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Spectroscopy and Photochromism of Triphenylformazan and Its Derivatives.

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SPECTROSCOPY AND PHOTOCHROMISM OF TRIPHENYLFORMAZAN AND ITS DERIVATIVES

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In memory of Ana

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TABLE OF CONTENTS

LIST OF ABBREVIATIONS

TPF	-	1,3,5-triphenylformazan
o-OH	-	3-(2-hydroxyphenyl)-1,5-diphenylformazan
OH-Cl	-	3-(2-hydroxy-5-chlorophenyl)-1,5-diphenyl-formazan
o-Cl	-	3-(2-chlorophenyl)-1,5-diphenylformazan
o-Br	-	3-(2-bromophenyl)-1,5-diphenylformazan
p-Cl	-	3-(4-chlorohenyl)-1,5-diphenylformazan
m-Br	-	3-(3-bromophenyl)-1,5-diphenylformazan
naphthyl	-	3-naphthyl-1,5-diphenylformazan
CNDO	-	Complete Neglect Differential Overlap
MO	-	Molecular Orbital
LCAO	-	Linear Combination Atomic Orbital
v.d.W 1,4	-	van der Waals dispersion forces between non bonded atoms
A	-	Absorbance
ϵ	-	molar absorption coefficient
λ	-	wavelength
M	-	Molarity
3MP	-	Trimethylpentane
osc. st.	-	oscillator strength

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The spectroscopic and photochromic characteristics of triphenylformazan and its derivatives were investigated. These derivatives were formed by adding substituents to the phenyl group attached to the carbon atom of the formazan ring or by replacing this phenyl group with a naphthyl group. Studies of the effect of the concentration, substituent, solvent and temperature on the absorption spectra of triphenylformazan were made. Molecular mechanics calculations were performed to generate two different geometries of triphenylformazan that were used in CNDO calculations to assign the electronic transitions observed in the absorption spectra.

In contradiction to what was stated in earlier investigations, the results of this work indicate that a second isomer of triphenylformazan is not formed only by irradiation but the two chelated forms exist in an equilibrium mixture. These two forms have different geometries and absorb at different wavelength in the visible region of electromagnetic spectrum. The results of the determinations of the effect of alcohols on the absorption spectra of triphenylformazans with an electron withdrawing group as O^- or Cl lead to a better

understanding of the strucure of these derivatives. The mechanism of stabilization of the formazan ring in these derivative with increasing temperature is also suggested by the results obtained in this investigation. The acidity of alcohols has a strong influence on the equilibrium between the chelated (or red or closed) form and the unchelated (or yellor or open) form of the ortho-hydroxy derivative. Resonance Raman and picosecond laser spectroscopy experiments are proposed to confirm the conclusions reached in this investigation.

CHAPTER I

A. Introduction.

This investigation was concerned primarily with the determination of the effect of concentration, substituent, solvent, and temperature on the spectroscopic characteristics and structure of triphenylformazan.

In Chapter I a literature review of the investigations of triphenylformazan and its derivatives is presented No major information about substitution in the ortho position of the phenyl group attached to the carbon atom of the formazan ring was found. A brief description of the compounds investigated in this work is given.

In Chapter II the experimental procedure used to prepare solutions and record the absorption spectra of triphenylformazan and its derivatives in the different solvents is described.

In Chapter III the experimental results of the different determinations performed in this investigation are reported. It includes the concentration and substituent effect on the absorption spectra of triphenylformazan in

different solvents. The results of the temperature dependence of the absorption spectra of the ortho-hydroxy derivative in alcohols, and of triphenylformazan and the naphthyl derivative in different solvents are reported. This chapter also contains the effect of different alcohols on the absorption spectra of ortho-hydroxy derivative.

In Chapter IV the results of molecular mechanics and CNDO calculations are reported. Two different geometries, planar and non-planar, are generated from molecular mechanics calculations. These geometries are used in CNDO calculations to assign the electronic transitions of the bands observed in the absorption spectra of triphenylformazan. The results of these calculations give credibility to the conclusion that two red forms exist in an equilibrium mixture in non-irradiated solutions; this conclusion was suggested by the experimental results.

In Chapter V a discussion of the experimental results is presented. In this discussion the absorption spectra of triphenylformazan are analyzed in terms of the spectroscospic and calculational results. The substituent effect is discussed in terms of the nature and position of the substitution. Solvent effects and the interaction between the ortho-hydroxy derivative and alcohols are also

discussed. The effect of the temperature is also discussed to explain the experimental results observed in the absorption spectra of the ortho hydroxy derivative.

In Chapter VI a summary of this work and the conclusions reached in this investigation are presented. Further experiments are proposed.

In summary, this work produced evidence for the equilibrium existence of two red forms of triphenylformazans, one of which does not have to be produced by irradiation. Calculational results provided much more detailed and believable geometries for the two red forms. The synthesis of 3-(2-hydroxyphenyl)-1,5-diphenylformazan was done in an attempt to find successive photochromic changes; while this hope was not realized the work with these compounds did provide the opportunity to study the thermal equilibrium between red and yellow forms and to study the effect of the acid strength of alcohols in this equilibrium. These results are new and significant contributions to triphenylformazan chemistry.

B. Literature Review.

Triphenylformazan is a highly photochromic molecule the structure, photophysics and photochemistry of which has been investigated for several decades.[1,2] Figure 1 shows the structure of the chelated form of triphenylformazan.

Triphenylformazan has unusual structural and spectroscopic characteristics that make this compound very interesting in many ways. Interest in triphenylformazan and in its derivatives has increased in recent years because of their practical uses. Several patents describing its use as image recording material have already appeared in the literature.[1-14] Triphenylformazan is used in electrolytic and chemical electrophotography; in these systems a ZnO resin photosensor is exposed to light and its image is developed with a triphenylformazan developing solution.[3-6] Heat bleachable antihalation or filter components are manufacturated from biimidazole compounds and triphenylformazan dyes in polymer binders. These substances are used in photothermographic elements.[7,8,9] Triphenyl-formazan compounds improve antifogant properties when they are added to photosensitive materials,[10,11] provide high contrast images that have good stability to silver halide photographic materials,[12] and are used in protect color

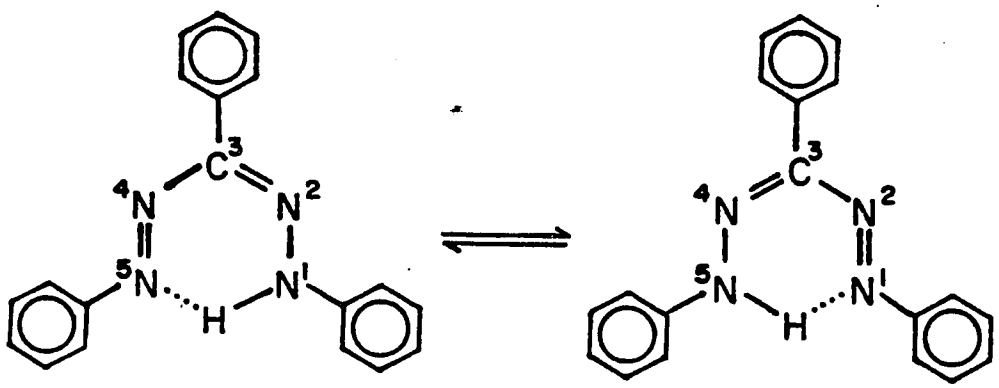


Figure 1

photographic material from the action of visible and ultraviolet radiation.[13] Some solutions of formazan dyes are useful as sharp cutoff optical filters in the ultraviolet, visible and near infrared regions.[14]

Irradiation of mixtures of triphenylformazan and dipyrromethenes form stable ion pairs that might be used as energy reservoirs for solar energy that has been absorbed.[15] Triphenylformazan also forms stable metal complexes with Co, Ni and Cu. Panyushkin et al.[16] studied the complex formation of tetrahalogen compounds of the group IV metals and formazan compounds, determined the position of the strongest nucleophilic center in the ligand molecule and obtained additional information about its structure. They determined from infrared and ultraviolet spectra and dipole moment measurements that these complexes are molecular compounds that have donor-acceptor bonds metal - nitrogen.

Triphenylformazan in biological systems has been studied.[17-23] It is used as an indicator of dehydrogenase activity in soils,[17,18,19,20] human cells,[21] and activated sludges.[22,23] In these determinations triphenyltetrazolium chloride is reduced to triphenylformazan.

In addition to studies of photochromic and biological behaviors, investigations of hydrogen bonds, mesomerism and tautomerism of triphenylformazans have produced interesting structural information.

The structure of formazans as been discussed by many authors.[2] As early as 1894 von Pechmann[24] in studying the reactions of formazans came to the conclusion that formazans obtained by two possible synthetic routes are identical. He concluded that formazans in the crystalline state exist in only one of the possible tautomeric forms, regardless of the mode of synthesis. The manifestation of tautomerism by formazans in cleavage reactions was shown in a study of unsymmetrically substituted triphenylformazans labeled with ^{14}C. In the case of symmetrically substituted formazans it is possible for the mesomeric system to exist. Nuclear Magnetic Resonance studies of ^{15}N-H coupling in unsymmetrically substituted triphenylformazan derivatives demonstrated that these components are not resonance hybrids but tautomeric pairs. It was further shown that the position of the tautomeric equilibrium is a function of the substituents present in the phenyl group on N_1 and N_5.[25] See Figure 1.

Infrared spectral data indicate that in the

crystalline state and in solution triphenylformazan contains a quasiaromatic ring in which there is a strong intramolecular hydrogen bond.[26] The totally symmetric ring breathing mode in the resonance Raman spectra is also an indication of a strong hydrogen bond.[27] The participation of the NH group in the formation of a stable hydrogen bond is shown by the absence of NH band in the 3400 - 2900 cm^{-1} region.[28,29]

Hunter and Roberts[30] showed that formazans have a chelated structure and are capable of forming complexes with certain metals. Magnetic susceptibility studies of metal complexes compounds of formazans (Co, Ni, Cu) indicate that the structure of these compounds corresponds to a planar arrangement of the atoms of the formazan group.[28,31] This planarity suggests that in the chelated ring formed by the hydrogen bond there is a leveling of the electron density; the formazan ring acquires a quasiaromatic character as a result of the delocalization of the six electrons of the system, (four π electrons in C=N and N=N double bonds and the two p electrons on the N_1). The hydrogen bond energy of triphenylformazan (7.0 kcal/mol) is high in comparison with that of 1,5 diphenylformazan (2.7 kcal/mol)[28]. This fact indicates that the 3-phenyl group participates in conjugation with other groups in the

formazan ring and has a determining effect in the stabilization of the hydrogen bond. The resonance energy of a tetrazole ring is 55,6 (kcal/ring) in tetrazole and 70,3 (kcal/ring) in 2,5-diphenyltetrazole. The resonance energy of benzene is 36.0 (kcal/ring).[32] The heat of combustion of diphenylformazan ($C_{13}H_{12}N_4$) is 174.9 (kcal/mol) and the heat of formation is 139.3 (kcal/mol).[33]

Several authors[26,34-41] have investigated the infrared spectra of triphenylformazan, some of its derivatives, and some of its metal complexes. The infrared absorption spectra of both the chelated and unchelated form of triphenylformazan have been studied by means of ^{15}N-labelling. The infrared bands are assigned on the basis of isotopic shifts. The nonsymmetric labeling gives characteristic labels for each formazan isomer.[42,43] Lewis and Sandorfy[27] studied the infrared and Raman spectra of triphenylformazan and some of its halogen derivatives in their chelated and unchelated forms. By means of ^{15}N-labelling and selective substitution on the phenyl group at N_1, it was suggested that only two isomers of the chelated and unchelated forms exist.

Triphenylformazan in solution undergoes a color change from red to yellow when it is irradiated with visible

light. Figure 2 shows the absorption spectra of triphenylformazan in a 3.96×10^{-4} M toluene solution at 25 (C). Curve A is the spectrum of the fresh unirradiated solution which contains the red form. Curve B is the spectrum of the same solution, after 12 minutes of irradiation with a 200 W tungsten lamp; the new absorption of the yellow form is apparent.

Hauser[44] investigated the quantum yield of the photochromic change from the red to the yellow form produced by visible light. The percentage of converted molecules was determined from integration of the visible absorption at 405 nm; it appears that 50 photons are absorbed for each molecule converted; only one of the 50 is active. A distinction is made between absorbed and active photons. Hauser[45] also reported that ultraviolet light converts tetrazolium chloride and triphenylformazan to the same product, 5-phenyl-2,3-dephenylenetetrazolium chloride.

The efficiency of disappearance of absorption of the red form is a function of the light intensity;[46,47] the efficiency increases as the light flux increases, until a limiting value is reached at high incident light levels.

Kuhn and coworkers[48-50] studied triphenylformazan in

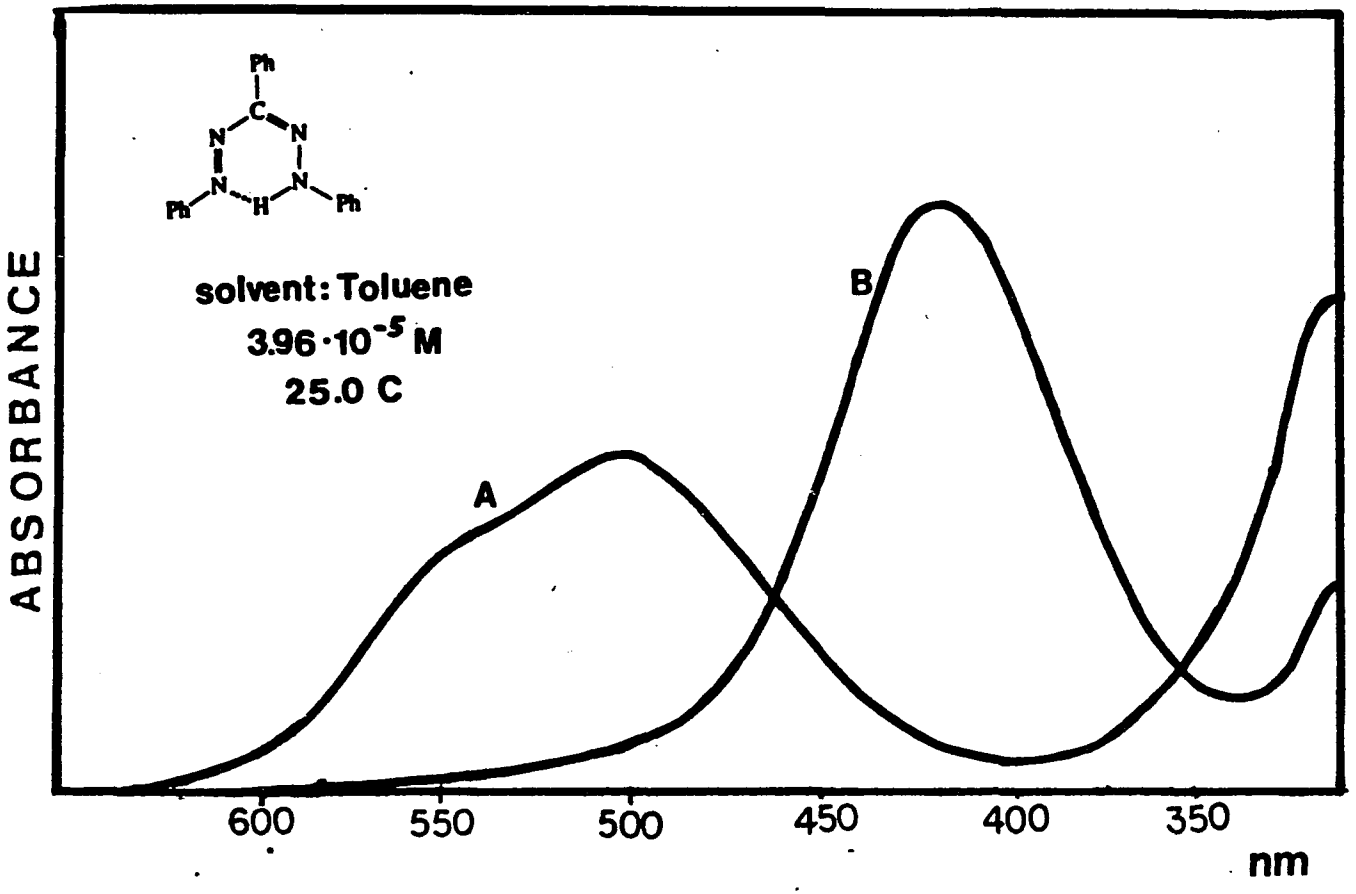
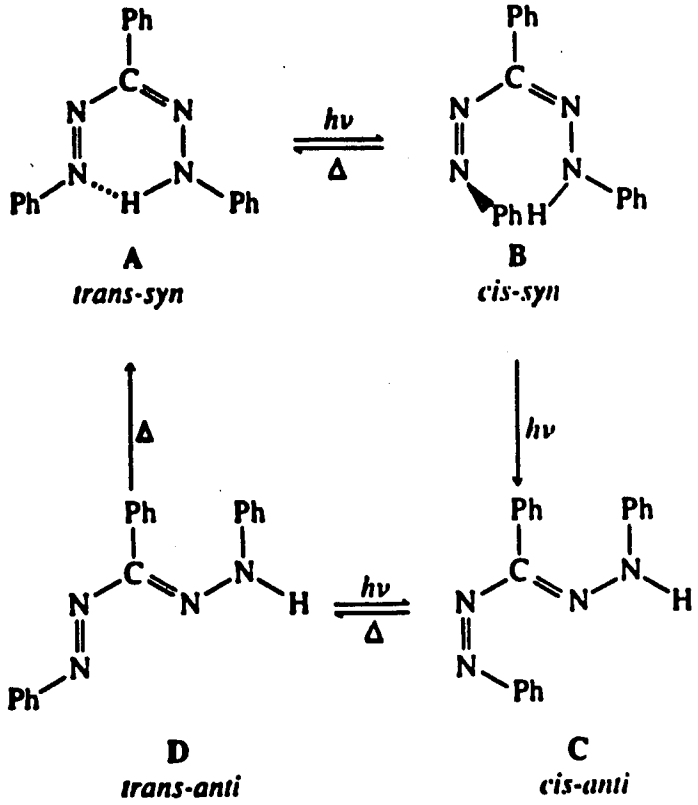

Ph
C
N
N
N
N
Ph
H
Ph
solvent: Toluene
3.96·10⁻⁵ M
25.0 C
A
B
ABSORBANCE
600
550
500
450
400
350
nm

Figure 2

detail and demonstrated that there must be at least two intermediates between the stable red form and the metastable yellow form. They also showed that there are two yellow forms involved in the sequence. Irradiation of a solution of the red form produces a yellow compound that changes to a second yellow form by a thermal process. Upon irradiation, the second yellow form returns to the initial photochemically produced yellow compound. Kuhn and Weitz[50] proposed the scheme shown in Figure 3 to account for the changes produced by irradiation of the several forms of triphenylformazan with visible light. In this scheme the prefixes cis and trans are used for the arrangement at the N=N double bond and come first; the prefixes syn and anti are used for the C=N double bond and syn is used when the arrangement of the substituents at the C=N is favorable for the formation of a hydrogen bond. The trans-syn form is arranged in a plane, is capable of forming an intramolecular hydrogen bond, and is considered to be the most stable form. From these results Kuhn and Weitz[50] concluded that the cycle takes place clockwise; on irradiation the trans-cis rearrangement at the azo group occurs more easily than the syn-anti conversion at the C=N double bond; in other words, a syn-anti conversion by an absorbed light quantum occurs only after the azo group has already been changed to a cis configuration by an earlier



Kuhn-Weitz Scheme

Figure 3

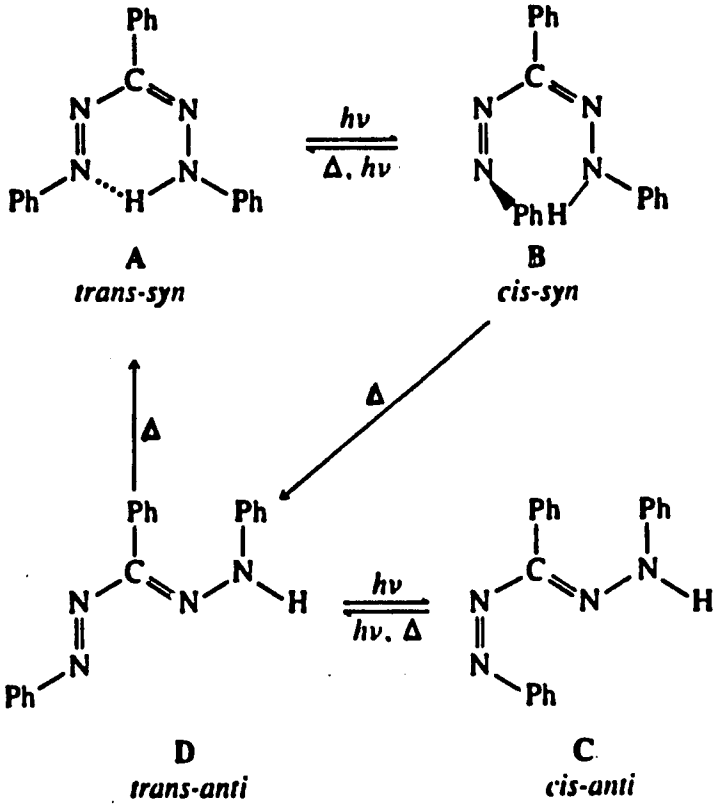
absorption process.

The rapid return of the red form B to red form A accounts in part for the intensity dependent quantum yield. The rate of this back reaction was too fast to permit Kuhn and Weitz to measure either an energy of activation or a preexponential factor. The reaction yellow C to yellow D was found to be insensitive to acid and base catalysis and had a preexponential factor of $6x10^{6}$ sec^{-1}. The thermal return of yellow D to red A was found to be extremely sensitive to catalysis and solvent purity. The preexponential factor reported for the process is $9.6x10^{-4}$ sec^{-1} but, because of the admitted sensitivity of this reaction to impurities, little significance can be attached to this value or to that of the energy of activation.

After consideration of the irradiation experiments and the absorption spectroscopic measurements in the temperature range 116-293 K Langbein[51] attempted to modify the cyclic isomerization scheme originally proposed by Kuhn and coworkers. Using Kuhn's assignments of the isomers of triphenylformazan to the spectroscopically observable species, Langbein[51] demonstrated that only the trans-cis isomerization of the azo group proceeds both photochemically and thermally and that photoinduced

isomerization about the C=N double bond could be excluded. Later, on the basis of flash photolysis experiments, Langbein and Grummt[52] proposed a modified scheme for the photochromic reaction of triphenylformazan that is shown in Figure 4. The results of their investigation indicate that the stable red form A of triphenylformazan is converted through a photochemical trans-cis isomerization about the N=N double bond into the isomer B which is also red and has a smaller molar absorption coefficient than isomer A. They postulate that the reason for the comparatively long wavelength of absorption of B might be that the species produced by a torsion about the C-N single bond could have a better conjugation in the azohydrazone (I) part of the molecule through the formation of a weak five membered cyclic hydrogen bond interaction. According to Grummt and Langbein, form B may revert photochemically as well as thermally to the original form. A competitive reaction that forms the trans-anti isomer D and has a comparable rate constant occurs at room temperature. The isomer C, that has a cis-anti configuration, is formed photochemically only from D. C is also yellow and has a smaller molar absorption coefficient than does D. The reverse reaction C $\longrightarrow$ D proceeds both photochemically and thermally.

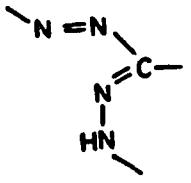
In spite of the differences between the schemes



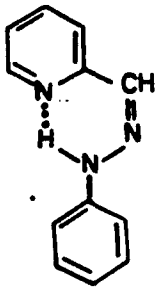
Langbein - Grummt Scheme

Figure 4

proposed by Kuhn-Weitz[50] and Grummt-Langbein[52], both suggest that under continous irradiation a photostationary state involving C and D should be achieved. Yet, such mixtures of isomers were not observed in the work of Lewis and Sandorfy;[27] consequently when this work was done confusion about the existence of multiple red and yellow forms existed.



(I)



(II)

Schulte-Frohlinde[53] measured the quantum yield for the syn-anti isomerization of the 2-pyridinecarboxaldehyde phenylhydrazone (II) and found ϕ= 0.02 for anti to syn and ϕ=0.008 to 0.006 for syn to anti. On comparing these values with an estimated 0.02 for triphenylformazan, he concluded that the red to yellow isomerization of the latter compound is a syn-anti (C=N) isomerization rather than a trans to cis isomerization of the azo group. However, he did not state to which of the two successive photochemical reactions required to get from red to yellow he meant this conclusion to apply.

Schiele[54] has proposed that the first step of the triphenylformazan photoisomerization is a conformational change involving one of the N-phenyl groups attached to the quasi-aromatic formazan ring. From resonance Raman results Lewis and Sandorfy[27] concluded that an excited state proton transfer is the initial photoinduced event in the photochromism of triphenylformazan.

Sueishi and Nishimura[55,56] investigated the mechanism of thermal reverse isomerization. They followed the rates of thermal isomerization around N=N (Process A) and C=N (Process B) of the substituted triphenylformazan at various temperatures and under high pressures. They found that kinetic substituents and pressure effects, together with the activation parameters, favor the inversion mechanism via a moderately polar transition state for both Processes A and B and fail to support the rotational mechanism via a very polar transition state.

Although the structural form of triphenylformazan does not suggest the presence of an unpaired electron, a strong ESR signal that has a g value of 2.0037, has been observed.[57] The signal observed is due to impurities formed during the synthesis of triphenylformazan. Repeated crystallizations eliminate the ESR signal. However, air

oxidation of formazans gives rise to a paramagmetic product, the room temperature ESR spectrum of which shows 9 lines that are easily explained by two pairs of equivalent nitrogens.[58]

Klyuev et al.[59] have considered the structure of some aryl and heteroarylformazans and they discuss their fragmentation patterns. They report the mass spectrum of triphenylformazan (peak intensity as percent of maximum), but they do not discuss its fragmentation pattern.

Ganyuk et al.[60] reported the luminescence of triphenylformazan. They observed two bands with maxima at 419 and 515 nm, and they attributed these bands to the two isomeric forms of triphenylformazan (red and yellow). According to Lewis [61] the observed luminescence is due to an impurity formed during the synthesis of triphenylformazan.

C. Triphenylformazan Derivatives.

The photochromic activity of triphenylformazan is affected by the presence of impurities, traces of acids and hydroxylic solvents. The lifetime of the yellow isomer in highly purified hydrocarbon solvents is normally of the

order of several hours or even days. The yellow isomer of triphenylformazan in toluene solution has been reported to have a lifetime of 96 hours. [15]

The sensitivity of triphenylformazan to the presence of other substances has been used to study the structure of triphenylformazan and its photochromic mechanism and to identify derivatives that would be appropiate for specific uses in the development of photographic material or analytical reagents.

These derivatives of triphenylformazan are modifications of the attachments to the basic formazan ring and are formed by adding substituents to a phenyl group or by replacing a phenyl group with other groups or atoms. There have been numerous reports in the literature[25,37,38,40,55,56,62-65] about the effect of substituents on the structure and photochromism of triphenylformazan, but most of these investigations are related to substitutions on the phenyl groups attached to N_1 and N_5 or to replacement of these phenyl groups by different groups or atoms.

There is a relatively small number of reports that include the effect of substitution of hydrogen atoms of the

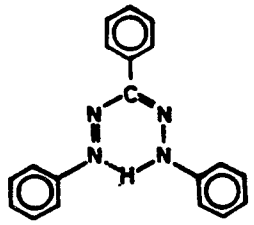
phenyl group attached to the carbon atom in the formazan ring or with complete substitution of this phenyl group. Even more important is the observation that no reference related to a substitution in the ortho position of this phenyl group was found. Avramenko et al.[65] studied the structure of a series of formazans which contain different number of naphthyl residues attached to the formazan ring. They demonstrated that the mononaphthyl formazans are in the chelated form in the crystalline state that has the intramolecular hydrogen bond, and they determined the δ(NH) proton signal of triphenylformazan to be at 15.28 ppm; the δ(NH) signal is shifted toward stronger fields in proportion to the number of replacements of the phenyl groups by naphthyl residues; the intramolecular hydrogen bond of naphthyl derivatives is weaker than that of the triphenylformazan.

The compounds investigated in this research project include triphenylformazan as a reference compound and seven derivatives that have substitutions in the phenyl group attached to the carbon atom of the formazan ring. They were prepared by Dr. Jerry W. Lewis by reducing triphenyltetrazolium chloride with dextrose in a basic solution and by means of the procedure of Neugebauer and Kuchler.[66] The derivatives were prepared by means of suitable

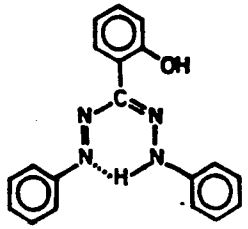
modifications of the Neugebauer procedure[15]. Figure 5 shows the chelated form of triphenylformazan and the derivatives studied in this investigation.

3-(2-hydroxyphenyl)-1,5-diphenylformazan and 3-(2-hydroxy-5-chlorophenyl)-1,5-diphenylformazan are not photochromic; they are stable in their red forms in hydrocarbon solutions and as an equilibrium mixture of both the red and the yellow isomers in methanol solutions. These compounds were synthesized because it was hoped that eventually a photochromic center that would have multichromophoric properties or successive photochromic stages upon irradiation could be prepared. Although the 3-(2-hydroxyphenyl) compounds are not photochromic, their behavior in temperature studies make them very valuable in the determination of the structure of triphenylformazan.

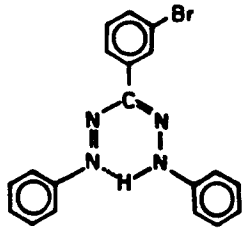
3-(2-chlorophenyl)-1,5-diphenylformazan and 3-(2-bromo-phenyl)-1,5-diphenylformazan exist, even in the crystalline form, as a mixture of the chelated and non-chelated forms. According to Lewis,[27] the fraction of the non chelated isomer in the crystalline state depends upon the conditions of the crystallization. The existence of these derivatives as the non chelated isomer could be



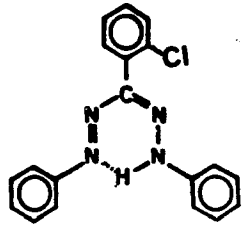
1,3,5- triphenylformazan



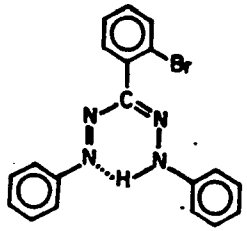
3-(2-hydroxypheny)-1,5-diphenylformazan



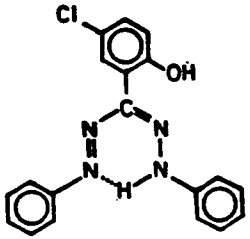
3-(3-bromophenyl)-1,diphenylformazan



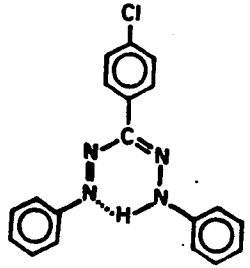
3-(2-chlorophenyl)-1,5-diphenylformazan



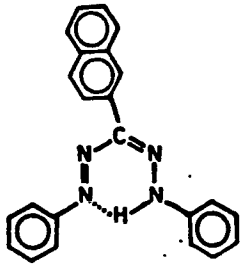
3-(2-bromophenyl)-1,5 diphenylformazan



3-(2-hydroxy,5-chlorophenyl)-1,5-diphenylformazan



3.-(4-chlorophenyl)-1,5-diphenylformazan



3-(2-naphthyl)-1,5-diphenylformazan

Figure 5

important in the field of organic semiconductors. Thin films of 1,3,5-triphenylformazan exhibit a photovoltaic spectrum that agrees well with the visible absorption spectrum of the non-chelated isomer[67]. Derivatives that exist in the solid phase as the non chelated isomer might exhibit even more interesting semiconductor properties.

CHAPTER II

EXPERIMENTAL

In order to record the spectrum of a solution in a 1.00 cm cell that would have a maximum absorbance between 0 and 1, the concentration of a triphenylformazan must be approximately 10^{-5} M. To obtain 50.0 cm^3 of a solution with such a small concentration, one must weigh about 0.3 mg of sample; since the precision of the balance was about 0.1 mg, the concentrations of the solutions could not be known sufficiently accurately if this direct method were used. Preparing larger volumes of solution in order to increase the precision was prohibitively expensive. In order to minimize the error in the calculation of molarities and absorption coefficients, calibration curves for each compound in the different solvents were prepared.

When spectroscopic grade solvents were available, no further purification was done. Reagent grade solvents were purified by passing them through an activated alumina column. The purified solvents were stored over metallic sodium under a nitrogen atmosphere. Methanol was purified by distilling it from calcium hydride. The solutions were prepared immediately after the solvents were purified. Triphenylformazan and its derivatives were used as

received. No purification or identification studies were made on the compounds before using them.

For each compound a 10^{-4} M solution was prepared by weighing the solute and transferring it to a 100 cm^3 volumetric flask. The solvent was added to make up approximately 50 cm^3 of total volume. The flask with the solution was weighed. Since the concentration was very low, the density of the solution was assumed to be the density of the pure solvent. The concentration was calculated from the weighed quantities. The concentration of a solution prepared in this way has a precision of about 1.3%. The spectrum of this solution was recorded, and the molar absorption coefficient, calculated from the maximum absorbance, was used to estimate the concentration required to obtain a 99% maximum absorbance.

Ten solutions that had concentrations differing from each other by 0.10 absorbance unit were prepared by dilution of the stock solution (10^{-4} M) to a standard volume. An empty flask was weighed, and the flask with the final solution was weighed . The density of the solution was assumed to be the density of the pure solvent, and the final concentrations were calculated from the weighed quantities. The concentrations of a solution prepared in

this way had a precision of almost 1.5%. The solutions of the photochromic compounds prepared in cyclohexane, carbon tetrachloride, toluene and dichloromethane were kept in the dark. The solutions of the non photochromic compounds in these solvents and the solutions of all the compounds in methanol were not protected from the light.

In order to make an accurate determination of the dependence of the molar absorption coefficient upon the concentration, three solutions which had concentrations that decreased by one order of magnitude each were prepared and were put in cells which had lengths that increased by one order of magnitude, and the spectra were recorded. If Beer's law was followed, the three spectra should be identical.

The solutions were prepared in the same manner that was used to prepare the solutions for the calibration curves, i.e., by diluting a stock solution, weighing the empty flask, weighing the flask with a quantity of stock solution and weighing the flask with the total volume of solution. The density of the solution was assumed to be the density of the pure solvent.

The spectra were recorded by means of a Cary 14

spectrophotometer with a 0.0 to 1.0 slide wire immediately after the solutions were prepared. The wavelength measurements were good to ± 0.3 nm when read from the wavelength indicator. The resolving power of the monochromator is reported by the manufacturer to be 0.1 nm throughout the range 190 to 1300 nm. The Cary 14 spectrophotometer was calibrated with a Neodymium glass at different wavelength. On the same chart were recorded the base line obtained when the solvent was in both the reference and the sample cells and the absorption spectra of the ten solutions. The absorbance read from the chart had an error of ±0.002. In order to obtain the spectra of the solutions at controlled temperature, the sample cell was kept in a cell holder through which ethylene glycol was circulated. The temperature of ethylene glycol was controlled in a circulator bath, Brinkman Lauda RC-6. The cell compartment was flushed with nitrogen to avoid condensation of water on the windows of the cell holder. The temperature was determined by means of a chromel-alumel thermocouple positioned outside the sample cell. The voltage read from a potentiometer had an error of ± 0.05 mV.

CHAPTER III

EXPERIMENTAL RESULTS

A. Concentration Effect.

Tables 1 through 39 present the results of the calibration curves for triphenylformazan and its derivatives in all the solvents. Each table presents the concentration of the stock solutions, the density of the solvent, temperatures, wavelengths of maximum absorbances in the visible and ultraviolet regions, and the concentrations maximal absorbances and molar absorption coefficient of the standard solutions.

Each set of data consisting of the maximum absorbances was fitted to a linear function of the concentration ($A=b+mC$) in which b, the intercept, corresponds to the absorbance A of a solution of zero concentration. The slope m corresponds to the molar absorption coefficient, ϵ, if there is no dependence of a on the concentration C. The statistical parameters, as well as the average value of the molar absorption coefficients, are presented at the end of each table. Two deviation values of the molar absorption coefficient are shown. The first value corresponds to the

statistical deviation of the calculated absorption coefficient; the second value, between parentheses, corresponds to the average value of the calculated deviations.

Although in almost every case the correlation coefficient r is 1.00, there are significant differences. The slope m is consistently lower than the average value of the molar absorption coefficient, and the intercept is in general greater than zero. For almost every compound, the calculated molar absorption coefficient decreases as the concentration increases. These observations indicate that there is no linear correlation between the concentration and the absorbance. No attempt was made to determine the correct dependence of the absorbance upon the concentration, but these results suggested that more than one molecular species absorbs in this region.

Figure 6 show the calibration curves of triphenyl-formazan in toluene. The results observed in the calibration curves were confirmed when the spectra of solutions differing by one order of magnitude from each other were recorded. Tables 40 through 44 present the results of these determinations. In every case in the visible range as well as in the ultraviolet range, there is

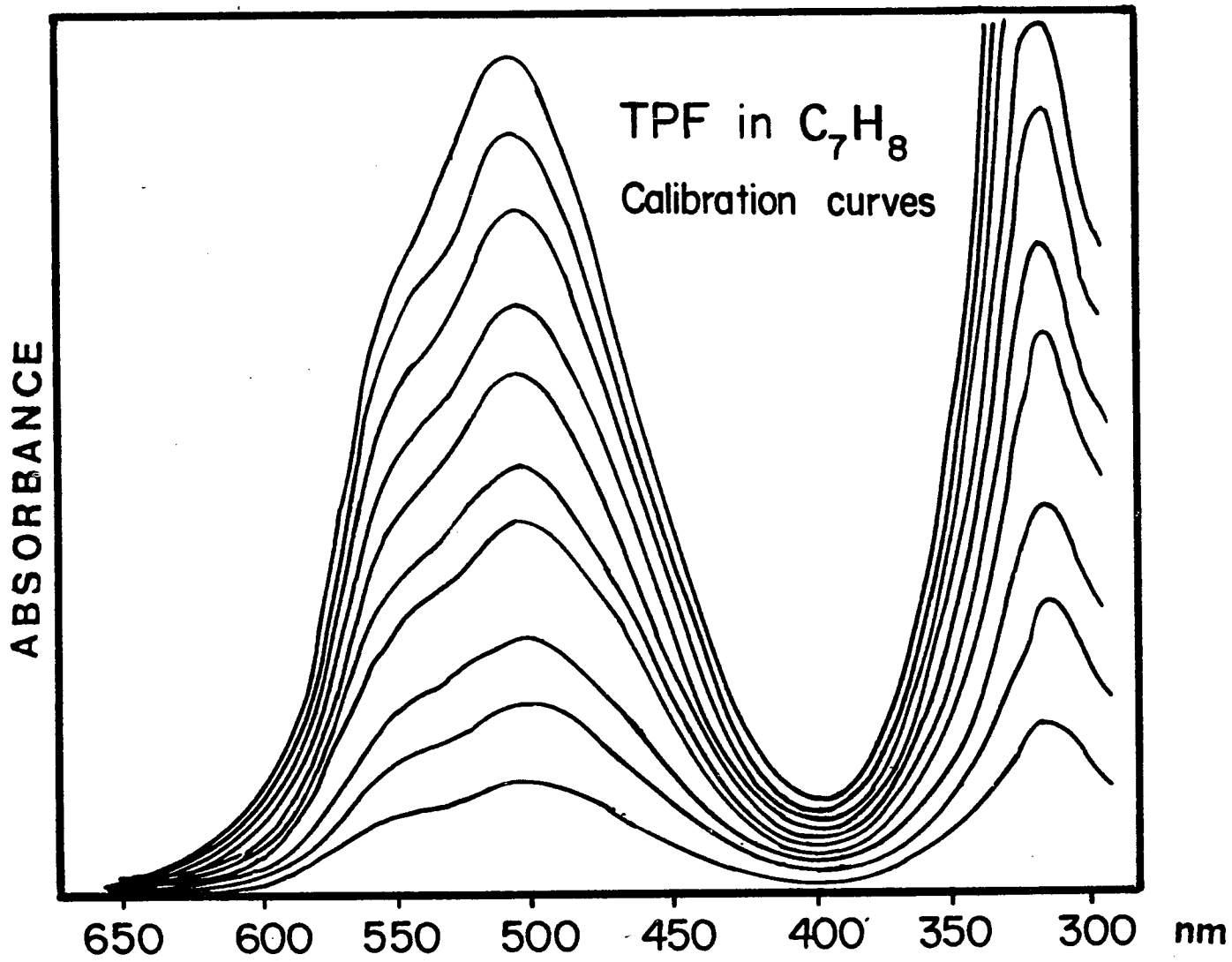

TPF in C_7H_8
Calibration curves
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 6

a dependence of the absorbance on the concentration. The molar absorption coefficient decreases as the concentration increases. The difference between the values of the two consecutive concentrations is larger than the calculated deviation of a single determination.

B. Substituent Effect.

1. 1,3,5-triphenylformazan.

The spectra of triphenylformazan in cyclohexane, carbon tetrachloride, toluene, dichloromethane and methanol are presented in Figure 7.

Triphenylformazan in different solvents has similar spectroscopic characteristics. See Table 45. The maximum absorbance of triphenylformazan in all the solvents except methanol in the visible range occurs near 490 nm. The maximum absorbance of triphenylformazan in methanol occurs at 482 nm. A second unresolved band appears between 530 and 540 nm. The ratio between absorbance at the maximum and the absorbance at 535 nm varies between 1.336 for triphenyl-formazan in toluene and 1.609 for triphenylformazan in methanol. The ratio generally increases with the polarity of the solvent, although the ratios corresponding to carbon

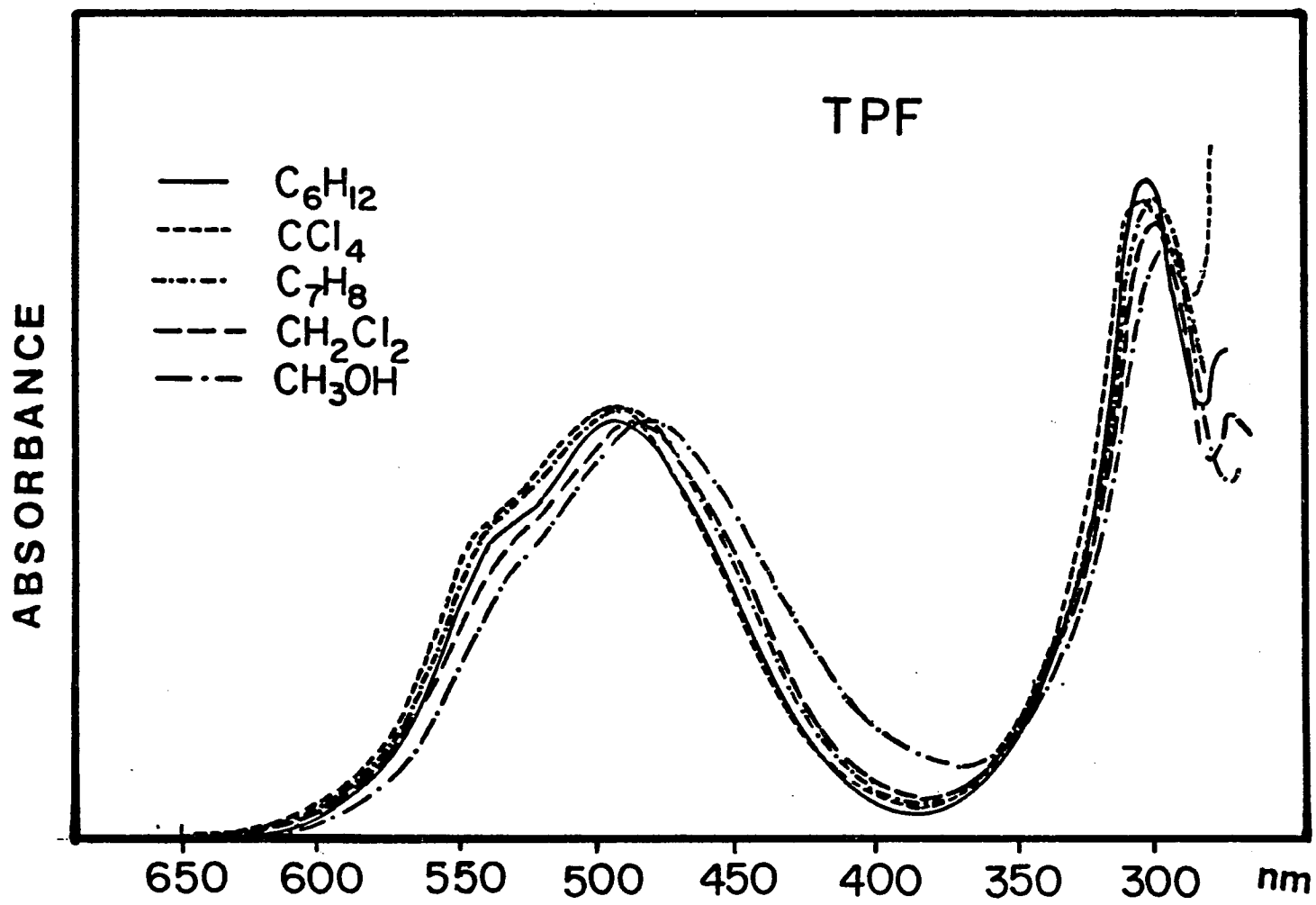

TPF
C_6H_{12}
CCl_4
C_7H_8
CH_2Cl_2
CH_3OH
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 7

tetrachloride and toluene solutions are lower than that of the cyclohexane solution. The visible molar absorption coefficient of triphenylformazan ranges from 15,574 to 17,676 ($M^{-1}cm^{-1}$). In the ultraviolet region the maximum absorbance occurs between 297 and 302 nm and the molar absorption coefficient ranges between 20,937 and 27,900 ($M^{-1}cm^{-1}$).

The molar absorption coefficients of triphenylformazan in both the visible and ultraviolet regions generally decrease as the solvent polarity increases. In non-polar carbon tetrachloride triphenylformazan has relatively low molar absorption coefficients, but it should be remembered that carbon tetrachloride is locally very polar. The relative effect of solvent polarity on the visible and ultraviolet transition is clear; a more polar solvent increases the molar absorption coefficient of the visible transition with respect to that of the ultraviolet transition. The ratio between the visible and ultraviolet molar absorption coefficient increases from 0.633 in cyclohexane to 0.745 in methanol.

The red producing band near 490 nm (482 nm in methanol solutions) corresponds to the absorption of the

formazan ring in the chelated isomers; this identification has been repeatedly reported in the literature [27,29,50,51,65]. The band near 300 nm corresponds to the absorption of the phenyl groups that is shifted to the red by the presence of the formazan ring. Benzene in cyclohexane absorbs between 220 and 270 nm.[68] Under the experimental conditions, (spectra recorded in the dark, room temperature), there is no evidence for the presence of the yellow isomers that absorb near 400 nm.[29,50,51]

2. 3-(4-chlorophenyl)-1,5-diphenylformazan. (para-chloro derivative).

In the para-chloro derivative the hydrogen in the para position of the phenyl group attached to the carbon atom in the formazan ring has been replaced by a chlorine atom. Its spectra in the different solvents are shown in Figure 8 and its spectroscopic characteristics are presented in Table 46.

The spectroscopic characteristics of this derivative are similar to those of triphenylformazan . See Figure 9. The maximum absorbance in the visible region occurs between 482 and 493 nm. It has a second unresolved band near 540 nm. In the ultraviolet region the maximum absorbance occurs between 305 and 308 nm. The absorption coefficients are

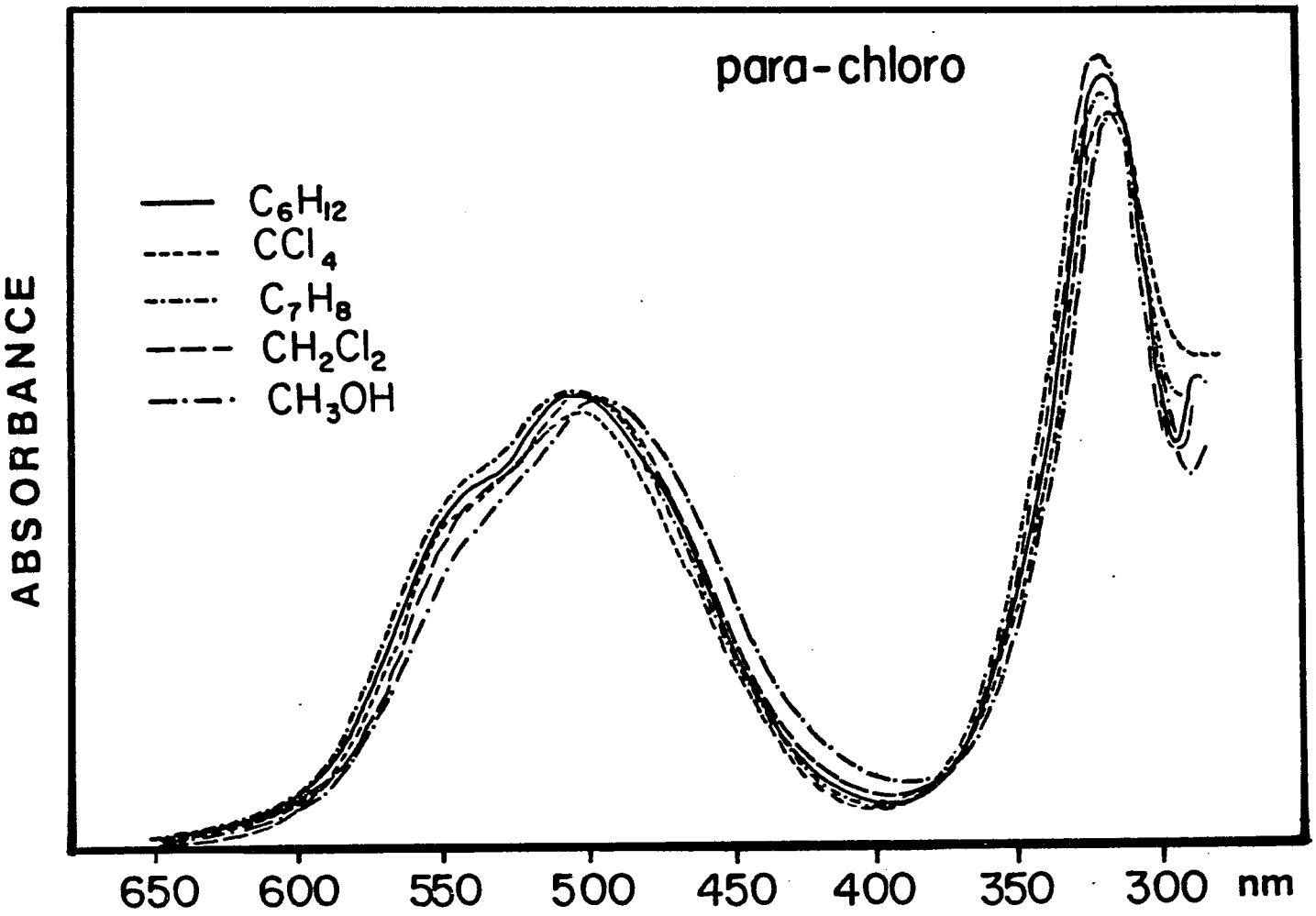

para-chloro
C_6H_{12}
CCl_4
C_7H_8
CH_2Cl_2
CH_3OH
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 8

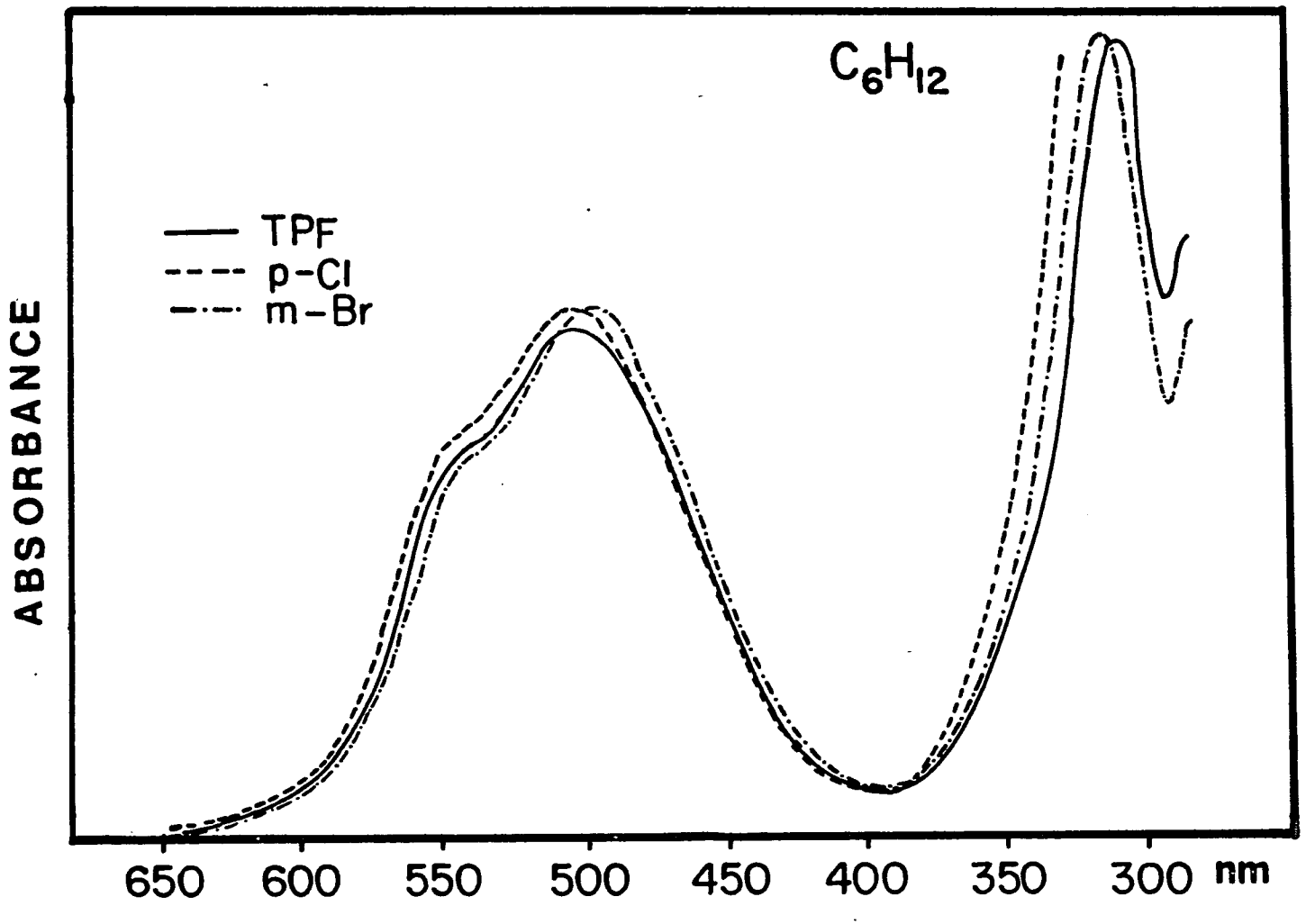

C_6H_{12}
TPF
p-Cl
m-Br
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 9

between 16,462 and 18,574 ($M^{-1}cm^{-1}$) in the visible region and between 26,864 and 32,337 ($M^{-1}cm^{-1}$) in the ultraviolet region. The ratio between the visible and the ultraviolet molar absorption coefficients varies from 0.574 to 0.613.

Although there is no clear effect of the solvent on the absorption characteristics of this derivative, an increasing polarity of the solvent appears to decrease the absorption coefficients in both the ultraviolet and visible range, the effect of dichloromethane is anomalous; the absorption coefficients are very large. The ratio between the visible and the ultraviolet molar absorption coefficients increases as the polarity of the solvent increases.

In general, the contours of the spectra of the para-chloro derivative are very similar to those of triphenylformazan, but comparison of the results with those for triphenylformazan presented in Table 45, indicates that: the visible maximum absorbance of the derivative is slightly shifted to the red by 1 to 2 nm with respect to that of triphenylformazan; the visible molar absorption coefficients are very similar for both compounds; the ultraviolet maximum absorbances are also shifted to the red by 6 to 8 nm; the derivative ultraviolet molar absorption

coefficients are 5.95 to 31.1% higher than those of triphenylformazan; and the shoulder at about 535 nm is more apparent in the spectra of the compound in non-polar solvents and less apparent in the spectra of the methanol solutions.

3. 3-(3-bromophenyl)-1,5-diphenylformazan. (meta-bromo derivative).

In the meta-bromo derivative, a hydrogen atom in the meta position of the phenyl group attached to the carbon atom in the formazan ring has been replaced by a bromine atom. Its spectra in the different solvents are shown in Figure 10. Its spectroscopic characteristics are presented in Table 47.

As in the case of the para-chloro derivative, the spectral contours of this derivative are very similar to those of triphenylformazan although its absorption characteristics are slightly different from those of triphenylformazan. See Figure 9.

The maximum absorbance in the visible region occurs between 482 nm in the case of the methanol solution and 493 nm in the case of carbon tetrachloride and toluene solutions. A second unresolved band appears near 540 nm. In

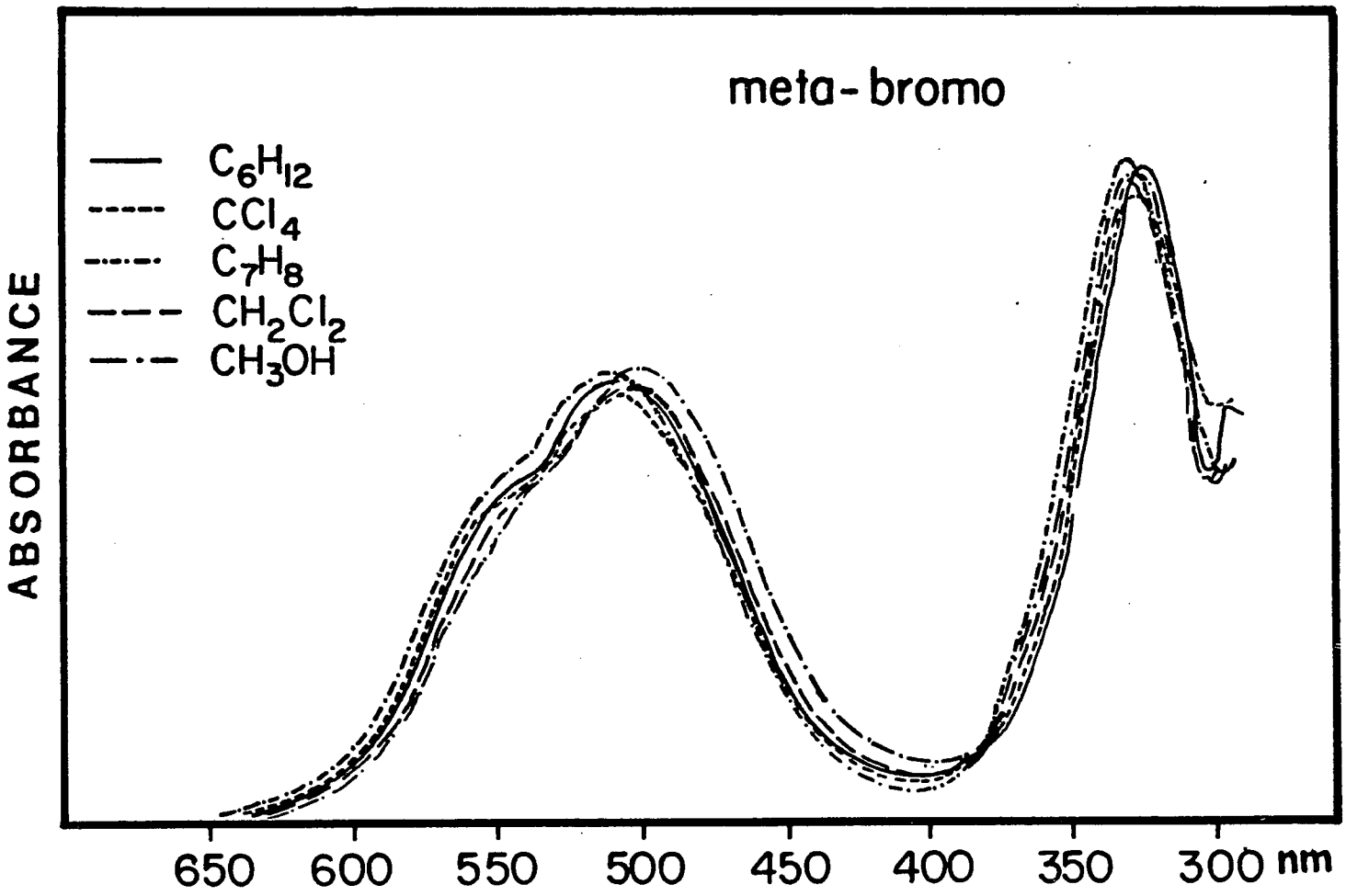

meta-bromo
C_6H_{12}
CCl_4
C_7H_8
CH_2Cl_2
CH_3OH
ABSORBANCE
650
600
550
500
450
400
350
300 nm

Figure 10

the ultraviolet region the maximum absorbance of the spectra of triphenylformazan are between between 304 nm in cyclohexane solutions and 314 nm in methanol solutions. The molar absorption coefficients vary between 17,080 and 18,231 ($M^{-1}cm^{-1}$) in the visible region and between 24,922 and 27,443 ($M^{-1}cm-1$) in the ultraviolet region. The ratio between the visible and ultraviolet absorption coefficients ranges between 0.664 and 0.690. No distinct trends are noticeable.

Although no clear effect of the solvent on the visible and ultraviolet molar absorption coefficient can be observed the changes observed in both regions are consistent. The wavelength at which the maximum absorbance occurs is more clearly affected by the polarity of the solvent; an increased polarity shifts the wavelength of maximum absorbance toward the blue in the visible region and towards the red in the ultraviolet region. Carbon tetrachloride is the exception; it shifts the wavelength of the visible maximum absorbance by 2 nm to the red with respect to that of triphenylformazan. The ratio between the visible and ultraviolet absorption coefficients also increases with the polarity of solvent.

Comparison of these results with those presented in Table 46 for the para-chloro derivative, shows that the

wavelength of the visible maximum absorbance of the meta-bromo derivative is consistently lower than those of the para-chloro derivative by 2 to 4 nm. A similar change in the ultraviolet maximum absorbance wavelength is observed except that in methanol the bromo derivative absorbs at a much higher wavelength than does the para-chloro derivative (8 nm shift to the red). The visible molar absorption coefficients of the meta-bromo derivative are higher than those of the para-chloro derivative and the ultraviolet molar absorption coefficients are lower than those of the para-chloro derivative. The ratio between the visible and the ultraviolet absorption coefficients of the meta-bromo derivative are higher those of the para-chloro derivative.

Comparison of these results with those of triphenylformazan shows that changes in the wavelength of the maximum absorbance depend on the solvent. No change or a very small change in the wavelength of the absorption of cyclohexane and carbon tetrachloride solutions is observed; the shift of the maximum absorbances of the meta-bromo compound in toluene and methanol is 2 to 3 nm to the blue with respect to those of triphenylformazan in the same solvents. The major change occurs in the spectra of dichloromethane solutions where a 5 nm shift to the blue occurs. In the ultraviolet region the spectra of carbon

tetrachloride solutions shift 5 nm to the red and those of methanol solutions shift 17 nm to the red. In the visible region the absorption coefficients of the meta-bromo derivative in cyclohexane and methanol are 3.14% and 16.5% higher than those of triphenylformazan in the same solvents. The ultraviolet absorption coefficients are, in general, lower than those of triphenylformazan by 2.59 to 8.58% except that in cyclohexane solutions the triphenylformazan molar absorption coefficient is 1.64% higher than that of the meta-bromo derivative in the same solvent. No major difference in the ratio of the visible and ultraviolet molar absorption coefficients of triphenylformazan and the meta-bromo derivative can be observed.

4. 3-(2-hydroxyphenyl)-1,5-diphenylformazan. (ortho-hydroxy derivative)

The ortho-hydroxy derivative shows spectroscopic characteristics different from those of triphenylformazan. The spectra of the compound in the different solvents are shown in Figure 11 and its spectroscopic characteristics are presented in Table 48.

The maximum absorbance of the compound in

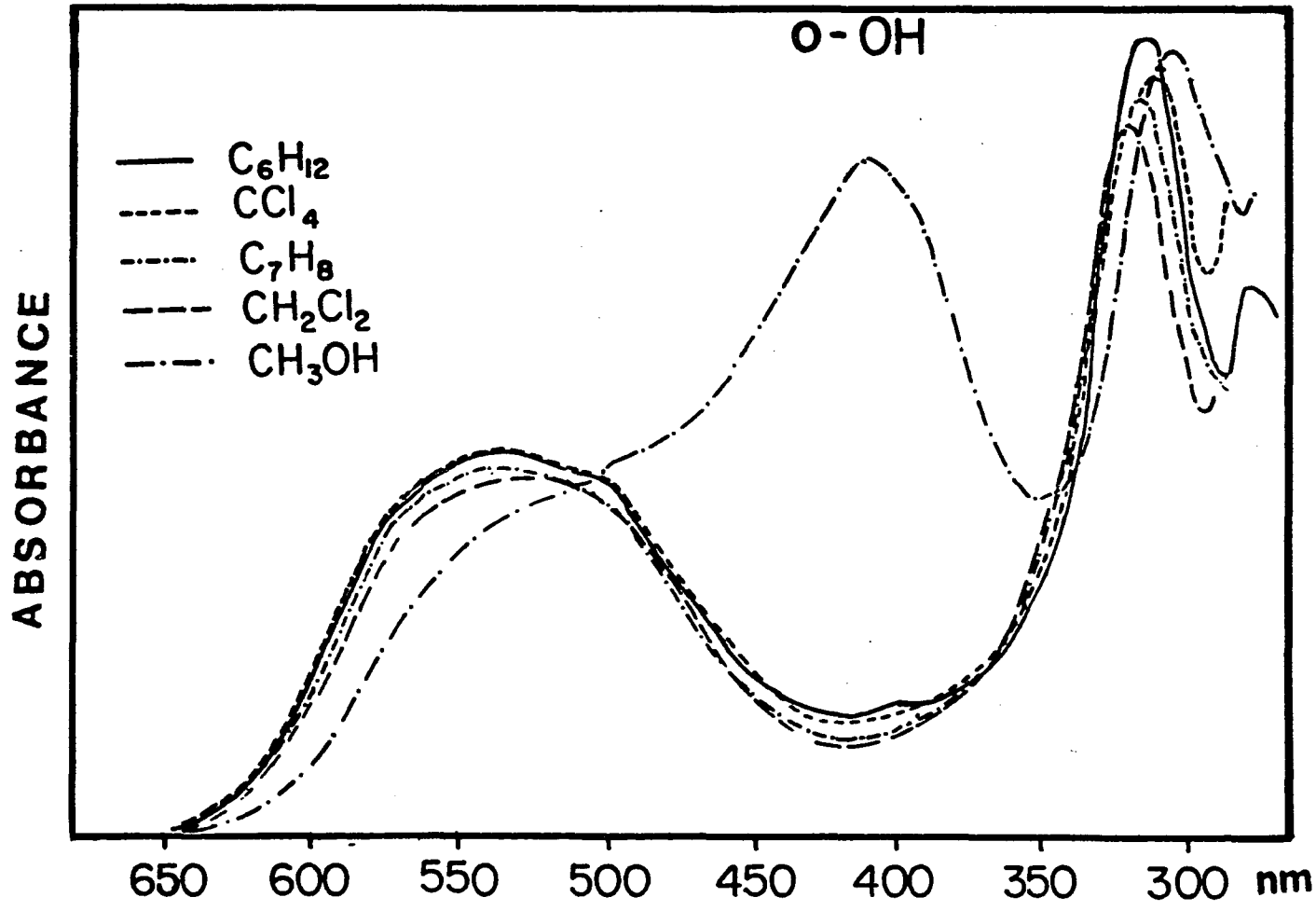

o-OH
C_6H_{12}
CCl_4
C_7H_8
CH_2Cl_2
CH_3OH
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure II

cyclohexane, carbon tetrachloride and toluene solutions in the visible region occurs at 535 nm. In these solvents the compound has an unresolved band near 500 nm. In dichloromethane solutions the maximum absorbance occurs at 525 nm. The visible absorption coefficients are between 11,472 and 12,774 ($M^{-1}cm^{-1}$). An unresolved band of low intensity in the spectra of the cyclohexane and carbon tetrachloride solutions appears between 360 and 430 nm. This low intensity band appears in the spectra of the toluene and dichloromethane solutions as a shoulder of the band in the ultraviolet region. The maximum absorbance in the ultraviolet region occurs at 310 - 311 nm and has absorption coefficients that vary between 23,774 and 26,469 ($M^{-1}cm^{-1}$). The ratio between the visible and the ultraviolet absorption coefficients is 0.417 to 0.500.

The contour of the spectra of the compound in different solvents shows that this derivative exists as an equilibrium mixture of the red and yellow isomers; the equilibrium favors the formation of the red form in all solvents except methanol in which the yellow form predominates. The relative intensities of the bands near 500-530 nm and 360-430 nm lead to this conclusion. Comparing the spectra shown in Figure 11, one can observe that a more polar solvent favors the formation of the red

form, shifts the wavelength of the maximum absorbance toward the blue, and suggests a redistribution of the red isomers. Also, a higher polarity in the solvent increases the molar absorption coefficients in both the visible and the ultraviolet region.

The effect of methanol on the absorption characteristics of the ortho-hydroxy derivative is completely different from that of the other solvents. The presence of the absorption of the yellow form at 406 nm and the broad shoulder in the vicinity of 530 nm can be observed. It is known that the maximum absorbance of a red isomer of the ortho-hydroxy derivative in hydrocarbon solutions occurs near 530 nm. The presence of these two bands in the spectrum indicates that there is an equilibrium between the red and the yellow forms, and no absolute value of the absorption coefficients can be calculated directly from these spectra. Methanol also changes the absorption characteristics of the phenyl group with respect to those observed in the spectra of this compound in hydrocarbon solutions. The maximum absorbance occurs at 302 nm, shifted by 8 to 10 nm to the blue with respect to that observed in the spectra of the derivative in hydrocarbon solutions. The absorption coefficient in the methanol solution is 16,242 ($M^{-1}cm^{-1}$), approximately

two thirds of those in hydrocarbon solutions.

Comparison of these results with those obtained for triphenylformazan shows major differences. See Figure 12. The principal band in the spectra of the derivative in hydrocarbon solutions in the visible region appears where the spectra of triphenylformazan in hydrocarbon solutions show an unresolved band, and the shoulder on principal band in the spectra of the derivative in the same solvents appears where the spectra of triphenylformazan hydrocarbon solutions show the maximum absorbance. The absorption coefficients of the ortho-hydroxy derivative are 23.7% to 30.9% lower than those of triphenylformazan. The presence of the yellow form could explain the smaller molar absorption coefficients of this derivative in the visible region.

The difference in wavelengths at which the spectra of this derivative and triphenylformazan show the maximum absorbances is large enough to assume that it is not a simple substituent effect. An explanation suggested to explain the different absorption wavelengths is the existence of two different structures (the two red isomers reported in literature[50,51]), that are present in an equilibrium mixture and absorb at different wavelengths.

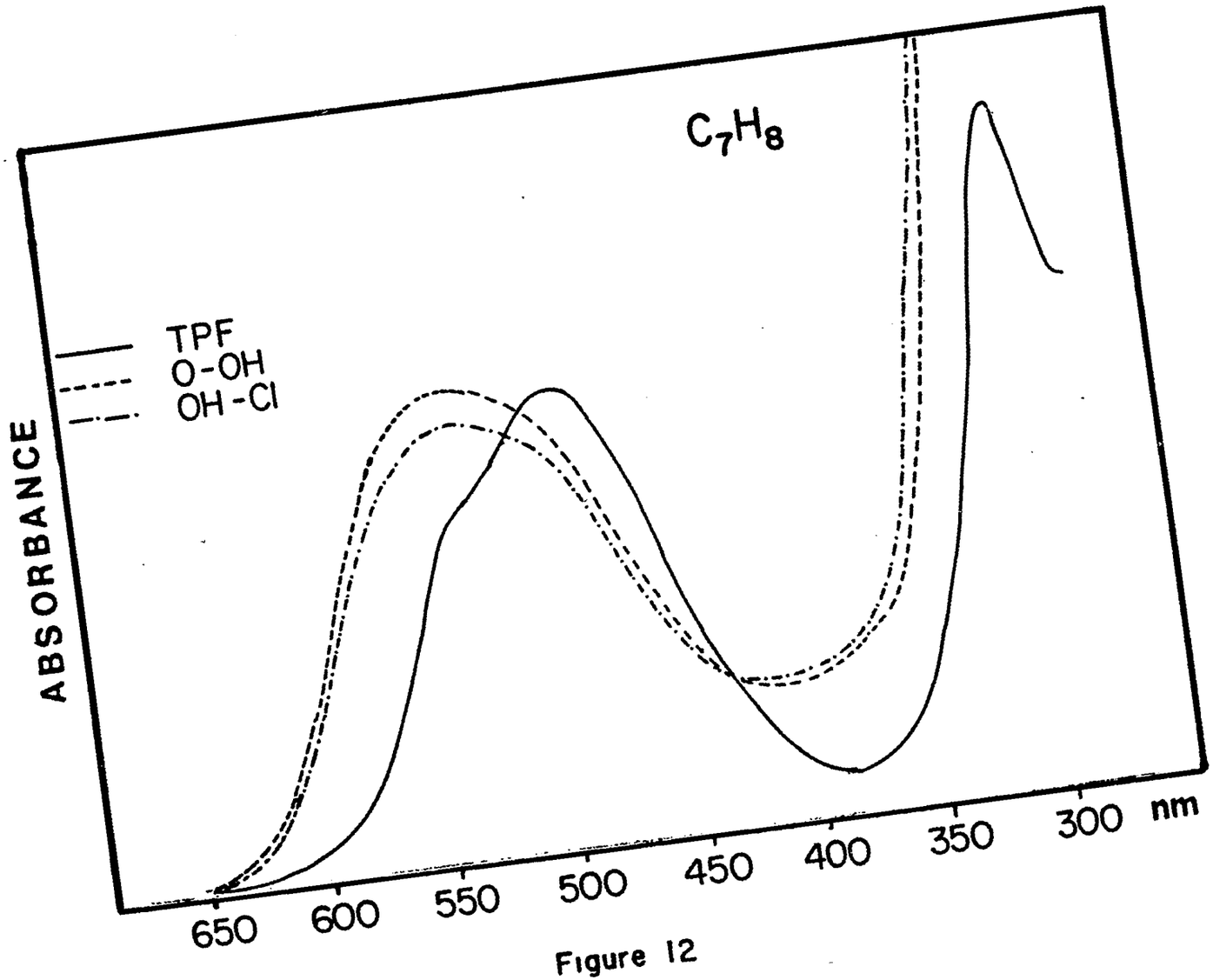

C_7H_8
TPF
O-OH
OH-Cl
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 12

The nature of these two structures of the red form is discused later. Due to the different nature of the predominant species in equilibrium, the spectroscopic characteristics of triphenylformazan and those of the ortho-hydroxy derivative in the visible region are the results of the absorption of very different distribution of red isomers and are not directly comparable.

Comparison of the ultraviolet bands shows that the hydroxy group in the ortho position of the phenyl group attached to the carbon atom of the formazan ring induces a 5 nm shift of this band to the red and the molar absorption coefficient of the phenyl group transition is decreased by 20.4% with respect to that of triphenylformazan in methanol. The band is much broader in the spectrum of the derivative than it is in the spectrum of triphenylformazan. The ultraviolet band in the spectra of the ortho-hydroxy derivative in hydrocarbon solutions is shifted 10 to 13 nm to the red with respect to that in the spectra of triphenylformazan in the same solvents. The ultraviolet molar absorption coefficients for triphenylformazan are slightly higher than those of the ortho hydroxy derivative in cyclohexane solutions, but as the polarity of the solvent increases, the molar absorption coefficient of the derivative becomes higher than that of

triphenylformazan.

5. 3-(2-hydroxy-5-chlorophenyl)-1,5-diphenylformazan (hydroxy-chloro derivative).

Results similar to those for the ortho-hydroxy derivative are observed for the hydroxy-chloro derivative in all the solvents. Figure 13 show the absorption spectra of this derivative in the different solvents. Table 49 presents its absorption characteristics.

The maximum absorbance in the spectra of this compound in cyclohexane, carbon tetrachloride, and toluene solutions occurs at 530 nm; a more polar solvent like dichloromethane shifts the wavelength of maximum absorbance 10 nm to the blue. The derivative absorption coefficient in these solvents increases from 12,315 to 13,246 ($M^{-1}cm^{-1}$) as the polarity of the solvent increases. The exception is cyclohexane; in these solutions the derivative absorption coefficient is 12,584 ($M^{-1}cm^{-1}$). The unresolved band appears near 490-500 nm. The presence of the yellow form is evidenced by a low intensity band between 370 and 430 nm; this band almost disappears as the polarity of the solvent increases. The ultraviolet maximum absorbance occurs between 318 and 320 nm and the absorption coefficients vary between 22,885 and 24,269 ($M^{-1}cm^{-1}$). In the ultraviolet

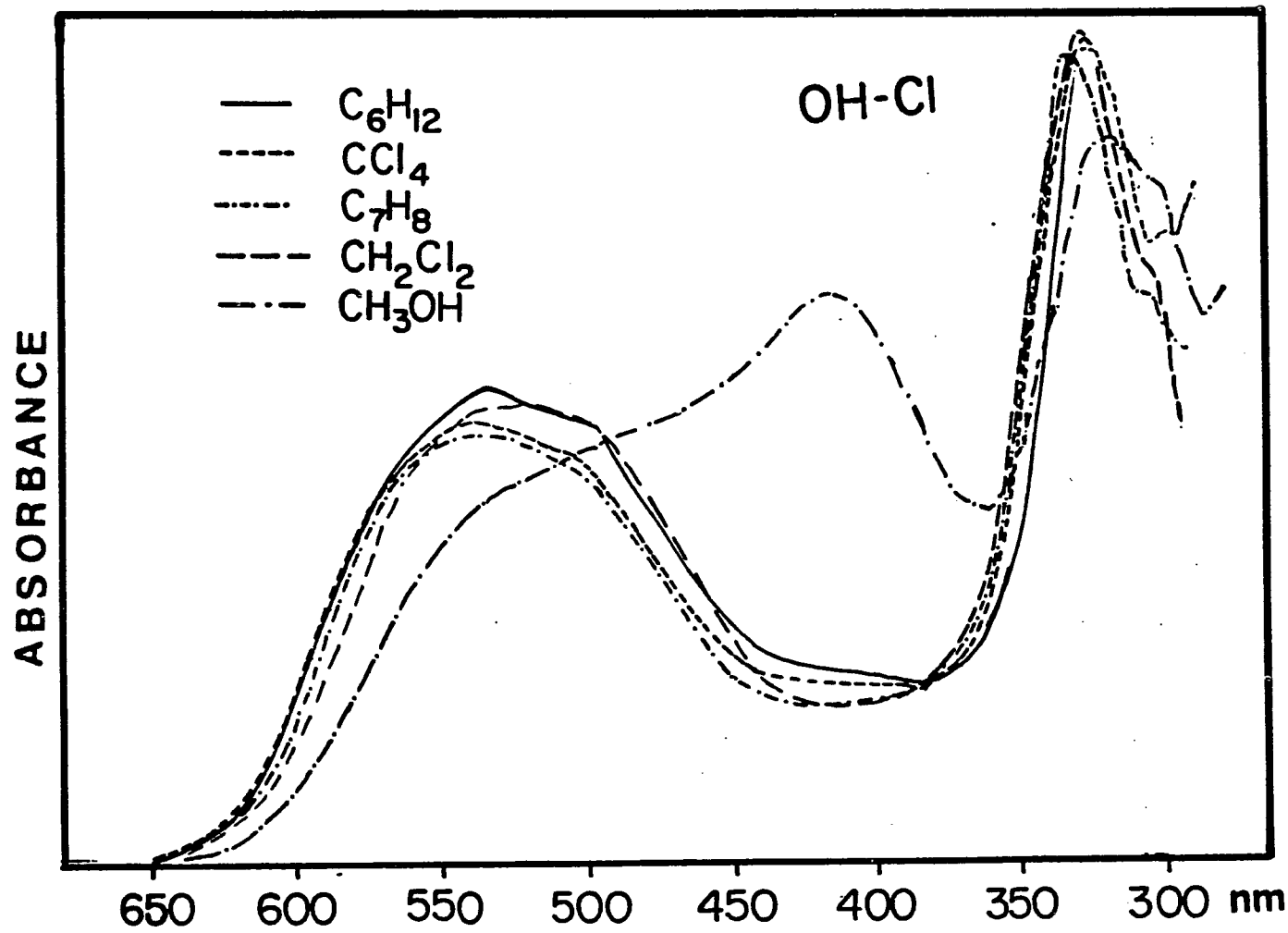

OH-Cl
C_6H_{12}
CCl_4
C_7H_8
CH_2Cl_2
CH_3OH
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 13

region, the molar absorption coefficient of cyclohexane solutions of the hydroxy-chloro derivative is greater than that found in very polar solutions of this derivative. The ratio between the visible and the ultraviolet molar absorption coefficients is 0.531 to 0.549.

In agreement with the behavior of the spectra of the ortho-hydroxy derivative, the spectra of the hydroxy-chloride derivative in methanol show different contours from those of hydrocarbon solutions. The maximum absorption band at 408 nm and a broad shoulder near 530 nm indicate the existence of an equilibrium between the red and yellow forms; the equilibrium favors the formation of the yellow form. The absorption characteristics of the phenyl group are also changed by methanol. The wavelength of maximum absorbance in the spectra of methanol solutions is shifted by 7 to 9 nm to the blue with respect to those of hydrocarbon solutions and the derivative molar absorption coefficient is about two thirds smaller than those determined for the substances in hydrocarbon solutions.

Although the spectra of both hydroxy derivatives have similar contours and different solvents have similar effects on their absorption characteristics, the presence of both the chlorine atom in the 5- position and the

hydroxy group in the 2- position of the phenyl group attached to the carbon atom of the formazan system produces definitive changes. See Figure 12. In the visible region the hydroxy-chloro derivative in hydrocarbon solutions has maximum absorbance that is shifted by 4 - 5 nm to the blue and by 2 nm to the blue for the compound in methanol solutions, with respect to that of the ortho-hydroxy derivative in the same solvents. In the ultraviolet region the shift of the maximum of the spectrum of the compound in all solvents is 8 to 9 nm to the red.

The hydroxy-chloro derivative in hydrocarbon solutions has a visible molar absorption coefficient that is increased by 0.135 to 7.35% and in methanol solutions it is decreased by 10.2%. with respect to that of the ortho-hydroxy derivative in the same solvents. In the ultraviolet region, the hydroxy-chloro absorption coefficients are 1.33% to 10.5% smaller than those of the ortho-hydroxy derivative. Both hydroxy derivatives have similar absorption characteristics; the same spectroscopic differences observed in the case of the ortho-hydroxy derivative with respect to triphenylformazan are valid in the case of the hydroxy-chloro derivative.

6. 3-(2-chlorophenyl)-1,5-diphenylformazan and 3-(2-bromophenyl)-1,5-diphenylformazan. (ortho-chloro and ortho-bromo derivatives).

The absorption spectra of the ortho-halogen derivatives in the different solvents are shown in Figures 14 and 15; their absorption characteristics are summarized in Tables 50 and 51. These derivatives are stable in equilibrium mixtures of the red and yellow isomers; the equilibrium favors the formation of the yellow form as the polarity of the solvent increases. The red form predominates in cyclohexane and carbon tetrachloride solutions and the yellow form is the main component of the equilibrium mixture in toluene, dichloromethane and methanol solutions. When the red form is the predominant species, an unresolved band near 540 nm can be observed.

Since there is a strong influence of the solvent polarity on the equilibrium between the red and yellow isomers, no conclusion or observations about the quantitative effect of the solvent on the molar absorption coefficients and wavelengths of maximum absorbance of the visible transition can be made. The numbers reported in Tables 50 and 51 reflect only the influence of the solvent on the equilibrium distribution and not on the absorption characteristics of either the red or the yellow form.

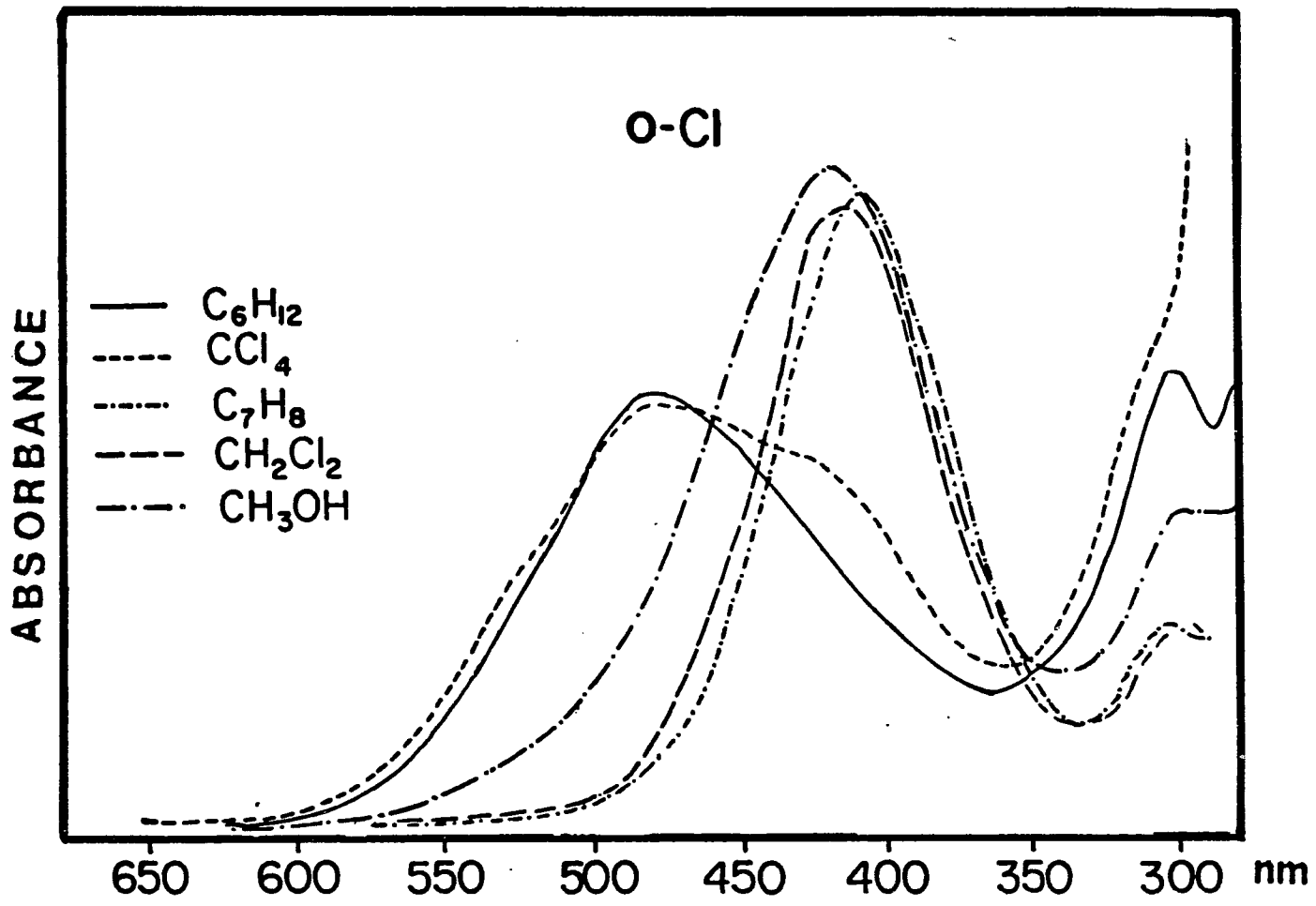

o-Cl
ABSORBANCE
C_6H_{12}
CCl_4
C_7H_8
CH_2Cl_2
CH_3OH
650
600
550
500
450
400
350
300
nm

Figure 14

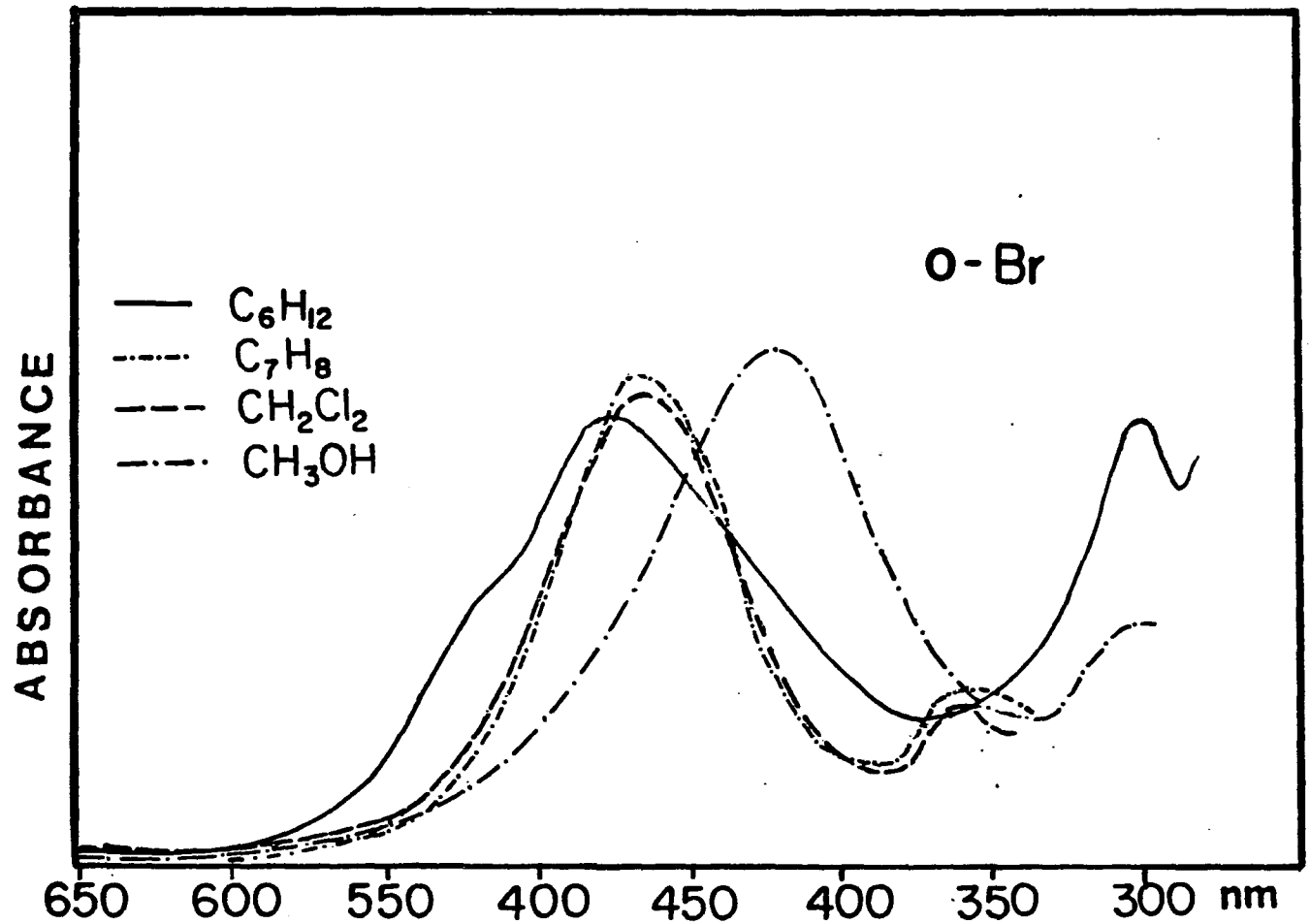

o-Br
C_6H_{12}
C_7H_8
CH_2Cl_2
CH_3OH
ABSORBANCE
650
600
550
400
450
400
350
300
nm

Figure 15

In the ultraviolet region, the band of maximum absorbance corresponds to the transition of the phenyl group. The position of this band shifts toward the red as the polarity of the solvent increases. The molar absorption coefficients are also affected by the nature of the solvent and these results are shown in Tables 50 and 51. Observe that the visible and ultraviolet molar absorption coefficients of both derivatives in cyclohexane solutions are of the same order of magnitude; the ratio between them is almost one. In those solvents in which the yellow form is the predominant species, the absorption coefficient of the phenyl group transition is decreased by approximately 35% with respect to the correponding value of the cyclohexane solutions. These observations are valid for the ortho-chloro as well as for the ortho-bromo derivative. It appears that the chelated ring interacts with the phenyl group much more strongly than does the open azo group.

These derivatives exist as equilibrium mixtures of both yellow and red isomers rather than as a single species in solution; therefore no comparison with triphenylformazan in the corresponding solutions can be made. See Figure 16. Under the experimental conditions, triphenylformazan is stable in its red form(s). Nevertheless, the effect of the size and electronegativity of the halogen placed in the

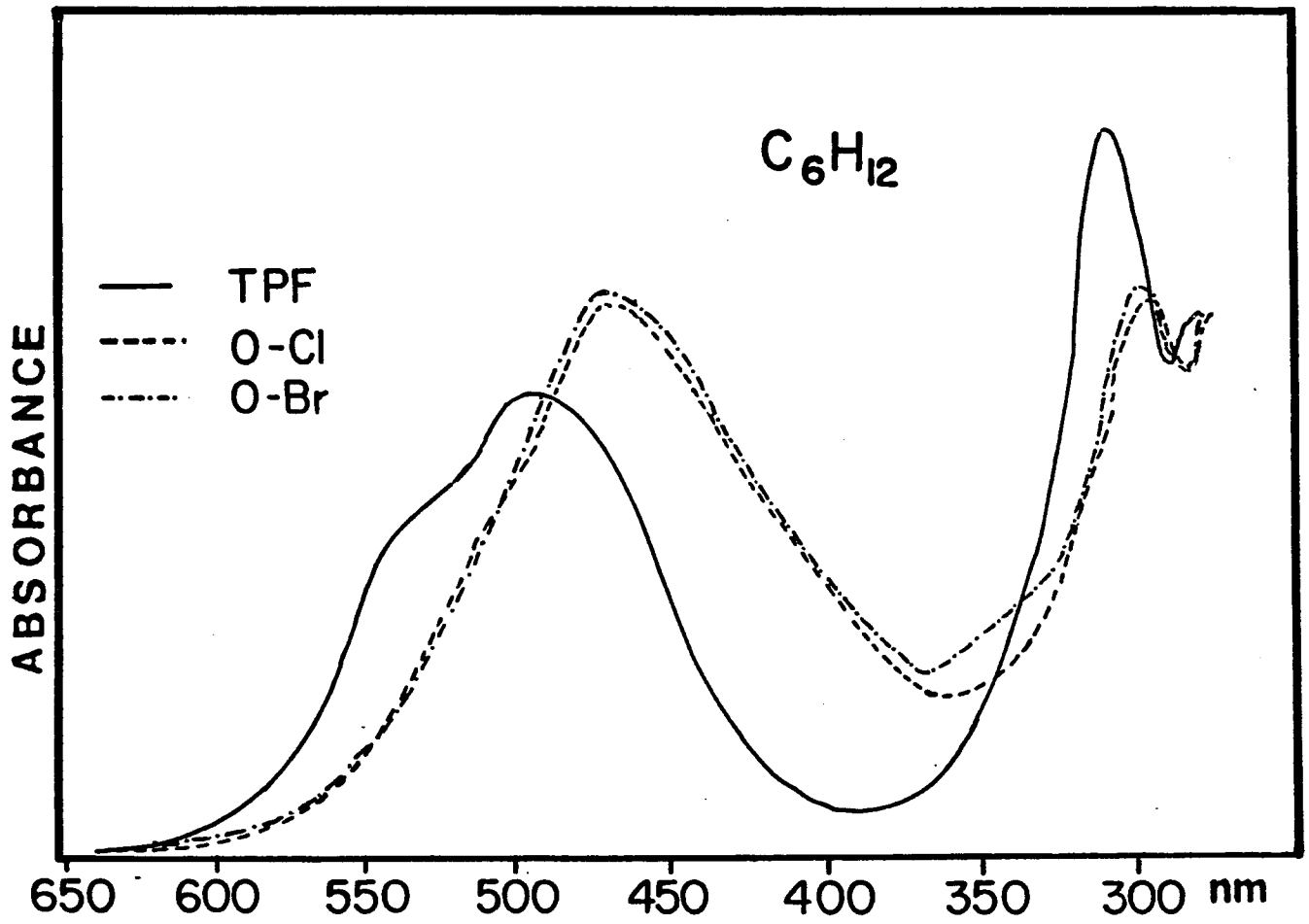

C_6H_{12}
TPF
O-Cl
O-Br
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 16

ortho position of the phenyl group attached to the carbon atom of the formazan ring can be observed in Tables 50 and 51. The larger halogen, the bromine atom, shifts the wavelength of maximum absorbance to the red and decreases the absorption coefficients in both the visible and the ultraviolet regions. This effect is opposite to the behavior of the same substituents in meta or para position in the same phenyl group (Tables 46 and 47); in both cases the effect is very small.

7. 3-(2-naphthyl)-1,5-diphenylformazan. (naphthyl derivative)

In this derivative the phenyl group attached to the carbon atom in the formazan ring has been replaced by a naphthyl group. Figures 17 show the absorption spectra of its cyclohexane, carbon tetrachloride, toluene, dichloromethane and methanol solutions. Table 52 presents its absorption characteristics of the different solutions.

The spectra of the naphthyl derivative in non-polar or low polarity solvents show the maximum absorbance in the visible region near 500 nm. The maximum absorbance is shifted to the blue with increasing polarity of the solvent. Carbon tetrachloride solutions are the exception;

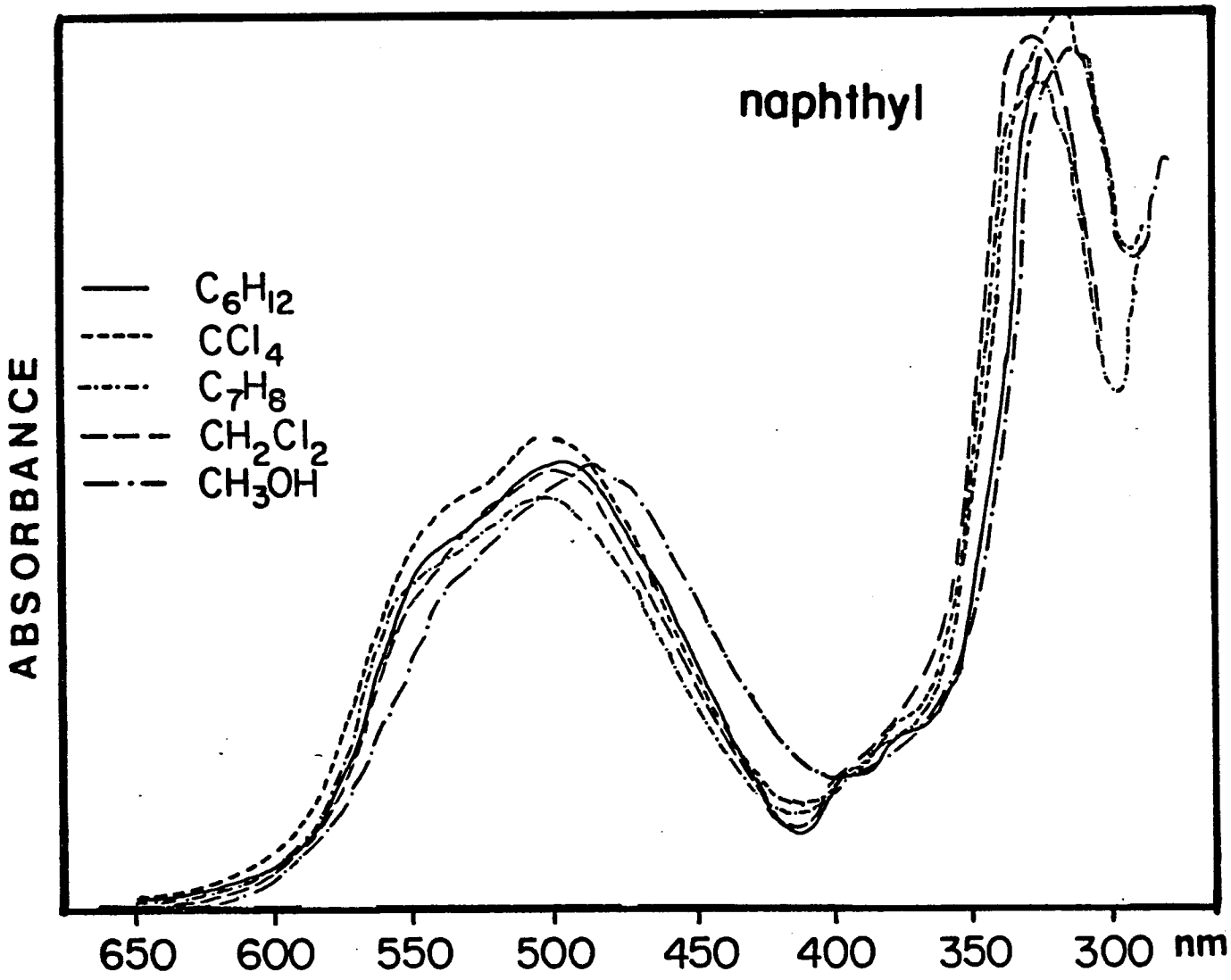

naphthyl
C_6H_{12}
CCl_4
C_7H_8
CH_2Cl_2
CH_3OH
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 17

the maximum absorbance band appears at 504 nm. There is a second unresolved band between 530 and 540 nm. The ratio between the maximum absorbance and the absorbance at 535 nm varies from 1.145 to 1.310. In general this ratio increases with the polarity of the solvent, but the ratio is less for carbon tetrachloride and toluene solutions than for cyclohexane solutions. The visible molar absorption coefficient of the derivative varies between 13,976 in methanol solutions and 15,366 ($M^{-1}cm^{-1}$) in cyclohexane solutions. In the ultraviolet region, the maximum absorbance appears between 317 and 320 nm in the spectra of hydrocarbon solutions. The position of this band is shifted to the red as the polarity of the solvent increases. The methanol solution shows the ultraviolet band at 316 nm. The ultraviolet molar absorption coefficients vary between 27,564 and 31,017($M^{-1}cm^{-1}$). There is a second band of much lower intensity near 330 nm. In general a polar solvent decreases the molar absorption coefficient of the naphthyl derivative in both the ultraviolet and visible region. The exception is dichloromethane; the ultraviolet absorption coefficient of the naphthyl derivative in dichloromethane solutions is very large. The ratio between the visible and the ultraviolet molar absorption coefficient varies between 0.494 and 0.531.

The band near 500 nm corresponds to the transition of the formazan ring in the red isomer. The band near 320 nm corresponds to the absorption of both the naphthyl and the phenyl group that are shifted to the red by the presence of the formazan system. The spectrum of naphthalene in 95% ethanol shows a band at 312 nm with a second smaller band near 320 nm[69].

The results of the naphthyl derivative present several differences with respect to the results of triphenylformazan. See Figure 18. The visible absorption band of the naphthyl derivative is shifted to the red with respect to that of triphenylformazan. The shift varies between 7 to 17 nm and it depends on the nature of the solvent. The derivative molar absorption coefficients in the visible range are 8.8% to 13.1% smaller than those of triphenylformazan. The ratio between the maximum absorbance and the absorbance at 535 nm of triphenylformazan is 1.2 times higher than that of the naphthyl derivative; the dependence of this ratio on the nature of the solvent is the same for both triphenylformazan and the naphthyl derivative. The nature of the unresolved band near 530 nm is discused later.

The naphthyl derivative exists as an equilibrium

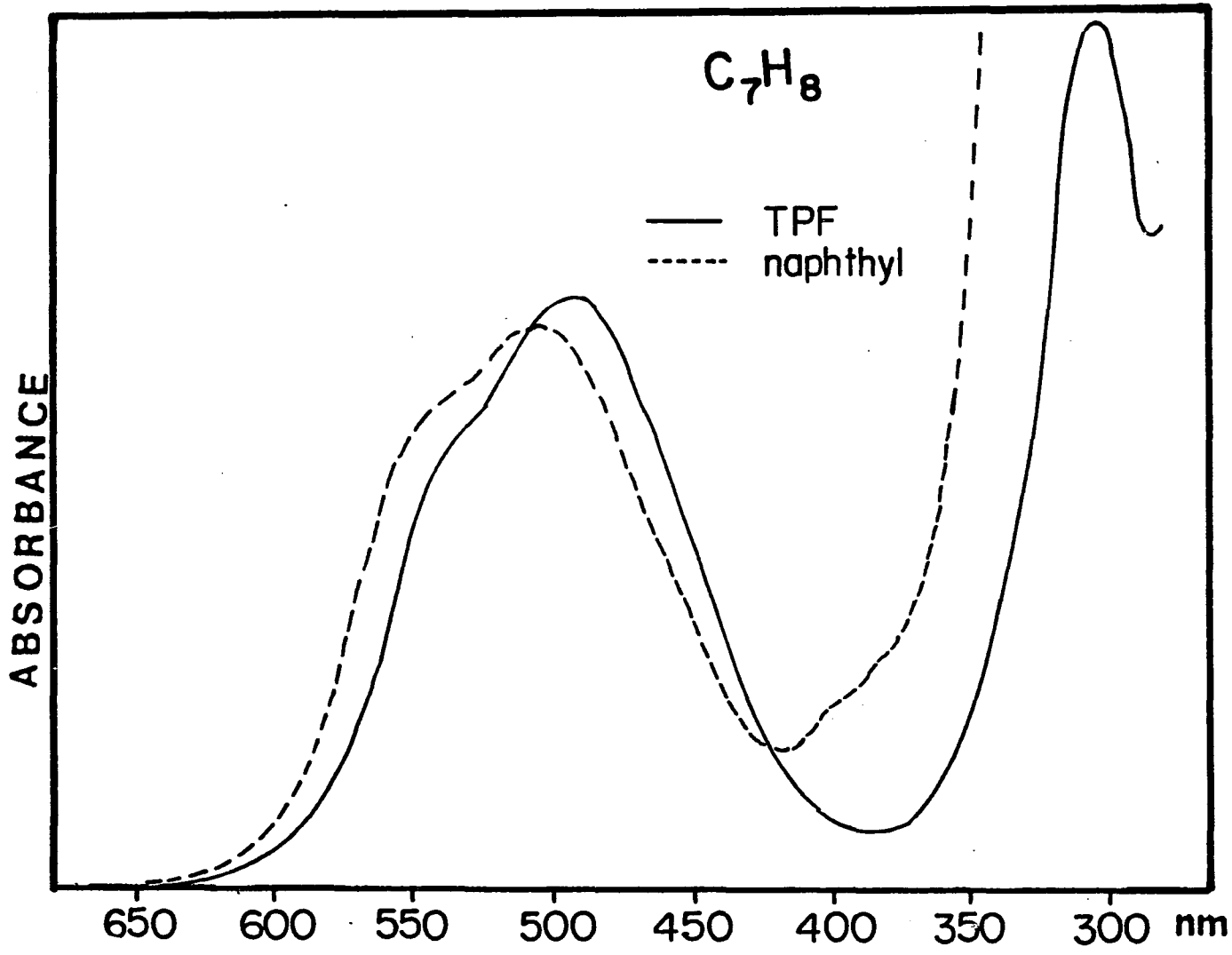

C_7H_8
TPF
naphthyl
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 18

mixture of the yellow and the red isomers; the equilibrium favors the formation of the red isomer. The presence of the yellow form is indicated by two low intensity bands between 370 and 400 nm the intensity and resolution of which depend on the nature of the solvent. In the spectra of methanol and dichloromethane solutions these bands appear only as an inflection on the side of the band at 320 nm. In the spectra of toluene solutions, the band near 400 nm is more easily seen but still unresolved from the band at 370 nm. The bands become differentiable as two shoulders in the spectra of carbon tetrachloride solutions and as two different bands in the spectra of cyclohexane solutions. The ratio between the absorbances at 370 and 395 nm increases with the polarity of the solvent.

The results reported in this section can be summarized:

- The substitution of a hydrogen atom in the para or meta position in the phenyl group attached to the carbon in the formazan ring by a halogen atom does not appreciably change the absorption characteristics of triphenylformazan.

- The substitution of a hydrogen atom in the ortho position in the same phenyl group by a halogen atom or a hydroxy group does affect appreciably the absorption characteristics of triphenylformazan. When the substituent

in the ortho position is a halogen atom, the formazan ring becomes very sensitive to the nature of the solvent. A highly polar solvent favors the formation of the yellow isomer; in a non polar solvent the stable form is the red isomer. The nature of the halogen atom substituent does not have a major effect upon the absorption characteristics of these derivatives. When the substituent in the ortho position is the hydroxy group, the compound is not photochromic and exists as an equilibrium mixture of the red and yellow isomers; the equilibrium favors the formation of the yellow form as the polarity of the solvent increases. The presence of an additional substituent in the same phenyl group does not change appreciably the spectrum of this derivative.

- When the C-phenyl group is replaced by a naphthyl group, the absorption characteristics of the formazan ring change. The nature of the species present in the equilibrium mixture depends on the nature of the solvent. The relative intensities of the band near 490 nm and the shoulder near 540 nm are different from those of the bands of triphenylformazan. This result gives an insight of the nature of the band appearing as a shoulder at 540 nm. Temperature studies and the effect of the solvent on the relative intensity between the absorbances at 490 nm and 540 nm suggest that they correspond to electronic

transitions of different structures of the red isomer. This result is partially confirmed by molecular mechanics and CNDO calculations made on the triphenylformazan molecule.

C. Temperature and Alcohol Effects on the Absorption Spectra of 3-(2-hydroxyphenyl)-1,5-diphenylformazan.

The absorption spectra of the ortho-hydroxy and the chloro-hydroxy derivatives in methanol solutions show contours different from those of the same compound in hydrocarbon solvents. The absorption of the yellow form at 406 nm and a broad shoulder in the vicinity of 530 nm can be observed. It is known from determinations of the spectrum of the compound in other solvents that the red form of the ortho hydroxy derivative has an absorption maximum near 530 nm. The presence of these two bands in the spectra indicates that there is an equilibrium between the red and the yellow forms which should be temperature dependent. Figure 19 presents the temperature dependent spectra of a $4.94*10^{-5}$ M solution of the ortho-hydroxy derivative in methanol. It can be observed that, as the temperature increases, the equilibrium is displaced towards the formation of the red form. The decrease in the absorbance of the yellow form is larger (0.412) than the

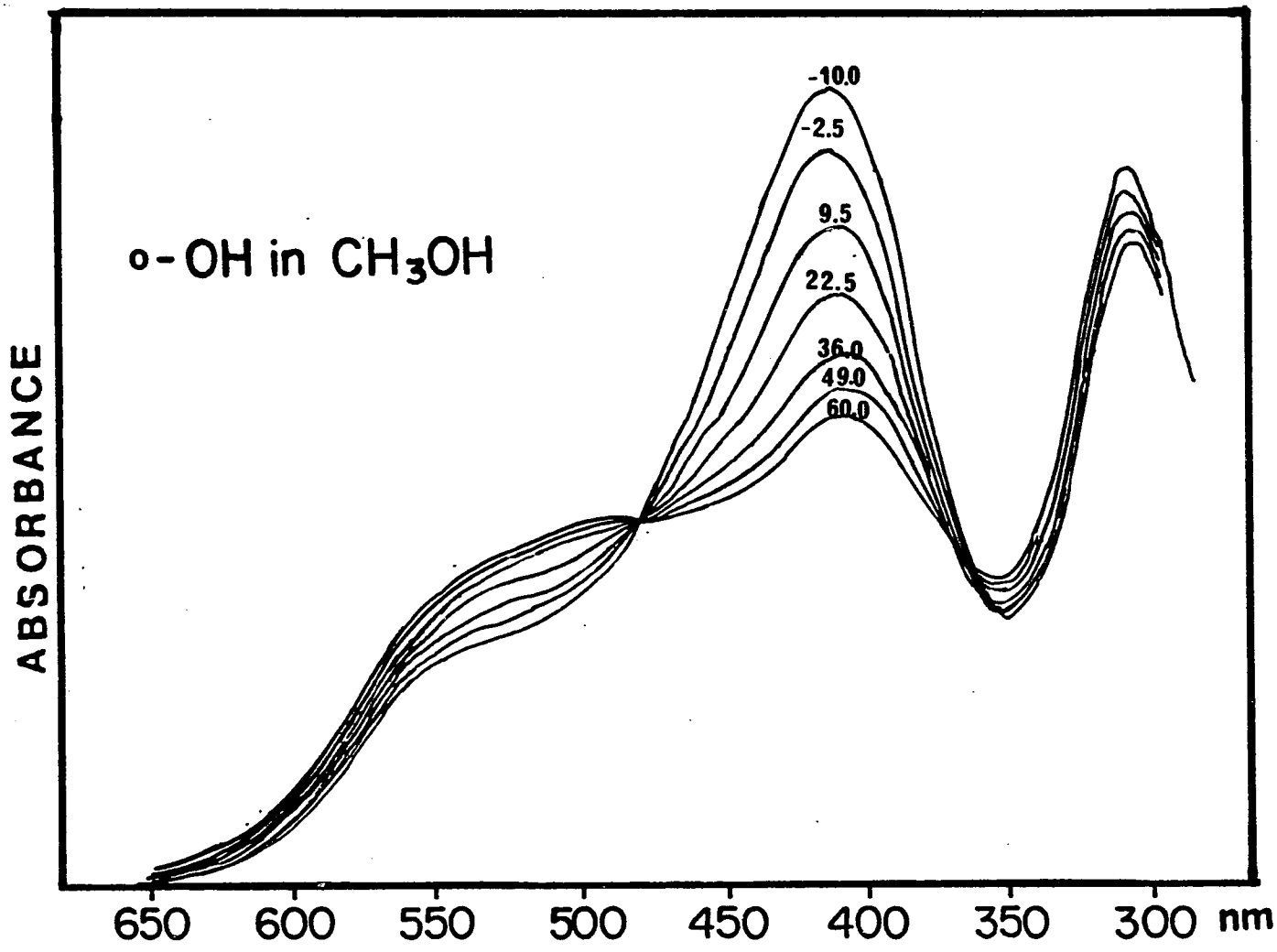
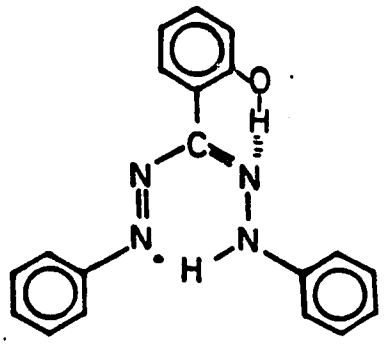

o-OH in CH3OH
-10.0
-2.5
9.5
22.5
36.0
49.0
60.0
ABSORBANCE
650
600
550
500
450
400
350
300
nm

Figure 19

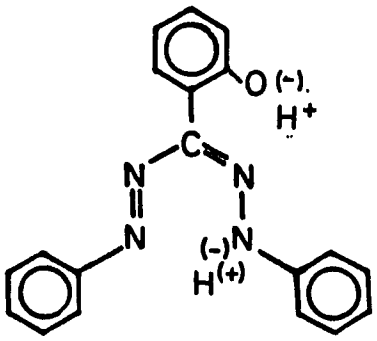
increase (0.276) in the absorbance of the red form. This relative difference may be due to the overlapping of the yellow and red absorptions and to differences between the molar absorption coefficients of the two isomers. As one absorption increases with the temperature, the other absorption decreases and there is a partial cancellation of the expected changes in the absorbances which results in a less marked change for the red form. In Figure 2 the contour of the absorption bands of the pure red and yellow forms of triphenylformazan in a toluene solution are presented.

These results for the temperature dependence of the absorption spectra of the ortho-hydroxy derivative in methanol solutions raise two questions: Why is the yellow form of this derivative more stable in a polar solvents and why is the equilibrium between the red and yellow forms displaced toward the formation of the red form as the temperature increases.

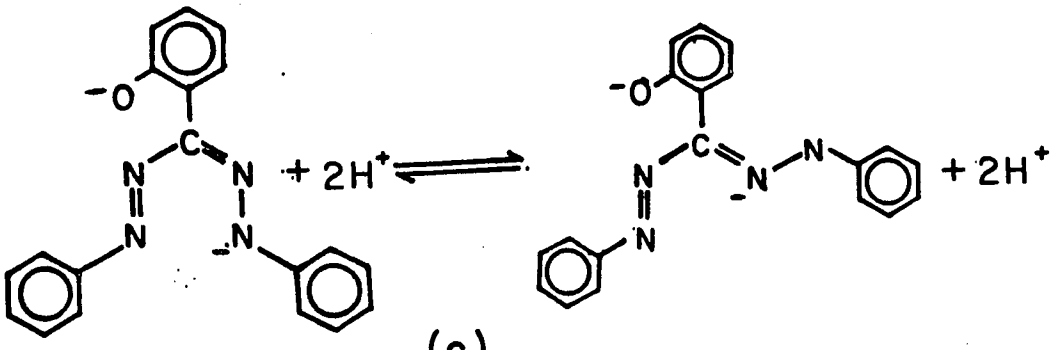
If the structure of the chelated form were as it is shown in Figure 20a, a strong hydrogen bond between the hydroxylic hydrogen and a nitrogen of the formazan ring would exist and the red form would predominate as it does in solvents less polar than methanol. An increase in the



(a)



(b)



(c)

Figure 20

temperature would promote the opening of the formazan ring to yield the yellow form. The experimental results show that the expected phenomenon does not occur and an explanation for these results could be the existence of a different structure for the red form of the ortho-hydroxy derivative in methanol; such a possibility is the one illustrated in Figure 20b.

The ^{1}H NMR spectra of the ortho-hydroxy derivative in cyclohexane and in acetonitrile were recorded by means of a 100 MHz NMR spectrometer. They are shown in Figures 21 and 22. In cyclohexane there are three main groups of bands at 15.3 ppm 10.5 ppm, and the characteristic bands of a phenyl group between 7 and 8 ppm. The peak at 15.3 ppm corresponds to the NH hydrogen,[65] and the band at 10.5 ppm to the OH hydrogen. These two bands were assigned on the basis of the results of the spectrum of the same solution with trace amounts of D_2O, which is supposed to eliminate the band of the OH hydrogen. Although both bands, due to OH and NH protons, decrease in intensity in the presence of D_2O, the decrease of the band at 10.5 ppm is greater than that for the band at 15.3 ppm. In acetonitrile, the bands at 15.3 and 10.5 ppm are almost completely eliminated, and one of the bands of the phenyl group has been completely eliminated.

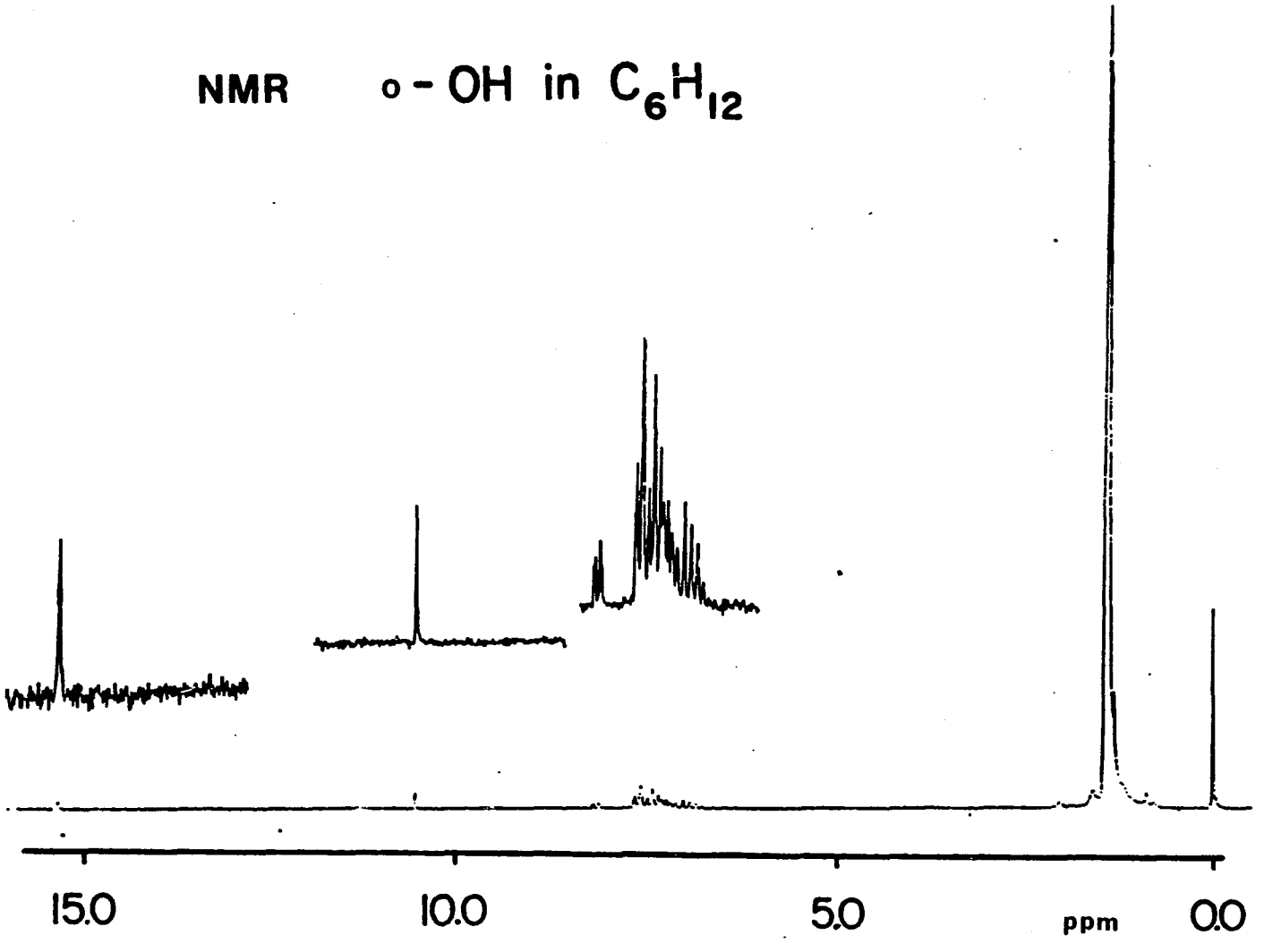


Figure 21

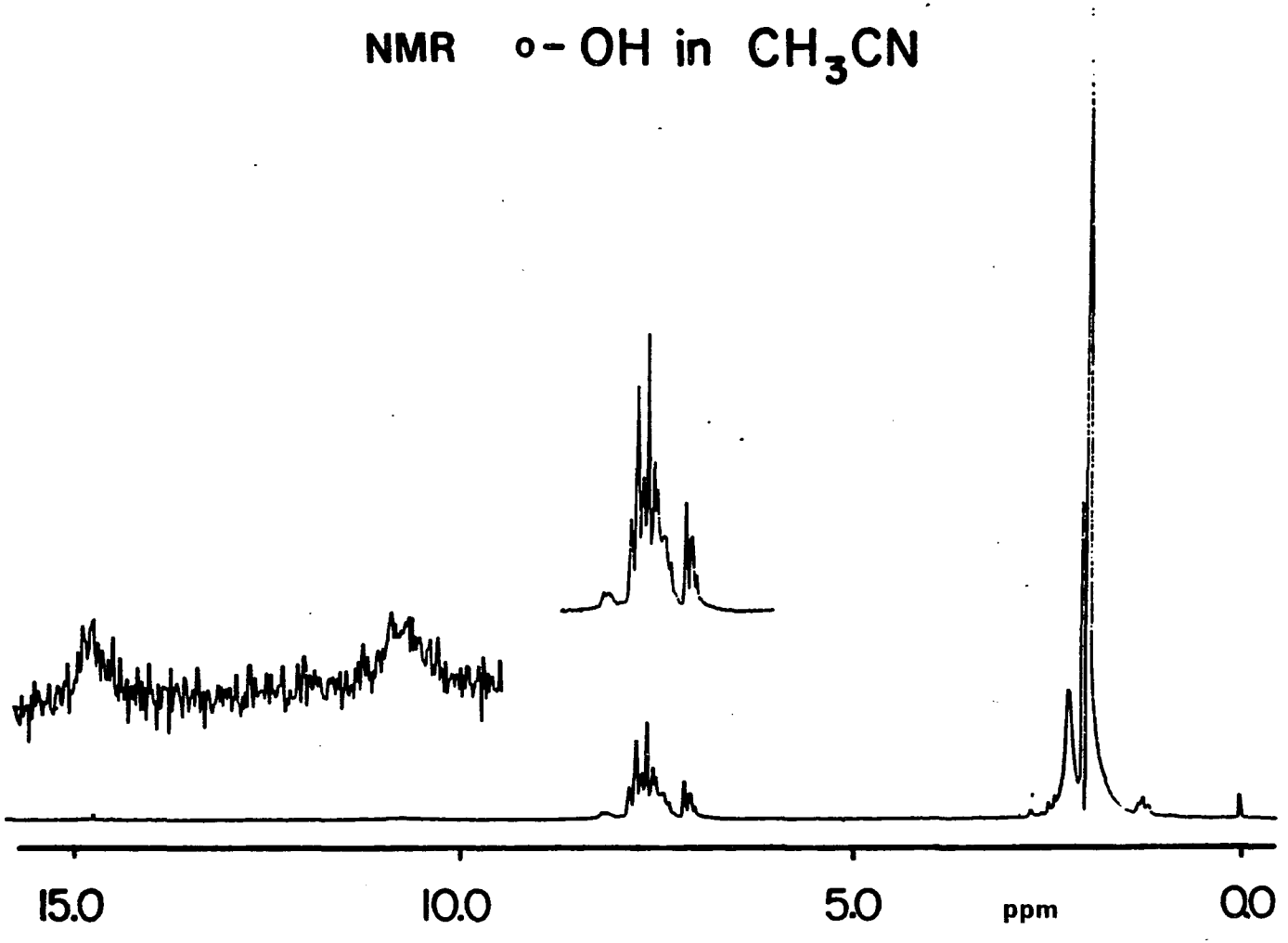


Figure 22

Although no complete assignment of all the bands in the spectrum were made, the disappearance of the bands of NH and OH in acetonitrile indicate that both hydrogens in a polar solvent are highly mobile. In the absorption spectrum of a 5.07x10-5 M solution of the ortho-hydroxy derivative in acetonitrile at room temperature, two absorption bands appear at 492 and 395 nm. This result indicates the presence of an equilibrium mixture of the yellow and the red forms. The high mobility of the NH and OH hydrogens in the ortho-hydroxy derivative explains the presence of the yellow form in polar solvents. See Figure 20c.

Figures 23 and 24 present the temperature dependence of the spectra of triphenylformazan in methanol and n-butanol solutions. The maximum absorbance of the red form of triphenylformazan near 480 nm decreases as the temperature increases in both methanol and n-butanol solutions. The wavelength of maximum absorbance shifts to the blue at higher temperatures. The ratio between the maximum absorbance and the absorbance at 535 nm also increases with temperature. The absorbance near 400 nm, where the absorption band of the yellow form appears, increases with temperature. This result indicates that triphenylformazan in methanol solutions also exists in an equilibrium mixture; the equilibrium is almost completely

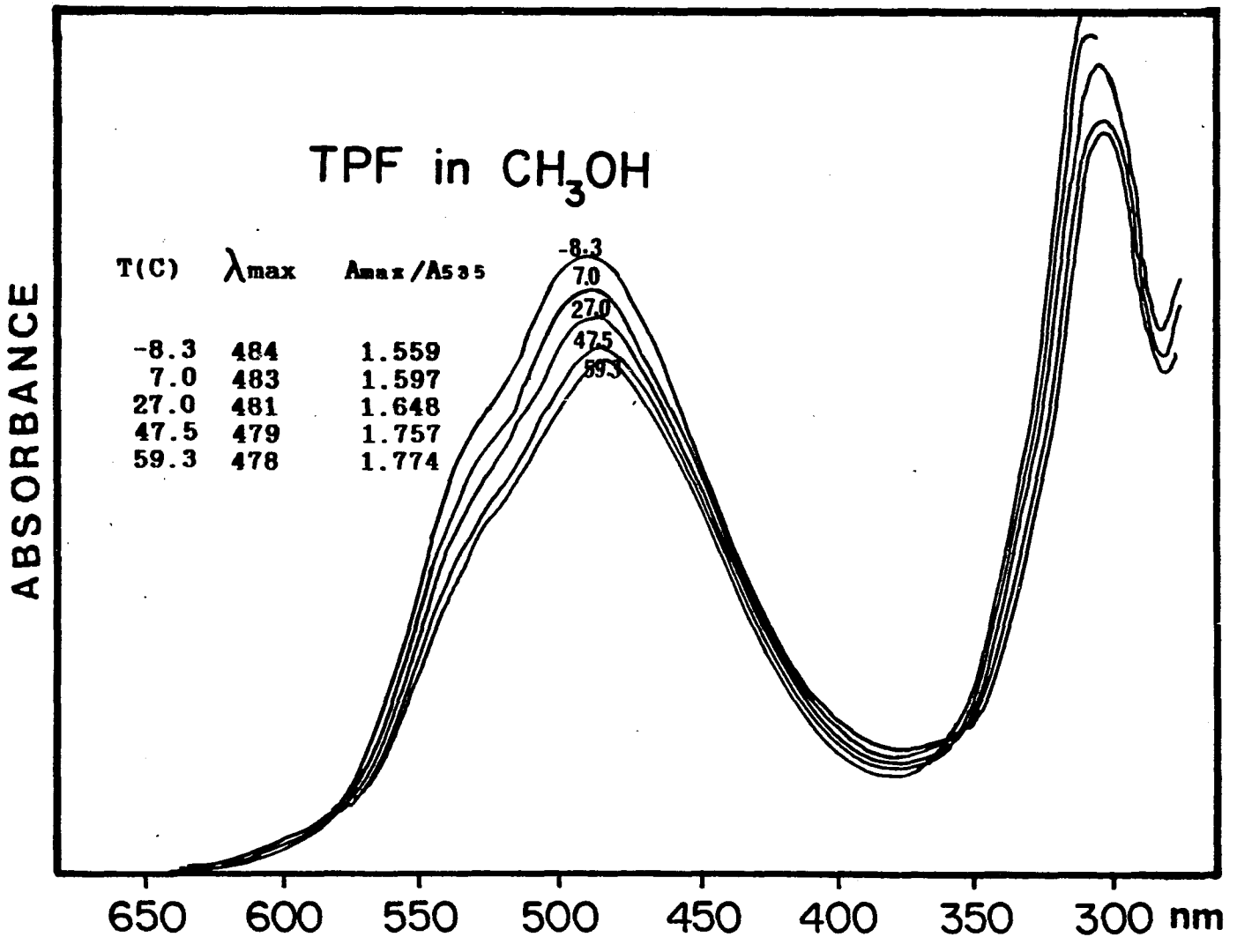

TPF in CH_3OH
T(C) λmax Amax/A535
-8.3 484 1.559
7.0 483 1.597
27.0 481 1.648
47.5 479 1.757
59.3 478 1.774
-8.3
7.0
27.0
47.5
59.3
ABSORBANCE
650 600 550 500 450 400 350 300 nm

Figure 23

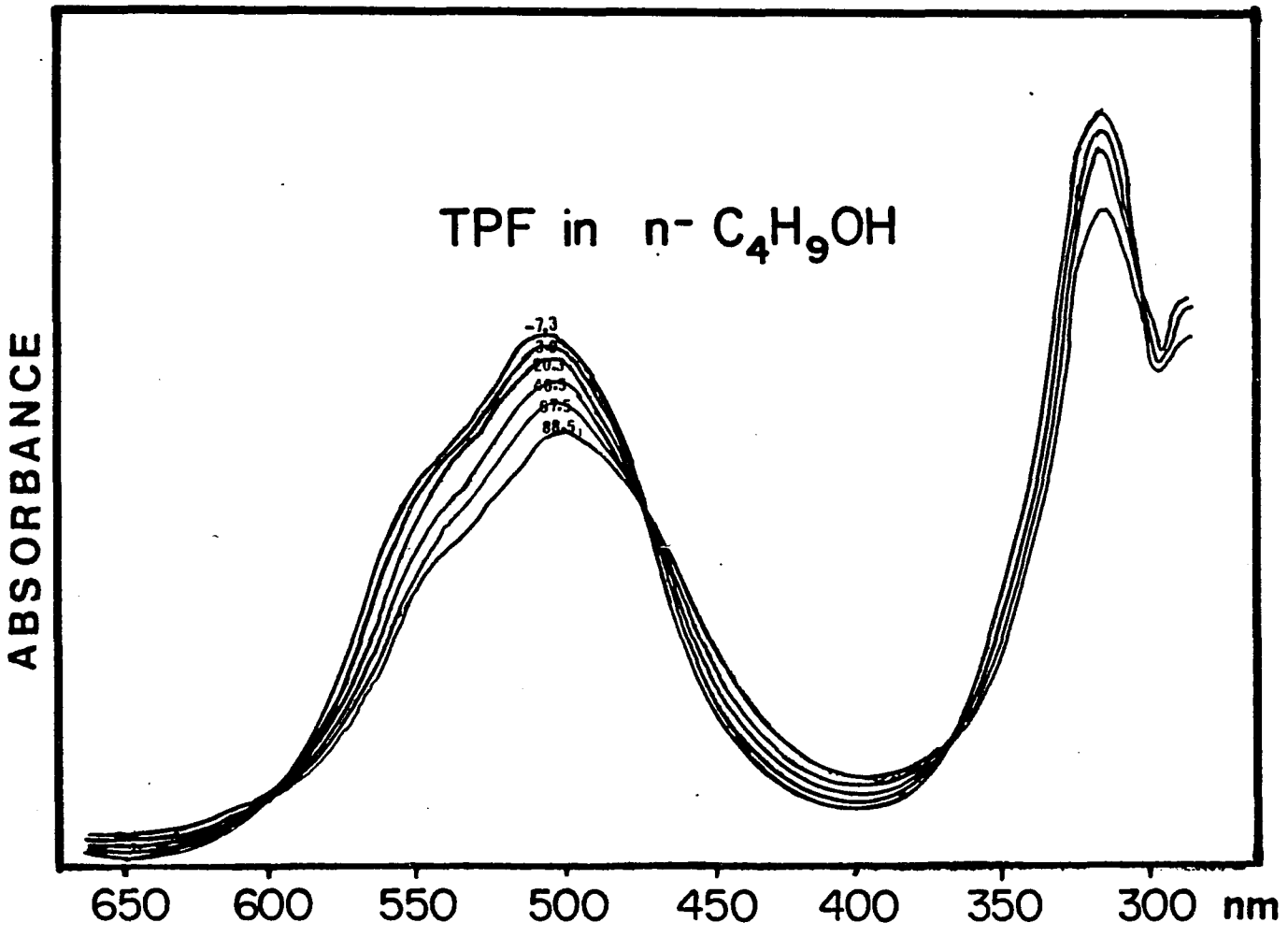
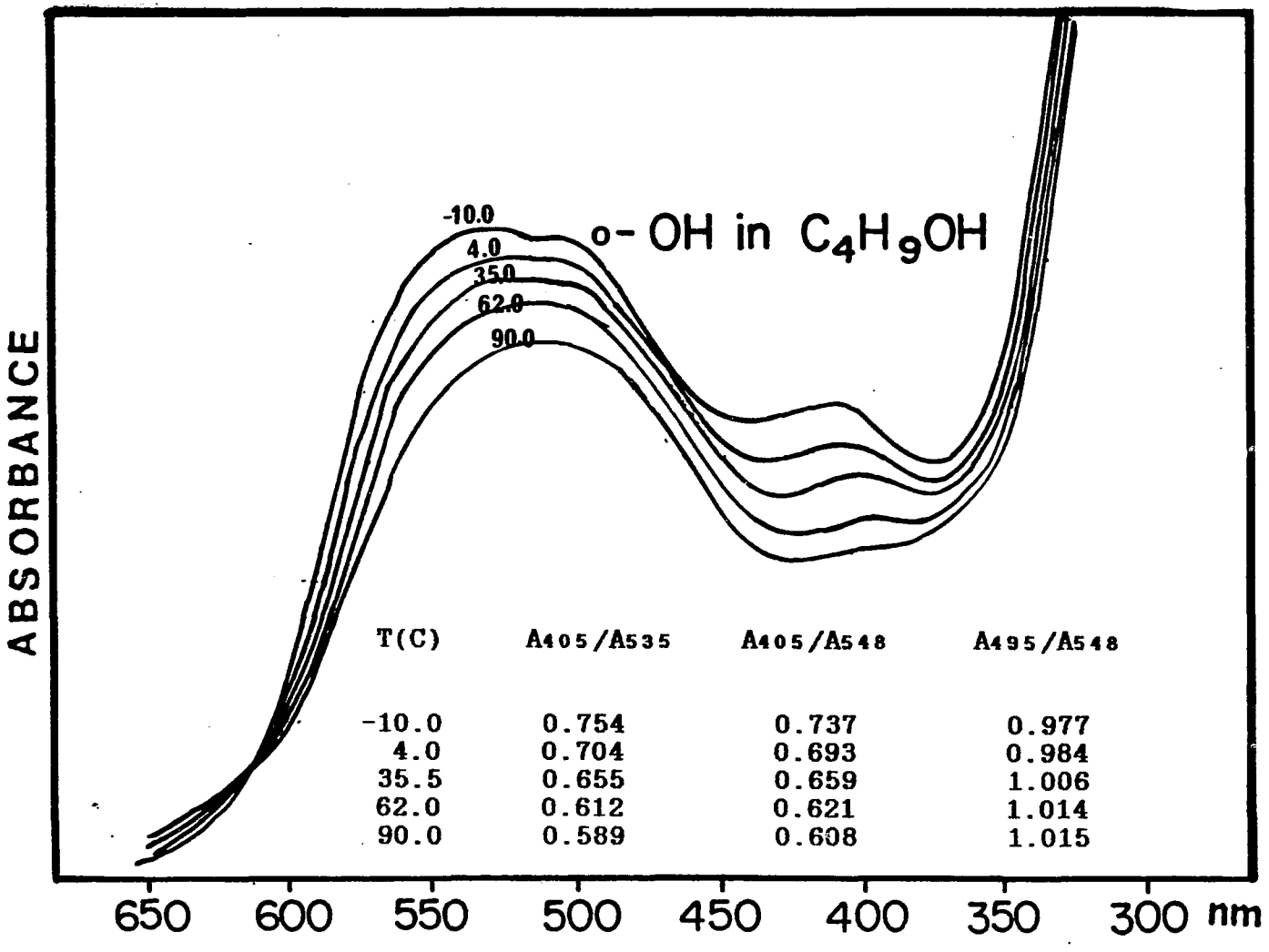


Figure 24

displaced toward the formation of the red form. However, in none of these alcoholic solvents is the equilibrium displaced enough to observe clearly the yellow band.

Figure 25 shows the temperature dependent spectra of the ortho-hydroxy derivative in a 4.28×10^{-5}M n-butanol solution. Both the yellow and the red forms are present in the mixture; the equilibria in the n-butanol solutions favor the formation of the red forms. The intensities of both the yellow and red absorption bands decrease as the temperature increases; nevertheless the ratio between the absorbance at 405 nm and the absorbance between 495 and 550 nm decreases as the temperature increases. (See Table in Figure 25). This result indicates that although both the red and the yellow bands have lesser intensities at higher temperatures the equilibria are displaced toward the formation of the red forms and the behavior is reminiscent of that of methanol solutions. The ratio between the absorbances at 495 and 550 nm also increases with temperature. A shift of the wavelength of maximum absorbance to the blue with increasing temperature is observed. The absence of isosbestic points suggests that more than two forms are involved in the equilibrium.

Figures 26 and 27 show the temperature dependent



T(C)	A405/A535	A405/A548	A495/A548
-10.0	0.754	0.737	0.977
4.0	0.704	0.693	0.984
35.5	0.655	0.659	1.006
62.0	0.612	0.621	1.014
90.0	0.589	0.608	1.015

Figure 25

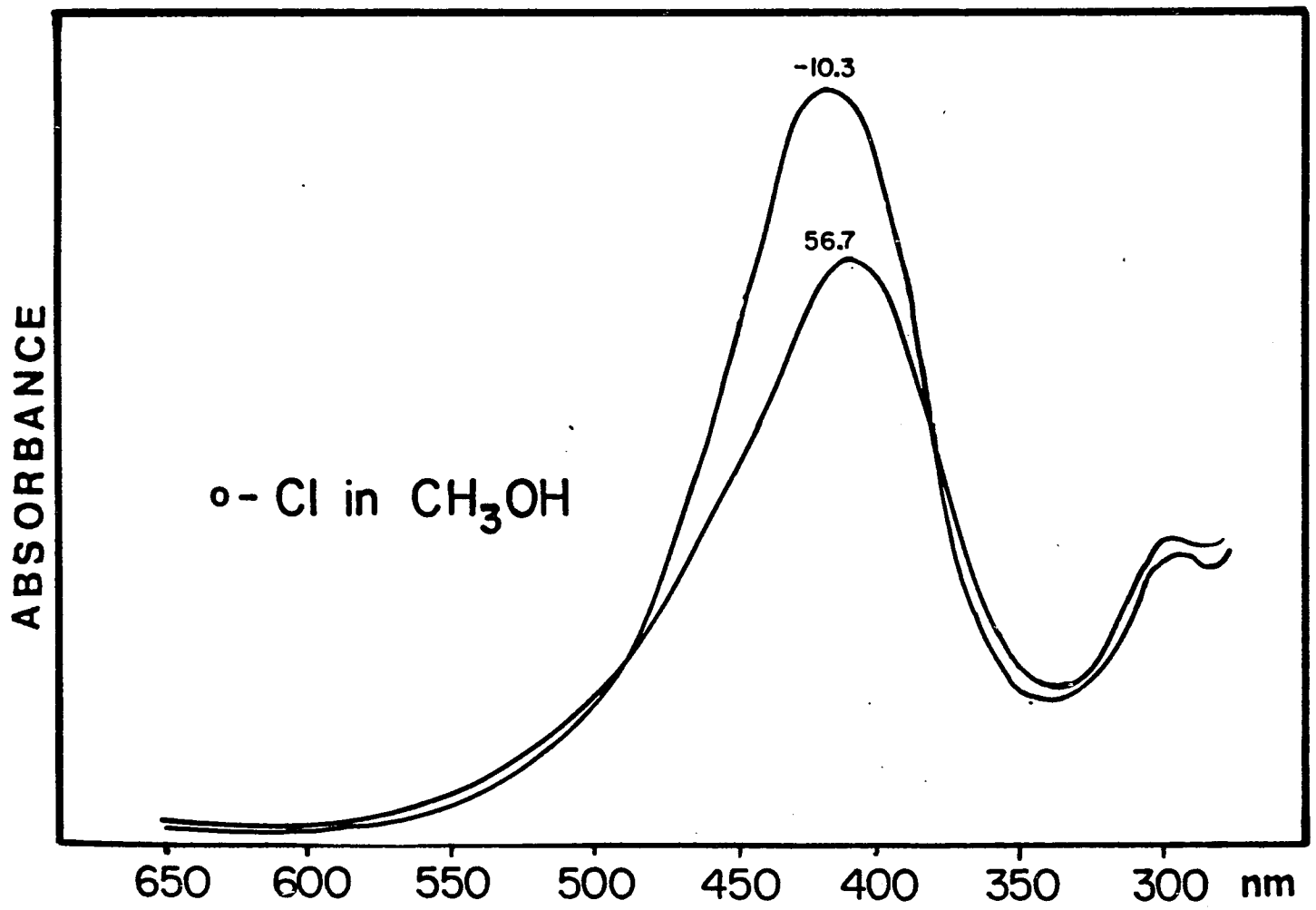

-10.3
56.7
o- Cl in CH_3OH
ABSORBANCE
650
600
550
500
450
400
350
300
nm

FIGURE 26

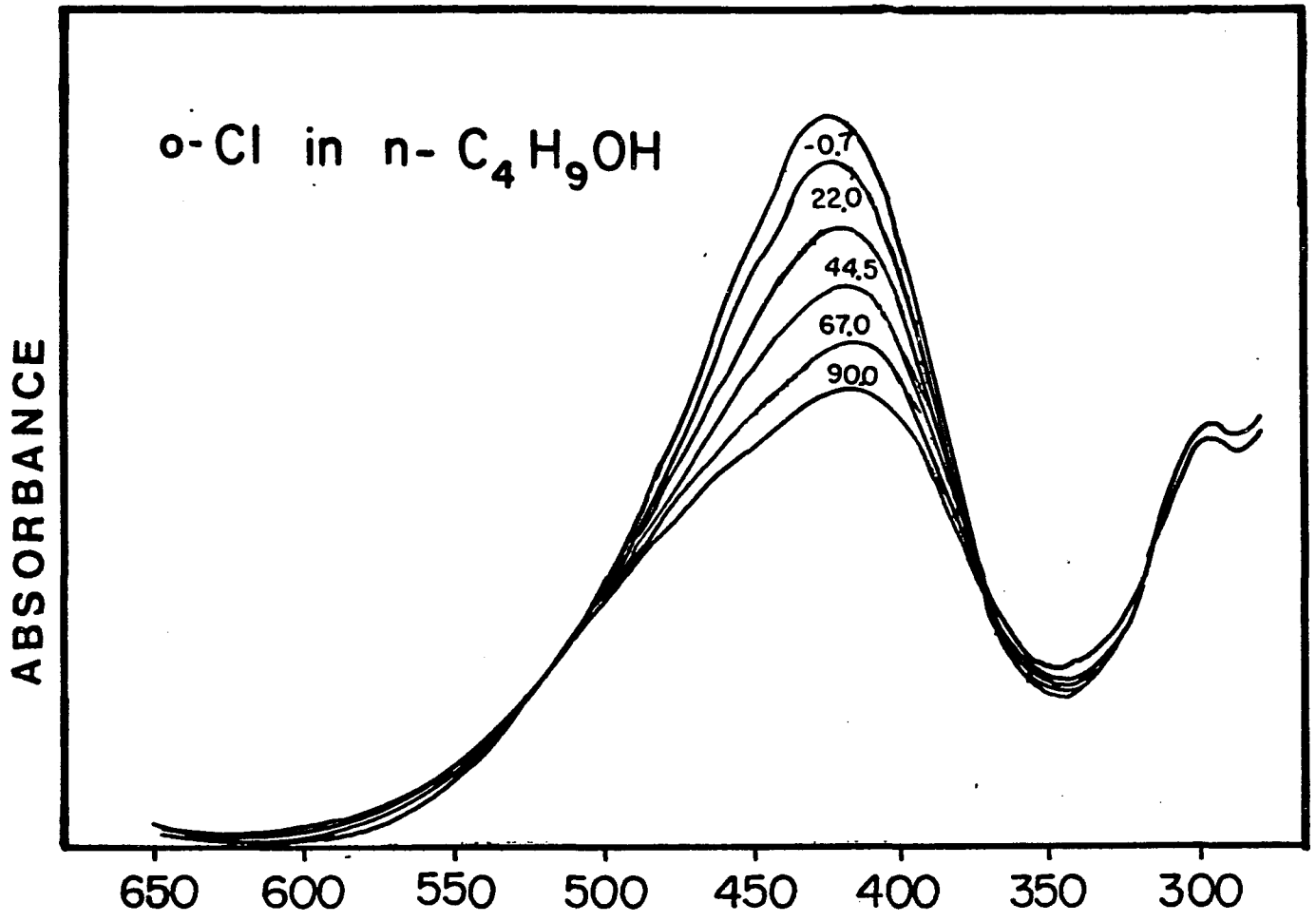

o-Cl in n- C_4H_9OH
-0.7
22.0
44.5
67.0
90.0
ABSORBANCE
650
600
550
500
450
400
350
300

Figure 27

spectra of the ortho-chloro derivative in methanol and n-butanol solutions. In alcoholic solutions of this derivative the yellow form is the predominant form in the equilibrium mixture. The absorption band of the yellow form appears near 410 nm; its intensity and the wavelength of maximum absorbance is shifted to the blue as the temperature increases. Although it is difficult to observe an absorption band of the red form in the spectra at low temperature, its presence becomes evident at higher temperatures; the absorbance between 480 and 550 nm increases. No major effect of the nature of the alcohol on the absorption characteristics of this derivative can be observed.

Comparison of the results of the temperature dependence of the spectra of triphenylformazan and the two derivatives in methanol and n-butanol solutions indicates that, in the cases of the ortho hydroxy and chloro derivatives, the equilibrium between the red and the yellow forms is displaced toward the formation of the red forms as the temperature increases. In the case of triphenylformazan high temperatures favor the yellow forms. The intensity of the red band in the spectra of triphenylformazan and that of the yellow band in the spectra of the ortho-chloro derivative decrease as the

temperature increases. This decrease in intensity is not only an effect of the change in the equilibria between the red and the yellow forms, but also an effect of the change in the distribution of the red forms. The maximum absorbance of the red as well of the yellow band is shifted to the blue as the temperature increases.

In the spectra of the ortho-hydroxy derivative, in which both the yellow and red forms have easily observable absorption bands, an effect of the nature of the solvent can be observed. In methanol solution the yellow form predominates in the equilibrium mixture while in n-butanol solutions, the equilibrium favors the formation of the red isomer. Figure 28 shows the spectra of the ortho-hydroxy derivative in a series of alcoholic solutions. A displacement of the equilibrium between the red and the yellow forms toward the formation of the red form is observed as the size of the alcohol molecules increases. Table 53 presents the values of the ratio between the maximum absorbance of the yellow form and the maximum absorbance of the red form. As the size of the aliphatic chain of the alcohol increases, this ratio decreases from 1.924 for methanol solutions to 0.633 for iso-butanol solutions. Notice that the value of this ratio for the methanol solution is almost twice the value for the ethanol

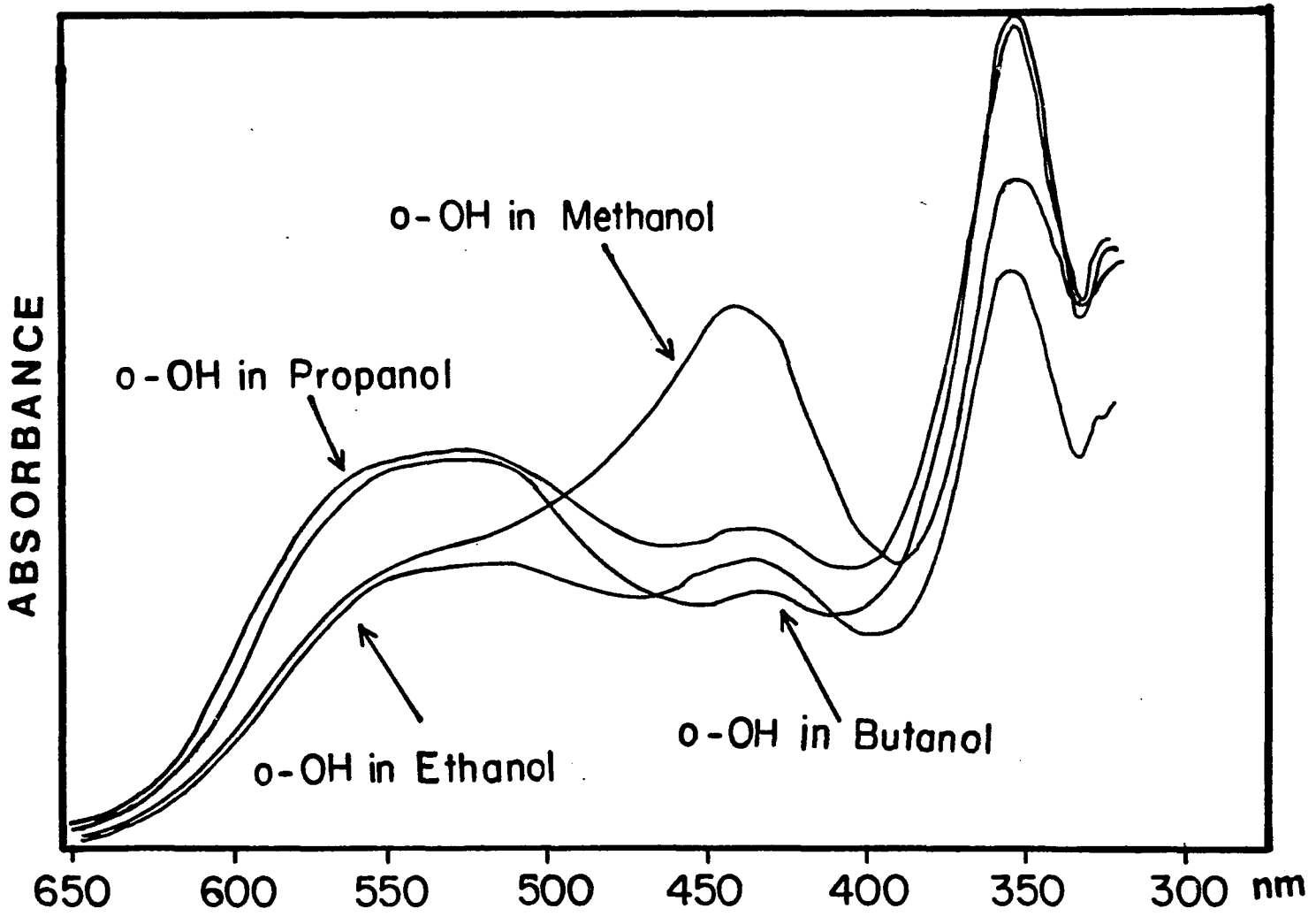

ABSORBANCE
o-OH in Methanol
o-OH in Propanol
o-OH in Ethanol
o-OH in Butanol
650
600
550
500
450
400
350
300
nm

Figure 28

solution. The difference between the values of this ratio for the methanol and ethanol solutions is 2.25 times the difference between the values for the ethanol and iso-butanol solutions.

In the spectrum of the methanol solution the red band appears as a shoulder of the yellow band. In the spectra of the other alcoholic solutions of the ortho-hydroxy derivative the red band is resolved from the yellow band and it is a broad band. Although the change is very subtle, the ratio between the absorbances at 495 and 525 nm also decreases as the size of the alcohol increases. See Table 53. The absorption spectra of triphenylformazan in alcoholic solutions do not present appreciable changes as the size of the alcohol solvent molecules increases.

D. 3-(2-naphthyl)-1,5-diphenylformazan.

Temperature Effect on the Relative Intensity of the Band near 490 nm and the Shoulder near 535 nm

The naphthyl derivative shows an appreciable change in the relative intensities of the absorption bands of the red form with respect to those of triphenylformazan; nevertheless it retains the same contour as triphenylformazan in the different solvents. In order to

investigate the nature or origin of the bands of the red form, the temperature dependence of the absorption spectra of triphenylformazan and the naphthyl derivative in the different solvents was studied. Figures 29 to 31 show the temperature dependence of the spectra of triphenylformazan in carbon tetrachloride, toluene and cyclohexane solutions respectively. Figure 19 shows the temperature dependence of the spectra of methanol solutions. Under the experimental conditions (solutions prepared in the dark and spectra recorded inmediately after the solutions were prepared), only the red form is stable in these solvents. There is no unequivocal evidence for the presence of the yellow form. The absorption intensity of the band of the red form decreases as the temperature increases. Since the molar absorption coefficient of the yellow form is, in general, larger than that of the red form, the small change in absorbance near 400 nm cannot represent the total amount of the red form that is apparently converted. Figures 19, and 29 to 31 include the values of the ratio between the maximum absorbance and the absorbance at 535 nm as a function of the temperature. For triphenylformazan in all the solvents this ratio increases as the temperature increases. However the increase of this ratio with the temperature is constant in all the solutions of triphenylformazan.

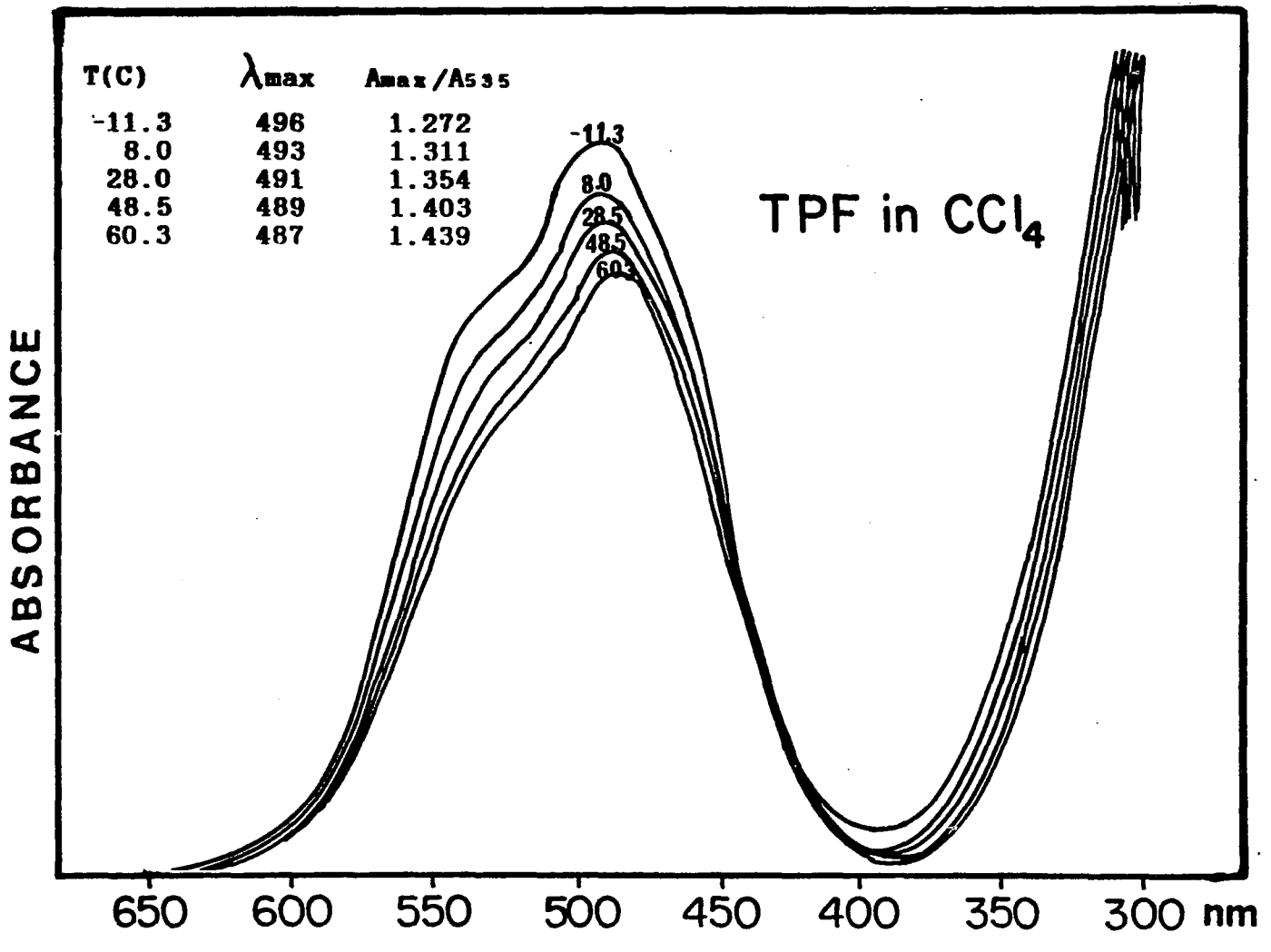

T(C) λmax Amax/A535
-11.3 496 1.272
8.0 493 1.311
28.0 491 1.354
48.5 489 1.403
60.3 487 1.439
-11.3
8.0
28.5
48.5
60.3
TPF in CCl4
ABSORBANCE
650 600 550 500 450 400 350 300 nm

Figure 29

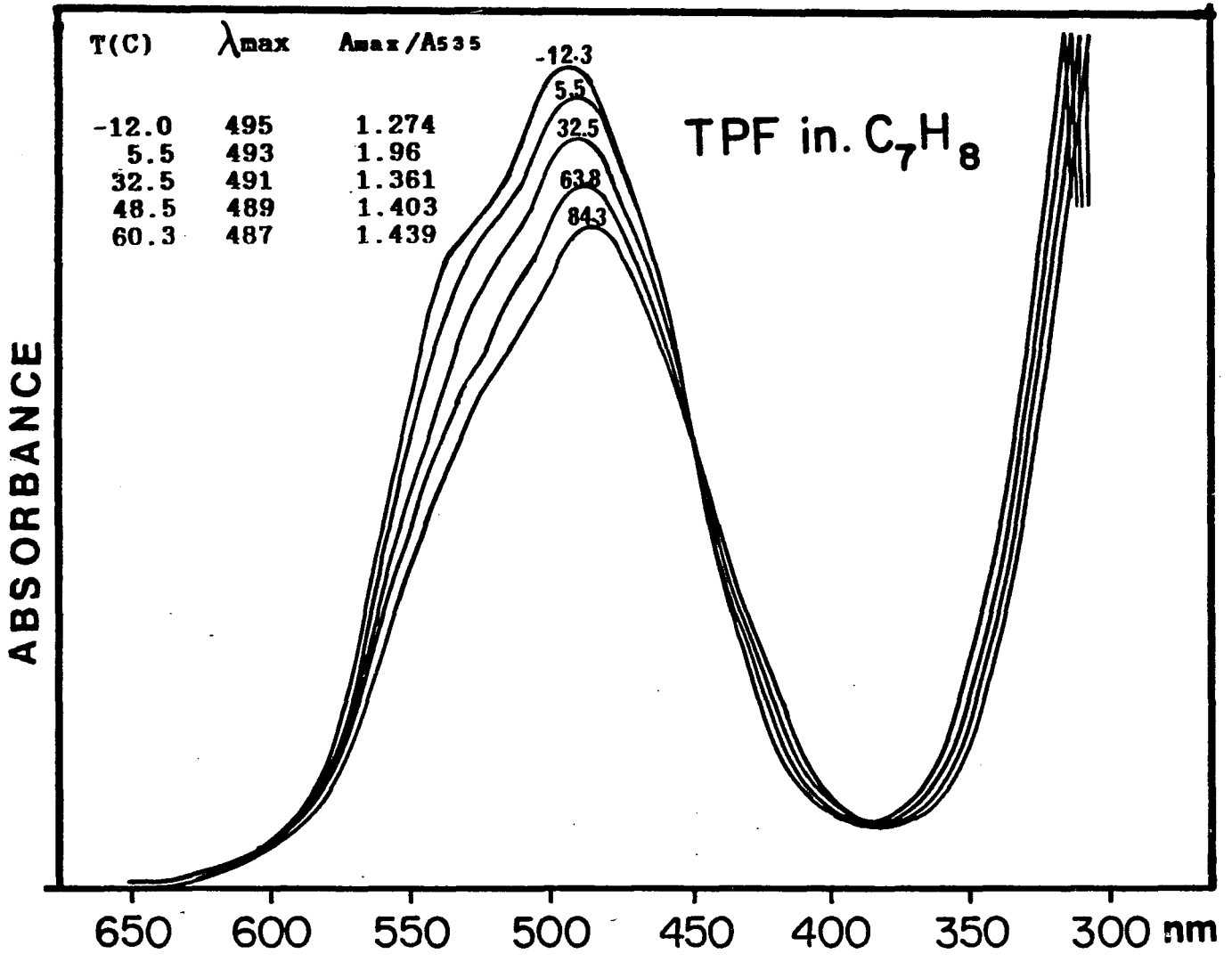

T(C) λmax Amax/A535
-12.0 495 1.274
5.5 493 1.96
32.5 491 1.361
48.5 489 1.403
60.3 487 1.439
-12.3
5.5
32.5
63.8
84.3
TPF in. C7H8
ABSORBANCE
650 600 550 500 450 400 350 300 nm

Figure 30

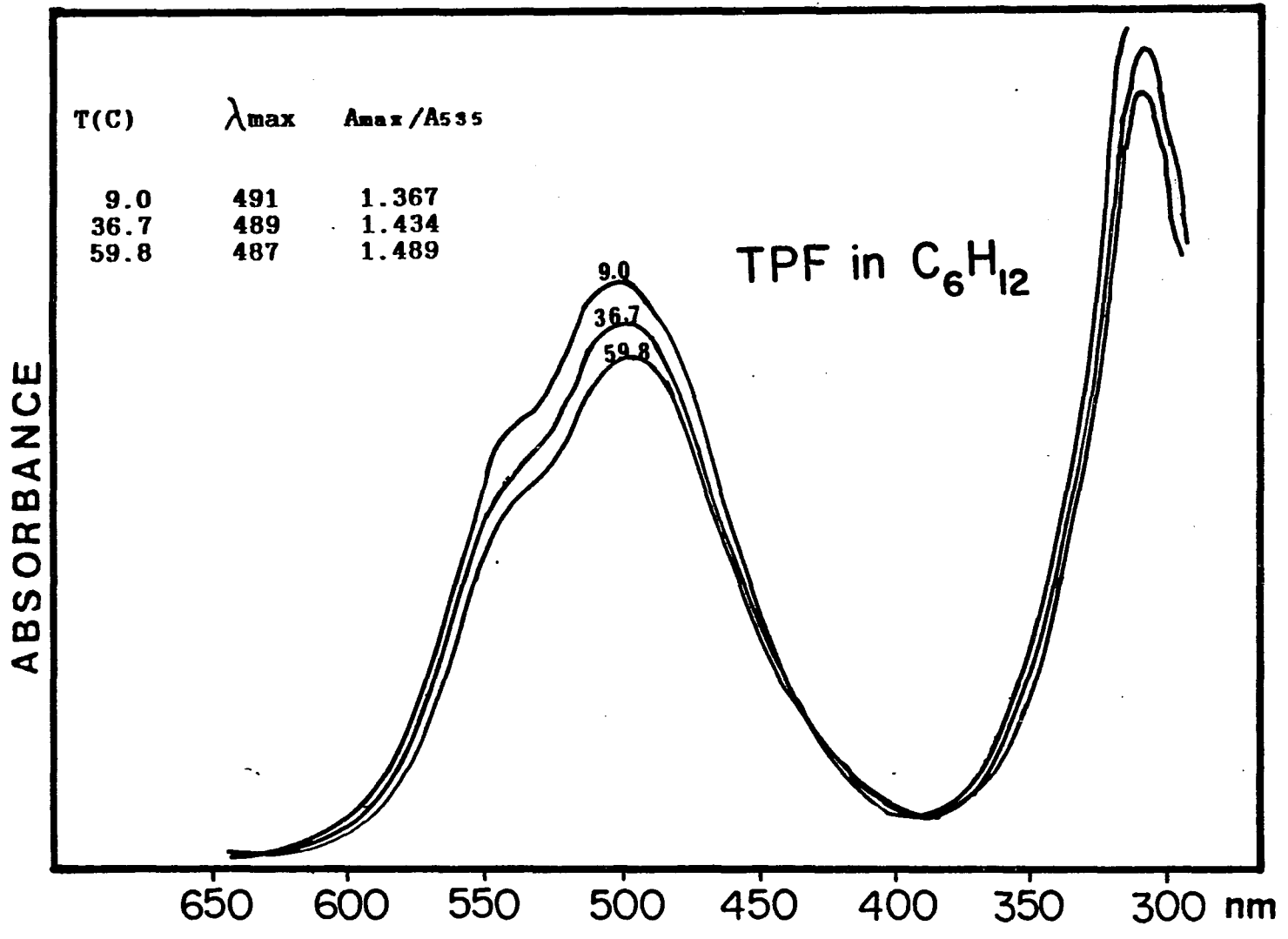

T(C) λmax Amax/A535
9.0 491 1.367
36.7 489 1.434
59.8 487 1.489
TPF in C_6H_{12}
9.0
36.7
59.8
ABSORBANCE
650 600 550 500 450 400 350 300 nm

Figura 31

Similar results are observed in the temperature dependent spectra of the naphthyl derivative in all the solvents. See Figures 32 to 35. The major difference is that the ratio between the maximum absorbance and the absorbance at 535 nm is smaller than that for triphenylformazan in every solvent. On the other hand, the increase of the ratio with temperature is the same for both triphenylformazan and the naphthyl derivative. The effect of the nature of the solvent on this ratio agrees with the results observed in spectra recorded at room temperature.

The facts that triphenylformazan and the naphthyl derivative have different values for the ratio between the maximum absorbance and the absorbance at 535 nm and that this ratio increases with temperature suggest that the band near 490 nm and the shoulder that appears in the 520 to 550 nm region in the spectra correspond to two different absorption bands of two different forms. The spectrum of triphenylformazan in a 3-methylpentane solution at 77 K recorded in the dark is shown in Figure 36. Two well defined bands at 503 and 546 nm can be observed. The band at 503 nm shows a shoulder near 468 nm. Four additional bands appear between 355 and 380 nm. The shoulder at 468 nm as well as the bands between 355 and 380 nm are not observable at room temperature. No band can be observed

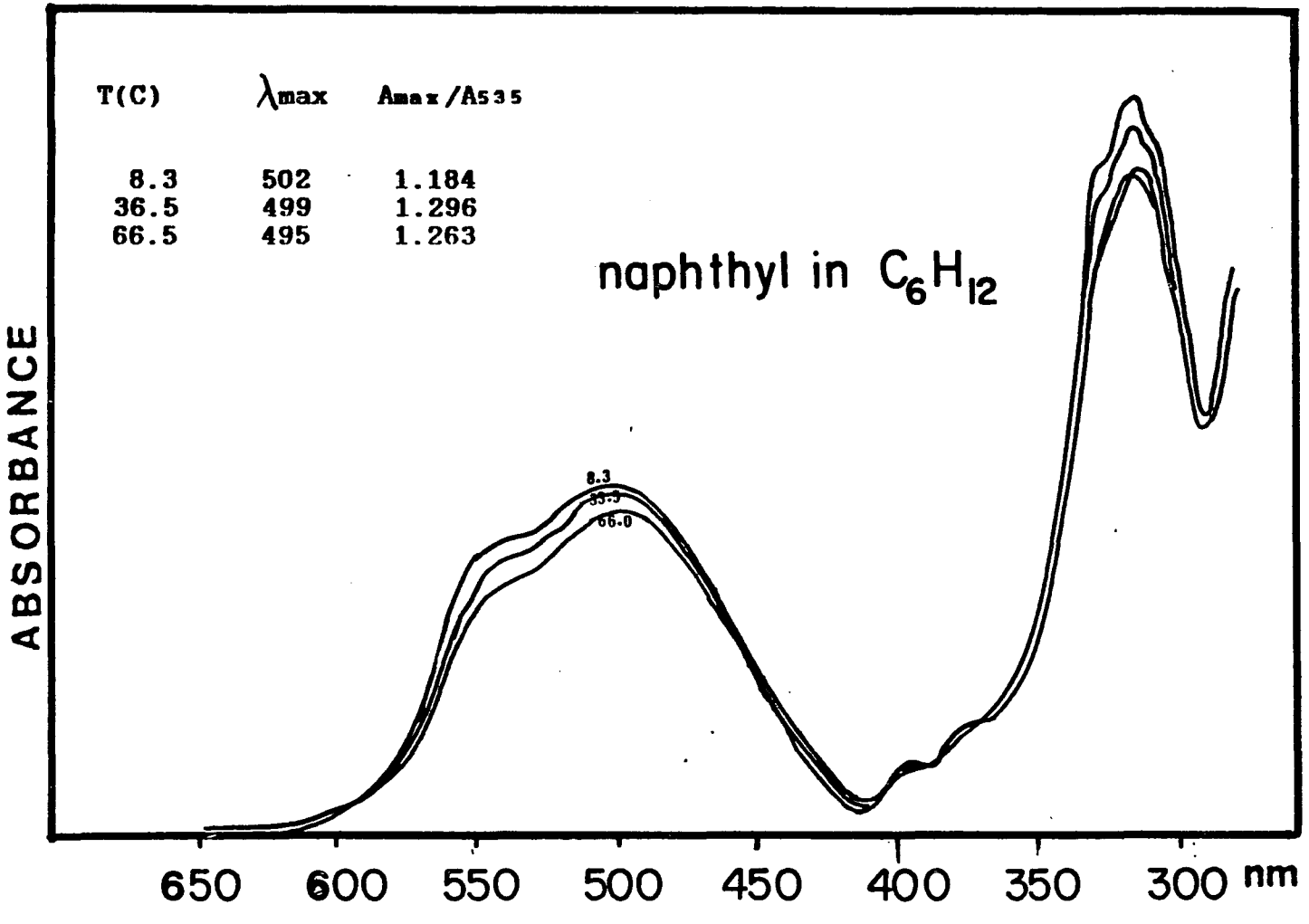

T(C) λmax Amax/A535
8.3 502 1.184
36.5 499 1.296
66.5 495 1.263
naphthyl in C_6H_{12}
ABSORBANCE
8.3
66.0
650 600 550 500 450 400 350 300 nm

Figure 32

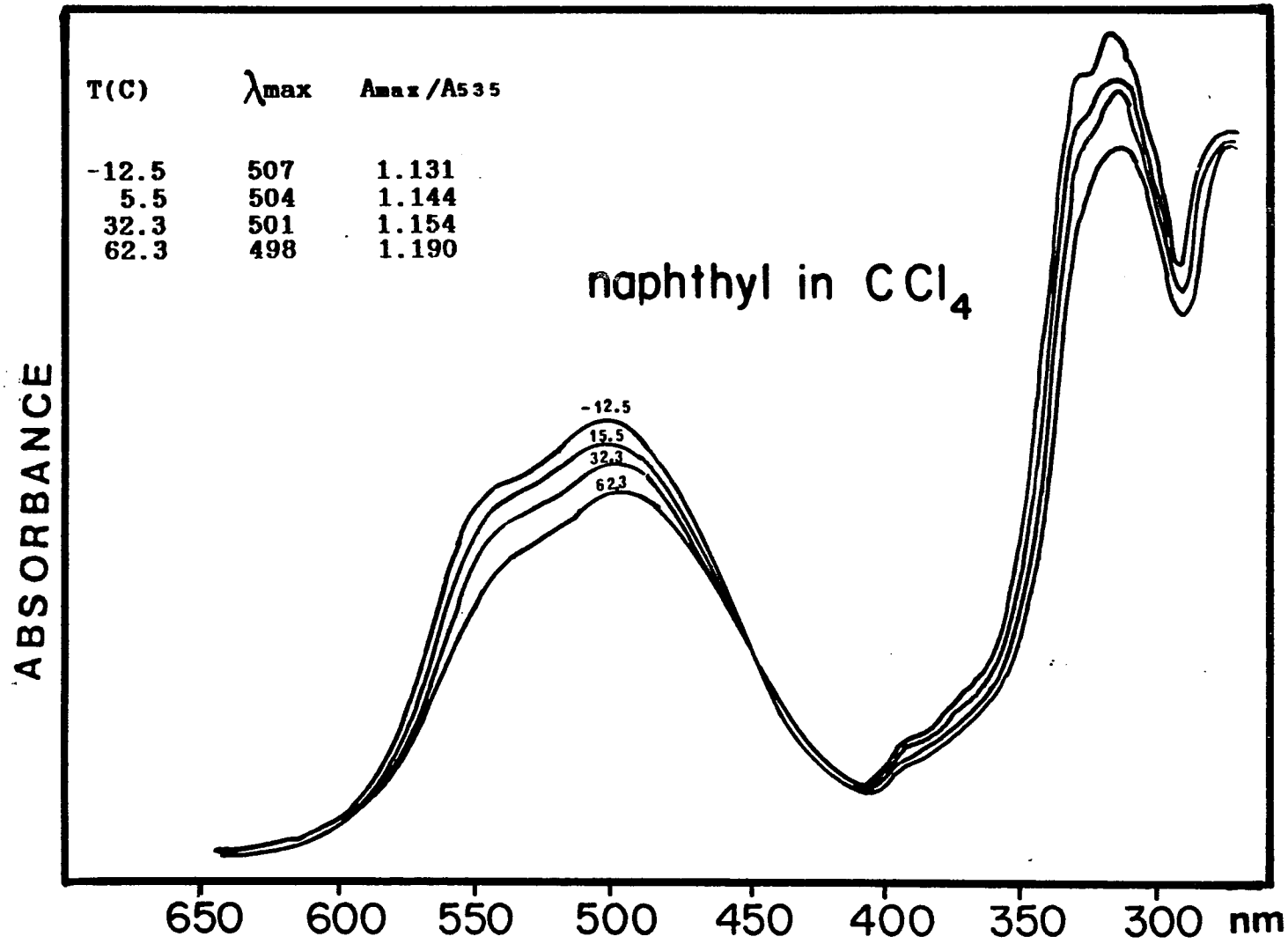

T(C) λmax Amax/A535
-12.5 507 1.131
5.5 504 1.144
32.3 501 1.154
62.3 498 1.190
naphthyl in CCl4
ABSORBANCE
-12.5
15.5
32.3
62.3
650 600 550 500 450 400 350 300 nm

Figure 33

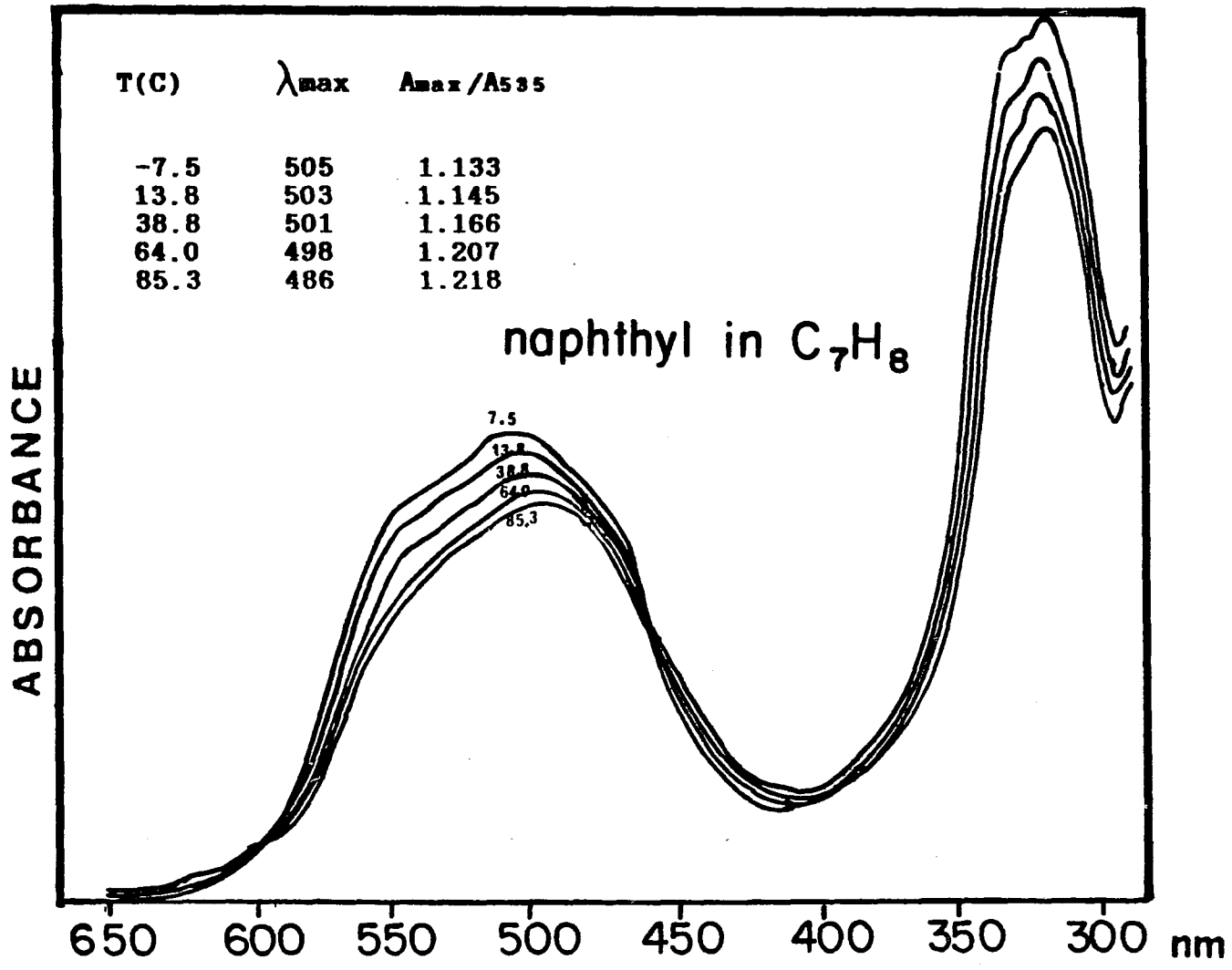

T(C) λmax Amax/A535
-7.5 505 1.133
13.8 503 1.145
38.8 501 1.166
64.0 498 1.207
85.3 486 1.218
naphthyl in C7H8
7.5
13.8
38.8
64.0
85.3
ABSORBANCE
650 600 550 500 450 400 350 300 nm

Figure 34

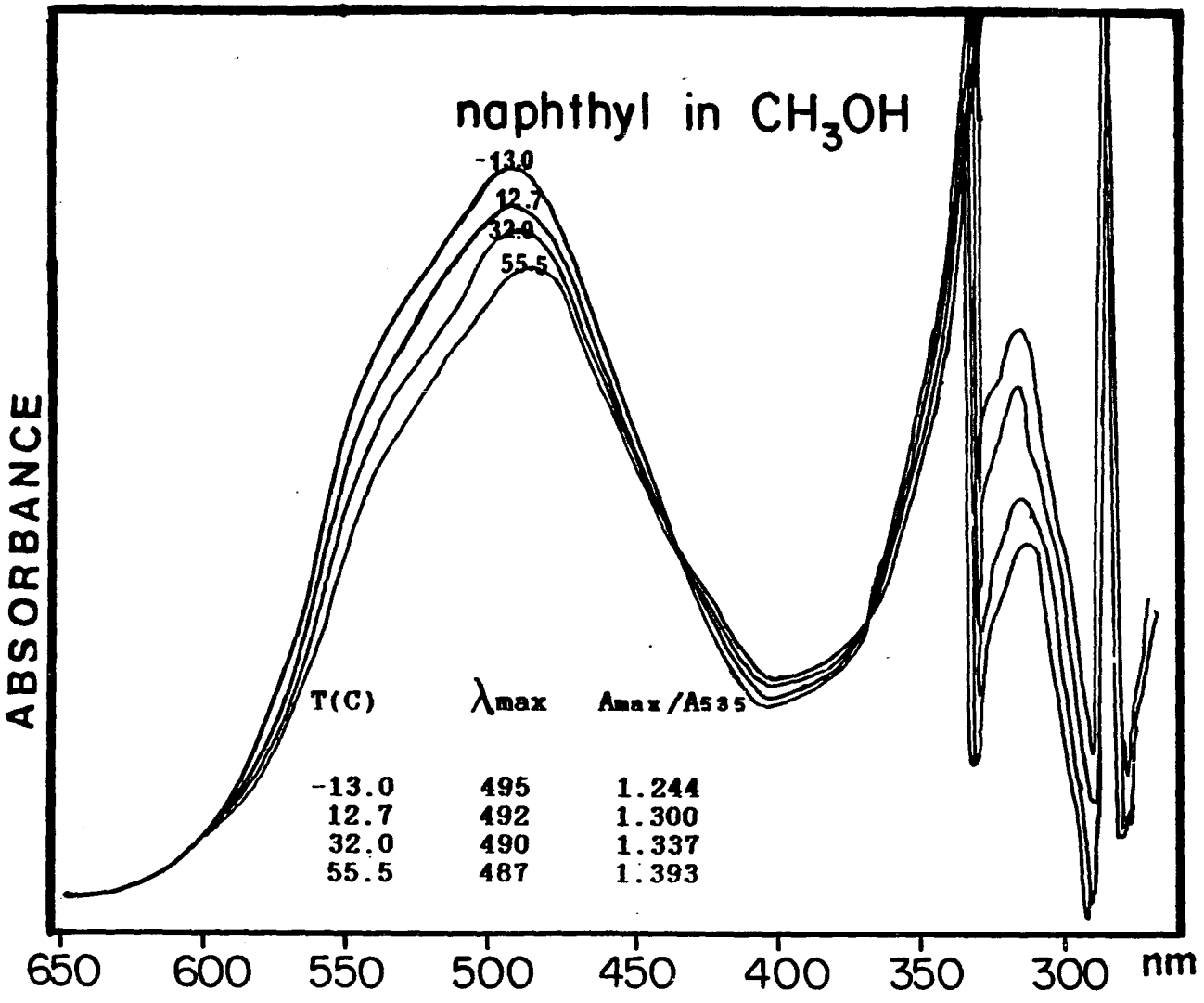

naphthyl in CH_3OH
-13.0
12.7
32.0
55.5
ABSORBANCE
T(C) λmax Amax/A535
-13.0 495 1.244
12.7 492 1.300
32.0 490 1.337
55.5 487 1.393
650 600 550 500 450 400 350 300 nm

Figure 35

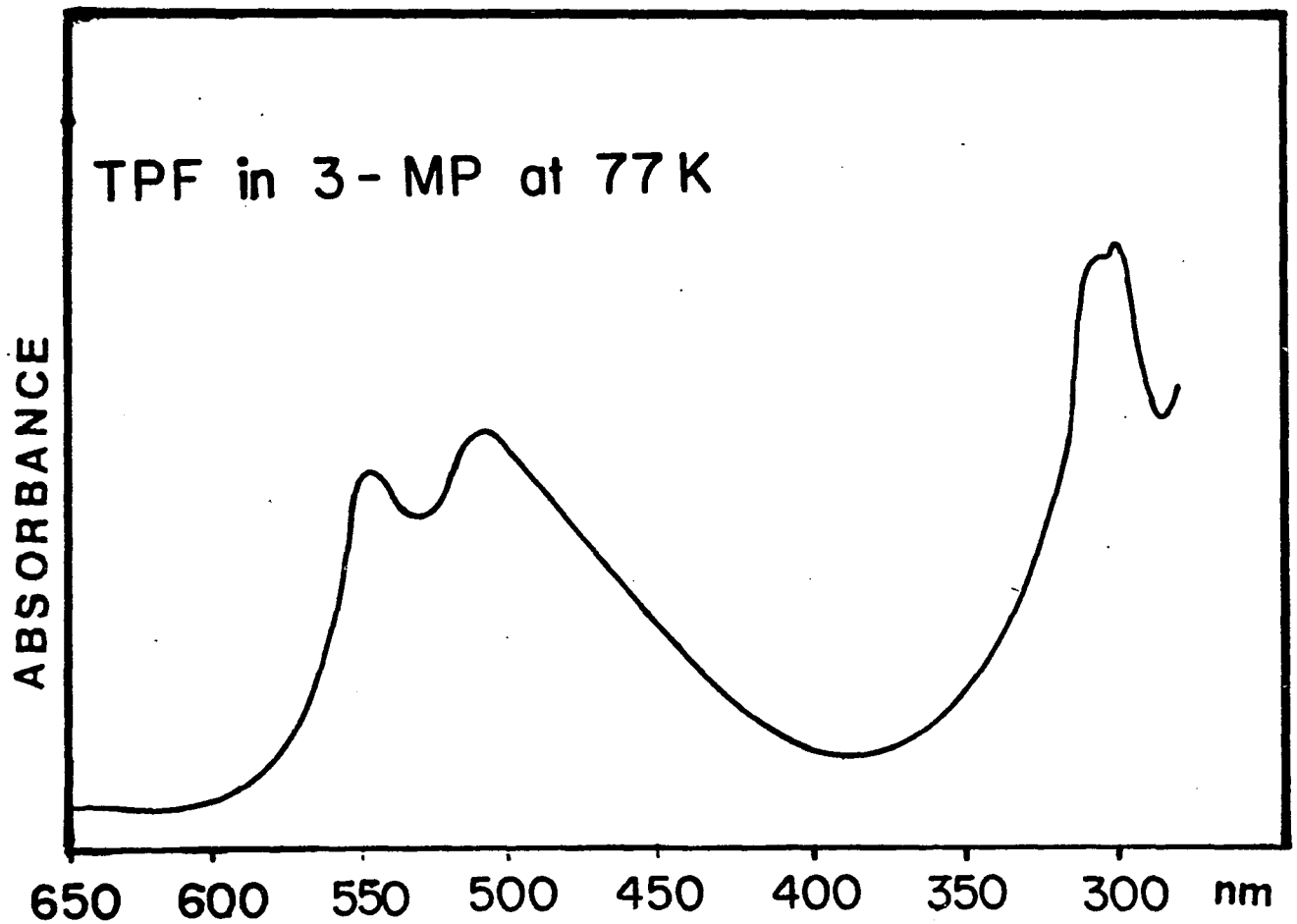


Figure 36

near 400 nm where the yellow form absorbs at room temperature. A calculation of the Boltzmann population at 77 K and at 298 K suggest that the band near 490 nm and the shoulder of this band near 535 nm correspond to the absorption bands of two different structures of the red form rather than to two absorptions from the same ground state of the triphenylformazan molecule.

CHAPTER IV

MOLECULAR MECHANICS AND CNDO CALCULATIONS

A. Introduction.

The second part of this work consists of molecular mechanics and CNDO calculations of the geometry and electronic transitions of triphenylformazan and some of its derivatives. The CNDO computations were done in order to assign the electronic transitions observed in the absorption spectrum of the red form of triphenylformazan and to investigate the origin of the long wavelength bands observed in the absorption spectrum of triphenylformazan. In the absence of light the red form is stable in solution and Kuhn and Weitz[50] report that irradiation produces a second red isomer that has a half-life of the order of 6 to 30 sec at 0(C). From determinations of extinction coefficients immediately before and after irradiation Kuhn and Weitz explained the existence of the second red form; yet they assumed that in absence of light, only one red form is stable. Earlier in this work, evidence for the existence of the two red isomers in an equilibrium mixture was suggested by the results of the temperature dependence and the solvent effects on the absorption characteristics of the red form. These two isomers are assumed to have

different structures. Calculations of the electronic transitions of different conformations of triphenylformazan were done in order to confirm the existence of these two isomers. The molecular mechanics calculations provided a rationale for the geometries of the slightly different red forms.

Neither electronic transitional quantum mechanical nor molecular mechanical calculations have been reported in the literature. Yurchenko and Kukushkina[80,71] and Zeif et al.[73] have determined the conformation of certain 1,5-diphenylformazans in solution by the simple MO LCAO method and they have used the Hückel method to estimate the dipole moments of formazans. These are the only three reports found in the literature that give results of calculations performed for triphenylformazan.

To date, all the reports found in the literature concerning the structure of triphenylformazan indicate that the formazan ring is planar and has a strong intramolecular hydrogen bond.[27-29,31] Molecular mechanics calculations were performed to determine the geometry of triphenylformazan. The molecular mechanics of the force field method has been reviewed several times[73-75] and will not be discussed here. Only a brief description of the

method is given here.

B. Molecular Mechanics.

Molecular mechanics or force field calculations are based on a simple classical mechanical model of molecular structure. The method treats the molecule as an array of atoms governed by a set of classical mechanical potential functions. These potential functions include bond stretching, angle bending and torsional potentials. These three potential functions constitute the valence force field. To improve the quality of the calculations, steric interactions are taken into account by means of including van der Waals potentials and cross terms which are related to the increase of the bond length as the angle between bonds decreases. Electrostatic terms are included when polar groups are present in a molecule. Each type of these potential functions is assumed to be transferable from molecule to molecule. This transferability means that a given type of bond, for instance, is assumed to have the same characteristics in each molecule in which it occurs. The force field defines the mechanical model used to represent a molecule and the purpose of the molecular mechanics program is to determine the optima structure and

energy that are consistent with this mechanical model.

The initial data of the input for the program must therefore define a starting structure for the molecule. Initial Cartesian coordinates (x,y,z) for the individual atoms and definitions of the bonds joining them must be provided. The nature of the molecular mechanics calculations requires that bonds be defined in the input; the model corresponds strictly to the classical valence bond picture of chemical bonding. For instance, carbon atoms may be either sp^3, sp^2 or sp; these three type of carbon atoms have completely different force fields. The bond description is the major difference between molecular mechanics and molecular orbital calculations. In the latter the electronic state determines the bonding pattern which is, therefore, not defined in the input. The details of the input to the program are included in the manual of the molecular mechanics program.[76] Clark developed excellent examples of the input and the output of the most recent version of the molecular mechanics program.[77]

The first step in the molecular mechanics calculations is the determination of the interatomic distances, bond angles and torsional angles in the starting geometry. These values are used in the different potential function

expressions to calculate an initial steric energy, which is the sum of the various potential energies calculated for all the bonds, bond angles, torsional angles and non-bonded pairs of atoms in the molecule. The structure is then optimized by means of finding a minimum with respect to the steric energy. The program uses a Newton-Raphson iteration method to optimize the geometry. Once optimization has converged (energy and structure remain constant from iteration to iteration), the program prints the final steric energy and the optimized geometry. This geometry is then used to calculate such properties as moment of inertia and dipole moment.

One serious problem is the determination of the force fields to be used for treating conjugated molecules. The transferability of potential functions from one molecule to another is no longer a good aproximation. Allinger and Sprage[78,79] have combined quantum mechanics and classical mechanics to treat conjugated molecules. A simple π-only MO section is included in the molecular mechanics program. The program uses the normal force fields for those parts of the molecule that are not involved in the conjugated system and the modified force field for the delocalized bonds; thereafter an ordinary geometry optimization is performed with this force field.

One of the most frequent problems encountered in molecular mechanics calculations is the determination or creation of the parameters needed to calculate the different potentials.[80] Osawa[81,82] has compiled a list of published ad hoc parameters for empirical force field calculations.

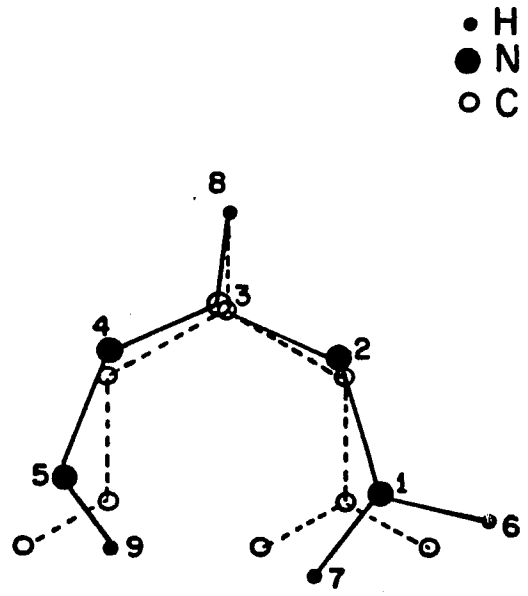
The program used for the molecular mechanics calculations reported in this work is the MMI/MMPI program created by Allinger and Yuh[76] in a version modified by Bill Colucci (CHCOLU.MM2.V05). This program calculates only force fields for localized electron systems. No version of the program including molecular orbital calculations for delocalized systems was available at LSU at the time these calculations were performed. Therefore, the results of the molecular mechanics calculations done in this work do not include those for the naphthyl derivative and in the triphenylformazan calculations a localized electron system in the formazan ring was assumed.

The starting point was a simple planar formazan molecule. Literature values[83] for bond lengths and angles were used to generate the initial Cartesian coordinates for the input to the molecular mechanics program. These Cartesian coordinates were generated by a program called

COORDANG which calculates x,y,z coordinates from bond lengths and angles between bonds. The force field parameters not available in the initial version of the program were added at the end of the input to the molecular mechanics program.[84-92]

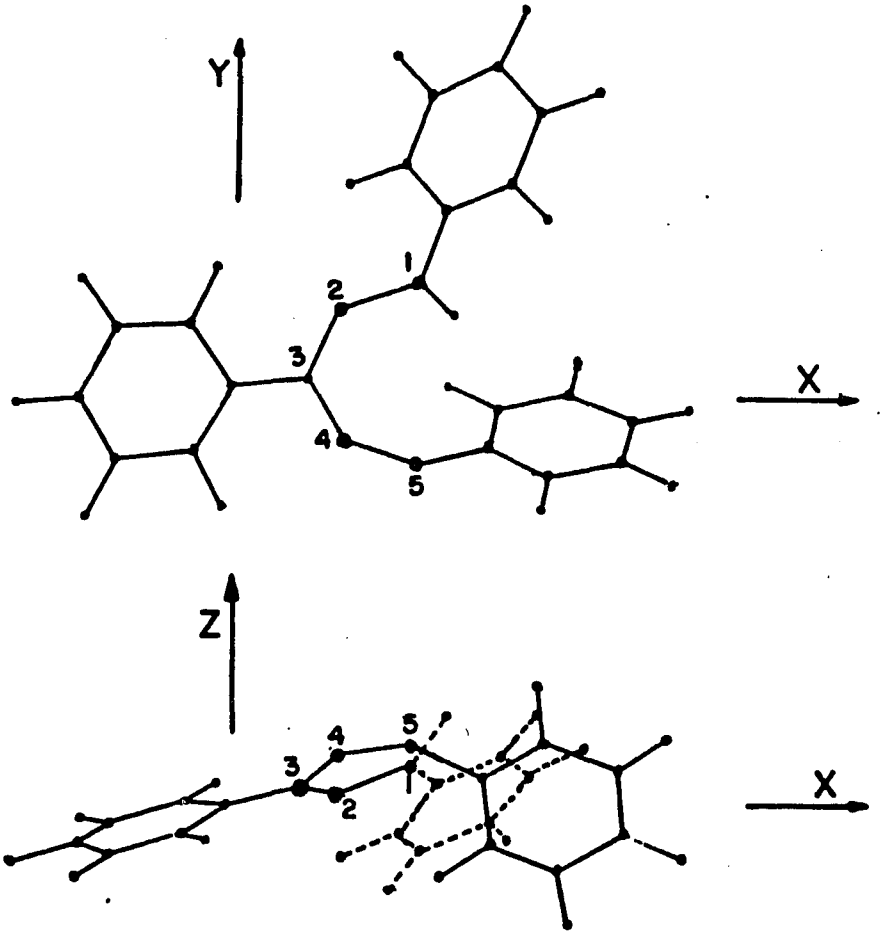
Figure 37 shows the x-y planar view of both the initial geometry and the optimized geometry of formazan calculated by means of the molecular mechanics program. The dotted lines represent the initial geometry and the solid lines correspond to the final calculated geometry. The small black dots are hydrogen atoms, the large black dots are nitrogen atoms and the white dot represents the carbon atom in the formazan ring. Notice that the optimized structure is planar and that the hydrogen atom attached to the N_5 is in a position that tends to close the formazan ring.

This optimized geometry of formazan was used to provide the initial data for the formazan ring with which the molecular mechanics program could be used to optimize the geometry of triphenylformazan. H_7, H_8 and H_9 were replaced by phenyl groups, for which conventional geometries were used. Figure 38 shows the x-y and x-z views of the final geometry of triphenylformazan that was



FORMAZAN

Figure 37



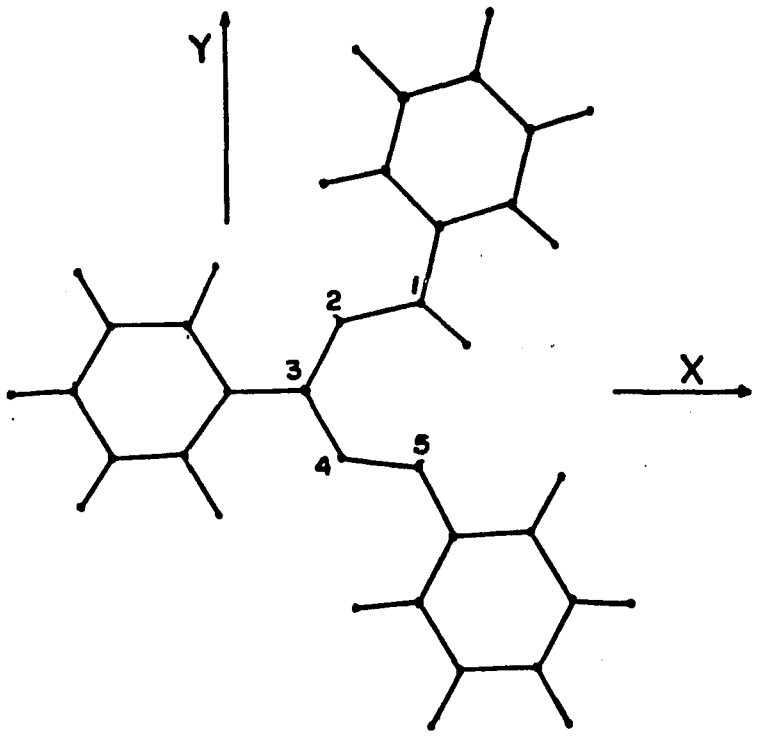
TRIPHENYLFORMAZAN
NON- PLANAR

Figure 38

generated by means of the molecular mechanics program. It can be observed that the formazan system and the phenyl group attached to the carbon atom of the formazan system are practically in the same plane and that the phenyl groups attached to the nitrogen atoms are rotated with respect to the plane of the formazan system. The x-z view shows that the the molecular mechanics program generates a clearly non-planar structure; it shows that the hydrogen bond between H_6 and N_5 is possible, even though in the x-y view it seems that H_6 and N_5 are too far apart to participate in hydrogen bonding.

A different initial geometry was used to generate a different structure of triphenylformazan. The same final coordinates previously generated for the formazan molecule were used, but the position of the H_9 atom was moved to a position outside the ring. A new geometry of triphenylformazan was generated and it is presented in Figure 39. Only the x-y view is shown because this structure of triphenylformazan is almost completely planar. Table 3 shows the coordinates of the optimized structure of triphenylformazan.

It is not surprising to obtain different optimized structures when one uses different initial geometries. It is



TRIPHENYLFORMAZAN
PLANAR

Figure 39

very possible that the potential energy surface of triphenylformazan contains more than one minimum in its potential function and the different minima correspond to different structures. The optimization leads to the minimal energy structures that most nearly resembles the initial structure; the calculated geometry depends on the potential functions as well as on the initial geometry.[93]

Table 54 shows the final energies and some properties calculated by means of the molecular mechanics program for both optimized structures of triphenylformazan. It should be emphasized that there is very little physical significance to the parameters and energies that result from molecular mechanics calculations. The values of the steric energy do not give any indication about which is the most stable form. Remember that the steric energy is specific to the force field, and it does not correspond to any classical definition of strain energy, although it is related to the heat of formation by a simple expression. The term that makes the major difference between the energy of both structures is the contribution of the torsional potential. This result explains why one structure is planar and the other is not planar.

The total dipole moment of a molecule can be considered

to be the vector sum of the dipoles attributable to each bond. In general, the isomer or conformation in which the total dipole moment is the lowest is the most stable one. According to this criterion, the non-planar conformer of triphenylformazan is more stable than the planar isomer even though the steric energy of the former one is higher than that of the latter one.

Similar calculations were performed for the ortho-hydroxy, ortho-chloro, ortho-bromo, para-chloro and meta-bromo derivatives. Table 55 shows the results of the calculations performed for some derivatives of triphenylformazan. The final geometry of the non-planar conformation of triphenylformazan was used as the initial geometry for each of the derivatives. No major difference in the values presented in Table 55 with respect to those of the non-planar triphenylformazan (Table 54) can be observed. The major contribution to the steric energy of the derivative is provided by the interaction between non-bonded atoms (van der Waals dispersion forces); this result is analogous to that for the triphenylforamzan. The bending term is the next major contributor to the energy followed by the dipole-dipole interactions. Compression and stretching-bending contributions are minimal. Another important term is the torsional energy which is the only negative contribution

to the total steric energy.

All the derivatives have higher steric energies than that of triphenylformazan. The position at which a hydrogen is substituted in the phenyl group attached to the carbon atom in the formazan ring changes the value of the steric energy of the molecule. Ortho-halogen derivatives have the highest steric energy (30.7 - 30.8 Kcal). Para-chloro, meta-bromo and ortho-chloro derivatives have lower steric energies (27.0 - 27.4 Kcal); peculiarly the nature of the halogen is not relevant to the value of the energy.

Since the main purpose of the molecular mechanics calculations is to determine a geometry to be used in the calculation and assignment of the electronic transitions in the absorption spectrum of triphenylformazan, no major discussion of the results obtained is done in this work. In order to be able to discuss other aspects of the results such as rotational barriers and heats of formation, a better version of the molecular mechanics program, which includes molecular orbital calculations for delocalized electron systems would be necessary.

Attempts to calculate the geometry of the naphthyl derivative were unsuccesful. Experimentally, it is found

that bond lengths in naphthalene are different; they vary between the single and double bond lengths. This variation is two thirds of the difference in length between a single and a double bond, and one third of the difference in length between a single and a double bond; thus, the phenyl group parameters are not adequate for representing structure of the naphthyl group. In the naphthyl group the bond lengths are determined by the bond order, therefore the initial molecular orbital calculations are necessary to determine the geometry of this derivative.[94,95]

C. CNDO Calculations.

The optimized geometries of both planar and non-planar conformations of triphenylformazan were used to provide geometries with which to perform CNDO calculations. This semiempirical method is a member of a series of molecular orbital techniques developed by J.A. Pople and his group[96] at a time when the available computers were able to handle ab initio calculations only on small systems. These methods were intended to reproduce electronic properties such as dipole moments. CNDO or Complete Neglect of Differential Overlap assumes that the atomic orbitals are to be spherically symmetrical when electron repulsion integrals are evaluated. The directionality of p-orbitals is included

only in the one electron resonance integrals, the sizes of which depend on the orientations and distances of the orbitals and on a constant assigned to each type of bond.

The CNDO/S method was introduced by del Bene and Jaffe[97] in order to correlate calculated transitional energies with electronic spectra. An extensive discussion of the CNDO/S method is given elsewhere.[98]

A CNDO/S-2 version of the original CNDO program was used in this work. In this modified version of CNDO/S the basis members have been expanded from 100 to 200 and the number of centers has been expanded from 31 to 99. Also, some flexibility on the amount of output was added. These modifications were performed by Drs. Jerry Darsey and Jerry Lewis and are part of the current LSU chemistry program library.

The results of CNDO calculations for both planar and non-planar conformations of triphenylformazan indicate that its ground state has an energy of 2669 - 2976 (eV). Two pieces of information are intended to be drawn from the results of these calculations:

1.- The nature of the transitions calculated, i.e., whether they are n - π^* or π - π^* transitions in both the

planar and the non-planar conformations of triphenylformazan.

2.- The correlation between the observed wavelength at which the transitions occur and the calculated wavelengths.

The eigenvector coefficients of the individual atomic orbitals involved in the molecular orbitals were all found to be different from zero,i.e., there is a mixture of orbitals that does not allow one to determine whether a transition is from a p electron or from a lone pair electron. In order to determine if this result is due to a problem in the CNDO program or to a strong interaction between the p electron system of the phenyl groups and the lone electron pairs in the nitrogen atoms of the formazan system, similar calculations for formazan and trimethylformazan were performed in order to study the mixture of orbitals that occurs when different groups are substituted in the formazan ring.

In the case of formazan the transitions are "pure",i.e.,there is no mixture of orbitals. For instance, in a $\pi - \pi^*$ transition the eigenvector coefficients for 2s, $2p_x$ and $2p_y$ atomic orbitals are zero and those for $2p_z$ are different from zero. This result is valid for all the atoms participating in the molecular orbitals involved in the

transition.

In the case of trimethylformazan there is a mixture of n and p orbitals but neither orbital predominates in the molecular orbital, i.e., the eigenvector coefficients for 2s, $2p_x$, $2p_y$ and $2p_z$ are of similar magnitude, which indicates that the presence of the methyl groups induces the participation of both n and p electrons in the transitions.

The results for both conformations of triphenylformazan show a clear predominance of the π character of the transition. In general the $2p_z$ coefficients are larger, in absolute value, than those of 2s, $2p_x$ and $2p_y$. This result is valid for all the atoms included in the molecular orbital involved in a transition.

These results lead to the conclusion that there is a strong interaction between the π electron system of the phenyl group attached to the formazan ring and the lone electron pairs in the formazan ring. This strong interaction is responsible for the "impure" mixture of $n - \pi^*$ and $\pi - \pi^*$ transitions of triphenylformazan.

Table 56 summarizes the principle effects of the orbital involved in the first nine transitions of formazan,

trimethylformazan and the planar and non-planar conformation of triphenylformazan. It also shows the character of the transitions that is estimated from the eigenvector coefficients.

Although there is no complete separation between the atomic orbitals, the eigenvector coefficients indicate that the main component of the transitions are n - π^* in the first transition and π - π^* in the second transition in both planar and non-planar conformation. This result is in agreement with the solvent effects on the absorption spectra of triphenylformazan and its derivatives that are observed. As the polarity of the solvent increases, from cyclohexane to methanol, the maximum absorbance of the band near 490 nm shifts from 488 nm in cyclohexane solutions to 482 nm in methanol solutions. This confirms that the electronic transition to be associated with this band is mainly n - π^*, although it is mixed with the π - π^* transitions due to the interaction between the π electron system in the phenyl groups and the lone electron pairs in the formazan ring.

Table 56 shows the observed wavelength in the spectra of triphenylformazan in 3-methylpentane at 77 K and the wavelength calculated by means of the CNDO program for the planar and non-planar conformation of triphenylformazan.

In the planar conformation, the long wavelength transition at 684.4 nm is forbidden (osc.st. $4x10^{-5}$) and the transition at 350 nm is not allowed either (osc.st.$1.3*10^{-4}$). The transitions at 427 and 296 nm are the most probable transitions (osc.st 0.237 and 0.347 respectively). In the non-planar conformation the most probable transition occurs at 284.2 nm (osc.st. 0.207). The other three transitions (465.5, 409.1 and 325.8) in the region where experimental data is available, have similar oscillator strengths (0.0865, 0.0937 and 0.0424), even though they are weaker than the corresponding transitions of the planar conformation (427.3, 295.8 nm).

The CNDO method normally predicts n - π^* transition energies that are lower than those observed experimentally; the predicted π - π^* transiton energies are higher than those observed experimentally.[98,99] However, this relationship seems to be a general trend for carbonyl compounds. A calculated n - π^* transition energy higher than that observed experimentally could be due to the participation of the π electrons in the transition. The part of the transition due to the π electrons increases the predicted energy and the part of the transition due to the n electrons decreases the predicted energy; the net effect is a calculated energy that is greater than that found for the

n - π* transition. Therefore, it can be assumed that the transition at 546 nm correponds to the transition at 465 nm calculated for the non- planar conformation and that the transition at 503 nm corresponds to the transition at 427.3 nm calculated for the planar conformation. The difference in energy between the transitions at 546 nm and 503 nm is 1,566 cm^{-1}. The difference in energy between the transition of the non-planar structure at 465 nm and the transition of the planar structure at 427 nm is 1,914 cm^{-1}. This result seems to indicate that even though the predicted transitions do not correspond with the experimental data, they are within the order of magnitude that the program can provide.

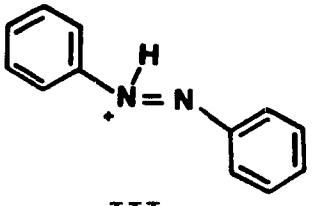
These results confirm to a certain extent that the absorption band near 490 nm and the shoulder near 530 nm that are observed in the absorption spectra of triphenylformazan in solution at room temperature and that are resolved as two distinct bands at 77 K, correspond to transitions from the two different chelated isomers of triphenylformazan that exist in an equilibrium mixture in the dark rather than to bands due to two vibronic structures of a single triphenylformazan species.

CHAPTER V

DISCUSSION OF THE RESULTS

A. Absorption Spectrum of Triphenylformazan.

The absorption spectra of triphenylformazan in different solvents show a long wavelength band in the vicinity of 490 nm. Solvent effects and empirical calculations indicate that this band corresponds to an n - π^* transition. This transition originates in the lone pair of electrons in the nitrogen atoms present in the formazan ring. Two functional groups -N=N- and -C=N- are present in the formazan ring. The azo group has an n - π^* absorption at 340 nm and the -C=N- group absorbs strongly at 190 nm (π - π^*) and at 300 nm (n - π^*).[100] The only compounds for which the absorption characteristics can be compared with those of triphenylformazan are azobenzene and the cyanine dyes. The conjugate acid of azobenzene (III) has an intense band at 420 nm. This band is assigned to a π - π^* transition.[101]



III

Cyanine dyes are of the type $Me_2N=CH-(C=H)_r-NMe_2$.[102] The wavelength of maximum absorbance of this general class of compounds varies linearly with r, the number of vinyl groups interposed between the end nitrogen atoms. For instance, the cyanine dye with r = 3 absorbs at 511 nm.

The conjugation of the n electrons with the π electrons shifts the absorption band of the formazan ring from 420 nm where the azobenzene molecule absorbs to 490 nm. Avramenko[64] indicates that the long wavelength absorption band is the result of a $\pi - \pi^*$ transition of the azohydrazone (I) moiety of the triphenylformazan molecule.

CNDO calculations performed for triphenylformazan show that both n and π orbitals are involved in the transitions of triphenylformazan, and that there is a strong participation of the π orbitals. The first transition, which is called the S_0-S_1 transition, has a predominant $n - \pi^*$ character.

An intense band appears in the spectra of triphenylformazan near 300 nm. As it was indicated in sction III.A.1, this band corresponds to the absorption of the phenyl groups attached to the formazan system.

From the study performed of the effect of the concentration on the spectra of triphenylformazan and its derivatives, it is concluded that there is no linear correlation between concentration and the maximum absorbance. Even though the concentrations are low enough to expect the Beer's law to be valid, a change in the molar absorption coefficient as a function of the concentration indicates that there is more than one absorbing species in equilibrium. The spectra of triphenylformazan at different concentrations show that even though there is a significant change in the molar absorption coefficient when concentrations differ at least by one order of magnitude, the wavelength of the corresponding absorbance remains constant. This constant absorption contour indicates that in a concentrated solution there might be aggregates of molecules that have similar absorptions but different molar absorption coefficients.

It is already known that two different red isomers of triphenylformazan exist, and other results suggest that these two forms exist in an equilibrium mixture; this equilibrium depends on the temperature and on the nature of the solvent. A higher concentration of triphenylformazan might favor the formation of the form absorbing at 535 nm,

such a process would explain the decrease of the molar absorption coefficient of the band at 490 nm.

B. Substituent Effect.

The results presented in Chapter III indicate that the absorption characteristics of the para-chloro and meta-bromo derivatives are very similar to those of triphenylformazan in different solvents. See Figure 9. Although the spectroscopic characteristics of the ortho-halophenyl derivatives are very different from those of triphenylformazan, there are no major differences between their absorption characteristics. See Figure 16. Likewise, the ortho hydroxy derivatives have distinct absorption spectra, that resemble one another, but that are different from those of triphenylformazan. See Figure 12. The naphthyl derivative is unique in its absorption characteristics and differs from all the other members of the series of compounds that were investigated. The effect of a substituent on the absorption spectra of triphenyl-formazan can be analyzed in terms of proton donating substituent (-OH), electron withdrawing substituent (-Cl) and electron deficient system (-naphthyl).

A group deficient in electrons (-naphthyl) tends to

attract the lone pair of electrons on the nitrogen atoms of the formazan ring. The result of this interaction is a decrease in the strength of the intramolecular hydrogen bond and the formazan ring is more susceptible to being excited with less energy than that required to excite triphenylformazan that has a strong hydrogen bond. This fact explains the absorption of the naphthyl derivative at longer wavelengths than those of the triphenylformazan absorption. See Figure 38.

In section III.D it was shown that the absorbance ratio between the band at 490 nm and the shoulder near 530 nm of the naphthyl derivative is lower than that of triphenylformazan. This result indicates that the presence of the naphthyl group tends to stabilize the conformer of triphenylformazan that absorbs at 535 nm and that the relative concentration of the red isomer absorbing at 490 nm decreases. This result agrees with the fact that the molar absorption coefficients of the naphthyl derivative are smaller than those of triphenylformazan.

The substitution of a halogen atom in the ortho position of the phenyl group attached to the carbon atom of the formazan ring has a peculiar effect on the absorption characteristics of the formazan ring. In the spectra of a

cyclohexane solution the contour of the absorption band of the red form is the same as that of triphenylformazan, but it is shifted 20 nm to the blue. This result indicates a stabilization of the formazan ring. On the other hand the presence of the yellow band is evident as a shoulder near 400 nm, and this band indicates that the equilibrium between the red and the yellow isomers has been displaced to the formation of the unchelated form by the presence of the halogen atom in the ortho position. The presence of the yellow form explains the lesser absorption coefficient with respect to that of triphenylformazan. The stabilization of the formazan ring is evident in cyclohexane and carbon tetrachloride solutions, but as the polarity of the solvent increases, the opening of the ring predominates; in carbon tetrachloride solutions the red form is the more stable, but the yellow form is present in higher proportion than that in cyclohexane solutions. This fact is shown by the smaller molar absorption coefficient of the red form in carbon tetrachloride with respect to that of the same form in cyclohexane solutions and by the increasing molar absorption coefficient of the yellow form in toluene and dichloromethane solutions. In these two solutions the red form is apparently absent. The effect of methanol is different. Even though the yellow form predominates, the red form is present in very low concentrations. This

presence of some red form explains the smaller molar absorption coefficient of the yellow form in methanol solutions. This reversal in the tendency to stabilize the yellow form in a polar solvent indicates that when methanol is the solvent, polarity is not the only factor that affects the absorption of the formazan ring.

The presence of a hydroxy group in the ortho position of the phenyl group attached to the carbon atom in the formazan ring has a strong effect on the spectroscopic and photochromic characteristics of the formazan ring. This derivative has no photochromic activity; both the red and the yellow forms exist in an equilibrium mixture. The presence of the hydroxy group also has an effect on the structure of the red form. The interaction between the OH group and the formazan ring produces the formation of a hydrogen bond and another ring external to the formazan ring is formed. For these two rings to coexist, a planar geometry must be relatively stable. The formation of this second ring destabilizes the formazan ring and produces a displacement of the equilibrium to the formation of the yellow form. This destabilization of the formazan ring implies that less energy is required to produce a transition and these derivatives absorb at longer wavelengths than does triphenylformazan. Thus, the substitution in the ortho position of the phenyl group

attached to the carbon atom of the formazan ring affects the structure of the red form and the equilibrium between the red and the yellow forms. The effect of the solvent on the ortho derivatives is stronger than that on triphenylformazan and the naphthyl derivatives.

C. Solvent Effects.

The position, shape and intensity of absorption bands are usually modified when the absorption spectra of a compound in solvents of different polarity are measured. These changes are a result of a physical intermolecular solute-solvent interaction caused by forces such as dipole-dipole, dipole-induced dipole, hydrogen bond, etc.[103] These interactions alter the energy difference between the ground and the excited state of the absorbing species. Theories of solvent effects[104,105] on the absorption spectra assume that the chemical state of the isolated and solvated molecule are the same and treat these effects only as physical perturbations. This assumption excludes spectral changes arising from alteration of the chemical nature of the solute by the solvent such as proton or charge transfer between solvent and solute, solute aggregates, ionization, complexation or isomerization equilibria.

Triphenylformazan and the naphthyl derivative demonstrate solvent effects that are the result of the interaction between the solute and the solvent and affect only the absorption band of the red form. The spectra of both compounds show a shift to the blue as the polarity increases. Since not enough different types of solvents were used to make a complete study of the effect of the solvent, the only qualitative information that can be drawn from the solvent studies concerns the relative polarity of the ground and excited states involved in the transition. An hypsochromic or blue shift occurs when the ground state is more dipolar than the excited state. The experimental results indicate that, upon irradiation, the excited state of the formazan ring must assume a less planar structure than that of the ground state. The observed shift to the blue agrees with the fact that the ratio between the absorbances of the red forms at 490 and 535 nm increases as the polarity of the solvent increases, i.e., a more polar solvent favors the displacement of the equilibrium between the two red isomers to the formation of the red form absorbing at 490 nm. The shift in the spectra is smaller for triphenylformazan than for the naphthyl derivative. This experimental result indicates that the naphthyl derivative has a weaker hydrogen bond. This fact favors the conversion between the red forms. A similar effect on the

spectra of all solutions of the ortho-hydroxy derivative is observed, except in the case of the ortho-hydroxy derivative methanol solutions.

As it was indicated in section III.B.6, solvents affect the equilibrium between the red and yellow forms of the ortho-halo substituted derivatives and it is not possible to detect the solvent-solute interaction in these compounds.

Of particular interest is the effect of methanol on the spectroscopic characteristics of the ortho-hydroxy derivative. NMR and temperature studies indicate that there is a strong interaction between the hydroxy group of methanol and the nitrogen atoms involved in the hydrogen bond of the ortho hydroxy derivatives. The two hydrogen atoms of the derivative are highly mobile in polar solvents due to the formation of hydrogen bonds with solvent molecules. It was discussed in section III.C that this high mobility of the hydrogens favors the displacement of the equilibrium to the formation of the yellow form. Another effect of this hydrogen bond interaction should be the stabilization of the planar structure of the molecule. In methanol solution this effect is not observed directly because of the predominance of the yellow form.

The spectra of the ortho-hydroxy derivative in different alcohols show that the red forms absorb with similar intensities at 490 and 535 nm, this result indicates that in alcohols both isomers are present in similar concentrations. This result is different from that observed from other solutions in which the red form at 535 nm predominates. Thus, the interaction between the alcoholic solvent molecules and the ortho-hydroxy molecules has an internal effect as well as an external effect on the spectroscopic characteristics of this derivative. The internal effect is on the structure of the red form and the external effect is on the equilibrium between the yellow and the red forms.

Observe that different alcohols do not have the same effect on the structure of the red form. It was indicated before (Section III.C.) that the change is very subtle. More accentuated is the effect of the type of alcohol on the equilibrium between the red and the yellow forms. It was indicated before that, from methanol to butanol, the equilibrium between the red and the yellow isomers is displaced to the formation of the red form. Since the change of the ratio A_{yellow}/A_{red} is constant from ethanol to butanol and the ratio is half that of methanol solutions, the size of the aliphatic chain in the alcohol

molecule does not explain the large change between methanol and ethanol. The effect is not due to the change in the value of the dielectric constant of the alcohols because no similar relation is detected for the other solvents that were used. Since hydroxylic groups are involved, it was suggested that the change of A_{yellow}/A_{red} with the type of alcohol is related to the acidity of the alcohol. Hine and Hine determined the relative acidity of several alcohols in isopropanol solutions.[106] Comparison of the relative acidity of alcohols and the values of A_{yellow}/A_{red} indicate that the nature of the interaction between alcohol and the ortho-hydroxy derivative is an acid-base equilibrium. Thus, the spectroscopic characteristics of the formazan ring of this derivative depend not only on the isomeric equilibrium between the red and the yellow form but also depend on the acid-base equilibrium between the ortho-hydroxy derivative and the solvent. The latter equilibrium predominates over the isomeric equilibrium.

D. Temperature Effect.

In spite of the effect of the acidity of alcohols upon the equilibrium between the yellow and the red forms, the temperature dependence study of both alcoholic solutions

show a displacement of the equilibrium to the formation of the red form as the temperature increases. This result indicates that the formazan ring becomes more stable at higher temperatures. This stabilization of the formazan ring is possible if the structure of the ortho-hydroxy derivative molecule in methanol solution is that shown in Figure 20b. If this is the structure of the solute molecule, an increase in the temperature would produce a rotation of the phenyl group attached to the carbon atom in the formazan system and therefore a stabilization of the formazan ring.

The same effect is observed when a chlorine atom is the substituent in the ortho position. The absorption intensity of the band of the red form increases as the temperature increases. No such effect is observed in the temperature dependence of the absorption spectra of triphenylformazan in alcohol. These results suggest that the presence of an electron donor group in the ortho position of the phenyl group attached to the carbon atom of the formazan system favors the stabilization of the formazan ring as the temperature increases by means of inducing a rotation about the bond between the phenyl group and the carbon atom. This rotation must occur much faster than the breaking of a hydrogen bond in order to stabilize

the ring before it opens.

The temperature dependence of the absorption spectra of triphenylformazan and the naphthyl derivative in different solvents, together with the effect of the solvent on the A_{490}/A_{525} ratio on both compounds indicate that, as it has been indicated in section III.B.7, the long wavelength band and its shoulder observed in the absorption spectra of triphenylformazan and those derivatives that are stable in the red forms, are the results of electronic transitions from two different isomers of triphenylformazan and are not the result of vibronic bands of a single transition. The spectrum of triphenylformazan in 3-methylpentane at 77 K confirms these results. Not only are both bands clearly resolved but also the Boltzman populations at 77 K and 298 K are significantly different.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The results of the studies on the concentration effect on the absorption spectra of triphenylformazan and its derivatives in solutions indicate that Beer's Law is not obeyed by these systems and therefore more absorbing species than one are present in solution. The possility of a permanent chemical reaction or internal polymerization can be eliminated because the process is reversible. Triphenylformazan does not show a permanent interaction; only the solvent effects due to physical intermolecular interactions are observed. In addition, the spectral maxima of the red and the yellow forms are not affected by a change in the concentration. Therefore, it can be concluded that two red isomers of triphenylformazan are present in a solution that has not been exposed to irradiation.

The presence of two red forms in equilibrium is shown by the relative change produced in the absorbances observed at 490 nm and 535 nm when the solvent and the temperature are varied. The presence of a hydroxy group in the ortho position of the phenyl group attached to the carbon atom of the formazan system and the substitution of

a naphthyl group for the phenyl group also affect the relative intensities of the absorbances at 490 and 535 nm.

To this time, it had been assumed that the second red form is formed by irradiation, but there was no conclusive evidence for the formation of this second red form. The results of this investigation indicate that the two different chelated isomers exist in an equilibrium mixture. The two red forms reported in literature, the stable form A and the transient form B, are shown in Figures 3 and 4. A planar geometry for the chelated form of triphenylformazan has been assumed by other authors because of the presence of a strong intermolecular hydrogen bond. It is highly improbable that form B has a planar geometry because the phenyl group attached to N_5 atom of the formazan ring would be forced out of place by the hydrogen on N_1.

Molecular mechanics calculations performed in this investigation indicate that a non-planar geometry for triphenylformazan is stable and has a lower dipole moment than that of a planar molecule. In this non-planar form the N_5 phenyl group is pointed toward the formazan ring in the general manner of form B of Figures 3 and 4, but both phenyl rings are tilted in a manner so that they avoid each other and so that the N_1 hydrogen atom can interact with

N_5. Molecular mechanics calculations also generated a different planar geometry for triphenylformazan in which the N_5 phenyl group is pointed away from the formazan ring. Therefore, it is concluded that the form A reported in literature has a planar geometry and the B form shown in Figures 3 and 4 has a non-planar geometry. Both forms are chelated and have similar dipole moments and ground state energies. They exist in an equilibrium mixture, and B does not have to be formed from A by irradiation. It is highly improbable that after the hydrogen bond is broken by irradiation there is a rotation about the double bond $N_4=N_5$.

These conclusions are further supported by the results of CNDO calculations for both the planar and non-planar geometries. These calculations indicate that the first electronic transition of these two forms occur at different wavelengths; although there is no perfect agreement with the position of the transitions observed in the absorption spectra, the agreement is sufficient to support the belief that the two bands are not vibronic bands but are bands of different geometric forms.

No conclusion about the number or nature of the yellow species present in a solution can be reached. Many

different geometries for the open non-hydrogen bonded form are possible. Temperature, solvent and substitution studies combined with molecular mechanics and CNDO calculations might provide information about minimal energy structure of the yellow isomer, but at this time the cost of making the necessary number of calculations is prohibitive.

The results of this investigation on the effect of methanol on the absorption spectra of the ortho-hydroxy derivative lead to a better understanding of the structure of this derivative. NMR and absorption spectra of this derivative in a very polar solvent show that the NH and OH hydrogens are very mobile. This high mobility favors the formation of a second ring by interaction between the oxygen atom and the lone electron pair in the N_2 atom of the formazan ring. This second ring destabilizes the formazan ring because it decreases the strength of the hydrogen bond in the formazan ring and favors its opening. The opening of the formazan ring is shown by the presence of the yellow and red producing bands in the absorption spectra of this derivative in methanol.

The results of the temperature dependence of the absorption spectra of this derivative in methanol solutions demonstrated that the formazan ring is stabilized as the

temperature increases. A higher temperature decreases the interaction between the oxygen atom and the N_2 atom of the formazan system and induces the rotation of the oxygen substituted phenyl group. As a result of these effects, the strength of the hydrogen bond of the formazan ring increases and the equilibrium between the red and yellow isomers is displaced to the formation of the red isomers. Similar results were observed in the temperature dependence of the absorption spectra of the ortho-chloro derivative in alcoholic solutions. Therefore, it is concluded that the presence of an electron withdrawing group such as O^- or Cl in the ortho position of the phenyl group attached to the carbon atom of the formazan system causes a destabilization of the formazan ring due to the formation of a second ring. This second ring is formed by the interaction between the electron withdrawing group and the lone electron pair in the N_2 atom of the formazan system.

The effect of the solvent is usually only a physical intermolecular interaction between the solvent and solute molecules, but alcohols cause a different behavior. A proton transfer from the solvent to the solute occurs and the equilibrium between the red and yellow forms is affected by the acidity of the solvent. A more acid solvent favors the formation of the unchelated form.

While many advances have been made in this work, other work has been suggested. A resonance Raman spectroscopy experiment would confirm the presence of the different structures in a solution of the chelated forms of triphenylformazan. Excitation in the low energy edge of the absorption spectra should excite only the vibration of one red form; excitation in the high energy edge of the first transition might excite primarily the vibration of tbe other red form. Excitation through the band should be done to determine the change in the Raman pattern as a function of the excitation energy. A picosecond laser excited resonance Raman experiment could confirm whether the rotation of the substituted phenyl group is a faster process than the breaking of the hydrogen bond in the formazan ring. The equipment will be soon available in this department, and time-resolved picosecond resonance Raman spectroscopy should make it possible to determine the order of occurrence of the various possible conformational changes.

The non-chelated form of formazan should phosphoresce. A kinetic study of the development of the phosphorescence should tell whether the excitation of the luminescence is a one or two photon process kinetically. Such information would provide another key to the understanding of the

initial steps in the photochromism. All these experiments can be done in the near future but could not be done while this work was in progress.

APPENDIX A

TABLES

TABLE 1

TRIPHENYLFORMAZAN IN CYCLOHEXANE

MOLECULAR WEIGHT = 300.363 (g/mol)
DENSITY = 0.775 (g/cc)
TEMPERATURE = 24.0 (C)
CONC. STOCK SOLUTION = $3.94*10^{-4} \pm 6.80*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 488.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.46*10^{-6} \pm 1.12*10^{-7}$	0.116 ± 0.001	$17,950 \pm 380$
$1.22*10^{-5} \pm 2.11*10^{-7}$	0.220 ± 0.001	$17,994 \pm 332$
$1.72*10^{-5} \pm 2.97*10^{-7}$	0.305 ± 0.001	$17,747 \pm 317$
$2.91*10^{-5} \pm 5.03*10^{-7}$	0.498 ± 0.001	$17,107 \pm 299$
$2.34*10^{-5} \pm 4.04*10^{-7}$	0.409 ± 0.001	$17,483 \pm 308$
$3.45*10^{-5} \pm 5.95*10^{-7}$	0.597 ± 0.001	$17,319 \pm 302$
$3.92*10^{-5} \pm 6.78*10^{-7}$	0.687 ± 0.001	$17,508 \pm 305$
$4.60*10^{-5} \pm 7.94*10^{-7}$	0.798 ± 0.001	$17,362 \pm 301$
$5.17*10^{-5} \pm 8.93*10^{-7}$	0.929 ± 0.002	$17,974 \pm 313$
$5.58*10^{-5} \pm 9.65*10^{-7}$	1.023 ± 0.002	$18,318 \pm 319$

b = -0.010
m = 17,982
r = 0.999

$17,676 \pm 380$ (310)

RANGE = ULTRAVIOLET
ABSORBANCE at = 297.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.46*10^{-6} \pm 1.12*10^{-7}$	0.218 ± 0.001	$3,733 \pm 622$
$1.22*10^{-5} \pm 2.11*10^{-7}$	0.349 ± 0.001	$8,545 \pm 506$
$1.72*10^{-5} \pm 2.97*10^{-7}$	0.475 ± 0.001	$7,639 \pm 484$
$2.91*10^{-5} \pm 5.03*10^{-7}$	0.780 ± 0.001	$6,794 \pm 465$
$2.34*10^{-5} \pm 4.04*10^{-7}$	0.630 ± 0.001	$6,929 \pm 469$
$3.45*10^{-5} \pm 5.95*10^{-7}$	0.948 ± 0.001	$7,501 \pm 477$
$3.92*10^{-5} \pm 6.78*10^{-7}$	1.071 ± 0.002	$7,294 \pm 475$
$4.60*10^{-5} \pm 7.94*10^{-7}$	1.312 ± 0.002	$8,546 \pm 495$
$5.17*10^{-5} \pm 8.93*10^{-7}$	1.548 ± 0.003	$9,950 \pm 521$
$5.58*10^{-5} \pm 9.65*10^{-7}$	1.788 ± 0.003	$2,017 \pm 556$

b = -0.057
m = 30,701
r = 0.992

$27,900 \pm 1055$ (487)

TABLE 2

ORTHO HYDROXY DERIVATIVE IN CYCLOHEXAN

MOLECULAR WEIGHT = 316.362 (g/mol)
DENSITY = 0.774 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $5.97*10^{-4} \pm 7.05*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 535.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$9.66*10^{-6} \pm 1.14*10^{-7}$	0.129 ± 0.001	$13,349 \pm 215$
$1.70*10^{-5} \pm 2.01*10^{-7}$	0.216 ± 0.001	$12,693 \pm 171$
$2.49*10^{-5} \pm 2.94*10^{-7}$	0.313 ± 0.001	$12,593 \pm 159$
$3.46*10^{-5} \pm 4.08*10^{-7}$	0.433 ± 0.001	$12,519 \pm 153$
$4.27*10^{-5} \pm 5.05*10^{-7}$	0.537 ± 0.001	$12,568 \pm 152$
$5.17*10^{-5} \pm 6.10*10^{-7}$	0.648 ± 0.001	$12,537 \pm 151$
$5.97*10^{-5} \pm 7.05*10^{-7}$	0.746 ± 0.001	$12,488 \pm 149$
$6.88*10^{-5} \pm 8.13*10^{-7}$	0.858 ± 0.001	$12,468 \pm 149$
$7.67*10^{-5} \pm 9.06*10^{-7}$	0.954 ± 0.001	$12,442 \pm 148$
$8.56*10^{-5} \pm 1.01*10^{-6}$	1.102 ± 0.002	$12,868 \pm 154$

b = -0.000
m = 12,597 $12,567 \pm 135$ (154)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 310.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$9.66*10^{-6} \pm 1.14*10^{-7}$	0.269 ± 0.001	$27,837 \pm 360$
$1.70*10^{-5} \pm 2.01*10^{-7}$	0.450 ± 0.001	$26,444 \pm 323$
$2.49*10^{-5} \pm 2.94*10^{-7}$	0.672 ± 0.001	$27,037 \pm 324$
$3.46*10^{-5} \pm 4.08*10^{-7}$	0.904 ± 0.001	$26,136 \pm 311$
$4.27*10^{-5} \pm 5.05*10^{-7}$	1.117 ± 0.001	$26,142 \pm 311$
$5.17*10^{-5} \pm 6.10*10^{-7}$	1.369 ± 0.002	$26,486 \pm 316$
$5.97*10^{-5} \pm 7.05*10^{-7}$	1.572 ± 0.002	$26,315 \pm 313$
$6.88*10^{-5} \pm 8.13*10^{-7}$	1.839 ± 0.003	$26,723 \pm 319$

b = 0.004
m = 26,405 $26,469 \pm 324$ (317)
r = 1.000

TABLE 3

HYDROXY-CHLORO DERIVATIVE IN CYCLOHEXAN E

MOLECULAR WEIGHT = 350.807 (g/mol)
DENSITY = 0.775 (g/cc)
TEMPERATURE = 24.0 (C)
CONC. STOCK SOLUTION = $4.58*10^{-4} \pm 5.75*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 530.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$8.60*10^{-6} \pm 1.08*10^{-7}$	0.112 ± 0.001	13,030 ± 232
$1.71*10^{-5} \pm 2.15*10^{-7}$	0.215 ± 0.001	12,585 ± 179
$2.60*10^{-5} \pm 3.27*10^{-7}$	0.331 ± 0.001	12,714 ± 169
$3.61*10^{-5} \pm 4.54*10^{-7}$	0.427 ± 0.001	11,833 ± 154
$4.27*10^{-5} \pm 5.37*10^{-7}$	0.536 ± 0.001	12,540 ± 161
$5.10*10^{-5} \pm 6.41*10^{-7}$	0.639 ± 0.001	12,528 ± 160
$5.87*10^{-5} \pm 7.38*10^{-7}$	0.735 ± 0.001	12,524 ± 159
$6.79*10^{-5} \pm 8.53*10^{-7}$	0.844 ± 0.001	12,434 ± 158
$7.68*10^{-5} \pm 9.66*10^{-7}$	0.960 ± 0.001	12,495 ± 158
$8.56*10^{-5} \pm 1.08*10^{-6}$	1.062 ± 0.002	12,413 ± 158

b = 0.002
m = 12,420
r = 1.000

12,584 ± 188 (170)

RANGE = ULTRAVIOLET
ABSORBANCE at = 318.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$8.60*10^{-6} \pm 1.08*10^{-7}$	0.208 ± 0.001	24,198 ± 346
$1.71*10^{-5} \pm 2.15*10^{-7}$	0.400 ± 0.001	23,414 ± 306
$2.60*10^{-5} \pm 3.27*10^{-7}$	0.622 ± 0.001	23,892 ± 305
$3.63*10^{-5} \pm 4.57*10^{-7}$	0.799 ± 0.001	22,001 ± 279
$4.27*10^{-5} \pm 5.37*10^{-7}$	1.000 ± 0.002	23,395 ± 299
$5.10*10^{-5} \pm 6.41*10^{-7}$	1.199 ± 0.002	23,508 ± 299
$5.87*10^{-5} \pm 7.38*10^{-7}$	1.381 ± 0.002	23,531 ± 298
$6.79*10^{-5} \pm 8.53*10^{-7}$	1.605 ± 0.003	23,646 ± 301
$7.68*10^{-5} \pm 9.66*10^{-7}$	1.831 ± 0.003	23,831 ± 302

b = -0.012
m = 23,774
r = 0.999

23,678 ± 278 (307)

TABLE 4

PARA-CHLORO DERIVATIVE IN CYCLOHEXANE

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 0.775 (g/cc)
TEMPERATURE = 24.0 (C)
CONC. STOCK SOLUTION = $3.08*10^{-4} \pm 5.32*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 490.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$5.68*10^{-6} \pm 9.79*10^{-8}$	0.098 ± 0.001	$17,267 \pm 388$
$1.20*10^{-5} \pm 2.07*10^{-7}$	0.207 ± 0.001	$17,209 \pm 319$
$1.76*10^{-5} \pm 3.04*10^{-7}$	0.305 ± 0.001	$17,285 \pm 309$
$2.37*10^{-5} \pm 4.09*10^{-7}$	0.414 ± 0.001	$17,440 \pm 307$
$2.98*10^{-5} \pm 5.14*10^{-7}$	0.518 ± 0.001	$17,376 \pm 303$
$3.55*10^{-5} \pm 6.12*10^{-7}$	0.610 ± 0.001	$17,187 \pm 299$
$4.16*10^{-5} \pm 7.17*10^{-7}$	0.720 ± 0.001	$17,319 \pm 301$
$4.75*10^{-5} \pm 8.19*10^{-7}$	0.830 ± 0.001	$17,482 \pm 303$
$5.36*10^{-5} \pm 9.25*10^{-7}$	0.924 ± 0.001	$17,236 \pm 298$
$5.94*10^{-5} \pm 1.02*10^{-6}$	1.026 ± 0.002	$17,269 \pm 300$

b = 0.001
m = 17,290
r = 1.000

$17,370 \pm 98$ (313)

RANGE = ULTRAVIOLET
ABSORBANCE at = 305.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$5.68*10^{-6} \pm 9.79*10^{-8}$	0.161 ± 0.001	$28,367 \pm 549$
$1.20*10^{-5} \pm 2.07*10^{-7}$	0.350 ± 0.001	$29,098 \pm 515$
$1.76*10^{-5} \pm 3.04*10^{-7}$	0.524 ± 0.001	$29,696 \pm 518$
$2.37*10^{-5} \pm 4.09*10^{-7}$	0.706 ± 0.001	$29,740 \pm 516$
$2.98*10^{-5} \pm 5.14*10^{-7}$	0.883 ± 0.001	$29,620 \pm 513$
$3.55*10^{-5} \pm 6.12*10^{-7}$	1.059 ± 0.002	$29,838 \pm 518$
$4.16*10^{-5} \pm 7.17*10^{-7}$	1.236 ± 0.002	$29,731 \pm 516$
$4.75*10^{-5} \pm 8.19*10^{-7}$	1.429 ± 0.003	$30,099 \pm 523$
$5.36*10^{-5} \pm 9.25*10^{-7}$	1.604 ± 0.003	$29,921 \pm 519$
$5.94*10^{-5} \pm 1.02*10^{-6}$	1.770 ± 0.003	$29,791 \pm 517$

b = -0.008
m = 30,043
r = 1.000

$29,560 \pm 504$ (520)

TABLE 5

META-BROMO DERIVATIVE IN CYCLOHEXANE

MOLECULAR WEIGHT = 379.259 (g/mol)
DENSITY = 0.775 (g/cc)
TEMPERATURE = 24.0 (C)
CONC. STOCK SOLUTION = $3.38*10^{-4} \pm 5.14*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 488.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$5.80*10^{-6} \pm 8.83*10^{-8}$	0.110 ± 0.001	18,953 ± 377
$1.13*10^{-5} \pm 1.72*10^{-7}$	0.211 ± 0.001	18,645 ± 310
$1.67*10^{-5} \pm 2.53*10^{-7}$	0.304 ± 0.001	18,249 ± 290
$2.29*10^{-5} \pm 3.48*10^{-7}$	0.414 ± 0.001	18,080 ± 282
$2.83*10^{-5} \pm 4.30*10^{-7}$	0.510 ± 0.001	18,034 ± 279
$3.40*10^{-5} \pm 5.17*10^{-7}$	0.615 ± 0.001	18,073 ± 278
$3.94*10^{-5} \pm 5.99*10^{-7}$	0.716 ± 0.001	18,166 ± 279
$4.49*10^{-5} \pm 6.83*10^{-7}$	0.812 ± 0.001	18,077 ± 277
$5.08*10^{-5} \pm 7.72*10^{-7}$	0.914 ± 0.001	18,003 ± 275
$5.64*10^{-5} \pm 8.58*10^{-7}$	1.017 ± 0.002	18,030 ± 277

b = 0.006
m = 17,923
r = 1.000

18,231 ± 316 (292)

RANGE = ULTRAVIOLET
ABSORBANCE at = 304.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$5.80*10^{-6} \pm 8.83*10^{-8}$	0.165 ± 0.001	28,430 ± 496
$1.13*10^{-5} \pm 1.72*10^{-7}$	0.317 ± 0.001	28,012 ± 444
$1.67*10^{-5} \pm 2.53*10^{-7}$	0.459 ± 0.001	27,554 ± 428
$2.29*10^{-5} \pm 3.48*10^{-7}$	0.625 ± 0.001	27,295 ± 420
$2.83*10^{-5} \pm 4.30*10^{-7}$	0.769 ± 0.001	27,193 ± 417
$3.40*10^{-5} \pm 5.17*10^{-7}$	0.934 ± 0.001	27,447 ± 419
$3.94*10^{-5} \pm 5.99*10^{-7}$	1.078 ± 0.002	27,350 ± 420
$4.49*10^{-5} \pm 6.83*10^{-7}$	1.228 ± 0.002	27,339 ± 419
$5.08*10^{-5} \pm 7.72*10^{-7}$	1.388 ± 0.003	27,339 ± 420
$5.64*10^{-5} \pm 8.58*10^{-7}$	1.549 ± 0.003	27,462 ± 421

b = 0.004
m = 27,283
r = 1.000

27,443 ± 238 (423)

TABLE 6

ORTHO-CHLORO DERIVATIVE IN CYCLOHEXANE

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 0.775 (g/cc)
TEMPERATURE = 24.0 (C)
CONC. STOCK SOLUTION = $3.01*10^{-4} \pm 5.01*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 468.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$6.23*10^{-6} \pm 1.04*10^{-7}$	0.092 ± 0.001	14,778 ± 335
$1.26*10^{-5} \pm 2.11*10^{-7}$	0.201 ± 0.001	15,892 ± 287
$1.89*10^{-5} \pm 3.16*10^{-7}$	0.297 ± 0.001	15,683 ± 272
$2.52*10^{-5} \pm 4.20*10^{-7}$	0.394 ± 0.001	15,641 ± 267
$3.14*10^{-5} \pm 5.24*10^{-7}$	0.487 ± 0.001	15,489 ± 262
$3.76*10^{-5} \pm 6.26*10^{-7}$	0.591 ± 0.001	15,726 ± 265
$4.39*10^{-5} \pm 7.31*10^{-7}$	0.682 ± 0.001	15,541 ± 261
$4.97*10^{-5} \pm 8.28*10^{-7}$	0.774 ± 0.001	15,585 ± 261
$5.62*10^{-5} \pm 9.37*10^{-7}$	0.891 ± 0.001	15,848 ± 265
$6.25*10^{-5} \pm 1.04*10^{-6}$	0.985 ± 0.001	15,749 ± 263

b = -0.004
m = 15,780
r = 1.000

15,684 ± 135 (267)

RANGE = ULTRAVIOLET
ABSORBANCE at = 290.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$6.23*10^{-6} \pm 1.04*10^{-7}$	0.095 ± 0.001	15,260 ± 341
$1.26*10^{-5} \pm 2.11*10^{-7}$	0.200 ± 0.001	15,813 ± 286
$1.89*10^{-5} \pm 3.16*10^{-7}$	0.295 ± 0.001	15,577 ± 270
$2.52*10^{-5} \pm 4.20*10^{-7}$	0.400 ± 0.001	15,879 ± 270
$3.14*10^{-5} \pm 5.24*10^{-7}$	0.501 ± 0.001	15,934 ± 269
$3.76*10^{-5} \pm 6.26*10^{-7}$	0.600 ± 0.001	15,965 ± 269
$4.39*10^{-5} \pm 7.31*10^{-7}$	0.695 ± 0.001	15,837 ± 266
$4.97*10^{-5} \pm 8.28*10^{-7}$	0.783 ± 0.001	15,766 ± 264
$5.62*10^{-5} \pm 9.37*10^{-7}$	0.920 ± 0.001	16,364 ± 274
$6.25*10^{-5} \pm 1.04*10^{-6}$	0.990 ± 0.001	15,829 ± 265

b = -0.005
m = 16,071
r = 1.000

15,722 ± 241 (237)

TABLE 7

ORTHO-BROMO DERIVATIVE IN CYCLOHEXANE

MOLECULAR WEIGHT = 379.259 (g/mol)
DENSITY = 0.775 (g/cc)
TEMPERATURE = 24.0 (C)
CONC. STOCK SOLUTION = $2.61*10^{-4} \pm 5.50*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 470.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$6.94*10^{-6} \pm 1.46*10^{-7}$	0.110 ± 0.001	$15,851 \pm 392$
$1.35*10^{-5} \pm 2.84*10^{-7}$	0.204 ± 0.001	$15,150 \pm 337$
$1.98*10^{-5} \pm 4.19*10^{-7}$	0.298 ± 0.001	$15,027 \pm 325$
$2.65*10^{-5} \pm 5.59*10^{-7}$	0.392 ± 0.001	$14,794 \pm 317$
$3.32*10^{-5} \pm 7.00*10^{-7}$	0.490 ± 0.001	$14,779 \pm 315$
$3.97*10^{-5} \pm 8.38*10^{-7}$	0.609 ± 0.001	$15,340 \pm 326$
$4.61*10^{-5} \pm 9.74*10^{-7}$	0.698 ± 0.001	$15,131 \pm 321$
$5.27*10^{-5} \pm 1.11*10^{-6}$	0.795 ± 0.001	$15,081 \pm 319$
$5.94*10^{-5} \pm 1.25*10^{-6}$	0.894 ± 0.001	$15,049 \pm 319$
$6.60*10^{-5} \pm 1.39*10^{-6}$	0.986 ± 0.001	$14,943 \pm 316$

b = 0.002
m = 14,496
r = 1.000

$15,032 \pm 177$ (322)

RANGE = ULTRAVIOLET
ABSORBANCE at = 291.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$6.94*10^{-6} \pm 1.46*10^{-7}$	0.112 ± 0.001	$16,139 \pm 370$
$1.35*10^{-5} \pm 2.84*10^{-7}$	0.205 ± 0.001	$15,224 \pm 330$
$1.98*10^{-5} \pm 4.19*10^{-7}$	0.303 ± 0.001	$15,279 \pm 326$
$2.65*10^{-5} \pm 5.59*10^{-7}$	0.394 ± 0.001	$14,870 \pm 316$
$3.32*10^{-5} \pm 7.00*10^{-7}$	0.488 ± 0.001	$14,719 \pm 312$
$3.97*10^{-5} \pm 8.38*10^{-7}$	0.613 ± 0.001	$15,441 \pm 327$
$4.61*10^{-5} \pm 9.74*10^{-7}$	0.697 ± 0.001	$15,109 \pm 320$
$5.27*10^{-5} \pm 1.11*10^{-6}$	0.800 ± 0.001	$15,176 \pm 321$
$5.94*10^{-5} \pm 1.25*10^{-6}$	0.901 ± 0.001	$15,167 \pm 321$
$6.60*10^{-5} \pm 1.39*10^{-6}$	0.992 ± 0.001	$15,034 \pm 318$

b = 0.002
m = 15,066
r = 1.000

$15,113 \pm 216$ (321)

TABLE 8

NAPTHYL DERIVATIVE IN CYCLOHEXANE

MOLECULAR WEIGHT = 350.422 (g/mol)
DENSITY = 0.775 (g/cc)
TEMPERATURE = 24.0 (C)
CONC. STOCK SOLUTION = $4.68*10^{-4} \pm 6.09*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 500.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.89*10^{-6} \pm 8.97*10^{-8}$	0.110 ± 0.001	$15,958 \pm 292$
$1.37*10^{-5} \pm 1.78*10^{-7}$	0.213 ± 0.001	$15,557 \pm 227$
$2.02*10^{-5} \pm 2.62*10^{-7}$	0.314 ± 0.001	$15,557 \pm 214$
$2.71*10^{-5} \pm 3.53*10^{-7}$	0.418 ± 0.001	$15,397 \pm 207$
$3.41*10^{-5} \pm 4.43*10^{-7}$	0.528 ± 0.001	$15,503 \pm 206$
$4.06*10^{-5} \pm 5.28*10^{-7}$	0.624 ± 0.001	$15,360 \pm 203$
$4.73*10^{-5} \pm 6.15*10^{-7}$	0.725 ± 0.001	$15,334 \pm 202$
$5.42*10^{-5} \pm 7.04*10^{-7}$	0.826 ± 0.001	$15,251 \pm 200$
$6.09*10^{-5} \pm 7.92*10^{-7}$	0.925 ± 0.001	$15,192 \pm 199$
$6.77*10^{-5} \pm 8.81*10^{-7}$	1.026 ± 0.002	$15,144 \pm 200$

b = 0.009
m = 15,075 $15,366 \pm 153$ (206)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 317.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.89*10^{-6} \pm 8.97*10^{-8}$	0.217 ± 0.001	$31,482 \pm 458$
$1.37*10^{-5} \pm 1.78*10^{-7}$	0.429 ± 0.001	$31,332 \pm 420$
$2.02*10^{-5} \pm 2.62*10^{-7}$	0.629 ± 0.001	$31,164 \pm 411$
$2.71*10^{-5} \pm 3.53*10^{-7}$	0.836 ± 0.001	$30,793 \pm 404$
$3.41*10^{-5} \pm 4.43*10^{-7}$	1.051 ± 0.002	$30,859 \pm 407$
$4.06*10^{-5} \pm 5.28*10^{-7}$	1.255 ± 0.002	$30,893 \pm 405$
$4.73*10^{-5} \pm 6.15*10^{-7}$	1.459 ± 0.002	$30,859 \pm 404$
$5.42*10^{-5} \pm 7.04*10^{-7}$	1.674 ± 0.003	$30,908 \pm 406$
$6.09*10^{-5} \pm 7.92*10^{-7}$	1.879 ± 0.003	$30,860 \pm 405$

b = 0.000
m = 30,752 $31,017 \pm 247$ (413)
r = 1.000

TABLE 9

TRIPHENYLFORMAZAN IN CARBON TETRACHLORIDE

MOLECULAR WEIGHT = 300.363 (g/mol)
DENSITY = 1.584 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $4.48*10^{-4} \pm 3.30*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 491.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$7.01*10^{-6} \pm 5.16*10^{-8}$	0.118 ± 0.001	16,839 ± 237
$1.45*10^{-5} \pm 1.07*10^{-7}$	0.244 ± 0.001	16,832 ± 158
$1.81*10^{-5} \pm 1.33*10^{-7}$	0.299 ± 0.001	16,506 ± 144
$2.42*10^{-5} \pm 1.78*10^{-7}$	0.410 ± 0.001	16,966 ± 138
$3.01*10^{-5} \pm 2.22*10^{-7}$	0.503 ± 0.001	16,706 ± 132
$3.64*10^{-5} \pm 2.68*10^{-7}$	0.604 ± 0.001	16,585 ± 128
$4.29*10^{-5} \pm 3.16*10^{-7}$	0.706 ± 0.001	16,449 ± 125
$4.85*10^{-5} \pm 3.57*10^{-7}$	0.786 ± 0.002	16,214 ± 128
$5.41*10^{-5} \pm 3.98*10^{-7}$	0.881 ± 0.002	16,293 ± 127
$6.06*10^{-5} \pm 4.46*10^{-7}$	1.006 ± 0.002	16,611 ± 128

b = 0.007
m = 16,300
r = 1.000

16,600 ± 243 (145)

RANGE = ULTRAVIOLET
ABSORBANCE at = 301.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$7.01*10^{-6} \pm 5.16*10^{-8}$	0.187 ± 0.001	26,686 ± 282
$1.45*10^{-5} \pm 1.07*10^{-7}$	0.363 ± 0.001	25,041 ± 209
$1.81*10^{-5} \pm 1.33*10^{-7}$	0.449 ± 0.001	24,786 ± 198
$2.42*10^{-5} \pm 1.78*10^{-7}$	0.597 ± 0.001	24,704 ± 191
$3.01*10^{-5} \pm 2.22*10^{-7}$	0.736 ± 0.001	24,444 ± 186
$3.64*10^{-5} \pm 2.68*10^{-7}$	0.885 ± 0.001	24,300 ± 183
$4.29*10^{-5} \pm 3.16*10^{-7}$	1.037 ± 0.001	24,161 ± 181
$4.85*10^{-5} \pm 3.57*10^{-7}$	1.130 ± 0.001	23,311 ± 174
$5.41*10^{-5} \pm 3.98*10^{-7}$	1.265 ± 0.002	23,394 ± 177
$6.06*10^{-5} \pm 4.46*10^{-7}$	1.477 ± 0.002	24,389 ± 183

b = 0.026
m = 23,327
r = 0.999

24,522 ± 943 (197)

TABLE 10

ORTHO-HYDROXY DERIVATIVE IN CARBON TETRACHLRIDE

MOLECULAR WEIGHT = 316.362 (g/mol)
DENSITY = 1.584 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $2.81*10^{-4} \pm 3.13*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 535.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$3.74*10^{-6} \pm 4.17*10^{-8}$	0.045 ± 0.001	$12,028 \pm 401$
$7.40*10^{-6} \pm 8.25*10^{-8}$	0.083 ± 0.001	$11,211 \pm 228$
$1.12*10^{-5} \pm 1.25*10^{-7}$	0.128 ± 0.001	$11,417 \pm 179$
$1.52*10^{-5} \pm 1.70*10^{-7}$	0.167 ± 0.001	$10,960 \pm 153$
$1.86*10^{-5} \pm 2.08*10^{-7}$	0.214 ± 0.001	$11,493 \pm 149$
$2.27*10^{-5} \pm 2.53*10^{-7}$	0.259 ± 0.001	$11,419 \pm 142$
$2.67*10^{-5} \pm 2.98*10^{-7}$	0.309 ± 0.001	$11,565 \pm 139$
$2.98*10^{-5} \pm 3.33*10^{-7}$	0.345 ± 0.001	$11,564 \pm 137$
$3.33*10^{-5} \pm 3.72*10^{-7}$	0.385 ± 0.001	$11,549 \pm 136$
$3.73*10^{-5} \pm 4.15*10^{-7}$	0.429 ± 0.001	$11,511 \pm 134$

b = -0.002
m = 11,587
r = 1.000

$11,427 \pm 273$ (180)

RANGE = ULTRAVIOLET
ABSORBANCE at = 311.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$3.74*10^{-6} \pm 4.17*10^{-8}$	0.109 ± 0.001	$29,135 \pm 498$
$7.40*10^{-6} \pm 8.25*10^{-8}$	0.183 ± 0.001	$24,718 \pm 335$
$1.12*10^{-5} \pm 1.25*10^{-7}$	0.279 ± 0.001	$24,886 \pm 305$
$1.52*10^{-5} \pm 1.70*10^{-7}$	0.393 ± 0.001	$25,793 \pm 302$
$1.86*10^{-5} \pm 2.08*10^{-7}$	0.452 ± 0.001	$24,274 \pm 281$
$2.27*10^{-5} \pm 2.53*10^{-7}$	0.543 ± 0.001	$23,940 \pm 274$
$2.67*10^{-5} \pm 2.98*10^{-7}$	0.645 ± 0.001	$24,140 \pm 274$
$2.98*10^{-5} \pm 3.33*10^{-7}$	0.715 ± 0.001	$23,966 \pm 271$
$3.33*10^{-5} \pm 3.72*10^{-7}$	0.791 ± 0.001	$23,728 \pm 268$
$3.73*10^{-5} \pm 4.15*10^{-7}$	0.885 ± 0.001	$23,746 \pm 267$

b = 0.022
m = 23,192
r = 1.000

$24,355 \pm 673$ (286)

TABLE 11

HYDROXY-CHLORO DERIVATIVE IN CARBON TETRACHLORIDE

MOLECULAR WEIGHT = 350.807 (g/mol)
DENSITY = 1.584 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $5.15*10^{-4} \pm 2.82*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 533.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$6.29*10^{-6} \pm 3.45*10^{-8}$	0.079 ± 0.001	$12,552 \pm 235$
$1.74*10^{-5} \pm 9.53*10^{-8}$	0.214 ± 0.001	$12,302 \pm 106$
$2.07*10^{-5} \pm 1.13*10^{-7}$	0.256 ± 0.001	$12,387 \pm 96$
$2.65*10^{-5} \pm 1.45*10^{-7}$	0.328 ± 0.001	$12,357 \pm 86$
$3.39*10^{-5} \pm 1.86*10^{-7}$	0.419 ± 0.001	$12,360 \pm 80$
$4.00*10^{-5} \pm 2.19*10^{-7}$	0.491 ± 0.001	$12,271 \pm 76$
$4.87*10^{-5} \pm 2.67*10^{-7}$	0.595 ± 0.001	$12,210 \pm 73$
$5.46*10^{-5} \pm 2.99*10^{-7}$	0.671 ± 0.001	$12,292 \pm 72$
$6.23*10^{-5} \pm 3.41*10^{-7}$	0.758 ± 0.002	$12,168 \pm 76$
$6.95*10^{-5} \pm 3.81*10^{-7}$	0.851 ± 0.002	$12,249 \pm 74$

b = 0.004
m = 12,174
r = 1.000

$12,315 \pm 108$ (98)

RANGE = ULTRAVIOLET
ABSORBANCE at = 319.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$6.29*10^{-6} \pm 3.45*10^{-8}$	0.144 ± 0.001	$22,879 \pm 257$
$1.74*10^{-5} \pm 9.53*10^{-8}$	0.389 ± 0.001	$22,361 \pm 147$
$2.07*10^{-5} \pm 1.13*10^{-7}$	0.469 ± 0.001	$22,693 \pm 142$
$2.65*10^{-5} \pm 1.45*10^{-7}$	0.594 ± 0.001	$22,379 \pm 134$
$3.39*10^{-5} \pm 1.86*10^{-7}$	0.758 ± 0.001	$22,359 \pm 129$
$4.00*10^{-5} \pm 2.19*10^{-7}$	0.897 ± 0.001	$22,417 \pm 128$
$4.87*10^{-5} \pm 2.67*10^{-7}$	1.087 ± 0.001	$22,307 \pm 126$

b = 0.004
m = 22,261
r = 1.000

$22,485 \pm 215$ (152)

TABLE 12

PARA-CHLORO DERIVATIVE IN CARBON TETRACHLORIDE

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 1.584 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $4.11*10^{-4} \pm 2.11*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 493.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$7.50*10^{-6} \pm 3.85*10^{-8}$	0.129 ± 0.001	$17,207 \pm 208$
$1.24*10^{-5} \pm 6.38*10^{-8}$	0.216 ± 0.001	$17,380 \pm 145$
$1.64*10^{-5} \pm 8.43*10^{-8}$	0.281 ± 0.001	$17,113 \pm 123$
$2.25*10^{-5} \pm 1.15*10^{-7}$	0.377 ± 0.001	$16,788 \pm 107$
$2.94*10^{-5} \pm 1.51*10^{-7}$	0.494 ± 0.001	$16,778 \pm 99$
$3.32*10^{-5} \pm 1.71*10^{-7}$	0.555 ± 0.001	$16,708 \pm 96$
$3.92*10^{-5} \pm 2.01*10^{-7}$	0.656 ± 0.004	$16,724 \pm 136$
$4.45*10^{-5} \pm 2.28*10^{-7}$	0.741 ± 0.002	$16,659 \pm 99$
$4.97*10^{-5} \pm 2.55*10^{-7}$	0.820 ± 0.002	$16,496 \pm 96$
$5.53*10^{-5} \pm 2.84*10^{-7}$	0.904 ± 0.002	$16,352 \pm 93$

b = 0.014
m = 16,249
r = 1.000

$16,834 \pm 340$ (116)

RANGE = ULTRAVIOLET
ABSORBANCE at = 308.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$7.50*10^{-6} \pm 5.39*10^{-8}$	0.222 ± 0.002	$29,612 \pm 366$
$1.24*10^{-5} \pm 8.94*10^{-8}$	0.362 ± 0.002	$29,127 \pm 276$
$1.64*10^{-5} \pm 1.18*10^{-7}$	0.464 ± 0.002	$28,257 \pm 245$
$2.25*10^{-5} \pm 1.61*10^{-7}$	0.625 ± 0.002	$27,832 \pm 224$
$2.94*10^{-5} \pm 2.12*10^{-7}$	0.823 ± 0.003	$27,952 \pm 223$
$3.32*10^{-5} \pm 2.39*10^{-7}$	0.908 ± 0.003	$27,335 \pm 214$
$3.92*10^{-5} \pm 2.82*10^{-7}$	1.070 ± 0.003	$27,278 \pm 209$
$4.45*10^{-5} \pm 3.20*10^{-7}$	1.210 ± 0.003	$27,203 \pm 206$
$4.97*10^{-5} \pm 3.57*10^{-7}$	1.317 ± 0.003	$26,494 \pm 199$
$5.53*10^{-5} \pm 3.97*10^{-7}$	1.437 ± 0.004	$25,994 \pm 198$

b = 0.046
m = 25,713
r = 1.000

$27,708 \pm 1106$(236)

TABLE 13

META-BROMO DERIVATIVE IN CARBON TETRACHLORIDE

MOLECULAR WEIGHT = 379.259 (g/mol)
DENSITY = 1.584 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $4.20*10^{-4} \pm 2.61*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 490.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$5.10*10^{-6} \pm 3.17*10^{-8}$	0.094 ± 0.001	18,426 ± 300
$1.36*10^{-5} \pm 8.45*10^{-8}$	0.246 ± 0.001	18,085 ± 153
$1.74*10^{-5} \pm 1.08*10^{-7}$	0.311 ± 0.001	17,889 ± 138
$2.27*10^{-5} \pm 1.41*10^{-7}$	0.407 ± 0.001	17,941 ± 128
$2.75*10^{-5} \pm 1.71*10^{-7}$	0.490 ± 0.001	17,789 ± 122
$3.43*10^{-5} \pm 2.13*10^{-7}$	0.595 ± 0.001	17,346 ± 115
$4.00*10^{-5} \pm 2.48*10^{-7}$	0.702 ± 0.001	17,554 ± 115
$4.56*10^{-5} \pm 2.83*10^{-7}$	0.802 ± 0.001	17,603 ± 114
$5.11*10^{-5} \pm 3.17*10^{-7}$	0.897 ± 0.001	17,562 ± 113
$5.69*10^{-5} \pm 3.53*10^{-7}$	0.995 ± 0.001	17,492 ± 111

b = 0.009
m = 17,353
r = 1.000

17,769 ± 325 (141)

RANGE = ULTRAVIOLET
ABSORBANCE at = 306.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$5.10*10^{-6} \pm 3.17*10^{-8}$	0.140 ± 0.001	27,443 ± 325
$1.36*10^{-5} \pm 8.45*10^{-8}$	0.355 ± 0.001	26,098 ± 193
$1.74*10^{-5} \pm 1.08*10^{-7}$	0.450 ± 0.001	25,884 ± 180
$2.27*10^{-5} \pm 1.41*10^{-7}$	0.589 ± 0.001	25,963 ± 173
$2.75*10^{-5} \pm 1.71*10^{-7}$	0.708 ± 0.001	25,703 ± 168
$3.43*10^{-5} \pm 2.13*10^{-7}$	0.880 ± 0.001	25,655 ± 165
$4.00*10^{-5} \pm 2.48*10^{-7}$	1.034 ± 0.001	25,856 ± 164
$4.56*10^{-5} \pm 2.83*10^{-7}$	1.162 ± 0.002	25,505 ± 166
$5.11*10^{-5} \pm 3.17*10^{-7}$	1.294 ± 0.002	25,335 ± 163
$5.69*10^{-5} \pm 3.53*10^{-7}$	1.403 ± 0.002	24,665 ± 158

b = 0.023
m = 24,729
r = 1.000

25,810 ± 703 (186)

TABLE 14

ORTHO-CHLORO DERIVATIVE IN CARBON TETRACHLORIDE

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 1.584 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $6.01*10^{-4} \pm 2.96*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 467.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$7.88*10^{-6} \pm 3.88*10^{-8}$	0.115 ± 0.001	$14,600 \pm 193$
$1.63*10^{-5} \pm 8.01*10^{-8}$	0.219 ± 0.001	$13,455 \pm 109$
$2.39*10^{-5} \pm 1.18*10^{-7}$	0.332 ± 0.001	$13,870 \pm 90$
$3.34*10^{-5} \pm 1.65*10^{-7}$	0.468 ± 0.001	$13,991 \pm 81$
$4.07*10^{-5} \pm 2.01*10^{-7}$	0.550 ± 0.001	$13,497 \pm 75$
$5.00*10^{-5} \pm 2.46*10^{-7}$	0.672 ± 0.001	$13,437 \pm 72$
$5.78*10^{-5} \pm 2.84*10^{-7}$	0.777 ± 0.002	$13,444 \pm 77$
$6.56*10^{-5} \pm 3.23*10^{-7}$	0.888 ± 0.002	$13,542 \pm 75$
$7.34*10^{-5} \pm 3.61*10^{-7}$	0.983 ± 0.002	$13,400 \pm 73$
$8.31*10^{-5} \pm 4.09*10^{-7}$	1.115 ± 0.003	$13,412 \pm 76$

b = 0.011
m = 13,291
r = 1.000

$13,665 \pm 387$ (192)

TABLE 15

NAPTHYL DERIVATIVE IN CARBON TETRACHLORIDE

MOLECULAR WEIGHT = 350.422 (g/mol)
DENSITY = 1.584 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $5.11*10^{-4} \pm 2.83*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 504.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$7.56*10^{-6} \pm 4.18*10^{-8}$	0.118 ± 0.001	$15,606 \pm 206$
$1.35*10^{-5} \pm 7.48*10^{-8}$	0.210 ± 0.001	$15,527 \pm 135$
$2.14*10^{-5} \pm 1.19*10^{-7}$	0.335 ± 0.001	$15,624 \pm 109$
$2.84*10^{-5} \pm 1.57*10^{-7}$	0.432 ± 0.001	$15,214 \pm 98$
$3.69*10^{-5} \pm 2.04*10^{-7}$	0.550 ± 0.001	$14,920 \pm 91$
$4.14*10^{-5} \pm 2.29*10^{-7}$	0.634 ± 0.001	$15,331 \pm 91$
$4.89*10^{-5} \pm 2.71*10^{-7}$	0.735 ± 0.001	$15,018 \pm 88$
$5.70*10^{-5} \pm 3.15*10^{-7}$	0.855 ± 0.002	$15,007 \pm 92$
$6.29*10^{-5} \pm 3.48*10^{-7}$	0.951 ± 0.002	$15,116 \pm 91$
$6.82*10^{-5} \pm 3.77*10^{-7}$	1.016 ± 0.002	$14,902 \pm 89$

b = 0.010
m = 14,816
r = 1.000

$15,227 \pm 280$ (109)

RANGE = ULTRAVIOLET
ABSORBANCE at = 318.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$7.56*10^{-6} \pm 4.18*10^{-8}$	0.225 ± 0.002	$29,757 \pm 338$
$1.35*10^{-5} \pm 7.48*10^{-8}$	0.399 ± 0.002	$29,501 \pm 232$
$2.14*10^{-5} \pm 1.19*10^{-7}$	0.633 ± 0.002	$29,523 \pm 194$
$2.84*10^{-5} \pm 1.57*10^{-7}$	0.827 ± 0.002	$29,124 \pm 179$
$3.69*10^{-5} \pm 2.04*10^{-7}$	1.037 ± 0.003	$28,131 \pm 173$
$4.14*10^{-5} \pm 2.29*10^{-7}$	1.199 ± 0.003	$28,993 \pm 174$
$4.89*10^{-5} \pm 2.71*10^{-7}$	1.382 ± 0.003	$28,237 \pm 166$
$5.70*10^{-5} \pm 3.15*10^{-7}$	1.627 ± 0.003	$28,557 \pm 166$
$6.29*10^{-5} \pm 3.48*10^{-7}$	1.792 ± 0.004	$28,484 \pm 168$
$6.82*10^{-5} \pm 3.77*10^{-7}$	1.872 ± 0.004	$27,457 \pm 161$

b = 0.032
m = 27,641
r = 0.999

$28,776 \pm 730$ (195)

TABLE 16

TRIPHENYLFORMAZAN IN TOLUENE

MOLECULAR WEIGHT = 300.363 (g/mol)
DENSITY = 0.865 (g/cc)
TEMPERATURE = 21.0 (C)
CONC. STOCK SOLUTION = $4.11*10^{-4} \pm 6.75*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 491.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$8.35*10^{-6} \pm 1.37*10^{-7}$	0.132 ± 0.001	15,813 ± 310
$1.44*10^{-5} \pm 2.37*10^{-7}$	0.225 ± 0.001	15,576 ± 274
$1.93*10^{-5} \pm 3.17*10^{-7}$	0.302 ± 0.001	15,647 ± 267
$2.83*10^{-5} \pm 4.65*10^{-7}$	0.441 ± 0.001	15,580 ± 261
$3.27*10^{-5} \pm 5.37*10^{-7}$	0.512 ± 0.001	15,667 ± 261
$3.92*10^{-5} \pm 6.44*10^{-7}$	0.616 ± 0.001	15,698 ± 260
$4.59*10^{-5} \pm 7.53*10^{-7}$	0.705 ± 0.001	15,375 ± 254
$5.22*10^{-5} \pm 8.57*10^{-7}$	0.808 ± 0.001	15,491 ± 256
$5.82*10^{-5} \pm 9.56*10^{-7}$	0.898 ± 0.001	15,428 ± 255
$6.38*10^{-5} \pm 1.05*10^{-6}$	0.987 ± 0.001	15,463 ± 255

b = 0.005
m = 15,378
r = 1.000

15,574 ± 136 (265)

RANGE = ULTRAVIOLET
ABSORBANCE at = 300.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$8.35*10^{-6} \pm 1.37*10^{-7}$	0.190 ± 0.001	22,761 ± 410
$1.44*10^{-5} \pm 2.37*10^{-7}$	0.330 ± 0.001	22,844 ± 388
$1.93*10^{-5} \pm 3.17*10^{-7}$	0.447 ± 0.001	23,160 ± 387
$2.83*10^{-5} \pm 4.65*10^{-7}$	0.648 ± 0.001	22,893 ± 379
$3.27*10^{-5} \pm 5.37*10^{-7}$	0.749 ± 0.001	22,920 ± 379
$3.92*10^{-5} \pm 6.44*10^{-7}$	0.911 ± 0.001	23,215 ± 383
$4.59*10^{-5} \pm 7.53*10^{-7}$	1.045 ± 0.002	22,790 ± 377
$5.22*10^{-5} \pm 8.57*10^{-7}$	1.203 ± 0.002	23,064 ± 381
$5.82*10^{-5} \pm 9.56*10^{-7}$	1.332 ± 0.003	22,885 ± 380
$6.38*10^{-5} \pm 1.05*10^{-6}$	1.467 ± 0.003	22,983 ± 381

b = 0.000
m = 22,960
r = 1.000

22,952 ± 153 (385)

TABLE 17

ORTHO-HYDROXY DERIVATIVE IN TOLUENE

MOLECULAR WEIGHT = 316.362 (g/mol)
DENSITY = 0.865 (g/cc)
TEMPERATURE = 21.0 (C)
CONC. STOCK SOLUTION = $4.84*10^{-4} \pm 6.32*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 535.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$9.39*10^{-6} \pm 1.23*10^{-7}$	0.113 ± 0.001	12,037 ± 218
$1.78*10^{-5} \pm 2.32*10^{-7}$	0.212 ± 0.001	11,905 ± 174
$2.70*10^{-5} \pm 3.52*10^{-7}$	0.321 ± 0.001	11,910 ± 164
$3.52*10^{-5} \pm 4.59*10^{-7}$	0.419 ± 0.001	11,901 ± 160
$4.40*10^{-5} \pm 5.74*10^{-7}$	0.521 ± 0.001	11,851 ± 158
$5.32*10^{-5} \pm 6.94*10^{-7}$	0.631 ± 0.001	11,866 ± 157
$6.16*10^{-5} \pm 8.04*10^{-7}$	0.729 ± 0.001	11,837 ± 156
$7.01*10^{-5} \pm 9.15*10^{-7}$	0.828 ± 0.001	11,812 ± 155
$7.83*10^{-5} \pm 1.02*10^{-6}$	0.927 ± 0.001	11,833 ± 155
$8.66*10^{-5} \pm 1.13*10^{-6}$	1.026 ± 0.002	11,845 ± 157

b = 0.002
m = 11,810 11,880 ± 65 (165)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 311.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$9.39*10^{-6} \pm 1.23*10^{-7}$	0.225 ± 0.001	23,968 ± 347
$1.78*10^{-5} \pm 2.32*10^{-7}$	0.417 ± 0.001	23,417 ± 316
$2.70*10^{-5} \pm 3.52*10^{-7}$	0.640 ± 0.001	23,746 ± 314
$3.52*10^{-5} \pm 4.59*10^{-7}$	0.834 ± 0.001	23,688 ± 312
$4.40*10^{-5} \pm 5.74*10^{-7}$	1.037 ± 0.001	23,588 ± 309
$5.32*10^{-5} \pm 6.94*10^{-7}$	1.264 ± 0.002	23,769 ± 313
$6.16*10^{-5} \pm 8.04*10^{-7}$	1.459 ± 0.002	23,690 ± 311
$7.01*10^{-5} \pm 9.15*10^{-7}$	1.674 ± 0.003	23,880 ± 315
$7.83*10^{-5} \pm 1.02*10^{-6}$	1.876 ± 0.003	23,948 ± 315

b = -0.008
m = 23,940 23,774 ± 188 (317)
r = 1.000

TABLE 18

HYDROXY-CHLORO DERIVATIVE IN TOLUENE

MOLECULAR WEIGHT = 350.807 (g/mol)
DENSITY = 0.865 (g/cc)
TEMPERATURE = 21.0 (C)
CONC. STOCK SOLUTION = $5.14*10^{-4} \pm 5.84*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 530.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$1.01*10^{-5} \pm 1.15*10^{-7}$	0.127 ± 0.001	$12,582 \pm 200$
$1.86*10^{-5} \pm 2.12*10^{-7}$	0.232 ± 0.001	$12,449 \pm 161$
$2.82*10^{-5} \pm 3.20*10^{-7}$	0.355 ± 0.001	$12,598 \pm 152$
$3.82*10^{-5} \pm 4.34*10^{-7}$	0.482 ± 0.001	$12,624 \pm 148$
$4.66*10^{-5} \pm 5.30*10^{-7}$	0.588 ± 0.001	$12,607 \pm 147$
$5.55*10^{-5} \pm 6.31*10^{-7}$	0.697 ± 0.001	$12,552 \pm 145$
$6.23*10^{-5} \pm 7.08*10^{-7}$	0.787 ± 0.001	$12,638 \pm 145$
$7.48*10^{-5} \pm 8.50*10^{-7}$	0.948 ± 0.001	$12,681 \pm 145$
$8.33*10^{-5} \pm 9.47*10^{-7}$	1.053 ± 0.002	$12,638 \pm 146$
$9.11*10^{-5} \pm 1.04*10^{-6}$	1.148 ± 0.002	$12,607 \pm 145$

b = -0.002
m = 12,650
r = 1.000

$12,598 \pm 63$ (153)

RANGE = ULTRAVIOLET
ABSORBANCE at = 300.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$1.01*10^{-5} \pm 1.15*10^{-7}$	0.230 ± 0.001	$22,787 \pm 295$
$1.86*10^{-5} \pm 2.12*10^{-7}$	0.419 ± 0.001	$22,483 \pm 267$
$2.82*10^{-5} \pm 3.20*10^{-7}$	0.644 ± 0.001	$22,854 \pm 265$
$3.82*10^{-5} \pm 4.34*10^{-7}$	0.881 ± 0.001	$23,075 \pm 265$
$4.66*10^{-5} \pm 5.30*10^{-7}$	1.064 ± 0.002	$22,812 \pm 264$
$5.55*10^{-5} \pm 6.31*10^{-7}$	1.279 ± 0.002	$23,034 \pm 265$
$6.23*10^{-5} \pm 7.08*10^{-7}$	1.424 ± 0.002	$22,867 \pm 262$
$7.48*10^{-5} \pm 8.50*10^{-7}$	1.734 ± 0.003	$23,195 \pm 267$
$8.33*10^{-5} \pm 9.47*10^{-7}$	1.944 ± 0.003	$23,331 \pm 268$

b = -0.014
m = 23,339
r = 1.000

$22,938 \pm 252$ (269)

TABLE 19

PARA-CHLORO DERIVATIVE IN TOLUENE

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 0.865 (g/cc)
TEMPERATURE = 21.0 (C)
CONC. STOCK SOLUTION = $3.66*10^{-4} \pm 6.10*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 493.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$7.67*10^{-6} \pm 1.28*10^{-7}$	0.125 ± 0.001	$16,306 \pm 328$
$1.28*10^{-5} \pm 2.13*10^{-7}$	0.214 ± 0.001	$16,680 \pm 299$
$1.91*10^{-5} \pm 3.17*10^{-7}$	0.313 ± 0.001	$16,421 \pm 283$
$2.56*10^{-5} \pm 4.25*10^{-7}$	0.428 ± 0.001	$16,743 \pm 284$
$3.15*10^{-5} \pm 5.25*10^{-7}$	0.520 ± 0.001	$16,482 \pm 278$
$3.79*10^{-5} \pm 6.30*10^{-7}$	0.623 ± 0.001	$16,452 \pm 276$
$4.40*10^{-5} \pm 7.33*10^{-7}$	0.722 ± 0.001	$16,391 \pm 275$
$5.05*10^{-5} \pm 8.40*10^{-7}$	0.836 ± 0.001	$16,550 \pm 277$
$5.69*10^{-5} \pm 9.46*10^{-7}$	0.942 ± 0.001	$16,559 \pm 277$
$6.28*10^{-5} \pm 1.04*10^{-6}$	1.030 ± 0.001	$16,401 \pm 274$

b = 0.001
m = 16,455 $16,472 \pm 105$ (285)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 307.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$7.67*10^{-6} \pm 1.28*10^{-7}$	0.210 ± 0.001	$27,393 \pm 492$
$1.28*10^{-5} \pm 2.13*10^{-7}$	0.360 ± 0.001	$28,060 \pm 480$
$1.91*10^{-5} \pm 3.17*10^{-7}$	0.538 ± 0.001	$28,225 \pm 475$
$2.56*10^{-5} \pm 4.25*10^{-7}$	0.728 ± 0.001	$28,479 \pm 477$
$3.15*10^{-5} \pm 5.25*10^{-7}$	0.860 ± 0.001	$27,259 \pm 456$
$3.79*10^{-5} \pm 6.30*10^{-7}$	1.033 ± 0.001	$27,280 \pm 455$
$4.40*10^{-5} \pm 7.33*10^{-7}$	1.196 ± 0.002	$27,151 \pm 455$
$5.05*10^{-5} \pm 8.40*10^{-7}$	1.376 ± 0.001	$27,240 \pm 454$
$5.69*10^{-5} \pm 9.46*10^{-7}$	1.538 ± 0.002	$27,035 \pm 452$
$6.28*10^{-5} \pm 1.04*10^{-6}$	1.712 ± 0.003	$27,260 \pm 456$

b = 0.017
m = 26,896 $27,538 \pm 513$ (465)
r = 1.000

TABLE 20

META-BROMO DERIVATIVE IN TOLUENE

MOLECULAR WEIGHT = 379.259 (g/mol)
DENSITY = 0.865 (g/cc)
TEMPERATURE = 21.0 (C)
CONC. STOCK SOLUTION = $3.26*10^{-4} \pm 5.30*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 488.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.64*10^{-6} \pm 1.08*10^{-7}$	0.116 ± 0.001	$17,471 \pm 355$
$1.23*10^{-5} \pm 2.01*10^{-7}$	0.213 ± 0.001	$17,255 \pm 303$
$1.81*10^{-5} \pm 2.94*10^{-7}$	0.303 ± 0.001	$16,747 \pm 283$
$2.42*10^{-5} \pm 3.93*10^{-7}$	0.418 ± 0.001	$17,298 \pm 287$
$3.01*10^{-5} \pm 4.89*10^{-7}$	0.513 ± 0.001	$17,039 \pm 281$
$3.61*10^{-5} \pm 5.87*10^{-7}$	0.615 ± 0.001	$17,022 \pm 279$
$4.16*10^{-5} \pm 6.76*10^{-7}$	0.709 ± 0.001	$17,046 \pm 279$
$4.75*10^{-5} \pm 7.72*10^{-7}$	0.811 ± 0.001	$17,074 \pm 279$
$5.35*10^{-5} \pm 8.70*10^{-7}$	0.903 ± 0.001	$16,866 \pm 275$
$5.69*10^{-5} \pm 9.25*10^{-7}$	0.967 ± 0.001	$16,986 \pm 277$

b = 0.004
m = 16,918
r = 1.000

17.080 ± 212 (290)

RANGE = ULTRAVIOLET
ABSORBANCE at = 306.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.64*10^{-6} \pm 1.08*10^{-7}$	0.174 ± 0.001	$26,206 \pm 476$
$1.23*10^{-5} \pm 2.01*10^{-7}$	0.309 ± 0.001	$25,032 \pm 423$
$1.81*10^{-5} \pm 2.94*10^{-7}$	0.452 ± 0.001	$24,982 \pm 414$
$2.42*10^{-5} \pm 3.93*10^{-7}$	0.613 ± 0.001	$25,367 \pm 416$
$3.01*10^{-5} \pm 4.89*10^{-7}$	0.752 ± 0.001	$24,977 \pm 409$
$3.61*10^{-5} \pm 5.87*10^{-7}$	0.888 ± 0.001	$24,578 \pm 401$
$4.16*10^{-5} \pm 6.76*10^{-7}$	1.031 ± 0.002	$24,788 \pm 407$
$4.75*10^{-5} \pm 7.72*10^{-7}$	1.179 ± 0.002	$24,822 \pm 406$
$5.35*10^{-5} \pm 8.70*10^{-7}$	1.332 ± 0.002	$24,879 \pm 407$
$5.69*10^{-5} \pm 9.25*10^{-7}$	1.416 ± 0.002	$24,873 \pm 406$

b = 0.007
m = 24,696
r = 1.000

$24,922 \pm 214$ (410)

TABLE 21

ORTHO-CHLORO DERIVATIVE IN TOLUENE

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 0.861 (g/cc)
TEMPERATURE = 26.0 (C)
CONC. STOCK SOLUTION = $2.64*10^{-4} \pm 5.97*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 400.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$3.72*10^{-6} \pm 8.42*10^{-8}$	0.103 ± 0.001	$27,689 \pm 733$
$7.23*10^{-6} \pm 1.64*10^{-7}$	0.209 ± 0.001	$28,927 \pm 683$
$1.05*10^{-5} \pm 2.38*10^{-7}$	0.299 ± 0.001	$28,426 \pm 657$
$1.39*10^{-5} \pm 3.15*10^{-7}$	0.399 ± 0.001	$28,640 \pm 656$
$1.74*10^{-5} \pm 3.94*10^{-7}$	0.499 ± 0.001	$28,665 \pm 654$
$2.09*10^{-5} \pm 4.72*10^{-7}$	0.601 ± 0.001	$28,817 \pm 656$
$2.43*10^{-5} \pm 5.51*10^{-7}$	0.701 ± 0.001	$28,806 \pm 654$
$2.76*10^{-5} \pm 6.25*10^{-7}$	0.794 ± 0.002	$28,742 \pm 655$
$3.11*10^{-5} \pm 7.03*10^{-7}$	0.887 ± 0.002	$28,549 \pm 650$
$3.46*10^{-5} \pm 7.82*10^{-7}$	0.991 ± 0.002	$28,668 \pm 652$

b = -0.001
m = 28,699 $28,693 \pm 151$ (657)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 292.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$3.72*10^{-6} \pm 8.42*10^{-8}$	0.044 ± 0.001	$11,828 \pm 465$
$7.23*10^{-6} \pm 1.64*10^{-7}$	0.074 ± 0.001	$10,242 \pm 303$
$1.05*10^{-5} \pm 2.38*10^{-7}$	0.105 ± 0.001	$9,983 \pm 263$
$1.39*10^{-5} \pm 3.15*10^{-7}$	0.143 ± 0.001	$10,264 \pm 253$
$1.74*10^{-5} \pm 3.94*10^{-7}$	0.165 ± 0.001	$9,478 \pm 229$
$2.09*10^{-5} \pm 4.72*10^{-7}$	0.197 ± 0.001	$9,446 \pm 224$
$2.43*10^{-5} \pm 5.51*10^{-7}$	0.227 ± 0.001	$9,328 \pm 219$
$2.76*10^{-5} \pm 6.25*10^{-7}$	0.255 ± 0.001	$9,231 \pm 215$
$3.11*10^{-5} \pm 7.03*10^{-7}$	0.288 ± 0.001	$9,270 \pm 215$
$3.46*10^{-5} \pm 7.82*10^{-7}$	0.323 ± 0.001	$9,344 \pm 215$

b = 0.011
m = 8,922 $9,621 \pm 421$ (237)
r = 0.999

TABLE 22

ORTHO-BROMO DERIVATIVE IN TOLUENE

MOLECULAR WEIGHT = 379.259 (g/mol)
DENSITY = 0.864 (g/cc)
TEMPERATURE = 23.0 (C)
CONC. STOCK SOLUTION = $2.91*10^{-4} \pm 5.62*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 402.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$4.21*10^{-6} \pm 8.14*10^{-8}$	0.106 ± 0.001	25,149 ± 590
$8.14*10^{-6} \pm 1.57*10^{-7}$	0.209 ± 0.001	25,685 ± 525
$1.20*10^{-5} \pm 2.32*10^{-7}$	0.300 ± 0.001	25,016 ± 497
$1.65*10^{-5} \pm 3.18*10^{-7}$	0.422 ± 0.001	25,637 ± 502
$2.02*10^{-5} \pm 3.91*10^{-7}$	0.524 ± 0.001	25,880 ± 504
$2.83*10^{-5} \pm 5.46*10^{-7}$	0.736 ± 0.002	26,029 ± 509
$3.19*10^{-5} \pm 6.16*10^{-7}$	0.818 ± 0.002	25,652 ± 500
$3.60*10^{-5} \pm 6.95*10^{-7}$	0.930 ± 0.002	25,818 ± 502
$4.02*10^{-5} \pm 7.76*10^{-7}$	1.038 ± 0.003	25,813 ± 505

b = -0.004
m = 25,954
r = 1.000

25,666 ± 335 (514)

RANGE = ULTRAVIOLET
ABSORBANCE at = 294.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$1.20*10^{-5} \pm 2.32*10^{-7}$	0.149 ± 0.001	12,424 ± 267
$1.65*10^{-5} \pm 3.18*10^{-7}$	0.167 ± 0.001	10,145 ± 214
$2.02*10^{-5} \pm 3.91*10^{-7}$	0.193 ± 0.001	9,532 ± 197
$2.42*10^{-5} \pm 4.67*10^{-7}$	0.212 ± 0.001	8,755 ± 179
$2.83*10^{-5} \pm 5.46*10^{-7}$	0.239 ± 0.001	8,452 ± 171
$3.19*10^{-5} \pm 6.16*10^{-7}$	0.277 ± 0.001	8,686 ± 173
$3.60*10^{-5} \pm 6.95*10^{-7}$	0.313 ± 0.001	8,689 ± 172
$4.02*10^{-5} \pm 7.76*10^{-7}$	0.347 ± 0.001	8,629 ± 170

b = 0.050
m = 7,161
r = 0.991

8,984 ± 617 (181)

TABLE 23

NAPHTHYL DERIVATIVE IN TOLUENE

MOLECULAR WEIGHT = 350.422 (g/mol)
DENSITY = 0.865 (g/cc)
TEMPERATURE = 21.0 (C)
CONC. STOCK SOLUTION = $5.29*10^{-4} \pm 6.97*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 501.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.96*10^{-6} \pm 9.19*10^{-8}$	0.102 ± 0.001	$14,645 \pm 280$
$1.35*10^{-5} \pm 1.78*10^{-7}$	0.198 ± 0.001	$14,633 \pm 219$
$2.11*10^{-5} \pm 2.78*10^{-7}$	0.299 ± 0.001	$14,199 \pm 199$
$2.79*10^{-5} \pm 3.67*10^{-7}$	0.401 ± 0.001	$14,396 \pm 197$
$3.43*10^{-5} \pm 4.52*10^{-7}$	0.486 ± 0.001	$14,168 \pm 191$
$4.12*10^{-5} \pm 5.43*10^{-7}$	0.573 ± 0.001	$13,914 \pm 187$
$4.76*10^{-5} \pm 6.27*10^{-7}$	0.670 ± 0.001	$14,087 \pm 188$
$5.50*10^{-5} \pm 7.25*10^{-7}$	0.765 ± 0.001	$13,919 \pm 185$
$6.14*10^{-5} \pm 8.10*10^{-7}$	0.871 ± 0.001	$14,175 \pm 188$
$6.86*10^{-5} \pm 9.05*10^{-7}$	0.960 ± 0.001	$13,987 \pm 186$

b = 0.007
m = 13,909
r = 1.000

$14,212 \pm 267$ (202)

RANGE = ULTRAVIOLET

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.96*10^{-6} \pm 9.19*10^{-8}$	0.198 ± 0.001	$28,428 \pm 426$
$1.35*10^{-5} \pm 1.78*10^{-7}$	0.390 ± 0.001	$28,823 \pm 394$
$2.11*10^{-5} \pm 2.78*10^{-7}$	0.586 ± 0.001	$27,828 \pm 373$
$2.79*10^{-5} \pm 3.67*10^{-7}$	0.791 ± 0.001	$28,398 \pm 378$
$3.43*10^{-5} \pm 4.52*10^{-7}$	0.963 ± 0.001	$28,074 \pm 372$
$4.12*10^{-5} \pm 5.43*10^{-7}$	1.131 ± 0.002	$27,464 \pm 366$
$4.76*10^{-5} \pm 6.27*10^{-7}$	1.321 ± 0.002	$27,774 \pm 369$
$5.50*10^{-5} \pm 7.25*10^{-7}$	1.516 ± 0.002	$27,583 \pm 366$
$6.14*10^{-5} \pm 8.10*10^{-7}$	1.741 ± 0.003	$28,334 \pm 377$
$6.86*10^{-5} \pm 9.05*10^{-7}$	1.921 ± 0.003	$27,989 \pm 372$

b = 0.004
m = 27,870
r = 1.000

$28,069 \pm 426$ (379)

TABLE 24

TRIPHENYLFORMZAN IN DICHLOROMETHANE

MOLECULAR WEIGHT = 300.363 (g/mol)
DENSITY = 1.317 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $3.79*10^{-4} \pm 7.27*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 488.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$7.90*10^{-6} \pm 1.51*10^{-7}$	0.138 ± 0.001	$17,477 \pm 380$
$1.16*10^{-5} \pm 2.22*10^{-7}$	0.198 ± 0.001	$17,089 \pm 350$
$1.67*10^{-5} \pm 3.20*10^{-7}$	0.281 ± 0.001	$16,827 \pm 334$
$2.32*10^{-5} \pm 4.45*10^{-7}$	0.387 ± 0.001	$16,675 \pm 325$
$2.92*10^{-5} \pm 5.60*10^{-7}$	0.485 ± 0.001	$16,591 \pm 322$
$3.42*10^{-5} \pm 6.55*10^{-7}$	0.568 ± 0.001	$16,620 \pm 321$
$4.08*10^{-5} \pm 7.82*10^{-7}$	0.685 ± 0.001	$16,789 \pm 324$
$4.58*10^{-5} \pm 8.78*10^{-7}$	0.769 ± 0.001	$16,789 \pm 323$
$5.20*10^{-5} \pm 9.98*10^{-7}$	0.868 ± 0.002	$16,677 \pm 323$
$5.85*10^{-5} \pm 1.12*10^{-6}$	0.977 ± 0.001	$16,696 \pm 321$

b = 0.003
m = 16,634
r = 1.000

$16,823 \pm 270$ (332)

RANGE = ULTRAVIOLET
ABSORBANCE at = 300.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$7.90*10^{-6} \pm 1.51*10^{-7}$	0.196 ± 0.001	$24,822 \pm 509$
$1.16*10^{-5} \pm 2.22*10^{-7}$	0.287 ± 0.001	$24,771 \pm 490$
$1.67*10^{-5} \pm 3.20*10^{-7}$	0.414 ± 0.001	$24,792 \pm 483$
$2.32*10^{-5} \pm 4.45*10^{-7}$	0.568 ± 0.001	$24,474 \pm 473$
$2.92*10^{-5} \pm 5.60*10^{-7}$	0.714 ± 0.001	$24,425 \pm 471$
$3.42*10^{-5} \pm 6.55*10^{-7}$	0.835 ± 0.002	$24,432 \pm 473$
$4.08*10^{-5} \pm 7.82*10^{-7}$	1.015 ± 0.002	$24,877 \pm 480$
$4.58*10^{-5} \pm 8.78*10^{-7}$	1.135 ± 0.002	$24,780 \pm 478$
$5.20*10^{-5} \pm 9.98*10^{-7}$	1.273 ± 0.003	$24,459 \pm 473$
$5.85*10^{-5} \pm 1.12*10^{-6}$	1.451 ± 0.003	$24,797 \pm 479$

b = -0.002
m = 24,714
r = 1.000

$24,663 \pm 188$ (481)

TABLE 25

ORTHO-HYDROXY DERIVATIVE IN DICHLOROMETHANE

MOLECULAR WEIGHT = 316.362 (g/mol)
DENSITY = 1.317 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $3.47*10^{-4} \pm 7.69*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 524.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$1.54*10^{-5} \pm 3.42*10^{-7}$	0.197 ± 0.001	12,791 ± 299
$2.31*10^{-5} \pm 5.13*10^{-7}$	0.296 ± 0.001	12,809 ± 291
$3.12*10^{-5} \pm 6.93*10^{-7}$	0.398 ± 0.001	12,762 ± 287
$3.89*10^{-5} \pm 8.64*10^{-7}$	0.496 ± 0.001	12,750 ± 285
$4.61*10^{-5} \pm 1.02*10^{-6}$	0.588 ± 0.001	12,745 ± 285
$5.45*10^{-5} \pm 1.21*10^{-6}$	0.696 ± 0.001	12,781 ± 285
$6.25*10^{-5} \pm 1.39*10^{-6}$	0.800 ± 0.002	12,794 ± 286
$6.96*10^{-5} \pm 1.55*10^{-6}$	0.892 ± 0.002	12,815 ± 286
$7.83*10^{-5} \pm 1.74*10^{-6}$	0.996 ± 0.002	12,717 ± 284

b = 0.001
m = 12,757
r = 1.000

12,774 ± 33 (208)

RANGE = ULTRAVIOLET
ABSORBANCE at = 310.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$7.45*10^{-6} \pm 1.65*10^{-7}$	0.205 ± 0.001	27,527 ± 640
$1.54*10^{-5} \pm 3.42*10^{-7}$	0.400 ± 0.001	25,972 ± 584
$2.31*10^{-5} \pm 5.13*10^{-7}$	0.592 ± 0.001	25,618 ± 572
$3.12*10^{-5} \pm 6.93*10^{-7}$	0.803 ± 0.002	25,749 ± 576
$3.89*10^{-5} \pm 8.64*10^{-7}$	1.001 ± 0.002	25,732 ± 574
$4.61*10^{-5} \pm 1.02*10^{-6}$	1.187 ± 0.002	25,728 ± 573
$5.45*10^{-5} \pm 1.21*10^{-6}$	1.392 ± 0.002	25,562 ± 569
$6.25*10^{-5} \pm 1.39*10^{-6}$	1.612 ± 0.003	25,781 ± 575
$6.96*10^{-5} \pm 1.55*10^{-6}$	1.815 ± 0.003	26,076 ± 581

b = 0.001
m = 25,789
r = 1.000

25,777 ± 170 (570)

TABLE 26

HYDROXY-CHLORO DERIVATIVE IN DICHLOROMETHANE

MOLECULAR WEIGHT = 350.807 (g/mol)
DENSITY = 1.317 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $5.59*10^{-4} \pm 6.70*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 520.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$8.38*10^{-6} \pm 1.01*10^{-7}$	0.122 ± 0.001	$14,561 \pm 243$
$1.37*10^{-5} \pm 1.65*10^{-7}$	0.205 ± 0.001	$14,935 \pm 207$
$2.41*10^{-5} \pm 2.90*10^{-7}$	0.325 ± 0.001	$13,482 \pm 172$
$2.98*10^{-5} \pm 3.58*10^{-7}$	0.400 ± 0.001	$13,414 \pm 168$
$3.87*10^{-5} \pm 4.65*10^{-7}$	0.517 ± 0.001	$13,368 \pm 165$
$4.65*10^{-5} \pm 5.59*10^{-7}$	0.611 ± 0.001	$13,144 \pm 161$
$5.53*10^{-5} \pm 6.65*10^{-7}$	0.727 ± 0.001	$13,136 \pm 160$
$6.16*10^{-5} \pm 7.41*10^{-7}$	0.814 ± 0.002	$13,211 \pm 163$
$7.04*10^{-5} \pm 8.46*10^{-7}$	0.924 ± 0.002	$13,124 \pm 161$
$7.74*10^{-5} \pm 9.30*10^{-7}$	1.013 ± 0.002	$13,091 \pm 160$

b = 0.019
m = 12,843 $13,246 \pm 156$ (164)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 318.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$8.38*10^{-6} \pm 1.01*10^{-7}$	0.226 ± 0.001	$26,974 \pm 366$
$1.37*10^{-5} \pm 1.65*10^{-7}$	0.370 ± 0.001	$26,956 \pm 340$
$2.41*10^{-5} \pm 2.90*10^{-7}$	0.612 ± 0.001	$25,389 \pm 311$
$2.98*10^{-5} \pm 3.58*10^{-7}$	0.723 ± 0.001	$24,246 \pm 295$
$3.87*10^{-5} \pm 4.65*10^{-7}$	0.926 ± 0.002	$23,944 \pm 294$
$4.65*10^{-5} \pm 5.59*10^{-7}$	1.101 ± 0.002	$23,684 \pm 289$
$5.53*10^{-5} \pm 6.65*10^{-7}$	1.350 ± 0.002	$24,393 \pm 296$
$6.16*10^{-5} \pm 7.41*10^{-7}$	1.508 ± 0.003	$24,474 \pm 299$
$7.04*10^{-5} \pm 8.46*10^{-7}$	1.726 ± 0.003	$24,514 \pm 298$
$7.74*10^{-5} \pm 9.30*10^{-7}$	1.819 ± 0.003	$23,506 \pm 285$

b = 0.033
m = 23,546 $24,269 \pm 586$ (296)
r = 1.000

TABLE 27

PARA-CHLORO DERIVATIVE IN DICHLOROMETHANE

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 1.317 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $3.33*10^{-4} \pm 6.86*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 487.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$4.85*10^{-6} \pm 9.99*10^{-8}$	0.096 ± 0.001	$19,801 \pm 501$
$1.06*10^{-5} \pm 2.19*10^{-7}$	0.202 ± 0.001	$19,024 \pm 414$
$1.66*10^{-5} \pm 3.42*10^{-7}$	0.304 ± 0.001	$18,328 \pm 387$
$2.22*10^{-5} \pm 4.57*10^{-7}$	0.413 ± 0.001	$18,625 \pm 389$
$2.76*10^{-5} \pm 5.69*10^{-7}$	0.514 ± 0.001	$18,598 \pm 387$
$3.19*10^{-5} \pm 6.57*10^{-7}$	0.594 ± 0.001	$18,630 \pm 386$
$3.76*10^{-5} \pm 7.75*10^{-7}$	0.682 ± 0.001	$18,124 \pm 375$
$4.12*10^{-5} \pm 8.49*10^{-7}$	0.751 ± 0.002	$18,219 \pm 379$
$4.95*10^{-5} \pm 1.02*10^{-6}$	0.929 ± 0.002	$18,777 \pm 389$
$5.50*10^{-5} \pm 1.13*10^{-6}$	1.036 ± 0.003	$18,840 \pm 392$

b = -0.000
m = 18,602
r = 0.999

$18,574 \pm 298$ (389)

RANGE = ULTRAVIOLET
ABSORBANCE at = 307.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$4.85*10^{-6} \pm 9.99*10^{-8}$	0.159 ± 0.001	$32,795 \pm 736$
$1.06*10^{-5} \pm 2.19*10^{-7}$	0.337 ± 0.001	$31,738 \pm 667$
$1.66*10^{-5} \pm 3.42*10^{-7}$	0.515 ± 0.001	$31,049 \pm 645$
$2.22*10^{-5} \pm 4.57*10^{-7}$	0.705 ± 0.001	$31,793 \pm 658$
$2.76*10^{-5} \pm 5.69*10^{-7}$	0.889 ± 0.002	$32,167 \pm 668$
$3.19*10^{-5} \pm 6.57*10^{-7}$	1.054 ± 0.002	$33,057 \pm 685$
$3.76*10^{-5} \pm 7.75*10^{-7}$	1.222 ± 0.003	$32,475 \pm 674$
$4.12*10^{-5} \pm 8.49*10^{-7}$	1.386 ± 0.003	$33,624 \pm 697$
$4.95*10^{-5} \pm 1.02*10^{-6}$	1.899 ± 0.003	$38,382 \pm 793$

b = -0.027
m = 33,534
r = 0.999

$32,337 \pm 823$ (677)

TABLE 28

META-BROMO DERIVATIVE IN DICHLOROMETHANE

MOLECULAR WEIGHT = 379.259 (g/mol)
DENSITY = 1.317 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $3.42*10^{-4} \pm 5.81*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 483.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$5.26*10^{-6} \pm 8.93*10^{-8}$	0.103 ± 0.001	$19,574 \pm 427$
$1.06*10^{-5} \pm 1.81*10^{-7}$	0.199 ± 0.001	$18,689 \pm 344$
$1.68*10^{-5} \pm 2.85*10^{-7}$	0.302 ± 0.001	$17,987 \pm 317$
$2.13*10^{-5} \pm 3.62*10^{-7}$	0.374 ± 0.001	$17,553 \pm 305$
$2.77*10^{-5} \pm 4.70*10^{-7}$	0.498 ± 0.001	$17,984 \pm 309$
$3.30*10^{-5} \pm 5.61*10^{-7}$	0.591 ± 0.001	$17,883 \pm 306$
$3.92*10^{-5} \pm 6.65*10^{-7}$	0.672 ± 0.001	$17,137 \pm 293$
$5.02*10^{-5} \pm 8.51*10^{-7}$	0.841 ± 0.002	$16,762 \pm 288$
$5.61*10^{-5} \pm 9.53*10^{-7}$	0.962 ± 0.002	$17,135 \pm 294$

b = 0.023
m = 16,698
r = 0.999

$17,810 \pm 830$ (318)

RANGE = ULTRAVIOLET
ABSORBANCE at = 306.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$5.26*10^{-6} \pm 8.93*10^{-8}$	0.156 ± 0.001	$29,646 \pm 570$
$1.06*10^{-5} \pm 1.81*10^{-7}$	0.291 ± 0.001	$27,329 \pm 482$
$1.68*10^{-5} \pm 2.85*10^{-7}$	0.451 ± 0.001	$26,862 \pm 464$
$2.13*10^{-5} \pm 3.62*10^{-7}$	0.555 ± 0.001	$26,048 \pm 447$
$2.77*10^{-5} \pm 4.70*10^{-7}$	0.736 ± 0.001	$26,578 \pm 454$
$3.30*10^{-5} \pm 5.61*10^{-7}$	0.864 ± 0.002	$26,144 \pm 449$
$3.92*10^{-5} \pm 6.65*10^{-7}$	1.001 ± 0.002	$25,527 \pm 437$
$4.30*10^{-5} \pm 7.30*10^{-7}$	1.116 ± 0.003	$25,932 \pm 446$
$5.02*10^{-5} \pm 8.51*10^{-7}$	1.253 ± 0.003	$24,974 \pm 428$
$5.61*10^{-5} \pm 9.53*10^{-7}$	1.418 ± 0.003	$25,257 \pm 432$

b = 0.034
m = 24,734
r = 1.000

$26,072 \pm 763$ (449)

TABLE 29

ORTHO-CHLORO DERIVATIVE IN DICHLOROMETHANE

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 1.317 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $2.98*10^{-4} \pm 6.34*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 402.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$3.24*10^{-6} \pm 6.89*10^{-8}$	0.101 ± 0.001	$31,171 \pm 793$
$6.80*10^{-6} \pm 1.45*10^{-7}$	0.208 ± 0.001	$30,594 \pm 683$
$9.78*10^{-6} \pm 2.08*10^{-7}$	0.294 ± 0.001	$30,074 \pm 655$
$1.37*10^{-5} \pm 2.90*10^{-7}$	0.411 ± 0.001	$30,090 \pm 648$
$1.66*10^{-5} \pm 3.53*10^{-7}$	0.498 ± 0.001	$30,025 \pm 644$
$2.00*10^{-5} \pm 4.25*10^{-7}$	0.601 ± 0.001	$30,032 \pm 642$
$2.28*10^{-5} \pm 4.85*10^{-7}$	0.686 ± 0.001	$30,092 \pm 643$
$2.73*10^{-5} \pm 5.80*10^{-7}$	0.816 ± 0.002	$29,889 \pm 640$
$2.97*10^{-5} \pm 6.32*10^{-7}$	0.891 ± 0.002	$29,974 \pm 641$
$3.16*10^{-5} \pm 6.71*10^{-7}$	0.990 ± 0.002	$31,334 \pm 670$

b = -0.004
m = 30,509
r = 0.999

$30,327 \pm 524$ (666)

RANGE = ULTRAVIOLET
ABSORBANCE at = 292.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$3.24*10^{-6} \pm 6.89*10^{-8}$	0.040 ± 0.001	$12,345 \pm 509$
$6.80*10^{-6} \pm 1.45*10^{-7}$	0.074 ± 0.001	$10,884 \pm 311$
$9.78*10^{-6} \pm 2.08*10^{-7}$	0.097 ± 0.001	$9,922 \pm 256$
$1.37*10^{-5} \pm 2.90*10^{-7}$	0.132 ± 0.001	$9,664 \pm 230$
$1.66*10^{-5} \pm 3.53*10^{-7}$	0.168 ± 0.001	$10,129 \pm 232$
$2.00*10^{-5} \pm 4.25*10^{-7}$	0.186 ± 0.001	$9,294 \pm 210$
$2.28*10^{-5} \pm 4.85*10^{-7}$	0.221 ± 0.001	$9,694 \pm 215$
$2.73*10^{-5} \pm 5.80*10^{-7}$	0.256 ± 0.001	$9,377 \pm 206$
$2.97*10^{-5} \pm 6.32*10^{-7}$	0.282 ± 0.001	$9,487 \pm 207$
$3.16*10^{-5} \pm 6.71*10^{-7}$	0.323 ± 0.001	$10,223 \pm 222$

b = 0.005
m = 9,530
r = 0.997

$9,836 \pm 465$ (210)

TABLE 30

ORTHO-BROMO DERIVATIVE IN DICHLOROMETHANE

MOLECULAR WEIGHT = 379.259 (g/mol)
DENSITY = 1.317 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $1.79*10^{-4} \pm 5.73*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 402.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$3.39*10^{-6} \pm 1.08*10^{-7}$	0.104 ± 0.001	$30,700 \pm 1067$
$6.82*10^{-6} \pm 2.18*10^{-7}$	0.200 ± 0.001	$29,336 \pm 961$
$1.03*10^{-5} \pm 3.31*10^{-7}$	0.304 ± 0.001	$29,378 \pm 949$
$1.40*10^{-5} \pm 4.48*10^{-7}$	0.401 ± 0.001	$28,625 \pm 921$
$1.76*10^{-5} \pm 5.62*10^{-7}$	0.509 ± 0.001	$28,961 \pm 930$
$2.06*10^{-5} \pm 6.59*10^{-7}$	0.598 ± 0.001	$29,039 \pm 931$
$2.42*10^{-5} \pm 7.73*10^{-7}$	0.699 ± 0.001	$28,924 \pm 927$
$2.76*10^{-5} \pm 8.83*10^{-7}$	0.805 ± 0.002	$29,151 \pm 936$
$3.11*10^{-5} \pm 9.95*10^{-7}$	0.904 ± 0.002	$29,046 \pm 932$
$3.43*10^{-5} \pm 1.10*10^{-6}$	0.999 ± 0.002	$29,124 \pm 934$

b = 0.002
m = 28,982 $29,065 \pm 226$ (936)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 294.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
$3.39*10^{-6} \pm 1.08*10^{-7}$	0.037 ± 0.001	$10,922 \pm 544$
$6.82*10^{-6} \pm 2.18*10^{-7}$	0.069 ± 0.001	$10,121 \pm 384$
$1.03*10^{-5} \pm 3.31*10^{-7}$	0.100 ± 0.001	$9,664 \pm 338$
$1.40*10^{-5} \pm 4.48*10^{-7}$	0.135 ± 0.001	$9,637 \pm 324$
$1.76*10^{-5} \pm 5.62*10^{-7}$	0.170 ± 0.001	$9,673 \pm 320$
$2.06*10^{-5} \pm 6.59*10^{-7}$	0.203 ± 0.001	$9,858 \pm 323$
$2.42*10^{-5} \pm 7.73*10^{-7}$	0.230 ± 0.001	$9,517 \pm 310$
$2.76*10^{-5} \pm 8.83*10^{-7}$	0.268 ± 0.001	$9,705 \pm 315$
$3.11*10^{-5} \pm 9.95*10^{-7}$	0.297 ± 0.001	$9,543 \pm 309$
$3.43*10^{-5} \pm 1.10*10^{-6}$	0.331 ± 0.001	$9,650 \pm 311$

b = 0.004
m = 9,501 $9,708 \pm 183$ (326)
r = 1.000

TABLE 31

NAPHTHYL DERIVATIVE IN DICHLOROMETHANE

MOLECULAR WEIGHT = 350.422 (g/mol)
DENSITY = 1.317 (g/cc)
TEMPERATURE = 25.0 (C)
CONC. STOCK SOLUTION = $3.28*10^{-4} \pm 6.87*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 495.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.69*10^{-6} \pm 1.40*10^{-7}$	0.103 ± 0.001	$15,400 \pm 386$
$1.36*10^{-5} \pm 2.85*10^{-7}$	0.199 ± 0.001	$14,629 \pm 323$
$2.05*10^{-5} \pm 4.29*10^{-7}$	0.304 ± 0.001	$14,854 \pm 319$
$2.69*10^{-5} \pm 5.64*10^{-7}$	0.403 ± 0.001	$14,970 \pm 318$
$3.41*10^{-5} \pm 7.14*10^{-7}$	0.506 ± 0.001	$14,844 \pm 314$
$4.07*10^{-5} \pm 8.52*10^{-7}$	0.618 ± 0.001	$15,183 \pm 320$
$4.75*10^{-5} \pm 9.94*10^{-7}$	0.717 ± 0.002	$15,103 \pm 320$
$5.44*10^{-5} \pm 1.14*10^{-6}$	0.813 ± 0.002	$14,936 \pm 315$
$6.08*10^{-5} \pm 1.27*10^{-6}$	0.887 ± 0.002	$14,585 \pm 308$
$6.79*10^{-5} \pm 1.42*10^{-6}$	0.988 ± 0.002	$14,550 \pm 306$

b = 0.008
m = 14,636
r = 0.999

$14,905 \pm 274$ (323)

RANGE = ULTRAVIOLET
ABSORBANCE at = 320.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.69*10^{-6} \pm 1.40*10^{-7}$	0.205 ± 0.001	$30,651 \pm 676$
$1.36*10^{-5} \pm 2.85*10^{-7}$	0.394 ± 0.001	$28,965 \pm 615$
$2.05*10^{-5} \pm 4.29*10^{-7}$	0.603 ± 0.001	$29,464 \pm 621$
$3.41*10^{-5} \pm 7.14*10^{-7}$	1.016 ± 0.002	$29,806 \pm 628$
$4.07*10^{-5} \pm 8.52*10^{-7}$	1.301 ± 0.003	$31,964 \pm 674$
$4.75*10^{-5} \pm 9.94*10^{-7}$	1.542 ± 0.003	$32,481 \pm 683$
$5.44*10^{-5} \pm 1.14*10^{-6}$	1.640 ± 0.003	$30,128 \pm 634$
$6.08*10^{-5} \pm 1.27*10^{-6}$	1.759 ± 0.004	$28,923 \pm 609$
$6.79*10^{-5} \pm 1.42*10^{-6}$	1.954 ± 0.004	$28,776 \pm 606$

b = 0.026
m = 29,424
r = 0.995

$30,166 \pm 128$ (639)

TABLE 32

TRIPHENYLFORMAZAN IN METHANOL

MOLECULAR WEIGHT = 300.363 (g/mol)
DENSITY = 0.807 (g/cc)
TEMPERATURE = 27.0 (C)
CONC. STOCK SOLUTION = $6.09*10^{-4} \pm 6.63*10^{-6}$ (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 482.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.10*10^{-6} \pm 6.65*10^{-8}$	0.099 ± 0.001	$16,227 \pm 292$
$1.22*10^{-5} \pm 1.33*10^{-7}$	0.193 ± 0.001	$15,809 \pm 208$
$1.88*10^{-5} \pm 2.05*10^{-7}$	0.294 ± 0.001	$15,640 \pm 186$
$2.49*10^{-5} \pm 2.71*10^{-7}$	0.385 ± 0.001	$15,480 \pm 178$
$3.12*10^{-5} \pm 3.39*10^{-7}$	0.485 ± 0.001	$15,564 \pm 175$
$3.71*10^{-5} \pm 4.05*10^{-7}$	0.575 ± 0.001	$15,481 \pm 173$
$4.33*10^{-5} \pm 4.71*10^{-7}$	0.672 ± 0.001	$15,526 \pm 172$
$4.99*10^{-5} \pm 5.43*10^{-7}$	0.777 ± 0.002	$15,570 \pm 175$
$5.57*10^{-5} \pm 6.07*10^{-7}$	0.855 ± 0.002	$15,349 \pm 172$
$6.13*10^{-5} \pm 6.68*10^{-7}$	0.944 ± 0.002	$15,388 \pm 172$

b = 0.000
m = 15,345 $15,603 \pm 254$ (190)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 297.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
$6.10*10^{-6} \pm 6.65*10^{-8}$	0.108 ± 0.001	$17,702 \pm 302$
$1.22*10^{-5} \pm 1.33*10^{-7}$	0.245 ± 0.001	$20,069 \pm 247$
$1.88*10^{-5} \pm 2.05*10^{-7}$	0.394 ± 0.001	$20,960 \pm 240$
$2.49*10^{-5} \pm 2.71*10^{-7}$	0.525 ± 0.001	$21,109 \pm 237$
$3.12*10^{-5} \pm 3.39*10^{-7}$	0.668 ± 0.001	$21,437 \pm 238$
$3.71*10^{-5} \pm 4.05*10^{-7}$	0.784 ± 0.001	$21,108 \pm 233$
$4.33*10^{-5} \pm 4.71*10^{-7}$	0.885 ± 0.001	$20,447 \pm 225$
$4.99*10^{-5} \pm 5.43*10^{-7}$	1.065 ± 0.002	$21,342 \pm 237$
$5.57*10^{-5} \pm 6.07*10^{-7}$	1.175 ± 0.002	$21,094 \pm 233$
$6.13*10^{-5} \pm 6.68*10^{-7}$	1.280 ± 0.003	$20,865 \pm 233$

b = -0.004
m = 21,098 $20,937 \pm 433$ (243)
r = 0.999

TABLE 33

ORTHO-HYDROXY DERIVATIVE IN METHANOL

MOLECULAR WEIGHT = 316.362 (g/mol)
DENSITY = 0.807 (g/cc)
TEMPERATURE = 27.0 (C)
CONC. STOCK SOLUTION = 6.58E-04 $\pm$ 6.09*10^{-6} (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 406.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
7.22*10^{-6} $\pm$ 6.69*10^{-8}	0.105 $\pm$ 0.001	14,552 $\pm$ 238
1.39*10^{-5} $\pm$ 1.29*10^{-7}	0.199 $\pm$ 0.001	14,268 $\pm$ 167
2.29*10^{-5} $\pm$ 2.12*10^{-7}	0.324 $\pm$ 0.001	14,174 $\pm$ 145
2.87*10^{-5} $\pm$ 2.66*10^{-7}	0.406 $\pm$ 0.001	14,132 $\pm$ 140
3.59*10^{-5} $\pm$ 3.32*10^{-7}	0.504 $\pm$ 0.001	14,054 $\pm$ 136
4.26*10^{-5} $\pm$ 3.95*10^{-7}	0.598 $\pm$ 0.001	14,033 $\pm$ 134
4.97*10^{-5} $\pm$ 4.60*10^{-7}	0.688 $\pm$ 0.001	13,845 $\pm$ 131
5.40*10^{-5} $\pm$ 5.00*10^{-7}	0.761 $\pm$ 0.002	14,085 $\pm$ 137
6.35*10^{-5} $\pm$ 5.88*10^{-7}	0.874 $\pm$ 0.002	13,773 $\pm$ 132
7.15*10^{-5} $\pm$ 6.62*10^{-7}	0.984 $\pm$ 0.002	13,771 $\pm$ 131

b = 0.011
m = 13,687 14,068 $\pm$ 240 (139)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 302.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
7.22*10^{-6} $\pm$ 6.69*10^{-8}	0.118 $\pm$ 0.001	16,354 $\pm$ 248
1.39*10^{-5} $\pm$ 1.29*10^{-7}	0.231 $\pm$ 0.001	16,563 $\pm$ 184
2.29*10^{-5} $\pm$ 2.12*10^{-7}	0.374 $\pm$ 0.001	16,361 $\pm$ 164
2.87*10^{-5} $\pm$ 2.66*10^{-7}	0.468 $\pm$ 0.001	16,291 $\pm$ 159
3.59*10^{-5} $\pm$ 3.32*10^{-7}	0.584 $\pm$ 0.001	16,285 $\pm$ 156
4.26*10^{-5} $\pm$ 3.95*10^{-7}	0.698 $\pm$ 0.001	16,379 $\pm$ 155
4.97*10^{-5} $\pm$ 4.60*10^{-7}	0.798 $\pm$ 0.001	16,058 $\pm$ 151
5.40*10^{-5} $\pm$ 5.00*10^{-7}	0.873 $\pm$ 0.002	16,158 $\pm$ 155
6.35*10^{-5} $\pm$ 5.88*10^{-7}	1.007 $\pm$ 0.002	15,869 $\pm$ 151
7.15*10^{-5} $\pm$ 6.62*10^{-7}	1.151 $\pm$ 0.003	16,108 $\pm$ 156

b = 0.001
m = 16,308 16,242 $\pm$ 197 (168)
r = 0.999

TABLE 34

HYDROXY-CHLORO DERIVATIVE IN METHANOL

MOLECULAR WEIGHT = 350.807 (g/mol)
DENSITY = 0.807 (g/cc)
TEMPERATURE = 27.0 (C)
CONC. STOCK SOLUTION = 1.80E-04 $\pm$ 4.36*10^{-6} (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 408.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
7.18*10^{-6} $\pm$ 1.73*10^{-7}	0.094 $\pm$ 0.001	13,088 $\pm$ 372
1.44*10^{-5} $\pm$ 3.47*10^{-7}	0.183 $\pm$ 0.001	12,737 $\pm$ 323
2.17*10^{-5} $\pm$ 5.24*10^{-7}	0.275 $\pm$ 0.001	12,678 $\pm$ 313
2.87*10^{-5} $\pm$ 6.94*10^{-7}	0.364 $\pm$ 0.001	12,663 $\pm$ 310
3.62*10^{-5} $\pm$ 8.74*10^{-7}	0.457 $\pm$ 0.001	12,622 $\pm$ 307
4.34*10^{-5} $\pm$ 1.05*10^{-6}	0.543 $\pm$ 0.001	12,503 $\pm$ 304
5.05*10^{-5} $\pm$ 1.22*10^{-6}	0.630 $\pm$ 0.001	12,480 $\pm$ 303
5.75*10^{-5} $\pm$ 1.39*10^{-6}	0.717 $\pm$ 0.001	12,473 $\pm$ 302
7.47*10^{-5} $\pm$ 1.80*10^{-6}	0.924 $\pm$ 0.001	12,364 $\pm$ 299

b = -0.008
m = 12,310
r = 1.000

12,263 $\pm$ 212 (315)

RANGE = ULTRAVIOLET
ABSORBANCE at = 311.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
7.18*10^{-6} $\pm$ 1.73*10^{-7}	0.118 $\pm$ 0.001	16,430 $\pm$ 443
1.44*10^{-5} $\pm$ 3.47*10^{-7}	0.234 $\pm$ 0.001	16,286 $\pm$ 405
2.17*10^{-5} $\pm$ 5.24*10^{-7}	0.350 $\pm$ 0.001	16,135 $\pm$ 395
2.87*10^{-5} $\pm$ 6.94*10^{-7}	0.463 $\pm$ 0.001	16,107 $\pm$ 392
3.62*10^{-5} $\pm$ 8.74*10^{-7}	0.580 $\pm$ 0.001	16,019 $\pm$ 389
4.34*10^{-5} $\pm$ 1.05*10^{-6}	0.690 $\pm$ 0.001	15,888 $\pm$ 385
5.05*10^{-5} $\pm$ 1.22*10^{-6}	0.800 $\pm$ 0.001	15,847 $\pm$ 384
5.75*10^{-5} $\pm$ 1.39*10^{-6}	0.912 $\pm$ 0.001	15,865 $\pm$ 384
7.47*10^{-5} $\pm$ 1.80*10^{-6}	1.170 $\pm$ 0.003	15,656 $\pm$ 380

b = 0.011
m = 15,603
r = 1.000

16,026 $\pm$ 241 (395)

TABLE 35

PARA-CHLORO DERIVATIVE IN METHANOL

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 0.807 (g/cc)
TEMPERATURE = 27.0 (C)
CONC. STOCK SOLUTION = 5.27E-04 ± 5.47*10^{-6} (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 482.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
5.79*10^{-6} ± 6.01*10^{-8}	0.101 ± 0.001	17,455 ± 304
1.20*10^{-5} ± 1.24*10^{-7}	0.200 ± 0.001	16,684 ± 210
1.80*10^{-5} ± 1.86*10^{-7}	0.299 ± 0.001	16,647 ± 190
2.41*10^{-5} ± 2.50*10^{-7}	0.401 ± 0.001	16,625 ± 182
3.05*10^{-5} ± 3.16*10^{-7}	0.504 ± 0.001	16,544 ± 178
3.61*10^{-5} ± 3.75*10^{-7}	0.596 ± 0.001	16,499 ± 176
4.21*10^{-5} ± 4.37*10^{-7}	0.692 ± 0.001	16,431 ± 174
4.84*10^{-5} ± 5.03*10^{-7}	0.791 ± 0.001	16,328 ± 172
5.46*10^{-5} ± 5.67*10^{-7}	0.891 ± 0.001	16,314 ± 171
6.04*10^{-5} ± 6.26*10^{-7}	0.971 ± 0.001	16,086 ± 169

b = 0.011
m = 16,072
r = 1.000

16,462 ± 194 (193)

RANGE = ULTRAVIOLET
ABSORBANCE at = 303.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
5.79*10^{-6} ± 6.01*10^{-8}	0.161 ± 0.001	27,824 ± 379
1.20*10^{-5} ± 1.24*10^{-7}	0.325 ± 0.001	27,112 ± 305
1.80*10^{-5} ± 1.86*10^{-7}	0.486 ± 0.001	27,058 ± 292
2.41*10^{-5} ± 2.50*10^{-7}	0.654 ± 0.001	27,113 ± 287
3.05*10^{-5} ± 3.16*10^{-7}	0.827 ± 0.001	27,146 ± 286
3.61*10^{-5} ± 3.75*10^{-7}	0.970 ± 0.001	26,852 ± 281
4.21*10^{-5} ± 4.37*10^{-7}	1.126 ± 0.002	26,735 ± 282
4.84*10^{-5} ± 5.03*10^{-7}	1.295 ± 0.002	26,732 ± 281
5.46*10^{-5} ± 5.67*10^{-7}	1.434 ± 0.003	26,256 ± 279
6.04*10^{-5} ± 6.26*10^{-7}	1.558 ± 0.003	25,810 ± 273

b = 0.023
m = 25,908
r = 1.000

26,864 ± 545 (295)

TABLE 36

META-BROMO DERIVATIVE IN METHANOL

MOLECULAR WEIGHT = 379.259 (g/mol)
DENSITY = 0.807 (g/cc)
TEMPERATURE = 27.0 (C)
CONC. STOCK SOLUTION = 3.64E-04 ± 4.30*10^{-6} (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 480.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
5.56*10^{-6} ± 6.56*10^{-8}	0.102 ± 0.001	18,358 ± 334
1.10*10^{-5} ± 1.30*10^{-7}	0.201 ± 0.001	18,239 ± 251
1.86*10^{-5} ± 2.19*10^{-7}	0.336 ± 0.001	18,091 ± 227
2.24*10^{-5} ± 2.64*10^{-7}	0.406 ± 0.001	18,140 ± 223
2.84*10^{-5} ± 3.35*10^{-7}	0.518 ± 0.001	18,255 ± 221
3.31*10^{-5} ± 3.91*10^{-7}	0.601 ± 0.001	18,143 ± 218
3.99*10^{-5} ± 4.71*10^{-7}	0.727 ± 0.001	18,201 ± 218
4.42*10^{-5} ± 5.22*10^{-7}	0.801 ± 0.001	18,104 ± 216
4.84*10^{-5} ± 5.71*10^{-7}	0.881 ± 0.002	18,208 ± 220
5.62*10^{-5} ± 6.63*10^{-7}	1.016 ± 0.002	18,086 ± 217

b = 0.001
m = 18,116
r = 1.000

18,182 ± 86 (235)

RANGE = ULTRAVIOLET
ABSORBANCE at = 314.0 (nm)

M (mol l^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
5.56*10^{-6} ± 6.56*10^{-8}	0.149 ± 0.001	26,818 ± 406
1.10*10^{-5} ± 1.30*10^{-7}	0.296 ± 0.001	26,859 ± 342
1.86*10^{-5} ± 2.19*10^{-7}	0.489 ± 0.001	26,329 ± 320
2.24*10^{-5} ± 2.64*10^{-7}	0.588 ± 0.001	26,272 ± 316
2.84*10^{-5} ± 3.35*10^{-7}	0.744 ± 0.001	26,220 ± 313
3.31*10^{-5} ± 3.91*10^{-7}	0.870 ± 0.001	26,264 ± 313
3.99*10^{-5} ± 4.71*10^{-7}	1.054 ± 0.001	26,388 ± 313
4.42*10^{-5} ± 5.22*10^{-7}	1.156 ± 0.001	26,128 ± 310
4.84*10^{-5} ± 5.71*10^{-7}	1.255 ± 0.002	25,938 ± 310
5.62*10^{-5} ± 6.63*10^{-7}	1.484 ± 0.003	26,416 ± 317

b = 0.004
m = 26,140
r = 1.000

26,363 ± 285 (326)

TABLE 37

ORTHO-CHLORO DERIVATIVE IN METHANOL

MOLECULAR WEIGHT = 334.808 (g/mol)
DENSITY = 0.807 (g/cc)
TEMPERATURE = 27.0 (C)
CONC. STOCK SOLUTION = 3.01E-04 ± 5.79*10^{-6} (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 308.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
4.72*10^{-6} ± 9.09*10^{-8}	0.109 ± 0.001	23,087 ± 536
9.48*10^{-6} ± 1.83*10^{-7}	0.215 ± 0.001	22,679 ± 462
1.38*10^{-5} ± 2.66*10^{-7}	0.310 ± 0.001	22,425 ± 444
1.89*10^{-5} ± 3.65*10^{-7}	0.422 ± 0.001	22,277 ± 436
2.34*10^{-5} ± 4.50*10^{-7}	0.520 ± 0.001	22,232 ± 432
2.83*10^{-5} ± 5.44*10^{-7}	0.628 ± 0.001	22,220 ± 431
3.28*10^{-5} ± 6.31*10^{-7}	0.726 ± 0.001	22,150 ± 429
3.74*10^{-5} ± 7.20*10^{-7}	0.830 ± 0.001	22,215 ± 430
4.19*10^{-5} ± 8.07*10^{-7}	0.926 ± 0.001	22,104 ± 427
4.68*10^{-5} ± 9.02*10^{-7}	1.018 ± 0.001	21,731 ± 421

b = 0.010
m = 21,718
r = 1.000

22,312 ± 362 (445)

RANGE = ULTRAVIOLET
ABSORBANCE at = 285.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
4.72*10^{-6} ± 9.09*10^{-8}	0.055 ± 0.001	11,650 ± 374
9.48*10^{-6} ± 1.83*10^{-7}	0.105 ± 0.001	11,076 ± 260
1.38*10^{-5} ± 2.66*10^{-7}	0.145 ± 0.001	10,489 ± 226
1.89*10^{-5} ± 3.65*10^{-7}	0.196 ± 0.001	10,347 ± 213
2.34*10^{-5} ± 4.50*10^{-7}	0.240 ± 0.001	10,261 ± 207
2.83*10^{-5} ± 5.44*10^{-7}	0.295 ± 0.001	10,438 ± 207
3.28*10^{-5} ± 6.31*10^{-7}	0.340 ± 0.001	10,373 ± 204
3.74*10^{-5} ± 7.20*10^{-7}	0.385 ± 0.001	10,304 ± 202
4.19*10^{-5} ± 8.07*10^{-7}	0.436 ± 0.001	10,407 ± 203
4.68*10^{-5} ± 9.02*10^{-7}	0.487 ± 0.001	10,396 ± 202

b = 0.005
m = 10,246
r = 1.000

10,574 ± 442 (230)

TABLE 38

ORTHO-BROMO DERIVATIVE IN METHANOL

MOLECULAR WEIGHT = 379.259 (g/mol)
DENSITY = 0.807 (g/cc)
TEMPERATURE = 27.0 (C)
CONC. STOCK SOLUTION = 2.51E-04 $\pm$ 4.61*10^{-6} (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 410.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1} cm^{-1})
2.34*10^{-6} $\pm$ 4.31*10^{-8}	0.053 $\pm$ 0.001	22,612 $\pm$ 733
5.19*10^{-6} $\pm$ 9.54*10^{-8}	0.116 $\pm$ 0.001	22,333 $\pm$ 492
7.30*10^{-6} $\pm$ 1.34*10^{-7}	0.165 $\pm$ 0.001	22,604 $\pm$ 458
9.21*10^{-6} $\pm$ 1.69*10^{-7}	0.208 $\pm$ 0.001	22,591 $\pm$ 442
1.20*10^{-5} $\pm$ 2.21*10^{-7}	0.268 $\pm$ 0.001	22,265 $\pm$ 425
1.45*10^{-5} $\pm$ 2.66*10^{-7}	0.324 $\pm$ 0.001	22,374 $\pm$ 422
1.67*10^{-5} $\pm$ 3.06*10^{-7}	0.370 $\pm$ 0.001	22,203 $\pm$ 417
1.90*10^{-5} $\pm$ 3.49*10^{-7}	0.425 $\pm$ 0.001	22,343 $\pm$ 417
2.13*10^{-5} $\pm$ 3.91*10^{-7}	0.473 $\pm$ 0.001	22,222 $\pm$ 414
2.38*10^{-5} $\pm$ 4.37*10^{-7}	0.532 $\pm$ 0.001	22,338 $\pm$ 415

b = 0.002
m = 22,219
r = 1.000

22,388 $\pm$ 157 (437)

RANGE = ULTRAVIOLET
ABSORBANCE at = 290.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1} cm^{-1})
2.34*10^{-6} $\pm$ 4.31*10^{-8}	0.025 $\pm$ 0.001	10,666 $\pm$ 634
5.19*10^{-6} $\pm$ 9.54*10^{-8}	0.055 $\pm$ 0.001	10,589 $\pm$ 335
7.30*10^{-6} $\pm$ 1.34*10^{-7}	0.074 $\pm$ 0.001	10,138 $\pm$ 269
9.21*10^{-6} $\pm$ 1.69*10^{-7}	0.095 $\pm$ 0.001	10,318 $\pm$ 244
1.20*10^{-5} $\pm$ 2.21*10^{-7}	0.121 $\pm$ 0.001	10,053 $\pm$ 219
1.45*10^{-5} $\pm$ 2.66*10^{-7}	0.150 $\pm$ 0.001	10,358 $\pm$ 214
1.67*10^{-5} $\pm$ 3.06*10^{-7}	0.169 $\pm$ 0.001	10,142 $\pm$ 205
1.90*10^{-5} $\pm$ 3.49*10^{-7}	0.195 $\pm$ 0.001	10,252 $\pm$ 202
2.13*10^{-5} $\pm$ 3.91*10^{-7}	0.215 $\pm$ 0.001	10,101 $\pm$ 197
2.38*10^{-5} $\pm$ 4.37*10^{-7}	0.240 $\pm$ 0.001	10,078 $\pm$ 194

b = 0.002
m = 10,045
r = 1.000

10,270 $\pm$ 215 (271)

TABLE 39

NAPHTHYL DERIVATIVE IN METHANOL

MOLECULAR WEIGHT = 350.422 (g/mol)
DENSITY = 0.807 (g/cc)
TEMPERATURE = 27.0 (C)
CONC. STOCK SOLUTION = 3.15E-04 ± 3.32*10^{-6} (mol/l)

RANGE = VISIBLE
ABSORBANCE at = 489.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
7.45*10^{-6} ± 7.85*10^{-8}	0.105 ± 0.001	14,095 ± 241
1.47*10^{-5} ± 1.55*10^{-7}	0.205 ± 0.001	13,951 ± 176
2.20*10^{-5} ± 2.32*10^{-7}	0.309 ± 0.001	14,022 ± 161
2.96*10^{-5} ± 3.12*10^{-7}	0.417 ± 0.001	14,092 ± 156
3.68*10^{-5} ± 3.88*10^{-7}	0.515 ± 0.001	13,978 ± 152
4.41*10^{-5} ± 4.64*10^{-7}	0.613 ± 0.001	13,906 ± 150
5.13*10^{-5} ± 5.41*10^{-7}	0.720 ± 0.001	14,028 ± 150
5.90*10^{-5} ± 6.21*10^{-7}	0.818 ± 0.001	13,870 ± 148
6.61*10^{-5} ± 6.96*10^{-7}	0.918 ± 0.001	13,892 ± 148
7.40*10^{-5} ± 7.79*10^{-7}	1.030 ± 0.001	13,922 ± 148

b = 0.003
m = 13,863 13,976 ± 81 (163)
r = 1.000

RANGE = ULTRAVIOLET
ABSORBANCE at = 316.0 (nm)

M (mol l^{-1})	A	ϵ (M^{-1}cm^{-1})
7.45*10^{-6} ± 7.85*10^{-8}	0.202 ± 0.001	27,116 ± 343
1.47*10^{-5} ± 1.55*10^{-7}	0.406 ± 0.001	27,629 ± 306
2.20*10^{-5} ± 2.32*10^{-7}	0.611 ± 0.001	27,726 ± 299
2.96*10^{-5} ± 3.12*10^{-7}	0.813 ± 0.001	27,474 ± 293
3.68*10^{-5} ± 3.88*10^{-7}	1.032 ± 0.002	28,010 ± 301
4.41*10^{-5} ± 4.64*10^{-7}	1.213 ± 0.002	27,518 ± 294
5.13*10^{-5} ± 5.41*10^{-7}	1.436 ± 0.002	27,782 ± 296
5.90*10^{-5} ± 6.21*10^{-7}	1.597 ± 0.002	27,079 ± 288
6.61*10^{-5} ± 6.96*10^{-7}	1.833 ± 0.003	27,739 ± 296
7.40*10^{-5} ± 7.79*10^{-7}	-0.003 ± 0.001	-41 ± -14

b = 0.002
m = 27,521 27,564 ± 307 (301)
r = 1.000

TABLE 40

CYCLOHEXANE

TRIPHENYLFORMAZAN

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
VISIBLE RANGE				
10.00	489	$3.90*10^{-6}\pm6.73*10^{-8}$	0.690±0.001	17,708±308
1.00	489	$3.95*10^{-5}\pm6.82*10^{-7}$	0.703±0.001	17,784±309
0.10	488	$3.94*10^{-4}\pm6.80*10^{-6}$	0.655±0.001	16,624±289
ULTRAVIOLET RANGE				
10.00	298	$3.90*10^{-6}\pm6.73*10^{-8}$	1.030±0.001	26,434±458
1.00	297	$3.95*10^{-5}\pm6.82*10^{-7}$	1.092±0.002	27,624±480
0.10	297	$3.94*10^{-4}\pm6.80*10^{-6}$	1.063±0.001	26,980±467

ORTHO-HYDROXY DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
VISIBLE RANGE				
10.00	536	$5.92*10^{-6}\pm7.00*10^{-8}$	0.724±0.001	12,221±146
1.00	536	$5.96*10^{-5}\pm7.04*10^{-7}$	0.738±0.002	12,379±151
0.10	536	$5.97*10^{-4}\pm7.05*10^{-6}$	0.670±0.002	11,223±138
ULTRAVIOLET RANGE				
10.00	309	$5.92*10^{-6}\pm7.00*10^{-8}$	1.550±0.003	26,163±314
1.00	309	$5.96*10^{-5}\pm7.04*10^{-7}$	1.566±0.003	26,267±315
0.10	310	$5.97*10^{-4}\pm7.05*10^{-6}$	1.440±0.003	24,121±290

cont. TABLE 40

HYDROXY-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	530	$4.75*10^{-6} \pm 5.97*10^{-8}$	0.601±0.001	12,640±161
1.00	530	$4.56*10^{-5} \pm 5.73*10^{-7}$	0.570±0.001	12,492±160
0.10	530	$4.58*10^{-4} \pm 5.75*10^{-6}$	0.558±0.001	12,183±156
ULTRAVIOLET RANGE				
10.00	317	$4.75*10^{-6} \pm 5.97*10^{-8}$	1.143±0.002	24,039±305
1.00	318	$4.56*10^{-5} \pm 5.73*10^{-7}$	1.075±0.002	23,560±300
0.10	317	$4.58*10^{-4} \pm 5.75*10^{-6}$	1.041±0.002	22,729±290

PARA-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	490	$3.22*10^{-6} \pm 5.56*10^{-8}$	0.560±0.001	17,402±304
1.00	490	$3.16*10^{-5} \pm 5.46*10^{-7}$	0.547±0.001	17,311±302
0.10	490	$3.08*10^{-4} \pm 5.32*10^{-6}$	0.509±0.001	16,526±289
ULTRAVIOLET RANGE				
10.00	304	$3.22*10^{-6} \pm 5.56*10^{-8}$	0.963±0.001	29,925±519
1.00	305	$3.16*10^{-5} \pm 5.46*10^{-7}$	0.942±0.001	29,811±517
0.10	304	$3.08*10^{-4} \pm 5.32*10^{-6}$	0.874±0.001	28,377±492

cont. TABLE 40

META-BROMO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	486	$3.39*10^{-6} \pm 5.15*10^{-8}$	0.623±0.001	18,380±283
1.00	485	$3.38*10^{-5} \pm 5.14*10^{-7}$	0.607±0.001	17,944±276
0.10	486	$3.38*10^{-4} \pm 5.14*10^{-6}$	0.595±0.001	17,604±271
ULTRAVIOLET RANGE				
10.00	302	$3.39*10^{-6} \pm 5.15*10^{-8}$	1.013±0.002	29,887±459
1.00	302	$3.38*10^{-5} \pm 5.14*10^{-7}$	0.917±0.001	27,107±414
0.10	303	$3.38*10^{-4} \pm 5.14*10^{-6}$	0.907±0.001	26,834±410

ORTHO-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	467	$3.18*10^{-6} \pm 5.30*10^{-8}$	0.511±0.001	16,052±271
1.00	468	$2.99*10^{-5} \pm 4.97*10^{-7}$	0.473±0.001	15,827±268
0.10	467	$3.01*10^{-4} \pm 5.01*10^{-6}$	0.439±0.001	14,585±247
ULTRAVIOLET RANGE				
10.00	290	$3.18*10^{-6} \pm 5.30*10^{-8}$	0.513±0.001	16,115±272
1.00	289	$2.99*10^{-5} \pm 4.97*10^{-7}$	0.476±0.001	15,927±269
0.10	289	$3.01*10^{-4} \pm 5.01*10^{-6}$	0.470±0.001	15,615±264

cont. TABLE 40

ORTHO-BROMO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
VISIBLE RANGE				
10.00	469	$2.78*10^{-6}\pm5.86*10^{-8}$	0.417±0.001	15,008±320
1.00	468	$2.60*10^{-5}\pm5.48*10^{-7}$	0.392±0.001	15,072±322
0.10	470	$2.61*10^{-4}\pm5.50*10^{-6}$	0.369±0.001	14,138±303
ULTRAVIOLET RANGE				
10.00	291	$2.78*10^{-6}\pm5.86*10^{-8}$	0.422±0.001	15,188±324
1.00	290	$2.60*10^{-5}\pm5.48*10^{-7}$	0.392±0.001	15,072±322
0.10	290	$2.61*10^{-4}\pm5.50*10^{-6}$	0.369±0.001	14,138±303

NAPHTHYL DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
VISIBLE RANGE				
10.00	500	$4.71*10^{-6}\pm6.14*10^{-8}$	0.718±0.001	15,229±200
1.00	500	$4.62*10^{-5}\pm6.01*10^{-7}$	0.704±0.001	15,234±201
0.10	500	$4.68*10^{-4}\pm6.09*10^{-6}$	0.676±0.001	14,444±190
ULTRAVIOLET RANGE				
10.00	318	$4.71*10^{-6}\pm6.14*10^{-8}$	1.457±0.002	30,904±405
1.00	316	$4.62*10^{-5}\pm6.01*10^{-7}$	1.425±0.002	30,835±404
0.10	316	$4.68*10^{-4}\pm6.09*10^{-6}$	1.392±0.001	29,744±388

TABLE 41

CARBON TETRACHLORIDE

TRIPHENYLFORMAZAN

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
VISIBLE RANGE				
10.00	492	$4.32*10^{-6}\pm3.18*10^{-8}$	0.711±0.002	16,459±132
1.00	491	$4.60*10^{-5}\pm3.39*10^{-7}$	0.740±0.001	16,073±122
0.10	493	$4.48*10^{-4}\pm3.30*10^{-6}$	0.708±0.001	15,804±121
ULTRAVIOLET RANGE				
10.00	301	$4.32*10^{-6}\pm3.18*10^{-8}$	1.039±0.002	24,052±185
1.00	300	$4.60*10^{-5}\pm3.39*10^{-7}$	1.083±0.001	23,523±176
0.10	300	$4.48*10^{-4}\pm3.30*10^{-6}$	1.042±0.001	23,259±174

ORTHO-HYDROXY DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
VISIBLE RANGE				
10.00	539	$2.74*10^{-6}\pm3.05*10^{-8}$	0.322±0.001	11,761±141
1.00	537	$2.71*10^{-5}\pm3.02*10^{-7}$	0.327±0.001	12,051±144
0.10	536	$2.81*10^{-4}\pm3.13*10^{-6}$	0.333±0.001	11,851±141
ULTRAVIOLET RANGE				
10.00	310	$2.74*10^{-6}\pm3.05*10^{-8}$	0.670±0.001	24,471±277
1.00	312	$2.71*10^{-5}\pm3.02*10^{-7}$	0.663±0.001	24,433±277
0.10	312	$2.81*10^{-4}\pm3.13*10^{-6}$	0.673±0.001	23,950±271

cont. TABLE 41

HYDROXY-CHLORIDE DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	532	$5.08*10^{-6} \pm 2.78*10^{-8}$	0.600±0.001	11,813± 70
1.00	531	$5.01*10^{-5} \pm 2.74*10^{-7}$	0.611±0.001	12,195± 73
0.10	530	$5.15*10^{-4} \pm 2.82*10^{-6}$	0.614±0.001	11,922± 71
ULTRAVIOLET RANGE				
10.00	319	$5.08*10^{-6} \pm 2.78*10^{-8}$	1.076±0.001	21,185±119
1.00	319	$5.01*10^{-5} \pm 2.74*10^{-7}$	1.094±0.002	21,835±128
0.10	320	$5.15*10^{-4} \pm 2.82*10^{-6}$	1.121±0.002	21,767±127

PARA-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	494	$4.02*10^{-6} \pm 2.90*10^{-8}$	0.668±0.002	16,602±132
1.00	493	$4.07*10^{-5} \pm 2.93*10^{-7}$	0.675±0.002	16,593±132
0.10	493	$4.11*10^{-4} \pm 2.96*10^{-6}$	0.660±0.002	16,058±128
ULTRAVIOLET RANGE				
10.00	308	$4.02*10^{-6} \pm 2.90*10^{-8}$	1.099±0.002	27,314±204
1.00	308	$4.07*10^{-5} \pm 2.93*10^{-7}$	1.097±0.003	26,966±209
0.10	308	$4.11*10^{-4} \pm 2.96*10^{-6}$	1.084±0.002	26,375±198

cont. TABLE 41

META-BROMO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε (M^{-1}cm^{-1})
VISIBLE RANGE				
10.00	488	$4.21*10^{-6}\pm2.62*10^{-6}$	0.731±0.002	17,369±794
1.00	488	$4.15*10^{-5}\pm2.58*10^{-5}$	0.719±0.001	17,306±754
0.10	489	$4.20*10^{-4}\pm2.61*10^{-4}$	0.693±0.001	16,500±754
ULTRAVIOLET RANGE				
10.00	306	$4.21*10^{-6}\pm2.62*10^{-6}$	1.071±0.002	25,448±814
1.00	307	$4.15*10^{-5}\pm2.58*10^{-5}$	1.047±0.001	25,200±660
0.10	304	$4.20*10^{-4}\pm2.61*10^{-4}$	1.018±0.002	24,238±862

ORTHO-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε (M^{-1}cm^{-1})
VISIBLE RANGE				
10.00	469	$5.76*10^{-6}\pm2.84*10^{-8}$	0.824±0.001	14,316± 75
1.00	468	$5.77*10^{-5}\pm2.85*10^{-7}$	0.811±0.002	14,048± 79
0.10	467	$6.01*10^{-4}\pm2.96*10^{-6}$	0.797±0.001	13,261± 69
ULTRAVIOLET RANGE				
10.00	290	$5.76*10^{-6}\pm2.84*10^{-8}$	0.896±0.002	15,566± 86
1.00	293	$5.77*10^{-5}\pm2.85*10^{-7}$	0.886±0.002	15,347± 85
0.10	291	$6.01*10^{-4}\pm2.96*10^{-6}$	0.870±0.002	14,476± 80

cont. TABLE 41

NAPHTHYL DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
VISIBLE RANGE				
10.00	505	$4.74*10^{-6}\pm2.63*10^{-8}$	0.705±0.002	14,862± 95
1.00	503	$5.21*10^{-5}\pm2.89*10^{-7}$	0.769±0.001	14,746± 86
0.10	503	$5.11*10^{-4}\pm2.83*10^{-6}$	0.735±0.002	14,384± 91
ULTRAVIOLET RANGE				
10.00	321	$4.74*10^{-6}\pm2.63*10^{-8}$	1.290±0.002	27,194±158
1.00	319	$5.21*10^{-5}\pm2.89*10^{-7}$	1.380±0.001	26,463±149
0.10	320	$5.11*10^{-4}\pm2.83*10^{-6}$	1.350±0.002	26,419±153

TABLE 42

TOLUENE

TRIPHENYLFORMAZAN

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	492	$4.26*10^{-6} \pm 6.99*10^{-8}$	0.657±0.001	15,435±256
1.00	492	$4.10*10^{-5} \pm 6.73*10^{-7}$	0.625±0.001	15,242±253
0.10	492	$4.11*10^{-4} \pm 6.75*10^{-6}$	0.624±0.001	15,182±252
ULTRAVIOLET RANGE				
10.00	300	$4.26*10^{-6} \pm 6.99*10^{-8}$	0.977±0.001	22,952±378
1.00	301	$4.10*10^{-5} \pm 6.73*10^{-7}$	0.925±0.001	22,558±372
0.10	300	$4.11*10^{-4} \pm 6.75*10^{-6}$	0.919±0.001	22,360±369

ORTHO-HYDROXY DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	535	$4.77*10^{-6} \pm 6.23*10^{-8}$	0.569±0.001	11,935±159
1.00	535	$4.82*10^{-5} \pm 6.29*10^{-7}$	0.563±0.001	11,691±155
0.10	536	$4.84*10^{-4} \pm 6.32*10^{-6}$	0.521±0.001	10,764±144
ULTRAVIOLET RANGE				
10.00	311	$4.77*10^{-6} \pm 6.23*10^{-8}$	1.150±0.001	24,123±316
1.00	311	$4.82*10^{-5} \pm 6.29*10^{-7}$	1.127±0.001	23,403±307
0.10	311	$4.84*10^{-4} \pm 6.32*10^{-6}$	1.042±0.002	21,529±285

cont. TABLE 42

HYDROXY-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	530	$5.19*10^{-6} \pm 5.90*10^{-8}$	0.661±0.001	12,742±147
1.00	531	$5.20*10^{-5} \pm 5.90*10^{-7}$	0.656±0.001	12,624±146
0.10	531	$5.14*10^{-4} \pm 5.84*10^{-6}$	0.636±0.001	12,374±143
ULTRAVIOLET RANGE				
10.00	320	$5.19*10^{-6} \pm 5.90*10^{-8}$	1.199±0.002	23,113±266
1.00	320	$5.20*10^{-5} \pm 5.90*10^{-7}$	1.195±0.002	22,996±265
0.10	320	$5.14*10^{-4} \pm 5.84*10^{-6}$	1.156±0.002	22,490±259

PARA-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	492	$3.66*10^{-6} \pm 6.11*10^{-8}$	0.603±0.001	16,453±277
1.00	492	$3.62*10^{-5} \pm 6.03*10^{-7}$	0.599±0.001	16,553±279
0.10	492	$3.66*10^{-4} \pm 6.10*10^{-6}$	0.589±0.001	16,093±271
ULTRAVIOLET RANGE				
10.00	306	$3.66*10^{-6} \pm 6.11*10^{-8}$	1.020±0.002	27,831±468
1.00	307	$3.62*10^{-5} \pm 6.03*10^{-7}$	0.997±0.001	27,551±461
0.10	309	$3.66*10^{-4} \pm 6.10*10^{-6}$	0.962±0.001	26,284±440

cont. TABLE 42

META-BROMO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	489	$3.31*10^{-6} \pm 5.38*10^{-8}$	0.562±0.001	16,977±279
1.00	488	$3.26*10^{-5} \pm 5.30*10^{-7}$	0.555±0.001	17,021±280
0.10	488	$3.26*10^{-4} \pm 5.30*10^{-6}$	0.546±0.001	16,748±276
ULTRAVIOLET RANGE				
10.00	306	$3.31*10^{-6} \pm 5.38*10^{-8}$	0.828±0.001	25,013±409
1.00	306	$3.26*10^{-5} \pm 5.30*10^{-7}$	0.812±0.001	24,903±407
0.10	308	$3.26*10^{-4} \pm 5.30*10^{-6}$	0.800±0.001	24,540±401

ORTHO-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	400	$2.71*10^{-6} \pm 6.12*10^{-8}$	0.778±0.002	28,738±655
1.00	400	$2.64*10^{-5} \pm 5.96*10^{-7}$	0.749±0.002	28,399±648
0.10	400	$2.64*10^{-4} \pm 5.97*10^{-6}$	0.739±0.002	27,992±639
ULTRAVIOLET RANGE				
10.00	293	$2.71*10^{-6} \pm 6.12*10^{-8}$	0.315±0.001	11,636±268
1.00	290	$2.64*10^{-5} \pm 5.96*10^{-7}$	0.246±0.001	9,327±218
0.10	293	$2.64*10^{-4} \pm 5.97*10^{-6}$	0.261±0.001	9,886±230

cont. TABLE 42

ORTHO-BROMO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	402	$3.02*10^{-6} \pm 5.84*10^{-8}$	0.758±0.002	25,080±490
1.00	402	$2.96*10^{-5} \pm 5.72*10^{-7}$	0.770±0.002	26,010±508
0.10	402	$2.91*10^{-4} \pm 5.62*10^{-6}$	0.736±0.002	25,292±494
ULTRAVIOLET RANGE				
10.00	293	$3.02*10^{-6} \pm 5.84*10^{-8}$	0.356±0.001	11,779±232
1.00	289	$2.96*10^{-5} \pm 5.72*10^{-7}$	0.274±0.001	9,256±185
0.10	293	$2.91*10^{-4} \pm 5.62*10^{-6}$	0.248±0.001	8,522±172

NAPHTHYL DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	500	$5.42*10^{-6} \pm 7.14*10^{-8}$	0.783±0.001	14,457±192
1.00	500	$5.31*10^{-5} \pm 6.99*10^{-7}$	0.741±0.001	13,960±186
0.10	500	$5.29*10^{-4} \pm 6.97*10^{-6}$	0.737±0.001	13,932±186
ULTRAVIOLET RANGE				
10.00	320	$5.42*10^{-6} \pm 7.14*10^{-8}$	1.577±0.002	29,118±386
1.00	320	$5.31*10^{-5} \pm 6.99*10^{-7}$	1.461±0.003	27,524±368
0.10	319	$5.29*10^{-4} \pm 6.97*10^{-6}$	1.433±0.002	27,089±359

TABLE 43

DICHLOROMETHANE

TRIPHENYLFORMAZAN

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
VISIBLE RANGE				
10.00	487	$3.49*10^{-6}\pm6.70*10^{-8}$	0.646±0.001	18,520±358
1.00	485	$3.73*10^{-5}\pm7.16*10^{-7}$	0.619±0.002	16,601±325
0.10	487	$3.79*10^{-4}\pm7.27*10^{-6}$	0.616±0.001	16,253±314
ULTRAVIOLET RANGE				
10.00	300	$3.49*10^{-6}\pm6.70*10^{-8}$	0.963±0.002	27,609±534
1.00	300	$3.73*10^{-5}\pm7.16*10^{-7}$	0.912±0.002	24,458±474
0.10	300	$3.79*10^{-4}\pm7.27*10^{-6}$	0.915±0.001	24,142±465

ORTHO-HYDROXY DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1}cm^{-1}$)
VISIBLE RANGE				
10.00	523	$3.37*10^{-6}\pm7.47*10^{-8}$	0.482±0.001	14,311±320
1.00	525	$3.41*10^{-5}\pm7.57*10^{-7}$	0.443±0.001	12,978±291
0.10	524	$3.47*10^{-4}\pm7.69*10^{-6}$	0.439±0.001	12,651±283
ULTRAVIOLET RANGE				
10.00	310	$3.37*10^{-6}\pm7.47*10^{-8}$	0.985±0.001	29,245±650
1.00	310	$3.41*10^{-5}\pm7.57*10^{-7}$	0.900±0.001	26,365±586
0.10	309	$3.47*10^{-4}\pm7.69*10^{-6}$	0.889±0.001	25,620±569

cont. TABLE 43

HYDROXY-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	521	$5.56*10^{-6} \pm 6.69*10^{-8}$	0.830±0.002	14,936±184
1.00	520	$5.57*10^{-5} \pm 6.71*10^{-7}$	0.742±0.001	13,310±162
0.10	520	$5.59*10^{-4} \pm 6.70*10^{-6}$	0.714±0.001	12,773±155
ULTRAVIOLET RANGE				
10.00	318	$5.56*10^{-6} \pm 6.69*10^{-8}$	1.503±0.002	27,047±328
1.00	318	$5.57*10^{-5} \pm 6.71*10^{-7}$	1.360±0.002	24,396±296
0.10	318	$5.59*10^{-4} \pm 6.70*10^{-6}$	1.279±0.002	22,880±277

PARA-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	488	$3.25*10^{-6} \pm 6.71*10^{-8}$	0.641±0.002	19,702±412
1.00	489	$3.37*10^{-5} \pm 6.95*10^{-7}$	0.605±0.001	17,954±373
0.10	488	$3.33*10^{-4} \pm 6.86*10^{-6}$	0.605±0.001	18,168±377
ULTRAVIOLET RANGE				
10.00	306	$3.25*10^{-6} \pm 6.71*10^{-8}$	1.079±0.002	33,164±688
1.00	307	$3.37*10^{-5} \pm 6.95*10^{-7}$	1.025±0.001	30,418±629
0.10	307	$3.33*10^{-4} \pm 6.86*10^{-6}$	1.005±0.002	30,180±625

cont. TABLE 43

META-BROMO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	485	$4.24*10^{-6} \pm 7.21*10^{-8}$	0.827±0.002	19,519±336
1.00	482	$3.39*10^{-5} \pm 5.77*10^{-7}$	0.616±0.002	18,178±316
0.10	482	$3.42*10^{-4} \pm 5.81*10^{-6}$	0.600±0.001	17,544±301
ULTRAVIOLET RANGE				
10.00	306	$4.24*10^{-6} \pm 7.21*10^{-8}$	1.235±0.002	29,149±499
1.00	305	$3.39*10^{-5} \pm 5.77*10^{-7}$	0.908±0.002	26,795±461
0.10	305	$3.42*10^{-4} \pm 5.81*10^{-6}$	0.891±0.001	26,053±445

ORTHO-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	400	$2.69*10^{-6} \pm 5.74*10^{-8}$	0.860±0.002	31,914±685
1.00	400	$2.96*10^{-5} \pm 6.31*10^{-7}$	0.888±0.003	29,967±647
0.10	401	$2.98*10^{-4} \pm 6.34*10^{-6}$	0.799±0.002	26,812±575
ULTRAVIOLET RANGE				
10.00	290	$2.69*10^{-6} \pm 5.74*10^{-8}$	0.331±0.001	12,283±267
1.00	292	$2.96*10^{-5} \pm 6.31*10^{-7}$	0.290±0.001	9,786±214
0.10	292	$2.98*10^{-4} \pm 6.34*10^{-6}$	0.268±0.001	8,993±197

cont. TABLE 43

ORTHO-BROMO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	402	$1.58*10^{-6} \pm 5.05*10^{-8}$	0.517±0.001	32,768±1053
1.00	401	$1.77*10^{-5} \pm 5.66*10^{-7}$	0.524±0.002	29,663±958
0.10	403	$1.79*10^{-4} \pm 5.73*10^{-6}$	0.436±0.001	24,358±784
ULTRAVIOLET RANGE				
10.00	293	$1.58*10^{-6} \pm 5.05*10^{-8}$	0.182±0.001	11,535±380
1.00	293	$1.77*10^{-5} \pm 5.66*10^{-7}$	0.188±0.001	10,642±350
0.10	293	$1.79*10^{-4} \pm 5.73*10^{-6}$	0.207±0.001	11,564±379

NAPHTHYL DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	493	$3.07*10^{-6} \pm 6.45*10^{-8}$	0.523±0.001	17,018±360
1.00	495	$3.25*10^{-5} \pm 6.81*10^{-7}$	0.481±0.001	14,818±314
0.10	495	$3.28*10^{-4} \pm 6.87*10^{-6}$	0.484±0.001	14,756±312
ULTRAVIOLET RANGE				
10.00	319	$3.07*10^{-6} \pm 6.45*10^{-8}$	1.029±0.002	33,483±706
1.00	317	$3.25*10^{-5} \pm 6.81*10^{-7}$	0.945±0.002	29,112±614
0.10	318	$3.28*10^{-4} \pm 6.87*10^{-6}$	0.949±0.002	28,933±610

TABLE 44

METHANOL

TRIPHENYLFORMAZAN

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	482	$5.79*10^{-6}\pm6.30*10^{-8}$	0.914±0.002	15,792±176
1.00	483	$5.89*10^{-5}\pm6.41*10^{-7}$	0.910±0.002	15,460±173
0.10	482	$6.09*10^{-4}\pm6.63*10^{-6}$	0.906±0.002	14,877±166
ULTRAVIOLET RANGE				
10.00	298	$5.79*10^{-6}\pm6.30*10^{-8}$	1.265±0.002	21,856±241
1.00	297	$5.89*10^{-5}\pm6.41*10^{-7}$	1.248±0.002	21,203±234
0.10	297	$6.09*10^{-4}\pm6.63*10^{-6}$	1.285±0.002	21,100±233

ORTHO-HYDROXY DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	406	$6.30*10^{-6}\pm5.83*10^{-8}$	0.910±0.002	14,456±138
1.00	405	$6.47*10^{-5}\pm5.99*10^{-7}$	0.908±0.002	14,033±134
0.10	405	$6.58*10^{-4}\pm6.09*10^{-6}$	0.888±0.001	13,495±127
ULTRAVIOLET RANGE				
10.00	302	$6.30*10^{-6}\pm5.83*10^{-8}$	1.089±0.003	17,299±168
1.00	304	$6.47*10^{-5}\pm5.99*10^{-7}$	1.070±0.002	16,536±157
0.10	304	$6.58*10^{-4}\pm6.09*10^{-6}$	1.033±0.003	15,699±153

cont. TABLE 44

HYDROXY-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	407	$1.77*10^{-6} \pm 4.30*10^{-8}$	0.230±0.001	12,968±324
1.00	407	$1.79*10^{-5} \pm 4.35*10^{-7}$	0.227±0.001	12,648±316
0.10	406	$1.80*10^{-4} \pm 4.36*10^{-6}$	0.220±0.001	12,222±306
ULTRAVIOLET RANGE				
10.00	312	$1.77*10^{-6} \pm 4.30*10^{-8}$	0.300±0.001	16,915±417
1.00	312	$1.79*10^{-5} \pm 4.35*10^{-7}$	0.291±0.001	16,213±401
0.10	310	$1.80*10^{-4} \pm 4.36*10^{-6}$	0.290±0.001	16,111±398

PARA-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	485	$5.07*10^{-6} \pm 5.27*10^{-8}$	0.899±0.002	17,719±189
1.00	482	$5.19*10^{-5} \pm 5.38*10^{-7}$	0.849±0.001	16,366±172
0.10	482	$5.27*10^{-4} \pm 5.47*10^{-6}$	0.842±0.002	15,977±171
ULTRAVIOLET RANGE				
10.00	304	$5.07*10^{-6} \pm 5.27*10^{-8}$	1.386±0.002	27,318±287
1.00	305	$5.19*10^{-5} \pm 5.38*10^{-7}$	1.372±0.002	26,447±278
0.10	304	$5.27*10^{-4} \pm 5.47*10^{-6}$	1.370±0.002	25,996±273

cont. TABLE 44

META-BROMO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	478	$3.68*10^{-6} \pm 4.35*10^{-8}$	0.693±0.001	18,833±226
1.00	478	$3.64*10^{-5} \pm 4.30*10^{-7}$	0.668±0.001	18,371±220
0.10	477	$3.64*10^{-4} \pm 4.30*10^{-6}$	0.656±0.001	18,022±216
ULTRAVIOLET RANGE				
10.00	302	$3.68*10^{-6} \pm 4.35*10^{-8}$	1.014±0.001	27,556±328
1.00	304	$3.64*10^{-5} \pm 4.30*10^{-7}$	0.968±0.001	26,621±317
0.10	305	$3.64*10^{-4} \pm 4.30*10^{-6}$	0.948±0.001	26,044±310

ORTHO-CHLORO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ϵ ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	410	$3.02*10^{-6} \pm 5.81*10^{-8}$	0.686±0.001	22,698±439
1.00	408	$2.99*10^{-5} \pm 5.74*10^{-7}$	0.657±0.001	22,003±426
0.10	408	$3.01*10^{-4} \pm 5.79*10^{-6}$	0.636±0.001	21,130±409
ULTRAVIOLET RANGE				
10.00	290	$3.02*10^{-6} \pm 5.81*10^{-8}$	0.303±0.001	10,025±198
1.00	285	$2.99*10^{-5} \pm 5.74*10^{-7}$	0.302±0.001	10,114±200
0.10	285	$3.01*10^{-4} \pm 5.79*10^{-6}$	0.290±0.001	9,635±191

cont. TABLE 44

ORTHO-BROMO DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	410	$2.47*10^{-6} \pm 4.53*10^{-8}$	0.553±0.002	22,429±422
1.00	409	$2.52*10^{-5} \pm 4.63*10^{-7}$	0.559±0.001	22,161±411
0.10	409	$2.51*10^{-4} \pm 4.61*10^{-6}$	0.543±0.001	21,633±401
ULTRAVIOLET RANGE				
10.00	286	$2.47*10^{-6} \pm 4.53*10^{-8}$	0.241±0.001	9,774±188
1.00	288	$2.52*10^{-5} \pm 4.63*10^{-7}$	0.255±0.001	10,109±194
0.10	288	$2.51*10^{-4} \pm 4.61*10^{-6}$	0.248±0.001	9,880±190

NAPHTHYL DERIVATIVE

CELL (cm)	λ (nm)	CONCENTRATION (mol cm^{-1})	A	ε ($M^{-1} cm^{-1}$)
VISIBLE RANGE				
10.00	490	$3.22*10^{-6} \pm 3.40*10^{-8}$	0.456±0.001	14,146±155
1.00	489	$3.19*10^{-5} \pm 3.36*10^{-7}$	0.445±0.001	13,941±153
0.10	489	$3.15*10^{-4} \pm 3.32*10^{-6}$	0.425±0.001	13,492±149
ULTRAVIOLET RANGE				
10.00	316	$3.22*10^{-6} \pm 3.40*10^{-8}$	0.906±0.002	28,105±304
1.00	316	$3.19*10^{-5} \pm 3.36*10^{-7}$	0.885±0.002	27,725±300
0.10	315	$3.15*10^{-4} \pm 3.32*10^{-6}$	0.839±0.002	26,635±290

TABLE 45

TRIPHENYLFORMAZAN

SOLVENT	λ_{vis}	ϵ_{vis}	λ_{uv}	ϵ_{uv}	$\epsilon_{vis}/\epsilon_{uv}$	$\epsilon_{max}/\epsilon_{535}$
C_6H_{12}	488	17,676	297	27,900	0.633	1.416
CCl_4	491	16,600	301	24,522	0.677	1.336
C_7H_8	491	15,574	300	22,952	0.679	1.337
CH_2Cl_2	488	16,823	300	24,663	0.682	1.478
CH_3OH	482	15,603	297	20,937	0.745	1.609

TABLE 46

PARA-CHLORO DERIVATIVE

SOLVENT	λ_{vis}	ϵ_{vis}	λ_{uv}	ϵ_{uv}	$\epsilon_{vis}/\epsilon_{uv}$
C_6H_{12}	490	17,307	305	29,560	0.585
CCl_4	493	16,834	308	27,708	0.608
C_7H_8	493	16,472	307	27,538	0.598
CH_2Cl_2	487	18,574	307	32,337	0.574
CH_3OH	482	16,462	306	26,864	0.613

TABLE 47

META-BROMIDE DERIVATIVE

SOLVENT	λ_{vis}	ϵ_{vis}	λ_{uv}	ϵ_{uv}	$\epsilon_{vis}/\epsilon_{uv}$
C_6H_{12}	488	18,231	304	27,443	0.664
CCl_4	490	17,769	306	25,810	0.688
C_7H_8	488	17,080	306	24,922	0.683
CH_2Cl_2	483	17,810	306	26,072	0.683
CH_3OH	480	18,182	314	26,363	0.690

TABLE 48

ORTHO-HYDROXY DERIVATIVE

SOLVENT	λ_{vis}	ϵ_{vis}	λ_{uv}	ϵ_{uv}	$\epsilon_{vis}/\epsilon_{uv}$
C_6H_{12}	535	12,567	310	26,469	0.475
CCl_4	535	11,472	311	24,355	0.471
C_7H_8	535	11,880	311	23,774	0.500
CH_2Cl_2	524	12,774	310	25,777	0.496
CH_3OH	406	14,068	302	16,242	0.866

TABLE 49

HYDROXY-CHLORO DERIVATIVE

SOLVENT	λ_{vis}	ϵ_{vis}	λ_{uv}	ϵ_{uv}	$\epsilon_{vis}/\epsilon_{uv}$
C_6H_{12}	530	12,584	318	23,678	0.531
CCl_4	533	12,315	319	242,885	0.538
C_7H_8	530	12,598	320	22,938	0.549
CH_2Cl_2	520	13,246	318	24,269	0.546
CH_3OH	408	12,632	311	16,026	0.788

TABLE 50

ORTHO-CHLORO DERIVATIVE

SOLVENT	λ_{vis}	ϵ_{vis}	λ_{uv}	ϵ_{uv}	$\epsilon_{vis}/\epsilon_{uv}$
C_6H_{12}	468	15,684	290	15,722	0.998
CCl_4	477	13,665	-	-	-
C_7H_8	400	28,693	292	9,621	2.982
CH_2Cl_2	402	30,327	294	9,724	3.119
CH_3OH	408	22,312	285	10,574	2.110

TABLE 51

ORTHO-BROMO DERIVATIVE

SOLVENT	λ_{vis}	ϵ_{vis}	λ_{uv}	ϵ_{uv}	$\epsilon_{vis}/\epsilon_{uv}$
C_6H_{12}	470	15,032	291	15,113	0.995
CCl_4	-	-	-	-	-
C_7H_8	402	25,666	294	8,984	2.857
CH_2Cl_2	402	29,065	294	9,708	2.994
CH_3OH	410	22,388	290	10,270	2.180

TABLE 52

NAPHTHYL DERIVATIVE

SOLVENT	λ_{vis}	ϵ_{vis}	λ_{uv}	ϵ_{uv}	$\epsilon_{vis}/\epsilon_{uv}$	$\epsilon_{max}/\epsilon_{535}$	$\epsilon_{370}/\epsilon_{395}$
C_6H_{12}	500	15,366	317	31,017	0.495	1.200	1.320
CCl_4	504	15,277	318	28,776	0.531	1.145	1.351
C_7H_8	501	14,212	320	28,069	0.506	1.155	1.282
CH_2Cl_2	495	14,905	320	30,166	0.494	1.227	1.240
CH_3OH	489	13,976	316	27,564	0.507	1.310	1.417

TABLE 53

ORTHO-HYDROXY DERIVATIVE IN DIFFERENT ALCOHOLS

SOLVENT	A_{yellow}/A_{red}	A_{495}/A_{535}	D	acidity strength
CH_3OH	1.924	1.115	32.63	4.0
C_2H_5OH	1.031	1.074	24.30	0.95
1-C_3H_8OH	0.809	1.027	21.10	0.5
2-C_3H_8OH	0.741	1.015	18.3	-
1-C_4H_9OH	0.643	0.989	17.8	0.5
2-C_4H_9OH	0.633	0.990	15.8	-
C_6H_{12}	0.456		2.20	
CCl_4	0.323		2.24	
C_7H_8	0.299		2.38	
CH_2CL_2	0.274		9.08	

TABLE 54

TRIPHENYLFORMAZAN MOLECULAR MECHANICS ENERGY

	Non planar (Kcal)	Planar (Kcal)
Compression	0.9108	0.9097
Bending	8.0041	4.2083
Stretching-bendin	0.1359	0.0690
v.d.W. 1,4	20.6891	21.1177
Other	-0.4977	0.3023
Torsional	-13.1037	-21.8669
Dipole	6.0154	5.3867
Final Steric Energy	22.1539	10.1267
Dipole moment	2.080 (D)	2.808 (D)
Dielectric constant	1.50	1.50

TABLE 55

DERIVATIVES MOLECULAR MECHANICS ENERGY

	ortho-hydroxy (Kcal)	para-chloro (Kcal)	ortho-chloro (Kcal)
Compression	1.1503	0.9265	1.1189
Bending	9.2678	10.2707	10.2514
Stretching-bending	0.1093	0.1436	0.1161
1,4 v.d.W.	20.7455	21.0536	21.2501
Other	0.9791	-0.6550	-0.9325
Torsional	-9.1038	-10.9962	-9.6810
Dipole	4.2083	6.5734	8.5854
Final Steric Energy	27.3566	27.3165	30.7083
Dipole moment	1.789 (D)	3.297 (D)	3.113 (D)
Dielectric constant	1.50	1.50	1.50

cont. TABLE 55

DERIVATIVES MOLECULAR MECHANICS ENERGY

	meta-bromo (Kcal)	ortho-chloro (Kcal)
Compression	0.9527	1.1929
Bending	10.7798	10.7595
Stretching-bending	0.1304	0.0884
1,4 v.d.W.	21.4440	21.5812
Other	-0.7518	-1.3826
Torsional	-12.3735	-9.5829
Dipole	6.7740	8.1364
Final Steric Energy	26.9557	30.7931
Dipole moment	1.990 (D)	0.716 (D)
Dielectric constant	1.50	1.50

TABLE 56

CNDO ELECTRONIC TRANSITIONS

FORMAZAN		TRIMETHYLFORMAZAN	
13 - 15	n - π*	22 - 24	n,π - π*
14 - 15	π - π*	21 - 24	n - π*
10 - 15	n - π*	23 - 24	n,π - π*
11 - 15	n - π*	22 - 25	n,π - n*,π*
13 - 16	n - π*	20 - 24	n,π - π*
12 - 15	π - π*	19 - 24	n,π - π*
14 - 16	π - π*	18 - 24	n - π*
14 - 17	π - n*	23 - 25	n,π - n*,π*
11 - 16	n - π*	21 - 25	n - n*,π*

TRIPHENYLFORMAZAN planar		TRIPHENYLFORMAZAN non-planar	
52 - 57	n - π*	52 - 57	n - π*
56 - 57	π - π*	55 - 57	π - π*
55 - 57	π - π*	50 - 57	n - π*
54 - 57	π - π*	56 - 58	π - π*
56 - 58	π - π*	54 - 57	π - π*
50 - 57	π - π*	51 - 57	n - π*
49 - 57	n - π*	53 - 57	n - π*
51 - 57	π - π*	56 - 59	π - π*
53 - 58	π - π*	56 - 61	π - π*

TABLE 57

TRIPHENYLFORMAZAN ABSORPTION WAVELENGTHS

exp at 77 (K) (nm)	calc (osc. st.) (nm)	
	non-planar	planar
		684.4 (4×10^{-6})
546		
503		
478		
	465.5 (0.0865)	
		427.3 (0.2370)
	409.1 (0.0937)	
364		
350		
		349.3 (1.3×10^{-5})
343		
330		
	325.2 (0.0424)	
		295.4 (0.3470)
	284.2 (0.2065)	
		283.4 (0.0834)
		270.6 (0.1849)

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