

GEOMETRY CHANGES IN EXCITED STATES

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ABSTRACT

A brief discussion of the experimental methods of obtaining geometrical information about the equilibrium geometry of molecules in their electronically excited states is followed by a sampling of geometrical information available at present. The significance of simple orbital and symmetry arguments exemplified by Walsh diagrams is stressed. The geometrical tendencies of alkane excited states are studied. We find an excited state of methane that is planar. The lowest excited state of ethane should have longer C—H bonds and a shorter C—C bond than the ground state, and should also prefer an eclipsed conformation. Excited cyclopropane breaks one C—C bond. The lowest n, π^* state of benzophenone is computed to be more planar than the ground state, and apparently does not become pyramidal at the carbonyl group. The isocyanide—cyanide rearrangement potential surface cautions us not to assume necessarily that excited state reaction is facilitated by a geometry change bringing closer the geometry of reactant to that of product.

Every state of a molecule may be represented by a potential energy surface. An excited state surface is one such surface, the ground state of an isomer another. The excited state surface potentially differs from that of the ground state as much as the latter does from the surface of an isomer of very different geometry. It is not surprising therefore that upon electronic excitation molecules may adopt equilibrium geometries very different from those in their ground states. I would like to report on some of these geometry changes here, with particular emphasis on the interaction between theory and experiment in this area.

Our primary source of experimental information on geometry changes remains the elucidation of the rotational fine structure of electronic transitions. The theoretical procedures leading from the observed high resolution spectrum to the moments of inertia of the molecule are summarized in the classic work of Herzberg¹. These procedures rank among the highest achievements of theoretical chemistry and physics.

The kind of information that emerges from spectroscopic studies is illustrated by the equilibrium bond length, the only free geometrical parameter, in various states of C_2 , listed in *Table 1*².

Each molecular orbital may be classified as bonding (σ_g, π_u) or antibonding (σ_u^*, π_g^*), and these tendencies may be graded. Occupation of bonding orbitals decreases the equilibrium internuclear separation, occupation of antibonding orbitals increases this separation. These arguments, now so

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familiar that we present them to freshman chemistry students, are due to Mulliken³. The trends exhibited in *Table 1* for C_2 may thus be rationalized and predictions for as yet unobserved states easily made^{2, 4}.

Table 1. Bond lengths for states of C_2

State	Bond length Å	$\sigma_g(2s)$	$\sigma_u^*(2s)$	Configuration $\pi_u(2p)$	$\sigma_g(2p)$	$\pi_g^*(2p)$
$^1\Sigma_g^+$	1.2422	2	2	4		
$^3\Pi_u$	1.3117	2	2	3	1	
$^1\Pi_u$	1.3280	2	2	3	1	
$^3\Sigma_g^-$	1.3693	2	2	2	2	
$^3\Pi_g$	1.2660	2	1	3	2	
$^1\Pi_g$	1.2730	2	1	3	2	
$^1\Sigma_u^+$	1.2378	2	1	4	1	
$^3\Pi_g$	1.5350	2	2	2	1	1
$^1\Sigma_g^+$	1.2518	2		4	2	

There are two further comments to be made on the distances shown in *Table 1*. Note that among the various states we have two pairs consisting of a singlet and triplet of the same spatial configuration: $^1, ^3\Pi_u$ and $^1, ^3\Pi_g$. These differ little in geometry, a fact that may be of some importance in interpretations of the difference between singlet and triplet reactivity in more complicated molecules⁵. The second point of interest is that in its ground and various excited states the C_2 molecule spans almost the entire range of

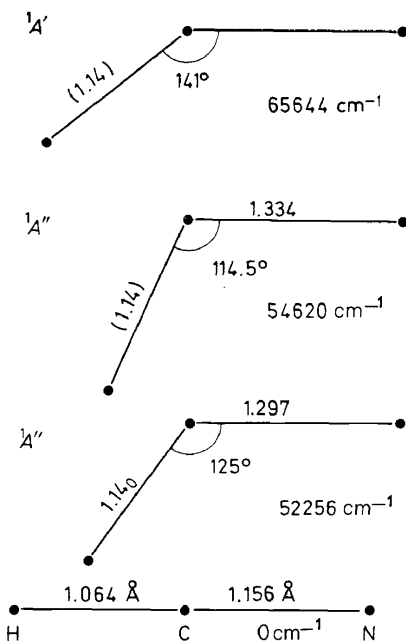


Figure 1. Geometrical parameters of the ground and three excited singlet states of HCN. The excitation energies appear below each geometry.

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carbon-carbon distances of organic molecules: the excited states of C_2 model the valence states of carbon in other molecular environments.

As we go on to larger molecules the experimental information becomes harder to extract, the geometrical parameters more interesting, and the interaction between theory and experiment more pronounced. Some representative results are the following:

(1) HCN, linear in its ground state has had three of its excited singlet states analysed^{1,6}. All are bent, with HCN angles of 125° , 114.5° and 141° , respectively. The geometries are drawn to scale in *Figure 1*.

(2) HCO, bent 119.5° in its ground state is linear in its lowest doublet excited state⁷.

(3) Almost all of the excited states of NH_3 are planar^{1,8}.

(4) Acetylene is *trans* bent, with a C—C distance of 1.39 \AA in its lowest singlet excited state⁹.

(5) Formaldehyde, planar in its ground state, is pyramidal in both the singlet and triplet n, π^* states¹⁰.

(6) Benzene in its ${}^1B_{2u}$ state appears to retain a D_{6h} geometry but with a longer C—C bond of 1.435 \AA ¹¹; in contrast the ${}^3B_{1u}$ appears to distort slightly to D_{2h} symmetry¹².

Most of these and other interesting geometry changes in small molecules can be rationalized on the basis of an extraordinarily simple and powerful device, the Walsh diagram¹³. I think it can be fairly said that the predictive capability of this model is responsible for any creditability that electronic structure calculators retain among professional spectroscopists.

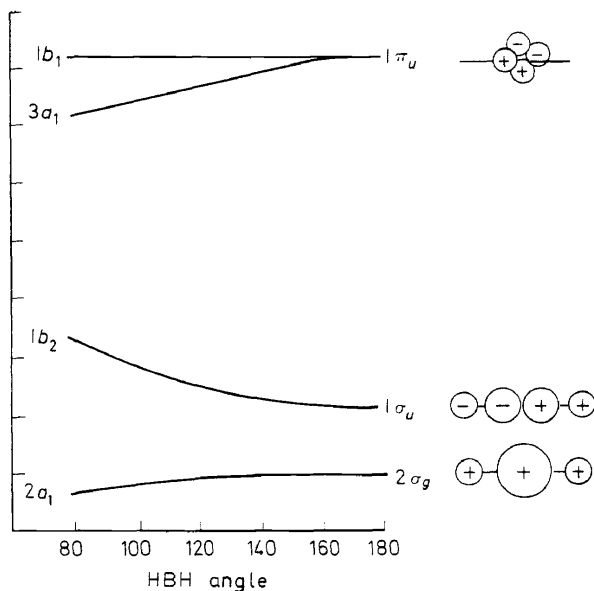


Figure 2. Walsh diagram for triatomic XH_2 , showing how the energy levels change with bending of the molecule. The diagram is modelled after that given by Allen in ref. 14.

In a Walsh diagram, an example of which is shown in *Figure 2*, one plots the orbital energies versus some angular variable, for example the HXH angle in XH_2 . The rough positioning of energy levels at either angular extreme is accomplished from either spectroscopic data, hybridization or bonding arguments, or calculation. The correlation of levels at intermediate angles is constrained by symmetry. The utility of such a diagram is apparent. Consider for example the problem of predicting whether the lowest singlet of methylene is more or less bent than the lowest triplet. The singlet is derived from the configuration $(2a_1)^2(1b_2)^2(3a_1)^2$ while the triplet comes from $(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^1$. Since the $3a_1$ orbital favours a bent molecule while $1b_1$ has to a first approximation no angular preference it is clear that one would predict the singlet to be more bent than the triplet.

Walsh diagrams are as powerful as their direct antecedents, the united atom-separated atoms correlation diagrams of Hund and Mulliken. The reasons for their success are the same—they are grounded in the most fundamental symmetry and bonding arguments. Their utility is not obviated by the problem that on further probing it is not so clear just what the orbital energy that is being plotted is¹⁴.

A sad reflection on the state of theoretical chemistry is the rarity of the situation where a computational prediction is in disagreement with an experimental result and the calculator has the courage to question the observation. I think such a rare situation presents itself in the case of the triplet ground state of methylene, CH_2 .

The search for the methylene spectrum is an interesting story in itself¹⁵. The lowest triplet and likely ground state has been assigned as $^3\Sigma_g^-$, and it has been concluded that the molecule is linear or nearly linear^{1, 15}. On the other hand nearly every theoretical calculation, semi-empirical or *ab initio*¹⁶, has given a bent triplet, with an HCH angle of 135° to 150° . The best of these calculations^{16g} approach the true wavefunction so closely that, in my opinion, it is safe to say that they are correct and the experimental conclusion must be questioned.

Discrete rotational structure often cannot be resolved or detected. In such cases band contours and specific vibrational progressions can provide fragmentary structural information. Even this is not available for some of the simplest molecules, e.g. butadiene, allene, ethane, cycloalkanes, ozone, acetaldehyde, acetone, pyridine, etc. Theory, or more precisely said, theoretical speculation, then becomes of prime importance. The strongest arguments are the simplest ones, those which are based on symmetry and bonding considerations, much as the Walsh diagrams discussed above. We have carried out a number of calculations on excited state geometries and in the remainder of this paper I would like to discuss some of our results.

ALKANES

Saturated hydrocarbons absorb in the far ultra-violet, and it is only recently that systematic spectroscopic studies of these spectra were undertaken¹⁷. The basic problem in the interpretation of the transitions of alkanes, whose spectra have not been definitively assigned, is that we do not know whether the transitions responsible for these spectra are best described as

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$\sigma \rightarrow \sigma^*$ molecular excitations, or as Rydberg transitions in which a σ electron is promoted to a diffuse higher principal quantum number orbital. We will base our geometrical discussion on the assumption that the $\sigma \rightarrow \sigma^*$ component dominates, though we will be able to model the Rydberg state by the ionized molecule.

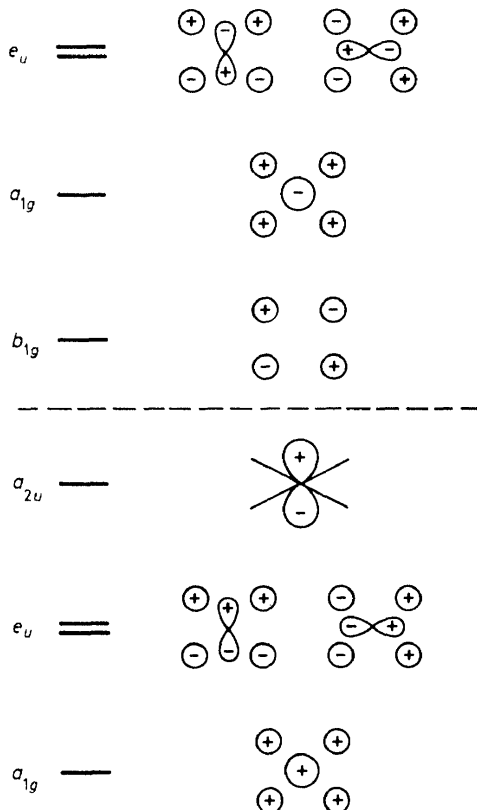


Figure 3. Molecular orbitals of a square planar methane.

Let us first consider methane. The proper symmetry-adapted molecular orbitals of CH_4 are ordered in energy as follows: $a_1 < f_2 < f_2 < a_1$. There is some doubt about the ordering of the last two levels. The ground state A_1 singlet is derived from the configuration $(a_1)^2(f_2)^6$. The excited configuration $(a_1)^2(f_2)^5(f_2)^1$ yields states $A_1 + E + F_1 + F_2$ with transition from the ground state allowed only to F_2 .

A methane molecule may distort to lower symmetry in a number of ways. The most interesting motions we have found are those that lead from a tetrahedron to a square via either a squashing (D_{2d}) or a twisting (D_2) motion. The molecular orbitals of a planar methane¹⁸ are shown in Figure 3, and a

correlation diagram for the squashing motion ($T_d \rightarrow D_{2d} \rightarrow D_{4h}$) is shown in Figure 4¹⁹.

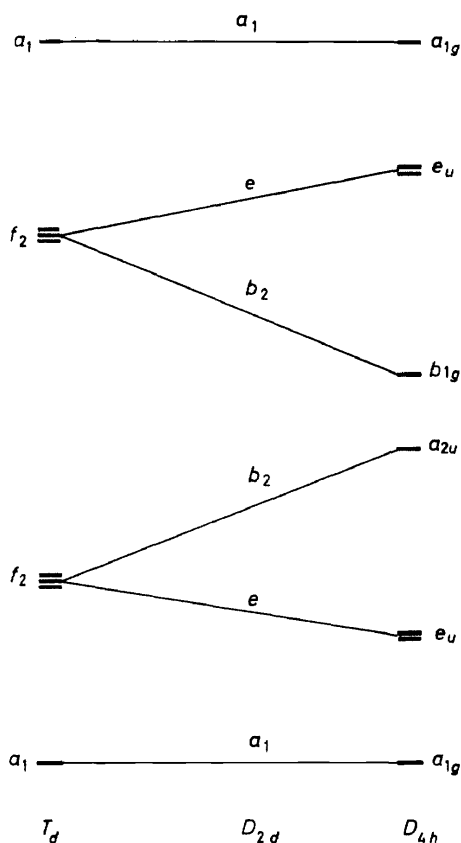


Figure 4. A level correlation diagram for the distortion of tetrahedral methane through a flattened tetrahedron (D_{2d}) to a square planar geometry.

The $b_2 \rightarrow b_2$ excitation, in which an electron is promoted from an energy level favouring a T_d geometry to one preferring D_{4h} , clearly favours a geometry change from T_d to D_{2d} and on to D_{4h} . This is confirmed by extended Hückel calculations²⁰. The excited state in question is A_1 in D_{2d} , and may be derived from either the A_1 or E excited state of methane.

If the lowest methane excited state is more Rydberg-like, i.e. possesses the configuration $(a_1)^2(f_2)^5(3s)^1$ then we would like to use CH_4^+ as a model for its geometrical proclivities. CH_4^+ is calculated to prefer a distortion to flattened tetrahedral²⁰ or C_{2v} geometry²¹.

We next turn to ethane where a fascinating counter-intuitive geometry change may be predicted. Let us first derive the molecular orbitals of ethane from those of two separate pyramidal methyl radicals. The three methyl C—H bonds give rise to an a and an e combination, as do the C—H σ^* levels.

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The radical lobe transforms as a . These orbitals are shown schematically in *Figure 5*. The molecular orbitals of ethane may now be formed by interaction of two such methyl radicals, as shown for an eclipsed D_{3h} ethane in *Figure 6*. An analogous picture holds for staggered D_{3d} ethane with the replacement of a'_1 by a_{1g} , a'_2 by a_{2u} , e' by e_u , e'' by e_g . The ground state configuration is $(a_{1g})^2(a_{2u})^2(e_u)^4(a_{1g})^2(e_g)^4$ and the lowest excitation is an $e \rightarrow e$ type²².

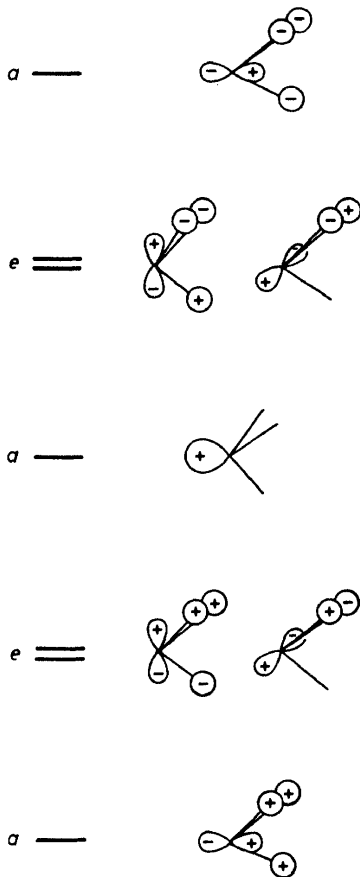


Figure 5. Schematic illustration of the molecular orbitals of a pyramidal methyl group. C_3 symmetry is used. The representation of the degenerate set is, of course, arbitrary.

The e' levels favour an eclipsed geometry, because they are H—H' bonding and the H—H' overlap is greater in the eclipsed conformation. Conversely the e'' levels favour a staggered geometry because they are H—H' antibonding. These preferences in fact are on the one-electron level the source of the ethane barrier. The various a levels are approximately cylindrically symmetrical and do not contribute to the barrier, whose origin may be traced to the e levels. In the interaction of the two methyl e orbitals to give e' and e'' the e'' orbital is raised more than the e' is depressed. This is the usual

consequence of including overlap in the calculations. Similarly the difference which ensues on internal rotation between e'' and e_g (favouring staggering) is greater than the difference between e' and e_u (favouring eclipsing). Thus ground state ethane is staggered. This argument has been independently presented by Lowe²³.

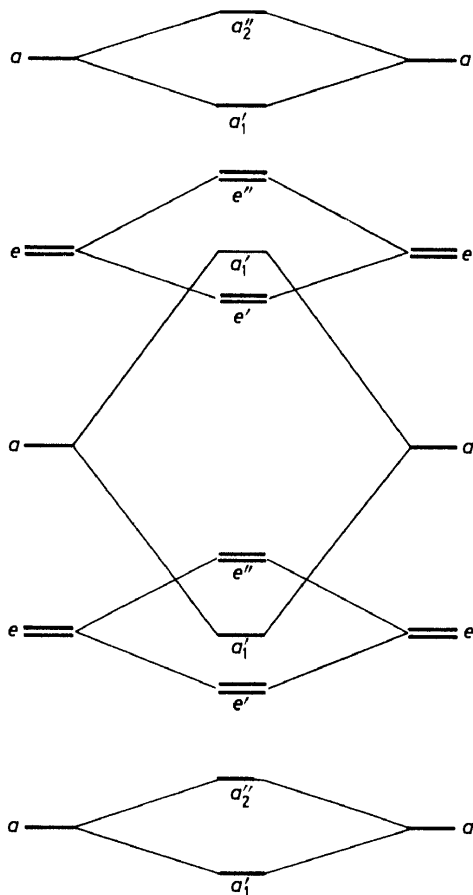


Figure 6. The molecular orbitals of an eclipsed ethane as derived from those of two methyl groups. The primary interaction is between methyl orbitals of the same energy. The non-bonding orbitals are optimally oriented for interaction and so split apart most.

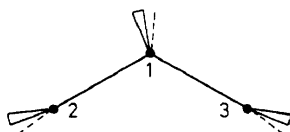
We now return to the geometry change anticipated for the $e_g \rightarrow e_u$ ($e'' \rightarrow e'$) excitation in ethane. The orbital from which the electron is taken is C—H bonding (it is derived from a methyl σ orbital), C—C antibonding (it has a node between the two carbons) and, as argued above, prefers a staggered conformation. The orbital to which the electron is excited is in contrast C—H antibonding, C—C bonding and prefers an eclipsed geometry. The excitation would thus be expected to weaken the C—H bond, strengthen the C—C bond and make the excited state eclipsed. That the C—H bond should

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be longer in the excited state is not unexpected. It is highly non-intuitive that a bond should become shorter in an excited state, as we predict here. Most of the time we like to think of bonds becoming weaker upon excitation. The reversal of the ground state conformational preference is also highly interesting.

An analysis of the vibrational structure of the electron impact spectrum of ethane by Lassetre and collaborators²⁴ indeed concludes that in the excited state the C—C distance is decreased to 1.39 Å, the CCH angle is increased 10° above tetrahedral, and the C—H bond is lengthened. No information is available on the predicted change to eclipsing. The theoretical rationalization of these changes, though put into slightly different words²⁴, is essentially identical to that presented here.

Cyclopropane absorbs at lower energy than other saturated hydrocarbons, consistent with its ethylene-like physical and chemical properties. The first excited state of cyclopropane, according to our calculations^{25,26} undergoes a severe geometry change. A carbon-carbon bond is broken and the excited cyclopropane is best described as a floppy trimethylene.



The optimum $C_2C_1C_3$ angle in the excited state is near 120° but it costs less than 8 kcal/mole to bend it 20° either way. There are only small barriers of less than 3 kcal/mole to twisting one or both terminal methylene groups into the plane of the carbons.

The general features of the excited state potential energy surface are not difficult to understand. The extended Hückel calculations give as the highest occupied and lowest unoccupied orbitals in cyclopropane precisely the linear combinations suggested by Walsh some time ago²⁷, and named as Walsh orbitals. In *Figure 7* these are illustrated; one specific form of the degenerate pair χ_1, χ_2 is chosen, namely that adapted to the ensuing stretching of the C_2-C_3 bond. The motion of the energy levels as one bond is slowly broken is apparent—those levels which are bonding in the region of bond cleavage are destabilized, while those antibonding in that region are stabilized. Promotion of an electron from χ_2 to χ_3 not only weakens C_2-C_3 bonding but also C_1-C_2 and C_1-C_3 as well, leading to a very flexible excited molecule.

It should be noted that other motions, such as twisting a single methylene group in place by 90° are also possible distortions for an excited cyclopropane²⁵. However, in so far as we can trust these calculations, it appears that breaking one C—C bond will be preferred to twisting. Thus our proposal²⁸ that a relative twist of both rings might be a likely mechanism for photochemical racemization of optically active spiropentanes, made before we studied the bond stretching, is probably incorrect.

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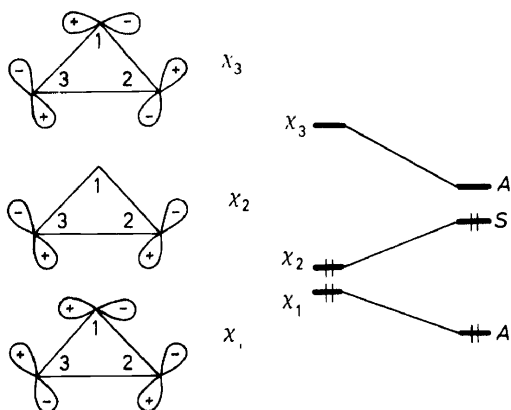
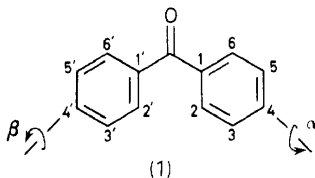


Figure 7. The Walsh orbitals of cyclopropane and their motion in energy as the C_2-C_3 bond is broken. χ_1 and χ_2 are originally degenerate.

BENZOPHENONE

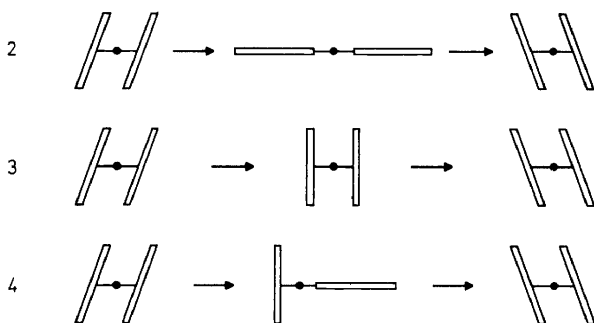
Our studies of geometry changes in excited states have recently led us to consideration of a most popular molecule among photochemists, benzophenone²⁹.



The ground-state equilibrium geometry of benzophenone is determined by a balance of steric and conjugative effects. Conjugation of the carbonyl group with the phenyl rings would favour a planar conformation. Steric repulsion between the H_2 and H'_2 hydrogen atoms prevents the attainment of coplanarity. Each of the phenyl rings must then be rotated by some angle, α and β (see structure 1), out of the plane formed by the carbonyl group and the adjacent phenyl carbon atoms. The mode of rotation which most efficiently relieves the steric problems of the planar geometry is a conrotatory one, i.e. α and β as defined in structure I both positive and probably of similar magnitude. This was obvious to early workers in the field³⁰ and is apparent in our calculated surface, Figure 8, where α and β are allowed to vary independently. The only minima in the surface are the conrotatory one at $\alpha = \beta = 38^\circ$ and its mirror image at $\alpha = -38^\circ$, $\beta = 142^\circ$. The agreement with various crystal structures of benzophenone derivatives³¹ is good.

The stable conformation of benzophenone is chiral. There arises immediately the problem of mechanisms for the conversion of one enantiomer into the other. Three possible geared motions, exemplified by their transition

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states 2, 3 and 4 may be considered. The activation energies may be read off from *Figure 8*, and it is clear that the last mechanism is favoured. The calculated activation energy is very small, ~ 1 kcal/mole.

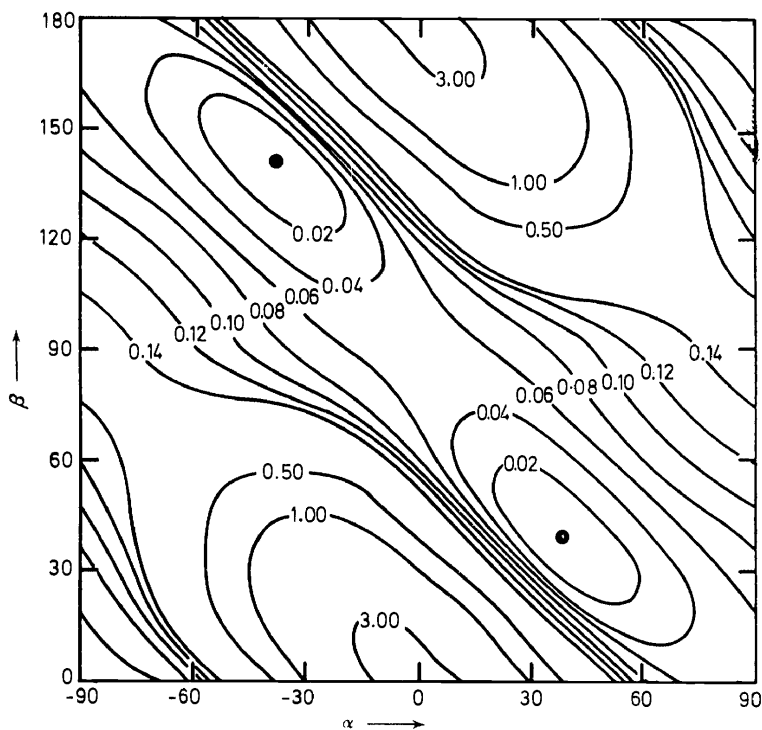


Figure 8. Contour diagram of the extended Hückel potential energy surface for the ground state of benzophenone. The signs of α and β are defined relative to the sense of rotation shown in structure 1. α and β are equal to zero for the planar conformation. The energy contours are in electron volts relative to the marked minima.

We now turn to a discussion of the excited state. *Figure 9* illustrates the extended Hückel surface for the (n, π^*) excited configuration of benzophenone. The angles are defined analogously to *Figure 8*, but the energy

contours are spaced at greater energy intervals. The only minima in this surface are once again the conrotatory ones for $\alpha = \beta = 32^\circ$ and $\alpha = -32^\circ$, $\beta = 148^\circ$. Loci such as $\alpha = 0^\circ$, $\beta = 90^\circ$ remain saddle points. New saddle points occur in the disrotatory regions, e.g. at $\alpha = -57^\circ$, $\beta = 57^\circ$ and $\alpha = 57^\circ$, $\beta = 123^\circ$.

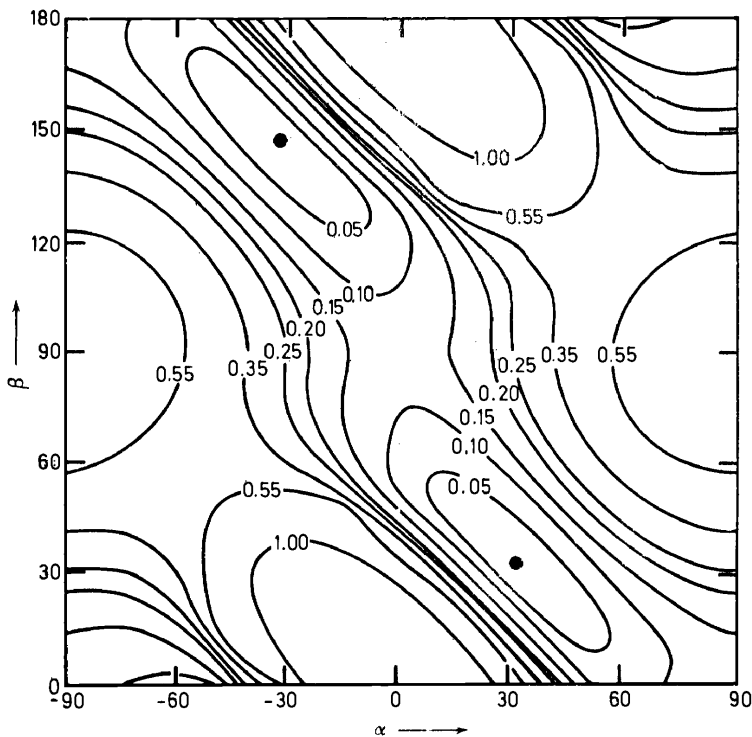


Figure 9. Contour diagram of the extended Hückel potential energy surface for the (n, π^*) excited configuration of benzophenone. See caption of Figure 8 for definition of angles.

The preference of the excited (n, π^*) configuration for a more nearly planar geometry is significant. The results were anticipated from the examination of the interaction diagram in Figure 10. On the left side of the diagram are the benzene π orbitals, taken twice. On the right side are carbonyl π and π^* orbitals. As a consequence of the greater electronegativity of the oxygen atom the centre of energy of the carbonyl orbitals is lower than that of the benzene orbitals. The molecular orbitals may be classified as symmetric, S , or antisymmetric, A , with respect to the molecular C_2 axis. The molecular orbitals are then allowed to interact; minimum interaction would correspond to $\alpha = \beta = 90^\circ$, maximum π -electron interaction would occur at $\alpha = \beta = 0^\circ$. The principal interaction is that of the carbonyl π^* with an unoccupied benzene orbital of the same symmetry. In the resulting stabilized MO, which is principally carbonyl π^* , the benzene π^* MO is mixed in a bonding

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way. Population of this MO in the (n, π^*) excited state results in both an increase in $C-C_1$ and $C-C_1'$ bond order and a greater tendency to planarity. The relative depths of ground- and excited-state minima are explained in the same manner.

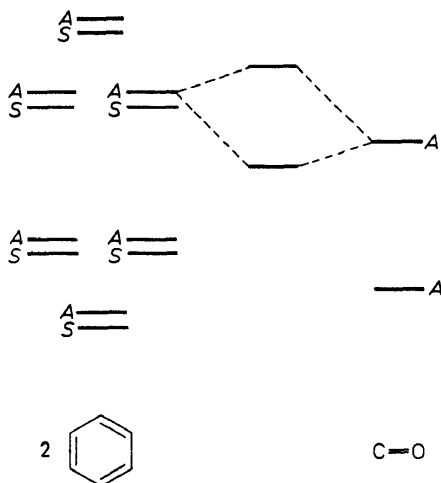
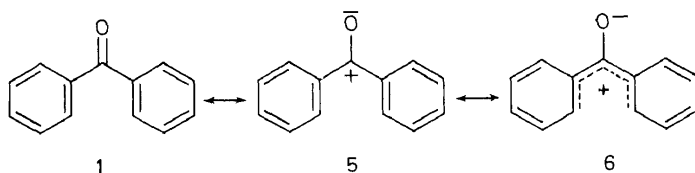


Figure 10. The interaction of the π levels of two phenyl groups with a carbonyl group, as in benzophenone. Only the most significant interaction is shown.

The preceding argument may also be used to account for the stabilization of the disrotatory region as manifested by the removal of the ground-state saddle point at $\alpha = -90^\circ, \beta = 90^\circ$ to $\alpha = -57^\circ, \beta = 57^\circ$. However, in the excited state, the disrotatory region may benefit from another electronic interaction, arising from the proximity of the two benzene rings. The polar valence bond structures 5 and 6 no doubt contribute to the best description of benzophenone. Pentadienyl cations, such as may be seen in part of structure 6, are expected theoretically³² and known experimentally³³ to undergo electrocyclic ring closure to cyclopentenyl cations in a conrotatory manner in the ground state and in a disrotatory manner in the excited state. The stabilizing interaction here is from the overlap of the C_2 and C_2' $2p$ orbitals.



The singlet and triplet (n, π^*) states of formaldehyde¹⁰ are pyramidal. We therefore studied the feasibility of the similar distortion in benzophenone excited states. CNDO/2 results for the formaldehyde excited-state geometry have been presented by Kroto and Santry³⁴. The calculated barrier to inversion is small. EH calculations predict an out-of-plane angle of 20°

and an inversion barrier of 0.0034 eV. The singlet state has in fact been analysed to have the oxygen out of the plane of the remaining atoms by 20° and to possess an inversion barrier of $\sim 650 \text{ cm}^{-1}$ or 0.080 eV^{10} . Thus both computational methods give much too small inversion barriers, though they confirm non-planarity.

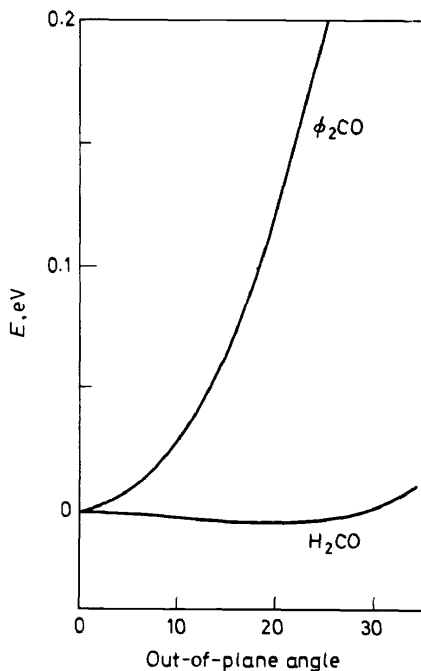


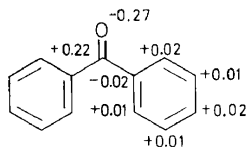
Figure 11. Comparison of calculated out-of-plane bending energy curves of formaldehyde and benzophenone. Both molecules are referred to the same energy zero for a planar geometry. The bending angle is defined in the plane perpendicular to the XCX plane and containing the bisector of the XCX angle. The bending angle is then the angle in the above defined plane by which the oxygen is out of planarity.

For the equilibrium conformation of the excited configuration of benzophenone ($\alpha = \beta = 32^\circ$) we studied a motion of the carbonyl oxygen out of its local molecular plane. The resulting potential energy curve (EH) is compared with that of formaldehyde in Figure 11. The planar conformation remains stable. However, in view of the fact that the EH method severely underestimates the barrier to inversion in formaldehyde, the only reliable conclusion that may be drawn is that the out-of-plane angle in benzophenone (if non-zero at all) is less than it is in formaldehyde.

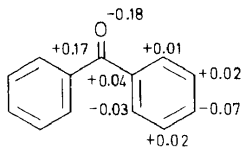
It should be noted from the potential surface of Figure 9 that in the excited state the same mechanism for interconversion of enantiomeric geometries is predicted as for the ground state. The activation energy is slightly higher.

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Our calculations also yielded the ground and excited configuration charge distributions for benzophenone. We consider the CNDO charge distributions more reliable and show below the carbon and oxygen charges computed by this method for a conrotatory geometry with $\alpha = \beta = 35^\circ$.



'ground state charge distribution'



'excited state charge distribution'

The charge redistribution in the excited state is not very great. This is the consequence of an n orbital which is not localized at oxygen, but significantly delocalized throughout the molecule. The absence of charge redistribution of a magnitude consistent with the classical picture of a fully localized oxygen lone pair is supported by recent measurements of the dipole moments of benzophenone excited states³⁵.

THE ISOCYANIDE-CYANIDE REARRANGEMENT

One of the possible uses of an excited state geometry determination is to provide a mechanism for a photochemical reaction. Thus the fact that we strongly suspect that the excited singlet and triplet of ethylene are twisted by 90° away from planarity immediately provides a mechanism for photochemical *cis-trans* isomerization. Occasionally such reasoning can be dangerous, and I would like to conclude by illustrating this point by one of

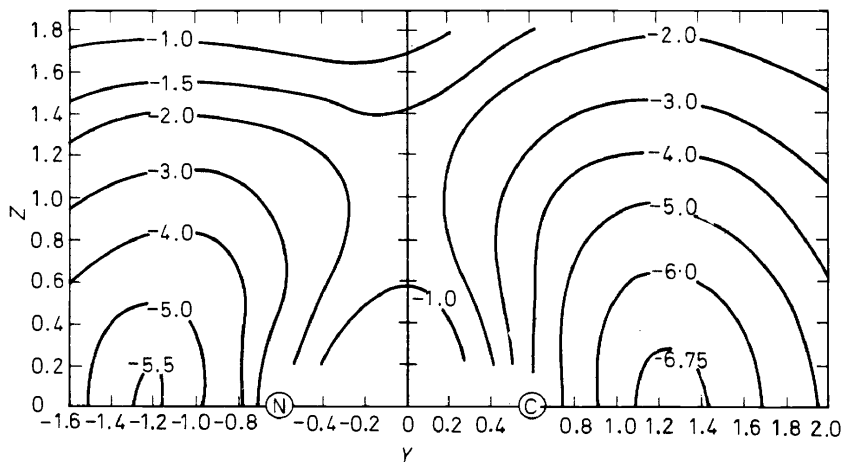
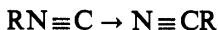


Figure 12. Energy contours (in electron volts) for the motion of a hydrogen near a C—N framework with fixed C—N distance of 1.20 Å. The axes are Cartesian coordinates in Å for the hydrogen. The energy surface has cylindrical symmetry around the C—N axis. Energies are separated H^+ and CN^- .

our calculated potential surfaces, that for the isocyanide-cyanide rearrangement³⁶. This reaction



is a well known thermal³⁷ and photochemical³⁸ process. *Figure 12* shows our computed potential surface for the model ground state reaction with $\text{R} = \text{H}$ moving about a fixed CN group. There are two minima for linear HCN and linear HNC , as expected.

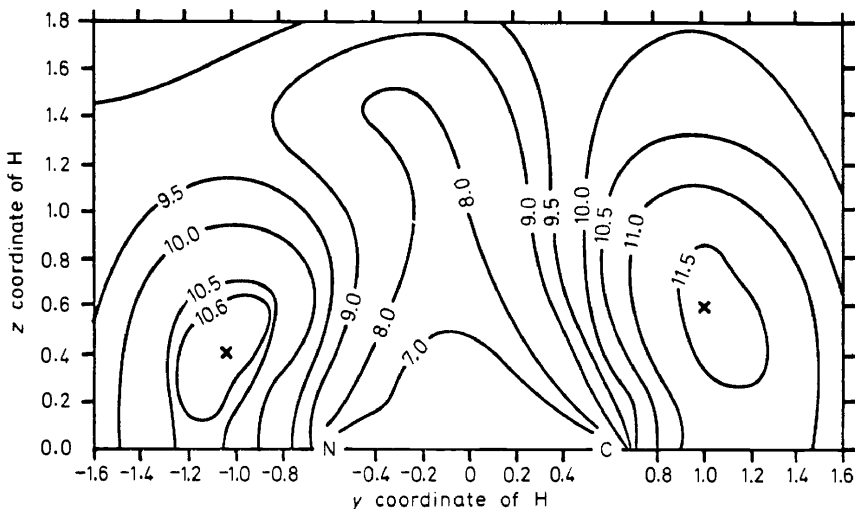


Figure 13. Calculated potential surface for the A' ($6a' \rightarrow 7a'$) excited state of HCN and HNC . The convention is that of *Figure 12* except that the contour labels are binding energies relative to an arbitrary energy zero.

The excited state surface for the A' excited state is next shown, *Figure 13*. This state of HCN is bent^{1,6}, and one would also anticipate a bent A' excited state of HNC . Our surface shows these tendencies clearly. The great temptation is to say that since a lesser relative motion of H and CN is required in the excited state to pass from a bent HCN to a bent HNC that the photochemical isomerization should be facilitated. The intervening contours show that this is not so.

ACKNOWLEDGEMENT

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