

The Electronic Spectra of Thioamides and Thiohydrazides

Part VIII.* Five- and Six-membered Thiolactams and Thioimides

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The ultraviolet spectra of some thiolactams, thioimides, and dithioimides have been recorded in polar and non-polar medium. The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies have been calculated with a LCAO-MO method and found to be in reasonable agreement with experimental results. The bathochromic shifts on going from five-membered to six-membered ring compounds are shown to be in agreement with theory if a departure from coplanarity of the substituents around the nitrogen atoms in the five-membered rings can be assumed. Such a departure is also indicated by the NMR spectra of the N-methyl derivatives.

Differences in physical properties between five-membered and six-membered cyclic amides and thioamides have been reported in several instances. Dipole moments have been recorded by Lee and Kumler.¹⁻³ The moments of five-membered imides are about one Debye unit lower than those of the six-membered analogues, which has been satisfactorily accounted for by differences in bond angles and ring flexibility. The moments of five- and six-membered lactams fall in the same order, but the differences are close to the experimental error. It has long been known (*cf.* Ref. 4) that the infrared stretching frequency of the carbonyl group in cyclic compounds decreases when the ring size increases up to six members, when the frequency is nearly the same as for saturated acyclic carbonyl compounds. This effect of ring size has been ascribed to changes in hybridization, the exocyclic double bond acquiring a higher s character and thus a higher force constant when the ring angles are diminished below 120° .^{5,6} The ultraviolet spectra are also affected by the ring size. Turner⁷ has found that succinimide and substituted succinimides have a $\pi \rightarrow \pi^*$ transition band at 191 nm, whereas the corresponding band for glutarimide falls at 198 nm. Flitsch⁸ has recorded ultraviolet spectra for five-, six-, and seven-membered N-methylimides, and he observed bathochromic shifts of both $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands with increasing ring size. Lee and Kumler² have

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recorded $\pi \rightarrow \pi^*$ bands for some thiolactams and found an increase from 262 to 278 nm when the ring increased from five to seven members. Potter⁹ has observed similar bathochromic shifts of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands when going from rhodanines to "propiorhodanines", i.e. tetrahydro-1,3-thiazin-4-one-2-thiones. Turner⁷ explained the bathochromic shift from succinimide to glutarimide by a steric effect, causing a departure from coplanarity of the imide chromophore in glutarimide.

This investigation has been undertaken to study the effect of ring size on the ultraviolet spectra of cyclic thioamides. For this purpose 2-thiopyrrolidone, 2-thiopiperidone, thiosuccinimide, dithiosuccinimide, thioglutarimide, dithioglutarimide, and all the corresponding N-methyl derivatives have been prepared. The spectra of thio- and dithiosuccinimides have previously been described by Cremlyn,¹⁰ but since his thiosuccinimides seem to have been contaminated by the dithio analogues, the recorded spectra are considerably in error. More recently Walter and Randau¹¹ have prepared the dithiosuccinimides in high purity, but they do not describe their electronic spectra.

The ultraviolet spectra of these compounds are recorded in Table 1 together with those of some related acyclic compounds.

It appears that the six-membered thiolactams and monothiomides have spectra rather similar to those of the corresponding acyclic analogues, whereas both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands of the five-membered compounds are shifted to shorter wave lengths. Potter⁹ has observed the same effect for the N-acyldithiocarbamate system, and this seems to make doubtful the explanation of Turner⁷ in terms of departure from coplanarity in the six-membered imides. Models show that the acyclic like the six-membered imides and thioimides can attain conformations where the delocalized systems have the planarity required for a maximal π electron interaction. It seems more profitable to discuss the effect of ring size on the ultraviolet spectra in terms of hybridization changes. The discussion will be based on calculation by the modified Hückel approximation, which is described in some detail in Ref. 14. It is obvious, however, that all effects of changing the ring size, such as changes in electron repulsion due to changed interatomic distances, cannot be accounted for in the Hückel approximation.

Hybridization changes due to diminishing bond angles motivate changes in Hückel parameters for different reasons. If the chromophoric system remains planar, the change will result in a redistribution of s and p character between the hybrid σ bonds. This redistribution gives a higher s character to the exocyclic double bond, thus accounting for the higher infrared stretching frequency.^{5,6} On the other hand, the increased p character in the ring bonds, reflected in decreased stretching frequencies,* should result in somewhat longer bonds with inferior overlap as a consequence. However, a survey of bond lengths of similar five- and six-membered compounds shows no consistent trend in this direction, and the effect, if any, can be expected to be small. As a first approximation, the redistribution of s and p character among the σ

* However, Colthup¹⁵ has been able to reproduce the effect of ring size on the vibration frequencies of both endo- and exocyclic double bonds by mechanical models without changing the force constants.

Table 1. Ultraviolet spectra of cyclic thioamides.

Compound	Solvent	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$		λ_{\max} nm	ϵ	Ref.
		λ_{\max} nm	ϵ	λ_{\max} nm	ϵ			
Thiopyrrolidone	Heptane + 20 % CH_2Cl_2 + 0.1 % CH_2Cl_2	335	47	270	14 800			
	Ethanol	319	66	266.5	14 400			
N-Methylthio- pyrrolidone	Heptane + 10 % CH_2Cl_2 + 0.05 % CH_2Cl_2	347.5	36	269	14 800			
	Ethanol	319.5	68	265	15 200			
Thiopiperidone	Heptane + 10 % CH_2Cl_2 + 0.05 % CH_2Cl_2	340	54	281	12 000			
	Ethanol	—	—	276	12 800			
N-Methylthio- piperidone	Heptane	361.5	32	275.5	13 800			
	Ethanol	320S	74	272	16 800			
N-Methyl- thioacetamide	Isooctane	360	26	264	11 000			12
	Ethanol	321	49	261	13 500			
N,N-Dimethyl- thioacetamide	Isooctane	365	41	272	15 500			12
	Ethanol	330	56	269	15 100			
Thiosuccinimide	Heptane + 25 % CH_2Cl_2 + 0.1 % CH_2Cl_2	398.5	20	265	18 000			
	Ethanol	392	21	269	20 900			
N-Methyl- thiosuccinimide	Heptane	394.5	33	269	23 000			
	Ethanol	386	30	271	22 400			
Thioglutarimide	Heptane + 20 % CH_2Cl_2 + 0.05 % CH_2Cl_2	417	27	276	17 800			
	Ethanol	413.5	25	279	20 300			
Acetyl- thioacetamide	Heptane	425	38	278.5	23 000			13
	Ethanol	429	32	282	20 000			
N-Methyl- thioglutarimide	Heptane + 10 % CH_2Cl_2 + 0.025 % CH_2Cl_2	424	32	278	20 300			
	Ethanol	417	30	279	20 700			
Dithiosuccinimide	Heptane + 12.5 % CH_2Cl_2 + 0.06 % CH_2Cl_2	406	158	315	35 400	234	4900	
	Ethanol	402	135	321	37 300	236.5	3600	
N-Methyl- dithiosuccinimide	Heptane	410	183	324	42 100	236	3900	
	Ethanol	395	162	320	42 200	238	4200	
Dithioglutarimide	Heptane + 10 % CH_2Cl_2 + 2 % CH_2Cl_2 + 0.05 % CH_2Cl_2	475.5	72	330.5	29 800	237	7000	
	Ethanol	427	175	336	32 200	237	6900	
N-Methyl- dithioglutarimide	Heptane + 10 % CH_2Cl_2 2 % CH_2Cl_2	500S	40					
		443	270					
		423	250					
	0.05 % CH_2Cl_2 Ethanol	435	250	333	35 000	234	4500	
		421	254	333.5	33 100	235	4200	

bonds should not affect the core potential for the π electrons in the unhybridized p orbital, and no change in Coulomb integral should be necessary.

It is also possible that one of the atoms in the delocalized system changes to a non-planar arrangement when the bond angles are diminished. This will necessitate more pronounced changes in Hückel parameters. The orbital, which participates in the delocalized system, will obtain some s character, and therefore the core attraction for the π electrons will increase, which must be reflected in the Coulomb integral. This orbital will also have its lobes directed somewhat away from the corresponding orbitals on the neighbouring atoms, with inferior overlap as a result. This can be accounted for by lowering the absolute values of the corresponding resonance integrals. It seems less probable that one of the carbonyl or thiocarbonyl carbon atoms should attain a non-planar arrangement, since they have been found to be planar in molecules such as ethylene carbonate,¹⁶ where the remainder of the ring is known to be puckered, ethylenethiourea,¹⁷ and succinimide.¹⁸ Instead, it can be assumed that the nitrogen atom changes from a planar to a non-planar arrangement. Such an arrangement has been found by Ehrlich¹⁹ for pyrazole, where the nitrogen-hydrogen bonds deviate 14° and 16° from the plane of the ring in two independent structures in the unit cell. Mason¹⁸ has also found by X-ray crystallography that the N-hydrogen atom in succinimide is not in the ring plane. Lumbroso *et al.*²⁰ reached the same conclusion from an analysis of the dipole moments of succinimide and some of its derivatives.

Rather more conclusive evidence can be obtained from the NMR spectra of N-methyl derivatives of five- and six-membered cyclic thioamides. It is well known²¹ that the magnetic anisotropy of the carbonyl group in amides like dimethylformamide and dimethylacetamide causes a shift to higher field of the resonance signal of the protons on the methyl group, which is closest to the carbonyl group. A similar effect though in the opposite direction has been found for thioamides.²² Pople²³ has given a theoretical treatment of the anisotropy in double bonds, and he has shown that the shielding effect is operative only in the nuclear plane of the carbonyl group, whereas protons above or below this plane should show small low field shifts. The NMR spectra of N-methylthiopyrrolidone, N-methylthiopiperidone, N-methyldithiosuccinimide, and N-methyldithioglutarimide (Fig. 1) are in good agreement with this theory, provided that the N-methyl group in the five-membered compounds deviates considerably more from the plane of the thiocarbonyl groups than in the six-membered compounds, since the resonances of the former appear at higher fields. Another explanation for the observed difference could be the somewhat greater distance between the methyl and thiocarbonyl groups in a *planar* five-membered thioimide than in the six-membered compound. This is far less likely, however, since the chemical shift between the two methyl groups in N,N-dimethylthioamides, where the distance between the remote methyl group and the thiocarbonyl group is far greater, is of the same order of magnitude as the difference between the methyl signals in five- and six-membered thioimides. It is also obvious that the methyl resonance appears at higher fields in the thiolactams than in the dithioimides, where the methyl group is exposed to the anisotropy of two thiocarbonyl groups. It is of interest to note that all proton resonances except the methyl signal

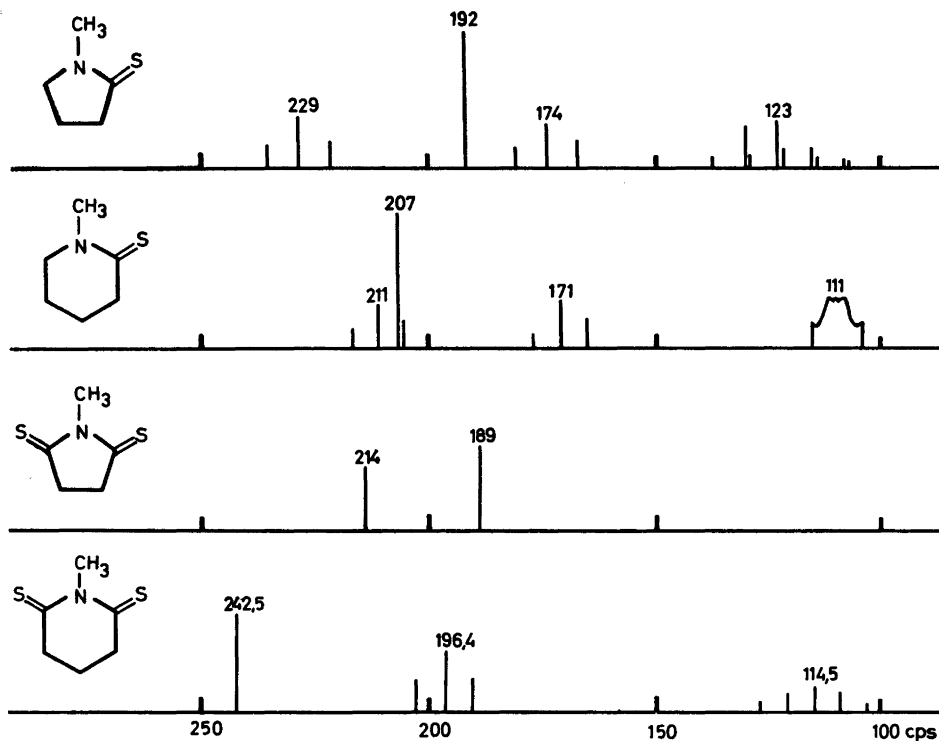
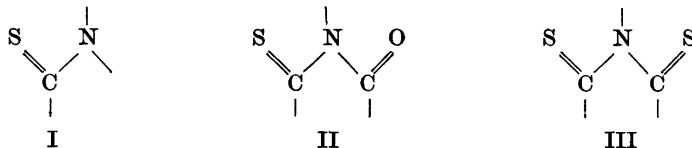


Fig. 1. NMR spectra in carbon tetrachloride (internal standard TMS).

in N-methylthiopyrrolidone fall at lower field than in N-methylthiopiperidone. This is according to expectations, if the C—H bonds in five-membered rings shall have a higher s character than in six-membered rings.

LCAO calculations have been performed for the systems (I—III), and the parameters have been changed to account for the change in hybridization discussed above. Different sets of parameters for treatment of molecules



containing heteroatoms were discussed in Ref. 14. Those designed as Set 1 have been used here as starting values. The system (II) has been treated previously,¹³ but the parameters then used for the carbonyl group were somewhat too high for a comparison with system (III). The effect of changing the nitrogen atom from an sp^2 towards an sp^3 state has been accounted for by

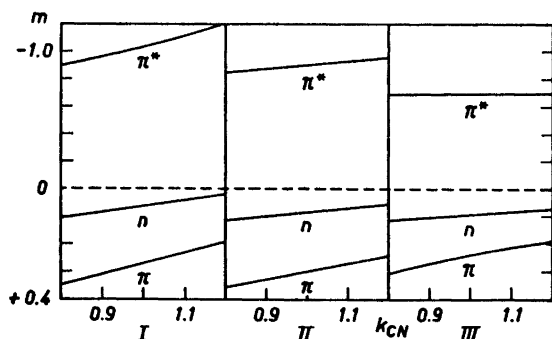


Fig. 2. HOMO(π), NBO(n) and LFMO(π^*) energies as function of k_{CN} with $h_N = 1.5$. Increase of h_N gives a slight parallel displacement of all curves towards lower energies.

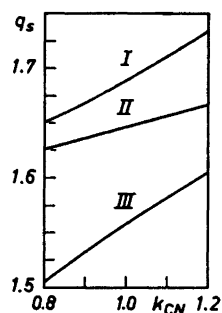


Fig. 3. π Electron density on the sulphur atom as function of k_{CN} with $h_N = 1.5$. Increase of h_N gives a parallel displacement of all curves towards lower charges.

giving h_N^* the values 1.7 and 1.9 and k_{CN}^* values from 1.2 to 0.8. The effects of these changes on the highest bonding and lowest antibonding π orbital and on the nonbonding orbital are shown in Fig. 2. It appears that the lowering of k_{CN} results in an almost linear decrease of all the orbital energies concerned, and that increasing the h_N values has the same effect. For the systems (II) and (III), increasing sp^3 character of the nitrogen atom causes a progressively more rapid decrease in the series π^* , n , π , which gives increased $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies, in agreement with the experimental results. For system (I), however, the rate of decrease with increasing sp^3 character increases in the series n , π^* , π , and the difference in rate of decrease between π^* and π is small. In this case we find increased energy for the $\pi \rightarrow \pi^*$ transition, in agreement with experiments, but decreased energy for the $n \rightarrow \pi^*$ transition, in contradiction to the experiments. However, Murrell²⁴ has pointed out that the electron distribution in the $n \rightarrow \pi^*$ state is of importance for the energy of this transition, since the π electrons on the atom with the non-bonding orbital will tend to stabilize the "hole" left by the excited non-bonding electron. It appears (Fig. 3) that increasing sp^3 character of the nitrogen atom will lead to decreasing charge on the sulphur atom in the $n \rightarrow \pi^*$ state in all the systems investigated. It is difficult to evaluate the magnitude of this effect in the present approximation, but it is obvious that it will increase the $n \rightarrow \pi^*$ transition energy, in agreement with the experimental results.

The transition energies calculated for the sp^2 hybridized nitrogen atom case fall in the same order as the experimental wavenumbers for both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions (Table 1 and Table 2). The shape and intensity of the $n \rightarrow \pi^*$ bands of the dithio compounds are rather different from those of the thioamides previously investigated. Several maxima occur (Fig. 4), which may be ascribed to vibrational fine structure. The intensity of the bands is also considerably higher than of normal $n \rightarrow \pi^*$ bands. Increased extinction

* $\alpha_N = \alpha_C + h_N \beta_{CC}$, $\beta_{CN} = k_{CN} \beta_{CC}$.

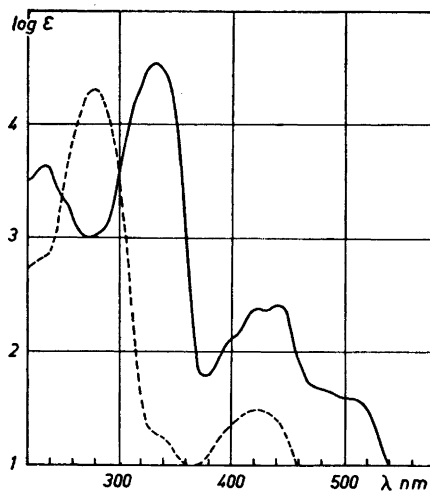


Fig. 4. Ultraviolet spectra of N-methylthioglutarimide (— — —) and N-methyldithioglutarimide (————) in heptane-methylene chloride (see Table 1 for solvent compositions)

coefficients of $n \rightarrow \pi^*$ bands have previously been noticed when a steric effect could be expected to cause a twist of the conjugated system, leading to overlap between n and π^* orbitals,¹³ but this effect can hardly be responsible here. The problem will be further investigated in connection with work on other cyclic thioamides.

EXPERIMENTAL

The cyclic thioamides and thioimides used in this work were prepared by refluxing the corresponding oxygen compounds with phosphorus pentasulphide in toluene or xylene. The products were purified by distillation or recrystallization, and, in the case of the thioimides, by chromatography on silica. The purity of the liquid compounds was checked by gas chromatography.

2-Thiopyrrolidone was prepared according to Tafel and Lawaczek²⁵ and obtained as colourless rods, m.p. 115–116° (Lit.²⁵ 116°).

N-Methyl-2-thiopyrrolidone has previously been described by Eilingsfeld *et al.*²⁶ It was obtained in 55% yield as a colourless liquid, b.p.₁₇ 146–147°, n_D^{20} 1.5821. (Found: C 51.6; H 7.87; N 12.1; S 27.9. C_5H_7NS (115.21) requires C 52.1; H 7.89; N 12.2; S 27.8).

Table 2. m_j in $\epsilon_j = \alpha + m_j\beta$ is tabulated.

	I	II	III
Lowest free molecular orbital (LFMO)	-1.209	-0.937	-0.706
Non-bonding orbital (NBO)	+0.029	+0.111	+0.143
Highest occupied molecular orbital (HOMO)	+0.388	+0.496	+0.368
$\Delta E_{n \rightarrow \pi^*}$	1.238	1.048	0.849
$\Delta E_{\pi \rightarrow \pi^*}$	1.597	1.433	1.074

Monothiosuccinimide and dithiosuccinimide. Succinimide (10 g) and phosphorus pentasulphide (22 g) were refluxed in xylene (100 ml) for 2.5 h. The filtered solution was evaporated, and the residue was subjected to vacuum sublimation. The solid sublimate (3.0 g) was shown by thin layer chromatography to contain two thiomides, and it was subjected to chromatography on silica. Chloroform eluted first dithiosuccinimide and then monothiosuccinimide as well separated yellow bands. The monothio compound (1.3 g, 11 % yield) crystallized from carbon tetrachloride as pale yellow prisms, m.p. 112–114° (Lit.¹⁰ 100–104°, Lit.¹¹ 109–112°). (Found: C 42.0; H 3.74; N 11.9; S 27.7. C_4H_5NOS (115.16) requires C 41.7; H 4.38; N 12.2; S 27.8).

The dithiosuccinimide (0.9 g, 7 % yield) crystallized from carbon tetrachloride as bright yellow prisms, m.p. 106–108° (Lit.¹⁰ 84–87°, Lit.¹¹ 108–109°). (Found: C 36.1; H 4.18; N 10.4; S 48.7. $C_4H_5NS_2$ (131.22) requires C 36.6; H 3.85; N 10.7; S 48.9).

N-Methylthiosuccinimide and N-methyldithiosuccinimide were prepared as the analogues in the preceding experiment. The monothio compound (10 % yield) crystallized from carbon tetrachloride as pale yellow needles, m.p. 59–60° (Lit.¹⁰ 52–54°). (Found: C 46.4; H 5.27; N 10.9; S 24.8. C_5H_7NOS (129.19) requires C 46.5; H 5.46; N 10.8; S 24.8). The dithio compound (20 % yield) crystallized from carbon tetrachloride as bright yellow rods, m.p. 112–113° (Lit.¹¹ 107°). (Found: C 41.1; H 5.43; N 9.69; S 44.1. $C_5H_7NS_2$ (145.24) requires C 41.3; H 4.86; N 9.64; S 44.1).

2-Thiopiperidone was prepared from 2-piperidone in the same way as the pyrrolidone analogue. The product (22 % yield) crystallized from cyclohexane as colourless rods, m.p. 95.5–96° (Lit.²⁷ 95–96°). (Found: C 51.9; H 7.68; N 12.5; S 28.0. C_6H_9NS (115.22) requires C 52.9; H 7.89; N 12.2; S 27.8).

N-Methyl-2-thiopiperidone. N-Methyl-2-piperidone (10.0 g, prepared by methylation of 2-piperidone with sodium hydride and methyl iodide in benzene) was refluxed with phosphorus pentasulphide (10 g) in benzene (200 ml) for 3 h. The filtered solution was evaporated, and the residue was distilled in vacuum. The main fraction (4.1 g, 37 % yield) b.p.₁₇ 155–158°, crystallized on standing, m.p. 36–39°. (Found: C 56.2; H 8.89; N 10.8; S 24.5. $C_6H_{11}NS$ (129.23) requires C 55.8; H 8.58; N 10.8; S 24.8).

Monothioglutaramide and dithioglutaramide. Glutarimide (15 g) and phosphorus pentasulphide (15 g) were refluxed in xylene (400 ml) for 1 h. The filtered solution was evaporated, and the residue was subjected to vacuum sublimation. The solid sublimate (9.4 g) was shown by thin layer chromatography to consist of a mixture of mono- and dithioglutaramide. Separation was effected by chromatography on silica. Chloroform eluted first dithioglutaramide and then monothioglutaramide. The monothio compound (2.9 g, 12 % yield) crystallized from benzene as pale yellow prisms, m.p. 118–119°. (Found: C 46.7; H 5.37; N 10.8; S 24.9. C_6H_7NOS (129.20) requires C 46.5; H 5.47; N 10.8; S 24.8).

The dithio compound (4.4 g, 23 % yield) crystallized from benzene as bright yellow rods, m.p. 105–106°. (Found: C 41.1; H 4.88; N 9.61; S 44.6. $C_6H_7NS_2$ requires C 41.3; H 4.87; N 9.64; S 44.2).

N-Methylmonothioglutaramide. N-Methylglutarimide (10.3 g, prepared by reaction between glutaric anhydride and methylamine and cyclization of the N-methylglutaramidic acid with acetic anhydride) and phosphorus pentasulphide (9.0 g) were refluxed in toluene (200 ml) for 2 h. After filtration and evaporation the reaction mixture was subjected to chromatography on silica. Chloroform eluted first the dithio compound (0.45 g) as a red liquid, and then the monothio compound (3.7 g, 32 % yield) as a pale yellow liquid. Gas chromatography showed a minor impurity, which was removed by repeated recrystallizations from light petroleum (b.p. 40–60°) at –30°, followed by vacuum distillation (b.p.₁₂ 137°). (Found: C 49.9; H 6.40; N 9.70; S 22.2. C_6H_9NOS (143.20) requires C 49.9; H 6.40; N 9.78; S 22.4).

N-Methyldithioglutaramide. N-Methylglutarimide (6.9 g) and phosphorus pentasulphide (5 g) were refluxed in xylene (150 ml) for 1 h. After filtration and evaporation the dithio compound was isolated by chromatography as in the preceding experiment. The product (2.0 g, 23 % yield) was purified by vacuum distillation (b.p.₁₁ 146°). On cooling, the distillate solidified and then showed m.p. 25–26°. (Found: C 45.4; H 5.86; N 8.89; S 40.4). $C_6H_9NS_2$ (159.26) requires C 45.2; H 5.70; N 8.79; S 40.3).

The recording of the ultraviolet spectra and the numerical calculations were performed as in the previous parts of this series. The NMR spectra were recorded with a Varian A-60 NMR spectrometer.

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