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The Electronic Spectra of Thioamides and Thiohydrazides

Part VI *. Conjugation and Steric Effects in Thiooxamide Derivatives

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The ultraviolet absorption spectra of cyanothioformamide, ethyl thiooxamate, monothiooxamide, dithiooxamide and most of their N-methyl derivatives have been recorded in ethanol and in hydroxyl-free solvents. The $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands appear at longer wavelengths than for simple thioamides, in harmony with the results of simple LCAO-MO calculations. Compounds with dimethylamino groups show the absorption bands at considerably shorter wavelengths, which is ascribed to a steric inhibition of resonance. The relations between the rotations around the carbon-carbon bond and the transition energies have been calculated and used in connection with experimental transition energies to evaluate angles of rotation. These rotations have been correlated with values obtained from geometrical models. The relations between steric factors and oscillator strengths are discussed, as is also the influence of solvation on the band positions.

In the previous parts of this series,[1–5] the ultraviolet absorption spectra of a number of conjugated thioamides have been recorded and correlated with transition energies calculated by a simple LCAO—MO method. It has been found that conjugation in general leads to bathochromic shifts of both the $n\rightarrow\pi^*$ and the first $\pi\rightarrow\pi^*$ bands, and that in several cases a band tentatively ascribed to a $n\rightarrow\sigma^*$ transition is relatively unaffected. Both spectra and calculated bond orders and π electron distributions indicate that the thioamide group is only moderately perturbed by the conjugation. Apparently the resonance stabilization of this group is quite strong, a conclusion which is supported by the tendency of heterocyclic thioamides to prevail in the thion form, even in cases where the tautomeric iminothiol form can profit of a complete aromatic π electron system.[6,7]

In Ref.[1] the hypsochromic shifts on the successive introduction of methyl groups on the nitrogen atom in thiobenzamide were tentatively explained as the result of a steric effect, which turned the thioamide group out of the

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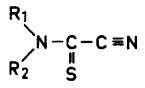
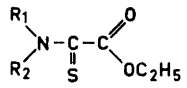
plane of the benzene ring. It has been regarded desirable to test this hypothesis further, and the four types of thiooxamide derivatives (I—IV) were thought to constitute a suitable material, in which the cyanothioformamides (I) should be insensitive to the steric effect.

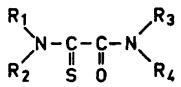


I

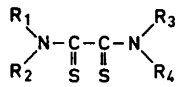


II

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$, $R_2 = H$
c, $R_1 = R_2 = CH_3$



III

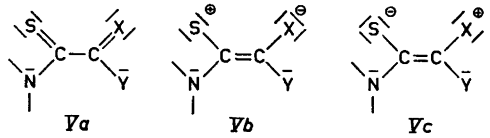


IV

a, $R_1 = R_2 = R_3 = R_4 = H$
b, $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$
c, $R_3 = CH_3$, $R_1 = R_2 = R_4 = H$
d, $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$
e, $R_1 = R_3 = CH_3$, $R_2 = R_4 = H$
f, $R_1 = R_2 = H$, $R_3 = R_4 = CH_3$
g, $R_1 = R_2 = R_3 = CH_3$, $R_4 = H$
h, $R_1 = R_3 = R_4 = CH_3$, $R_2 = H$
i, $R_1 = R_2 = R_3 = R_4 = CH_3$

a, $R_1 = R_2 = R_3 = R_4 = H$
b, $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$
c, $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$
d, $R_1 = R_3 = CH_3$, $R_2 = R_4 = H$
e, $R_1 = R_2 = R_3 = R_4 = CH_3$

An inspection of the colour of these compounds indicates a considerable conjugation over the carbon-carbon bond, since (IVa) is red, (IVb) and (IVd) are orange, and (Ia), (Ic), (IIa), and (IIIa) are deep yellow, whereas simple thioamides are colourless. Furthermore, methyl groups have a profound effect in the systems (II), (III) and (IV), where increasing methyl substitution leads to a gradual disappearance of the colour. The results of an X-ray crystallographic examination of the structure of dithiooxamide [8] seem to contradict a strong conjugation, since the length of the carbon-carbon bond was found to be 1.53—1.54 Å. A possible explanation is that intermolecular forces in the crystal cause a stretching of the bond, since the length of a bond between two sp^2 hybridized carbon atoms should be 1.51 ± 0.01 Å [9] in the absence



Va *Vb* *Vc*

of conjugation. Simple resonance theory predicts some double bond character for the central bond in (V). Furthermore, the corresponding bond length in oxamide has been determined to 1.49 Å,[10] and in glyoxal and biacetyl to 1.47 Å.[11] The latter values are of particular interest since they have been

determined in the gas phase. On the other hand, in α- and β-oxalic acids, with strong intermolecular forces, the even more extreme values of 1.56 and 1.59 Å are found.[12,13]

The conformation of the thiooxamide derivatives is also of interest for the interpretation of their spectra. The systems (II), (III), and (IV) can assume a planar conformation either in the s-*cis* or the s-*trans* form. In the crystalline state dithiooxamide,[8] oxamide,[10] oxalic acid,[12,13] and dimethyl oxalate[14] are centrosymmetric, *i.e.* in the s-*trans* form, and glyoxal and biacetyl have been shown by electron diffraction to be planar and in the s-*trans* form in the gas phase.[11] Furthermore, Scott and Wagner[15] and Milligan *et al.*[16] have shown by examination of the infrared spectra that symmetrical derivatives of oxamide and dithiooxamide have the s-*trans* conformation. These results mostly originate from solid state spectra, but considerations of dipole-dipole interaction would tend to favour the *trans* conformation also in solution. For dithiooxamide, molecular models indicate a noticeable interference between the sulphur atoms in the *cis* form.

Ultraviolet spectra. With the exception of three cases, where low solubility precluded the use of a hydroxyl-free solvent, the spectra have been recorded in absolute ethanol and in a hydroxyl-free solvent (heptane, methylene chloride or a mixture of these). The results are recorded in Table 1. An inspection of the table reveals that all spectra contain one weak band at relatively long wavelength, in many cases extending into the visible region and then responsible for the colour, and at least one strong band at shorter wavelength. It can safely be assumed that the weak band is due to a $n \rightarrow \pi^*$, and the strong band to a $\pi \rightarrow \pi^*$ transition. It appears that conjugation of two thioamide groups, as in dithiooxamide, causes greater bathochromic shifts of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands than conjugation of a thioamide group with a nitrile group as in (I), with an ester group as in (II), or with an amide group as in (III).

In the cyanothioformamide series (I) only the parent compound (Ia) and the dimethyl derivative (Ic) are available. The exchange of two hydrogen atoms for methyl groups causes a small hypsochromic shift (about 200 cm^{-1}) of the $n \rightarrow \pi^*$ band and a greater bathochromic shift (about 1600 cm^{-1}) of the $\pi \rightarrow \pi^*$ band. In the thiooxamate series (II) one methyl group causes a moderate hypsochromic shift (about 750 cm^{-1}) of the $n \rightarrow \pi^*$ band and a small bathochromic shift (about 200 cm^{-1}) of the $\pi \rightarrow \pi^*$ band. Two N-methyl groups have a much more striking effect and shift the $n \rightarrow \pi^*$ band about 4500 cm^{-1} and the $\pi \rightarrow \pi^*$ band about 2500 cm^{-1} towards shorter wavelengths. In the monothiooxamide series (III), the effect of methyl substitution depends on wether the substitution occurs on the amide or thioamide nitrogen atom. One methyl group on the amide nitrogen atom has a very small effect, whereas on the thioamide nitrogen atom it causes a blueshift of about 1000 cm^{-1} of the $n \rightarrow \pi^*$ band and a shift of the $\pi \rightarrow \pi^*$ band of about 300 cm^{-1} in the same direction. The effect of one methyl group on each of the nitrogen atoms is about the same as of only one on the thioamide nitrogen atom. Two methyl groups on the same nitrogen atom cause substantial hypsochromic shifts of both bands, but here the effect is smaller (shift of $n \rightarrow \pi^*$ band 3300 *versus* 3500 cm^{-1},or $\pi \rightarrow \pi^*$ band 1300 *versus* 3100 cm^{-1}) when substitution occurs in the thioamide than in the

Table 1.

Compound	Solvent	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$					
		λ_{max} Å	ε	λ_{max} Å	ε	Θ	f	λ_{max} Å	ε
$H_2NCS \cdot CN$ (Ia)	CH_2Cl_2	4380	32	—	—	—	—	—	—
	Heptane with 0.5 % of CH_2Cl_2	—	—	2940	7 400	—	0.181	—	—
	Ethanol	4220	31	3010	8 200	—	—	—	—
$(CH_3)_2NCS \cdot CN$ (Ic)	Heptane	4330	21	3085	9 300	—	0.192	—	—
	Ethanol	4170	23	3120	9 300	—	—	—	—
$H_2NCS \cdot CO_2Et$ (IIa)	Heptane with 10 % of CH_2Cl_2	4540	26	—	—	—	—	—	—
	Heptane with 0.05 % of CH_2Cl	—	—	3010	7 300	0°	0.161	—	—
	Ethanol	3900S[a]	28	2900	7 200	—	—	—	—
$CH_3NHCS \cdot CO_2Et$ (IIb)	Heptane with 2 % of CH_2Cl_2	4390	18	—	—	—	—	—	—
	Heptane with 0.1 % of CH_2Cl_2	—	—	3030	8 100	0°	0.183	—	—
	Ethanol	3820	27	2960	6 700	—	—	—	—
$(CH_3)_2NCS \cdot CO_2Et$ (IIc)	Heptane	3780	55	2820	12 800	65°	0.240	2390	8 500
	Ethanol	3550S	62	2800	11 400	—	—	2380	6 700
$H_2NCS \cdot CONH_2$ (IIIa)	Ethanol	4110	29	3010	6 600	0°	0.156	2290	4 600
$CH_3NHCS \cdot CONH_2$ (IIIb)	CH_2Cl_2	3990	25	3000	7 000	0°	0.149	—	—
	Ethanol	3940	25	2980	7 200	—	—	2230S	4 800
$H_2NCS \cdot CONHCH_3$ (IIIc)	Ethanol	4070	34	3030	6 100	0°	0.152	2400	5 500
$(CH_3)_2NCS \cdot CONH_2$ (IIId)	CH_2Cl_2	3700S	55	—	—	—	—	—	—
	Heptane with 0.5 % of CH_2Cl_2	—	—	2900	9 500	50°	0.229	—	—
	Ethanol	3600S	52	2785	11 800	—	—	2380	5 300
$CH_3NHCS \cdot CONHCH_3$ (IIIe)	Heptane with 10 % of CH_2Cl_2	4000	28	—	—	—	—	—	—
	Heptane with 0.05 % of CHCl	—	—	2975	7 000	10°	0.153	2400	6 400
	Ethanol	3925	33	2980	6 300	—	—	2380	6 100
$H_2NCS \cdot CON(CH_3)_2$ (IIIf)	CH_2Cl_2	3750	42	—	—	—	—	—	—
	Heptane with 0.5 % of CH_2Cl_2	—	—	2780	7 200	58°	0.216	—	—
	Ethanol	3580	43	2750	9 300	—	—	2300S	5 400
$(CH_3)_2NCS \cdot CONHCH_3$ (IIIg)	Heptane with 10 % of CH_2Cl_2	3910	68	—	—	—	—	—	—
	Heptane with 0.05 % of CH_2Cl	—	—	2900	9 000	50°	0.239	—	—
	Ethanol	3620	52	2790	12 800	—	—	2320	5 900

[a] S = Shoulder

Table 1. (cont.)

Compound	Solvent	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$					
		λ_{max}Å	ε	λ_{max}Å	ε	Θ	f	λ_{max}Å	ε
$CH_3NHCS \cdot CON(CH_3)_2$ (IIIh)	Heptane with 50 % of CH_2Cl_2	3690	44	—	—	—	—		—
	Heptane with 0.25 % of CH_2Cl_2	—	—	2760	6 900	55°	0.241	—	—
	Ethanol	3520	43	2710	10 200	—	—	2330	5 800
$(CH_3)_2NCS \cdot CON(CH_3)_2$ (IIIi)	CH_2Cl_2	3590	53	—	—	—	—	—	—
	Heptane with 1 % of CH_2Cl_2	—	—	2810	10 300	66°	0.218	2380S	5 200
	Ethanol	3550	49	2795	11 300	—	—	2350	6 800
$H_2NCS \cdot CSNH_2$ (IVa)	Ethanol	4830	22	3120	11 200	0°	0.271	—	—
$CH_3NHCS \cdot CSNH_2$ (IVb)	Heptane with 10 % of CH_2Cl_2	4860	19	—	—	—	—	—	—
	Heptane with 0.1 % of CH_2Cl_2	—	—	3100	10 200	0°	0.233	—	—
	Ethanol	4640	19	3070	10 900	—	—	—	—
$(CH_3)_2NCS \cdot CSNH_2$ (IVc)	Heptane with 0.5 % of CH_2Cl_2	3700S	450	—	—	—	—	—	—
	Heptane with 0.0025 % of CH_2Cl_2	—	—	3010	6 000	50°	0.411	2690	9 000
	Ethanol	3500S	440	2700	16 500	—	—	—	—
$CH_3NHCS \cdot CSNHCH_3$ (IVd)	Heptane with 10 % of CH_2Cl_2	4620	17	—	—	—	—	—	—
	Heptane with 0.05 % of CH_2Cl_2	—	—	3040	12 400	0°	0.274	—	—
	Ethanol	4400S	20	3025	11 600	—	—	—	—
$(CH_3)_2NCS \cdot CSN(CH_3)_2$ (IVe)	Heptane with 0.5 % of CH_2Cl_2	3650	375	—	—	—	—	—	—
	Heptane with 0.025 % of CH_2Cl_2	—	—	2750	18 800	89°	0.615	2620S	16 100
	Ethanol	3450S	500	2720	19 300	—	—	—	—

amide group (Fig. 1). The same difference is observed between the two trimethyl derivatives (IIIg) and (IIIh), and in the tetramethyl derivative (IIIi) the shifts are still somewhat greater. In the dithiooxamide series (IV) one methyl group shifts both bands moderately towards the blue, and a further methyl group on the other nitrogen atom causes additional shifts of the same order of magnitude ($n \rightarrow \pi^*$ band about 1000 cm^{-1}, $\pi \rightarrow \pi^*$ band about 500 cm^{-1}). In N,N-dimethyldithiooxamide the $n \rightarrow \pi^*$ band is shifted about 7000 cm^{-1}

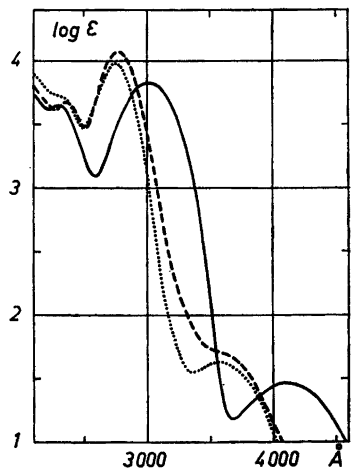


Fig. 1. Ultraviolet spectra of thiooxamide (IIIa, ————), N^s,N^s - dimethylthiooxamide (III d, — — —), and N^o,N^o - dimethylthiooxamide (III f, ...) in absolute ethanol.

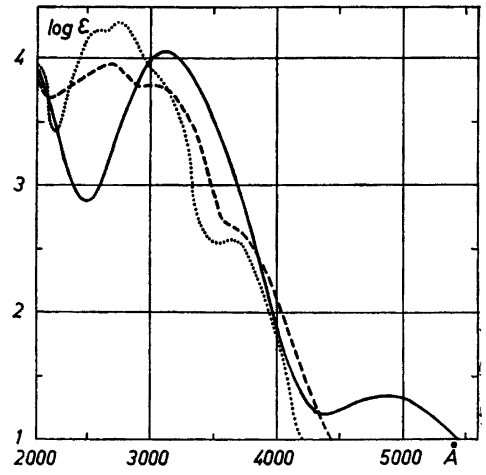


Fig. 2. Ultraviolet spectra of dithiooxamide (IVa, ————) in ethanol, N,N-dimethyldithiooxamide (IVc, — — —) and tetramethyldithiooxamide (IVe, ...) in heptane and methylene chloride.

towards the blue, and in the region of $\pi\rightarrow\pi^*$ transitions two bands appear, which are resolved in heptane but not in ethanol solution. They both appear at considerably shorter wavelength than the $\pi\rightarrow\pi^*$ band in dithiooxamide. The spectrum of tetramethyldithiooxamide is similar to that of the N,N-dimethyl derivative, the main differences being a further blueshift of the $\pi\rightarrow\pi^*$ bands and a different intensity relation between these (Fig. 2).

In several of the spectra a second strong band appears at shorter wavelengths. It seems most likely that these bands are due to higher $\pi\rightarrow\pi^*$ transitions, since they do not show the large blueshifts with increasing solvent polarity that can be expected for $n\rightarrow\sigma^*$ transitions.

LCAO-MO calculations. The energy levels, π electron distributions, and bond orders for the systems (I)—(IV) have been calculated by the modified Hückel method used in the previous parts of this series. This method is similar to the one devised by Janssen.[17] The main difference lies in the treatment of double bonds. In the formula (1), where n denotes the n:th iteration and p_{n-1}

$$(\beta_{cx})_n = (\beta_{cx})_1 (1 + 0.5p_{n-1}) \quad (1)$$

the bond order for the C—X bond obtained in the $(n-1)$:th iteration, Janssen uses the single bond values for $(\beta_{cx})_1$, whereas in this series the double bond values have been used. For the simple thioamides identical results were obtained since $\beta_{c=s}$ was given the value $0.6\beta = \beta_{c-s}$, but for other systems the present method gives greater weight to double bonds. The Coulomb and resonance integrals which have been used previously are summarised in Ref.[2], p. 681. The carbon-carbon bond resonance inte-

gral is given the value β. The nitrile group has not been treated previously. Only the π bond which overlaps with the π electron system in the thioamide group is taken into account. The Coulomb integrals are given the values $\alpha_C = \alpha$ and $\alpha_N = \alpha + 0.5\beta$, *i.e.* no allowance is made for the higher electronegativity of digonally hybridized atoms.[18] This higher value must have effect mainly for the σ bonds, and as a first approximation the screening of the nucleus from the electrons in a p orbital should not depend on the state of hybridization of the other orbitals. The length of the carbon-nitrogen triple bond is assumed to be 1.16 Å as in cyanogen.[19] If the resonance integral for the carbon-nitrogen bond in thioamides, 1.2β, (bond length 1.31—1.32 Å[8,20]) is taken as standard and assuming proportionality between resonance and overlap integrals, a resonance integral of 1.6β for the nitrile bond is arrived at. Davies and Jones[21] have treated the nitrile group in cyanamide with the simple Hückel approximation. They use three sets of parameters, in which α_C ranges from α to $\alpha + 0.2\beta$, α_N from $\alpha + 0.8\beta$ to $\alpha + 1.3\beta$, and β_{CN} from 0.9β to 1.3β. They do not discuss the influence of the state of hybridization on the Coulomb integrals, but it is apparent that their Coulomb integrals correspond to higher electronegativities than the set used in the present work. Our high value of β_{CN} should be seen in relation to the comparatively high values of all the resonance integrals used in this series.

Table 2. Energy levels, transition energies and stabilization energies in units of β.

	I	II	III	IV
Antibonding orbitals	−2.524 −0.956	−2.771 −0.982	−2.779 −0.989	−2.005 −0.600
Nonbonding orbital	0.059	0.066	0.064	0.102
Bonding orbitals	0.406 2.367 3.206 —	0.421 2.168 2.834 4.430	0.419 1.431 2.685 3.832	0.323 0.615 2.482 3.185
$\Delta E_{n\rightarrow\pi^*}$ $\Delta E_{\pi\rightarrow\pi^*}$	−1.015 −1.362	−1.048 −1.403	−1.053 −1.408	−0.702 −0.923
ΔE_π ("Extra π energy")	−0.234	−0.186	−0.206	−0.378

The calculated energy levels and transition and stabilization energies are recorded in Table 2, and the π electron distributions and bond orders are found in Fig. 3.

DISCUSSION

The effect of conjugation is in qualitative agreement with the results of the LCAO calculations. The $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transition energies in Table 2 are considerably smaller for the system (IV) than for the other systems, the

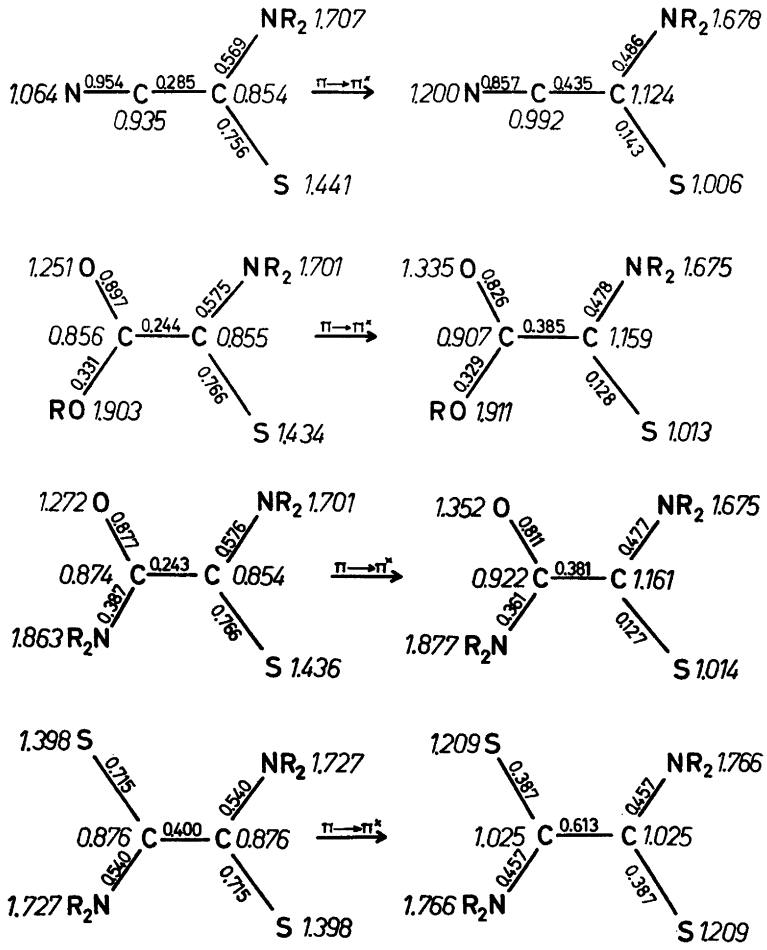


Fig. 3. Calculated π electron densities and π bond orders in ground and excited states.

values for which, on the other hand, are fairly similar and smaller than for an unconjugated thioamide.[1] The quantitative agreement is satisfactory for the systems (I), (II), and (III), whereas the calculated effect of conjugation is greatly exaggerated in (IV). The experimental $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ absorption maxima of the unsubstituted compounds (when necessary extrapolated to nonpolar solvent values with the aid of the solvent shifts of the monomethyl derivatives) and those calculated with thioacetamide as reference are found in Table 3. The reason for the failure with the system (IV) is not known, but investigations of other systems with two thiocarbonyl groups in conjugation have given similar results.

Table 3. Calculated and experimental wavelengths (Å) of absorption maxima (non-polar solvents).

	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	
	Calc.	Exptl.	Calc.	Exptl.
Thioacetamide	—	3670	—	2670
Cyanothioformamide (Ia)	4480	4370	3130	2940
Ethyl thiooxamate (IIa)	4330	4540	3040	3010
Thiooxamide (IIIa)	4310	4170[a]	3030	3030[a]
Dithiooxamide (IVa)	6470	5070[a]	4620	3150[a]

[a] Extrapolated assuming the same solvent shift as in the monomethyl derivatives.

Methyl substitution on the nitrogen atoms can influence the spectra in different ways. The conjugated system is extended by hyperconjugation, and the electronegativity of the nitrogen atoms is lowered by the inductive effect. Furthermore, steric hindrance to coplanarity will affect the conjugation and thereby the energy levels. Janssen [22,23] discusses the effect of alkyl substitution on the spectra of different thiocarbonyl compounds. In simple thioamides, one methyl group causes hypsochromic shifts of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands, whereas a second methyl group shifts the bands back to the neighbourhood of the positions for the unsubstituted compound. Janssen gives no explanation for this peculiarity, but in a later work [24] he stresses the importance of hyperconjugation in the excited state. An examination of molecular models indicates that one methyl group on each nitrogen atom can be accomodated in a planar molecule without steric interference. Its influence should then only be hyperconjugative and inductive. No treatment of the possible effect of hyperconjugation in these compounds has yet been performed, but the inductive effect on $\pi \rightarrow \pi^*$ transitions can be correlated with the change in π electron distribution on excitation [25,26] (Fig. 3). If the electron density on the nitrogen atom is increased by the excitation, a hypsochromic shift should result, whereas a decreasing charge should cause a shift in the opposite direction. An increasing π electron density on excitation is calculated for the thioamide nitrogen atom in dithiooxamide and for the amide nitrogen atom in monothiooxamide, whereas for all other nitrogen atoms a decrease is calculated. Experimentally, a bathochromic shift is observed in (II), in harmony with calculations, and for substitution on the amide nitrogen in (III), against calculations. Hypsochromic shifts are observed for substitution on the thioamide nitrogen atoms in (III) and (IV), where only the last shift is in agreement with calculation. In the system (I) the monomethyl derivative is not available. The observed discrepancies may of course be explained by an unsatisfactory description of the charge distribution by the simple calculation method, but it is also possible that the shifts are due to superposition of more than one effect, *e.g.* that hyperconjugation is also of importance.

Two methyl groups on the same nitrogen atom cause large hypsochromic shifts of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands in (II), (III), and (IV), whereas in (I) the $n \rightarrow \pi^*$ band is hardly affected and the $\pi \rightarrow \pi^*$ band undergoes a bathochromic shift. These effects can readily be explained by a steric hindrance to coplanarity, since molecular models show a considerable interference between the methyl groups and either the oxygen or sulphur atom (in the *trans* form) or the other amino group (in the *cis* form). The occurrence of a steric effect in the systems (II), (III), and (IV) is further supported by the absence of hypsochromic shifts in (I), where the structure of the molecule makes a steric interference impossible.

The steric strain can be relieved either by a rotation around the carbon-carbon bond or by a rotation of the substituted amide nitrogen atom out of the plane of the molecule. In the first case the conjugation between the two halves is diminished, and in the latter case the resonance in the amide or thioamide group is disturbed. Janssen [17] has calculated the stabilization energy of a thioamide group, *i.e.* the energy due to interaction between the amino group and the thiocarbonyl group, to be 1.106β. With the parameters used here the corresponding value for the amide group is 0.562β. The "extra stabilization energy", ΔE_π, due to conjugation over the carbon-carbon bond, *i.e.* the total π electron energy of the molecule minus the π electron energies of the two parts joined by the carbon-carbon bond, has values between 0.18β and 0.38β (Table 2). Therefore, a rotation around a carbon-nitrogen bond is more detrimental to the stabilization of the molecule than a rotation around the carbon-carbon bond. Probably both kinds of rotation occur to such an extent that the loss of stabilization is minimized, but the rotation around the carbon-carbon bond can be expected to be the most important. The effect of this rotation on the energy levels can be calculated by giving values to the carbon-carbon resonance integral ranging from 1.0β, corresponding to coplanarity, to zero, corresponding to a rotation of 90°. Suzuki [27] has pointed out that the overlap and thus the resonance integral of a bond is diminished by a rotation which causes departure from coplanarity of two conjugated systems both because the p orbitals are no longer parallel and because the bond is lengthened as a result of the diminished conjugation. Assuming proportionality between overlap and resonance integrals,[28] the first effect can be accounted for by the relation (2).

$$\beta_\Theta = \beta_0 \cos\Theta \tag{2}$$

A proper treatment of the bond lengthening effect requires a knowledge of the variation of overlap with bond length and of bond length with angle of rotation, Θ. In the present case the bond length data necessary for the treatment of the bond lengthening effect are not available. However, as a first approximation this effect can be neglected compared with the effect of diminished parallelism of the p orbitals. A variation in bond length between 1.48 and 1.51 Å corresponds to a variation in overlap integral between 0.213 and 0.199,[29] whereas a variation in Θ between 0° and 90° corresponds to a variation in overlap integral between 0.2 and zero. An attempt to calculate the angles of rotation of the most probable conformations of the N,N-dimethyl derivatives of (II), (III), and (IV) has been made in the following way. The

wavenumbers of the $\pi \rightarrow \pi^*$ band maxima, $\bar{\nu}_{max}$, and the calculated transition energies, $\Delta E_{\pi \rightarrow \pi^*}$, have been assumed to obey a linear relation (3).

$$\bar{\nu}_{max} = A \times \Delta E_{\pi \rightarrow \pi^*} + B \quad (3)$$

The values of A and B for each system have been calculated from (3) by using the known $\bar{\nu}_{max}$ and $\Delta E_{\pi \rightarrow \pi^*}$ values for the unsubstituted thiooxamide derivative ($\Theta = 0°$) and for thioacetamide ($\Theta = 90°$). By performing the LCAO calculations for (II), (III), and (IV) with suitably chosen β_{cc} values, graphs

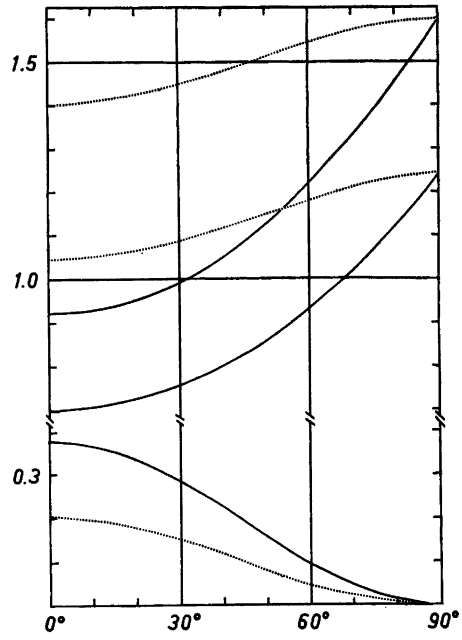


Fig. 4. $\Delta E_{\pi \rightarrow \pi^*}$ (top line), $\Delta E_{n \rightarrow \pi^*}$ (middle line), and ΔE_{π} (lowest line) as functions of Θ for thiooxamate and thiooxamide (II and III, ·····) and for dithiooxamide (IV, ————). The graphs for (II) and (III) are undistinguishable.

showing the relation between $\Delta E_{\pi \rightarrow \pi^*}$ and Θ could be constructed (Fig. 4). The Θ values were obtained from (2), where the β value from the last iteration was used for β_Θ. $\bar{\nu}_{max}$ was taken from the $\pi \rightarrow \pi^*$ bands, since these are less sensitive to solvent and substituent effects than are the $n \rightarrow \pi^*$ bands. In two cases, however, only spectra in ethanol were available, and for these the same solvent shifts as for the most similar monomethyl derivatives were assumed and used for correction to non-polar solvent values. The non-steric effect of methyl substitution also had to be accounted for. The effect of methyl substitution on the amide nitrogen atom in monothiooxamide was neglected. One methyl group on a thioamide nitrogen atom was corrected for by subtraction of 500 cm^{-1}, and for two methyl groups on the same nitrogen atom the shift from thioacetamide to N,N-dimethylthioacetamide, *i.e.* an addition of 1000 cm^{-1}, was used as correction. From the corrected $\bar{\nu}_{max}$ values, the relation (3), and Fig. 4, values for Θ were obtained, which are shown in Table 1. The calculations have been performed only for non-polar solvent values, since

they are least affected by solute — solvent interactions. It is of interest to note that the Θ value for (IIId) is smaller than for (IIIf), and that the same order is shown by (IIIg) and (IIIh). The first member in each pair contains a methyl group in opposition to an oxygen atom, the second one in opposition to a sulphur atom, and it is to be expected that the greater van der Waals radius of the latter atom should cause a larger angle of twist of the pivot bond. The spectrum of N,N-dimethyldithiooxamide (IVc) contains two bands in the $\pi \rightarrow \pi^*$ region (Fig. 3). The long-wavelength band corresponds to $\Theta = 50°$ and the short-wavelength band to $\Theta = 90°$. It is possible that the energy of the molecule has two minima corresponding to different angles of twist, and that the two bands are due to transitions from these. A similar spectrum is shown by tetramethyldithiooxamide, but there the two bands appear at shorter wavelengths. It is possible that twisting of carbon-nitrogen bonds is involved here, since that could explain the unexpectedly short wavelength of the less intense maximum.

If all bond lengths, angles and radii of interaction were known, it should be possible to calculate the angles of twist. Since the necessary data are not known, an attempt has been made assuming a simplified geometry. All bond angles have been put equal to 120°, and the bond lengths have been given the following values: C—C: 1.48 Å, C=S: 1.74 Å, C=O: 1.22 Å, C—N: 1.32 Å, CH_3—N: 1.44 Å. Suzuki [30] has obtained reasonable values for the angles of twist in diphenyl and stilbene systems by using the van der Waals radii for the interference distances. However, these radii are generally regarded as being too large,[31] since the potential at first rises rather slowly when the interatomic distance is decreased below the potential minimum value. The angle of twist, Θ, was calculated for C=S...H_3C—N and C=O...H_3C—N oppositions with different values for the radii of interaction. The full van der Waals radii (r_{vdW}) were found to give improbably high Θ values. Then 0.9, 0.85, 0,8 and 0.7 of r_{vdW} were tried, and as can be seen from Table 4, a value in the neighbourhood of $0.85 r_{vdW}$ gives Θ values similar to those from the spectra (Table 1).

Oscillator strengths. The absorption intensities are most profitably discussed in terms of oscillator strengths, f, which have been calculated from spectra in hydroxyl-free solvents (where possible) by the formula (4). The values are recorded in Table 1. It appears that the oscillator strengths for the representa-

$$f = 4.32 \times 10^{-9} \int \varepsilon \times d\bar{\nu} \qquad (4)$$

tives of systems (I), (II), and (III), where coplanarity is possible, are lower than for thioacetamide (0.258). This means that in these the absorption intensity is diminished by the conjugation, which is a rather unusual effect. In (IV) it is only slightly increased. In the compunds where dimethylamino groups prevent a planar conformation, the oscillator strengths are considerably higher, and the values for the thiooxamates (II) and monothiooxamides (III) come close to that for thioacetamide. The oscillator strengths for the dithiooxamides (IV) are much more increased by the steric effect, and for the tetramethyl derivative the value is more than twice that for thioacetamide. For the cyanothioformamides an increase is also observed, when two methyl groups are introduced, but it is smaller than for the other systems. These observations

Table 4. Angles of twist around the pivot bond calculated from a geometric model.

Radii of interaction	C=S...CH_3N	C=O...CH_3N
r_{vdW}	98°	89°
$0.9r_{vdW}$	76°	65°
$0.85r_{vdW}$	65°	52°
$0.8r_{vdW}$	54°	37°
$0.7r_{vdW}$	28°	0°

are in harmony with a considerably twisted conformation in the N,N-dimethyl derivatives of (II), (III), and (IV), where the chromophore responsible for the long wavelength absorption is much more like an unconjugated thioamide group, or two such groups in (IV), than in the planar molecules. Thus, the interpretation of the spectral shifts as results of steric effects is corroborated by the substituent effects on the absorption intensities.

Table 5. Calculated and experimental oscillator strengths.

Compound	Calc.		Exptl.
	S-*cis*	S-*trans*	
Thioacetamide	0.676		0.258
N,N-Dimethylthioacetamide	0.676		0.268
Cyanothioformamide (Ia)	0.630		0.181
Ethyl thiooxamate (IIa)	0.538	0.650	0.161
Monothiooxamide (IIIa)	0.516	0.640	0.156
Dithiooxamide (IVa)	0.432	1.276	0.271

The oscillator strengths have been calculated by a crude approximation employing the LCAO—MO functions obtained previously. The method of calculation is essentially the one given by Sandorfy.[32] For calculation of the components, Q_x and Q_y, of the transition moment Q, the relation (5) was used,

$$Q_x = \sqrt{2}\int \varphi_i \times x \times \varphi_j d\tau \approx \sqrt{2}\sum_n c_{in}c_{jn}x_n \qquad (5)$$

where φ_i and φ_j represent the highest occupied and lowest empty orbital, n denotes atom number n with x-coordinate x_n, and c_{in} and c_{jn} are the corresponding LCAO coefficients. The same molecular geometries as in the calculations of the angles of twist were used, and the lengths of the carbon-oxygen bonds in thiooxamate were given the same values as in methyl acetate.[33] The f values were obtained from the relation (6) and are found in Table 5.

$$f = 1.085 \times 10^{-5}\,(Q_x^2 + Q_y^2)\,\bar{\nu}_{max} \qquad (6)$$

The values are as usual several times higher than the experimental ones, but it is satisfying that the values for the systems (I), (II), and (III) are all considerably lower than for a simple thioamide whereas that for (IV) is higher. Thus, the order between the experimental values is reproduced. Just as with the transition energies, the f value for (IV) is greatly exaggerated. The inclusion of overlap (see Ref.,[32] p. 95) lowers the f values somewhat, but it seems questionable to use this improvement here when it was neglected in the construction of the molecular orbitals.

Hosoya *et al.*[34] found that the moment of the $\pi \rightarrow \pi^*$ transition corresponding to the 2610 Å band in thioacetamide follows near the direction through the sulphur and nitrogen atoms. The direction of the calculated moment nearly bisects the angle between this direction and the carbon-sulphur bond, a deviation of less than 10°, which is not too serious regarding the approximations made.

It has previously been observed [1,2] that a steric effect which causes a deviation from coplanarity in a conjugated thioamide also effects an increase in the intensity of the $n \rightarrow \pi^*$ band. Among the systems treated in this study increases in extinction coefficient by a factor of two are found in the thiooxamate and monothiooxamide series, whereas increases by a factor of ten are found in the dithiooxamide series. This intensity enhancement is regarded as being due to overlap between the lone pair orbital on the sulphur atom and the π orbitals, whereby the $n \rightarrow \pi^*$ transition borrows intensity from the $\pi \rightarrow \pi^*$ transition. The oscillator strength of the $n \rightarrow \pi^*$ transition is proportional to the square of the integral of overlap between the lone pair and π orbitals[35], and it is possible that the greater intensity of the $n \rightarrow \pi^*$ transitions in the hindered dithiooxamides is due to a greater overlap integral, which in turn could arise from the greater diffuseness of the π orbitals caused by exchange of oxygen for sulphur.

Solvent effects. The effect of solvent polarity and hydrogen bonding on the wavelength of absorption is governed by the interaction between solvent molecules and molecules of the general type (V), in their ground and excited states, where X is N (in the nitrile group), O, or S. In non-polar solvents the interaction can be expected to be weak and as a first approximation of the same order of magnitude in the ground and excited state. Therefore, the wavelength shifts when going from a non-polar to a hydroxylic solvent are determined mainly by the interaction between the solute molecules in the ground and excited states and the hydroxylic solvent molecules, and among these interactions hydrogen bonding is of paramount importance. In all the systems (V), an $n \rightarrow \pi^*$ transition involves the excitation of one electron from a lone pair on the sulphur atom to an antibonding π orbital. This must cause nearly complete breaking of the hydrogen bonds to the sulphur atom, but on the other hand the excited electron may be so distributed that it increases the basicity of other atoms. If one of these is already the donor in a hydrogen bond, the energy of this bond will be increased, and even if no bond exists, solvent molecules may be so oriented that a new hydrogen bond can be formed without so great changes in position of the nuclei that the Franck-Condon rule is violated. Thus, as was the case with N-acetylthioamides,[2] the loss of energy of solvation at the thiocarbonyl group may be more than balanced by

the gain at other positions, and the net result of excitation is an increase in energy of solvation, which appears as a redshift when going from non-polar to hydroxylic solvents. In less extreme cases the excitation causes a loss in energy of solvation, but the consequent blueshift is smaller than for simple thioamides, where no compensating increase in solvation occurs. In all thioamide systems so far investigated, the calculations have shown a strong decrease of the polarity of the thiocarbonyl group as a result of a $\pi \rightarrow \pi^*$ transition involving promotion of one electron from the highest bonding to the lowest antibonding orbital. In most cases even a reversal of the polarity is indicated. If this is correct, the transition must cause a considerable lowering of the basicity of the sulphur atom with consequent loss of hydrogen bonding energy. Since the lone pair is still intact, no complete breaking of hydrogen bonds should take place. The change in polarity must also diminish solvation by dipole-dipole interaction, and if no other changes occur, the result will be a blueshift of the $\pi \rightarrow \pi^*$ bands with increasing solvent polarity, though the shift should be smaller than for $n \rightarrow \pi^*$ bands. This is also observed with simple thioamides.[1,22,23] In the cyanothioformamide, thiooxamate and monothiooxamide systems the calculated charge on the atom X is increased by the $\pi \rightarrow \pi^*$ transition, which counteracts the changes at the thiocarbonyl group. This effect may even dominate and cause a redshift, as is found with some N-acetylthioamides.[2] However, superimposed upon the solvation induced shifts is a general redshift caused by increased solvent polarisability,[36] and this is responsible for part of the observed effect.

Among the dithiooxamides (IV), the calculated charge distributions (Fig. 3) are such that excitation should lead to decreased energy of solvation at both sulphur atoms, and in harmony with this blue shifts are observed both for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands. The cyanothioformamide, thiooxamate, and monothiooxamide systems all contain an atom X (V), the π electron charge of which is increased by both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In all cases the $n \rightarrow \pi^*$ bands undergo blue shifts, and therefore the increase in energy of solvation at atom X is less than the loss of hydrogen bonding energy at the sulphur atom. The $\pi \rightarrow \pi^*$ bands of the cyanothioformamides undergo considerable redshifts, and therefore the loss of energy of solvation at the thiocarbonyl group in this case should be balanced by the gain at the cyano group. As can be seen in Fig. 3, the π electron charge at the cyano nitrogen atom is considerably increased by the $\pi \rightarrow \pi^*$ transition. The redshift observed should indicate that the nitrile group already in the ground state in ethanol solution is surrounded by solvent molecules with such orientations that they can take full advantage of the increased polarity of the nitrile group. All three ethyl thiooxamates (II) show blueshifts of the $\pi \rightarrow \pi^*$ bands, and the same applies to most of the monothiooxamides (III). Thus, in these cases the increase in energy of solvation at the carbonyl group should be smaller than the decrease at the thiocarbonyl group. The representatives of the systems (II), (III), and (IV) which contain dimethylamino groups constitute a separate class, where the conjugation between the two halves of the molecule is so weak that the transitions can be regarded as taking place in isolated thioamide groups. Therefore, it is natural that these compounds should display the same type of solvent dependence as simple thioamides.

EXPERIMENTAL

Cyanothioformamide (Ia) was prepared mainly according to Anschütz [37] by bubbling hydrogen sulphide into a solution of cyanogen in ethanol at −30° until the yellow solution began to turn reddish, evaporating the solution and recrystallizing the residue from chloroform. Yellow prisms, m.p. 87−89° (Lit.[37] 87−90°). (Found: N 32.3. $C_3H_2N_2S$ (86.12) requires N 32.5). ν_{CN}: 2250 cm^{-1} (KBr).

Attempts to prepare N-methylcyanothioformamide (Ib) along several routes have been in vain. *N-Methylcyanoformamide*, which was used as starting material in one case, has previously been prepared by Slotta and Tschesche [38] by condensation of methyl isocyanate with hydrogen cyanide in the presence of triethylphosphine. A simpler method was found in the reaction between N-methyloxamide and phosphorus pentoxide. An intimate mixture of methyloxamide (10 g) and phosphorus pentoxide (12 g) was heated to 160° at 10 mm Hg in a vacuum sublimation apparatus. A sublimate of colourless prisms formed on the cold finger and was recrystallized from carbon tetrachloride to remove an insoluble impurity. Long colourless prisms (3.2 g, 39 % yield) were formed, m.p. 80−81° (Lit.[38] 80°). (Found: N 33.1. $C_3H_4N_2O$ (84.08) requires N 33.3).

This compound (3.2 g) and phosphorus pentasulphide (4 g) were refluxed in toluene (50 ml) for 6 h. The cooled, filtered solution was subjected to chromatography on silica. Elution with chloroform gave first an orange solid (0.52 g, 11 % yield), identified by m.p., mixed m.p., and thin layer chromatography on silica as monomethyldithiooxamide (IVb), to be described later. Further elution with chloroform gave a yellow solid (0.48 g, 9 % yield), identified as above as N°-monomethylmonothioxamide* (IIIc). With shorter reaction time the amount of the latter compound increased. Hydrogen sulphide must have been evolved during the reaction and added to the cyano group, and by thorough drying of the reagents it was made sure that the hydrogen atoms could only have come from the N-methylcyanoformamide Thus, the theoretical yield of (IIIc) and (IVb) together is only 33 %.

A further attempt to prepare (Ib) was made by reaction between cyanothioformamide (Ia) and methylamine at room temperature and at reflux. In both cases the only product that could be isolated when the evaporation residue was subjected to chromatography on alumina was N,N′-dimethyldithiooxamide (IVd, 20 % yield). In this case, decomposition of the cyanothioformamide must have occurred with formation of hydrogen sulphide, which may then have added to unchanged cyanothioformamide with formation of dithiooxamide. This in turn can react with methylamine to form (IVd).

Attempts to prepare (Ib) by pyrolysis of monomethyldithiooxamide (IVb) likewise were in vain. Only the unchanged starting material sublimed away even from an intimate mixture with lead(II) oxide. A similar result was obtained when a mixture of N^s-monomethylmonothiooxamide (IIIb) with phosphorus pentoxide was heated to 170° at 10 mm Hg.

N,N-Dimethylcyanothioformamide (Ic). Dithiooxamide (14.4 g) and 0.75 N dimethylamine in ethanol (300 ml) were refluxed for 1 h. The dark brown solution, which smelt strongly of hydrogen sulphide, was evaporated to dryness, and the residue was subjected to vacuum sublimation at 1 mm Hg and 170°C. A yellow, solid deposit was formed (7.9 g), which was dissolved in benzene and subjected to chromatography on alumina. Benzene first eluted sulphur (1.44 g) and then a yellow solid (3.6 g), which crystallized from chloroform-light petroleum (b.p. 40−60°) as yellow plates, m.p. 60−61°. (Found: C 41.8; H 5.16; N 24.2; S 28.3. $C_4H_6N_2S$ (114.17) requires C 42.1; H 5.30; N 24.5; S 28.1). $\bar{\nu}_{CN}$: 2210 and 2230 cm^{-1} (weak, in CCl_4).

Ethyl thiooxamate (IIa) was prepared according to Boon.[40]

Ethyl N-methylthiooxamate (IIb) was prepared according to Walter and Bode.[41] However, this product showed several spots on thin layer chromatography on silica. A pure specimen was obtained by chromatography on silica followed by vacuum distillation. Orange liquid, b.p.$_4$ 120°, n_D^{20} 1.5423. (Found: C 40.6; H 6.42; N 9.41; S 22.3. $C_5H_9NO_2S$ (147.19) requires C 40.8; H 6.16; N 9.52; S 21.8).

* Notation according to Milligan and Swan.[39]

Ethyl N,N-dimethylthiooxamate (IIc). Ethyl thiooxamate (2.6 g) was dissolved in 2.2 N dimethylamine in ethanol (10 ml). After three days the mixture was evaporated, and the oily residue was extracted several times with ether. On evaporation the colourless residue crystallized (1.7 g, 53 % yield). From toluene-light petroleum large rhombic prisms were obtained, m.p. 45–46°. (Found: C 44.8; H 6.84; N 8.72; S 20.0. $C_6H_{11}NO_2S$ (161.22) requires C 44.7; H 6.88; N 8.69; S 19.9). This compound has previously been described by Walter and Bode,[41] who obtained it by reaction between the oxygen analogue and phosphorus pentasulphide and report m.p. 46–47°.

Monothiooxamide (IIIa) was prepared according to Weddige.[42]

N^s-Methylmonothiooxamide (IIIb) was prepared according to Welcher *et al.*[43]

N^o-Methylmonothiooxamide (IIIc) was prepared according to Slotta and Tschesche.[38]

N^s,N^s-Dimethylmonothiooxamide (IIId). Monothiooxamide (2.1 g) was refluxed in 2 N dimethylamine in ethanol (30 ml) for 2 h. The solution was evaporated and gave a crystalline residue of 2.6 g (100 % yield) of fairly pure (IIId). It crystallized from ethanol as colourless pointed prisms, m.p. 140–141°. (Found: C 36.3; H 6.10; N 21.3; S 24.1. $C_4H_8N_2OS$ (132.18) requires C 36.3; H 6.10; N 21.2; S 24.3).

*N^o,N^s-*Dimethylmonothiooxamide *(IIIe).* Ethyl N-methylthiooxamate (IIb, 1.6 g) was dissolved in 2 N methylamine in ethanol (6 ml). The orange colour soon faded, and yellow prisms separated (0.97 g. 73 % yield), which crystallized from ethanol as yellow rhombic plates, m.p. 134–135°. (Found: C 36 3; H 5.94; N 21.1; S 24.3. $C_4H_8N_2OS$ (132.18) requires C 36.3; H 6.10; N 21.2; S 24.3). The same compound was obtained when the thiooxamates (IIa) and (IIc) were treated with an excess of methylamine in ethanol at room temperature

N^o,N^o-Dimethylmonothiooxamide (IIIf) was prepared according to Atkinson.[44] However, our preparation showed m.p 108–109.5°, whereas Atkinson reports m.p. 120–121°. The m.p. did not rise in spite of chromatography on alumina followed by recrystallization from toluene. As the preparation gave only one spot on paper and thin layer chromatograms and gave analytical figures deviating by less than 0.2 % (absolute values) from the calculated figures, the deviation in m.p. may be ascribed to dimorphism.

N^o,N^s,N^s-Trimethylmonothiooxamide (IIIg). N^o-Monomethylthiooxamide (IIIc, 2.0 g) was refluxed for 1 h with 2.7 N dimethylamine in ethanol (10 ml). Evaporation gave a red, semisolid residue. This was purified by vacuum sublimation followed by chromatography on alumina. Ether eluted a colourless crystalline product (1.1 g, 39 % yield), which crystallized from carbon tetrachloride as colourless rods, m.p. 85–86°. (Found: C 40.8; H 6.56; N 19.3; S 21.6. $C_5H_{10}N_2OS$ (146.21) requires C 41.1; H 6.89; N 19.2; S 21.9).

N^o,N^o,N^s-Trimethylmonothiooxamide (IIIh). N^o,N^o-Dimethylmonothiooxamide (IIIf, 4.0 g) was refluxed with 2.1 N methylamine in ethanol (30 ml) for 10 h. Evaporation gave a yellow oil, which was shown by paper chromatography to contain at least two major components. It was dissolved in benzene and subjected to chromatography on alumina. Ether with 10 % (v/v) of ethanol eluted a colourless oil, which slowly solidified (0.84 g, 19 % yield). The product crystallized from a mixture of carbon tetrachloride and light petroleum at −20° as colourless prisms, m.p. 68–70°. (Found: C 40.9; H 6.95; N 19.0; S 21.9. $C_5H_{10}N_2OS$ (146.16) requires C 41.1; H 6.89; N 19.2; S 21.9).

Tetramethylmonothiooxamide (IIIi). The above preparation was repeated with dimethylamine instead of methylamine. The yield of (IIIi) after elution with benzene from alumina was 82 %. It had a low tendency to crystallize, and in spite of several recrystallizations as above, no sharp m.p. could be obtained. A product with m.p. 73–78° gave only one UV-absorbing spot on a paper chromatogram and gave satisfactory analytical figures. (Found: C 44.8; H 7.53; N 17.7; S 19.9. $C_6H_{12}N_2OS$ (160.24) requires C 45.0; H 7.54; N 17.5; S 20.0).

Dithiooxamide (IVc) was a commercial quality (Merck *pro analysi*).

Methyldithiooxamide (IVb) and *N,N'-dimethyldithiooxamide (IVd).* Dithiooxamide (9.6 g) was refluxed in ethanol (200 ml) and one equivalent of methylamine in ethanol, (40 ml) was gradually added during one hour. The solution was filtered and evaporated and the dark brown residue was dissolved in benzene and subjected to chromatography on alumina. Benzene eluted a yellow solid (1.5 g, 13 % yield), which crystallized from butanol as yellow plates, identified by m.p., 137–138°, and mixed m.p. with N,N'-dimethyldithiooxamide prepared according to Wallach and Reinhard.[45] On continued chromatography, ether eluted an orange solid (2.0 g, 19 % yield), which crystallized from ethanol as orange pointed prisms, m.p. 131–132°, consisting of methyldithio-

oxamide. (Found: C 27.0; H 4.58; N 21.3; S 47.6. $C_3H_6N_2S_2$ (134.23) requires C 26.9; H 4.51; N 20.9; S 47.7).

N,N-Dimethyldithiooxamide (IVc). A solution of N,N-dimethylcyanothioformamide (Ic, 0.5 g) in benzene (10 ml) containing one drop of diethylamine was saturated with hydrogen sulphide. On the following day the solution was evaporated, and the residue (0.64 g, 98 % yield) crystallized from toluene as colourless rods, m.p. 134—135°. (Found: C 32.3; H 5.43; N 19.0; S 43.0. $C_4H_8N_2S_2$ (148.26) requires C 32.4; H 5.44; N 18.9; S 43.3).

Tetramethyldithiooxamide (IVe). Tetramethylmonothiooxamide (IIIi, 1.5 g) and phosphorus pentasulphide (1.5 g) were refluxed in toluene (50 ml) for 10 h. The solution was filtered hot and evaporated. The brown, half-crystalline residue was dissolved in benzene and subjected to chromatography on alumina. Benzene eluted first a small amount of sulphur and then a pale yellow solid (0.50 g, 30 % yield), which crystallized from benzene as pale yellow prisms, m.p. 137—138°. (Found: C 40.7; H 6.59; N 15.9; S 36.7. $C_6H_{12}N_2S_2$ (176.31) requires C 40.9; H 6.86; N 15.9: S 36.4). This compound has previously been prepared by Klöpping and van der Kerk [46] by reaction between tetramethyloxamide and phosphorus pentasulphide. They report m.p. 137°.

The recording of the ultraviolet spectra and the numerical calculations were performed as in the previous parts of this series.

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