The Electronic Spectra of Thioamides and Thiohydrazides
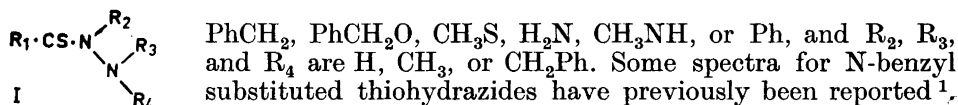
Part III *. Thiohydrazides

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Ultraviolet absorption spectra of a number of thiohydrazides have been recorded in solvents of different polarity and pH. The spectra are rather similar to those of the corresponding thioamides. Attempts to interpret the differences in terms of a simple LCAO−MO model have not been successful. The thiohydrazides are considerably stronger acids than the corresponding thioamides, and the strong absorption maxima in general undergo hypsochromic shifts on ionization. The pK_a values of some representative thiohydrazides have been correlated with the calculated π electron distribution.

In the first two parts of this series, the effects of conjugation with phenyl and acetyl groups on the ultraviolet spectrum of the thioamide group have been examined. The investigation has now been extended to thiohydrazides. A number of compounds of the general type (I) has been prepared, where R_1 is

$R_1 \cdot CS \cdot N \underset{\underset{R_4}{N}}{\overset{R_2}{\underset{R_3}{\diagup}}}$

I

$PhCH_2$, $PhCH_2O$, CH_3S, H_2N, CH_3NH, or Ph, and R_2, R_3, and R_4 are H, CH_3, or CH_2Ph. Some spectra for N-benzyl substituted thiohydrazides have previously been reported [1].

Ultraviolet spectra. These are recorded in Table 1, in some representative cases together with the wavenumber shifts relative to the same bands in the corresponding simple thioamides. It appears that the $n \rightarrow \pi^*$ bands in particular, but also the $\pi \rightarrow \pi^*$ bands, undergo hypsochromic shifts on the introduction of the amino group. In most cases the $n \rightarrow \pi^*$ band is only visible as a shoulder in nonpolar solvents and is completely covered by the $\pi \rightarrow \pi^*$ band in ethanol. It can also be seen (Fig. 1) that the bands of the thiohydrazides are broader and more diffuse than those of the thioamides. In the case of 2-methyl-thiobenzhydrazide in particular, this makes the exact location of the absorp-

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Table 1.

| Compound	Solvent	n → π* λmax Å	n → π* log ε	n → π* Δν[a]	π → π* λmax Å	π → π* log ε	π → π* Δν[a]	λmax Å	log ε	Ref.
PhCH₂CSNHNH₂	Heptane	—	—	—	2660	3.93[b]	420			3
	Chloroform	3250[c]	2.0	2200	—	—	—			
PhCH₂CSN(CH₃)NH₂	Ethanol	—	—	—	2650	3.95[b]	—			4
	Heptane	—	—	—	2780	4.07	—			
	Chloroform	3250[c]	2.2	—	—	—	—			
PhCH₂CSNHNHCH₂Ph	Ethanol	—	—	—	2780	4.08	—			4
PhCH₂OCSNHNH₂	Ethanol	2850[c]	2.3	1200	2815	3.98	—			11
	N NaOEt	*Only end absorption*			2600	3.91	500			
CH₃SCSNHNH₂	Heptane	3300[c]	1.8	1400	2420	4.02	1200	2540[c]	3.78	12
	Carbon tetrachloride	3360	1.87	—	—	—	—	—	—	
	Ethanol	*Only end absorption*			2400	4.01	—	—	—	
	NaOEt	—	—	—	—	—	—	—	—	
CH₃SCSN(CH₃)NH₂	Heptane	3250[c]	2.2	—	2710	3.92	900	2450	3.94	13
	Carbon tetrachloride	—	—	—	—	—	—	2510	3.86	
	Ethanol	—	—	—	2690	4.01	—	—	—	
	NaOEt	—	—	—	—	—	—	—	—	
	N HCl	3250[c]	1.8	—	2750	4.00	—	—	—	
H₂NCSNHNH₂	Heptane	—	—	—	2750	4.01	0	2580[c]	3.92	14
	Carbon tetrachloride	—	—	—	—	—	—	—	—	
	Ethanol	—	—	—	2730	4.07	—	—	—	
	Ethanol	—	—	—	2420	4.10	—	—	—	
	N NaOH	—	—	—	2350	4.07	—	—	—	
H₂NCSN(CH₃)NH₂	Ethanol	—	—	—	2400	4.10	—	—	—	15
H₂NCSNHN(CH₃)₂	Ethanol	—	—	—	2440	4.10	—	—	—	16
H₂NCSN(CH₃)NHCH₃	Ethanol	—	—	—	2430	4.10	—	—	—	17
(CH₃)₂NCSNHNH₂	Ethanol	—	—	—	2410	4.12	—	—	—	
CH₃NHCSN(CH₃)NH₂	Ethanol	—	—	—	2380	4.10	—	—	—	
PhCSNHNH₂	Heptane	3810	2.45	2000	2860	3.78	1400	2400	3.99	
	Carbon tetrachloride	—	—	—	—	—	—	—	—	
	Ethanol	—	—	—	2820	3.73	—	—	—	
PhCSN(CH₃)NH₂	Heptane	—	—	—	2890	3.90	—	2270	3.10	18
	Carbon tetrachloride	3580[c]	2.7	—	—	—	—	—	—	
	Ethanol	—	—	—	2820	4.02	—	2230	4.13	

[a] $\Delta\nu = \nu_{thiohydrazide} - \nu_{thioamide}$ [b] Unstable   [c] Shoulder

tion maximum somewhat uncertain. In alkaline medium the $\pi \to \pi *$ bands in general undergo blueshifts, and the $n \to \pi *$ bands disappear. The same is true for thioacetamide, as has recently been shown by Edward and Wang [2]. In very dilute solutions in N sodium ethoxide, thiosemicarbazide undergoes a rapid change, which leads to the appearance of a new absorption band at 2700 Å, and which is not reversed on neutralization with acetic acid.

Acidity constants. pK_a values for four N-benzyl substituted thiohydrazides in 20 % and 3 % aqueous ethanol (w/w) were reported in Ref.[1] pK_a values for 1-benzyl-thiophenylacethydrazide (I, $R_1 = R_4 = PhCH_2$, $R_2 = R_3 = H$) and 1-benzylthiosemicarbazide (I, $R_1 = H_2N$, $R_2 = R_3 = H$, $R_4 = CH_2Ph$) have now been determined in the same way in 20 % ethanol, and the results are given in Table 3. Jensen *et al.*[4] have reported pK_a values in 50 % ethanol for several thiohydrazides with $R_1 =$ alkyl, aralkyl or aryl.

LCAO—MO calculations. Even if it can be assumed that the electron distributions in a thiohydrazide and the corresponding thioamide are not very much different, the spectra in Table 1 show that the new amino group must shift the energy levels to some extent. Its effect may be purely inductive, or it may take part in the delocalized system. In the latter case the interaction can be expected to be rather weak, since the amino group is likely to be nearly sp[3] hybridized, and therefore its lone pair orbital will have a component directed away from the neighbouring nitrogen atom. In fact, valence bond structures (II) do not allow participation of the amino group in the conjugated system without invoking very unlikely structures such as (II c). The naive calculations,
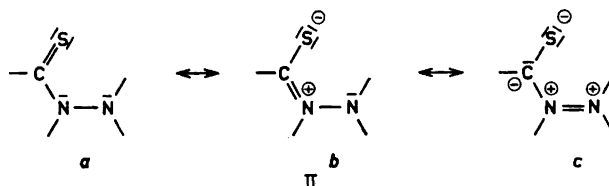
described in part I, give as one result that the charge on the nitrogen atom in thioacetamide and thiobenzamide is unchanged by a $\pi \to \pi *$ transition, and therefore a substituent on the nitrogen atom with purely inductive effect should be without influence on the energy of such a transition. However, one of the main deficiencies of the calculation method employed is the neglect of repulsion between electrons on different atoms, and this can be expected to be particularly serious in molecules like thiohydrazides, where two neighbouring atoms carry lone electron pairs. Still, it was considered worth-while to try to explain the spectral shifts from thioamides to thiohydrazides in terms of a LCAO—MO model, where the new amino group was treated as part of the conjugated system. The parameters for the thioamide group were the same as those used previously [5]. For the amino group a Coulomb integral of $\alpha + 0.9\beta$ was derived from the value for the ionization potential for ethylamine [6]. Values between 0.2β and 1.0β were tried in the simplest system for the resonance integral of the N—N bond. The resulting shifts of the energy levels were in the same directions, and the magnitude of the effects increased with the

Table 2. Calculated transition energies for thioamides, ΔE_1, and thiohydrazides, ΔE_2.

R_1	$n \to \pi *$		$\pi \to \pi *$	
	ΔE_1	ΔE_2	ΔE_1	ΔE_2
Alkyl	-1.193β	-1.202β	-1.623β	-1.561β
RO	-1.401β	-1.410β	-1.776β	-1.755β
RS	-1.229β	-1.206β	-1.623β	-1.600β
H_2O	-1.428β	-1.436β	-1.772β	-1.761β
C_6H_5	-0.794β	-0.791β	-1.182β	-1.125β

absolute value of β_{NN}. A value of 0.5β was chosen as a compromise and used for the other systems. The iterative calculation method described in Ref.[5] was used. However, the thioncarbazate and thiosemicarbazide systems did not give convergent results with the ordinary procedure, and therefore all the systems involved in the discussion had to be recalculated with $\omega = 0.8$. ω determines the influence of the positive charge, q, of an atom, x, on its Coulomb integral according to $a_{q,x} = a_x + \omega q\beta$. The results of the calculations are given in Tables 2 and 3. These calculations were performed before the mean value technique described in Part II was available, and it was not considered necssary to repeat the calculations.

An attempt was also made to calculate the spectral shifts following ionization. According to the iterative procedure the appearance of a unit negative charge on the nitrogen atom should give it a Coulomb integral of $\alpha + 0.5\beta$. However, no convergent results could be obtained using this parameter, not even with $\omega = 0.8$. With $a_N = \alpha + \beta$ and $\omega = 0.8$ convergent results were obtained in some cases, but the energies of the $\pi \to \pi *$ transitions were found to be unchanged. This discrepancy between calculated and experimental transition energies may be due to increased electron repulsion in the anion.
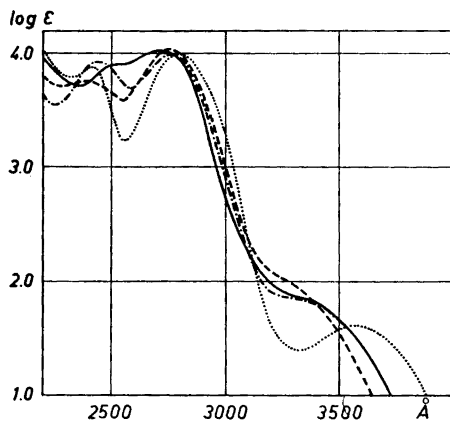

Fig. 1. Ultraviolet absorption spectra of $CH_3S.CS.NHNH_2$ in heptane (————) and in N HCl (—·—·—) and of $CH_3S.CS.NH_2$ in heptane (·····) and in water (- - - -).

DISCUSSION

An inspection of Table 2 reveals that the calculations predict shifts which are too small to be significant and which occur in either direction. For the $n \to \pi^*$ bands the shifts are between 0.01β and 0.02β, corresponding to $250-500$ cm^{-1}. The experimental $n \to \pi^*$ band shifts are in general considerably larger and always hypsochromic, and therefore they are not accounted for in the present approximation. The same can be said about the $\pi \to \pi^*$ bands. As the calculation method predicted shifts of correct direction and order of magnitude for thiobenzamides and N-acetylthioamides (Part I and II), the failure in the present case is ascribed to the unusually high electron repulsion. In harmony with this, the spectrum of methyl dithiocarbazate in N HCl, where the compound is fully protonated, shows a $n \to \pi^*$ band, and the spectrum is very similar to that of methyl dithiocarbamate in water (Fig. 1). This shows that the protonated amino group is without influence on the spectrum. Thus, the effect of the free amino group on the spectrum cannot be purely inductive, as it then should have been increased by protonation and not counteracted.

However, the π electron distribution is often more accurately given by an approximate calculation than are the energy levels, and attempts have therefore been made to relate the pK_a values of the thiohydrazides to the calculated π electron density, q_N, on the secondary nitrogen atom (Table 3 and Fig. 2). In some cases [7-9] linear relations have been found to exist between π electron densities and pK_a values in series of closely related acids, where the proton is attached to an atom belonging to the conjugated system. Longuet-Higgins [7] has given a theoretical explanation for these results. For the thiohydrazides the differing inductive effects of the groups R_1 (I) can be expected to confuse the issue, but it is seen in Table 3 and Fig. 2 that a reasonable correlation exists. The deviation of the thiophenylacethydrazide may be ascribed to the inverted inductive effect of the group R_1. Simple thioamides are weaker acids than the corresponding thiohydrazides. Edward and Wang [2] have recently determined pK_a for thioacetamide in water to be 13.4, and Baggesgaard Rasmussen [10] has found pK_a 13.3 for thiobenzamide in water. The pK_a values in Table 3 are probably $0.1-0.2$ units higher than if they had been determined in water.

The q_N values in Table 2 are not very different for the pairs of corresponding thioamides and thiohydrazides. If the q_N values for the thioamides are

Table 3. pK_a values (in 20 % ethanol w/w) for $R_1 \cdot CS \cdot NHNHCH_2Ph$ and calculated q_N values for thioamides and thiohydrazides.

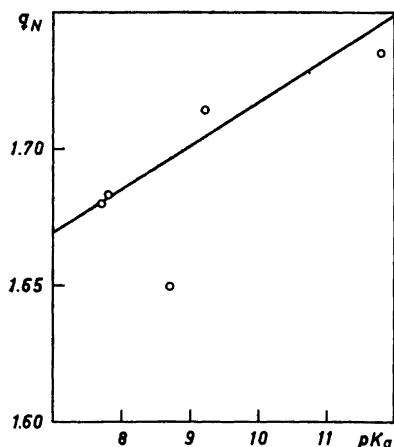| R_1	pK_a	q_N for thioamide	q_N for thiohydrazide
$PhCH_2$	8.7	1.668	1.649
CH_3O	9.2	1.727	1.714
CH_3S	7.7	1.688	1.680
H_2N	11.8	1.747	1.735
Ph	7.8	1.702	1.683

Fig. 2. Plot of pK_a values of 1-benzyl-thiohydrazides in 20 % aqueous ethanol *versus* calculated q_N values.

entered on the line in Fig. 2, far too low pK_a values are obtained. The higher acidity of the thiohydrazides can therefore only to a small extent be explained by their lower q_N values, possibly resulting from a resonance interaction with the amino group. Instead, the inductive effect of the amino group is believed to be the most important of the factors determining the acidity. The differences between the individual thiohydrazides are to a great extent determined by resonance effects already present in the thioamides. Therefore, considering both spectra and acidity constants, the conclusion is drawn that the interaction between the amino and thioamide groups is based chiefly on repulsion between π electrons, and on attraction of the amino group on the σ electrons in the N—N bond.

EXPERIMENTAL

Of the thiohydrazides only 1,1- and 1,2-dimethylthiosemicarbazide appear not to have been described before.

1,1-Dimethylthiosemicarbazide. Asymm. dimethylhydrazine (0.6 g) was added to a 0.69 N aqueous solution of thiocyanic acid (17 ml), and the mixture was evaporated to dryness. The residue was carefully heated to 160°. After three minutes a sudden reaction occurred, and an oily red residue was obtained. On treatment with water (1 ml) it solidified, and the product (0.3 g) crystallized from ethanol as colourless prisms, m.p. 163°. (Found: C 30.5; H 7.4. $C_3H_9N_3S$ (119.18) requires C 30.2; H 7.6.)

1,2-Dimethylthiosemicarbazide. This compound was prepared in very much the same way as the 1,1-isomer, using *sym.* dimethylhydrazine. A 75 % yield of crude product was obtained, which crystallized from ethanol as colourless prisms, m.p. 130°. (Found: N 35.5. $C_3H_9N_3S$ requires N 35.3.)

The other thiohydrazides were prepared according to known methods. Literature references are given in Table 1 except for 1-benzylthiosemicarbazide, which was prepared according to Hoggarth and Young [19]. The recording of the spectra and the numerical calculations were performed as usual (see Part I), and the acidity constants were determined as described in Ref.[1]

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