

The Electronic Spectra of Thioamides and Thiohydrazides

Part IV*. Alkylidene and Aralkylidene Thiohydrazides

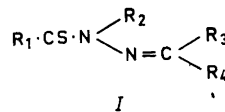
JAN SANDSTRÖM

Department of Organic Chemistry, University of Lund, Lund, Sweden

The ultraviolet absorption spectra of a number of hydrazones of different thiohydrazides with unconjugated, α,β -unsaturated, and aromatic carbonyl compounds have been recorded. Progressive bathochromic shifts of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are observed with increasing conjugation, in harmony with the results of simple LCAO-MO calculations. The spectra of the thiohydrazones are discussed in relation to the possible existence of tautomeric forms.

In Parts I¹ and II² of this series it has been shown that the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands undergo bathochromic shifts when the thioamide group is conjugated at the carbon atom with a benzene ring or at the nitrogen atom with an acetyl group. The thiohydrazones present another type of conjugated thiocarbonyl compounds, suitable for testing the validity of the assignments of absorption bands to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions made in Part I.

In the present investigation the spectra of a number of compounds of the general structure (I) have been recorded, where R_1 is PhCH_2 , CH_3O , CH_3S , H_2N , or Ph , R_2 is H or CH_3 , and R_3 and R_4 are H , alkyl, alkenyl, or aryl. The compounds are numbered 1-25. The results have been correlated with the transition energies predicted from LCAO-MO calculations. It should have been desirable to include compounds with $R_1 = \text{CH}_3$, but unfortunately these are very unstable, as has been pointed out by Jensen *et al.*³ However, no great error is introduced if thiohydrazones without conjugation in the group R_1 are represented by phenylthioacethydrazones ($R_1 = \text{PhCH}_2$), since the spectra of thioacetamide and phenylthioacetamide are fairly similar with the $\pi - \pi^*$ bands at 2670 and 2690 Å and the $n \rightarrow \pi^*$ bands at 3670 and 3650 Å, respectively (in heptane).



* Part III. *Acta Chem. Scand.* 17 (1963) 731.

No.	Compound	Solvent	$\eta \rightarrow \pi^*$		$\pi \rightarrow \pi^*$		$\lambda_{\max} \text{ \AA}$	$\log \epsilon$	Ref.
			$\lambda_{\max} \text{ \AA}$	$\log \epsilon$	$\lambda_{\max} \text{ \AA}$	$\log \epsilon$			
1	PhCH ₂ CSNHN:CHPh	Heptane	—	—	3360	3.83	2500 ^a	3.56	3
2	PhCH ₂ CS-N(CH ₃)N:CHCH ₃	Ethanol	—	—	3360	4.42	2470	3.79	—
3	PhCH ₂ CSN(CH ₃)N:CHPh	CHCl ₃	3800	2.13	—	—	—	—	—
4	CH ₃ O-CS-NHN:C(CH ₃) ₂	Ethanol	3730	2.07	—	—	—	—	—
5	CH ₃ O-CS-NHN:CHPh	Heptane	—	—	3350	4.60	2450	3.76	4
6	CH ₃ S-CS-NHN:CHCH ₃	Ethanol	3080 ^a	2.78	3340	4.59	2010	4.24	—
7	CH ₃ S-CS-NHN:C(CH ₃) ₂	Heptane	—	—	2760	4.29	2030	4.17	—
8	CH ₃ S-CS-NHN:C(CH ₃) ₂	Ethanol	—	—	2750	4.32	2030	4.17	—
9	CH ₃ S-CS-NHN:CHPh	Ethanol	—	—	3140	4.48	2250	4.04	—
10	CH ₃ S-CS-NHN:C(CH ₃)COOH	Heptane	3500 ^a	2.13	2985	4.23	2735	4.09	5
11	CH ₃ S-CS-NHN:C(CH ₃) ₂	Ethanol	3450 ^a	2.2	2970	4.32	2720	4.11	—
12	CH ₃ S-CS-NHN:C(CH ₃) ₂	Heptane	3590	2.40	3020	4.29	2730	4.14	—
13	CH ₃ S-CS-NHN:C(CH ₃) ₂	CCl ₄	—	—	—	—	—	—	—
14	CH ₃ S-CS-NHN:C(CH ₃) ₂	Ethanol	—	—	3010	4.31	2710	4.08	—
15	CH ₃ S-CS-NHN:C(CH ₃) ₂	0.6 N NaOEt	—	—	2500	3.98	2290	3.97	—
16	CH ₃ S-CS-NHN:C(CH ₃) ₂	Heptane	4200 ^a	1.6	3150	4.28	2780	4.00	6
17	CH ₃ S-CS-NHN:C(CH ₃)COCH ₃	Ethanol	—	—	3220	4.27	2850 ^a	3.9	—
18	C ₂ H ₅ S-CS-NHN:C(CH ₃)COOH	Heptane	3850 ^a	2.40	3200	4.42	—	—	—
19	CH ₃ S-CS-NHN:CHPh	Ethanol	—	—	3240	4.42	2610	3.74	7
20	CH ₃ S-CS-NHN:C(CH ₃) ₂	Ethanol	—	—	3200	4.30	—	—	—
21	CH ₃ S-CS-NHN:CHPh	Heptane	—	—	3295	4.53	2310	4.11	—
22	CH ₃ S-CS-NHN:C(CH ₃) ₂	Ethanol	—	—	3320	4.56	—	—	—
23	CH ₃ S-CS-NHN:C(CH ₃) ₂	0.6 N NaOEt	—	—	3520	4.23	—	—	—
24	CH ₃ S-CS-NHN:C(CH ₃) ₂	Ethanol	—	—	3330	4.45	2320	3.77	6
25	CH ₃ S-CS-NHN:CH:CH:CHPh	Ethanol	—	—	3520	4.74	2160	4.16	10
26	CH ₃ S-CS-NHN:CH:CH:CHPh	Ethanol	—	—	3420	4.63	2550	3.74	10
27	CH ₃ S-CS-NHN:CH:CH:CHPh	Ethanol	—	—	3630	4.81	2680	4.28	—
28	CH ₃ S-CS-NHN:CH:CH:CHPh	Ethanol	—	—	3790	4.95	2760	4.30	—
29	CH ₃ S-CS-N(CH ₃)N:CH ₃	CCl ₄	3760	2.15	3015	4.39	—	—	5
30	CH ₃ S-CS-N(CH ₃)N:CH:CH:CHCH ₃	Ethanol	3550	2.21	2960	4.39	—	—	—
31	CH ₃ S-CS-N(CH ₃)N:CH:CH:CHCH ₃	Water	3500 ^a	2.1	2940	4.33	2420 ^a	3.65	—
32	CH ₃ S-CS-N(CH ₃)N:CH:CH:CHCH ₃	Heptane	—	—	3270	4.57	—	—	—
33	CH ₃ S-CS-N(CH ₃)N:CH:CH:CHCH ₃	Ethanol	—	—	3210	4.57	—	—	—
34	H ₂ N-CS-NHN:C(CH ₃) ₂	Ethanol	—	—	3330	4.56	—	—	—
35	H ₂ N-CS-NHN:C(CH ₃) ₂	Ethanol	—	—	2710	4.33	2285	3.85	5
36	H ₂ N-CS-NHN:C(CH ₃) ₂	Ethanol	—	—	3015	4.56	2460	4.01	8
37	H ₂ N-CS-NHN:CH:CH:CH-C ₃ H ₇	Ethanol	—	—	3070	4.54	—	—	8
38	PhCSNHN:CHPh	Heptane	—	—	3125	3.82	2370	4.20	9
39	Ph-CS-NHN:CH:CH:CHPh	Ethanol	—	—	3150	3.77	2360	4.15	9
40	Ph-CS-NHN:CH:CH:CHPh	Ethanol	—	—	3280	3.77	2390	4.23	9
41	Ph-CS-NHN:CH:CH:CHPh	Ethanol	—	—	3650	4.18	2660	4.32	10

^a) Shoulder.

Ultraviolet spectra. The absorption maxima and the corresponding $\log \epsilon$ values are recorded in Table 1. An inspection of the table reveals that the group R_1 has an influence similar to the one found in simple thioamides^{10,11} and also in N-acetylthioamides² and in thiohydrazides (Part III)¹². The wavelengths of the $\pi - \pi^*$ bands of the different derivatives of the same unconjugated carbonyl compound decrease in the order $R_1 = \text{Ph}, \text{PhCH}_2, \text{CH}_3\text{S}, \text{CH}_3\text{O}, \text{H}_2\text{N}$. This means that PhCH_2 (or CH_3) and CH_3S and also CH_3O and H_2N have been interchanged as compared with the previous sequences. The derivatives of the individual thiohydrazides show successive bathochromic shifts of the $\pi \rightarrow \pi^*$ bands on increasing conjugation in the carbonyl compound. The thiosemicarbazones and thiobenzhydrazones show no $n - \pi^*$ bands. In the other series, the acetone derivatives have their $n \rightarrow \pi^*$ bands at longer wavelengths than the corresponding thioamides, and the $n \rightarrow \pi^*$ bands of the mesityl oxide and diacetyl derivatives of methyl dithiocarbazate (8 and 9) appear at still longer wavelengths. Because of the enhanced intensity and width of the $\pi \rightarrow \pi^*$ bands, the $n \rightarrow \pi^*$ bands are obscured in the more extended conjugated systems.

The effect of a carbonyl group in conjugation is nearly the same as that of a vinyl group, since the diacetyl and pyruvic acid derivatives (9) and (10) have their $\pi \rightarrow \pi^*$ bands close to those of the crotonaldehyde and mesityl oxide derivatives (18) and (8).

The effect of methyl substitution in general is small. When substitution occurs on the nitrogen atom 2, no significant wavelength shifts are observed. Methyl substitution on the carbon atom of the azomethine group may cause small bathochromic shifts of the $\pi \rightarrow \pi^*$ bands (6, 7) or have an influence only on the absorption intensity (11, 12). In no case is found an effect of the same order of magnitude as for the $n \rightarrow \pi^*$ bands of the simple thioamides¹¹.

The effect of solvent polarity in most cases parallels the one found for simple thioamides. The $n \rightarrow \pi^*$ bands are shifted considerably towards shorter wavelengths with increasing solvent polarity, and the $\pi \rightarrow \pi^*$ bands, with few exceptions, undergo small shifts in the same direction under these circumstances.

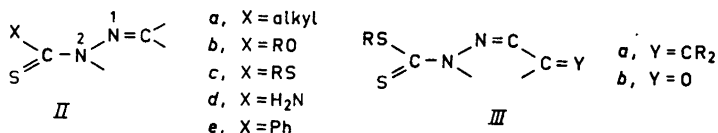
It may also be pointed out that whereas the intensity of the $\pi \rightarrow \pi^*$ bands in the other series increase considerably with increasing conjugation, the $\pi \rightarrow \pi^*$ bands of the thiobenzhydrazones show only a very moderate increase (23, 24, 25).

It is natural that the spectra of hydrazine derivatives of carbonyl compounds should have attracted the interest of spectroscopists. Most of the attention has been centered on semicarbazones and thiosemicarbazones and in particular on 2,4-dinitrophenylhydrazones. The effect of alkyl substitution is different in these classes of compound. The spectra of semicarbazones and thiosemicarbazones^{8,13} are very little affected by alkyl groups, and the positions of the $\pi \rightarrow \pi^*$ maxima are mainly determined by the degree of unsaturation in the carbonyl compound. On the other hand, in the spectra of 2,4-dinitrophenylhydrazones¹⁴ a methyl group attached to a double bond in the hydrazone may cause a bathochromic shifts of the $\pi \rightarrow \pi^*$ band of the order of $500-1000 \text{ cm}^{-1}$, which is of the same order of magnitude as the shifts caused by a new double bond ($1000-1500 \text{ cm}^{-1}$) and much smaller than the

shift caused by a new double bond in the semicarbazone-thiosemicarbazone series (about 3500 cm^{-1}). The different effect of double bonds has been commented on by Braude *et al.*¹⁴, who ascribe it to the lower "chromolatory" effect of the NH group in 2,4-dinitrophenylhydrazones as compared with the same group in semicarbazones and thiosemicarbazones. This may well be explained by a difference in hybridization. The NH group in 2,4-dinitrophenylhydrazones should be nearly sp^3 hybridized like the amino group in aniline, whereas in thiohydrazones like in thioamides¹⁵ it should be sp^2 hybridized. In the latter case the overlap of the lone pair orbital on the nitrogen atom with the two parts of the conjugated system should be better and therefore also its ability to transmit the conjugation.

A further difference is found in the effect of a carbonyl group in conjugation with the azomethine group. In the thiohydrazone series this causes a bathochromic shift of the same magnitude as a carbon-carbon double bond, whereas in the 2,4-dinitrophenylhydrazone series a hypsochromic shift is obtained¹⁶.

LCAO—MO calculations. In order to study the influence of conjugation of a thioamide group with an azomethine group on the energy levels, calculations have been performed for the systems (II, a—e). Furthermore, the systems (III, a, b)



have been investigated. The parameters for the thioamide group are the same as those proposed by Janssen¹² and used in the previous parts of this series (summarized in Ref.², Table 3). The resonance integral for the nitrogen-nitrogen bond was estimated with the aid of the assumption due to Mulliken¹⁷ that the resonance and overlap integrals for a bond are proportional. The β_{NN} value was determined in relation to the β_{CN} value of 1.2β for the carbon-nitrogen bond in the thioamide moiety. The length of the carbon-nitrogen bond was taken to be 1.32 \AA as in thioacetamide¹⁵. The nitrogen-nitrogen bond, between two sp^2 hybridized nitrogen atoms, was assumed to be equal to the nitrogen-nitrogen bond in diformylhydrazine, which has been determined by Tomiie¹⁸ to be 1.39 \AA . The carbon-nitrogen and nitrogen-nitrogen overlap integrals were determined from the tables of Mulliken *et al.*¹⁹, and were found to have the ratio 1.27:1.0. Therefore the values 1.0β and 0.9β were tried for β_{NN} . The nitrogen atom 1 (II) only gives up one π electron to the delocalized bond, whereas two come from the other nitrogen atom. The former atom therefore must have a lower value for the coefficient of β in the Coulomb integral than the latter. The parameter for the secondary nitrogen atom 2 is $\alpha + 1.5\beta$, and Gerson and Heilbronner²⁰ have shown that $\alpha + 0.5\beta$ is a reasonable value for the sp^2 hybridized nitrogen atoms in an azo group. These parameters are the same as those proposed by Streitwieser²¹. The azomethine carbon-nitrogen bond was assumed to be a nearly pure double bond, which is supported by the calculated bond order (Fig. 1). The bond length was taken to be 1.27 \AA as in the oximes,²² and in the same way as for the nitrogen-nitrogen

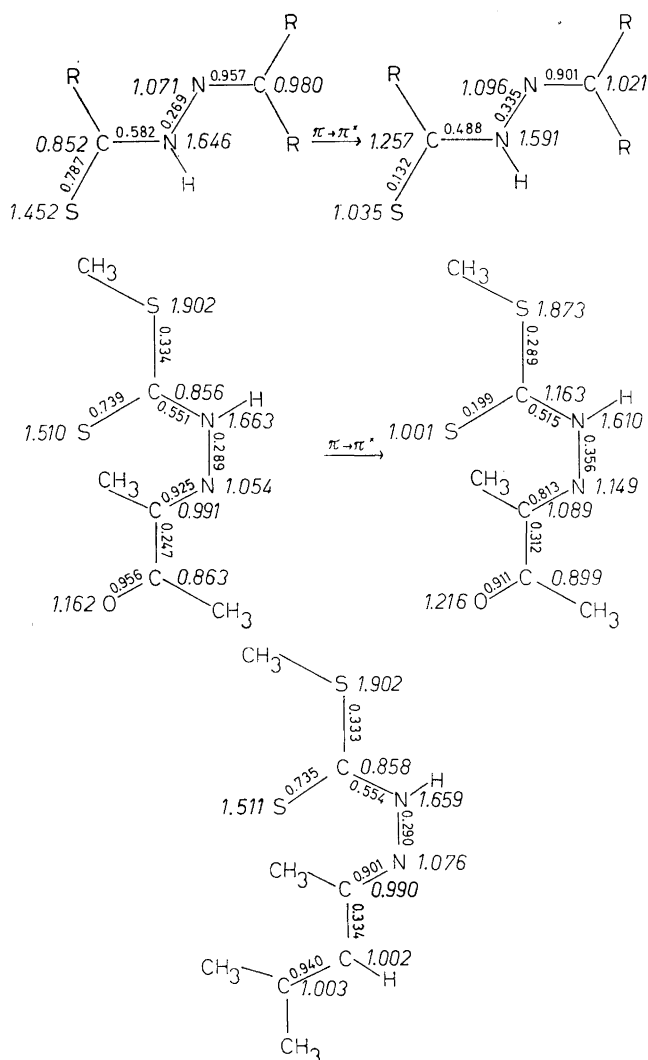


Fig. 1. π Electron distribution and π bond orders for ground and excited states of (II a), (IIIa), and (III b).

bond a resonance integral of 1.4β was derived. For the carbon atoms and carbon-carbon bonds the parameters α and β were used. For the carbonyl group the same parameters, $\alpha + 1.1 \beta$ and 1.8β were used as in Ref.² The mean value technique described in Ref.² was found to give convergent results in the systems tried. The energy levels and transition energies for the systems (II) and (III) are recorded in Table 2, and some charge distributions and bond orders for ground and excited states are shown in Figure 1.

Table 2. Energy levels and transition energies for the systems (II) and (III). $\beta_{\text{NN}} = 1.0 \beta$

	II X = alkyl	II X = CH ₃ O	II X = CH ₃ S	II X = H ₂ N	II X = Ph	III Y = CR ₂	III Y = O
Antibonding levels	$a - 2.086 \beta$ $a - 1.122 \beta$	$a - 2.126 \beta$ $a - 1.440 \beta$	$a - 2.097 \beta$ $a - 1.233 \beta$	$a - 2.133 \beta$ $a - 1.494 \beta$	$a - 2.788 \beta$ $a - 2.110 \beta$ $a - 1.713 \beta$ $a - 1.333 \beta$ $a - 0.764 \beta$	$a - 2.482 \beta$ $a - 1.447 \beta$ $a - 1.043 \beta$	$a - 2.756 \beta$ $a - 1.685 \beta$ $a - 1.158 \beta$
Nonbonding level	$a + 0.048 \beta$	$a - 0.106 \beta$	$a - 0.065 \beta$	$a - 0.141 \beta$	$a + 0.066 \beta$	$a - 0.011 \beta$	$a - 0.010 \beta$
Bonding levels	$a + 0.394 \beta$ $a + 1.915 \beta$ $a + 3.399 \beta$	$a + 0.165 \beta$ $a + 1.653 \beta$ $a + 3.015 \beta$ $a + 4.233 \beta$	$a + 0.307 \beta$ $a + 1.130 \beta$ $a + 2.004 \beta$ $a + 3.389 \beta$	$a + 0.094 \beta$ $a + 1.430 \beta$ $a + 2.519 \beta$ $a + 3.585 \beta$	$a + 0.371 \beta$ $a + 1.311 \beta$ $a + 1.347 \beta$ $a + 2.000 \beta$ $a + 2.710 \beta$ $a + 3.468 \beta$	$a + 0.274 \beta$ $a + 1.032 \beta$ $a + 1.396 \beta$ $a + 2.321 \beta$ $a + 3.451 \beta$	$a + 0.284 \beta$ $a + 1.146 \beta$ $a + 1.921 \beta$ $a + 3.216 \beta$ $a + 3.633 \beta$
$\Delta E_{n \rightarrow \pi}$	-1.170β	-1.334β	-1.168β	-1.353β	-0.830β	-1.032β	-1.148β
$\Delta E_{\pi \rightarrow \pi}$	-1.516β	-1.605β	-1.540β	-1.588β	-1.135β	-1.317β	-1.442β

DISCUSSION

The calculated $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies (Table 2) are smaller than for the corresponding thioamides both when β_{NN} is 0.9β and 1.0β , and this is in agreement with the experimental results (Table 3). As could have been expected, the higher absolute value of the resonance integral for the nitrogen-nitrogen bond, corresponding to a more efficient conjugation, gives lower

Table 3. $\Delta E_{\text{Thioamide}} / \Delta E_{\text{Thiohydrazone}}$

System	$n \rightarrow \pi^*$			$\pi \rightarrow \pi^*$		
	Calc.		Found ^a	Calc.		Found ^a
β_{NN}	0.9β	1.0β		0.9β	1.0β	
IIa	1.05	1.06	1.04	1.04	1.05	1.12
IIb	1.07	1.08	1.06 ^b	1.06	1.07	1.14
IIc	1.10	1.11	1.01	1.02	1.03	1.08
IId	1.08	1.09	—	1.06	1.07	1.12
IIe	1.02	1.02	—	1.02	1.02	1.05
IIIa	1.25	1.26	1.18 ^b	1.20	1.21	1.17
IIIb	1.12	1.13	1.08 ^b	1.09	1.10	1.15

^a From non-polar solvents.

^b Shoulder.

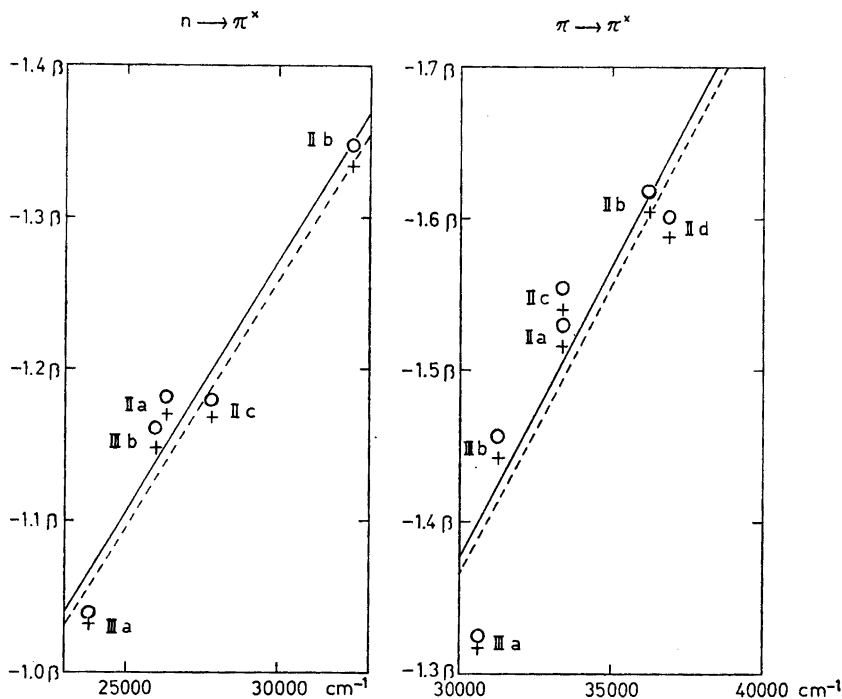


Fig. 2. Plots of calculated transition energies versus wavenumbers of the extinction maxima for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. (O —, $\beta_{NN} = 0.9\beta$; + ----, $\beta_{NN} = 1.0\beta$).

transition energies, but the differences are small. For the $n \rightarrow \pi^*$ transitions the value 0.9β gives slightly better agreement with the experimental results than does 1.0β , but the experimental values are few and somewhat uncertain, since some of the bands appear as shoulders, and therefore no great weight can be given to this evidence. For the $\pi \rightarrow \pi^*$ transitions the value 1.0β gives the better agreement.

According to the calculations the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies are smaller for a dithiocarbazate derivative of an α,β -unsaturated carbonyl compound than for a derivative of an α -dicarbonyl compound. This is in agreement with the experimental results. The influence of the group X in the systems (II, a–d) is also fairly well reproduced by the LCAO–MO model. The calculated transition energies for the systems (II, a–d) and (III, a and b) have been plotted against the wavenumbers of the corresponding absorption bands (Fig. 2). The best straight lines have been computed by the method of least squares. From their slopes spectroscopic β values have been calculated (Table 4), which are in reasonable agreement with the values of 23 000 and 32 000 cm^{-1} proposed by Platt²³. The value for the thiobenzhydrazone (II e) has been omitted, since this system is too different from the simpler (II, a–d) to allow a quantitative comparison. On the whole, the agreement

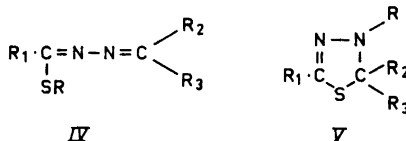
Table 4. Spectroscopic β values (cm^{-1}).

	$\beta_{\text{NN}} = 0.9 \beta$	$\beta_{\text{NN}} = 1.0 \beta$
$n \rightarrow \pi^*$	30 500	31 100
$\pi \rightarrow \pi^*$	26 200	26 400

between calculated and experimental transition energies is sufficiently good to lend strong support to the assignment of the low-intensity absorption band to a $n \rightarrow \pi^*$ transition and the long-wavelength, high-intensity absorption band to a $\pi \rightarrow \pi^*$ transition. Thereby the arguments for the assignments made in Ref.¹ are also strengthened.

The blue shift of the $n \rightarrow \pi^*$ bands with increasing solvent polarity is in agreement with the general behaviour of this type of band, as has been discussed in the previous parts of this series. Most of the $\pi \rightarrow \pi^*$ bands show small blue shifts under the same conditions, and this can be explained in the same way as for the simple thioamides¹. As is seen in Fig. 1; the polarity of the thione group is reversed by a $\pi \rightarrow \pi^*$ transition, just as it is for thioacetamide and thiobenzamide. It may be worth noticing that the $\pi \rightarrow \pi^*$ band of the diacetyl derivative (9) is shifted towards the red with increasing solvent polarity. Unfortunately, the $\pi \rightarrow \pi^*$ band is considerably broadened in ethanol and obscures the $n \rightarrow \pi^*$ band. Therefore the solvent dependence of the latter band cannot be studied, but it is possible that the behaviour of the $\pi - \pi^*$ band can be ascribed to preferential solvation at the carbonyl group, as was proposed to explain similar shifts of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands of N-acetylthioamides². As is seen in Fig. 1, the charge on the oxygen atom is increased by the excitation.

Structure of the thiohydrazones. Though the structure (I) is the most likely one for thiohydrazones, other possibilities exist when $R_2 = \text{H}$. The imidothiol structure (IV, $R = \text{H}$) could be expected to give a more favourable conjugation, especially in more extended conjugated systems. The thiadiazoline structure (V, $R = \text{H}$) is also possible and may be taken into account in order to explain the facile oxidation of several benzaldehyde thiohydrazones to 1,3,4-thiadiazoles^{6,24,25}.



The presence of these isomers cannot be excluded on the basis of the available evidence, but it is very unlikely that the absorption bands discussed above are due to either of them. Compounds with the structure (V, $R = \text{CH}_2\text{Ph}$) have been described previously²⁶. The carbon atom from the carbonyl group is sp^3 hybridized, and thus the chromophores in the carbonyl compound

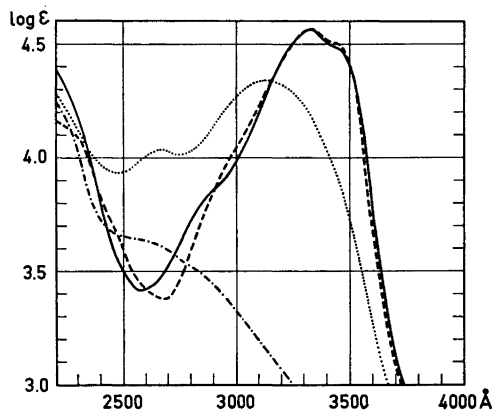
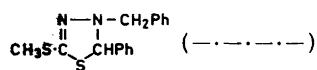


Fig. 3. Ultraviolet absorption spectra in ethanol of $\text{CH}_3\text{S-CS-NHN:CHPh}$ (—), $\text{CH}_3\text{S-CS-N(CH}_3\text{)N:CHPh}$ (---), $\text{C}_2\text{H}_5\text{S-C(SCH}_2\text{Ph):N-N:CHPh}$ (.....), and



moiety are effectively isolated from the other chromophores in the molecule. In harmony with this the thiadiazolines were found to be without selective absorption in the near ultraviolet region (Fig. 3). Therefore the tautomers (V, R = H) cannot be responsible for the absorption bands under discussion.

Compounds of the type (IV, R = alkyl) have not been obtained in a crystalline state from derivatives of simple carbonyl compounds. Benzaldehyde and *p*-nitrobenzaldehyde derivatives have been obtained crystalline, and they absorb at somewhat shorter wavelengths and with lower intensity than the isomers (I, R₂ = CH₃). However, the spectra of some of the free thiohydrazones are so characteristically similar to those of the 2-methyl analogues (Figure 3) that the isomers (IV, R = H) must be without importance. This conclusion

Table 5.

Compound No.	Solvent	M.p.	Formula	C		H		N		S	
				found	calc.	found	calc.	found	calc.	found	calc.
2	Heptane	74–75°	C ₁₁ H ₁₄ N ₂ S	64.4	64.0	7.13	6.84	13.5	13.6	15.6	15.5
3	Heptane	104–105°	C ₁₆ H ₁₆ N ₂ S	71.6	71.6	5.99	6.01	10.4	10.3	12.0	11.9
4	Toluene-heptane	99–100°	C ₆ H ₁₀ N ₂ OS	41.1	40.9	6.89	6.84	19.2	19.3	21.9	21.8
5	Toluene	124.5–125°	C ₉ H ₁₀ N ₂ OS	55.6	55.4	5.19	5.27	14.4	14.3	16.5	16.4
7	Toluene-heptane	117–118°	C ₆ H ₁₀ N ₂ S ₂	37.2	37.0	6.10	6.22	17.1	17.3	39.5	39.5
8	Petroleum ether	73.5–74°	C ₈ H ₁₄ N ₂ S ₂	47.4	47.5	7.01	6.97	13.9	13.9	31.6	31.7
9	Ethanol	152.0–152.5°	C ₆ H ₁₀ N ₂ OS ₂	38.0	37.9	5.33	5.30	14.7	14.7	33.8	33.7
15	Butanol	199–200°	C ₉ H ₉ N ₃ O ₂ S ₂	42.4	42.3	3.44	3.55	16.3	16.5	24.9	25.1
16	Ethanol	177–178°	C ₁₁ H ₁₅ N ₃ O ₂	52.4	52.1	6.07	5.97	16.5	16.6	25.1	25.3
18	Petroleum ether	63–64°	C ₇ H ₁₂ N ₂ S ₂	44.6	44.8	6.43	6.48	14.9	14.8	34.1	33.6

is also supported by the infrared spectra in chloroform of the free thiohydrazones, which show no absorption bands in the S—H stretching region around 2500 cm^{-1} , but strong narrow bands around 3350 cm^{-1} and broad bands at slightly lower frequency, corresponding to NH stretching modes of monomers and associated forms.

EXPERIMENTAL

A number of the thiohydrazones used in this work are new. They were in general prepared by reaction between equimolecular amounts of thiohydrazide and carbonyl compound in ethanol. If the products did not separate spontaneously, they were precipitated by the addition of water, and in all cases they were purified by repeated recrystallizations from suitable solvents or solvent mixtures. The melting points, solvents for recrystallization, and analytical results are summarized in Table 5.

Methyl thioncarbazate does not seem to have been described earlier. For the preparation of compounds (4) and (5) a water solution was used, which was obtained by reaction of the sodium salt of O-methyl-S-carboxymethyl-thionthiolcarbonate²⁷ with hydrazine.

Literature references for the known thiohydrazones are given in Table 1. The recording of the ultraviolet spectra and the numerical calculations were performed as in the previous parts of this series.

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