

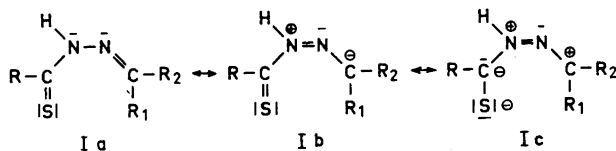
## The Electronic Spectra of Thioamides and Thiohydrazides Part V\*. N-Acetylthiohydrazides and N-Phenylthio- hydrazides. A Comparison with Thiohydrazones

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The ultraviolet absorption spectra of a series of N-acetylthiohydrazides and N-phenylthiohydrazides have been recorded in polar and nonpolar solvents. The spectra in most cases are rather similar to those of the parent thioamides, indicating only a rather weak conjugation over the nitrogen-nitrogen bond. The energy levels and charge distributions have been calculated by a LCAO-MO method. For the acetylthiohydrazides the calculated shifts are found to be in the right direction and of the right order of magnitude, but for the  $n \rightarrow \pi^*$  bands of the phenylthiohydrazides divergent results are obtained, which is ascribed to a higher electron repulsion. The effect of solvent polarity is correlated with the charge distribution in the ground and excited states. The possible existence of tautomeric forms of the acetylthiohydrazides is discussed. The extra  $\pi$  electron stabilisations due to conjugation between the thioamide parts and the acetamide and aniline parts in acetylthiohydrazides and phenylthiohydrazides have been calculated and found to be smaller than the corresponding stabilisations in thiohydrazones and N-acetylthioamides.

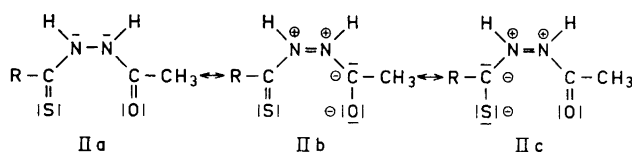
In the previous part of this series<sup>1</sup> a comparison was made between calculated and experimental  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transition energies for a number of thiohydrazones (I). A considerable conjugation between the thioamide and azomethine groups was observed, in agreement with the calculations. In the simple resonance theory this is explained by a resonance which also



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includes the valence bond structures (Ib) and the less probable (Ic), both of which give some double bond character to the N—N bond. A structure similar to (Ib) has previously been proposed to explain the difference in cyclization tendency between carboxymethyl dithiocarbazates and their hydrazones<sup>2</sup>. The importance of structure (Ib) increases with conjugation, since, if  $|\beta_{NN}|$  is increased, the calculations give an increasing positive charge on the thioamide nitrogen atom and a decreasing positive charge on the azomethine carbon atom, and at the same time the N—N bond order is increased.

In acetylthiohydrazides (II) the valence bond structures which give double bond character to the N—N bond are high energy structures, which violate the adjacent charge rule<sup>3</sup>, and therefore the conjugation between the thioamide and amide parts of the molecule can be expected to be weak.



A still weaker conjugation can be expected to occur in 1-phenylthiohydrazides (III), where a thioamide and an aniline part are combined and the overlap of the lone pair orbitals of the nitrogen atoms is inferior to that for the same bond in the acetylthiohydrazides. In order to investigate the effect of conjugation on the ultraviolet spectra, a series of N-acetylthiohydrazides (II, R = PhCH<sub>2</sub>, CH<sub>3</sub>O, CH<sub>3</sub>S, H<sub>2</sub>N, and Ph) and N-phenylthiohydrazides (III, R the same as above) have now been prepared.

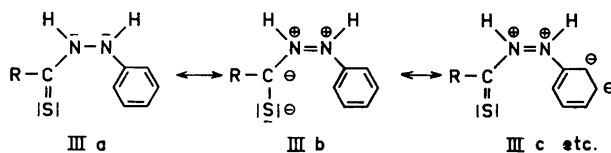


Table 1. Ultraviolet spectra of R·CS·NHNHCOCH<sub>3</sub>

R	Solvent	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$			
		$\lambda_{\max} \text{ \AA}$	$\log \epsilon$	$\lambda_{\max} \text{ \AA}$	$\log \epsilon$	$\lambda_{\max} \text{ \AA}$	$\log \epsilon$
PhCH <sub>2</sub>	Heptane	—	—	2890	4.10	—	—
	Ethanol	3350 <sup>a</sup>	1.94	2770	4.15	—	—
CH <sub>3</sub> O	Heptane	—	—	2570	4.12	—	—
	Ethanol	—	—	2445	4.12	—	—
CH <sub>3</sub> S	Heptane	—	—	2825	4.15	2700 <sup>a</sup>	4.14
	Ethanol	3350 <sup>a</sup>	1.8	2780	4.09	2465	3.97
H <sub>2</sub> N	Ethanol	—	—	2465	4.10	—	—
Ph	Heptane	—	—	3140	3.88	2630	4.06
	Ethanol	3780 <sup>a</sup>	2.30	3000	3.87	2450	4.12

<sup>a</sup> Shoulder

*Ultraviolet spectra.* It appears that the strong absorption bands of the acetylthiohydrazides fall at somewhat longer wavelengths than the same bands of the corresponding simple thioamides (Table 1). These strong bands in most cases undergo considerable hypsochromic shifts with increasing solvent polarity. Only three of the acetylthiohydrazides (II, R = PhCH<sub>2</sub>, CH<sub>3</sub>S, and Ph) show  $n \rightarrow \pi^*$  bands as shoulders in ethanol, whereas in heptane these low-intensity bands are shifted to shorter wavelengths and are completely covered by the strong bands.

Table 2. Ultraviolet spectra of R-CS-NHNHPh

R	Solvent	$\pi \rightarrow \pi^*$						Ref.
		$\lambda_{\max} \text{Å}$	$\log \epsilon$	$\lambda_{\max} \text{Å}$	$\log \epsilon$	$\lambda_{\max} \text{Å}$	$\log \epsilon$	
PhCH <sub>2</sub>	Heptane <sup>a</sup>	2870	4.17	2330	4.36	—	—	18
	Ethanol	2890	4.02	2350	4.16	—	—	
CH <sub>3</sub> O	Heptane <sup>a</sup>	2510	4.03	2285	4.11	—	—	19
	Ethanol	2470	4.17	2350 <sup>b</sup>	4.11	—	—	
CH <sub>3</sub> S	Heptane <sup>a</sup>	2830	4.13	2380 <sup>b</sup>	4.15	—	—	20
	Ethanol	2795	4.10	2415	4.09	—	—	
H <sub>2</sub> N	Methylene dichloride	2540	4.29	—	—	—	—	21
	Ethanol	2460	4.31	—	—	—	—	
Ph	Heptane	3330	3.84	2595	3.63	2410	4.08	22
	Ethanol	3250	3.85	—	—	2400	4.24	

<sup>a</sup> With 0.3 % of methylene dichloride

<sup>b</sup> Shoulder

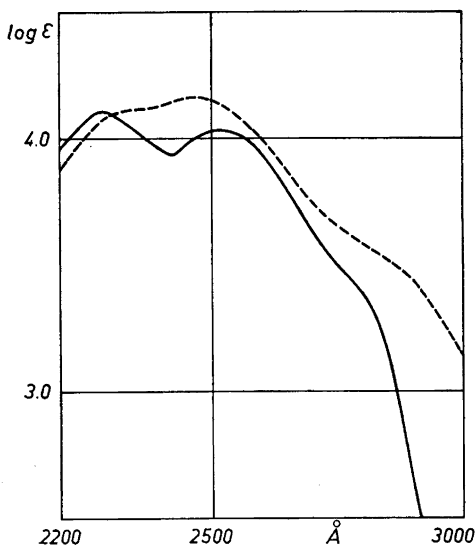


Fig. 1. Ultraviolet spectrum of methyl 3-phenylthioncarbazate (III, R = CH<sub>3</sub>O) in heptane (—) and in ethanol (-----).

The phenylthiohydrazides also show strong bands, more or less displaced towards the red as compared with the thioamide bands (Table 2). The greatest shift ( $3500\text{ cm}^{-1}$ ) is shown by phenylthiobenzhydrazide, the smallest one (*ca.*  $100\text{ cm}^{-1}$ ) by methyl 3-phenyldithiocarbazate. In the spectra of methyl 3-phenylthiocarbazate (III, R =  $\text{CH}_3\text{O}$ ) and 1-phenylthiosemicarbazide (III, R =  $\text{H}_2\text{N}$ ) weak shoulders appear at about  $2800\text{ \AA}$  with  $\epsilon$  *ca.* 2000 (Fig. 1). These are probably due to transitions in the aniline chromophore, since aniline has  $\lambda_{\text{max}}$ :  $2800\text{ \AA}$  with  $\epsilon$ :  $1430^4$ . The strong bands in most cases undergo hypsochromic shifts with increasing solvent polarity. The one exception is 2-phenyl-thiophenylacetylhydrazide (III, R =  $\text{PhCH}_2$ ), and there the deviation may be due to superposition of the band from the aniline chromophore. None of these compounds showed a  $n \rightarrow \pi^*$  band.

*Calculations.* The energy levels,  $\pi$  bond orders and  $\pi$  electron distributions in the acetylthiohydrazides and phenylthiohydrazides were calculated by the LCAO-MO method used in the previous parts of this series. The parameters for the amide and thioamide groups were the same as in the previous parts (summarized in Ref.<sup>5</sup>). The resonance integral for the N—N bond in the acetylthiohydrazides should be about the same as for the thiohydrazones<sup>1</sup>, since the bond combines two  $\text{sp}^2$  hybridized nitrogen atoms in both cases. In Ref.<sup>1</sup> the  $\beta_{\text{NN}}$  values  $0.9\beta$  and  $1.0\beta$  were tried, and in general the transition energies calculated with the latter value gave the closest fit with the experimental results, and therefore it has also been used in this work.

For the phenylthiohydrazides the Coulomb integral of the aniline nitrogen atom was given the value  $\alpha + 0.9\beta$ , as was discussed in Part III<sup>6</sup> for the thiohydrazides. As there, the resonance integral for the N—N bond was given the value  $0.5\beta$ . The resonance integral for the C—N bond in the aniline moiety,  $0.6\beta$ , was taken from the work of Fischer-Hjalmars<sup>7</sup>, and it seems reasonable with regard to the bond length ( $1.39\text{ \AA}$ ) and the  $\text{sp}^3$  hybridization of the nitrogen atom, which will result in an inferior overlapping of its lone pair orbital with the neighbouring  $\pi$  orbitals.

The mean value technique described in Ref.<sup>5</sup> gave convergent results in all these systems. The calculated energy levels and transition energies are found in Table 3, and the  $\pi$  bond orders and  $\pi$  electron distributions of ground and excited states of the simplest systems are shown in Fig. 2.

## DISCUSSION

The results of the calculations on the acetylthiohydrazides indicate that some interaction between the amide and thioamide parts of the molecule occurs. The energies of the  $\pi \rightarrow \pi^*$  transitions are found to be slightly smaller, and those for the  $n \rightarrow \pi^*$  transitions mostly slightly larger, than those for the corresponding thioamide transitions, and this is in harmony with the experimental results (Table 4). A satisfactory description of the acetylthiohydrazides shall also explain the large hypsochromic shifts of the  $\pi \rightarrow \pi^*$  bands and the bathochromic shifts of the  $n \rightarrow \pi^*$  bands with increasing solvent polarity. The first shift requires that the ground state in the acetylthiohydrazides is more stabilized by increasing solvation relative to the excited state than in the thio-

Table 3. Energy levels and transition energies for acetyl- and phenylthiohydrazides. (m) in  $\epsilon_j = \alpha + m_j\beta$  is tabulated)

	II R = Alkyl	II R = CH <sub>3</sub> O	II R = CH <sub>3</sub> S	II R = H <sub>2</sub> N	II R = Ph	III R = Alkyl	III R = CH <sub>3</sub> O	III R = CH <sub>3</sub> S	III R = H <sub>2</sub> N	III R = Ph
Antibonding orbitals					-2.788					-3.150
					-2.478					-2.693
	-2.480	-2.484	-2.481	-2.484	-1.814	-2.693	-2.693	-2.693	-2.693	-1.806
-1.279	-1.606	-1.388	-1.658	-0.840	-1.351	-1.351	-1.351	-1.351	-1.351	-1.398
										-1.642
										-1.395
										-1.351
										-0.811
Nonbonding orbitals	-0.022	-0.151	-0.075	-0.179	±0.000	+0.010	-0.134	-0.054	-0.165	+0.031
Bonding orbitals	+0.223	+0.063	+0.149	+0.014	+0.224	+0.297	+0.109	+0.207	+0.050	+0.291
	+1.278	+1.066	+0.939	+0.938	+1.046	+0.780	+0.707	+0.708	+0.677	+0.739
	+2.967	+2.588	+1.512	+2.139	+1.345	+1.322	+1.322	+1.219	+1.322	+1.322
	+3.891	+3.711	+2.985	+3.242	+1.617	+1.550	+1.517	+1.322	+1.471	+1.347
		+4.263	+3.884	+3.909	+2.615	+2.677	+2.373	+1.575	+1.915	+1.371
				+3.107	+2.952	+2.713	+2.681	+2.697	+1.600	
				+3.899		+4.184	+2.982	+3.348	+2.551	
									+2.703	
										+3.150
$\Delta E_{n \rightarrow \pi}$	-1.257 $\beta$	-1.455 $\beta$	-1.313 $\beta$	-1.479 $\beta$	-0.840 $\beta$	-1.239 $\beta$	-1.453 $\beta$	-1.286 $\beta$	-1.477 $\beta$	-0.842 $\beta$
$\Delta E_{\pi \rightarrow \pi}$	-1.502 $\beta$	-1.669 $\beta$	-1.537 $\beta$	-1.676 $\beta$	-1.069 $\beta$	-1.526 $\beta$	-1.696 $\beta$	-1.543 $\beta$	-1.692 $\beta$	-1.102 $\beta$

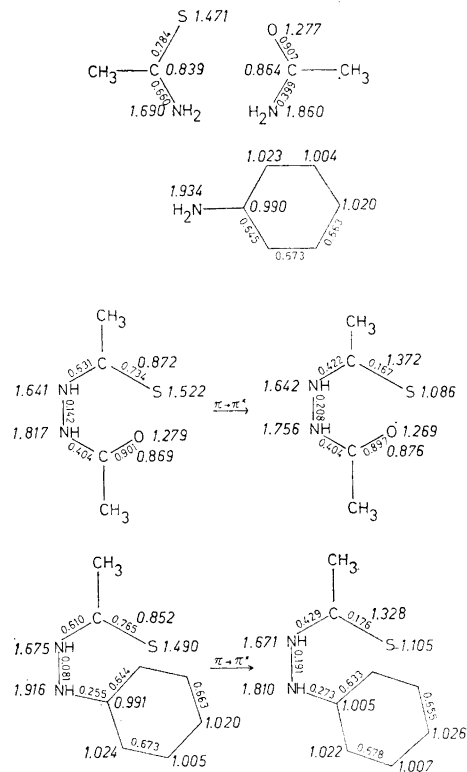


Fig. 2. Calculated  $\pi$  electron distributions and bond orders for the ground states of acetamide, thioacetamide, and aniline, and of the ground state and first excited state of a simple N-acetylthiohydrazide and N-phenylthiohydrazide.

amides. This may be explained by the assumption that the carbonyl and thiocarbonyl groups are independently solvated, and that the solvation of both groups is decreased by the excitation. The charge diagram (Fig. 2) shows that the electron density is decreased both at the sulphur and at the oxygen atom on excitation, and this should diminish their basicity and thus the energy of solvation. The total decrease should be greater than for thioamides, where only the thiocarbonyl group is affected.

The redshift of the  $n \rightarrow \pi^*$  bands with increasing solvation has previously been observed in the spectra of the N-acetylthioamides<sup>5</sup>, and there it was explained by a preferential solvation at the carbonyl group. A similar effect may explain the same type of shift here. The arguments put forward for the greater energy of solvation at the carbonyl group than at the thiocarbonyl group are equally valid here. In a  $n \rightarrow \pi^*$  transition an electron from the lone pair on the sulphur atom is promoted to an antibonding  $\pi$  orbital, and it is shared by all atoms in the delocalized system. Therefore, the electron density

Table 4.  $\Delta E_{\text{thioamide}} / \Delta E_{\text{thiohydrazide}}$  in non-polar solvent.

R	II				III			
	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$		$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	
	calc.	found	calc.	found	calc.	found	calc.	found
PbCH <sub>2</sub>	0.985	—	1.063	1.074	0.999	—	1.047	1.067
CH <sub>3</sub> O	0.989	—	1.025	1.060	0.990	—	1.009	1.035
CH <sub>3</sub> S	0.986	—	1.036	1.014	1.007	—	1.032	1.014
H <sub>2</sub> N	0.993	—	1.017	—	0.995	—	1.005	1.054
Ph	1.007	—	1.091	1.054	1.005	—	1.048	1.107

on the oxygen atom is also increased, and the energy of solvation at this point should also be increased. If this gain more than balances the loss at the sulphur atom, the observed spectral shift is explained. It must be emphasized that solvation, and in particular hydrogen bonding, in the excited state is not optimal, since according to the Franck-Condon principle the nuclei cannot rearrange during the transition to meet the requirements of the changed polarity<sup>8</sup>.

The  $\pi \rightarrow \pi^*$  transition energies calculated for the phenylthiohydrazides are somewhat smaller than for the corresponding thioamides, and the  $n \rightarrow \pi^*$  transition energies are practically unchanged (Table 4). For methyl 3-phenyl-

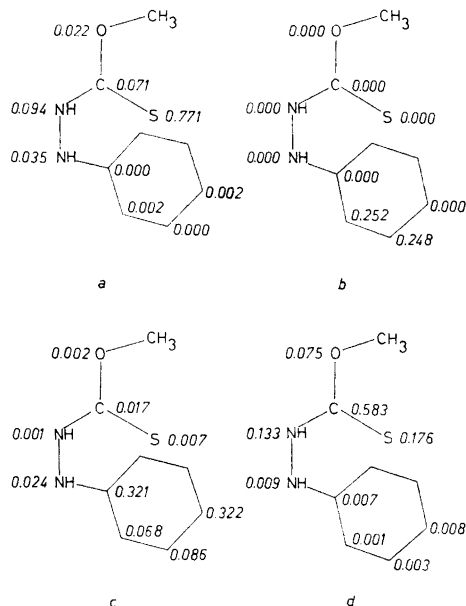


Fig. 3. Calculated distributions of one  $\pi$  electron in the highest occupied and three first excited orbitals of methyl 3-phenylthioncarbazate (III, R = CH<sub>3</sub>O).

thioncarbazate (III, R = CH<sub>3</sub>O) and 1-phenylthiosemicarbazide (III, R = H<sub>2</sub>N) the lowest  $\pi \rightarrow \pi^*$  transitions have not been chosen for the correlation, since they occur between orbitals which are localized in quite different parts of the molecule (Fig. 3) and should therefore occur with low probability. The transition chosen for the correlation are those between orbitals localized in the thioamide group. For the other thiohydrazides these are the lowest transitions. Experimentally, small bathochromic shifts of the  $\pi \rightarrow \pi^*$  bands are observed, but no  $n \rightarrow \pi^*$  bands appear, and it is obvious that the  $n \rightarrow \pi^*$  transition energies are considerably greater than for the corresponding thioamides, which is at variance with the results of the calculations. A similar discrepancy was observed in the case of the thiohydrazides<sup>6</sup>, where it was tentatively explained as the result of electron repulsion in excess of what is found in the thioamides. A similar explanation may be valid for the phenylthiohydrazides. The effect of solvent polarity on the positions of the  $\pi \rightarrow \pi^*$  bands in most cases parallels the one found for thioamides, and this is in agreement with the view that the transition is mostly localized in the thioamide part of the molecule.

No thermochemical data are at present available to estimate the effect of conjugation in the ground state, but it is of interest to compare the additional stabilizations caused by the interaction over the N—N bond as it is obtained by subtracting the sums of the calculated  $\pi$  electron energies of the thioamide, resp. azomethine, acetamide, and aniline parts from the calculated total  $\pi$  electron energies for thiohydrazones (I), acetylthiohydrazides (II), and phenylthiohydrazides (III). The total  $\pi$  electron energies and the differences are found in Table 5. It can be seen that the stabilization of the thiohydrazones is very uniform and amounts to about  $-0.3 \beta$ . With a  $\beta$  value of about  $-20$  kcal/mole, this means a stabilization of about 6 kcal/mole. For the acetylthiohydrazides the corresponding values are between  $-0.16 \beta$  and  $-0.19 \beta$  (3–4 kcal/mole), and for the phenylthiohydrazides between  $-0.04 \beta$  and  $-0.06 \beta$  (0.8–1.2 kcal/mole), *i.e.* almost insignificant. These values probably fall in the right order, and they give the same order of ground state stabilization as can be

Table 5. Calculated  $\pi$  electron energies ( $\Sigma E$ ) and extra stabilization energies ( $\Delta E$ ) in units of  $-\beta$ . The *a* terms are omitted, since they cancel in  $\Delta E$ .

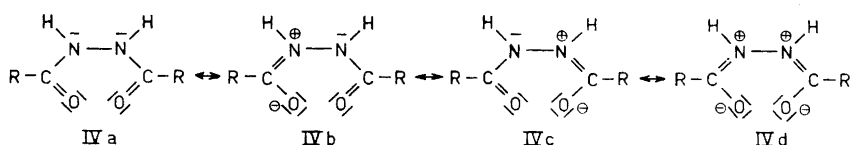
R	Thioamide	I		II		III		N-Acetylthioamide			$\Sigma E$
	$\Sigma E$	$\Sigma E$	$\Delta E$	$\Sigma E$	$\Delta E$	$\Sigma E$	$\Delta E$	$\Sigma E$	$\Delta E$		
Alkyl	6.416	11.416	0.290	16.718	0.190	19.156	0.064	13.362	0.406	Acetamide	10.112
CH <sub>3</sub> O	13.126	18.132	0.296	23.382	0.144	25.850	0.048	20.092	0.426	> C = N—	4.710
CH <sub>3</sub> S	8.662	13.660	0.288	18.938	0.164	21.388	0.050	15.624	0.422	Aniline	12.676
H <sub>2</sub> N	10.246	15.256	0.300	20.484	0.126	22.960	0.038	17.224	0.438	> C=O	6.540
Ph	17.410	22.414	0.294	27.706	0.184	30.148	0.062	—	—		



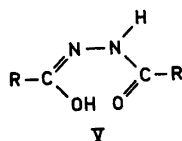
reached by the qualitative resonance arguments discussed in the introduction. It can be mentioned that the stabilization energies for the conjugation of thioamide groups with a carbonyl group in the N-acetylthioamides fall between  $-0.41 \beta$  and  $-0.44 \beta$  (8.2–8.8 kcal/mole), indicating a more efficient conjugation.

#### THE STRUCTURE OF THE ACETYLTHTIOHYDRAZIDES

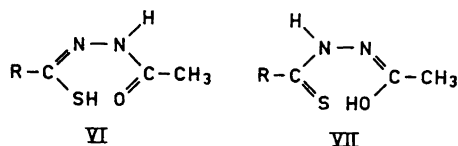
Arndt *et al.*<sup>9,10</sup> discussed the structure of the diacylhydrazines (IV) and came to the conclusion that they occur as the monoimidol tautomers (V) in many cases, especially when R is aliphatic or aromatic but not when R is an amino group.



The reason for this should be the unfavourable charge distribution in (IV), caused by the contribution of the resonance structure (IVd), and termed the "dication effect". The same effect should be at work in the acetylthiohydrazides, particularly as the charge separation in thioamides is greater than in



amides (Fig. 2), and consequently the acetylthioamides should occur in either of the forms (VI) or (VII). However, the infrared spectra of the acetylthiohydrazides give no indication of the existence of either (VI) or (VII). No SH



stretching bands appear, but strong carbonyl bands are found in the region 1625–1670  $\text{cm}^{-1}$ , and two strong bands appear in the region of stretching vibrations of associated NH groups, 3140–3300  $\text{cm}^{-1}$ . (For solubility reasons the spectra had to be recorded in potassium bromide discs). Therefore it is concluded that the acetylthiohydrazides are best represented by the structure (II). It is of interest to note that the calculated positive charge on the nitrogen atoms is greater in (II) than in the separated amides and thioamides (Fig. 2).

## EXPERIMENTAL

*N*<sub>2</sub>-Acetylthiophenylacetylhydrazide (II, R = PhCH<sub>2</sub>). Acetylhydrazide (0.9 g) was added to a solution of carboxymethyl dithiophenylacetate<sup>11</sup> (2.3 g) in N NaOH (10 ml). A clear solution was formed, but within a few minutes an oil began to separate, which presently crystallized (1.6 g, 76 % yield). The crude product was dissolved in N NaOH, filtered, and precipitated with acetic acid at -10°, and finally recrystallized from chloroform-petroleum ether (b.p. 40–60°) at -30°. Colourless, rhombic plates, m.p. 113–114°. (Found: C 57.4; H 5.68; N 13.6; S 15.2. C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>OS (208.28) requires C 57.7; H 5.81; N 13.5; S 15.4).

*Methyl 3-acetylthioncarbazate* (II, R = CH<sub>3</sub>O). Acetylhydrazide (1.8 g) was added to a solution of O-methyl S-carboxymethyl thionthiolcarbonate<sup>12</sup> (3.3 g) in N NaOH (20 ml). On the following day the clear solution was evaporated to about one third of the original volume. On scratching, a solid product began to separate (1.7 g, 58 % yield), which crystallized from toluene as colourless rods, m.p. 112–114°. (Found: C 32.4; H 5.47; N 19.0; S 21.6. C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S (148.18) requires C 32.4; H 5.44; N 18.9; S 21.6).

*Methyl 3-acetyldithiocarbazate* (II, R = CH<sub>3</sub>S). Acetylhydrazide reacted with methyl carboxymethyl trithiocarbonate as the components in the preceding experiment and gave 60 % yield of a crude product, which crystallized from a mixture of toluene and butanol as colourless plates, m.p. 125–126°. (Found: N 16.9; S 38.5. C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>OS<sub>2</sub> (164.24) requires N 17.1; S 39.0). This compound has previously been described by Hoggarth<sup>13</sup>, who reports m.p. 122–123°.

The preparation of *methyl carboxymethyl trithiocarbonate* has not been described previously. Holmberg<sup>14</sup> prepared the ethyl analogue by reacting carbon disulphide with potassium ethylmercaptide and treating the resulting ethyl potassium trithiocarbonate with sodium chloroacetate. The methyl ester was obtained in the following way, which obviates the use of methanethiol. Sodium trithiocarbonate (1 mole) was prepared by turbinating carbon disulphide (1.2 moles) with sodium sulphide (1 mole) in water (700 ml) until all was dissolved. The excess carbon disulphide evaporated during the process. Chloroacetic acid (100 g) was dissolved in water (150 ml) and neutralized with solid sodium bicarbonate. The solution was added dropwise with stirring and external cooling during one hour to the trithiocarbonate solution. After 3 h dimethyl sulphate (126 g) was added in the same way. On the following day a small amount of dimethyl trithiocarbonate was taken up in chloroform, and the water solution was acidified with 5 N HCl (250 ml). A clear yellow oil separated, which soon solidified. The crude product was contaminated with dicarboxymethyl trithiocarbonate. It was extracted with chloroform (3 × 250 ml), which does not dissolve the impurity, and the pure acid (130 g, 73 % yield) separated as yellow flakes, m.p. 72–73°, when petroleum ether (40–60°, 1500 ml) was added to the filtered chloroform solution. (Found: S 53.0; equiv.wt. 180. C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>S<sub>3</sub> (182.27) requires S 52.8; equiv.wt. 182).

*1-Acetylthiosemicarbazide* (II, R = H<sub>2</sub>N) was prepared according to Freund and Meinelcke<sup>15</sup>, dried *in vacuo* over phosphorus pentoxide and recrystallized from absolute ethanol to remove the water of crystallization.

*N*<sub>2</sub>-Acetylthiobenzhydrazide (II, R = Ph). Acetylhydrazide and carboxymethyldithiobenzoate<sup>16</sup> reacted as in the preparation of acetyl-thiophenylacetylhydrazide and gave 66 % yield of a crude product. It was purified in the same way as acetyl-thiophenylacetylhydrazide and formed colourless rods, m.p. 113–113.5°. (Found: C 55.4; H 5.27; N 14.6; S 16.3. C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>OS (194.25) requires C 55.6; H 5.19; N 14.4; S 16.5). This compound is probably also formed in the reaction between thiobenzhydrazide and carboxymethyl thiolacetate<sup>17</sup>, but it is then cyclized to 2-methyl-5-phenyl-1,3,4-thiadiazole. Acetylthiobenzhydrazide is quite labile, and all operations with the compound in solution were performed below 20°. The N-phenylthiohydrazides (III) were prepared according to known methods (see Table 2 for references).

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

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