

The Electronic Spectra of Thioamides and Thiohydrazides

Part II *. N-Acetylthioamides

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The ultraviolet absorption spectra of a number of simple N-acetylthioamides have been recorded in solvents of different polarity. A long-wavelength, weak absorption maximum is assigned to a $n \rightarrow \pi^*$ transition, and a stronger absorption maximum at shorter wavelength to a $\pi \rightarrow \pi^*$ transition. Both maxima are shifted towards longer wavelengths with respect to the same maxima in the corresponding unacetylated thioamides. This behaviour is in good agreement with the results of a simple LCAO—MO calculation. The effect of methyl substitution is discussed in relation to the change in π electron distribution caused by excitation to the lowest antibonding π orbital. The dependence of the $n \rightarrow \pi^*$ bands on solvent polarity is found to be abnormal, and a possible explanation is discussed.

In Part I, the long-wavelength strong absorption maximum in thioacetamide was assigned to a $\pi \rightarrow \pi^*$ transition with reference to the bathochromic shift caused by conjugation of the thioamide group with a benzene ring. The simple LCAO—MO method proposed by Janssen¹ was shown to give a qualitatively correct picture of the changes in the energy levels on conjugation. It was considered to be of interest to test the applicability of this method of calculation to other similar systems, and to investigate further the effect of conjugation on the absorption spectrum of the thioamide group. The simple N-acetylthioamides (I a—h) were chosen as suitable objects of investigation. Goerdeler and Horstmann^{2,3} have recently prepared a series of acylated thio-benzamides, and Horstmann⁴ has discussed their ultraviolet spectra. He showed that the low-intensity ($n \rightarrow \pi^*$) band of thiobenzamide is subject to successive redshifts when first one and then two acyl groups are introduced. Most of the N-acetylthioamides used in the present investigation have been described before. Walter⁵ has given a brief description of the ultraviolet spectrum of acetylthioacetamide, Potter⁶, in an investigation of the ultraviolet spectra of rhodanine derivatives, has also recorded the spectrum of

* Part I. *Acta Chem. Scand.* 16 (1962) 1616.

Table 1.

	Solvent	Parent compound						N-Acetyl derivative					
		λ_{\max} Å	log ϵ	λ_{\max} Å	log ϵ	λ_{\max} Å	log ϵ	λ_{\max} Å	log ϵ	λ_{\max} Å	log ϵ	λ_{\max} Å	log ϵ
CH ₃ CS·NH ₂	Heptane	3670	1.55	2670	4.14	2310	3.77	4250	1.58	2785	4.36	2120	3.63
	Ethanol	3270	1.71	2660	4.10	2100	3.63	4290	1.50	2820	4.30	—	—
CH ₃ O·CS·NH ₂	Heptane	2950	1.88	2425	4.08	2030	3.70	—	—	2570	4.15	2020	3.95
	CHCl ₃ Ethanol	—	—	—	4.17	—	3.68	3330 3410	1.98 1.87	— 2610	— 4.15	— 2060	— 3.89
CH ₃ OCS·NHCH ₃	Heptane	2850 ^a	1.9	2414	4.11	—	—	3450	1.81	2630	4.01	2040	3.83
	Ethanol	—	—	2405	4.18	—	—	3460	1.74	2640	3.99	2120	3.76
CH ₃ S·CS·NH ₂	Heptane	3570 ^b	1.60	2790 ^b	3.91	2410 ^b	3.81	—	—	3050	4.12	2545	4.15
	CHCl ₃ Ethanol	—	—	—	—	—	—	3970 4050	1.71 1.60	— 3070	— 4.14	— 2585	— 4.09
CH ₃ S·CS·NHCH ₃	Heptane	3430 ^b	1.59	2740 ^b	3.90	2470 ^b	3.89	4100	1.69	3060	4.07	2640	4.07
	Ethanol	3200 ^{a,b}	1.81	2680 ^b	4.00	2510 ^b	3.93	4120	1.67	3080	4.01	2660	4.02
H ₂ N·CS·NH ₂	Heptane	—	—	—	—	—	—	—	—	—	—	—	—
	Ethanol	2800 ^{a,b}	2	2420 ^b	4.11	—	—	—	—	2770	4.10	2080	4.07
(CH ₃) ₂ N·CS·NH ₂	Heptane	—	—	—	—	—	—	—	—	—	—	—	—
	CHCl ₃ Ethanol	—	—	—	—	—	—	3820 3880	1.62 1.64	— 2920	— 4.20	— 2310	— 4.31
(CH ₃) ₂ N·CS·NH ₂	Heptane	2850 ^{a,b}	—	2430 ^b	4.14	—	—	3380	2.60	2770	4.17	2030	4.13
	Ethanol	—	—	—	—	—	—	3350	2.52	2750	4.20	2120	4.11

a) Shoulder.

 b) From Ref.⁸

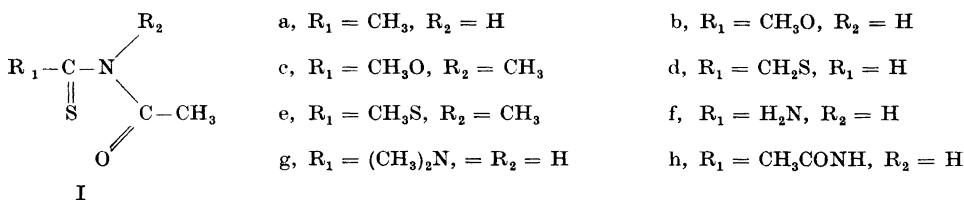
c) Monoacetyl derivative.

d) Diacetyl derivative.

ethyl N-acetyldithiocarbamate, and Zahradnik⁷ has recorded the strong absorption bands of N-acetylthiourea and N,N'-diacetylthiourea in water solution.

Ultraviolet spectra. In Table 1 the absorption maxima and $\log \epsilon$ values of the simple thioamides and their N-acetyl derivatives are given. The values for the simple thioamides are to a great extent taken from the work of Janssen⁸. Several of the same spectra have also been recorded by the present author, and in all cases the agreement is good.

It can be seen that the two long-wavelength maxima in the spectra of the parent compounds in general undergo considerable redshifts on acetylation. The low-intensity bands of acetylthioacetamide (I a) and the acetyldithiocarbamates (I d, e) extend into the visible region, and these compounds have a clear yellow colour.



In the simple thioamides N-methyl substitution and increasing solvent polarity cause hypsochromic shifts of the two long-wavelength bands. In the case of the $n \rightarrow \pi^*$ bands the shifts are of considerable magnitude. The effect on the spectra of the N-acetyl derivatives is rather different. Both solvent and substituent effects are small, and in most cases bathochromic shifts are observed. In 95 % sulphuric acid the compounds are decomposed with varying rate, and no reliable spectra could be measured. Methyl N-acetyldithiocarbamate (I d) showed the greatest stability. Its low-intensity band did not disappear on dissolution but showed up at the same place as a shoulder on the broadened neighbouring band. The N-methyl analogue (I e) also gave a yellow solution, which faded much more rapidly, and acetylthioacetamide (I a) was decomposed immediately.

LCAO—MO calculations. The Coulomb and resonance integrals are found in Table 2. The parameters for the thioamide group are the same as proposed by Janssen¹ and used in Part I. The Coulomb integral for the carbonyl carbon atom was derived from the differences in electronegativity between oxygen and carbon⁹. The value for the ether oxygen atom was shown by Janssen¹ to give the closest fit to a linear relation between calculated and experimental $n \rightarrow \pi^*$ transition energies for simple thioamides, and the same is true for the $\beta_{\text{C}=\text{O}}$ value. For $\beta_{\text{C}=\text{O}}$ the values 1.6β , 1.8β , and 2.0β were tried*, and though all gave qualitatively similar results, the value 1.8β was preferred, since it gave a closer numerical agreement for the $n \rightarrow \pi^*$ transitions. On the whole, the resonance integrals have higher values than what is becoming common practice¹², but this should not affect the reliability of the results, as long as the comparisons are restricted to a group of closely related compounds.

* cf. Refs. ^{10,11}

Table 2. Coulomb and resonance integrals.

Heteroatom X	Coulomb integral	Resonance integral for C-X
N	$\begin{array}{l} \diagup \\ \text{N} - \\ \diagdown \end{array} \quad a + 1.5\beta$	1.2 β
O	$=\text{O} \quad a + 1.1\beta$	1.8 β
	$-\text{O}- \quad a + 3\beta$	1.4 β
S	$=\text{S} \quad a + 0.5\beta$	0.6 β
	$-\text{S}- \quad a + 1.0\beta$	

The results of the calculations are shown in Table 3 and in Figure 1.

For comparison the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies for the corresponding simple thioamides, $\Delta E'$, are given below those of the acetylthioamides in Table 3. The values are taken from Ref.¹ except those for the thioncarbamate which have been recalculated with $\alpha_{\text{O}} = \alpha + 3.0 \beta$ and $\beta_{\text{C-O}} = 1.4 \beta$.

As before, the final Coulomb integral of the sulphur atom is taken as an approximate value for the energy of the lone pair electrons, the nonbonding orbital. The energy of the oxygen lone pair electrons is far lower, and their $n \rightarrow \pi^*$ transition will be overlapped by the stronger $\pi \rightarrow \pi^*$ transition.

Table 3. Energy levels and transition energies for N-acetylthioamides.

	CH ₃ CSNHAc	CH ₃ O.CS.NHAc	CH ₃ S.CS.NHAc	H ₂ N.CS.NHAc	(AcNH) ₂ CS
Antibonding orbitals	$\alpha - 2.501\beta$	$\alpha - 2.527\beta$	$\alpha - 2.509\beta$	$\alpha - 2.530\beta$	$\alpha - 2.608\beta$
	$\alpha - 1.081\beta$	$\alpha - 1.420\beta$	$\alpha - 1.202\beta$	$\alpha - 1.481\beta$	$\alpha - 1.359\beta$
Nonbonding orbitals	$\alpha + 0.077\beta$	$\alpha - 0.087\beta$	$\alpha + 0.006\beta$	$\alpha - 0.125\beta$	$\alpha - 0.090\beta$
Bonding orbitals	$\alpha + 0.459\beta$	$\alpha + 0.204\beta$	$\alpha + 0.320\beta$	$\alpha + 0.124\beta$	$\alpha + 0.174\beta$
	$\alpha + 2.337\beta$	$\alpha + 1.963\beta$	$\alpha + 1.205\beta$	$\alpha + 1.638\beta$	$\alpha + 1.573\beta$
	$\alpha + 3.885\beta$	$\alpha + 3.563\beta$	$\alpha + 2.403\beta$	$\alpha + 2.905\beta$	$\alpha + 2.589\beta$
		$\alpha + 4.316\beta$	$\alpha + 3.884\beta$	$\alpha + 3.945\beta$	$\alpha + 3.670\beta$
$\Delta E_{n \rightarrow \pi^*}$	-1.158 β	-1.333 β	-1.208 β	-1.356 β	-1.269 β
$\Delta E'_{n \rightarrow \pi^*}$ ^a	-1.244 β ^b	-1.439 β	-1.295 β ^b	-1.469 β ^b	-1.469 β ^b
$\Delta E_{\pi \rightarrow \pi}$	-1.540 β	-1.624 β	-1.522 β	-1.605 β	-1.533 β
$\Delta E'_{\pi \rightarrow \pi}$ ^a	-1.599 β ^b	-1.711 β	-1.592 β ^b	-1.701 β ^b	-1.701 β ^b

a) Value for the parent compound.

b) From Ref.¹

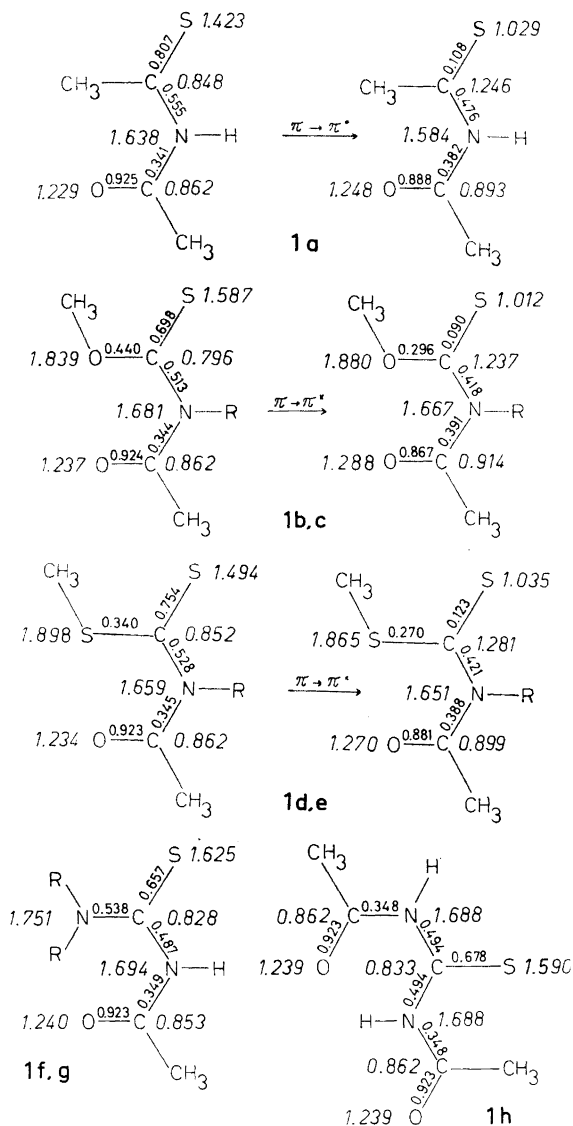


Fig. 1. π Electron distribution and bond orders in ground and excited states of N-acetylthioamides.

DISCUSSION

The results in Table 3 show that acetylation can be expected to lead to lower transition energies for both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Therefore, the long-wavelength, low-intensity bands in all the investigated compounds are confidently ascribed to $n \rightarrow \pi^*$ transitions, and the first strong

Table 4. $\Delta E'/\Delta E$ in non-hydroxylic solvent.

R_1 ($R_2=H$)	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	
	calc.	found	calc.	found
CH_3	1.07	1.16	1.04	1.04
CH_3O	1.08	1.13	1.05	1.06
CH_3S	1.07	1.11	1.05	1.09
NH_2	1.08	—	1.06	1.14
CH_3CONH	1.16	—	1.11	1.21

bands to $\pi \rightarrow \pi^*$ transitions. The numerical agreement can be tested by a graphic procedure, since the calculated transition energies and the wave numbers of the experimental absorption maxima shall show a linear relationship. As is seen from Fig. 2, the values for the $n \rightarrow \pi^*$ bands show a reasonable linearity, whereas for the $\pi \rightarrow \pi^*$ bands the agreement is less satisfactory. From the slope of the best straight line for the $n \rightarrow \pi^*$ bands a spectroscopic

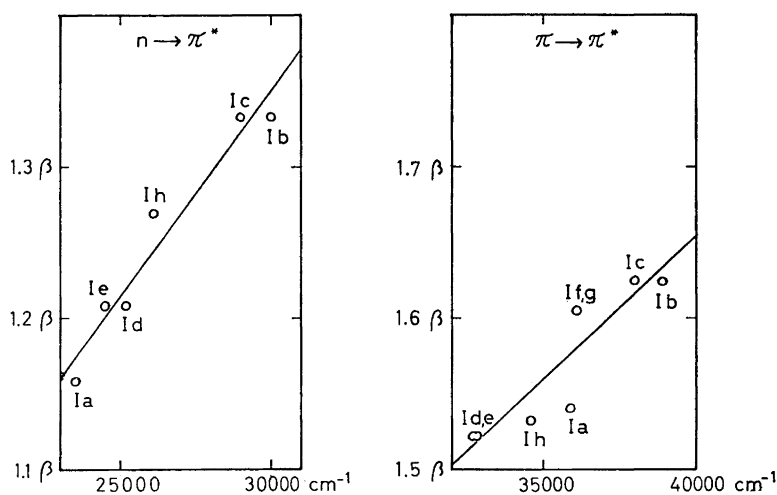


Fig. 2. Plots of calculated transition energies versus wave numbers of absorption maxima for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of N-acetylthioamides.

β value of 37 000 cm^{-1} can be derived, in moderate agreement with the values between 23 000 and 32000 cm^{-1} given by Platt¹³. The agreement between calculated and experimental transition energies is often better, when each parent thioamide is compared with its N-acetyl derivative (Table 4).

When a methyl group is introduced on the acetylated nitrogen atom in (I b) and (I d), bathochromic shifts of both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands result. The shifts of the latter bands may at least partly be explained as an inductive substituent effect. Coulson¹⁴ has shown that if a substituent can be regarded as changing the Coulomb integral of the substituted atom r by a quantity $d\alpha_r$, the change in $\pi \rightarrow \pi^*$ transition energy is given by (2)

$$d(\varepsilon_{n+1} - \varepsilon_n) = (c_{r,n+1}^2 - c_{r,n}^2)d\alpha_r \quad (2)$$

ε_{n+1} is the energy of the lowest antibonding π orbital and ε_n that of the highest bonding one. $c_{r,n+1}$ and $c_{r,n}$ are the corresponding LCAO coefficients for the atom r . It can be seen from Fig. 1 that $(c_{r,n+1}^2 - c_{r,n}^2)$ is negative for the nitrogen atom in (I b) and (I d), since its charge is diminished by the $\pi \rightarrow \pi^*$ transition. Since $d\alpha_r$ is positive for +I substituents such as methyl groups, $d(\varepsilon_{n+1} - \varepsilon_n)$ is negative, *i.e.* the transition energy is lowered. However, the change in charge distribution is small, and it is probable that other effects, in the first hand hyperconjugation, must be invoked to explain the shifts. The bathochromic shifts of the $n \rightarrow \pi^*$ bands on methylation cannot be explained by the model used for this work. A calculation was performed for N-acetyldithiocarbamate with α_N changed from $\alpha + 1.5\beta$ to $\alpha + 1.4\beta$, and it was found that the nonbonding and lowest antibonding orbitals were raised by nearly the same small amounts of energy. Hyperconjugation is probably of importance also in this case, as it has been shown to be for the $n \rightarrow \pi^*$ bands in simple thioamides by Janssen *et al.*¹⁵, though there the shifts are hypsochromic.

The effect of solvent polarity is at first rather surprising, particularly regarding the $n \rightarrow \pi^*$ bands, which, with one exception, undergo redshifts with increasing solvent polarity and do not disappear in acid solution. Previously¹⁶ the "negative solvatochromy", *i.e.* the blue shift on increasing solvent polarity, was regarded as one of the main evidences for the assignation of weak absorption bands to $n \rightarrow \pi^*$ transitions. The blue shift is generally explained by the assumption that the ground state is more stabilized by increasing solvent polarity and in particular by hydrogen bonding than the excited state. Bayliss¹⁷ has shown that increasing solvent polarisability gives a general red shift due to the "assistance" of the transition by the moments induced by the solute transition moment in the solvent molecules. This red shift is always superimposed on the shifts caused by differences in energy of solvation in the ground and excited state, and it may at least partly be responsible for the red shifts observed in the spectra of the N-acetylthioamides. In any case the absence of a blue shift requires that the total energy of solvation of the molecule is only slightly changed by the transition. To explain this, it can be assumed that solvation and in particular hydrogen bonding occur mainly at the carbonyl group, and that the energy of solvation lost on excitation at the thiocarbonyl group is nearly balanced by the gain at the carbonyl group. A comparison of the base strengths of

Table 5. van't Hoff i factors for methyl N-acetyldithiocarbamate in 100 % sulphuric acid.

m	$\Delta t^\circ\text{C}$	i
0.0244	0.304	2.03
0.0340	0.443	2.12
0.0419	0.591	2.29

acetamide ($\text{p}K_a = +0.37^{18}$) and thioacetamide ($\text{p}K_a = -1.76^{19}$) indicates that the first assumption is correct. The difference of two powers of ten in K_a must reflect a considerable difference in strength of hydrogen bonding. A cryoscopic determination of the van't Hoff i -factor in 100 % sulphuric acid (Table 5) shows that methyl N-acetyldithiocarbamate (I d) is monoprotated in this solvent, and it is rather probable that the proton is attached to the oxygen atom. According to the calculations on acetylthioacetamide, excitation increases the π electron density on the oxygen atom by 0.06 electronic units and on the carbonyl carbon atom by only about 0.03 units. This should increase both polarity of the carbonyl group and basicity of the oxygen atom with increasing energy of solvation and particularly of hydrogen bonding as results. Obviously the red shifts of the $\pi \rightarrow \pi^*$ bands can be explained along the same lines. The $\pi \rightarrow \pi^*$ band of monoacetylthiourea (I f) and the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands of N,N-dimethyl-N'-acetylthiourea (I g) all undergo small blue shifts when going from heptane as solvent to ethanol. This may be ascribed to the greater basicity of the sulphur atom in thiourea. Janssen²⁰ has determined $\text{p}K_a$ values for thiourea (-1.19) and tetramethylthiourea (-1.0), and Zahradnik⁷ obtained a similar value (-1.26) for thiourea. The appearance of a $n \rightarrow \pi^*$ band in the spectrum of (I g) but not in that of the simple acetylthiourea (I f) can probably be explained by a steric hindrance to coplanarity, similar to the one Janssen⁸ has proposed for tetramethylthiourea. It is apparent that both for tetramethylthiourea and (I g) the $n \rightarrow \pi^*$ band is considerably stronger than for the compounds where coplanarity is possible. This can be explained by a mixing of the n and π orbitals, made possible by the deviation from coplanarity. (See part I for a discussion of a similar case with references.)

However, it is clear that these arguments count rather heavily upon the reliability of the naive calculations, and a definite conclusion about the cause of the redshifts of the $n \rightarrow \pi^*$ bands necessitates a better knowledge of the cybotactic conditions around the molecule.

The origin of the absorption bands at shorter wavelengths is less clear. The band at 2120 Å in the spectrum of acetylthioacetamide is probably due to a similar transition as the band at 2310 Å of thioacetamide. It may be ascribed to a $n \rightarrow \sigma^*$ transition on the following grounds. Since the $n \rightarrow \sigma^*$ transition is localized in the thiocarbonyl group, it cannot be expected to increase the energy of solvation of the carbonyl group, whereas that of the thiocarbonyl group is certainly lowered. The result of increasing the solvent polarity will therefore be to increase the transition energy. The expected blueshift actually also occurs, since no absorption maximum is found above 2000 Å in ethanol

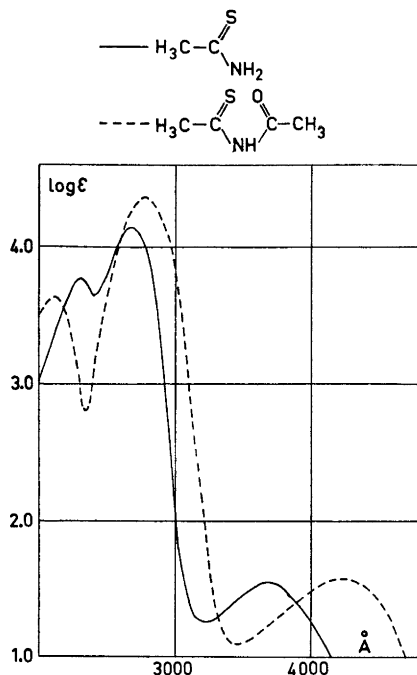
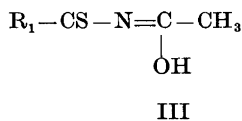
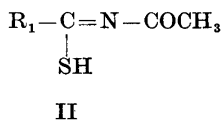


Fig. 3. Ultraviolet absorption spectra of thioacetamide (—) and N-acetylthioacetamide (---) in heptane.

solution. Furthermore, the σ^* level can be expected to be only slightly affected by acetylation. On the other hand, the nonbonding level on the sulphur atom is lowered from $\alpha + 0.029 \beta$ to $\alpha + 0.077 \beta$, and consequently acetylation should result in a hypsochromic shift of a $n \rightarrow \sigma^*$ band. The calculated shift is 1200 cm^{-1} and the experimental one is 3900 cm^{-1} in heptane. Rosen-gren²¹ in his recent investigation of the ultraviolet spectra of simple aliphatic thials and thions finds evidence for $n \rightarrow \sigma^*$ bands between 2200 and 2300 \AA , and he also proposes that the 2310 \AA band in thioacetamide is due to a $n \rightarrow \sigma^*$ transition. The second strong bands of the other acetylthioamides in general show an opposite kind of solvent dependence, and they may be due to higher $\pi \rightarrow \pi^*$ transitions.

The infrared spectra in chloroform show no absorption bands that can be ascribed to S—H or C=N stretching vibrations, and therefore the possible tautomers (II) and (III) need not be considered. The same conclusion can be drawn from the similarity of the spectra of the N-methyl derivatives with those of the N-unsubstituted compounds.



The acetylthioamides are considerably stronger acids than the simple thioamides. This can be explained in a qualitative way by the action of two

electron-withdrawing groups on the NH group. In harmony with this, the LCAO—MO calculations give π electron densities around the nitrogen atoms that are 0.05—0.10 electronic units lower than in the corresponding simple thioamides.

EXPERIMENTAL

N-Acetylthioacetamide (I a). Thioacetamide (30 g) and acetic anhydride (150 ml) were heated on a boiling water bath until hydrogen sulphide began to appear. The solution was evaporated *in vacuo* at 80°, and the residue (20.5 g) crystallized on cooling. It was purified by vacuum sublimation at 50° and 1 mm and crystallized from benzene-light petroleum as bright yellow rods, m.p. 62—62.5°. The yield of sublimed product was 41 %. (Found: C 41.0; H 5.95; N 12.0; S 27.4. C_4H_7NOS (117.17) requires C 41.0; H 6.02; N 12.0; S 27.4). This compound has previously been described by Walter⁶ and by Goerdeler and Porrmann²².

Methyl N-acetylthioncarbamate (I b) was prepared according to Wheeler and Johnson²³. (Found: N 10.4; S 24.2. $C_4H_7NO_2S$ (133.17) requires N 10.5; S 24.1.) M.p. 79—80°, in agreement with Ref.²³

Methyl N-acetyl-*N*-methylthioncarbamate (I c). *O*-Methyl-*S*-carboxymethylthionthiolcarbonate²⁴ (83 g) in 2 N NaOH (400 ml) was added to a solution of methylammonium chloride (40 g) in water (100 ml). A colourless oil separated and was taken up in ether, dried and distilled. A fraction was obtained, b.p._{4 mm}: 70—71° (35 g, 67 % yield), which consisted of methyl *N*-methylthioncarbamate. (Found: C 34.1; H 6.49. C_3H_7NOS (105.17) requires C 34.2; H 6.73.) n_D^{20} : 1.5355. This compound has previously been prepared by Delépine and Schwing²⁵, who give no data.

Attempts to acetylate this amide with acetic anhydride led to incomplete reaction, and due to the similar boiling points of the starting material and the product, no efficient separation could be achieved by distillation. However, acetylation with acetyl chloride in pyridine gave a better result. The ester (21 g) was dissolved in absolute ether (250 ml) and pyridine (32 ml), and acetyl chloride (16 g) in absolute ether (50 ml) was added dropwise with stirring. The temperature was kept below +10° by external cooling. When the addition of acetyl chloride was completed, the mixture was refluxed for one hour and then poured onto ice. The ether layer was separated, dried, and distilled. A pale yellow liquid was obtained, b.p. 6 mm: 83° (15 g, 50 % yield), consisting of the desired acetyl derivative (I c). (Found: C 41.0; H 6.28; N 9.60; S 22.0. $C_5H_9NO_2S$ (147.19) requires C 40.8; H 6.15; N 9.52; S 21.8.) n_D^{20} : 1.5085.

Methyl N-acetyldithiocarbamate (I d). This compound was prepared according to Delépine²⁶.

Methyl N-acetyl-*N*-methyldithiocarbamate (I e). This compound has previously been prepared by Delépine (Ref.²⁶, p. 59), who did not get a pure specimen. When the preparation was performed as described for (I c) a good yield (90 %) of a pure product was obtained. The crude product crystallized when the ether was evaporated, and purification was effected by distillation at 3 mm in a vacuum sublimation apparatus. The product crystallized from benzene-petroleum ether as bright yellow plates, m.p. 39—40°. (Found: C 37.0; H 5.65; N 8.56; S 39.6. $C_5H_9NOS_2$ (163.25) requires C 36.8; H 5.55; N 8.58; S 39.3.)

Mono-acetylthiourea (I f) and *N,N'*-diacetylthiourea (I h) were prepared according to the directions of Kohlmann²⁷.

N,N-Dimethyl-*N'*-acetylthiourea (I g). Methyl *N*-acetyldithiocarbamate (I d, 3.0 g) was dissolved in ethanol (25 ml), and dimethylamine (1.5 g) in water (5 ml) was added. After 10 h the solution was evaporated, and a residue of colourless, rhombic prisms was obtained (2.9 g = 100 % yield), m.p. 100—101° after recrystallization from toluene-heptane. (Found: C 41.5; H 7.06; N 19.0; S 21.8. $C_5H_{10}N_2OS$ (146.21) requires C 41.1; H 6.90; N 19.2; S 21.9.)

Solvents. Heptane was shaken first with concentrated sulphuric acid and then with water, dried with Drierite, and distilled through a 60 cm Vigreux column. The distillate was allowed to flow through a column of silica, activated at 350°. Ethanol was treated as described in Part I.

Spectra. The ultraviolet spectra down to 2200 Å were recorded with a Beckman DU spectrophotometer with photomultiplier attachment. Between 2000 and 2200 Å the spectra were recorded with a Perkin-Elmer Model 137 recording spectrophotometer.

The cryoscopic measurements were performed as described in Part I. The deviation from 2 in the later i values is probably due to decomposition, since the depression of the freezing point was found to increase with time. Since it was necessary to change the temperature during the experiment, no attempt was made to correct for the decomposition. When a fresh solution of (I d) in 100 % sulphuric acid was poured into water, the compound was recovered in good yield.

Calculations. The calculations were performed on the electronic digital computer "SMIL" at the Department of Numerical Analysis of the University of Lund. The program for the calculations was changed in order to avoid divergent results in some cases. From the first and second sets of parameters the arithmetic means were formed and used in the following calculation. In the subsequent steps the mean values of the parameters obtained in the last calculation and the previous set of mean values were used. This led to a much more rapid convergency, and a complete agreement was obtained with the convergent results from previous calculations. For acetylthiourea divergent results were obtained with the original program, whereas with the mean value technique convergency was achieved.

Acknowledgements. The author thanks the Swedish Natural Science Research Council for financial support, Fil.Kand. Leif Robertsson for programming the calculations, and Laborator Carl-Erik Fröberg for valuable advice concerning the calculations.

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Received September 10, 1962.

Acta Chem. Scand. **17** (1963) No. 3