ACTA CHEMICA SCANDINAVICA 23 (1969) 2888–2899

Tautomeric Cyclic Thiones

Part IV.* The Thione-Thiol Equilibrium in some Azoline-2-thiones

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The position of the thione-thiol equilibrium has been studied by the basicity method in a series of methyl and phenyl substituted oxazoline-, thiazoline-, and imidazoline-2-thiones. Tautomeric ratios in the range 10^5-10^8 have been obtained, with the highest values for the imidazoline-2-thiones. A deviation from the normal Hammett relation is observed. Spectroscopic and basicity data have been used to estimate the position of the equilibrium in the excited state. Correlation of tautomeric ratios and spectral transition energies with molecular orbital data has been attempted.

Thione-thiol tautomerism in six-membered heteroaromatic compounds has been the subject of extensive and accurate investigation during the last decade (*cf.* Ref. 1 for a review), but corresponding data for five-membered compounds are much more scarce and generally of a more qualitative nature. We have now performed an investigation of the tautomeric equilibria in the systems Ia $\rightleftharpoons$ Ib. Qualitative studieds indicated in all cases such a predominance of form Ib that no hope existed for a direct measurement of the concentration of the thiol form. We therefore chose an indirect method, which seemed well suited for the determination of large tautomeric ratios, and which depends on the measurements of the acidity constants of the conjugate acids of the tautomers *** (K_{HA}) and their *N*- and *S*-methyl derivatives (K_{NMe} and K_{SMe}). When these constants are known, the tautomeric ratio $K_T=[Ib]/[Ia]$ can be obtained from eqns. (1) or (2).[2]

* Part III. *Acta Chem. Scand.* **23** (1969) 2879.

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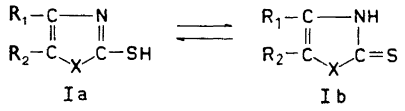
*** K_{HA} is an apparent acidity constant, but in the present systems it is indistinguishable from the constant of the conjugate acid of the thione tautomer.



Ia Ib

$R_1, R_2 = CH_3, CH_3; H, Ph; Ph, H$
$X = O, S, NCH_3$

$$K_T = K_{NMe}/K_{SMe} \quad (1)$$

$$K_T = (K_{HA}/K_{SMe})-1 \quad (2)$$

Eqns. (1) and (2) are obtained by substituting the acidity constants of the *N*- and *S*-methyl derivatives for the generally non-available constants of the tautomers Ia and Ib. The justification for this substitution rests on the assumption that methylation has little influence on the basicity of the molecules. The influence is composed of inductive and steric effects, of which the former should enhance and the latter probably diminish the basicity. Both kinds of effects should be larger in the *N*- than in the *S*-methyl derivatives, and therefore formula (2) should be the best one for the systems under study here. Since phenyl substitution generally lowers the basicity (Table 1)

Table 1. pK_T values for Ia and Ib and pK_a values for their conjugate acids.

R_1	R_2	X	pK_{HA}	pK_{NMe}	pK_{SMe}	$pK_T(1)$[b]	$pK_T(2)$
CH_3	CH_3	O	$-3.9\pm0.2(1)$[a]	$-4.3\pm0.3(3)$	$2.5\ \pm0.1(2)$	-6.8 ± 0.4	-6.4 ± 0.3
Ph	H	O	$-4.6\pm0.2(4)$	$-4.9\pm0.1(6)$	$0.3\ \pm0.1(5)$	-5.2 ± 0.2	-4.9 ± 0.3
H	Ph	O	$-4.5\pm0.2(7)$	$-4.8\pm0.1(9)$	$1.0\ \pm0.1(8)$	-5.8 ± 0.2	-5.5 ± 0.3
CH_3	CH_3	S	$-2.8\pm0.2(10)$	$-3.0\pm0.1(12)$	$3.3\ \pm0.1(11)$	-6.3 ± 0.2	-6.1 ± 0.3
Ph	H	S	$-3.3\pm0.1(13)$	$-3.6\pm0.1(15)$	$1.5\ \pm0.1(14)$	-5.1 ± 0.2	-4.8 ± 0.2
H	Ph	S	$-3.5\pm0.2(16)$	$-3.7\pm0.2(18)$	$1.8\ \pm0.1(17)$	-5.5 ± 0.3	-5.3 ± 0.3
CH_3	CH_3	NH	$-1.2\pm0.1(19)$	$-1.4\pm0.1(21)$	$6.85\pm0.06(20)$	-8.3 ± 0.2	-8.1 ± 0.2
CH_3	CH_3	NCH_3	$-1.4\pm0.1(21)$	$-1.6\pm0.2(23)$	$6.68\pm0.02(22)$	-8.3 ± 0.2	-8.1 ± 0.1
Ph	H	NH	$-1.7\pm0.2(24)$	$-2.0\pm0.2(26)$	$4.94\pm0.02(25)$	-6.9 ± 0.2	-6.6 ± 0.2
H	Ph	NH	$-1.7\pm0.2(24)$	$-2.0\pm0.2(27)$	$4.94\pm0.02(25)$	-6.9 ± 0.2	-6.6 ± 0.2
Ph	H	NCH_3	$-2.0\pm0.2(27)$	$-2.2\pm0.2(30)$	$5.47\pm0.05(28)$	-7.7 ± 0.3	-7.5 ± 0.3
H	Ph	NCH_3	$-2.0\pm0.2(26)$	$-2.2\pm0.2(30)$	$4.67\pm0.05(29)$	-6.9 ± 0.3	-6.7 ± 0.3

[a] Refers to numbers given to the compounds in Part III.
[b] Calculated by formula (1).

a steric effect which diminishes the coplanarity of the phenyl and the heterocyclic ring might be base-strengthening. However, a comparison of corresponding pK_{HA} and pK_{NMe} values (Table 1) shows that the simple steric effect, which hinders protonation of the thione group, more than outweighs the sum of the inductive effect and the base-strengthening steric effect.

The free acids and their *N*-methyl derivatives are quite weak bases, which has necessitated the determination of the acidity constants of their conjugate acids by Hammett's method [3] from spectral measurements in aqueous sulphuric acid at known H_0 values. The constants for the *S*-methyl derivatives could

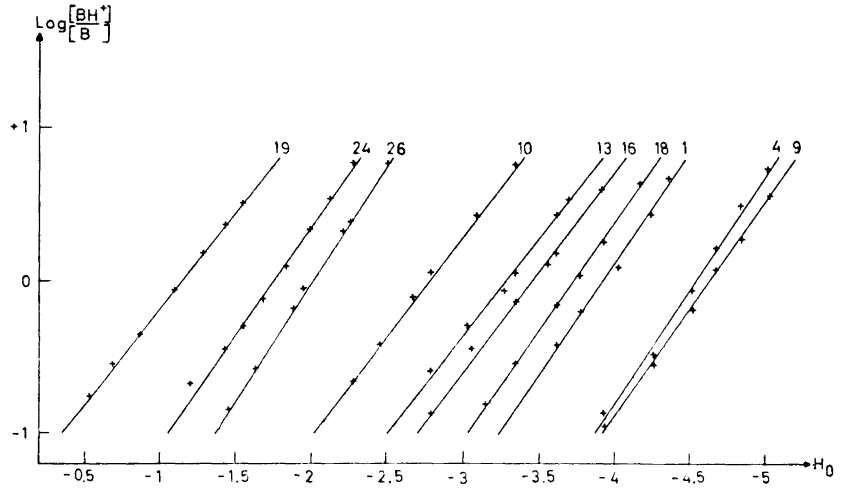


Fig. 1. Deviations from the Hammett equation. The numbers are thosen given to the compounds in Part III.

be determined by spectral measurements in aqueous solutions of known pH or by titrating the free base with standard hydrochloric acid and measuring the pH with a glass electrode. The pK_a and pK_T values are summarised in Table 1. In all cases, the thione form is found to dominate greatly, particularly in the imidazole series. The pK_T values previously reported for thiopyridones and analogs fall in the range 3.0—5.8 (excluding zwitterionic species)[4,5] and thus the dominance of the thione is greater in five-membered than in six-membered rings. The difference is probably at least partly due to a relatively greater aromatic stabilisation of the thiol form in the six-membered systems, in agreement with MO data (Table 3). Unfortunately, the exact quantitative significance of the pK_a and pK_T values is not quite clear, since the thiones do not behave as ideal Hammett bases. If log ($[BH^+]/[B]$) is plotted against H_0, straight lines are obtained, but their slopes, instead of being unity as required by theory, fall between 1.25 and 1.50 (Fig. 1). Edward and Stollar [6] have found similar discrepancies for a series of thiolactams with slopes in the range 1.4—2.0, and Janssen [7] reports values between 1.3 and 1.5 for *N*,*N*-dimethylthioamides. On the other hand, Katritzky *et al.*[8] have found slopes lower than unity for a series of amides. In this case the problem was solved by elaboration of a new acidity function, H_A, based on amides.[9] This method is not so feasible for the thiones since they show fairly large individual differences, and the slope of log ($[BH^+]/[B]$) *versus* H_0 does not increase

monotonously with decreasing basicity of the thiones, but varies in a more irregular manner. An acidity function for thiones, H_T, should be intermediate between H_0 and H_R, the acidity function for carbonium ions,[10] but it could accomodate all thiones in a very approximate way only, and therefore it was regarded of doubtful value. Arnett [11] lists a number of deviations from ideal Hammett behaviour and ascribes them in part to differences in activity coefficients, caused by differences in solvation between the bases in question and the Hammett indicators. An inspection of the H_R, H_0, and H_A functions [9,11] shows that they are very similar in shape, mainly differing in slope. Therefore, it can confidently be concluded that the measured K_A values fall in the right order, but that they are lower than the actual thermodynamic constants.

MO CALCULATIONS

π-Electron energies, π-bond orders, and charge distributions have been calculated, as in part II of this series,[12] by the HMO method with α- and β-variation described by Janssen [13] and Janssen and Sandström.[14] The parameters are those designated as set 3 in Ref. 14 (Table 2). The π-electron energies

Table 2. Parameters for the molecular orbital calculations. $\alpha_X = \alpha_C + h_X\beta_{CC}$; $\beta_{C-X} = k_{C-X}\beta_{CC}$; $\omega = 1.0$.

Atom	h_X	Bond	k_{C-X}
C	0	C—C	0.75
N̈	0.5	C—N	0.7
N̈	1.5	C—O	0.6
Ö	2.5	C—S	0.4
Ṡ	0.5		
S̈	1.0		

of the highest occupied (HOMO) and lowest free molecular orbital (LFMO), total π-electron energy ($\sum E_\pi$), difference between total π-electron energy of thione and thiol form (ΔE_π), and energy of the lowest $\pi \rightarrow \pi^*$ transition, all in units of β, are given in Table 3, together with the π-electron density on the nitrogen atom 3 in the thiol forms (q_N) and on the thiocarbonyl sulphur atoms in the thione forms (q_S). Molecular diagrams for some representative systems are presented in Fig. 2.

DISCUSSION

The dominance of the thione over the thiol form in these and similar systems depends on a combination of different factors. Among these, the difference in π-electron energy should be a major one, but differences in energy of solvation may also be important. Beak and Bonham [15] have shown

Table 3. Molecular orbital energies and π-electron densities.

R_1	R_2	X	Structure	HOMO	LFMO	$\sum E\pi$	$\Delta E\pi$	$\Delta E\pi\rightarrow\pi^*$	q_N	q_S
CH_3	CH_3	O	thione	0.312	−0.716	13.032	0.361	1.028		1.423
CH_3	CH_3	O	thiol	0.628	−0.850	12.671		1.478	1.206	
Ph	H	O	thione	0.303	−0.715	21.260	0.364	1.018		1.422
Ph	H	O	thiol	0.560	−0.752	20.896		1.312	1.208	
H	Ph	O	thione	0.294	−0.673	21.284	0.326	0.967		1.419
H	Ph	O	thiol	0.496	−0.658	20.922		1.154	1.202	
CH_3	CH_3	S	thione	0.289	−0.705	10.001	0.372	0.995		1.424
CH_3	CH_3	S	thiol	0.617	−0.825	9.629		1.442	1.210	
Ph	H	S	thione	0.281	−0.703	18.234	0.375	0.984		1.422
Ph	H	S	thiol	0.546	−0.735	17.859		1.281	1.211	
H	Ph	S	thione	0.275	−0.662	18.254	0.370	0.937		1.420
H	Ph	S	thiol	0.488	−0.645	17.884		1.134	1.206	
CH_3	CH_3	NR	thione	0.153	−0.863	11.404	0.290	1.016		1.520
CH_3	CH_3	NR	thiol	0.581	−1.040	11.114		1.621	1.247	
Ph	H	NR	thione	0.151	−0.790	19.648	0.310	0.941		1.514
Ph	H	NR	thiol	0.517	−0.847	19.347		1.364	1.248	
H	Ph	NR	thione	0.151	−0.790	19.648	0.289	0.941		1.514
H	Ph	NR	thiol	0.464	−0.762	19.359		1.227	1.240	

Table 3. Continued.

Structure	HOMO	LFMO	$\sum E\pi$	$\Delta E\pi$	$\Delta E\pi\rightarrow\pi^*$	q_N	q_S
2-Thiopyridone	0.095	−0.537	10.856	0.046	0.668		1.563
2-Pyridinethiol	0.804	−0.925	10.810		1.729	1.139	
4-Thiopyridone	0.109	−0.591	10.874	0.064	0.700		1.517
4-Pyridinethiol	0.843	−0.941	10.810		1.784	1.136	

by equilibration studies that the enthalpy difference between *N*-methyl-2-pyridone and 2-methoxypyridine is shifted 4 kcal/mole in favour of the methoxypyridine when going from the neat liquid to the gaseous state. For the 4-analogs the shift is 6 kcal/mole in the same direction. Clearly, solvation is an important factor in stabilizing the pyridones relative to the methoxypyridines, and it is likely that the same relation applies to thiones relative to thiols.

Table 3 shows that in all cases the thione forms have a greater π-electron stabilization than the corresponding thiols, and the differences, $\Delta E\pi$, are also greater for five-membered than for six-membered ring systems. The differences in K_T between the individual five-membered ring systems are, however, not very well reproduced. The $\Delta E\pi$ values fall in the range 0.289β—0.375β, but the smallest differences are found for the imidazoles, which have

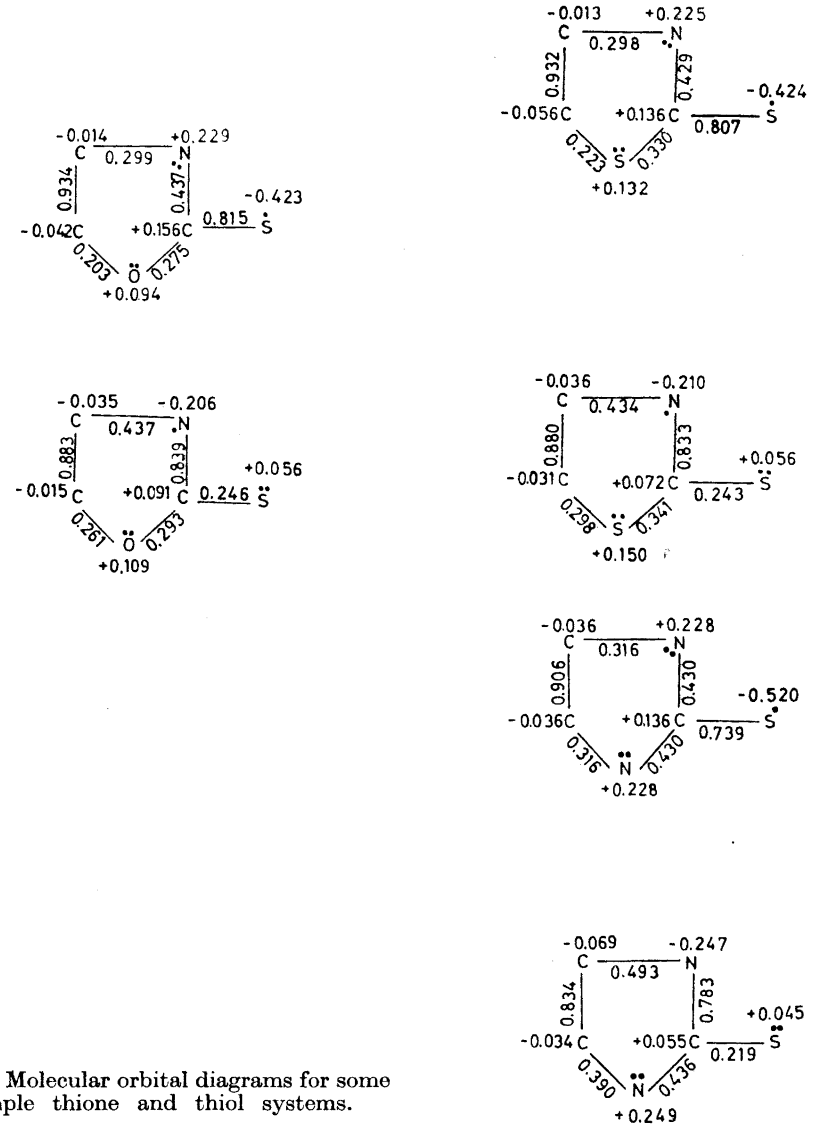


Fig. 2. Molecular orbital diagrams for some simple thione and thiol systems.

the highest K_T values, whereas the reverse is true for the thiazoles. This discrepancy must not necessarily be ascribed to a shortcoming in the calculations, since the thiocarbonyl sulphur atom has a much greater π-electron density, q_S, in the imidazolinethiones than in the other thiones (Fig. 2). This difference, which is due to the greater electron-donating capacity of the second nitrogen atom, obviously leads to a higher basicity for the imidazolinethiones (Table 1)

and should also give them greater energy of solvation. For the oxazole and thiazole systems, the standard parameters give almost the same ΔE_π and q_S values. However, it has been observed previously [16] that the

Table 4. Ultraviolet spectra of Ia (methylthio-azole) and Ib (thione) as free bases in water and as conjugate acids.

No.	R_1	R_2	R_3	X	Structure	Free base		Conjugate acid	
						λ_{max} nm	ε_{max}	λ_{max} nm	ε_{max}
1	CH_3	CH_3	H	O	Ib	271	14 600	258	9 100
2	CH_3	CH_3	CH_3	O	Ia	251	6 800	262	10 300
3	CH_3	CH_3	CH_3	O	Ib	269.5	14 400	257	8 800
4	Ph	H	H	O	Ib	270.5	21 200	249	14 500
5	Ph	H	CH_3	O	Ia	251	14 800	258	15 400
6	Ph	H	CH_3	O	Ib	266	21 600	250	11 400
7	H	Ph	H	O	Ib	300	24 600	280	17 400
						216	13 400		
8	H	Ph	CH_3	O	Ia	289	21 500	287	19 800
						248(S) [a]	7 000		
9	H	Ph	CH_3	O	Ib	300	23 800	282	17 500
						218	13 400		
10	CH_3	CH_3	H	S	Ib	316.5	14 400	296	9 800
11	CH_3	CH_3	CH_3	S	Ia	284.5	7 900	302	11 400
12	CH_3	CH_3	CH_3	S	Ib	312.4	13 400	293	9 000
13	Ph	H	H	S	Ib	316	15 800	302	6 900
								247	11 700
14	Ph	H	CH_3	S	Ia	268	12 200	303	10 300
						238	18 000	261	10 200
								240	12 300
15	Ph	H	CH_3	S	Ib	309	15 400	290	8 800
								234	8 900
16	H	Ph	H	S	Ib	333.5	23 200	315	14 800
17	H	Ph	CH_3	S	Ia	309	22 900	318	22 000
								252	4 800
18	H	Ph	CH_3	S	Ib	331	20 300	314	14 200
								244	5 700
19	CH_3	CH_3	H	NH	Ib	261	14 600	250	8 800
20	CH_3	CH_3	CH_3	NH	Ia	254	7 400	259	8 900
								233(S)	4 900
21	CH_3	CH_3	CH_3	NH	Ib	259	14 300	250	9 800
						209	6 800		
22	CH_3	CH_3	CH_3	NCH_3	Ia	257	6 600	259	7 700
23	CH_3	CH_3	CH_3	NCH_3	Ib	257	13 000	251	7 600
24	Ph	H	H	NH	Ib	285	18 400	264	17 500
						216	13 600		
25	Ph	H	CH_3	NH	Ia	269	19 400	270	22 000
26	Ph	H	CH_3	NH	Ib	266	16 600	250	13 700
27	Ph	H	H	NCH_3	Ib	288	17 400	263	17 200
						218	13 700		
28	Ph	H	CH_3	NCH_3	Ia	265	14 800	260	14 400
29	H	Ph	CH_3	NCH_3	Ia	266	17 200	270	16 600
30	H	Ph	CH_3	NCH_3	Ib	261	19 200	252	13 400

[a] S = shoulder.

customary α_{-S-} and β_{C-S-} values underestimate the electron-donating capacity of a thioether sulphur atom, when it is attached to a strongly electron-attracting group. This discrepancy was ascribed to a contraction of the polarisable $3p$ orbitals on the sulphur atom, which to a first approximation should be reflected in an increase in the resonance integral. If the β_{C-S-} value is increased in the thiazolinethione, both ΔE_π and q_S increase, and the observed differences in K_T and basicity between the oxazole and thiazole systems are reproduced.

The phenyl derivatives in all cases are weaker bases than the corresponding 4,5-dimethyl derivatives. These differences are not reproduced by the q_S, q_N, or ΔE_π values, but it is possible that they are at least partly due to entropy effects.

The ultraviolet absorption spectra are collected in Table 4. Generally, the wavelengths of the absorption maxima fall in the order thiazole>oxazole ≈imidazole, which is reproduced by the calculated transition energies. A phenyl group in position 5 has a bathochromic effect in both methylthioazoles and thiones as expected, and in agreement with calculations. More remarkable is the effect of a phenyl group in position 4 of the oxazoles and thiazoles. In the free acids (Ib, R_3=H) the substituent does not shift the position of the first absorption maximum, and in the *N*- and *S*-methyl derivatives the effect is hypsochromic. *N*-Methyl groups adjacent to phenyl groups have considerable hypsochromic effects (Fig. 3), which can be ascribed to an

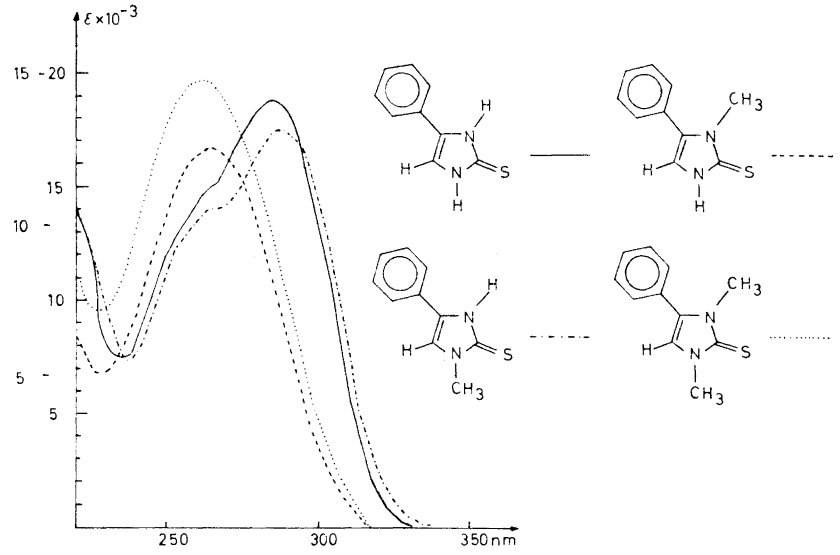


Fig. 3. Ultraviolet spectra in water.

enforced deviation of the phenyl ring from coplanarity. Tensmeyer and Ainsworth [17] have observed equivalent steric effects on the NMR spectra of *N*-phenylpyrazoles. This can be part of the explanation for the hypsochromic

effect observed in the *N*-methyl-oxazoline- and -thiazoline-thiones, but not in the *S*-methyl analogs. The calculated transition energies do not explain the hypsochromic shifts, though they are considerably larger for the 4-phenyl derivatives than for their 5-phenyl analogs (Table 3). An inspection of the changes in π-electron density in positions 4 and 5 on excitation reveals that the LFMO has a node close to carbon atom 4 in the thiones, which is not the case with carbon atom 5. Consequently, the inductive effect ($-I$) of the phenyl group opposes the loss of charge in position 4 on excitation, and a hypsochromic shift should result, which might more than outweigh a small bathochromic effect due to conjugation. In the thiols, position 4 does not have a node in the LFMO, but the calculated loss in π-electron density on excitation is quite large, 0.061 e.u. in the oxazole and 0.066 e.u. in the thiazole. It is about 50 % larger than in position 5, and also in this case a hypsochromic shift is expected on consideration of the inductive effect alone. Plattner and Heilbronner [18] have shown how the differences in π-electron densities between HOMO and LFMO for azulene can very precisely explain the effect of methyl substitution on the absorption spectrum of this molecule.

Generally, the strong chromophoric effect of the thione group causes heterocyclic thiones to absorb at longer wavelength than their methylthio analogs.[4,12] This is also true for the systems in the present study, and the effect is reproduced by the calculated transition energies (Fig. 4). On protonation, the thiones as a rule undergo hypsochromic shifts, and their methylthio analogs bathochromic shifts. As a first approximation, one should expect the corresponding protonated forms to have the same spectra, since they have the same π-electron structures. The deviations observed can be ascribed to

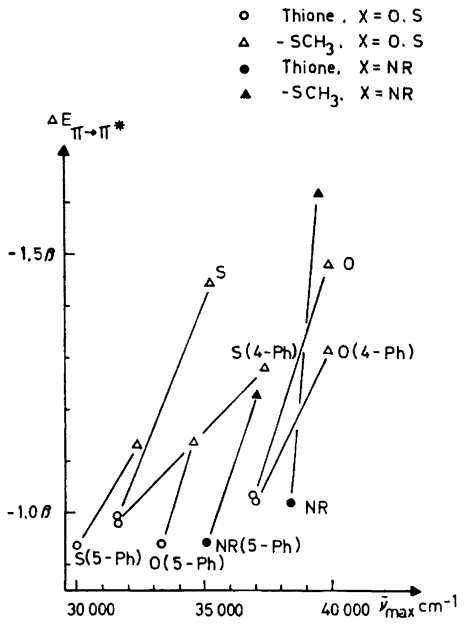


Fig. 4. Correlation between calculated and experimental transition energies.

the different effects of *N*- and *S*-methylation, and to the solvent shifts in sulphuric acid.

Murrell [19] has shown how "Förster's cycle" [20] can be used to calculate a crude approximation to the pK_a value of an excited state (pK_a^*) from the positions of the absorption maxima of an acid and its conjugate base, if the pK_a value of its ground state is known. The expression (3) is derived under

$$pK_a^* = \frac{\bar{\nu}_B - \bar{\nu}_{BH^+}}{477} + pK_a \qquad (3)$$

the assumption that the entropy of ionisation is the same in the ground and excited states. Application of (3) to the compounds 1—30 shows that the basicity of all thiones decreases, mostly by several pK_a units (Table 5).

Table 5. Excited state properties.

R_1	R_2	X	pK_{HA}^*	$pK_{NCH_3}^*$	$pK_{SCH_3}^*$	$pK_T^*(1)$	$pK_T^*(2)$	Δq_S	Δq_N
CH_3	CH_3	O	− 7.8(1)	− 8.1(3)	6.0(2)	−14.1	−13.8	−0.343	−0.015
Ph	H	O	−11.3(4)	−10.0(6)	2.6(5)	−12.6	−13.9	−0.325	−0.057
H	Ph	O	− 9.5(7)	− 9.3(9)	0.5(8)	− 9.8	−10.0	−0.303	−0.025
CH_3	CH_3	S	− 7.4(10)	− 7.5(12)	7.6(11)	−15.1	−15.0	−0.326	−0.012
Ph	H	S	− 6.4(13)	− 8.0(15)	10.5(14)	−18.5	−16.9	−0.293	−0.036
H	Ph	S	− 7.2(16)	− 7.1(18)	3.7(17)	−10.8	−10.9	−0.320	−0.056
CH_3	CH_3	NH	− 4.7(19)	− 4.3(21)	8.4(20)	−12.7	−13.1	−0.441	−0.011
CH_3	CH_3	NCH_3	− 4.3(21)	− 3.6(23)	7.3(22)	−10.9	−11.6	−0.441	−0.011
Ph	H	NH	− 7.6(24)	− 7.1(26)	5.2(25)	−12.3	−12.8	−0.550	−0.088
Ph	H	NCH_3	− 7.6(24)	− 8.9(27)	5.2(25)	−14.1	−12.8	−0.550	−0.088
H	Ph	NH	− 8.9(27)	− 5.1(30)	4.0(28)	− 9.1	−12.9	−0.550	−0.060
H	Ph	NCH_3	− 7.1(26)	− 5.1(30)	3.5(29)	− 8.6	−10.6	−0.550	−0.060

This decrease in basicity reflects the general tendency for π-electron migration from the thiocarbonyl sulphur atom in $\pi \rightarrow \pi^*$ transitions in thioamides, which is also manifested by increasing blue-shifts of the corresponding absorption bands with increasing solvent polarity.[21] The methylthio compounds, on the other hand, with two exceptions show increases in basicity on excitation. The calculations indicate large decreases in π-electron density on the thiocarbonyl sulphur atom (Δq_S) in the thione and small decreases on nitrogen atom 3 (Δq_N) in the thiol form on excitation (Table 5). The result of these basicity changes is a spectacular increase in K_T, *i.e.* the dominance of the thione form is considerably greater in the excited state than in the ground state. It is true that the use of Förster's cycle involves some approximations. $\bar{\nu}_B$ does not give the energy of the 0—0 transition, since, according to the Franck-Condon principle, the solvent cage cannot reorient during the excitation, and consequently the transition ends in a state in which the solvent molecules are in a rather unstable orientation. The solute molecules are also in a vibrationally excited state, and consequently $\bar{\nu}_B$ gives the energy of transition to a state considerably above the vibrational ground level of the excited state

with equilibrium between solute and solvent molecules, in which pK_a^* should be measured. This means that $\bar{\nu}_B$ is too large, but the same is true for $\bar{\nu}_{BH^+}$, and the errors will at least partly cancel. Mason *et al.*[22] have used both Förster's cycle and fluorescence measurements at different pH values to estimate pK_a^* for 3-hydroxyquinoline, and the two methods gave almost identical results. On the other hand, Wehry and Rogers[23] have found differences of up to two pK_a^* units for phenols between estimates by the two methods. In the present case the effects are so large that one can safely conclude that the calculated shift of the thione-thiol equilibrium still more in favour of the thione form is real and quite substantial. This is also in agreement with the MO energies given in Table 3, since the ΔE_π^* values can be obtained by the relation (4):

$$\Delta E_\pi^* = \Delta E_\pi + [\Delta E_{\pi\to\pi^*}(\text{thiol}) - \Delta E_{\pi\to\pi^*}(\text{thione})] \quad (4)$$

It is also interesting to note that the observed (Table 4) and calculated (Table 3) difference between thiol and thione transition energies is smallest for the 5-phenyl substituted systems, for which also the smallest changes in K_T on excitation are observed.

Jaffé *et al.*[24] have used Förster's cycle to calculate K_T^* for a series of conjugate acids of substituted *p*-dimethylamino-azo- and -azoxy-benzenes. In these, the equilibrium is shifted from the ammonium to the azonium form on excitation, and the authors point out the possible importance of the tautomeric equilibrium in the excited state for the mechanisms of photochemical reactions.

EXPERIMENTAL

The preparation of the compounds used in this investigation is described in Part III.

The pK_a values of the thiones were determined by the spectroscopic method. The concentrations of the aqueous sulphuric acids were determined by titrating weighed samples with standard sodium hydroxide, and their H_0 values were obtained from the tables collected by Paul and Long.[25] The UV spectra were recorded alternatively with a Cary Model 15 and a Unicam Model SP 800 B ultraviolet-visible spectrophotometer. The compounds were dissolved in ethanol, and the solutions were diluted with acid so that the final ethanol concentration was 2 %. For each compound the spectrum was recorded at 25.0°C and 5–7 different H_0 values, and the ionization ratios I were obtained from the relation (5).

$$I = \frac{[BH^+]}{[B]} = (\varepsilon_B - \varepsilon)/(\varepsilon - \varepsilon_{BH^+}) \quad (5)$$

The extinction was measured at wavelengths both above and below the isosbestic point in order to minimize solvent effects,[26] and ε_B and ε_{BH^+} were obtained at H_0 values 1.5–2.0 units above and below that corresponding to $I = 1.0$. The limits of error given in Table 1 represent the scatter within one series of measurements.

The pK_a values of the weakly basic methylthio compounds ($pK_a = 0.3-3.3$) were obtained in a similar way by spectroscopic measurements in solutions containing hydrochloric acid and sodium chloride with a total concentration of one mole per liter. In this way concentration constants in media of approximately the same ionic strengths were obtained.

The more basic methylthio compounds were measured by potentiometric titration with 0.02 N hydrochloric acid in solutions with a total base concentration of less than 10^{-3}, using a Metrohm Model E 300 pH meter. This technique gives approximately thermodynamic constants, but on the present level of approximation they can safely be

compared with those obtained by the two other methods, since the expression for K_a contains the ratio of the activities of two positive ions. Their activity coefficients will at least partly cancel, and therefore medium effects are not extremely important.

The molecular orbital calculations were performed with the electronic digital computer SMIL of the Department of Numerical Analysis of the University of Lund.

Acknowledgement. This work has been supported by *the Swedish Natural Science Research Council.*

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Received December 19, 1968.