SCF MO CI CALCULATIONS FOR ANIONS OF MERCAPTO DERIVATIVES OF BENZENES, NAPHTHALENES, PYRIDINES AND PYRIMIDINES[1]

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The semiempirical Pariser-Parr-Pople type calculations are used to predict the singlet--singlet ($\pi \to \pi^*$ type) electronic transition energies, oscillator strengths and transition polarizations for thirty three sulfur-containing aromatic and heterocyclic compounds (benzenes, naphthalenes, pyridines, pyrimidines). Special consideration is devoted to the anionic forms of the molecules. The core integral for the $-S^-$ substituent is treated as an empirical parameter and its value is chosen to fit results for mercaptobenzene anion and then applied for the molecules with the $-S^-$ substituents. In general, the calculated spectra of the anions under study, as well as neutral mercapto and methylthio substituted compounds, agree well with experimental measurements for transitions in the whole ultraviolet absorption region.

1. Introduction

Quantum mechanical studies of electronic structures and spectra of sulfur-containing compounds by means of the semiempirical and *ab initio* methods have contributed to understanding of many physical and chemical properties (*e. g.* Zahradník 1965; the reader is also referred to a forthcoming review[2] on the quantum chemistry of sulfur compounds by Fa-

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bian 1970). Semiempirical Pariser-Parr-Pople type calculations (here referred to as PPP method), have proved to be particularly useful, and during the last three years this method has frequently been employed for succesful interpretations of a number of spectral properties of neutral sulfur-compounds.

However, the interpretation of electronic absorption spectra of ionized forms within this method is very incomplete so far. Recent papers (Nishimoto and Forster 1968, Tichý and Zahradník 1969, Berndt and Kwiatkowski 1970; comp. also Zahradník 1968) have shown that the electronic spectra of some anionic species of a number of hydroxy derivatives of aromatic and heterocyclic molecules can be succesfully interpreted by the PPP method. The aim of the present paper is to extend this type of calculations for anions of some mercapto derivatives of benzene, naphthalene, pyridine and pyrimidine. We shall also compare the spectra of the anions with those of the corresponding neutral and methylthio derivatives of molecules. The list of the examined compounds and their numbering are given in Fig. 1.
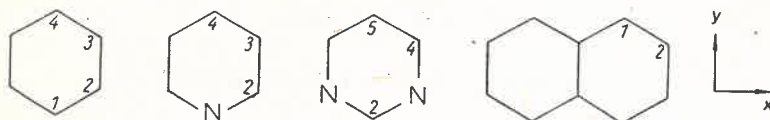

Fig. 1. The numbering systems adopted for the parent molecules. The polarization direction (angle Θ) is measured positive towards the y axis with respect to the x one.

Molecules under study:

(1) mercaptobenzene
(2) methylthiobenzene
(3) mercaptobenzene anion

(4) 1-mercaptonaphthalene
(5) 1-mercaptonaphthalene anion
(6) 2-mercaptonaphthalene
(7) 2-mercaptonaphthalene anion

(8) 1,2-dimercaptobenzene
(9) 1,2-dimercaptobenzene anion (2-S⁻)
(10) 1,2-dimercaptobenzene dianion
(11) 1,3-dimercaptobenzene
(12) 1,3-dimercaptobenzene anion (3-S⁻)
(13) 1,3-dimercaptobenzene dianion
(14) 1,4-dimercaptobenzene
(15) 1,4-dimercaptobenzene anion (4-S⁻)
(16) 1,4-dimercaptobenzene dianion

(17) 2-methylthiopyridine
(18) 2-mercaptopyridine anion
(19) 3-methylthiopyridine
(20) 3-mercaptopyridine anion
(21) 4-methylthiopyridine
(22) 4-mercaptopyridine anion
(23) 2-methylthiopyrimidine
(24) 2-mercaptopyrimidine anion
(25) 4-methylthiopyrimidine
(26) 4-mercaptopyrimidine anion
(27) 5-mercaptopyrimidine
(28) 5-methylthiopyrimidine
(29) 5-mercaptopyrimidine anion

(30) 4-amino-2-methylthiopyrimidine
(31) 4-amino-2-mercaptopyrimidine anion (thiocytosine anion)
(32) 2-amino-4-methylthiopyrimidine
(33) 2-amino-4-mercaptopyrimidine anion (isothiocytosine anion)

It should be noted, that the spectra of several neutral molecules, for which the theoretical calculations are presented in this paper, have already been investigated by means of the PPP method. Namely, the absorption spectra of mercaptobenzene and methylthiobenzene were succesfully interpreted by Kimura and Nagakura (1965), Nishimoto (1967), Fabian et al.

(1967), Hartmann and Fabian (1969). The results of our calculations for the above compounds are given here only in order to compare them with the results obtained for the mercapto-benzene anion.

One of the authors and his co-workers (Fabian *et al.* 1967) have carried out similar calculations for neutral forms of dimercaptobenzenes and mercaptonaphthalenes. The obtained results were superimposed on experimental spectral curves in the same way as it is done in the present paper. Therefore, we shall only present the theoretical results for the anions of the compounds mentioned above in this way, giving the results for the corresponding neutral forms in tables and correlation plots. It is noteworthy that, as far as we know, the electronic spectra of methylthio substituted pyridines and pyrimidines have not been interpreted by the PPP method.

2. *Calculations*

The semiempirical PPP method (see *e. g.* Parr 1963) with the zero differential overlap approximation has been adopted. The reader is also referred to our previous paper (Berndt and Kwiatkowski 1970) on similar calculations for anions of hydroxycompounds. Since the details of the present calculations are the same as those in the paper mentioned above, we are only reporting all the applied parameters in Table I.

TABLE I

Semiempirical parameters used in the calculations[1]

Atom		$-W_p$(in eV)	γ_{pp}(in eV)
Carbon (*tr tr tr* π)		11.16[2]	11.13[2,3]
Nitrogen (*tr*² *tr tr* π)		14.12[2]	12.34[2,3]
Sulfur	in $-$SH group	21.26 $(10.46^{[4]}+\gamma_{SS})$	
(*tr*² *tr tr* π²)	in $-$SCH₃ group	20.24 $(9.44^{[4]}+\gamma_{SS})$	10.8[3]
Sulfur	in $-$S⁻ group	19.0 $(8.2^{[5]}+\gamma_{SS})$	
(*tr*² *tr*² *tr* π²)			

Bond	Distance (in Å)	$\beta_{pq}^{[6]}$(in eV)
C$-$C	1.397	$-$2.294
C$-$N	1.34	$-$2.402
C$-$S	1.75	$-$1.6

[1] The values of the parameters are similar to those used in the previous papers of the third author (Fabian *et al.* 1967, Hartmann and Fabian 1969).

[2] From Hinze and Jaffé (1962).

[3] $\gamma_{pp} = I_p - A_p$. The values of the ionization potentials (I_p) and electron affinities (A_p) of appropriated valence states were taken from Hinze and Jaffé (1962).

[4] Experimental values of ionization potentials of the H₂S (10.46 eV) and HSCH₃ (9.44 eV) molecules (Watanabe *et al.* 1962).

[5] The value determined by comparison of the experimental and theoretical first singlet-singlet transition energies for the mercaptobenzene anion.

[6] The resonance integrals β_{pq} were considered only for the nearest neighbours.

However, the way of estimating the value of the core integral

$$W_{-S^-} = \langle \Phi(i)|T(i) + U^{++}(i)|\Phi(i)\rangle$$

for the $-S^-$ substituent should be explained. We assume, analogously as in the previous paper (Berndt and Kwiatkowski 1970) that the removal of the proton of the $-SH$ group leaves the hybridization of the valence electrons of sulfur atom unchanged so that there are two π-electrons of $-S^-$ conjugated with the π-electron system of the ring. Consequently, the integral W_{-S^-} is approximated in the following way

$$W_{-S^-} = -I(-S^-) - \gamma_{SS},$$

where $I(-S^-)$ is the ionization potential of these lone pair electrons of the $-S^-$ substituent, which are conjugated with the π-electrons of the parent molecule. The value of the two-electron one-center Coulomb repulsion integral γ_{SS} is put to be equal to 10.8 eV (see Table I).

Unfortunately, the value of $I(-S^-) = -[W_{-S^-} + \gamma_{SS}]$ remains unknown and it must be estimated empirically. The application of different values of $I(-S^-)$, when keeping all the other parameters of the calculations unchanged, has allowed to find the value of $I(-S^-)$ = 8.2 eV exactly reproducing the experimental value of the first singlet-singlet transition energy for the anion of mercaptobenzene. It may be worthwhile to note that the value found in this way depend on the values of other integrals used in the calculations, particularly on the value of the β_{CS} resonance integral.

As far as the two-center Coulomb repulsion integrals are concerned we adopted the Nishimoto and Mataga approximation to estimate their values. As to the excited states, the configuration interaction was admitted and all the singly excited configurations have been included in the configuration interaction treatment.

The calculations reported here have been based on the assumption that the anionic forms may be represented by electronic structures with the negative charges concentrated on the sulfur atom. This assumption, which is rather evident as far as the anions of mercapto derivatives of hydrocarbons are concerned, requires a detailed investigation in the case of the anions of mercapto derivatives of N-heterocyclic compounds. It is known that the mercapto substituted pyridines and pyrimidines are capable of thiol-thione tautomerism, because the labile hydrogen atom may be attached to either the nitrogen or the sulfur atoms (comp. Jones and Katritzky 1958, Albert and Barlin 1959, Mason 1960). Thus, for instance, the existence of 2- and 4-mercaptopyridines in the forms of pyrid-2- and pyrid-4-thiones, respectively, has been confirmed by X-ray measurements (Penfold 1953), infrared spectroscopic studies (Katritzky and Ambler 1963) and some studies on ionization constants[3] (Jones and Katritzky 1958).

The investigations of the ultraviolet absorption spectra of some monosubstituted pyrimidines (Boarland and McOmie 1952a) confirm the fact that 2- and 4-mercaptopyrimidines in neutral solutions exist mainly in the thione structures (as pyrimid-2- and pyrimid-4-

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[3] Jones and Katritzky (1958), using a reasonable assumption that the basicities of the individual tautomers are not greatly affected by N- or S-alkylation, have shown that thione forms are preferred by factors of about $10^{4.5}$ and about 10^4 for 2- and 4-mercaptopyridines, respectively.

-thiones, respectively), The similar conclusion for the latter pyrimidines is deduced from infrared spectroscopic investigations (see Katritzky and Ambler 1963).

Unfortunately, no experimental data, except the ultraviolet absorption spectral evidence, concerning the electronic structures of the anions of mercapto derivatives of N-heterocyclic compounds are available. Therefore, by analogy to the corresponding anions of hydroxypyridines and pyrimidines (Berndt and Kwiatkowski 1970) electronic structures with the negative charges concentrate on the sulfur atoms have been assumed for all the anions under study.

In the calculations for pyridines and pyrimidines we have also included those for corresponding methylthio derivatives which are the neutral forms having the π-electronic structures similar to the anionic ones assumed in our calculations.

3. Results and discussion

Below we present the results of the calculations for all the compounds under study, comparing them with the corresponding experimental data available.

Some of the experimental data have been taken from literature (all references are given in the tables). However, as far as we are aware, no experimental results concerning the spectra of the anions of mercapto substituted benzenes and naphthalenes have been published. Therefore, the necessary measurements for these compounds have been done in the present work. Some details of the measurements are described in the Experimental part.

3.1. Experimental part

Mercaptobenzene was available as a commercial product (Schuchard München). It was purified by destillation ($3\times$) through a Vigreux column (b.p.$_{.30} = 77°$, $n_D^{20} = 1.5895$). Mercaptonaphthalenes were prepared according to A. W. Wagner's method (*Chem. Ber.* **99**, 375 (1966)) by HJ reduction of the sulfochlorides (1-mercaptonaphthalene: b.p.$_{.20} = 161$, $n_D^{20} = 1.6801$, yield $= 82\%$; 2-mercaptonaphthalene m.p. $= 80$-81, yield $= 80.5\%$). The methylation was done in the common manner (methylthiobenzene: b.p.$_{.14} = 76.5$-77, yield $= 72.5\%$; 1-methylthionaphthalene: b.p.$_{.0.05} = 99$-97, yield $= 71.5\%$; 2-methylthionaphtalene: b.p.$_{.2} = 130$-132, m.p. $= 59.5$-60.5, yield $= 73\%$).

The purity of all the investigated compounds was ensured gaschromatographically. The preparation was done by G. Tröger (*Diplomarbeit* 1966/1967). The UV spectral data were recorded by means of the Hungarian spectrophotometer "Spectromom 201" (MOM Budapest). The mistakes were estimated to be below 100 cm^{-1} and 10% for the transition energies and molar extinction coefficients, respectively.

The solvents were purified as described in literature (M. Pestemer, *Angew. Chem.*, **67**, 740 (1955)).

All the experimental measurements were done in the Sulfur Group headed by Professor R. Mayer (Technical University of Dresden).

3.2. Monosubstituted benzenes and naphthalenes

An examination of the electronic absorption spectra of mercaptobenezene and 1- and 2-mercaptonaphthalenes shows that there are great differences between the spectra of the

TABLE II

Monosubstituted benzenes and naphthalenes — the singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f, transition polarizations, Θ (in degrees), logarithms of molar extinction coefficients, log ε

Theoretical			Experimental[1]		
ΔE	f	Θ	ΔE (log ε)		
			(1) Mercaptobenzene		
			(He)[2]	(gas)[3]	(Cy)[4]
4.555	0.012	0	4.56	4.58 (f = 0.013)	4.58 (2.8)
5.533	0.251	90	5.3	5.30 (f = 0.347)	5.25 (3.9)
6.428	0.643	0		6.22 (f = 0.398)	
6.451	0.782	90		6.79 (f = 0.587)	
7.384	0.474	0		~7.3 (f = 0.438)	
7.503	0.230	90			
			(2) Methylthiobenzene		
			(He)[2]		
4.435	0.021	0	4.37		
5.152	0.362	90	4.88		
6.026	0.269	0			
6.338	0.493	90			
7.137	0.839	0			
7.306	0.427	90			
			(3) Mercaptobenzene anion		
			(W, 4% KOH)[5]		
4.118	0.037	0	4.11 (2.9)		
4.585	0.433	90	4.72 (4.17)		
5.546	0.080	0			
6.258	0.317	90			
7.024	1.001	0			
7.157	0.133	90			
			(4) 1-Mercaptonaphthalene		
			(Cy, Ace)[5,6]		$(i-C_8H_{18})$[7]
3.930	0.009	−2			
4.122	0.283	84	4.15 (3.8)		4.17 (3.4)
5.340	0.458	3			
5.464	0.336	−1	} 5.58 (4.7)		
5.630	0.046	66			
5.685	0.999	−2			
			(5) 1-Mercaptonaphthalene anion		
			(W, 4% KOH)[5]		
3.551	0.323	80	3.71 (3.95)		
3.765	0.042	11			
4.851	0.241	−1	5.00 (4.23)		
4.878	0.038	−12			
5.124	0.117	−87			
5.673	0.823	−1			

TABLE II continued

Theoretical			Experimental[1]
ΔE	f	Θ	ΔE (log ε)
			(6) 2-Mercaptonaphthalene
			(Cy, Ace)[5,6] $\qquad\qquad$ $(i-C_8H_{18})$[7]
3.875	0.022	−53	~3.9 (3.05) $\qquad\qquad$ 3.87 (3.1)
4.295	0.170	−69	4.4 (3.9) $\qquad\qquad$ 4.25 (3.7), 4.4 (3.9)
5.279	0.391	12	5.15 (4.6) $\qquad\qquad$ 5.12 (4.7)
5.483	0.235	27	5.52 (4.5) $\qquad\qquad$ 5.51 (4.6)
5.666	0.120	15	~5.8 (4.5)
5.976	0.609	−53	
			(7) 2-Mercaptonaphthalene anion
			(W, 4% KOH)[5]
3.488	0.101	−26	3.60 (3.29)
4.086	0.202	−9	4.09 (4.05)
4.683	0.710	36	
4.821	0.254	42	} 4.77 (4.49)
5.353	0.002	−26	
5.773	0.277	−24	

[1] Solvent: He — hexane, Cy — cyclohexane, Ace — acetonitrile, W — water. The values of log ε are given in the parentheses.

[2] Mangini et al. (1967).

[3] Kimura and Nagakura (1965).

[4] A. P. I. Research Project No 44 II (1955), 586. See *Organic Electronic Spectral Data*, Interscience Publishers, Inc., New York, 1960, Vol. II (1953–1955).

[5] Present work. See *Experimental Part*.

[6] Fabian et. al. (1967) and unpublished results of Fabian and Tröger.

[7] Williams and Offenhauer (1957).

compounds measured in nonpolar solvents (hexane, cyclohexane) and those measured in aqueous KOH. Absorption bands of the anionic forms of the molecules mentioned above are largely shifted towards the longer wavelengths and their intensities are stronger compared to those of the corresponding neutral forms of the compounds[4] (see Fig. 2).

As seen from Table II and Fig. 2, theoretical results correctly predict these characteristic features of the spectra of the considered molecules (it should, however, be remembered that here the mercaptobenzene anion is treated as a reference molecule). It can also be seen that in the case of naphthalenes the differences between the experimental and calculated transition energies are not higher than 0.2 eV.

Under substitution of the mercapto group at the carbon atom C_1 of the naphthalene ring, the first two near ultraviolet absorption bands of naphthalene (^1L_a and ^1L_b bands according to Platt's notation, Platt 1949) displace towards longer wavelengths with respect to those of the unsubstituted naphthalene. However, it seems that the substitution of the

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[4] We do not know the reason of the longwavelength absorption of the mercaptonaphthalenes anions, having the values of log ε of the order ~1-2 (see Fig. 2). This absorption can probably be due to an $n \rightarrow \pi^*$ transition (from the nonbonding orbital at the sulfur of the −S⁻ group to the antinonbonding π^* orbitals).

1-SH group does not produce any change in the sequence of the bands (*i. e.* the weak band corresponding to ^1L_a band of naphthalene is placed in the region of longer wavelengths with respect to the strong band being ascribed to ^1L_b). Theoretical results (comp. also Fa-
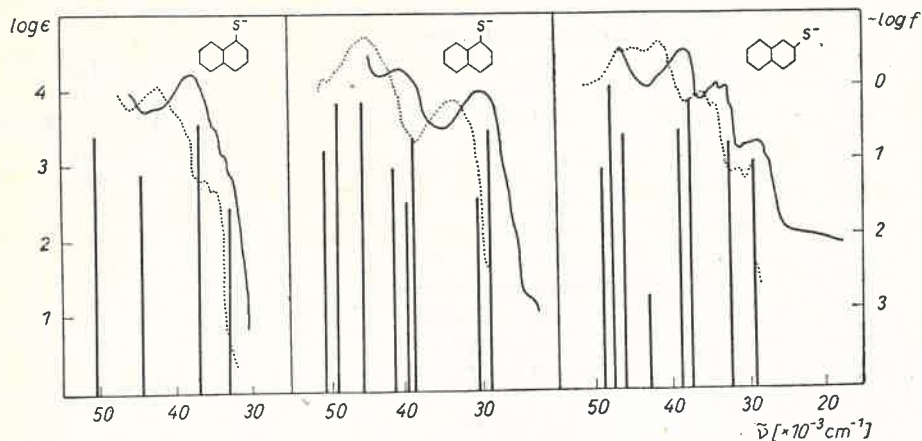

Fig. 2. Absorption curves of mercaptobenzene and mercaptonaphtalenes in 4% aqueous KOH (anions — full lines) and in cyclohexane (neutral compounds — dotted lines). The results of the PPP type calculations for the singlet-singlet transition energies and oscillator strengths for the anions are indicated by vertical straight lines

bian *et al.* 1967) confirm this fact as well. But it should be noted, that the 1-S$^-$ substituent produces stronger shifts of the bands than the 1-SH substituent and it is very probable that the sequence of the bands in the case of 1-mercaptonaphthalene anion is converted. The results of the present calculations indicate the occurrence of the conversion. One should remember, however, that the classification of the absorption bands by means of the calculated quantities ($\Delta E, f, \theta$) seems to be less reliable than that based on an experimental evidence.

On the other hand, when comparing the bands presented in Fig. 2, it can be seen that the substitution of —SH and —S$^-$ groups in the position 2 are connected with considerable shifts of the bands ^1L_a and ^1L_b of naphthalene, but do not change the sequence of the bands. Theoretical results confirm this fact.

3.3. Disubstituted benzenes

Similarly as in the case of mercaptobenzene and mercaptonaphthalenes, there are great differences between the spectra of neutral forms of dimercaptobenzenes and those of the corresponding anions (Fig. 3). The results presented in Fig. 3 and Table III show that the PPP method satisfactorily interpret the spectra of dimercaptobenzene anions. Generally, the greatest differences between the theoretical and experimental transition energies, both for the neutral and anionic forms, are of the order of 0.3 eV (except the case of the second transition for 1,4-dimercaptobenzene, where it is of the order of 0.45 eV).

A comparison between experimental and theoretical data is better illustrated in Fig. 4. As it can be seen from the diagram, the experimentally observed shifts of the first two bands of benzene under the substitution of —SH and —S$^-$ groups are, in general, properly interpreted by the present calculations.
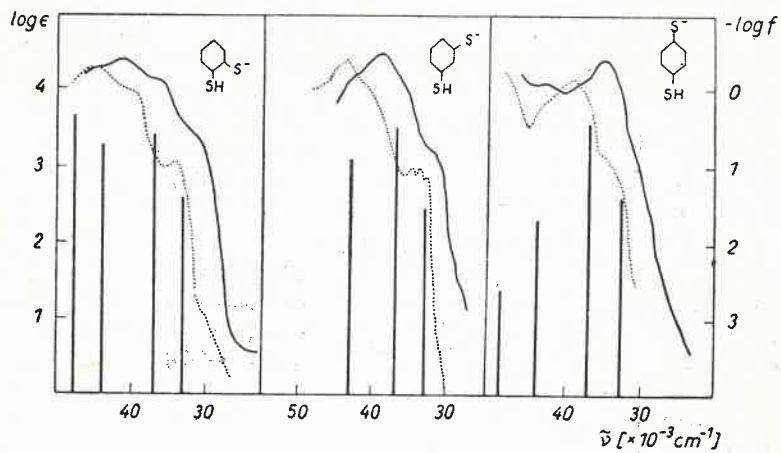
Fig. 3. Absorption curves of dimercaptobenzenes in 4% aqueous KOH (anions) and in cyclohexane (neutral compounds). For details see the caption to Fig. 2
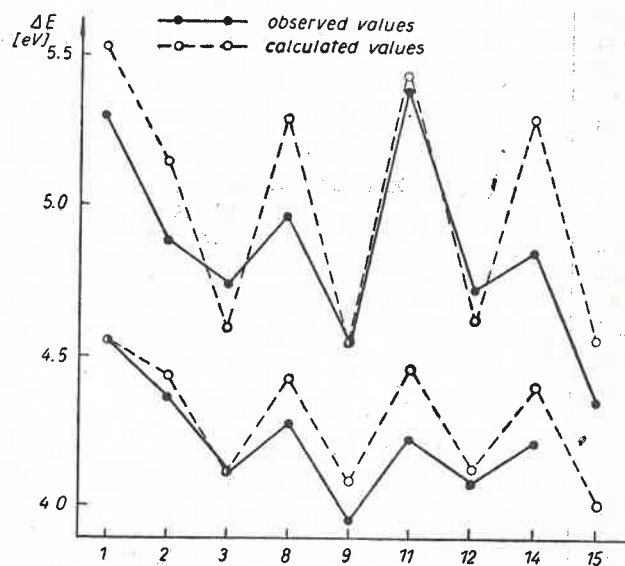

Fig. 4. Comparison between observed and calculated singlet-singlet transition energies for mono- and disubstituted benzenes under study. Actual data and numbering of the molecules are given in Tables II, III and Fig. 1

TABLE III

Disubstituted benzenes — the singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f, logarithms of molar extinction coefficients, log ε, transition polarization, Θ (in degrees)

Theoretical			Experimental[1] ΔE (log ε)
ΔE	f	Θ	
			(8) 1,2-Dimercaptobenzene
			(Cy, Ace)[2,3]
4.436	0.019	−60	4.28 (3.05–3.1)
5.294	0.146	30	4.96 (4.0)
6.003	0.986	−60	5.58 (4.3–4.45)
6.245	0.590	30	
7.254	0.137	−60	
7.267	0.008	30	
			(9) 1,2-Dimercaptobenzene anion
			(W, 4% KOH)[3]
4.008	0.049	−37	3.95 (3.46)
4.538	0.331	76	4.54 (4.15)
5.431	0.226	−21	5.12 (4.38)
5.864	0.516	−15	
6.722	0.649	1	
6.897	0.088	62	
			(10) 1,2-Dimercaptobenzene dianion
3.911	0.080	−60	
4.276	0.216	30	
5.086	0.747	−60	
5.122	0.065	30	
6.066	0.028	−60	
6.495	0.166	30	
			(11) 1,3-Dimercaptobenzene
			(Cy, Ace)[2,3]
4.456	0.010	60	4.24 (3.0)
5.427	0.101	−30	5.39 (4.4)
5.885	0.973	60	
6.187	0.589	−30	
7.037	0.297	−30	
7.047	0.107	60	
			(12) 1,3-Dimercaptobenzene anion
			(W, 4% KOH)[3]
4.189	0.029	−88	4.08 (3.28)
4.622	0.411	28	4.71 (4.50)
5.413	0.148	−41	5.27 (4.20)
5.660	0.495	69	
6.657	0.594	−28	
6.847	0.281	82	

TABLE III continued

Theoretical			Experimental[1]
ΔE	f	Θ	ΔE (log ε)
			(13) 1,3-Dimercaptobenzene dianion
3.997	0.030	60	
4.615	0.156	−30	
4.693	0.739	60	
4.924	0.164	−30	
6.088	0.034	60	
6.579	0.351	−30	
			(14) 1,4-Dimercaptobenzene
			(Cy, Ace)[2,3]
4.397	0.035	0	4.22 (3.15)
5.286	0.421	90	4.8–4.84 (4.15–4.25)
6.412	0.714	0	
6.455	0.871	90	
6.593	0.000	90	
6.660	0.000	90	
			(15) 1,4-Dimercaptobenzene anion
			(W, 4% KOH)[3]
4.014	0.055	0	4.35 (4.40)
4.564	0.518	90	5.46 (4.20)
5.482	0.026	0	
6.036	0.003	90	
6.481	0.767	90	
6.499	0.548	0	
			(16) 1,4-Dimercaptobenzene dianion
3.791	0.068	0	
4.322	0.661	90	
5.014	0.000	90	
5.244	0.000	90	
5.812	0.150	0	
6.330	0.546	90	

[1] Solvent: Ace — acetonitrile, Cy — cyclohexane, W — water. The values of log ε are given in the parentheses.

[2] Fabian et al. (1967) and unpublished results of Fabian and Tröger.

[3] Present work. See *Experimental Part*.

3.4. Monosubstituted pyridines and pyrimidines

Absorption spectra of anionic and neutral forms of monomercapto substituted pyridines and pyrimidines do not show analogies occurring in the case of the mercapto derivatives of both benzene and naphthalene. It is caused by the fact that pyridine and pyrimidine exist in thione forms (or as dipolar ions, see e.g. Mason 1960). Pyrid-2-, pyrid-4- and pyrimid -2- and pyrimid-4-thiones absorb in different spectral regions than the corresponding 2-

TABLE IV

Monosubstituted pyridines — the singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f, molar extinction coefficients, ε (or log ε), transition polarization, Θ (in degrees)

Theoretical			Experimental[1]
ΔE	f	Θ	ΔE (ε or log ε)
			(17) 2-Methylthiopyridine
			(pH = 6)[2]
4.381	0.129	5	4.25 (4200)
5.223	0.342	−45	5.02 (8700)
5.992	0.061	44	
6.473	0.350	−41	
7.136	0.926	45	
7.346	0.464	−56	
			(18) 2-Mercaptopyridine anion
			(pH = 12)[2] (0.1 N NaOH)[3,4]
4.003	0.140	4	4.00 (4700) 4.02 (5600)
4.681	0.396	−43	4.70 (12500) 4.73 (12800)
5.548	0.003	64	
6.386	0.219	−31	
7.091	0.778	45	
7.149	0.339	86	
			(19) 3-Methylthiopyridine
			(pH = 9)[2]
4.350	0.097	−20	4.22 (2500)
5.129	0.307	34	4.90 (8700)
5.918	0.178	76	
6.480	0.404	13	
7.245	0.898	−64	
7.454	0.347	43	
			(20) 3-Mercaptopyridine anion
			(pH = 10)[2]
3.917	0.096	−21	3.96 (2600)
4.568	0.375	35	4.61 (13500)
5.487	0.077	52	5.66 (9800)
6.380	0.253	13	
7.038	0.177	−50	
7.213	0.888	−75	
			(21) 4-Methylthiopyridine
			(pH = 12)[2] (0.1 N NaOH)[3] (0.1 N NH$_3$+EtOH)[5]
4.609	0.003	0	? ? ?
5.026	0.365	90	4.70–4.71 (12500) 4.68 (12200) 4.77 (4.2*)
5.956	0.381	0	5.79 (9500)
6.350	0.476	90	
7.469	0.663	0	
7.536	0.453	90	

TABLE IV continued

Theoretical			Experimental[1]			
ΔE	f	Θ	ΔE (ε or $\log \varepsilon$)			
			(22) 4-Mercaptopyridine anion			
			(pH = 12)[2]	(0.1 N NaOH)[3]	(0.1 N NaOH)[4]	
4.344	0.003	0	?	?	?	
4.460	0.439	90	4.32 (4.18*)	4.37 (138000)	4.38	
5.496	0.219	0	5.58 (4.04)	5.61 (9400)	5.61	
6.286	0.352	90				
7.298	0.802	0				
7.320	0.025	90				

[1] All data in aqueous solution unless otherwise indicated. Values in parentheses are ε, except those marked by (*) which are $\log \varepsilon$.

[2] Albert and Barlin (1959). *Cf.* Mason (1960).

[3] Jones and Katritzky (1958).

[4] Láng (1963).

[5] Ross (1951).

TABLE V

Monosubstituted pyrimidines — the singlet-singlet transition energies, ΔE (in eV), scillator strengths, f, molar extinction coefficients, ε (or $\log \varepsilon$), transition polarization, Θ (in degrees)

Theoretical			Experimental[1]			
ΔE	f	Θ	ΔE (ε or $\log \varepsilon$)			
			(23) 2-Methylthiopyrimidine			
			(pH = 7)[2]	(EtOH)[3]	(pH = 6.98)[3]	
4.410	0.090	0	4.43 (2500)	4.34 (3.30*)	?	
5.182	0.455	90	4.96 (14000)	4.94 (4.20*)	4.96 (4.12*)	
5.908	0.000	0				
6.598	0.187	90				
7.293	0.965	0				
7.294	0.469	90				
			(24) 2-Mercaptopyrimidine anion			
			(pH = 13)[3,4]	(pH = 11)[5]	(pH = 11)[6]	
3.941	0.067	0	?	4.13 (2500)	?	
4.666	0.504	90	4.59 (4.23*)	4.61 (17000)	4.61 (13150)	
5.516	0.021	0	5.37 (3.69*)		5.28 (3750)	
6.546	0.110	90				
7.096	0.141	90				
7.290	0.949	0				
			(25) 4-Methylthiopyrimidine			
			(pH = 11)[7]			
4.558	0.151	35	4.48 (10000)			
5.146	0.268	17	?			
5.945	0.216	−74	5.82 (7000)			
6.496	0.353	27				
7.327	0.744	−72				
7.622	0.482	8				

TABLE V continued

Theoretical			Experimental[1] ΔE (ε or log ε)		
ΔE	f	Θ			
			(26) 4-Mercaptopyrimidine anion		
			(pH = 13)[3]	(pH = 11)[6]	(pH = 11)[8]
4.196	0.203	41	4.22–4.25 (4.04*)	4.23 (13300)	4.25 (16000)
4.613	0.301	15			
5.572	0.088	−63			
6.410	0.287	40			
7.243	0.827	−67			
7.277	0.000	−53			
			(27) 5-Mercaptopyrimidine		
4.526	0.102	0			
5.471	0.324	90			
6.418	0.104	0			
6.814	0.600	90			
7.479	0.912	0			
7.577	0.132	90			
			(28) 5-Methylthiopyrimidine		
4.269	0.100	0			
5.058	0.375	90			
5.924	0.008	0			
6.689	0.346	90			
7.351	0.249	90			
7.401	1.004	0			
			(29) 5-Mercaptopyrimidine anion		
3.736	0.078	0			
4.481	0.420	90			
5.556	0.006	0			
6.519	0.171	90			
6.976	0.055	90			
7.355	0.561	90			

[1] All data in aqueous solution unless otherwise indicated. Values in parentheses are ε, except those marked by (*) which are log ε.

[2] Data for 2-methylthio-6-methylpyrimidine (Marshall and Walker 1951).

[3] Boarland and McOmie (1952a).

[4] Brown and Teitei (1965).

[5] Data for the 2-mercapto-4-methylpyrimidine anion (Marshall and Walker 1951).

[6] Koppel et al. (1961).

[7] Data for 4-methylthio-6-methylpyrimidine (Marshall and Walker 1951).

[8] Data for the 4-mercapto-6-methylpyrimidine anion (Marshall and Walker 1951).

and 4-methylthio derivatives of pyridine and pyrimidine, but their absorption bands are very close to the corresponding N-methyl derivatives (comp. Láng 1963, Mason 1960). The anions of 2- and 4-mercapto substituted pyridines and pyrimidines have spectra which are analogous to those of 2- and 4-methylthio derivatives of pyridine and pyrimidine, respec-

tively. The spectra of the anions are shifted towards longer wavelengths with respect to the corresponding spectra of methylthio compounds.

Tables IV and V show that the calculation results well agree with the experimental data (the differences between the theoretical and experimental transition energies do not exceed 0.2 eV). Figures 5 and 6 illustrate the differences between the spectra of the neutral
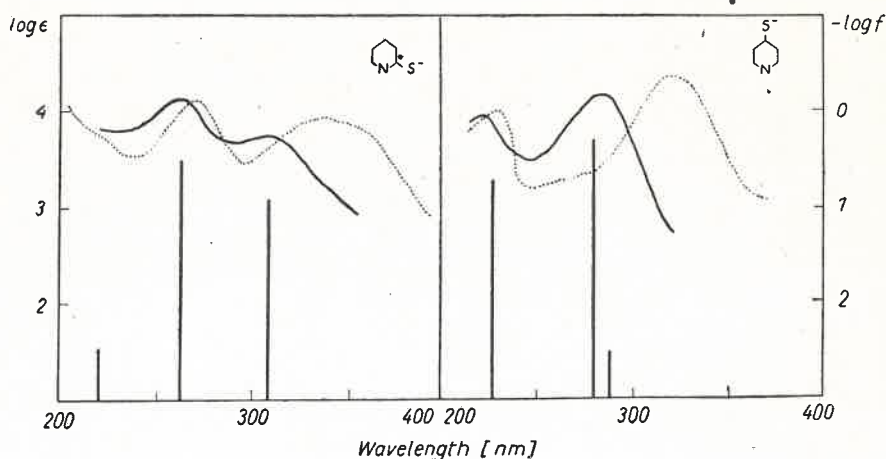

Fig. 5. Absorption curves of 2- and 4-mercaptopyridine in 0.1 N NaOH (anions) and in aqueous solution at the neutral pH (neutral compounds) — see Láng (1963). For details see the caption to Fig. 2
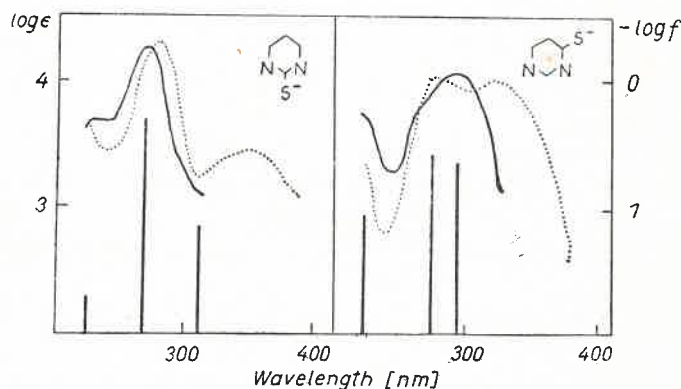

Fig. 6. Absorption curves of 2- and 4-mercaptopyrimidines in aqueous solution at pH = 13 (anions) and the neutral pH (neutral compounds) — see Boarland and McOmie (1952a). For details see the caption to Fig. 2

compounds and their anionic forms. As it can be seen, the calculated positions of the maxima of the absorption bands for the anions agree with the data obtained experimentally.

The correlation diagram in Fig. 7 shows the experimental and theoretically predicted locations of the maxima of the first two absorption bands of pyridine and pyrimidine depen-

TABLE VI

Disubstituted pyrimidines — the singlet-singlet transition energies, ΔE (in eV), oscillator strengths, f, logarithms of molar extinction coefficients, log ε, transition polarization, Θ (in degrees)

Theoretical			Experimental[1]
ΔE	f	Θ	ΔE (log ε)

(30) 4-Amino-2-methylthiopyrimidine

$(W, \text{pH} = 7.8)$[2] $\qquad\qquad (W, \text{pH} = 6.98)$[3]

ΔE	f	Θ	ΔE (log ε)	
4.412	0.124	34	4.35 (3.79)	4.43 (3.87)
5.224	0.343	−73	4.96 (4.00)	5.00 (4.08)
5.652	0.491	56	5.54 (4.31)	5.51 (4.34)
5.842	0.173	9		
6.785	0.317	−51		
6.995	0.422	6		

(31) 4-Amino-2-mercaptopyrimidine anion (Thiocytosine anion)

$(W, \text{pH} = 13.3)$[2]

ΔE	f	Θ	ΔE (log ε)
4.104	0.100	31	4.16 (3.80)
4.738	0.478	−85	4.70 (4.13)
5.297	0.117	57	
5.686	0.356	28	5.59 (4.32)
6.682	0.353	−55	
6.953	0.465	6	

(32) 2-Amino-4-methylthiopyrimidine

$(W, \text{pH} = 7.0)$[4]

ΔE	f	Θ	ΔE (log ε)
4.363	0.185	22	4.13 (4.02)
5.223	0.181	17	5.30 (3.90)
5.625	0.614	88	
6.009	0.239	22	
7.024	0.264	−67	
7.124	0.281	−34	

(33) 2-Amino-4-mercaptopyrimidine anion (Isothiocytosine anion)

$(W, \text{pH} = 10.4)$[2] $\qquad\qquad (W, \text{pH} = 11.0)$

ΔE	f	Θ	ΔE (log ε)	
4.166	0.277	31	3.97 (4.16)	3.99 (4.12)
4.760	0.201	23	4.72 (3.77)	4.73 (3.78)
5.319	0.207	−52		
5.718	0.480	70		
7.023	0.063	30		
7.030	0.514	−54		

[1] Solvent: W — water.

[2] Brown and Teitei (1965).

[3] Boarland and McOmie (1952b). Data for 4-amino-2-methylthio-6-methylpyrimidine. The data recorded in ethanol for the same compound are as follows (ΔE in eV, log ε): 4.39 (3.85), 5.00 (4,07), 5.51 (4.37) — see Boarland and McOmie (1952a).

[4] Koppel et al. (1961). They have also measured absorption bands of 2-amino-4-methylthio-6-methylpyrimidine in aqueous solution receiving following results (ΔE in eV, ε): 4.13 ($\varepsilon = 13900$), 5.32 ($\varepsilon = 10900$) at pH = 1.0 and 4.16 ($\varepsilon = 10300$), 5.34 ($\varepsilon = 12100$) at pH = 11.0.

ding on the kind of substituent ($-SCH_3$ or $-S^-$) and the position of substitution. As we see, there are correct predictions of the behaviour of the absorption spectra of pyridine and pyrimidine under $-SCH_3$ or $-S^-$ substitutions.
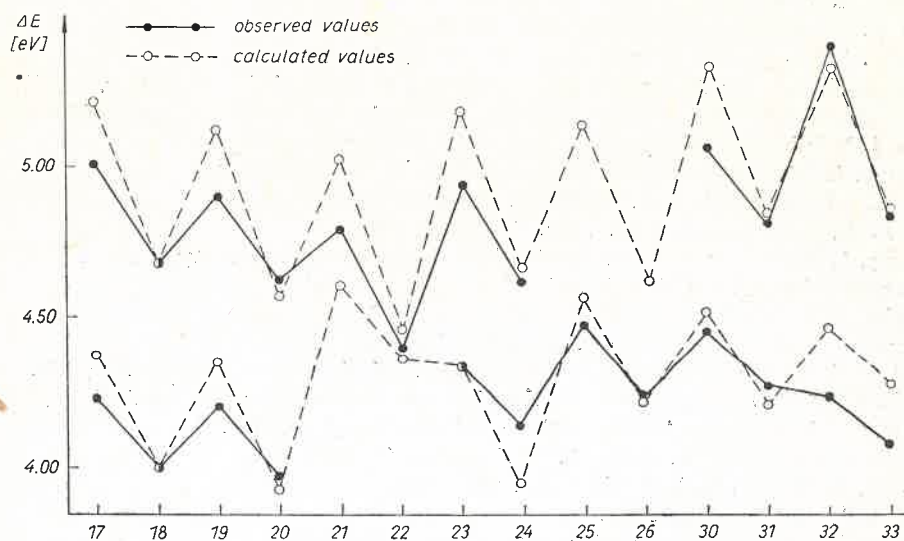

Fig. 7. Comparison between observed and calculated singlet-singlet transition energies for mono- and disubstituted pyridines and pyrimidines. Actual data and numbering of the molecules are given in Tables IV, V, VI and Fig. 1

3.5. Thiocytosine and isothiocytosine anions

It has been shown with the aid of ultraviolet and nuclear magnetic resonance spectroscopies (Brown and Lyall 1962, Katritzky and Waring 1963) that cytosine in aqueous solution exists as 4-amino-1,2- dihydro-2-oxypyrimidine (comp. also recent absorption spectra studies by Morita and Nagakura 1968). In the cases of isomers of cytosine and also their thio analogues and thiocytosine, amino-oxo and amino-thio structures have been indicated, respectively (Brown and Teitei 1965). But it was not possible in any case to allot a predominant tautomeric form with hydrogen atom attached to N_2 or N_3 on an experimental evidence. From the comparison of the absorption spectra it may also seen that the spectra of the neutral forms of thiocytosine and isothiocytosine are different from those of 4-NH_2-2-SCH_3- and 2-NH_2-4--SCH_3-pyrimidines, rspectively. On the other hand, the absorption bands of the latter compounds are similar to those of the anionic for of thiocytosine and isothiocytosine. Our theoretical results properly reproduce these experimental findings.

In a conclusion, it should be emphasized, however, that the resulting agreement between the theoretical and experimental data in our calculations cannot be treated as an evidence proving the existence of the anions of mercapto derivatives of pyridines and pyrimidines in the electronic forms having the structures assumed in the calculations. It can only be concluded that the assumptions made do not lead to uncorrect results.

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