AM1 studies of photoelectron spectra
11.* 10-Alkylphenothiazines

V. K. Turchaninov, N. N. Chipanina, and A. I. Vokin*

Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 ul. Favorskogo, 664033 Irkutsk, Russian Federation. Fax: +7 (395 2) 35 6046. E-mail: root@irioch.irkutsk.su

Deep-lying π- and σ-orbitals of 10-alkylphenothiazines were studied by photoelectron spectroscopy and quantum-chemical AM1 calculations. It was demonstrated that in 10-ethylphenothiazine the lone electron pair of the S atom interacts with the π-system of the aromatic fragments. The π-MOs, whose energies are a function of the dihedral angle between the planes of the benzene rings of phenothiazines and are independent of the degree of pyramidality of the N atom, were found. The differences in the energy of these MOs were used for estimating equilibrium dihedral angles of tricyclic molecules in the gaseous phase. These values differ only slightly from those observed in the solid phase. The replacement of the hydrogen atom at position 10 by the methyl group leads to a decrease in the dihedral angle, leaving the orientation of the substituent unchanged. The orbital energies of phenothiazines, which were calculated by the AM1 method, adequately reflect the order of changes in the ionization potential. However, contributions of the two highest occupied π-MOs to the total charges on the N and S atoms are inconsistent with the experimental data.

Key words: photoelectron spectroscopy, molecular conformation, semiempirical quantum-chemical calculations, phenothiazines.

The photoelectron spectra of phenothiazine and a series of its *N*- and *C*-substituted derivatives have been adequately studied.[2–4] For the low-energy region (≤11 eV), the assignment of most of the ionization potentials was made.[2,3] It was demonstrated[3] that, unlike processes of one-electron oxidation in the liquid phase in which the substituent at the N atom reduces the activity of phenothiazine, the reverse situation is observed in the gaseous phase, namely, alkylation at position 10 leads to a decrease in the first ionization potential.

The causes of the differences in the gas-phase and liquid-phase properties of phenothiazines were analyzed within the framework of two hypotheses.[3] According to the first hypothesis, the inconsistency between the behavior of phenothiazines in solutions and the classical concept of the effect of saturated hydrocarbon radicals on the electron-withdrawing ability is attributed to conformational factors. Thus, the replacement at position 10 results in the transformation of the quasi-equatorial spatial and electronic structure of the predominant conformer into the quasi-axial structure (Fig. 1). According to the second hypothesis, the lower values of potentials of electrochemical oxidation and lower energies of transitions in the charge transfer spectra are due to ionic solvation, *i.e.*, to stronger stabilization of the π radical-cation or the product of partial transfer of the electron pair in NH-containing compounds.

Based on the above-mentioned normal effect of the alkyl group in the gaseous phase and on the fact that the first band in the photoelectron spectra of all studied phenothiazines is substantially wider than the next individual band regardless of the type and structure of the substituent at the N atom, preference was given to the second hypothesis. The above-mentioned facts are indicative of a substantial contribution of the p_z-AO of the N atom to the HOMO and of the pyramidal configuration of the bonds formed by the N atom, *i.e.*, in all cases the predominant conformers have similar spatial structures.[3] Therefore, it was noted that the *N*-substituted phenothiazines differ from each other only in the conformation of the hydrocarbon chain of the substituent.

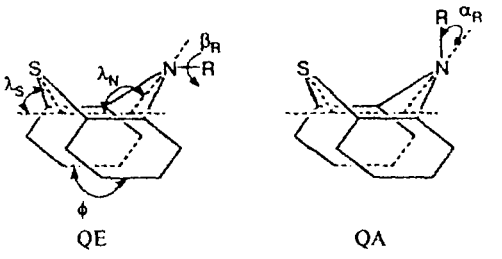


Fig. 1. Stereoisomers of phenothiazines; QE and QA are the quasi-equatorial and quasi-axial isomers, respectively.

* For Part 10, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1542–1548, August, 1998.

1066-5285/98/4708-1498 $20.00

In our opinion, the available data are insufficient to reject the first hypothesis. It was necessary to ascertain that a change in the phase state does not cause a selective change in the conformation of substituted phenothiazines. For this purpose, we found π-MOs whose energies depend only on the dihedral angle ϕ. The values of the energy gap between these MOs were used for estimating the equilibrium values of this angle in phenothiazines in the gaseous phase.

In addition, there was a need to analyze electronic manifestations of stereoisomerism of phenothiazines, which is, apparently, associated with a complicated internal motion. This motion may involve pyramidal inversion of the N atom, internal rotation of the substituent, and bending of the heterocycle accompanied by a change in the dihedral angle ϕ between the planes of the benzene rings (motion of the "butterfly wing" type). In the general case, all the above-mentioned factors determine not only the molecular conformation but also the electronic structure of phenothiazines, and hence, details of their photoelectron spectra.

The available experimental data are inadequate to analyze the situation where the geometric parameters that affect the photoelectron spectra may be changed simultaneously as a result of a change of the substituent or the phase state of phenothiazines. Conformational analysis based on the results of photoelectron spectroscopy has been carried out only for chalcogen-containing analogs of 9,10-dihydroanthracene.[5,6] In the present work, the photoelectron spectrum of 10-ethylphenothiazine (10-EPTZ), a representative of the series of 10-alkylphenothiazines, was interpreted using empirical approaches and the results of semiempirical AM1 calculations. The spectra of a number of other heteronuclear tricyclic compounds, in particular, 2-chlorophenothiazine (2-CPTZ), were analyzed.

Experimental

The photoelectron spectra of phenothiazines were recorded on an ES-3201 electron spectrometer. The resonance band of He(I) (21.21 eV) was used for excitation. The energy scale was calibrated against the first ionization potentials of argon (15.76 eV) and chlorobenzene (9.06 eV).

Quantum-chemical calculations of orbital energies of phenothiazines and their analogs were carried out by the AM1 method.[7] The ionization potentials were calculated using the formalism of configuration interaction according to a known procedure,[8] which consists in imposing 100 low-energy ionic configurations that occur for 12 MOs, namely, five unoccupied, one partially occupied, and six fully occupied orbitals.

Results and Discussion

Empirical analysis of photoelectron spectra. The photoelectron spectrum of 10-ethylphenothiazine and the spectra of phenothiazine and thianthrene used for comparison are shown in Fig. 2. In the energy region lower than 11 eV, the spectra of 10-ethylphenothiazine and thianthrene are characterized by identical sets of bands. The ratios of their peak intensities are similar. Based on the results obtained for thianthrene,[9] the two lowest-energy bands of these compounds are assigned to the two highest occupied $\pi_{8,7}$-MOs. The band that corresponds to the first ionization potential of 10-ethylphenothiazine has a very large half-width. This is consistent with the data on other phenothiazines studied previously and is attributable to flattening of the amine fragment on going from the neutral state to the radical-cation form. The highest occupied MO to which the p_π-AO of the N atom makes a substantial contribution may be arbitrarily called the "N-centered" orbital.

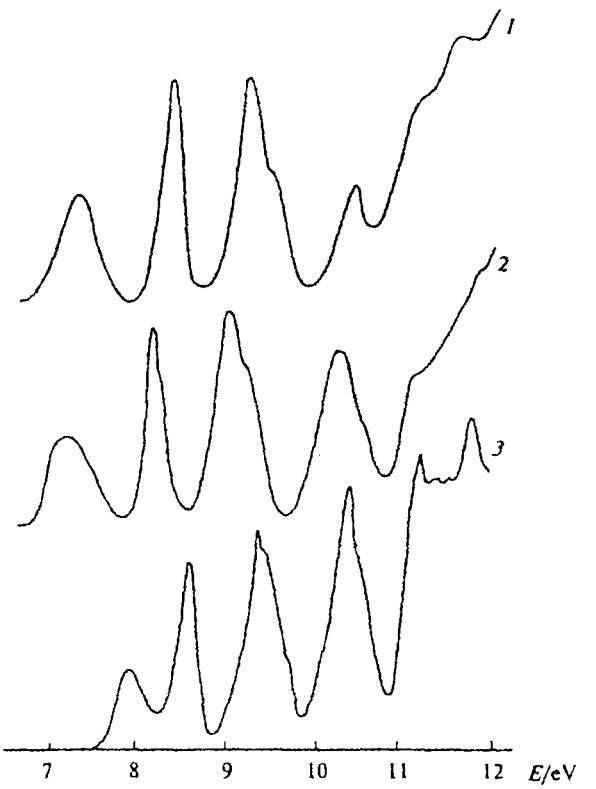


Fig. 2. Photoelectron spectra of phenothiazine (*1*), 10-ethylphenothiazine (*2*), and thianthrene (*3*).

On the contrary, the second band in the photoelectron spectrum is narrow and analogous in this characteristic to the corresponding band of thianthrene. Judging from the published data,[3,10] the spectra of phenoxathiin, 10-methylphenothiazine, and phenothiazine and the spectra of 2-chlorophenothiazine and 10-vinylphenothiazine measured by us exhibit the same characteristic feature. This suggests that the π_7-MO of 10-ethylphenothiazine and the analogous MOs of the above-mentioned other heterocycles make a small contribution to the electron density on the N or O atoms (arbitrary called "S-centered" MOs). This conclusion agrees with the conclusions[3] made based on the fact that *N*-alkyla-

tion leads to a change in the half-width of the bands of phenothiazine under consideration.

The third and fourth bands in the photoelectron spectra of 10-ethylphenothiazine and thianthrene are broad and intense (see Fig. 2). Based on the assignment made,[9] they should be ascribed to two quasi-degenerate sets of π-MOs, the $\pi_{5,6}$(Ph)- and $\pi_{4,3}$-MO, respectively. The $\pi_{5,6}$(Ph)-MOs are orbitals with nodes on both heteroatoms and with the electron density located totally on the benzene fragments. Three arguments can be adduced in favor of quasi-degeneration of the π_3- and π_4-MOs of 10-ethylphenothiazine: 1) the above-mentioned similarity of its photoelectron spectrum to the spectrum of more symmetrical thianthrene; 2) the twofold decrease in the intensity of the fourth band in the photoelectron spectrum (see Fig. 2) when the ethyl group of phenothiazine is replaced by the H atom (in this case, its energy position is approximately retained but its half-width is sharply decreased); the fourth band in the photoelectron spectrum is changed in exactly the same fashion when one S atom of thianthrene is replaced by the O atom (see Refs. 9 and 10); and 3) the presence of two closely-spaced bands (10.24 and 10.4 eV)[3] in this region of the photoelectron spectrum of 10-methylphenothiazine and the presence of one relatively narrow band in the spectrum of 10-vinylphenothiazine (this spectrum will be discussed in detail in the following paper).

The π_3-MO of phenothiazine possesses the higher energy and is characterized by the maximum at 11.1—11.6 eV. This is directly evidenced by the facts that the number of bands is constant and their contours are approximately retained in the low-energy regions of the spectra of phenothiazine and 10-ethylphenothiazine as

Table 1. Vertical ionization potentials (*IP*) of thianthrene and its heteronuclear analogs (X = S)

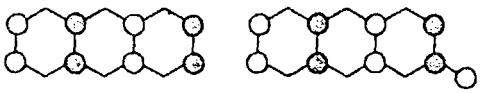
Y	R	*IP*/eV						Method	Literature	φ /deg	Method[a]
		π_8	π_7	π_6	π_5	π_4	π_3				
S	H	7.94	8.43	9.30	9.45	10.20	10.36	PES	9	128.1	XRD
		7.93	8.43	9.32	9.46	10.40	10.40	PES	16	131.4	ED
		7.95	8.58	9.33	9.50	10.40	10.55 sh	PES	[b]	132	PES[b]
		7.35	8.16	9.34	9.43	10.88	11.07	AM1[c,d]	[b]	116	PES[e]
										168.4	AM1[b]
O	H	7.72	8.71	9.40	9.60	10.63	11.70	PES	6	147.8	XRD
		7.35	8.73	9.27	9.47	10.86	12.13	AM1[c,d]	[b]	141	PES[b]
										136	PES[e]
										170.9	AM1[b]
NH	H	7.31	8.41	9.25	9.44	10.43		PES	2	158.5	XRD
		7.26	8.35	9.22	9.44	10.43		PES	3	153.5	XRD
		7.25	8.33	9.23	9.44	10.45	11.51	PES	[b]	158	PES[b]
		7.21	8.29	9.14	9.34	10.36		PES	4	165.1	AM1[b]
		6.96	8.31	9.16	9.37	10.68	11.55	AM1[c]	[b]	159.2	PM3
		7.10	8.69	9.70	10.04	10.45		AM1 (CI)	[b]		
NCH_3	H	7.15	8.23	9.06	9.25	10.24	10.43	PES	3	143.7	XRD
		6.97	8.24	9.08	9.31	10.54	10.77	AM1[c]	[b]	152	PES[b]
										152.0	AM1[b]
NC_2H_5	H	7.10	8.15	9.00	9.17	~10.20	10.22	PES	[b]	135.0	XRD
		6.88	8.21	9.08	9.29	10.61	10.76	AM1[c]	[b]	158.5	AM1[b]
$N(CH_2)_2N(CH_3)_2$	H	7.20	8.26	9.00	9.44	10.26		PES	3		
		π_9	π_8	π_7	π_6	π_5	n_{Cl}				
NH	2-Cl	7.31	8.39	9.20	9.35	10.37	11.24	PES	[b]	164.5	AM1[b]
		7.08	8.45	9.28	9.38	10.35	11.10	AM1[c]	[b]		
$N(CH_2)_2N(CH_3)_2$	2-Cl	7.16	8.25 ~8.5(n_N)	8.99	9.27	10.22[f]	11.24	PES	3	139.1	XRD
		7.34	8.39	9.06	9.27	10.29[f]		PES	4	149.5	AM1[b]
		7.09	8.29	9.19	9.30	10.52	11.08	AM1[c]	[b]		
		8.78(n_N)	[e]		10.75(π_4)						
Effect of halogen		0.05	0.05	0.00	−0.11	−0.03		PES	[b]		

Note. PES, XRD, ED, and CI are photoelectron spectroscopy, X-ray diffraction, gas phase electron diffraction, and configuration interaction, respectively.

[a] Data of X-ray diffraction studies and gas-phase electron diffraction studies have been published previously.[11—15] [b] This work. [c] Ionization potentials according to the Koopmans theorem with the scale factor of 0.93. [d] With the angle φ according to the data of photoelectron spectroscopy. [e] See Ref. 5. [f] The band corresponds to two quasi-degenerate π-MOs.

well as by the presence of an intense band at 11.51 eV in the spectrum of phenothiazine unlike the spectra of 10-ethylphenothiazine (see Fig. 2) and other 10-alkylphenothiazines.[3] A substantial effect of the substituent on the energy of the π_3-MO is indicative of a substantial contribution of the p_π-AO of the N atom to this orbital. Therefore, the π_4-MOs of phenothiazines are "S-centered," while their π_3-MOs are "N-centered."

We hope to obtain additional information on the electron density distribution over π-MOs of phenothiazines by considering the effect of the halogen atom in the aromatic fragment, which consists in the following: the MOs with nodes on the C atom are stabilized under the effect of the halogen atom and the halogen atom does not perturb or destabilizes only slightly the π-MOs that are characterized by the presence of the antibonding electron density on the C—Cl bond. When the replacement occurs at position 2 of phenothiazines, the effect of the halogen atom on their photoelectron spectra is very poorly pronounced. According to the experimental data (Table 1), among the highest occupied π-MOs of these compounds, only the π_5-MO is substantially perturbed. Its stabilization in 2-chlorophenothiazine indicates that this MO has a structure similar to that shown below.



π_5-MO (phenothiazine) π_6-MO (2-CPTZ)

It is conceivable that the two remaining bands in the photoelectron spectrum of 10-ethylphenothiazine with the maxima at 11.1 and 11.8 eV belong to the two highest occupied σ-MOs. On the one hand, the energies of their highest σ-levels in thianthrene are very close. On the other hand, if these orbitals are σ-MOs, their mutual energy arrangement should obey one of the relationships[17] for the highest occupied σ-levels of sulfur-containing compounds. When the molecule of 10-ethylphenothiazine in the gaseous phase is substantially nonplanar and the lone electron pair of the S atom in this molecule virtually does not interact with the π-system of the benzene rings, the relationship between the ionization potentials $IP_1(\sigma)$ and $IP_2(\sigma)$ will be identical to that for saturated derivatives of divalent sulfur (dimethyl sulfide, diethyl sulfide, diisopropyl sulfide, diallyl sulfide, 2,5-dihydro- and tetrahydrothiophenes, tetrahydrothiopyran, 9-thiabicyclo[3.3.1]nonane, and 9-thiabicyclo[3.3.1]nonene):[14,18–22]

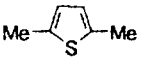
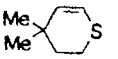
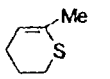
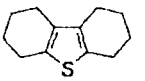
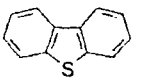
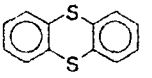
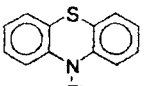
$$IP_2(\sigma) = (-7.5\pm1.3) + (1.8\pm0.1)IP_1(\sigma),\ r = 0.985,\ n = 9.$$

Otherwise, 10-ethylphenothiazine will manifest itself as an unsaturated compound (Table 2):

$$IP_2(\sigma) = (-6.5\pm0.8) + (1.65\pm0.07)IP_1(\sigma),\ r = 0.988,\ n = 16.$$

Analysis demonstrates that the energies of the maxima of the high-energy bands of 10-ethylphenothiazine under consideration as well as those of thianthrene fit the correlation that characterizes a series of unsaturated sulfur compounds. Therefore, the lone electron pair of the S atom in 10-ethylphenothiazine efficiently interacts with the π-system of the aromatic fragments.

Table 2. Ionization potentials of the highest occupied σ-MOs of unsaturated sulfur-containing compounds

Compound	$IP_1(\sigma)$	$IP_2(\sigma)$	Literature
	/eV		
	11.86	13.10	23
	12.00	13.11	24
	11.90	13.10	[a]
	12.10	13.30	[a]
	11.80	13.00	23
	11.82	13.02	[b]
	11.50	12.52	[b]
	11.94	13.10	23
	11.90	13.06	[b]
	11.78	12.75	[b]
	11.55	12.60	[a]
$MeSCH{=}CH_2$	11.55	12.50	20
	11.60	12.65	[b]
MeSCH=CHSMe (*cis*)	11.15	11.85	25
MeSCH=CHSMe (*trans*)	11.20	11.78	25
$(MeS)_2C{=}CH_2$	11.10	11.80	25
$(MeS)_2C{=}C(SMe)_2$	11.40	12.20	25
$CH_2{=}CHSCH{=}CH_2$	11.56	12.65	[b]
$CH_2{=}C{=}CHSCH{=}CH_2$	11.95	13.18	[b]
	11.20	11.70	20
	10.75	11.20	21
	10.86	11.45	[b]
	11.38	12.18	26
	11.17	11.75	9
	11.23	11.78	[b]
	11.18		16
	11.10	11.80	[b]

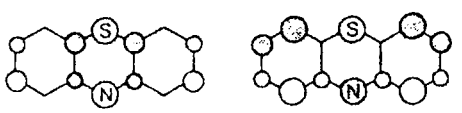
[a] For references, see Refs. 18 and 27. [b] This work; see also Refs. 16 and 17.

Conformational analysis of phenothiazines based on the results of photoelectron spectroscopy. The determination of a particular geometric characteristic of the molecular conformation by photoelectron spectroscopy is preceded by a search for π-MOs sensitive to this characteristic.[28] In the series of phenothiazines, absolute values and tendencies for a change in the dihedral angle φ in the gaseous phase under the action of the substituent are of prime interest to us.

For homonuclear and heteronuclear chalcoanthrenes, we compared the folding angles in the central boat of the heterocycle, which were calculated based on the data on dipole moments, with the characteristics of the photoelectron spectra. It was found that in these compounds the energy gap between the highest occupied orbital and the preceding occupied π-MO is conformation-dependent. Details of the calculations and analysis have been reported previously.[9,10] The results were systematized in Ref. 29.

Unfortunately, this approach cannot be applied to photoelectron spectra of phenothiazines because the energy positions of their frontier MOs depend not only on the angle φ but also on the degree of pyramidality of the N atom. That is the reason that "S-centered" MOs, *i.e.*, the above-mentioned π_7- and π_4-MOs, should be used in the conformational analysis of phenothiazines. It is also desirable to use these characteristics for other reasons. First, the consideration of the gaps between these π-MOs will allow one to carry out a comparative analysis throughout a series of heteronuclear sulfur-containing derivatives of 9,10-dihydroanthracene. The narrowest bands (except for the fourth band of thianthrene, which is associated with two π-MOs) correspond to these MOs. Second, the energy gap between the π_7- and π_4-MOs of thianthrene increases (according to the X-ray diffraction data, see Table 1), which can be considered as a qualitative argument in favor of its conformational sensitivity.

Generally, the data on MOs of complex molecules whose energies depend on conditions of the overlap of AOs of binding centers can be obtained experimentally or theoretically. The orbital energies of tricyclic heteroaromatic systems calculated by the AM1 and CNDO/2 methods agree qualitatively (for some π-MOs, quantitatively) with the experimental data within the framework of the Koopmans theorem (see Refs. 3 and 4 and Table 1), which is not true for the compositions of these MOs, in particular, of the π_7- and π_8-MOs. Thus, the CNDO/2 calculations demonstrated that both orbitals are localized on the S atom to a larger extent than on the N atom (42% and 18% for the π_8-MO and 28% and 17% for the π_8-MO, respectively).[3] This result is in contradiction with the experimental data.



π_8-MO π_7-MO

The AM1 method also poorly reproduces the compositions of the highest occupied π-MOs that correspond to the first and second ionization potentials of phenothiazines: the contribution of the p_π-AO of the S atom to the π_8-MO is overestimated, while the contribution of the AO of the N atom to the π_7-MO is underestimated. The use of the multiconfiguration theory did not remedy the situation. The AM1 (configuration interaction) calculations indicate that the π_8-MO and π_7-MO correspond to the first and second ionization potentials, respectively (see Table 1). Therefore, the drawbacks of orbital structures of phenothiazines calculated in the AM1 approximation are identical to those of orbital structures calculated by the CNDO/2 method. The behavior of the two above-mentioned π-MOs cannot be adequately described by these methods by varying the dihedral angle φ or the degree of pyramidality of the amine fragment of the molecule.

On the contrary, the empirical correlation diagrams, which can be readily constructed based on orbitals of diphenylamine and diphenyl sulfide (Fig. 3), agree well with the experimental data. From these diagrams it immediately follows that the π_4- and π_7-MOs are most sensitive to conditions of the overlap in the series of phenothiazines and phenochalcogens.

From the scheme of one-center orbital interactions it follows that the energy gap between the π-MOs under consideration ($\Delta_{4,7}$) is determined by Eq. (1):

$$\Delta_{4,7} = |\Delta_\perp^2 + 4\beta^2(\varepsilon)|^{1/2}, \qquad (1)$$

where $\Delta_\perp$ is the characteristic of the orthogonal conformer ($\varepsilon = 90°$), ε is the angle between the p_π-AOs of the fragments, and β(ε) is the energy of their interaction. From the practical viewpoint, the approximate form of this equation (Eq. (1a)), where β(ε) is approximated by the function β(0)cos(ε), is more convenient:

$$\Delta_{4,7}(\varepsilon) = \Delta_\perp + 4\beta^2(0)\cos^2\varepsilon/\Delta_\perp. \qquad (1a)$$

For phenothiazines and related tricyclic compounds, ε is the angle between the normal to the plane of the benzene ring and the normal to the plane in which the C—S bond is located. Therefore, this value can be readily determined from the experimental values: $\cos\varepsilon = \sin(\phi/2)\cos\lambda_S$ (see Fig. 1).

Previously,[5] an alternative equation was used in the analysis of the dependence of the first ionization potentials of analogs of 9,10-dihydroanthracene on the dihedral angles: $\phi = 180 - 2\arctan(0.5\tan\varepsilon)$. The dihedral angles of thianthrene (S, S) and phenoxathiin (S, O) are given in Table 1. We determined the angles λ_S by Eq. (2) based on the results of X-ray diffraction analysis of seven phenothiazine derivatives (10-R = H, Me, Et, $CHMe_2$, $(CH_2)_2CN$, $(CH_2)_2CN$, $(CH_2)_2COOH$, or 2′-$MeOC_6H_4$), its complex with 1,3,5-trinitrobenzene, and the radical-cation of 10-ethylphenothiazine, which has the planar structure.[12,15,32,33]

$$\cos\lambda_S = \sin(90 + \delta - 0.5\varphi_1)/\cos(0.5\varphi_2), \qquad (2)$$

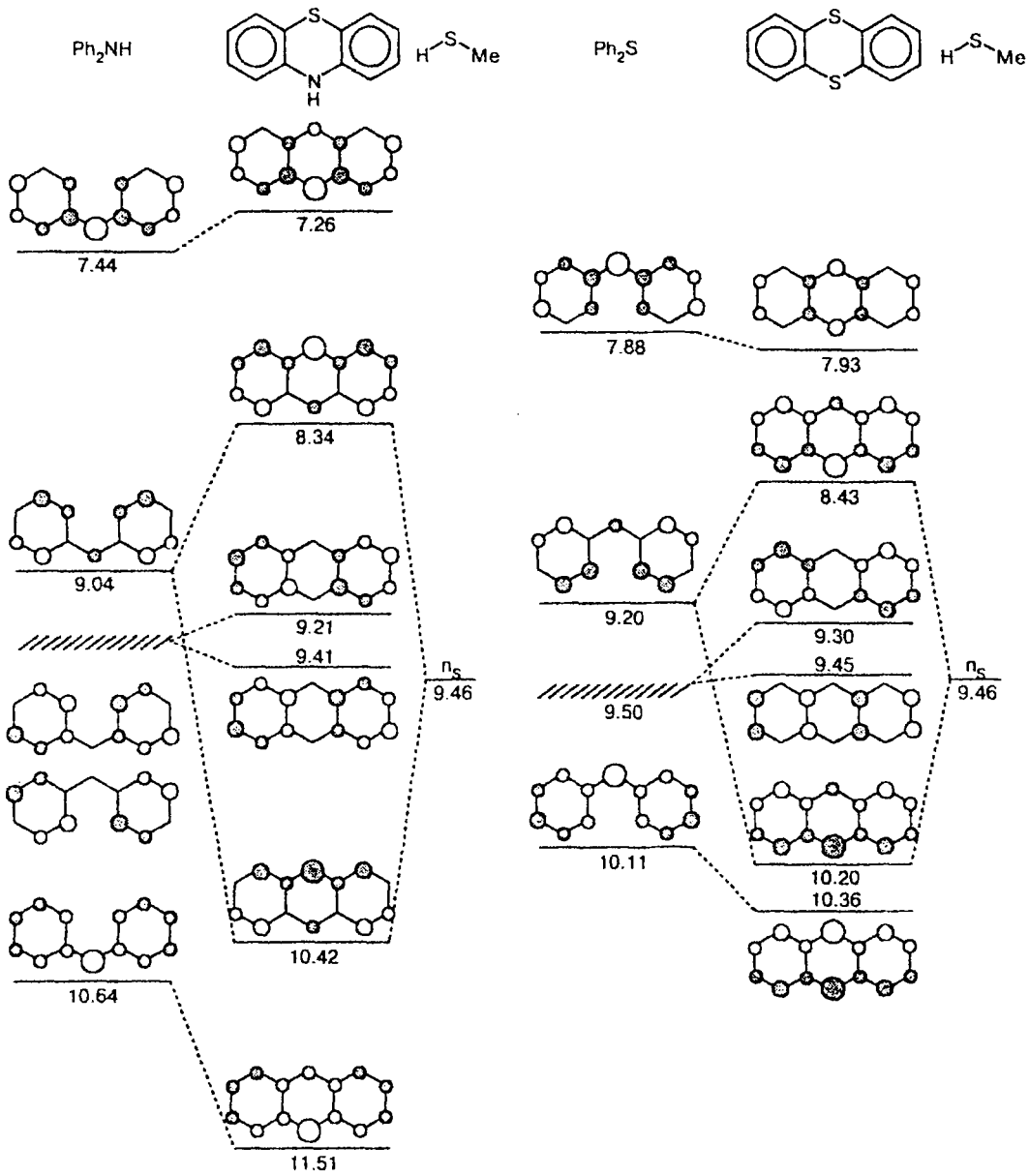
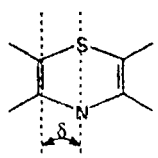


Fig. 3. Orbital correlation diagrams of diphenylamine, diphenyl sulfide, phenothiazine, and thianthrene. The published data[30,31] on the ionization potentials of Ph_2S and Ph_2NH were used.

$$\tan\delta = |l_{CS}\sin(0.5\varphi_2) - l_{CN}\sin(0.5\varphi_3)|/l_{CC},$$

where d_{CS}, d_{CN}, and d_{CC} are the bond lengths, φ_1, φ_2, and φ_3 are the SCC, CSC, and CNC bond angles, and δ is the angle between the C=C bond of the ring and the SN axis. For the neutral forms, $\delta \approx 5°$. For the radical-cation, this angle is 5.5°.



Based on the calculated values, it was found that λ_S depends nonlinearly on φ. Therefore, one would expect a simple relationship between cose and ϕ. Actually, empirical analysis gave the following dependence (Fig. 4):

$$\cos^2\varepsilon = \text{const} + 0.90(\phi/\pi)^2.$$

Taking into account this equation, Eq. (1a) takes the following form, which is very convenient in practical use: $\Delta_{4,7}(\varepsilon) = \Delta_\perp + \alpha 0.90(\phi/\pi)^2/\Delta_\perp$, where $\alpha = 1.03$ (see Ref. 36).

With the aim of using the last-mentioned equation in the conformational analysis based on the photoelectron spectra, its parameters were calibrated using the gas-

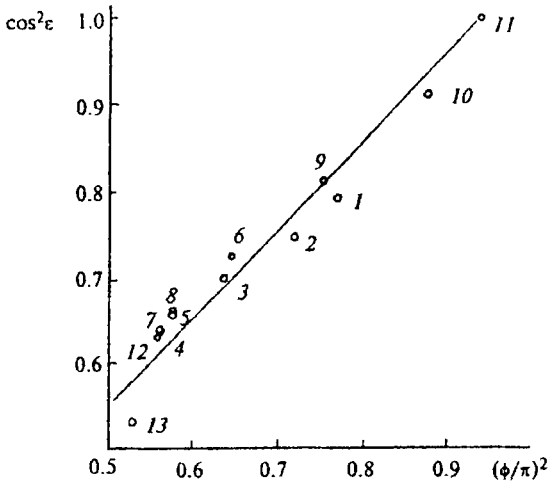


Fig. 4. Functional dependence of the angle ε between the p_π-AOs of the fragments on the dihedral angle ϕ for phenothiazines with 10-R = H (*1* and *2*), Me (*3*), Et (*4*), $CHMe_2$ (*5* and *6*), $(CH_2)_2CN$ (*7*), $(CH_2)_2COOH$ (*8*), and 2'-$OMeC_6H_4$ (*9*), the complex of phenothiazine with 1,3,5-trinitrobenzene (*10*), the radical-cation of 10-ethylphenothiazine (*11*), thioxane (for the geometric parameters, see Ref. 34) (*12*), and 2,7-Me_2-thianthrene (for the geometric parameters, see Ref. 35) (*13*).

phase characteristics of thianthrene ($\Delta_{4,7}$ = 1.85 eV, ϕ = 131.4°, see Table 1):

$$\Delta_{4,7} = 1.35 + 0.93(\phi/\pi)^2. \quad (3)$$

The values of ϕ determined by this procedure (see Table 1) allow two conclusions: a) the solid→gas phase transition affects only slightly the dihedral angles; b) the replacement of the H atom at position 10 of phenothiazines by the methyl group causes a decrease in the dihedral angle ϕ rather than a change from the quasi-equatorial to the quasi-axial conformer both in the solid and gaseous phases. Therefore, the results of this work allow one to reject the first of the above-mentioned hypotheses.

References

1. V. K. Turchaninov, N. N. Chipanina, T. N. Aksamentova, M. S. Sorokin, and V. A. Pestunovich, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 236 [*Russ. Chem. Bull.*, 1998, **47**, 231 (Engl. Transl.)].
2. H. J. Haink and J. R. Huber, *Chem. Ber.*, 1975, **108**, 1118.
3. L. N. Domelsmith, L. L. Munchausen, and K. N. Houk, *J. Am. Chem. Soc.*, 1977, **99**, 6506.
4. P. K. Basu and C. N. R. Rao, *Spectrochim. Acta*, 1978, **34A**, 845.
5. O. G. Rodin, V. F. Traven', V. V. Redchenko, M. Yu. Eismont, and B. I. Stepanov, *Zh. Obshch. Khim.*, 1983, **53**, 2537 [*J. Gen. Chem. USSR*, 1983, **53** (Engl. Transl.)].
6. V. F. Traven', *Elektronnaya struktura i svoistva organicheskikh molekul* [*Electronic Structure and Properties of Organic Molecules*], Khimiya, Moscow, 1989, 384 pp. (in Russian).
7. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
8. A. I. Vokin and V. K. Turchaninov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2365 [*Russ. Chem. Bull.*, 1995, **44**, 2261 (Engl. Transl.)].
9. G. Distefano, V. Galasso, K. I. Jrgolic, and G. C. Pappalardo, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1109.
10. F. P. Colonna, G. Distefano, V. Galasso, K. I. Jrgolic, C. E. King, and G. C. Pappolardo, *J. Organomet. Chem.*, 1978, **146**, 235.
11. I. Hargittai, *The Structure of Volatile Sulfur Compounds*, D. Reidel Publishing Co., Dordrecht, 1985.
12. I. Rowe and B. Post, *Acta Crystallogr.*, 1985, **11**, 372.
13. A. I. Fitzgerald, J. C. Gallucci, and R. E. Gerkin, *Acta Crystallogr.*, 1991, **C47**, 381.
14. J. D. Bell, J. F. Blount, O. V. Briscoe, and H. C. Freeman, *J. Chem. Soc., Chem. Commun.*, 1968, 1656.
15. V. K. Turchaninov, L. M. Sinegovskaya, S. V. Eroshchenko, A. F. Ermikov, and B. A. Trofimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2317 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2029 (Engl. Transl.)].
16. J. P. Reboul and B. Gristau, *J. Chim. Phys., Phys. Chim. Biol.*, 1978, **75**, 1109.
17. V. I. Nefedov and V. I. Vovna, *Elektronnaya struktura organicheskikh i elementoorganicheskikh soedinenii* [*Electronic Structure of Organic and Organometallic Compounds*], Nauka, Moscow, 1989, 199 pp. (in Russian).
18. K. Kimura, S. Hatsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Halsted press, Tokyo—New York, 1981, 270 pp.
19. A. A. Planckaert, J. Doucet, and C. Sandorfy, *J. Chem. Phys.*, 1974, **60**, 4846.
20. C. Batich, E. Heilbronner, C. B. Quinn, and J. R. Wiseman, *Helv. Chim. Acta*, 1976, **59**, 512.
21. H. Schmidt and A. Schweig, *Tetrahedron Lett.*, 1973, 1437.
22. V. F. Traven', V. V. Rudenko, and B. I. Stepanov, *Zh. Obshch. Khim.*, 1981, **51**, 1293 [*J. Gen. Chem. USSR*, 1981, **51** (Engl. Transl.)].
23. A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, 1970, **42**, 1046.
24. L. Klasinc, A. Subljic, G. Kluge, J. Rieger, and V. Scholz, *J. Chem. Soc., Perkin Trans. 2*, 1982, 539.
25. H. Bock, G. Wagner, K. Wittel, J. Saner, and D. Seebach, *Chem. Ber.*, 1974, **107**, 1869.
26. B. Ruscic, B. Kovac, L. Klasinc, and H. Gusten, *Z. Naturforsch.*, 1978, **A33**, 1006.
27. V. I. Vovna and F. I. Vilesov, in *Uspekhi fotoniki* [*Progress in Photonics*], Izd-vo LGU, Leningrad, 1975, 3 (in Russian).
28. R. S. Brown and F. S. Jorgensen, in *Electron Spectroscopy*, Academic Press, London—New York, 1984, **5**, 1.
29. C. Canletti and G. Distefano, in *Chemistry of Organic Selenium and Tellurium Compounds*, Academic Press, London—New York, 1987, **2**, 1.
30. F. P. Colonna, G. Distefano, G. Reichenbach, and S. Santini, *Z. Naturforsch.*, 1975, **A30**, 1213.
31. H. J. Haink, J. E. Adams, and J. R. Huber, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 436.
32. C. J. Fretchie, *J. Chem. Soc. (A)*, 1969, 1328.
33. L. Youcheng, D. Yanbing, and L. Zhongli, *Jiegon Huaxue (J. Struct. Chem.)*, 1989, **8**, 140.
34. J. A. Gillean, D. W. Phelps, and A. W. Cordes, *Acta Crystallogr.*, 1973, **B29**, 2296.
35. C. H. Suanwei, *Acta Crystallogr.*, 1971, **B27**, 1523.
36. V. K. Turchaninov, A. I. Vokin, D.-S. D. Toryashinova, and S. E. Korostova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 869 [*Russ. Chem. Bull.*, 1993, **42**, 822 (Engl. Transl.)].

Received October 27, 1997