

AM1 studies of photoelectron spectra

12.* Photoelectron spectrum and stereoisomerism of 10-vinylphenothiazine

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Empirical analysis of the photoelectron spectrum of 10-vinylphenothiazine demonstrated that in the gaseous phase, this compound exists as two stereoisomers that differ in the electronic structure. One of them contains the planar amine fragment. The second stereoisomer is characterized by the quasi-axial orientation of the substituent. The X-ray diffraction data for the molecules and donor-acceptor complexes of phenothiazine derivatives as well as for the radical-cation of 10-ethylphenothiazine were used for obtaining structure correlations. These correlations and the results of AM1 calculations indicate that pyramidal inversion of the nitrogen atom occurs simultaneously with inversion of the ring. In the stereoisomer containing the planar heterocyclic fragment, the dihedral angle between the planes of the benzene rings is 180°. According to the data of photoelectron spectroscopy, this stereoisomer is characterized by a substantial deviation of the vinyl group from the plane of the heteronucleus. In the stereoisomer with the quasi-axial arrangement of the substituent, the dihedral angle between the planes of the benzene rings is 150°. Similar values of the angles were obtained in the AM1 calculations of the potential of internal motion of 10-vinylphenothiazine.

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

In the preceding work¹ devoted to analysis of the photoelectron spectra of 10-ethylphenothiazine and the related heterocycles, we stated a number of problems associated with their stereoelectronic structures. Some of these problems can be solved with the use of photoelectron spectra of phenothiazines containing an unsaturated substituent at the N atom, by studying the stereochemistry of heterocyclic systems of this type in the gaseous phase, and by elucidating the effect of phase transition on the structures of the stereoisomers. In this work, we studied 10-vinylphenothiazine (10-VPTZ) and considered the characteristic features of its stereoisomerism in the gaseous phase.

Experimental

The photoelectron spectra of phenothiazines were recorded on an ES-3201 electron spectrometer. The resonance transition 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 potentials of internal motion and orbital energies of 10-vinylphenothiazine were carried out by the AM1 method.² The theoretical value of the equilibrium dihedral angle ϕ corresponds to the minimum on

the potential energy (static model). In the case of the dynamic model, the expected value of ϕ was calculated according to the equation for the classical rotamer ($T = 293$ K):

$$\langle \phi \rangle = \frac{\int_a^b \phi \exp\left[-\frac{V(\phi)}{RT}\right] d\phi}{\int_a^b \exp\left[-\frac{V(\phi)}{RT}\right] d\phi}.$$

The potential of internal motion $V(\phi)$ calculated by the AM1 method was approximated by the power series:

$$V(\phi) = \sum_{k=1}^n V_k \phi^{k-1}, \quad n = 6.$$

The integrals were calculated by the method of trapezoids. The limits of integration were chosen so that they correspond to the separation of $V(\phi)$ from the minimum on the potential energy by $2kT$.

Results and Discussion

Empirical analysis of the photoelectron spectrum of 1-vinylphenothiazine. The low-energy regions of the photoelectron spectra of 10-vinylphenothiazine and 10-ethylphenothiazine (10-EPTZ) (given for comparison) are shown in Fig. 1. Analysis of the spectrum of 10-ethylphenothiazine demonstrated¹ that ionization of six π -MOs and two σ -MOs is observed in this energy region. Several first low-energy bands in its photoelec-

* For Part 11, see Ref. 1.

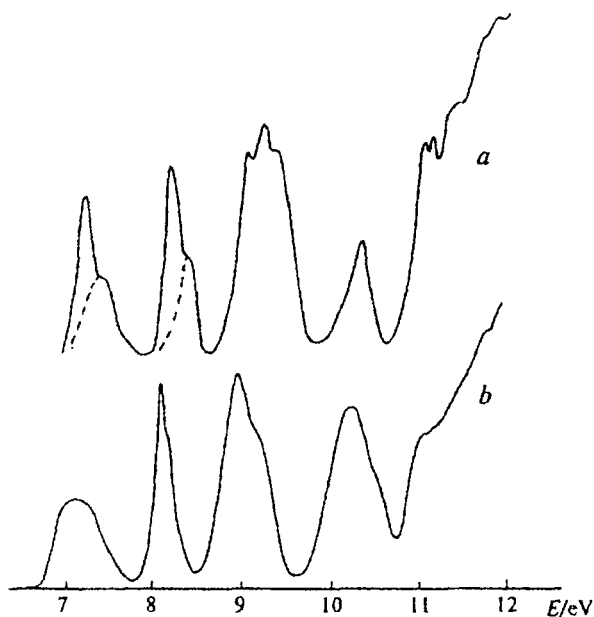


Fig. 1. Photoelectron spectra of 10-vinylphenothiazine (a) and 10-ethylphenothiazine (b).

tron spectrum are individual and correspond to the π_8 - and π_7 -MOs.

The contribution of the p_π -AO of the N atom to the π_8 -MO ("N-centered" MO) prevails. Therefore, the band corresponding to this AO has a large half-width (see Fig. 1). The contribution of the p_π -AO of the S atom to the π_7 -MO ("S-centered" MO) of 10-ethylphenothiazine prevails. The third band in the photoelectron spectrum of the *N*-ethyl derivative occurs due to the quasi-degenerate π_5 - and π_6 -MOs with nodes on both heteroatoms. The fourth band in the photoelectron spectrum corresponds to the quasi-degenerate π_4 - and π_3 -MOs. The p_π -AO of the S atom makes the major contribution to the π_4 -MO, and the p_π -AO of the N atom makes the major contribution to the π_3 -MO. Because of this, the fourth band in the photoelectron spectrum of 10-ethylphenothiazine has a large half-width and high peak intensity. Two high-energy maxima at 11.1 and 11.8 eV belong to σ -MOs of this compound.

A comparison of the photoelectron spectra of 10-ethylphenothiazine and 10-vinylphenothiazine revealed a number of characteristic features of the latter compound. 1. For 10-VPTZ and 10-EPTZ, the difference in the number of the bands in the energy region lower than 11.0 eV is more substantial than was expected. Actually, if the π -MO of the exocyclic double bond interacts with the "N-centered" π -MOs of the heterocyclic fragment, six bands corresponding to π -MOs should be observed in this region of the spectrum. If the molecular conformation of 10-vinylphenothiazine is such that its vinyl group lies exactly in the bisecting plane of the central boat of the tricyclic system, the spectrum

should contain five bands caused by ionization of π -MOs. However, eight bands are actually observed in this region of the photoelectron spectrum of 10-vinylphenothiazine (see Fig. 1). 2. For 10-VPTZ, the first band in the photoelectron spectrum, unlike that for 10-EPTZ, is narrow, and a less intense but broader component is superimposed on the high-energy slope of this band. 3. The second band in the photoelectron spectrum of 10-VPTZ is also characterized by the doublet structure. 4. The third band in the spectrum of 10-VPTZ consists of three components, two of which are absent in the corresponding region of the spectrum of 10-EPTZ. 5. When the ethyl group is replaced by the vinyl group, the fourth band in the photoelectron spectrum changes substantially, namely, it becomes twice as narrow as in the first case and its intensity is halved (see Fig. 1). 6. In the region of the spectrum in which bands of σ -MOs of 10-EPTZ are observed, at least one more band at 11.16 eV is observed in the case of 10-VPTZ, and its fine structure ($\sim 1000\text{ cm}^{-1}$) is typical of ionic states of the π type.

It is conceivable that the remaining bands in the photoelectron spectrum of 10-VPTZ with the maxima at 11.4 and 11.85 eV (see Fig. 1) correspond to the highest occupied σ -MOs. If this is the case, their energies should obey correlation equation (1), which relates the ionization potentials $IP_1(\sigma)$ and $IP_2(\sigma)$ of sulfur-containing compounds. Note that the highest occupied σ -MOs of 10-EPTZ and thianthrene obey this equation.¹

$$IP_2(\sigma) = (-6.5 \pm 0.8) + (1.65 \pm 0.07)IP_1(\sigma), \quad (1)$$

$$r = 0.988, n = 16.$$

However, the positions of the above-mentioned bands in the photoelectron spectrum of 10-VPTZ do not fit correlation equation (1), while the relative positions of the bands at 11.16 and 11.85 eV are rather adequately determined by Eq. (1). What this means is the highest occupied σ -MO and the π -MO of 10-VPTZ are quasi-degenerate, and the band with the maximum at 11.4 eV belongs to π -MOs rather than to σ -MOs. Therefore, throughout the region under consideration, eleven bands, which are caused by transitions into ionic π - and σ -states, are observed. This unambiguously indicates that in the case of the *N*-vinyl derivative of phenothiazine, an ensemble of two stereoisomers (A and B) exists in the gaseous phase. This is the first example of the manifestation of stereoisomerism in the photoelectron spectra of compounds of this type.

The correlation diagram (Fig. 2) shows the arrangement of the electronic π -levels of the isomers of 10-VPTZ on the energy scale. Form A is characterized by a very narrow band that corresponds to the "N-centered" MO ($IP_1 = 7.22\text{ eV}$) from which it follows that this form contains the planar or almost planar amine fragment. The fine structure of the band at 11.16 eV, which belongs to this fragment, provides additional evidence of its planar structure in stereoisomer A. Apparently, the second form (B) has the nonplanar structure. On the

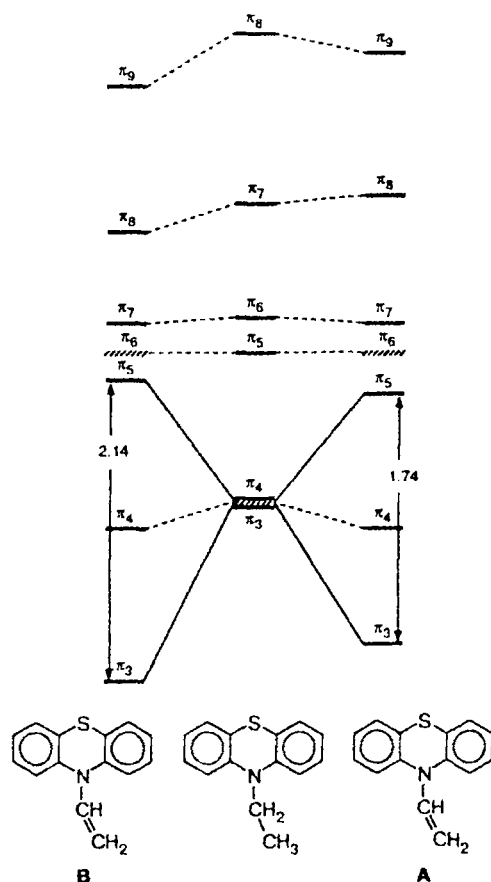


Fig. 2. Correlation diagrams of the energy levels of π -MOs of 10-ethylphenothiazine (see Ref. 1) and of two stereoisomers of 10-vinylphenothiazine (A and B).

one hand, interaction between the "N-centered" π -MO of the heteronucleus and the π -MO of the double bond is more efficient in form B (see Fig. 2). On the other hand, its band corresponding to the first ionization potential ($IP_1 = 7.44$ eV) is wider than that of form A.

If the nonplanar quasi-equatorial structure (Fig. 3) of 10-VPTZ corresponds to form B, the double bond should lie almost in the bisecting plane of the central boat of the heterocycle. In the case of this orientation of the vinyl group, the π -MO of the double bond cannot be noticeably mixed with the p_z -AO of the N atom. However, we observed the very efficient π -interaction. Hence, the quasi-axial (QA) structure can be assigned to form B of 10-VPTZ (see Fig. 3). When this structure of the stereoisomer is realized, the high value of the first ionization potential is attributed to a decrease in the contribution of the p_z -AO of the N atom to the π_9 -MO of 10-VPTZ.

Two alternative structures can be suggested for form A of 10-VPTZ, namely, the nonplanar structure with the planar amine fragment and the completely planar structure. It is impossible to unambiguously choose between

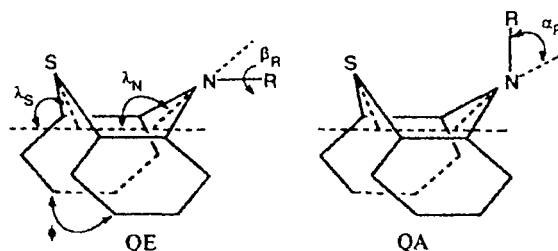


Fig. 3. Stereoisomers of phenothiazines; QE and QA are the quasi-equatorial and quasi-axial isomers, respectively.

these structures based only on the photoelectron spectrum. In this connection, we studied correlations between the geometric parameters in the series of phenothiazines and performed the conformational analysis of 10-VPTZ taking into account the data of photoelectron spectroscopy (PES).

Structure correlations and the dynamic aspect of stereoisomerism of phenothiazines. To answer the question of whether the presence of the planar amine fragment is evidence of planar structures of phenothiazine derivatives, we considered the relationship between the dihedral angle λ_N , the CNC bond angle, and the dihedral angle ϕ (see Fig. 3). This relationship was established based on the X-ray diffraction data for phenothiazine derivatives, which exist in the quasi-equatorial (QE) form, for the complexes of phenothiazine with 1,3,5-trinitrobenzene (TNB) and 7,7',8,8'-tetracyanoquinodimethane (TCQD), and for the planar radical-cation of 10-EPTZ (Table 1). The values of λ_N were estimated according to Eq. (2):

$$\sin(\lambda_N - 90) = [\sin(90 - \delta - 0.5\phi_1)] / \cos(0.5\phi_2), \quad (2)$$

$$\tan \delta = [l_{CS} \sin(0.5\phi_3) - l_{CN} \sin(0.5\phi_2)] / l_{CC},$$

where l_{CS} , l_{CN} , and l_{CC} are the bond lengths in the central boat of the heterocycle, ϕ_1 , ϕ_2 , and ϕ_3 are the NCC, CNC, and CSC bond angles, and δ is the angle between the C=C bond of the central boat and the SN axis. For the molecules,¹ $\delta \approx 5^\circ$.

The relationship between λ_N and ϕ is nonlinear in the range $\phi = 130$ – 180° (Fig. 4). The angle λ_N increases as ϕ increases, and when $\phi = 180^\circ$, $\lambda_N = 180^\circ$. Simultaneously, the CNC bond angle increases. In the planar form, ϕ_2 is 129.5° , i.e., this value is the average of the CNC angles in the planar phenothiazine molecule that enters into the composition of the complex with 7,7',8,8'-tetracyanoquinodimethane and in the planar radical-cation of 10-EPTZ. The CNC angles in the planar forms of phenothiazines were determined with a substantially poorer accuracy than the corresponding values in the neutral molecules.^{4–6} To put it differently, the degree of pyramidity of the amine fragment decreases as the benzene rings tend to the coplanar arrangement, and when $\phi = 180^\circ$, the fragment becomes planar.

Table 1. Structural parameters of the molecules, complexes, and ionic forms of 10-R-phenothiazines in the solid phase according to the data of X-ray diffraction analysis³⁻⁶

Com- pound	R	State	ϕ	λ_N	ϕ_2	λ_S	ϕ_3
deg							
1	H	Molecule	158.5	155	124.4	25	100.9
2	H	Molecule	153.3	150	121.5	27	99.6
3	H	Complex with TNB	165–172	164.5	126	23.5	102
4	H	Complex with TCQD	180	180	134	0	104
5	Me	Molecule	143.7	142	118.0	28	97.4
6	Et	Molecule	135.0	138.5	116.7	30	97.4
7	Et	Radical cation	180	180	124.8	0	103.2
8	CHMe ₂	Molecule	136.1	140	117.4	29	97.3
9	CHMe ₂	Molecule	146.8	143.5	118.6	27	98.9
10	CH ₂ CH ₂ CN	Molecule	135.4	141.5	118.1	30	98.7
11	CH ₂ CH ₂ COOH	Molecule	136.5	137.5	115.4	27	98.5
12	CH ₂ Ph	Molecule	148.3	—	120.4	—	98.9
13	CH ₂ Ph	Molecule	150.1	—	120.7	—	99.1
14	2'-OMeC ₆ H ₄	Molecule	157.5	151	122.5	23.5	100.7
15	CH ₂ CH(Me)NMe ₂	Salt with HCl	141.8	139	116.5	29	97.5
16	CH ₂ CH(Me)NMe ₂	Salt with HBr	140.6	139.8	118.5	28	98.9
17	CH ₂ CH(Me)NMe ₂	Salt with MgSO ₄	135.6	139.5	117.2	30.5	98.0
18	CH ₂ CH(Me)NEt ₂	Salt with HCl	138.0	140	116.4	29	97.5
19	CH ₂ CH(Me)NEt ₂	Salt with HCl	138.5	141	117.6	28	98.2

The conclusion about flattening of the central ring in the case of $\phi = 180^\circ$ follows also from the X-ray diffraction data on the angles λ_S and CSC (Figs. 4 and 5). In this case, the angle λ_S is calculated by Eq. (3) (ϕ_4 is the SCC angle):

$$\cos \lambda_S = [\sin(90 + \delta - 0.5\phi_4)] / \cos(0.5\phi_3). \quad (3)$$

The above-mentioned conclusion is common to all quasi-equatorial forms because phenothiazines containing different unsaturated substituents (of various nature, with different structures, and with various states of valence shells) at position 10 were included in the consideration (see Table 1), and hence, their quasi-equatorial→quasi-equatorial (QE→QE) transition occurs through pyramidal inversion of the N atom (N-inversion) accompanied by a change in the angle ϕ .

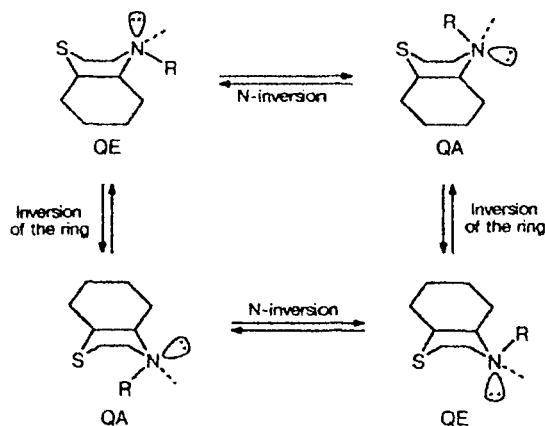
The correlations between the CNC and CSC angles and the dihedral angle ϕ were also established.² However, because the values of ϕ vary within a narrow range (135–159°), the reliability of these correlations is poor ($r \approx 0.8$). The use of the data on the phenothiazine complexes and on the π -radical-cation of 10-EPTZ allowed us to substantially improve the quality of the correlations (Eqs. (4) and (5)):

$$\phi_2 = (77^\circ \pm 4^\circ) + (0.29 \pm 0.02)\phi, \quad r = 0.950, \quad n = 17, \quad (4)$$

$$\phi_3 = (80^\circ \pm 1^\circ) + (0.13 \pm 0.01)\phi, \quad r = 0.955, \quad n = 19. \quad (5)$$

Previously,⁶ the internal motion of phenothiazines was considered as two different inversion processes (Scheme 1).

It was assumed that the inversion of the ring proceeds with retention of the configuration of the bonds in

Scheme 1

the amine fragment, while the N-inversion leads to a change in the configuration passing through the planar sp^2 -state of the N atom. In both inversion processes, the QE→QA transition is realized.

According to the obtained structure correlations, the pyramidal inversion of the N atom proceeds through the state with the completely planar heterocyclic fragment. When 10-R = H, this motion is analogous to the inversion transition of chalcocanthrenes and occurs between two energetically identical mirror isomers. When 10-R has a more complex structure, such as in 10-EPTZ, the quasi-equatorial forms become nonequivalent (Scheme 2).

In the general case, the C—X bond is not located exactly in the bisecting plane of the central boat of the

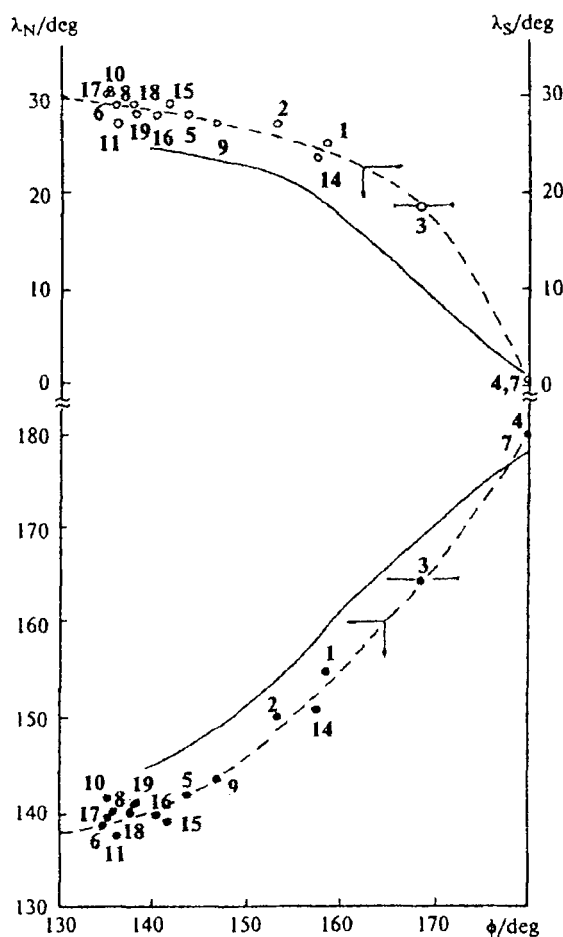


Fig. 4. Empirical dependences of the angles λ_N and λ_S on the dihedral angle ϕ between the planes of the benzene rings of phenothiazines. For the atomic numbering schemes for the compounds under study, see Table 1. The theoretical dependences, which were determined for phenothiazine in the AM1 approximation with the use of the structure correlations, are indicated by solid lines.

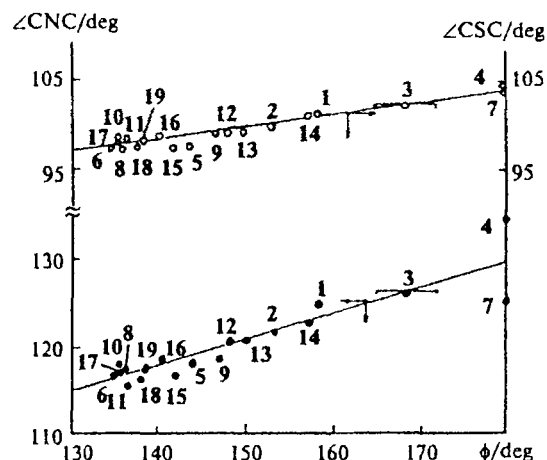


Fig. 5. Dependences of the CNC and CSC bond angles on the dihedral angle ϕ of phenothiazines. For the atomic numbering schemes for the compounds under study, see Table 1.

double bond in the quasi-axial isomer of 10-VPTZ occupies two equivalent positions, which are most favorable for π -electron interactions, when the plane corresponding to this bond forms an almost right angle with the axis of the lone electron pair of the N atom.

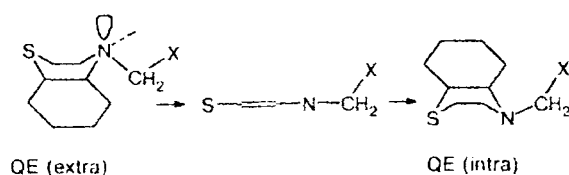
Since we found that the pyramidal inversion of the N atom is not independent motion in phenothiazines, in the case of stereoisomer A of 10-VPTZ we can exclude the nonplanar form containing the planar amine fragment from consideration and give preference to the planar structure.

Conformational analysis of 10-vinylphenothiazine based on the data of photoelectron spectra. Previously,¹ it has been found that the value of the energy gap (Δ) between "S-centered" MOs should be used in the conformational analysis of phenothiazines based on the characteristics of their photoelectron spectra. In stereoisomers A and B of 10-VPTZ, the "S-centered" MOs are the π_3 - and π_4 -MOs (Table 2). The angles ϕ for the two

heterocycle. Because of this, the statistical factor of the quasi-equatorial structures is equal to two. The QE \rightarrow QA transition may be caused by internal rotation of the substituent in the planar form (Scheme 3).

The QA \rightarrow QA transition is analogous to internal rotation about the N—C bond. In particular, the exocyclic

Scheme 2



Scheme 3

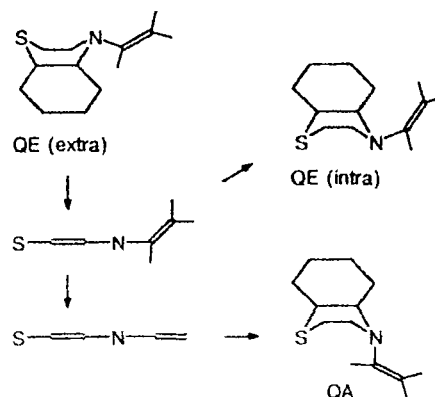


Table 2. Ionization potentials (*IP*) of π -MO and the dihedral angles (ϕ) of the stereoisomers of 10-vinylphenothiazine

Stereo-isomer	<i>IP</i> /eV							Method	ϕ /deg	Method
	π_9	π_8	π_7	π_6	π_5	π_4	π_3			
A	7.22	8.14	9.06	^a	9.42	10.35	11.16	PES	173	PES
A	6.80	8.19	9.14	9.35	9.82	10.60	11.09	AM1 ^b	179 ^c	AM1
B(QA)	7.44	8.38	9.06	^a	9.26	10.35	11.4	PES	147	PES
B(QA)	7.12	8.17	9.14	9.37	9.40	10.81	11.43	AM1 ^b	150	AM1

^a Was not observed because of the overlapping of the bands in the photoelectron spectrum that belong to the π_6 -MO and π_5 -MO of stereoisomers **A** and **B**. ^b $I_i = -0.93\epsilon_i$. ^c The dynamic model; limits of integration are from $\phi = 138^\circ$ to $\phi = 218^\circ$.

forms of 10-VPTZ were calculated by the following equation:¹

$$\Delta_{4,8} = 1.35 + 0.93(\phi/\pi)^2. \quad (6)$$

The values of ϕ , which were calculated according to Eq. (6) (see Table 2), coupled with the above-mentioned data allow the following conclusions. 1. The heterocyclic fragment of form **A** of 10-VPTZ is nearly planar; however, the conditions of overlapping of the p_z -AO of the N atom and the π -MO of the exocyclic double bond are not optimum in this molecule. From this it follows that the double bond deviates substantially from the plane of the heteronucleus. 2. In the gaseous phase, the dihedral angle ϕ in form **B** is similar to that in 10-methylphenothiazine (see Table 1 and Ref. 1), and the interaction between the vinyl group and the remaining π -system of the heterocycle is maximum. These requirements are best met by the quasi-axial form of 10-VPTZ. 3. Orbital perturbations of the π -system of the heteronucleus of phenothiazines caused by the double bond at the N atom disturb the equilibrium between resonance and nonbonded interactions, which occurs in phenothiazine and 10-alkylphenothiazines. As a result, the equilibrium molecular conformation sharply changes. Thus, for phenothiazine, 10-methylphenothiazine, and other *N*-alkylphenothiazines, only the quasi-equatorial stereoisomer was detected by photoelectron spectroscopy, while for 10-VPTZ, two stereoisomers are simultaneously observed. One of them is the quasi-axial isomer, while in the case of the second isomer these definitions are inapplicable.

Theoretical studies of stereoisomerism and of the photoelectron spectrum of 10-vinylphenothiazine. According to the data reported previously,¹ the equilibrium dihedral angles ϕ of phenothiazine and 10-methylphenothiazine are rather adequately calculated by the AM1 method. The geometric parameters of phenothiazines are fully optimized in the procedure of calculations used. However, in this case the energy barriers to transition caused by N-inversion are very low (for example, ~ 0.3 kcal mol⁻¹ for phenothiazine).

Strictly speaking, the low barrier that separates the quasi-equatorial forms of phenothiazine causes one to reject the static model of its stereoisomerization. However, in the case of phenothiazine, the results obtained

with the use of the dynamic model are inconsistent with the experimental data. The photoelectron spectrum is determined by the nonplanar quasi-equatorial form, and when the barrier is low, excitation of large-amplitude vibrations should provide, on average, the planar structure. The results obtained for the compounds related to phenothiazine, such as thianthrene and phenoxathiin, also set one thinking (the stability of their planar forms is substantially overestimated by the AM1 method).

These facts called for the modification of the scheme of calculations of optimum pathways of internal motion over the hypersurface with the use of the structure correlations. The modification consists in the following. The dihedral angle ϕ was used as the reaction coordinate (one of a few), which allows one to visualize stereoisomerism. When the angle ϕ was varied, the geometric parameters that are slightly affected by the phase transition (the l_{CS} and l_{CN} bond lengths and the CSC and CNC bond angles) were changed in a fashion typical of a series of the structures studied by X-ray diffraction analysis (Tables 1, 3, and 4; Eqs. (4) and (5)). The remaining parameters were completely relaxed in the course of the inversion process.

The relationships $\lambda_N \sim f(\phi)$ and $\lambda_S \sim f(\phi)$ for the quasi-equatorial isomers of phenothiazine with the use of the structure correlations are analogous to the corresponding empirical correlations (see Fig. 4). Therefore, it was theoretically confirmed that the completely planar structure of phenothiazine corresponds to the barrier between the quasi-equatorial forms. The stable quasi-equatorial stereoisomer of phenothiazine is characterized by the angle ϕ (Fig. 6, *a*) whose value coincides with that estimated based on the results of photoelectron spectroscopy.¹ For this compound, a stable quasi-axial form was not found (a search for this form was carried out by reversing the sign of α_R in the scheme with full relaxation of the geometry). The barrier to inversion motion of the N atom in phenothiazine determined by the method of structure correlations is ~ 2.5 kcal mol⁻¹ (see Fig. 6, *a*). It is somewhat lower than that obtained in the case of thianthrene for which $V_0 \geq 4$ kcal mol⁻¹ in the gaseous phase¹⁸ and $\Delta H_E \approx 3.5$ kcal mol⁻¹ in the polymeric matrix.¹⁹ This fact is consistent with a more planar structure of phenothiazine.

Based on the results obtained previously,^{19,20} it is this decrease in the barrier that would be expected when

the S atom in thianthrene is replaced by the NH group. Thus, the activation energy (U) of inversion motion is 6.2 and 2.4 kcal mol⁻¹ for thianthrene and phenothiazine, respectively.²⁰ The values of U were estimated according to the following equation:

$$U = 0.5(H_{CSC}r_S^2\Delta\Psi_S^2 + H_{CNC}r_N^2\Delta\Psi_N^2),$$

where H_{CXC} are the angular force constants, r_X are the equilibrium bond lengths, and $\Delta\Psi_X$ is the difference in the CXC bond angles in the equilibrium and planar forms of the molecule. The theoretical values of $\Delta\Psi_X$ were obtained for phenothiazine:²⁰ $\Delta\Psi_S = 14^\circ$ and $\Delta\Psi_N = 6^\circ$. However, the empirical relationships found in this work are somewhat different: $\Delta\Psi_S \approx \Delta CSC = 2.5\text{--}4^\circ$ and $\Delta\Psi_N \approx \Delta CNC = 5.0\text{--}8.0^\circ$. In this case, the

Table 3. Dihedral angles (ϕ) and the C—S bond lengths (l_{CS}) in the tricyclic heteroaromatic compounds according to the data of X-ray diffraction studies^a

Compound (R)	ϕ/deg	$l_{CS}/\text{\AA}$
10-R-Phenothiazines		
(H)	158.5	1.762
(H)	153.3	1.770
(H) (complex with TNB)	165—172	1.76
(Me)	143.7	1.764
(Et)	135.0	1.766
(CHMe ₂)	136.1	1.762
(CHMe ₂)	146.8	1.753
(CH ₂ CH ₂ CN)	135.4	1.76
(CH ₂ CH ₂ COOH)	136.5	1.77
(CH ₂ CH(Me)NMe ₂ · HCl)	141.8	1.77
(CH ₂ CH(Me)NMe ₂ · HBr)	140.6	1.768
(CH ₂ CH(Me)NMe ₃ · CH ₃ SO ₄)	135.6	1.772
(CH ₂ CH ₂ NEt ₂ · HCl)	138.0	1.766
(CH ₂ CH(Me)NEt ₂ · HCl)	138.5	1.766
((2'-OMe)C ₆ H ₄)	157.5	1.756
R-Thioxanthenes		
(CH ₂)	135.3	1.77
(CH ₂)	141.3 (ED) ^b	1.769 (ED) ^b
(HCCHMe ₂)	138.9	1.768
(MeCCHMe ₂)	143.0	1.761
(MeCCHMe ₂)	144.2	1.765
Methixene	137.9	1.765
Thioxanthone	169.0 (ED) ^b	1.751 (ED) ^b
Thianthrene	128.1	1.77
Thianthrene	131.4 (ED) ^b	1.770 (ED) ^b
2,7-Dimethylthianthrene	131.1	1.765
Phenoxathiin	147.8	1.762
Planar forms ($l_{CS} = 1.746 \text{ \AA}$)		
Phenothiazine (complex with TCQD)	180	1.73
10-Methylphenothiazine	180	1.754
(π -radical-cation) ^c		
Dinaphtho[2,3- <i>b</i> ,2',3'- <i>e</i>]dithiin-5,7,12,14-tetraone	180 ^b	1.754 ^b

Note: ED is gas phase electron diffraction.

^a See Refs. 3—6 and 8—11. ^b See Ref. 12. ^c The " π -centered" radical-cation.⁶

contribution of deformations of the bond angles to the barrier to inversion motion of phenothiazine is no more than 0.6 kcal mol⁻¹ in magnitude.

According to our empirical and theoretical estimates, deformations of the CS and the CN bond make the major contribution to the barrier (see Table 3). Therefore, care is required in the extension of the structure correlations that characterize phenothiazine (and, primarily, its *N*-alkyl derivatives) to the quasi-equatorial forms of 10-EPTZ, which contains the additional unsaturated fragment at the N atom. These correlations can be qualitatively extended to the quasi-axial isomers only in the case of substantially nonplanar conformations.

The AM1 calculations, which were carried out taking into account the structure correlations, predicted the existence of two quasi-equatorial forms (intra and extra) of 10-VPTZ, which are similar in energy and are separated by the barrier of ~4.5 kcal mol⁻¹ (see Fig. 6, *c*). This result is contradictory to the experimental data and the general concepts. First, both quasi-equatorial structures of 10-VPTZ appeared to be nonplanar (see Fig. 6, *c*). Second, when $\phi = 180^\circ$, the barrier is higher rather than lower compared to phenothiazine. The last-men-

Table 4. Dihedral angles (ϕ) and CN bond lengths (l_{CN}) in the tricyclic heteroaromatic compounds according to the data of X-ray diffraction analysis^a

Compound (R)	ϕ/deg	$l_{CN}/\text{\AA}$
10-R-Phenothiazines		
(H)	158.5	1.399
(H)	153.3	1.406
(H) (complex with TNB)	165—172	1.40
(Me)	143.7	1.402
(Et)	135.0	1.412
(CHMe ₂)	136.1	1.410
(CHMe ₂)	146.8	1.414
(CH ₂ CH ₂ CN)	135.4	1.42
(CH ₂ CH ₂ COOH)	136.5	1.43
(CH ₂ CH(Me)NMe ₂ · HCl)	141.8	1.42
(CH ₂ CH(Me)NMe ₂ · HBr)	140.6	1.413
(CH ₂ CH(Me)NMe ₃ · CH ₃ SO ₄)	135.6	1.411
(CH ₂ CH ₂ NEt ₂ · HCl)	138.0	1.415
(CH ₂ CH(Me)NEt ₂ · HCl)	138.5	1.42
((2'-OMe)C ₆ H ₄)	157.5	1.418
5-(3-Dimethylaminopropyl)-10,11-dihydro-5 <i>H</i> -dibenzo[<i>b</i> , <i>j</i>]azepine · HCl	130.3	1.422
<i>N,N'</i> -Dimethyldihydrophenazine	123.0	1.427
(complex with TCQD)	165.0	1.386
Planar forms ($l_{CN} = 1.363 \text{ \AA}$)		
Phenothiazine (complex with TCQD)	180	1.36
<i>N</i> -Methylphenazine (cation)	180	1.366,
		1.356
<i>N</i> -Ethylphenothiazine		
(radical-cation) ^b	180	1.362
3,6-Diaminoacridine · 2HCl	178.7	1.381
9-Chloromethylacridine · HCl	178.4	1.348

^a See Refs. 3—6 and 13—17 and references therein. ^b The " π -centered" radical-cation.⁶

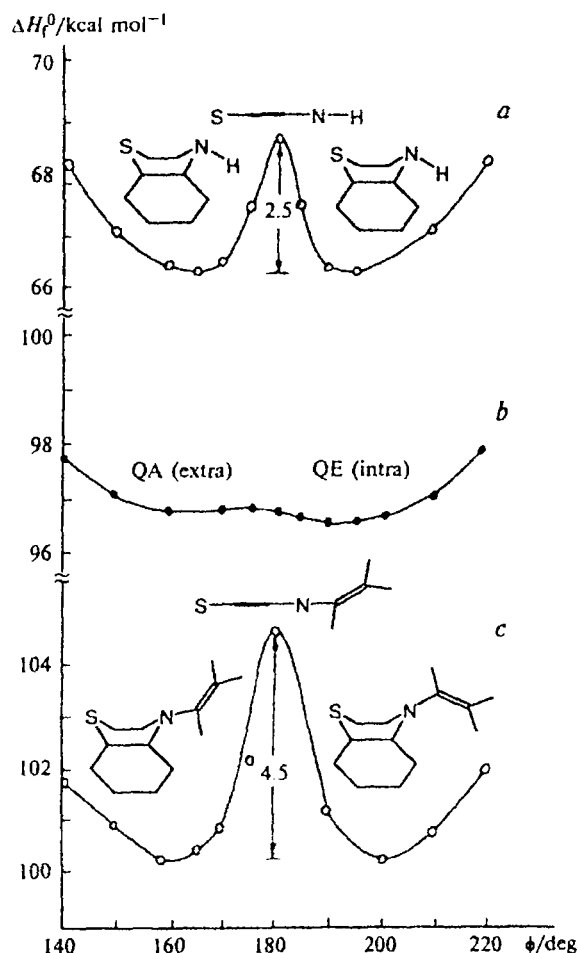


Fig. 6. Sections of hypersurfaces of inversion motion of phenothiazines along its coordinate for phenothiazine (a) and 10-vinylphenothiazine without taking into account (b) and taking into account (c) the structure correlations.

tioned fact is contradictory, in particular, to the fact that the barrier to pyramidal inversion of the N atom in vinylamine (~ 1 kcal mol $^{-1}$) is ~ 5 times lower than those in methylamine or ammonia.²¹

The pathway of the QE \rightarrow QE transition, which is realized upon relaxation of all geometric parameters except for the selected reaction coordinate, is also realized between two nonplanar energetically similar conformations (see Fig. 6, b). However, in this case the barrier is more than one order of magnitude lower. The use of the dynamic model of stereoisomerism of 10-VPTZ (integration over an interval from 0 to $2kT$; $T = 293$ K) gave a value of ϕ equal to $\sim 179^\circ$, which agrees satisfactorily with the experimental data. Therefore, in the case of 10-VPTZ the actual situation is, apparently, better predicted by calculations with full geometry optimization. Unfortunately, we failed to substantiate this suggestion in more detail because the number of structures, which exhibit the geometric features of the amine fragment of 10-VPTZ, is inadequate.

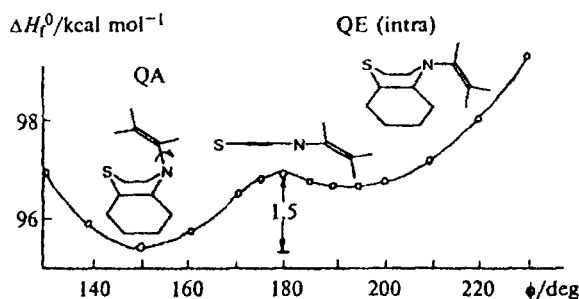


Fig. 7. Section of the hypersurface of inversion motion along its coordinate, which was calculated for 10-vinylphenothiazine in the AM1 approximation with full optimization of all geometric parameters except for this coordinate.

Within the framework of the calculation procedure with full relaxation of the structural parameters, the transition between the QE (intra) and QA forms of 10-VPTZ is described as inversion of the ring with an almost invariant configuration of the bonds in the $NCH=CH_2$ fragment (Fig. 7). The quasi-axial isomer of 10-VPTZ is nonplanar with $\phi \approx 150^\circ$. The calculated value of ϕ virtually coincides with those estimated from the data of photoelectron spectroscopy. The quasi-axial stereoisomer of 10-VPTZ is energetically more favorable (by ~ 1.3 kcal mol $^{-1}$) than the quasi-equatorial (intra) isomer. Because the ratio between the quasi-equatorial and quasi-axial structures is determined not only by the difference in the energy but also by statistical factors, which are larger for the quasi-equatorial forms, it is believed that the calculation scheme with full relaxation of the geometric parameters gives results consistent with the experimental data. The theoretical barrier to transition between the quasi-axial and quasi-equatorial forms of 10-VPTZ is ~ 1.5 kcal mol $^{-1}$.

The determined average values of the dihedral angles ϕ for the quasi-axial and quasi-equatorial stereoisomers of 10-vinylphenothiazine were used for comparing the calculated energies of π -MOs with the experimental values of ionization potentials within the framework of the Koopmans theorem. The comparison (see Table 2) indicated that AM1 calculations with the use of the above-mentioned values of ϕ adequately reproduced the ionization potentials of π -MOs.

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