

Thermodynamics of the Transformation of Spiranes of the Perimidine Series into Quinonimines*

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Abstract—Thermodynamic equilibrium between the spirane and quinonimine structures of photochromic perimidine derivatives was studied by electron absorption spectroscopy and semiempirical quantum-chemical methods (AM1 and PM3). The experimental data showed that the reaction entropy ΔS_0 in octane weakly depends on the substituent structure (0.015–0.024 kJ mol⁻¹ K⁻¹) and that the enthalpy of the reaction for the compound with bulky isobutyl substituent ($\Delta H_0 = 7.1$ kJ/mol) is lower than for those containing hydrogen and methyl group (12.9 and 13.1 kJ/mol, respectively). According to the calculations, in the spirane structure the orientation of lone electron pairs on the perimidine nitrogen atoms may be both cisoid or transoid for different orientations of the cyclohexadiene fragment which adopts a *boat* conformation. The quinonimine isomer can also exist in different stable conformations.

Thermodynamic equilibrium between the spirane and quinonimine structures of photochromic perimidine derivatives **I** (Scheme 1) [1–12] involves cleavage of the N–C_{sp³} bond and intramolecular proton transfer [1, 4–6]. The detailed mechanism of this process is difficult to elucidate because of the lack of the corresponding quantitative thermodynamic parameters and information on possible conformers of the cyclic and open structures. In the present communication we report the results of our study on the thermodynamics of the transformation of the spirane structure into quinonimine by electron absorption

spectroscopy and quantum-chemical calculations of the geometry of tautomeric forms.

The experimental results are summarized in Table 1 and Fig. 1. The entropy of the reaction ΔS_0 determined in a nonpolar solvent (octane) only slightly depends on the R substituent; it ranges from 0.015 to 0.024 kJ mol⁻¹ K⁻¹, being almost similar for compounds **Ia** and **Ic**. The enthalpy of the reaction for compound **Ic** having a bulky isobutyl group ($\Delta H_0 = 7.1$ kJ/mol) is considerably lower than ΔH_0 for

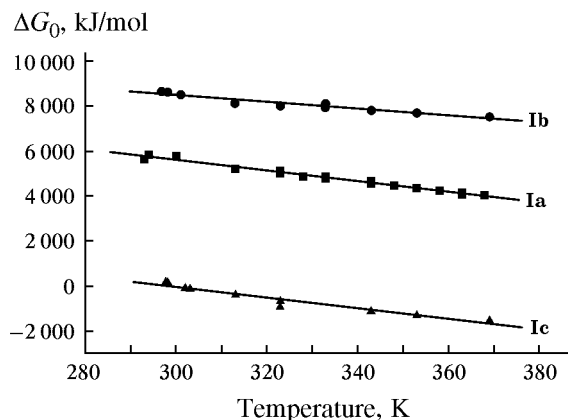
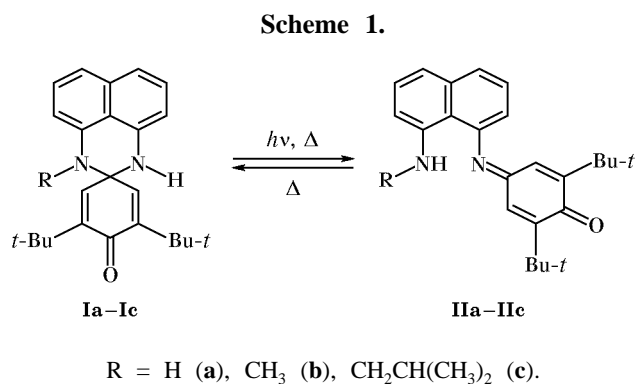


Fig. 1. Temperature dependences of the Gibbs energy ΔG_0 of the transformation of the spirane structure into quinonimine for compounds **Ia–Ic** in octane (experimental data).

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Table 1. Gibbs energies ΔG_0 (kJ/mol, 293 K), enthalpies ΔH_0 (kJ/mol), and entropies ΔS_0 (kJ mol⁻¹ K⁻¹) of the transformation of the spirane structure of compounds **Ia–Ic** into quinonimines **IIa–IIc**

Reaction	Parameter	Experimental data (octane)	Calculation ^a	
			AM1	PM3
Ia \rightleftharpoons IIa	ΔG_0	5.7	–	–
	ΔH_0	12.9±0.3	8.8	57.7
	ΔS_0	0.024±0.001	–	–
Ib \rightleftharpoons IIb	ΔG_0	8.6	–	–
	ΔH_0	13.1±0.5	-7.4	56.6
	ΔS_0	0.015±0.002	–	–
Ic \rightleftharpoons IIc	ΔG_0	0.2	–	–
	ΔH_0	7.1±0.6	–	–
	ΔS_0	0.024±0.002	–	–

^a For most stable conformers.

Table 2. Experimental (X-ray diffraction data [4]) and calculated (AM1, PM3) bond lengths and bond and torsional angles of compound **Ib** (conformer **C**)

Bond (angle)	Calculation		Experiment [4]
	AM1	PM3	
Bond lengths, Å			
C ¹ –C ²	1.3928	1.3806	1.369(3)
C ² –C ³	1.4098	1.4108	1.400(3)
C ³ –C ⁴	1.3730	1.3698	1.364(4)
C ⁴ –C ¹⁰	1.4211	1.4203	1.402(3)
C ⁹ –C ¹⁰	1.4123	1.4075	1.413(3)
C ¹ –N ¹¹	1.4052	1.4312	1.382(2)
C ⁸ –N ¹³	1.4041	1.4323	1.394(2)
N ¹¹ –C ¹²	1.4814	1.5027	1.458(2)
N ¹³ –C ¹²	1.4820	1.5007	1.480(2)
C ¹² –C ¹⁴	1.5343	1.5153	1.506(2)
C ¹⁴ –C ¹⁵	1.3410	1.3409	1.331(2)
C ¹⁵ –C ¹⁶	1.4880	1.4969	1.488(3)
C ¹⁸ –C ¹²	1.5366	1.5181	1.492(3)
C ¹⁶ –O ¹⁹	1.2354	1.2150	1.219(3)
Angles, deg			
N ¹¹ C ¹² N ¹³	112.7	109.2	106.8
C ¹⁴ C ¹² C ¹⁸	108.7	109.7	112.0
α	23.5	27.7	41.6
β_1	28.3	29.6	10.8
β_2	32.4	31.7	21.3
γ	83.8	92.1	87.8

compounds **Ia** and **Ib** (12.9 and 13.1 kJ/mol, respectively). These data show that there is no correlation between thermodynamic parameters of the transformation **I** \rightleftharpoons **II** and electronic properties of the R substituent {the donor effect increases in the series H < CH₃ < CH₂CH(CH₃)₂ [13]}. Presumably, the main factor affecting ΔH_0 is steric interaction between the substituent and spirane framework. In order to check this assumption we performed quantum-chemical calculations by the AM1 and PM3 methods of possible structures of compounds **Ia** and **Ib**. The results are presented in Tables 1–3 and Figs. 2 and 3.

According to the calculations, molecules **Ia** and **Ib** can exist as spirane conformers **A–D**. Conformers **A** and **C** of **Ia** are enantiomeric (Fig. 2). Compound **Ic** gives rise to a larger number of conformers due to nonrigidity of the isobutyl group. The PM3 heats of formation increase in the series **A** < **B** < **C** < **D** (Fig. 2) for compound **Ib**, the energy difference between conformers **A** and **D** being 8.8 kJ/mol. According to the AM1 calculations, the heats of formation change in the series **B** < **A** < **D** < **C**, and the energy difference between the most and least stable conformers is 6.5 kJ/mol. The opposite results were also obtained by the AM1 and PM3 calculations of compound **Ia**: the most stable conformers are **D** (AM1) and **B** (PM3), but the differences between the most and least stable conformers are considerably lesser, 0.9 (AM1) and 1.3 kJ/mol (PM3).

All conformers of **Ia** and **Ib** are characterized by a folding angle of 20–30° along the N–N axis in the perimidine fragment, and the cyclohexane fragment has a *boat* conformation with a folding angle of 25–35° (Table 2). The calculated data are well consistent with those obtained by X-ray analysis of compound **Ib** [4] (Table 2). However, the calculations showed that the spirane structure can be characterized by not only cisoid orientation of lone electron pairs on the nitrogen atoms in the perimidine fragment (conformers **A** and **C**; it is observed experimentally [4]) but also transoid orientation (conformers **B** and **D**). Moreover, the presence of *tert*-butyl groups is responsible for the *boat* conformation of the cyclohexadienone fragment. Analogous calculations of model compounds having no *tert*-butyl groups predict a planar structure of this fragment.

The quinonimine isomer of compounds **Ia** and **Ib** can exist as conformers **A** and **B** shown in Fig. 3 (Table 3). The cyclohexadienone fragment in these conformers also adopts a *boat* conformation, which was found experimentally for some compounds with electron-acceptor substituents in the crystalline phase [6]. Both AM1 and PM3 data indicate that conformer

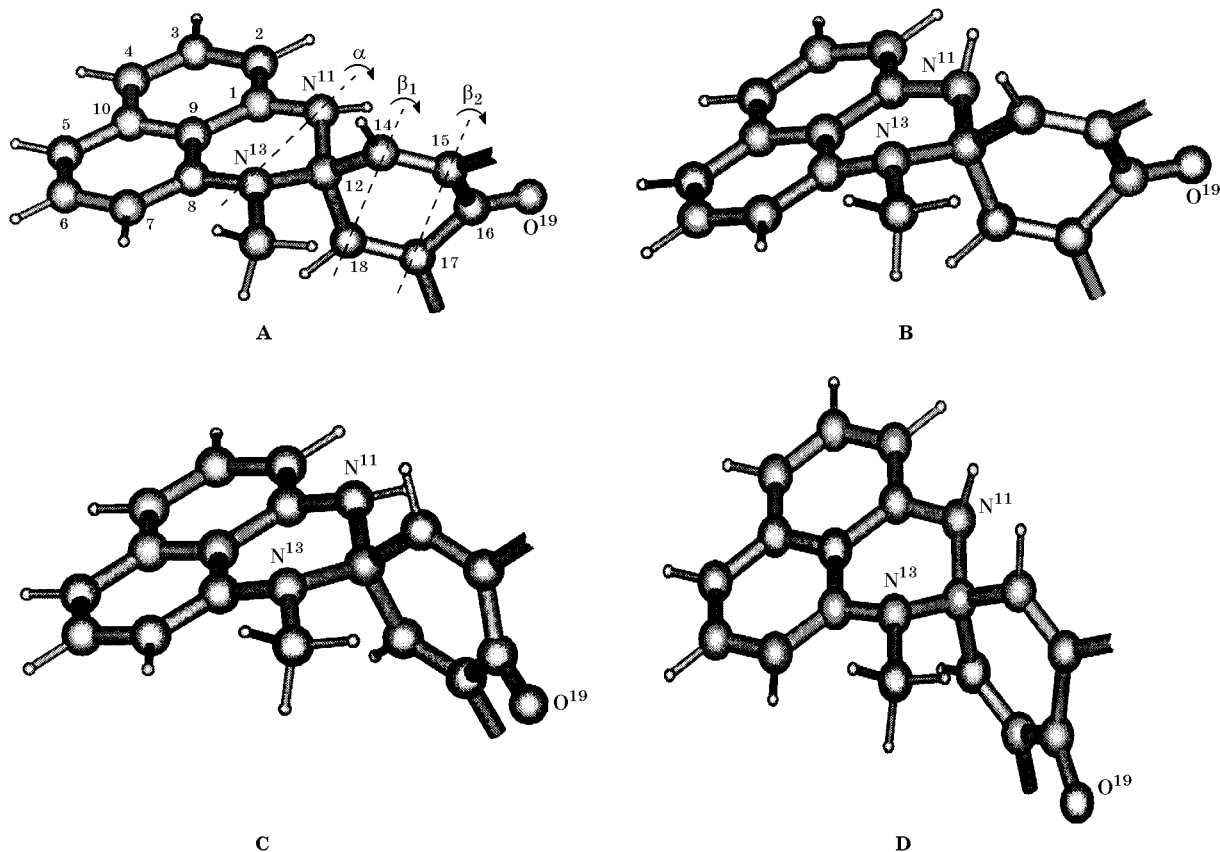


Fig. 2. Spirane structure of compound **Ib** (conformers **A**, **B**, **C**, and **D**), according to AM1 and PM3 quantum-chemical calculations; *tert*-butyl groups are not shown. Conformers of compound **Ia** have similar structures; conformers **A** and **C** are enantiomers.

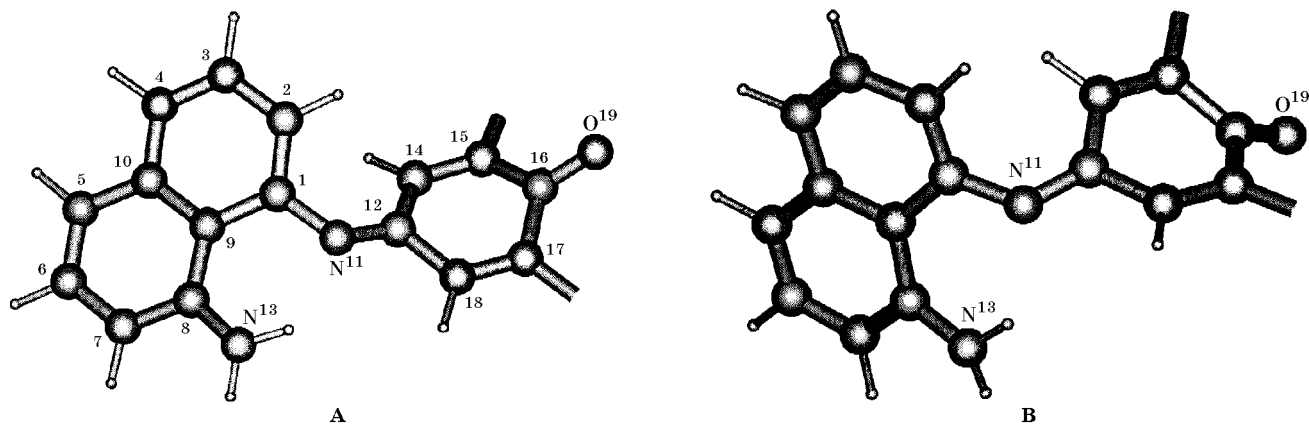


Fig. 3. Quinonimine structure of compound **Ia** (conformers **A** and **B**), according to AM1 and PM3 quantum-chemical calculations; *tert*-butyl groups are not shown. Conformers of compound **Ib** have similar structures.

A of structures **IIa** and **IIb** is more favorable than **B**: the energy difference is 3.1–3.2 kJ/mol.

Using the results of quantum-chemical calculations, we estimated the enthalpies of reactions $\mathbf{I} \rightleftharpoons \mathbf{II}$ as the difference between the heats of formation of the

most stable conformers of the spirane and quinonimine structures. The calculated enthalpies were compared with the experimental data (Table 1). Both AM1 and PM3 calculations show that spirane structure **Ia** is more stable than quinonimine isomer **IIa**, but the

Table 3. Calculated (AM1, PM3) bond lengths and bond and torsional angles in quinonimine structure **IIa** (conformer **A**; for atom numbering, see Fig. 3)

Bond (angle)	AM1	PM3
Bond lengths, Å		
C ¹ –C ²	1.3928	1.3806
C ² –C ³	1.4098	1.4108
C ³ –C ⁴	1.3730	1.3698
C ⁴ –C ¹⁰	1.4211	1.4203
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C ¹⁴ –C ¹⁵	1.3410	1.3409
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C ¹⁶ –O ¹⁹	1.2354	1.2150
Angle, deg		
N ¹¹ C ¹² N ¹³	112.7	109.2
C ¹⁴ C ¹² C ¹⁸	108.7	109.7
α	23.5	27.7
β ₁	28.3	27.7
β ₂	32.4	30.3

ΔH_0 value obtained by the AM1 method is better consistent with the experimental data. According to the PM3 calculations, the spirane isomer **Ib** is also more stable than quinonimine **IIb**, but in poor agreement with the experimental data. Contrary to the latter, the AM1 procedure predicts greater stability of quinonimine structure **IIb**.

EXPERIMENTAL

Compounds **I** were synthesized [1, 4–6], purified, and put at our disposal by V.N. Komissarov. Solvents of ultrapure grade were used in experiments. The electron absorption spectra were recorded on a Specord M-40 spectrophotometer (Germany). The temperature was maintained with an accuracy of ± 1 K using a temperature-controlled unit.

The enthalpies ΔH_0 and entropies ΔS_0 of the transformations **I** \rightleftharpoons **II** were determined from the temperature dependence of the Gibbs energy ΔG_0 using the known formulas $\Delta G_0 = \Delta H_0 - T \Delta S_0$ and $K_{\text{eq}} = \ln([Q]/[S]) = -\Delta G_0/RT$, which interrelate thermo-

dynamic parameters and equilibrium constant K_{eq} . The equilibrium concentrations of the quinonimine ([Q]) and spirane structures ([S]) were determined spectrophotometrically from the optical density at the long-wave absorption maximum of quinonimine **II**, its molar absorption coefficient, and overall concentration. Below are given λ_{max} (ϵ) for the quinonimine isomers of the compounds under study: **IIa**, 584 nm ($5330 \text{ l mol}^{-1} \text{ cm}^{-1}$); **IIb**, 620 nm ($4670 \text{ l mol}^{-1} \text{ cm}^{-1}$); **IIc**, 630 nm ($4200 \text{ l mol}^{-1} \text{ cm}^{-1}$) [7]. A correction was introduced, which took into account variation of the concentration due to thermal expansion.

AM1 and PM3 quantum-chemical calculations of the spirane (**I**) and quinonimine structures (**II**) were performed using Gaussian 94W software [14].

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ΔG_0 , kJ/mol
Temperature, K