PHOTO- AND THERMOCHROMIC SPIRANS.

13.* CALCULATION OF THE PATHWAYS OF THE THERMAL ELECTROCYCLIC REACTIONS OF CHROMENES AND THEIR STRUCTURAL ANALOGS BY THE MINDO/3 METHOD

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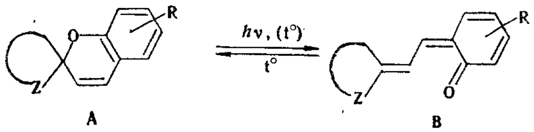
The mechanisms of the electrocyclic reactions of oxetene (I), 2H-pyran (II), 2-amino-2H-pyran (III), 2H-thiopyran (IV), and chromene (V) in the ground, first singlet, and triplet excited states were studied by means of the MINDO/3 method. The enthalpies of excitation are 125 (I, S_0), 32 (I, S_1), 113 (I, T_1), 188 (II, S_0), 109 (III, S_0), 150 (IV, S_0), and 239 kJ/mole (V, S_0). The number of isomers of the open form in S_0 is determined by the nature of the substituent attached to the final carbon atom. It was observed that π donors stabilize both the transoid isomer and the cisoid isomer, which is twisted 20° with respect to the formally single β—γ carbon—carbon bond. Bulky substituents cause ∿105° rotation about the same bond.

The mechanism of the photoreactions and thermal reactions of spiropyrans and chromenes is based on an electrocyclic reaction of the A ⇄ B type:



Despite the enormous volume of accumulated experimental data on the synthesis of spiropyrans and the relationship between their working characteristics and their structure [2, 3], an understanding of the detailed pathways of not only the photoreactions but also the thermal reactions of the indicated type, including the possible intermediates, the structure of the transition states, and the nature of the reaction coordinates, has not yet been achieved. The principal theoretical research on spiropyrans has set out to either calculate the relative stabilities of the valence tautomers (A and B) [5-11] or to calculate their spectral characteristics and the nature of the electron transitions [7, 8, 12-14], i.e., they have been devoted to the study of the most stable structures on the potential energy surface (PES) of the reaction, whereas the entire region of the PES between the indicated structures, which determines the detailed mechanism of the reactions, has for all practical purposes not previously been subjected to theoretical study. Although attempts to qualitatively explain the peculiarities of the mechanisms of reactions involving opening of spiropyran ring A have been made in a number of studies [7, 15-18], estimates of the energy barriers of the reactions were not obtained in them, and the structures of the transition states of the reactions were not established.

The important problem regarding the magnitudes of the barriers of adiabatic forward and reverse photoreactions and thermal reactions that was posed in the course of experimental investigations has not been subjected to theoretical study. The accumulated experimental data on the effect of electronic and steric factors on the rates of the A ⇄ B reactions require their own theoretical explanation, on the basis of which it would be possible to predict the barriers of previously uninvestigated reactions. In the present research we

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*See [1] for Communication 12.

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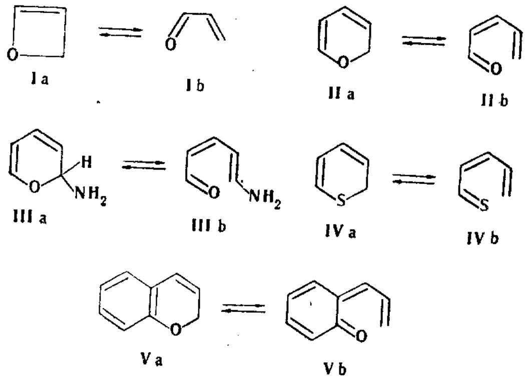
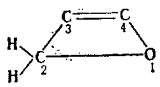
used the semiempirical MINDO/3 method [19] to calculate the pathways of the reactions in series of electrocyclic transformations of the *a* ⇄ b type for systems I-V in the ground, first singlet, and triplet excited states. The reaction 2H-oxetane ⇄ acrolein (Ia ⇄ Ib) serves as the simplest heterocyclic analog of the electrocyclic reaction cyclobutene ⇄ butadiene which has been theoretically investigated in detail [20-22]. The reaction IIa ⇄ IIb characterizes the valence-tautomeric equilibrium 2H-pyran ⇄ cis-dienone [23-25], whereas the III and IV system differ from the preceding system with respect to the introduction of a substituent or replacement of the ring heteroatom. Finally, the reaction Va ⇄ Vb corresponds to interconversions of 2H-chromene and o-quinoneallide, which were first studied experimentally in [26].

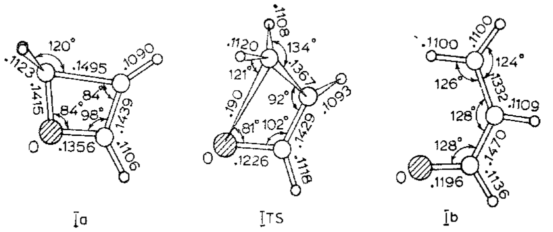


The Oxetene ⇄ Acrolein Reactions (Ia ⇄ Ib)

The mechanism of the reaction in the ground state has been previously investigated by means of ab initio calculations in the 4-31G basis [27]. In order to compare the possibilities of the MINDO/3 method for the calculation of similar reactions we made a detailed investigation of the energy profile of the Ia ⇄ Ib reaction under conditions of a reaction coordinate [28] with complete optimization of all of the geometrical parameters. The C—O distance was selected as the reaction coordinate. The results of our calculations, together with the data in [27], are presented in Tables 1 and 2. Both methods predict greater stability of acrolein as compared with oxetene: 68 kJ/mole greater by the MINDO/3 method and 179 kJ/mole in the case of ab initio calculations. The barriers of the Ia→Ib reaction are 125 (MINDO/3) and 96 kJ/mole (ab initio), as compared with 193 and 275 kJ/mole, respectively, for the reverse reaction. It is easy to note that the barriers of the forward reaction obtained by the MINDO/3 method and by ab initio calculations are in satisfactory agreement both with themselves and with the experimental values of 105 kJ/mole [29] for tetramethyl-substituted oxetene and 100 kJ/mole [30] for unsubstituted oxetene. A close value of the energy of activation of the Ia→Ib reaction (130 kJ/mole) was obtained by Fiquera and co-workers [31] also by means of calculations by the MINDO/3 method, in which continuous opening of the $C_{(4)}C_{(2)}C_{(3)}$ and $OC_{(3)}C_{(2)}$ angles in oxetene, which smoothly converts the molecule to acrolein, was selected as the reaction coordinate.

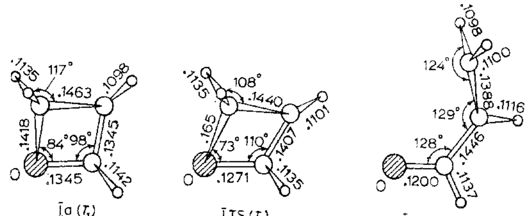


The geometrical characteristics of the ground states of oxetene and acrolein and the structure of the transition state of the Ia ⇄ Ib reaction are presented in Fig. 1. It is interesting to compare the structure of the transition state (ITS) with the calculated structures of the transition states for the 1,3-butadiene ⇄ cyclobutene interconversion [20-22, 32]. In contrast to this reaction, the possibility of the development of two reaction pathways, viz., conrotatory and disrotatory [33], the transition states of which differ substantially, is absent in the Ia ⇄ Ib process. In the case of the more favorable conrotatory pathway the transition state is noncoplanar [22], and the dihedral angle is 26°; for the disrotatory mechanism the transition state has a planar carbon skeleton. The geometry of the transition state of the Ia ⇄ Ib reaction, which is shown in Fig. 1, corresponds more to the geometry of the transition state of the "permitted" conrotatory mechanism than to the geometry of the disrotatory mechanism (with a dihedral angle of 13°). The bulk of the energy of activation is consumed in stretching the broken C—O bond (90%), disruption



Ia ITS Ib

Fig. 1



Ia (T_1) ITS (T_1) Ib (T_1)

Fig. 2

Fig. 1. Geometrical characteristics of oxetene (Ia), acrolein (Ib), and the transition state (ITS) of the Ia $\rightleftarrows$ Ib reaction in the ground state.

Fig. 2. Geometrical characteristics of oxetene [Ia (T_1)], acrolein [Ib (T_1)], and the transition state [ITS (T_1)] of the Ia $\rightleftarrows$ Ib reaction in the triplet state.

of the coplanarity of the skeleton of the oxetene molecule, and rotation of the methylene fragment, which commence after stretching of the C–O bond.

In the excited states the reaction barrier decreases substantially and becomes equal to 113 kJ/mole (T_1) and 32 kJ/mole (S_1). Let us note that the potential energy curves of the ground and first excited states do not overlap, and this constitutes evidence for the absence of a nonadiabatic reaction pathway. The geometries of oxetane, acrolein, and the transition state of the reaction of I in the first triplet state are presented in Fig. 2. The carbon skeleton of both oxetene and acrolein is noncoplanar, and the transition state also has a nonplanar structure. The known results of ab initio calculations [35] of the structure of acrolein in the excited state are in agreement with our data. Let us note that the length of the C–O bond in the transition structure in the excited states is substantially shorter than in the ground state. As a consequence of this, the barriers of the reactions of these compounds decrease appreciably. The changes in the geometry in the course of the Ia $\rightleftarrows$ Ib reaction in the first singlet state are similar to the changes in the first triplet state, and we therefore cite only the latter.

The *a* $\rightleftarrows$ b Reaction in Systems II-V

The energy characteristics of these reactions are presented in Table 2. The transition from the oxetene ring to the 2H-pyran ring changes the relative stability of the valence tautomers. Thus, whereas the open form is stable for oxetene, in the case of system II 2H-pyran is 51 kJ/mole more stable than pentadienal. This value is close to the experimental data [24] on the valence isomerization of substituted 2H-pyrans (the difference in the free energies is ∿25 kJ/mole). Somewhat greater disparity between the calculated and experimental relative stabilities of the closed and open structures was noted in the calculation of the cyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene (the error was 71 kJ/mole by the MINDO/2 method) [34].

Greater stability of the cyclic structure is also retained for systems III-V. In all likelihood, this is associated with both the difference in the aromatic character of oxetene (four π electrons) and 2H-pyran (six π electrons) and with the greater strain energy of the oxetene ring. The introduction of an amino group increases the relative stability of the open form significantly, and this has been observed experimentally [25]. Benzoannelation of 2H-pyran, on the other hand, leads to greater (by 143 kJ/mole) destabilization of the open form as compared with the closed form. This result is in agreement with our previous calculations [6], which constitute evidence for the substantial effect of the aromatic character on the relative stabilities of the open and closed forms. Replacement of the oxygen atom by a sulfur atom [2H-thiopyran (VI)] leads to a similar (as in the case of benzoannelation) change in the relative stability, i.e., to greater stabilization (∿128 kJ/mole) of the closed structure. The barrier of the forward reaction for 2H-pyran is 188 kJ/mole; the experimental value for 1-oxa-2,5,5,8a-tetramethyl-1,5,6,7,8,8a-hexahydronaphthalene is 113 kJ/mole [24] (the error is 75 kJ/mole).

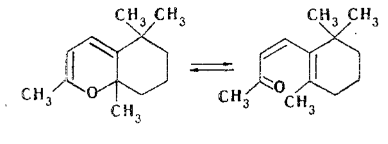


TABLE 1. Comparison of the Results of Calculations of the Ia ⇄ Ib Reaction in the Ground State by the MINDO/3 and ab initio Methods

Parameter	Structure*					
	Ia	ITS†	Ib	Ia	ITS†	Ib
	ab initio [27]			MINDO/3		
$R\,[C_{(2)}C_{(3)}]$, nm	0,1539	0,145	0,1337	0,1495	0,1367	0,1332
$R\,[C_{(3)}C_{(4)}]$, nm	0,1331	0,141	0,1491	0,1439	0,1429	0,1470
$R\,[C_{(4)}O]$, nm	0,1422	0,133	0,1211	0,1356	0,1226	0,1196
$\angle C_{(2)}C_{(3)}C_{(4)}$, deg	89	98	121	84	92	128
$\angle C_{(3)}C_{(4)}O$, deg	97	104	124	98	102	128
$\angle\theta$, deg	0	18	0	0	13	0

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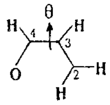
*The numbering of the atoms is as follows: 

†Transition state.

TABLE 2. Energy Characteristics of the Reactions of I-V (kJ/mole)

Reaction (state)	ΔH_{fa}*	ΔH_{fb}†	ΔH_f‡	$\Delta\Delta H_{a\to b}$	$\Delta\Delta H_{b\to a}$	$\Delta\Delta H_{a\text{-}b}$
I (S_0)	−15,0	−82,8	110,3	125,3	193,1	67,8
I (S_0) [27]	0,0	−179,4	96,1	96,1	275,5	179,4
I (S_1)	291,3	103,2	323,1	31,8	219,9	188,1
I (T_1)	183,9	100,7	296,8	112,9	196,1	83,2
II (S_0)	−79,0	−28,4	108,7	187,7	137,1	−50,6
III (S_0)	−91,1	−79,0	17,6	108,7	96,6	−12,1
IV (S_0)	73,2	201,1	222,8	149,6	21,7	−127,9
V (S_0)	−13,4	130,0	225,7	239,1	95,7	−143,4

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*The heat of formation of the cyclic structure.
†The heat of formation of the open form.
‡The heat of formation of the transition state.

Let us note that the barrier of the electrocyclic cyclobutene ⇄ butadiene reaction calculated by the MINDO/3 method is also 55 kJ/mole higher than the experimental value (the calculated energy of activation is 205 kJ/mole, and the experimental value is 150 kJ/mole).

The introduction of an amino group lowers the barrier of the ring-opening reaction substantially (108.7 kJ/mole), which was also observed in [25]. In the case of 2H-thiopyran the decrease in the barrier of the forward reaction is 38 kJ/mole; at the same time, the barrier of the reverse reaction (ring-closing) decreases by 115 kJ/mole and is 21.7 kJ/mole. This result makes it possible to expect that the thioquinoneallide (open) form is not characteristic for 2H-thiopyrans. Annelation of 2H-pyran increases the barrier of the ring-opening reaction by 51 kJ/mole and lowers the barrier of the reverse reaction by approximately the same value.

The geometrical characteristics of 2H-pyran, 2H-aminopyran, 2H-thiopyran, and chromene (closed form, structure of the transition state, and open form) are presented in Figs. 3 and 4. The region of cleavage of the C—O bond (the length of the C—O bond in the transition state) is virtually almost identical both in the case of 2H-pyran and in the case of 2H-aminopyran and chromene (0.195 nm). The introduction of an amino group stretches the C—O bond slightly (0.002 nm) in the cyclic structure, and this leads to a decrease in the barrier of the forward reaction. Attention is directed to the fact that the lengths of the C—C bonds in the transition state become almost equal, i.e., the structure tends to approach the aromatic delocalized state (this is particularly clearly noted in aminopyran). In the transition state the six-membered ring remains virtually planar [the $C_{(6)}$ atom deviates 0.001 nm from the plane], and stretching of the bond leads to a small change in the angle between the plane of the ring and the $RC_{sp^3}H$ plane (R = H, NH_2).

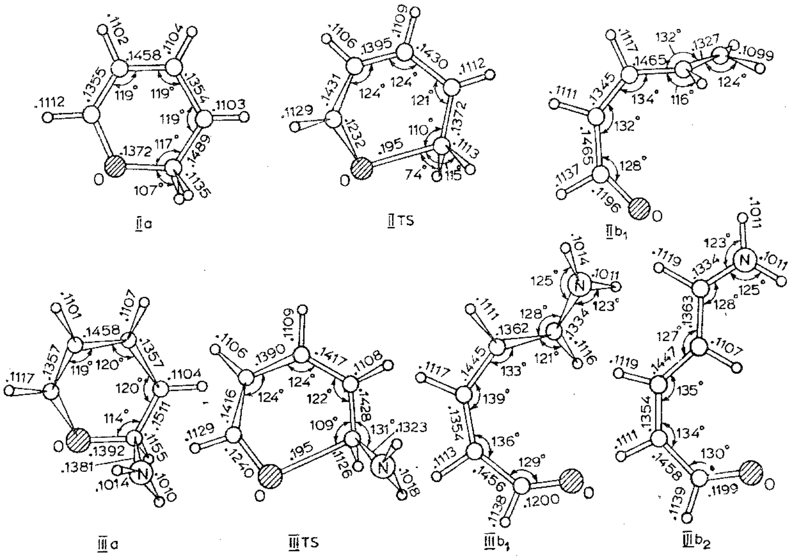


Fig. 3. Changes in the geometries of the 2H-pyran (II) and 2H-aminopyran (III) molecules in the course of the electrocyclic reaction (*a* pertains to the cyclic forms, TS pertains to the transition state, and b_1 and b_2 pertain to the open forms).

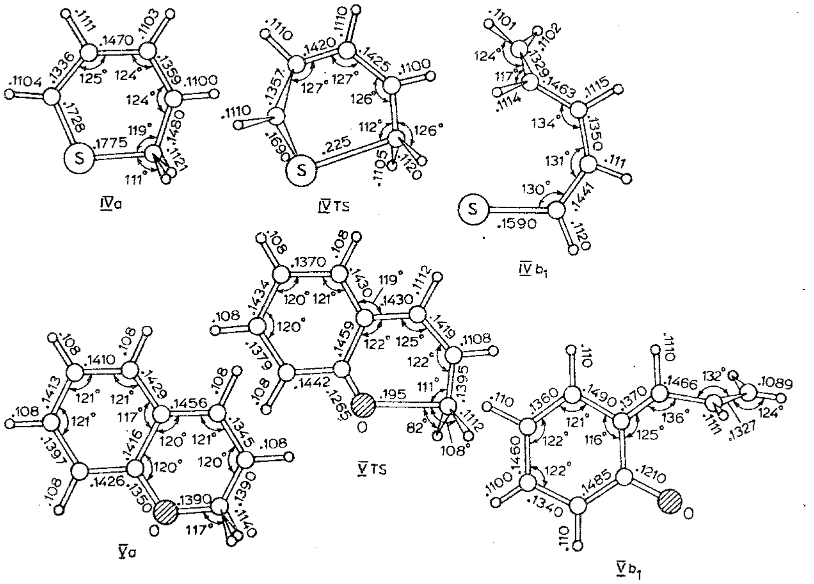


Fig. 4. Changes in the geometries of the 2H-thiopyran (IV) and chromene (V) molecules in the course of the electrocyclic reaction (*a* pertains to the cyclic forms, TS pertains to the transition state, and b_1 pertains to the open forms).

Structurally, the mechanism of the reaction can be represented as follows. When the C—O bond is stretched to 0.195 nm (the transition state), the plane of the ring rotates simultaneously 20° relative to the $HC_{sp^3}H$ plane. Stretching of the C—O bond also leads to changes in the bond angles (up to 5°) and rearrangement of the bond lengths. The further change in the geometry is associated with an increase in the C_{sp^3}—O distance and rotation of the $HC_{sp^3}H$ plane relative to the plane of the ring, which converts to rotation about the $C_{(2)}$—$C_{(3)}$ bond (angle φ, Figs. 5 and 6). It is interesting to note that rotation at angle θ occurs after the transition state is reached in the region R = 0.36 nm.

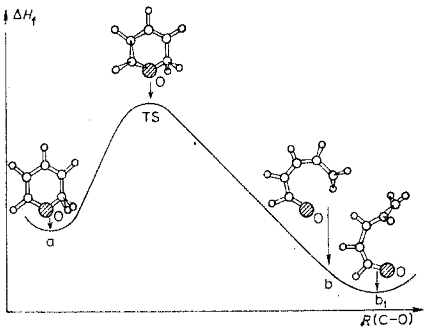


Fig. 5

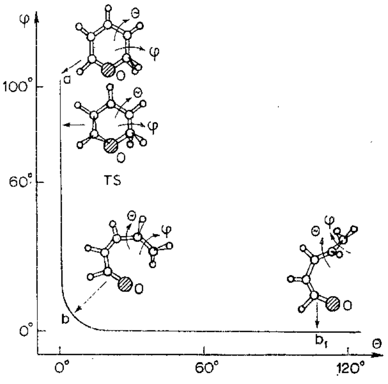


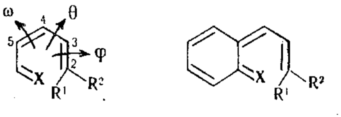
Fig. 6

Fig. 5. Energy profile of the reactions of II-V. The successive change in the geometry of the pyran fragment is shown.

Fig. 6. Changes in angles φ and θ in the course of the electrocyclic reactions of II-V.

Geometrical Isomers of the Open Forms

A knowledge of the relative stabilities of the geometrical isomers of the open forms of chromenes and spiropyrans is extremely important for the explanation of the spectral behavior, particularly the position of the long-wave absorption, which is one of the properties to which special attention is directed from a practical point of view. We calculated the barriers to rotation about the $C_{(3)}$—$C_{(4)}$ (angle θ) and $C_{(4)}$—$C_{(5)}$ (angle ω) bonds of the open forms of structures II-V (see above).



X=O, S; R^1 = H, CH_3; R^2 = H, NH_2

A minimum corresponding to the planar cis-cisoid structure is absent for all of the structures that we investigated. The existence of cis-cisoid isomers of the IIb-Vb type, in which the C—X bond is cleaved but isomerization to the final product has not occurred, is frequently postulated to explain the mechanisms of the reactions of chromenes and their analogs [36-39]. Our data constitute evidence for the absence of this sort of intermediate on the potential energy surface (PES) of the ring-opening reaction. In the case of 2-amino-2H-pyrans there is a minimum on the PES that corresponds to a structure that is rotated 20° about the $C_{(3)}$—$C_{(4)}$ bond. The geometrical characteristics of this isomer (IIIb$_1$) are presented in Fig. 3. Replacement of the hydrogen atom by a bulkier substituent, particularly a methyl group, leads to a slight increase in the noncoplanarity angle ($\theta = 32°$).

Unsubstituted 2H-pyrans, 2H-thiopyrans, and 2H-chromenes also do not have a minimum in the cis-cisoid structure. The minimum in the gauche form corresponds to these systems, and the angle of noncoplanarity along the $C_{(3)}$—$C_{(4)}$ bond ranges from 90 to 105°, depending on the specific case. The calculated barrier to rotation about the $C_{(3)}$—$C_{(4)}$ bond ranges from 13 to 29 kJ/mole. The geometry of the isomer obtained for 2H-pyran is shown in Fig. 3 (IIb$_1$).

The fact that the trans,trans isomer also does not correspond to the minimum on the PES of the reaction for any of the systems except 2H-aminopyrans is extremely interesting. The principal reason for destabilization of the planar trans,trans structure is the short H—X distance (X = O, S), which in the planar form is less than the sum of the van der Waals radii of the H and X atoms (Figs. 3 and 4). At the same time, for 2H-aminopyrans there is a minimum that corresponds to the planar trans,trans structure. The potential energy surface (PES) in coordinates of θ and ω is presented in Fig. 7. On the surface there are two minima that correspond to the planar trans,trans form ($\omega = 0°$, $\theta = 180°$) and a somewhat noncoplanar cis,cis structure ($\omega = 0°$, $\theta = 20°$). A comparison of the geometrical characteristics of the open forms of 2H-pyran and 2H-aminopyran makes it possible to understand the difference in the stabilities of the geometrical isomers and their structures. The geo-

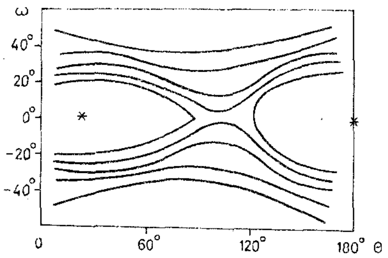


Fig. 7. Potential energy surface (PES) of rotation about the $C_{(3)}$—$C_{(4)}$ (angle θ) and $C_{(4)}$—$C_{(5)}$ (angle ω) bonds for 2-amino-2H-pyran. The minima on the PES are indicated by asterisks.

TABLE 3. Charges on the Atoms in the Merocyanine Forms of II and III

Structure	Atom No.*						
	1	2	3	4	5	6	7
IIb	−0,485	−0,013	0,007	0,155	−0,174	0,623	—
IIIb$_1$†	−0,520	0,237	−0,218	0,229	−0,246	0,647	−0,132
IIIb$_2$†	−0,509	0,234	−0,218	0,225	−0,235	0,645	−0,135

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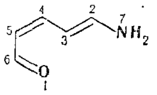
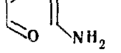
*The numbering of the atoms is 

†See Fig. 3.

metrical isomers of 2H-pyran (IIb$_1$, θ = 105°) and 2H-aminopyran (IIIb$_1$, b$_2$, θ = 20°) are presented in Fig. 3. The introduction of an amino group leads to an increase in the contribution of the $\overset{-}{\text{O}}\text{—CH=CH—CH=CH—CH=}\overset{+}{\text{N}}\text{H}_2$ dipolar structure to the resonance hybrid, which is reflected in the lengths of the 2—3 and 3—4 bonds (the 2—3 bond is lengthened by 0.003 nm, and the 3—4 bond is shortened by 0.002 nm). As a consequence of this, the O···H distance is increased, and the nonvalence repulsion, which leads to destabilization of the planar structure, decreases substantially. In addition, as a consequence of the decrease in the length of the $C_{(3)}$—$C_{(4)}$ bond, the barrier to rotation increases, which ultimately leads to stabilization of the noncoplanar cis,cis isomer (IIIb$_1$).

In agreement with our previous calculations within the π-electron approximation [1, 6], the MINDO/3 method indicates virtually equal energic stabilities of the possible isomers of the open form. The heats of formation of some isomers of the open form of 2H-aminopyran are presented below. Similar results were also obtained for the remaining investigated structures II-V.

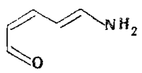


III b$_1$

$\Delta H_f = -78{,}0$ kJ/mole

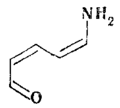
III o$_3$

$\Delta H_f = -80{,}7$ kJ/mole



III b$_2$

$\Delta H_f = -82{,}2$ kJ/mole



III b$_4$

$\Delta H_f = -84{,}9$ kJ/mole

Thus the introduction of an amino group leads to the development of two isomers relative to the $C_{(3)}$—$C_{(4)}$ bond. The first of these isomers, viz., the cis-cisoid isomer ($IIIb_1$), is responsible, in all likelihood, for the short-wave (with a brief lifetime) absorption, while the second, viz., the cis,trans isomer ($IIIb_2$), determines the long-wave absorption. The barriers of the transitions from the first to the second and vice versa are, respectively, 4.6 and 9.2 kJ/mole. The isomerization to structure IIIb is associated with rotation about the $C_{(4)}$—$C_{(5)}$ double bond. According to our calculations (disregarding double configuration interaction) is 74.4 kJ/mole, which is in agreement with the barriers to rotation about the double bond in similar compounds [40, 41]. Minima corresponding to a structure that is "twisted" along the double bond are absent on the potential energy surface (Fig. 7) [1].

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ARYLOXAZOLYL-SUBSTITUTED RHODAMINE C DERIVATIVES

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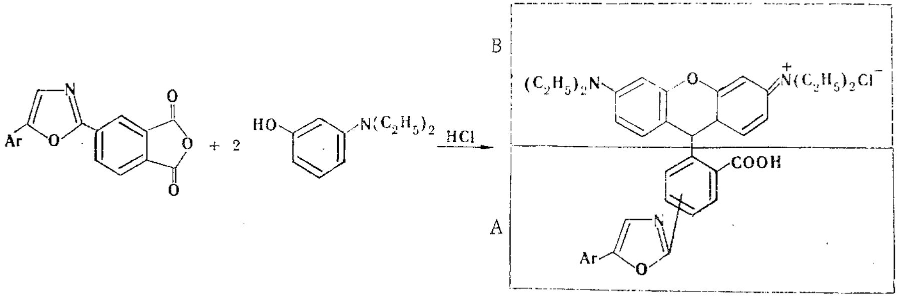
Aryloxazolyl-substituted rhodamine C derivatives were synthesized by condensation of 4-(5-aryloxazol-2-yl)phthalic anhydrides with m-diethylaminophenol, and their spectral-luminescence properties were investigated. The individual compounds and their mixtures with 4-aminonaphthalic acid phenylimide were used to obtain daytime fluorescent pigments and paints. Effective intermolecular transfer of the electronic excitation energy is observed in mix compositions, and its mechanism is discussed.

Rhodamine dyes and their derivatives are widely used as luminophores in daytime fluorescent pigments and paints [1], in tunable lasers [2], as active dyes in biological investigations [3], and for other purposes.

We have synthesized aryloxazolyl derivatives of rhodamine C (I) — compounds that contain two fluorophores with a common aromatic ring — by using our previously described 4-(5-aryloxazol-2-yl)phthalic anhydrides [4].



I a $Ar = C_6H_5$; b $Ar = 4\text{-}CH_3O\text{-}C_6H_4$; c $Ar = 2\text{-}C_{10}H_7$

Ia-c

The synthesis of Ia-c was realized by fusing 4-(5-aryloxazol-2-yl)phthalic anhydrides with m-diethylaminophenol at 180-190°C in a molar ratio of 1:2. The probability of the formation of two isomers that differ with respect to the mutual orientation of the aryloxazole residue and the pyrone ring in the carboxy-containing aromatic ring is not excluded in the reaction of aryloxazolylphthalic anhydrides with m-diethylaminophenol. Considering the fact that the visible color and fluorescence of rhodamines is due to the structure of the xanthene part of their molecules, which is in a mutually perpendicular plane with the carboxyphenyl group [5], the isomers should not differ substantially with respect to their spectral-luminescence properties. We therefore investigated the compounds obtained after chromatographic purification without isolation of the individual isomers (Table 1).

The absorption spectrum of Ia (Fig. 1) consists of two disconnected bands with a distance of 235 nm between the maxima. The short-wave band is due to transitions that are localized in the diphenyloxazole fragment and is identical to the absorption spectrum of 2-(p-carboxyphenyl)-5-phenyloxazole [λ_{max} 315 nm (ε = 37,000)]. Lengthening of the conjuga-

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