PHOTO- AND THERMOCHROMIC SPIRANS.

17.* THEORETICAL PREDICTION OF BARRIERS OF THERMAL REACTIONS INVOLVING VALENCE ISOMERIZATION OF SPIROPYRANS

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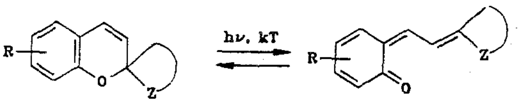
The mechanisms of the valence isomerization of 2H-pyrans and chromene were calculated by means of the MINDO/3 method. A correlation between the magnitude of the barrier of activation of the electrocyclic reaction and the differences in the energies of the π bonds of the tautomeric forms was noted. A simple scheme that makes it possible to estimate the magnitude of the activation barrier of the thermochromic transformations of spiropyrans on the basis of quantum-chemical calculations by the Pariser–Parr–Pople (PPP) method is proposed.

The photo- and thermochromic properties of spiropyrans are due to valence isomerization of the 2H-pyran fragment [2, 3]:



A B

Z=O, NR', S

The optimization of the operating characteristics of spirans involves an analysis of dependences of the structure–property type that are based on quantum-chemical calculations of valence isomers A and B. We have previously carried out theoretical investigations of the following parameters of these compounds: the long-wave absorption [4, 5], the relative stabilities of forms A and B [5], and the length of the cleaved $C_{(2)}$–O bond, which is comparable with the ability of A to manifest photochromic properties [6]. At the same time, virtually no study has been devoted to one of the most important parameters – the magnitude of the barriers of the thermal reaction A $\rightleftarrows$ B, which determines the lifetime of colored form B. This is associated, on the one hand, with the difficulties involved in the experimental determination of the kinetics of these processes and, on the other, with the complexity of the quantum-chemical calculation of the potential energy surface (PES) and the localization of the transition state (TS).

In this paper we propose a simple scheme for the semiquantitative evaluation of the activation barriers of the thermal reactions A → B of compounds that contain a 2H-pyran fragment. The data obtained by means of the proposed scheme make it possible to single out the structural factors that determine the relative magnitude of the barriers of the reactions. Previous calculations of the PES of the ground states of 2H-pyran, 2-amino-2H-pyran, and 2H-chromene by the MINDO/3 method [7] showed that the reaction coordinate of opening of the pyran ring is determined almost completely by stretching of the $C_{(2)}$–O bond length of 0.195 nm corresponds to the transition state of the thermal reaction A $\rightleftarrows$ B; this value remains virtually constant in the series of investigated reactions. This fact makes it possible to propose the following method for the calculation of the barriers of the thermal reactions of the investigated class of compounds. The heats of formation of forms A and B are determined in calculations with complete optimization of the geometry, while the heats of formation of the structures of the transition states are determined at a fixed $C_{(2)}$–O bond length of 0.195 nm with complete optimization of all of the remaining geometrical parameters. The character

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*See [1] for Communication 16.

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TABLE 1. Heats of Formation (ΔH), Enthalpies of Activation ($\Delta\Delta H^{\neq}$), Lengths of the $C_{(2)}$—O Bonds in Isomer A, Charges of the Bonds, and Some Energy Characteristics of the Thermal Reaction A → B

R_i	ΔH_A, kJ/mole	$\Delta\Delta H^{\neq}$,* kJ/mole	$R_{C_{(2)}-O}$, nm	E_{C-O}†, eV	$\lvert q_C\rvert+\lvert q_O\rvert$‡	$\Delta E_{TS-A}^{\pi b}$**, eV	$\Delta E_{B-A}^{\pi t}$**, eV	ΔH_B, kJ/mole
				Compound I				
H	−79,0	187,7	0,1372	−16,38	0,851	−1,348	−3,445	−28,4
2,2-(OH)$_2$	−440,9	90,8	0,1422	−16,72	1,431	−3,366	−4,316	−492,4
2-NH$_2$—5-CHO	−274,2	112,7	0,1411	−14,77	1,002	−1,881	−3,666	−215,4
2-NH$_2$	−101,4	119,0	0,1392	−16,01	1,008	−1,625	−3,602	−79,0
2-OH	−276,8	123,1	0,1394	−16,50	1,151	−1,580	−3,594	—
2-CHO	−203,4	152,7	0,1390	−15,38	0,750	−1,513	−3,734	−156,7
6-NH$_2$	−162,4	159,3	0,1371	−16,45	0,933	−1,424	−3,518	−128,1
5-OH	−293,6	180,1	0,1362	−16,67	0,818	−1,324	−3,433	
5-CHO	−238,0	181,0	0,1381	−16,00	0,841	−1,543	−3,444	−133,7
5-NH$_2$	−99,6	184,5	0,1365	−16,67	0,833	−1,324	−3,434	−37,2
5-NO$_2$	−174,4	201,8	0,1377	−15,71	0,823			
				Compound II				
H	−13,4	239,1	0,1390	−17,08	0,843	−0,860	−2,745	130,0

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*The energy barrier is reckoned from closed form A.

†The contribution of the $C_{(2)}$—O bond to the total energy [9].

‡Approximate measure of the polarity of the $C_{(2)}$—O bond.

**See below.

of the heteroring with the Z atom has a relatively slight effect on the structure of the 2H-pyran fragment [6]. In this connection we restricted ourselves to calculations of substituted 2H-pyrans (I) and 2H-chromene (II) by the MINDO/3 method.

I II

R^1, R^2, R^3, R^4=H, OH, NH$_2$, CHO, NO$_2$

The nature of the stationary points obtained in calculations with a fixed $C_{(2)}$—O bond length was verified by analysis of the matrix of the force constants by the McIver—Komornicki method [8]. Only a negative eigenvalue of this matrix was found in all cases for the hypothetical transition states; this makes it possible to classify the structures determined in this way as true transition states of the reaction A ⇄ B. It must be noted that the structural mechanism of the cleavage of the $C_{(2)}$ —O bond of the investigated comopunds is similar to that of unsubstituted 2H-pyran. Rotation of the R^1CR^2 fragment at a small angle relative to the plane of the pyran ring is realized synchronously with stretching of the $C_{(2)}$—O bond. The heats of formation of the transition states evaluated by the method set forth above are presented in Table 1 along with the heats of forms A and B and the activation barriers of the A ⇄ B processes. The lengths of the $C_{(2)}$—O bonds of cyclic structure A are also presented in Table 1. In connection with the fact that the length of the $C_{(2)}$—O bond in the transition state does not depend on structural variations and has a constant value, whereas in cyclic form A it varies over a wide range, one might expect symbatic character of the activation barriers and the lengths of the $C_{(2)}$—O bond. However, an analysis of the data in Table 1 does not reveal this sort of correlation. Moreover, other characteristics of the bond undergoing cleavage, which are also presented in Table 1, also do not correlate with the activation barriers. Thus the following questions can be formulated. 1. Why is a correlation of the characteristic of the cleavable bond—energy of activation type absent? 2. How do substituents affect the length of the $C_{(2)}$—O bond? 3. What explains the absence of this sort of the effect on the magnitude of this bond in the transition state?

For the study of these questions we examined the results of reconstruction analysis of the MO of 2H-pytan from the MO oxadiene (OD) fragment OCH=CH—CH=CH and the MO of OD and CH_2 group. For simplification, only the interactions of the MO of OD and CH_2 that lead to the formation of the spiro node are presented in Fig. 1. The interaction of the σ_2 MO of CH_2 and the nonbonding MO [lowest vacant mole-

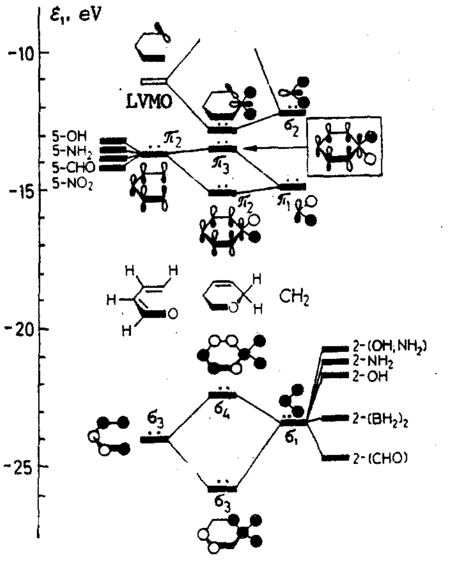


Fig. 1

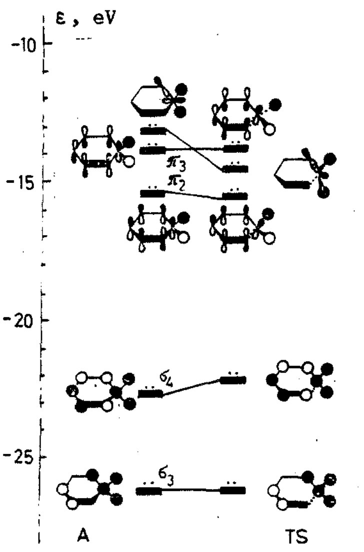


Fig. 2

Fig. 1. Reconstruction analysis of the MO that form the spiro node from the MO of the oxadiene (OD) fragment and CH_2. Results of calculations by the extended Hückel method (EHM).

Fig. 2. Correlation diagram of the change in the energies of the orbitals that form the spiro node during the reaction A → B.

cular orbital (LVMO)] of OD is responsible only for the $C_{(2)}$–$C_{(3)}$ bond (ones attention should be directed to the directed character of the corresponding orbitals, Fig. 1). Overlapping of the σ_3 MO of OD and the σ_1 MO of CH_2 leads to the formation of the σ_3 and σ_4 orbitals, the latter of which has a node in the $C_{(2)}$–O bond. An increase in the difference in the σ_3 and σ_1 energy levels by varying the substituents attached to $C_{(2)}$ (Fig. 1) decreases their interaction and, as a consequence, decreases the strength of the $C_{(2)}$–O bond and increases its length. A similar approach was previously used by Hoffman and co-workers [10] to explain the change in the lengths of the bonds in three-membered sulfur-containing rings. Mixing of the π_2 orbital of OD and the π_1 orbital of CH_2 leads to the formation of the low-lying π_2 MO of 2H-pyran, which has a node in the $C_{(2)}$–O bond, and the higher-lying π_3 MO, which has a bonding component along the $C_{(2)}$–O bond. π-Acceptor substituents in the pyran ring, which decrease the energy of the π_2 orbital of OD, therefore lead to an increase in the splitting of the π_2 and π_3 MO of 2H-pyran and, as a consequence, increase the length of the $C_{(2)}$–O bond. π-Donor substituents increase the energy of the π_2 orbital of OD and decrease the length of the $C_{(2)}$–O bond. In connection with the fact that the examined interaction is quite small, the effect of substituents of the pyran part on the length of the $C_{(2)}$–O bond is weaker than the effect of the substituents attached to $C_{(2)}$.

In the transition state of the reaction A $\rightleftarrows$ B (Fig. 2) the interaction of the σ_3 MO of OD and the σ_1 MO of CH_2 leads only to the formation of a $C_{(2)}$–$C_{(3)}$ bond [the density-matrix element (DME) is 0.292] and not to the formation of a $C_{(2)}$–O bond (the corresponding DME is only 0.007). The bonding of the O and $C_{(2)}$ atoms in the transition state is realized only through overlapping of their p_x AO [the x axis is directed along the $C_{(2)}$–O bond], and the corresponding DME is 0.357. It should once again be emphasized that the A → B transformation is associated not simply with stretching of the $C_{(2)}$–O bond but also with simultaneous rotation of the R^1CR^2 fragment relative to the plane of the pyran ring [7]. As a consequence of this, the unshared pairs of the substituents attached to $C_{(2)}$ do not overlap with the orbitals of the $C_{(2)}$–O bond. The orbitals of the substituents of the pyran part also do not interact with the orbitals of the $C_{(2)}$–O bond of the transition state (they are orthogonal). In the series of compounds I and II (Table 1) the $C_{(2)}$–O distance in the transition state therefore remains constant. Since the coordinate of the thermal opening of the pyran ring is determined not only by stretching of the $C_{(2)}$–O bond but also by rotation of the fragment attached to $C_{(2)}$, correlations of the property of the cleavable bond–energy of activation type are absent.

TABLE 2. Correlation of the Experimental Activation Parameters of the Thermal Opening of Spiropyrans with the Difference in the Energies of the π Bonds of Isomers A and B ($\Delta E^{\pi b}_{B-A}$)

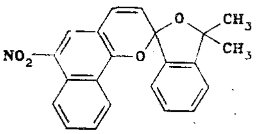
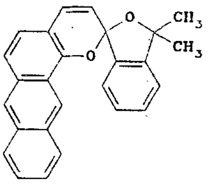
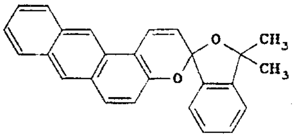
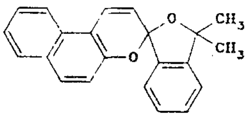
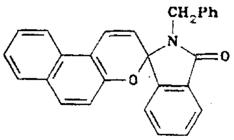
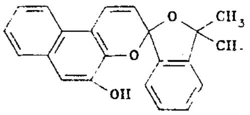
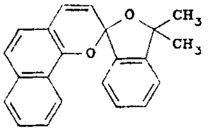
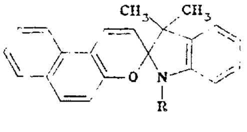
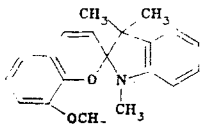
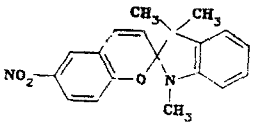
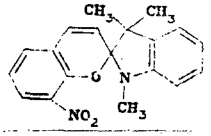
Spiropyran	Solvent*	$\Delta\Delta H^{\neq}$, kJ/mole	$\Delta G^{\neq}$, kJ/mole	$\Delta E_{B-A}^{\pi b}$, eV
1	2	3	4	5
	HCB	41,1±6,3	73,3±1,3	−4,5578
	HCB	62,0±9,6	78,8±1,7	−4,5394
	HCB	65,8±6,3	80,4±1,3	−4,5430
	HCB NB	70,6±0,8 72,5±2,9	82,5 81,7	−4,5310
	DCB NB	75,8±2,5 72,9±1,3	86,3 83,8	−4,0047
	HCB BN	78,8±2,1 89,7±0,8	78,8 82,1	−4,5321
	HCB BN	93.8±0.8 98,9±1,7	84,6 89,2	−4,5289
	HCB (R=CH₃) BN (R=CH₃) CT (R=CH₃) CT (R=C₂H₅) DCB (R=C₂H₅) DCB (R=CH₂Ph)	114.8±2,5 113.5±2.9 108,1±4,6† 120.2±4.2‡	85.1 94,7 84,2 82,1 87,2 92,5	−3,2060
	CT	—	101.4±1.7	−2,9139

Table 2 (continued)

Spiropyran	Solvent *	$\Delta\Delta H^{\neq}$ kJ/mole	$\Delta G^{\neq}$, kJ/mole	$\Delta E_{B-A}^{\pi b}$, eV
1	2	3	4	5
	ЧХ	—	102,2±1,7	−2,8748
	ЧХ	—	104,3±1,7	−2,7503

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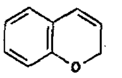
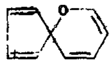
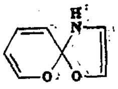
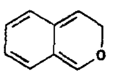
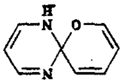
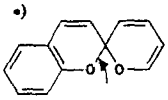
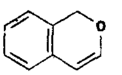
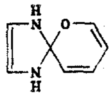
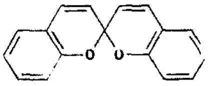
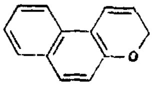
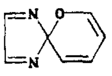
*The activation parameters were measured in the following solvents: hexachlorobenzene (HCB), benzonitrile (BN), dichlorobenzene (DCB), nitrobenzene (NB), and carbon tetrachloride (CT).

†Obtained by coalescence of the PMR signals of the 3',3'-methyl groups.

‡Obtained by coalescence of the PMR signals of the methylene protons of the benzyl group.

TABLE 3. Effect of Structural Modifications on the $\Delta E^{\pi b}_{B-A}$ Values

Structure	$\Delta E_{B-A}^{\pi b}$, eV	Structure	$\Delta E_{B-A}^{\pi b}$, eV	Structure	$\Delta E_{B-A}^{\pi b}$, eV
	−2,7450		−3,9488		−4,2787
	−4,1412		−6,3805	*) 	−5,1721
	−2,7567		−3,6177		−4,9426
	−3,0470		−4,0353		

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*The arrow shows the bond that undergoes cleavage.

Wilcox and Carpenter [11] have previously noted a correlation of the magnitudes of the activation barriers of electrocyclic reactions of hydrocarbons with the difference in the energies of the π bonds of the transition state and the starting structure ($\Delta E^{\pi b}_{TS-A}$). Using the proposed method we calculated the $\Delta E^{\pi b}_{TS-A}$ value, as well as the difference in the energies of the π bonds of the merocyanine and pyran structures ($\Delta E^{\pi b}_{B-A}$), correlation of which with the $\Delta\Delta H^{\neq}$ value might have been expected on the basis of the BEP principle. In conformity with the results in [11], it was assumed that the transition state on the pathway of the reaction $A \rightleftarrows B$ is a cis-pentadienal, turned at an angle of 70° with respect to the terminal double bond. The $\Delta E^{\pi b}_{TS-A}$ and $\Delta E^{\pi b}_{B-A}$ values calculated by the Pariser – Parr – Pople (PPP) method are presented in Table 1. The indicated values correlate satisfactorily with the barriers of activation of the thermal reactions; calculation of $\Delta E^{\pi b}_{B-A}$ is sufficient for a rough estimate. Calculations of the $\Delta E^{\pi b}_{B-A}$ values of spiropyrans (Table 2), the barriers of which were measured in [12, 13], may serve as yet another confirmation of the dependence that we observed. Taking into account the accuracy of the experimental data (the scatter in the values, the dependence of the $\Delta G^{\neq}$ and $\Delta\Delta H^{\neq}$ values on the solvent, and the selected method of measurement) the agreement between the $\Delta E^{\pi b}_{B-A}$ values and the experimental characteristics is good, and the value $\Delta E^{\pi b}_{B-A} = -2.7503$ eV, which corresponds to $\Delta G^{\neq} = 104$ kJ/mole (25 kcal/mole), characterizes the upper boundary of the thermochromic transformations of spiropyrans.

The proposed method can be used for the semiquantitative evaluation of the effect of structural modifications on the thermochromic properties of spiropyrans. The data presented in Table 3 provide evidence that varying the heterene fragment has the greatest effect on the magnitude of the barrier of activation of the thermal reactions of spiropyrans.

The authors thank V. A. Lokshin and N. A. Voloshin for providing us with data on the barriers of thermochromic transformations of spiropyrans.

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FORMATION OF 5-OXOINDENO[1,2-b]PYRAN DERIVATIVES IN CYCLIZATION OF 1,5-DIKETONES OF THE INDIAN-1,3-DIONE SERIES

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D. Kh. Mutsenietse, and G. Ya. Dubur

UDC 547.442.5'665'816.07:
543.422.25:541.634

Indeno[1,2-b]pyrans, including 2-methylene and 2-acetoxy derivatives of 3-ethoxycarbonyl-4-phenyl-5-oxo-3,4-dihydroindeno[1,2-b]pyran, are formed in the cyclization of 4-(indan-1',3'-dion-2'-yl)-4-phenyl-2-butanone and its 3-ethoxycarbonyl derivative in acetic anhydride in the presence of sulfuric acid.

One method for the synthesis of pyrans is ring closing of pentane-1,5-dione derivatives with splitting out of water. The use of cycloaliphatic 1,5-diketones instead of aliphatic 1,5-diketones leads to condensed pyrans, including indenopyrans [1].

In the present research we investigated reactions involving the cyclization of 1,5-diketones of the indan-1,3-dione series, i.e., indan-1,3-dione derivatives that contain a CO group in the composition of the substituent attached to the $C_{(2)}$ atom, particularly the cyclization of 4-(indan-1',3'-dion-2'-yl)-4-phenyl-2-butanone (Ia) and its 3-ethoxycarbonyl analog Ib in an acidic medium.

In solution in acetic anhydride in the presence of catalytic amounts of sulfuric acid the above-mentioned 1,5-diketones readily undergo ring closing to give a pyran ring and form 5-oxoindeno[1,2-b]pyran derivatives. In the absence of an electron-acceptor substituent attached to the $C_{(3)}$ atom in the molecule of the starting compound, i.e., in the cyclization of 4-(indan-1',3'-dion-2'-yl)-4-phenyl-2-butanone (Ia), the only reaction product is 2-methyl-4-phenyl-5-oxo-4H-indeno[1,2-b]pyran (IIa).

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