PHOTO- AND THERMOCHROMIC SPIRANS.

15.* EFFECT OF STRUCTURAL FACTORS ON THE LENGTH OF THE C_{spiro}—O BOND

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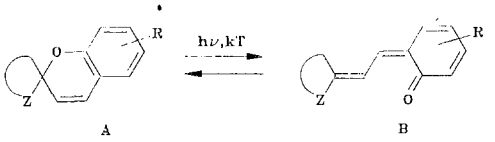
Calculations of a large number of compounds that contain a 2H-pyran fragment were made by means of the MINDO/3 method. A correlation between the magnitude of the barrier to opening of the pyran ring and the length of the C_{spiro}—O bond was noted. Structural factors that determine the length of the C_{spiro}—O bond were discovered. Spiropyran structures that have extremal lengths of the C_{spiro}—O bonds were predicted on the basis of the correlations obtained.

The valence tautomerism of spiropyrans (A $\rightleftarrows$ B), which determines their photo- and thermochromic properties, has been sufficiently well studied both experimentally [2-6] and theoretically [1, 7-13].



A B

The principal trend of research in this field has involved the study of the effect of structural factors of A and B on the efficiency of photoreactions, as well as on the efficiency of the forward and reverse thermal reactions. In this connection calculations that correctly model the effect of electronic and steric factors of the structure on the physicochemical properties of spiropyrans (SPP) have become particularly important. We have previously thoroughly analyzed the effect of structural modifications on the electronic spectra [12, 14] and on the kinetic [12] and thermodynamic [13] stabilities of an extensive class of spiropyran systems and, by means of the MINDO/3 method, have made detailed calculations of the pathways of minimal energy of reactions involving the electrocyclic opening of the 2H-pyran and 2H-chromene rings [1]. The calculations showed that in the ground and lower triplet electronic states the largest part of the energy of activation of opening of the six-membered ring is consumed in stretching of the C_{spiro}—O bond of the 2H-pyran ring. The length of this bond in the initial step of the transformation extremely accurately describes the total reaction coordinate.

These results can be coordinated with the results of x-ray diffraction studies of a number of spiropyrans of the A type [15-24], which have displayed significant variations in the lengths of the C_{spiro}—O bonds (up to 0.01 nm) as a function of the type of heterocyclic fragment and substituents R. In agreement with the calculations [1] and the principles of structural modeling of the pathways of the chemical reactions [25, 26] it might be expected that the length of the C_{spiro}—O bond in spiropyrans would correlate with the energy barriers to the electrocyclic thermal reaction or photoreaction A → B [23, 27]. In this case an analysis of the characteristics of this bond would make it possible to predict spiropyrans with the required kinetic characteristics without performing calculations of the entire potential energy surface of the A $\rightleftarrows$ B reaction.

The aim of the present research was a quantum-chemical analysis by means of the MINDO/3 method [28] of the factors that determine the strength of the C_{spiro}—O bond and the predic-

*See [30] for communication 14.

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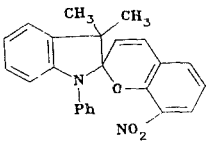
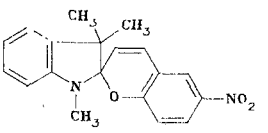
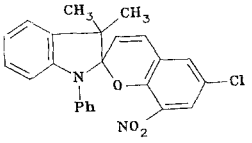
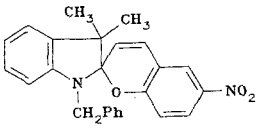
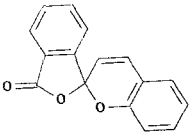
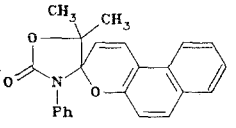
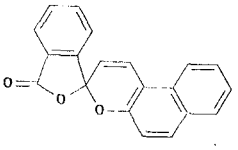
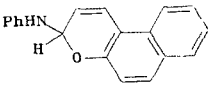
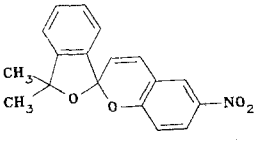
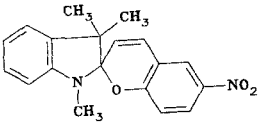
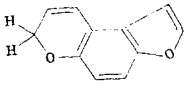
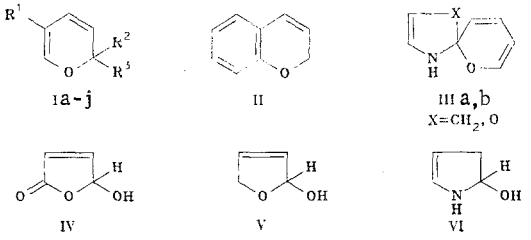
TABLE 1. C_{spiro}—O Bond Lengths and Photo- and Thermochromic Properties of Spiropyrans

Spiropyran	R[C_{spiro}—O], nm	Photochromism	Thermochromism	Spiropyran	R[C_{spiro}—O], nm	Photochromism	Thermochromism
	0,1492 [15]	+	+		0,1487 [20]	+	+
	0,1497 [16]	+	+		0,1478*	+	+
	0,1418 [17]	–	–		0,1439 [21]	+	–
	0,1399 [18]	–	–		0,1442 [22]	+	+
	0,1454 [19]	+	–		0,1495 [23]	+	+
					0,1421 [24]	+	–

*The crystals were triclinic with a = 13.534(2), b = 10.173(1), c = 8.372(1) Å, α = 105.66(1), β = 104.91(1), γ = 73.02(1)°, Z = 2, space group P1, and R = 0.043 for 2738 reflections.



tion of some structures in which the extremal characteristics of this bond should arise. The currently available data on the lengths of the C_{spiro}—O bonds in spiropyrans (R[C_{spiro}—O]) are presented in Table 1. The available experimental data basically determined the selection of systems for the model calculations (I–VI). The effect of the heterocyclic fragment on the C_{spiro}—O bond is modeled in the IV-VI systems. The results of the calculations are presented in Table 2.

Systematic understatement of the calculated C_{spiro}—O bond lengths as compared with the experimental values (≈0.005-0.006 nm) is observed. This fact has been previously noted by Dewar [29] for all C—O bonds and is not due to the peculiarities of the investigated com-

TABLE 2. Calculated Lengths and Polarities of the C_{spiro}–O Bonds of Model Compounds

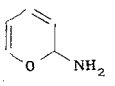
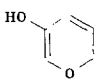
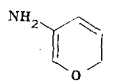
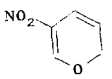
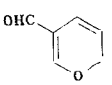
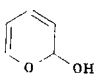
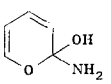
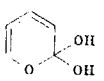
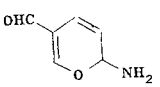
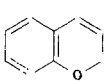
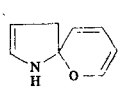
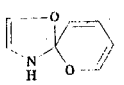
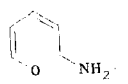
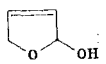
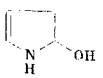
Compound		R[C_{spiro}–O], nm	Charge on C_{spiro}	Charge on O	Barrier to the thermal reaction, kJ/mole
1		2	3	4	5
	Ia [1]	0,1372	0,374	−0,422	187,7
	Ib [1]	0,1392	0,392	−0,447	108,7
	Ic	0,1362	0,435	−0,383	179,7
	Id	0,1365	0,440	−0,393	189,48
	Ie	0,1377	0,432	−0,391	201,3
	If	0,1381	0,438	−0,403	182,0
	Ig	0,1394	0,695	−0,456	124,7
	Ih	0,1420	0,7831	−0,4400	—
	Ii	0,1422	0,917	−0,514	91,0
	Ij	0,1400	0,543	−0,459	134,3
	II	0,1390	0,423	−0,420	239,1
	IIIa	0,1391	0,417	−0,488	—
	IIIb [13]	0,1442	0,719	−0,488	—
	Ia (T_1)	0,1384	0,321	−0,400	96,7

TABLE 2 (Continued)

1		2	3	4	5
	Ib (T_1)	0,1423	0,317	−0,369	33,4
	IV	0,1365	0,671	−0,511	—
	V	0,1378	0,684	−0,550	—
	VI	0,1372	0,470	−0,510	—

pounds. A combined analysis of Tables 1 and 2 makes it possible to draw the following conclusions.

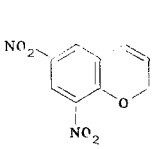
1. Calculations of a large number of compounds with a 2H-pyran ring reveal a correlation between the magnitude of the energy barrier to ring opening and the length of the C_{spiro}—O bond (this correlation is observed only over the range of elongated C_{spiro}—O bonds; see below).

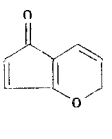
2. The introduction of π-acceptor substituents into the pyran part of the molecule leads to lengthening of the C_{spiro}—O bond. σ-Acceptor substituents attached to the spiro carbon atom have the same effect. The transition from the 2H-pyran structure (Ia) to the 2H-chromene structure (II) increases the bond length by 0.002 nm. This change exceeds the effect of acceptor substituents. In model structure IV the effect of a donor substituent is weakened by interaction with the carbonyl group, and this ultimately leads to shortening of the investigated bond.

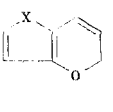
A correlation between the length of the bond and its polarity is not observed.

3. A comparison of the lengths of the C_{spiro}—O bonds of structures Ib, VI, and IIIa and Ih and IIIb shows that the bond length is determined by the 2H-pyran fragment, perturbation of which correctly describes the electronic effects in real spiropyrans. At the same time, the length of the bond in structure VI with a similar structure of the spiro node differs from the length in IIIb and IIIa by 0.002 nm.

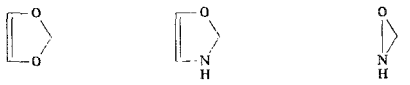
On the basis of the correlations obtained spiropyran and 2H-chromene structures with maximal and minimal lengths of the C_{spiro}—O bonds and extremal values of the energy barriers can be predicted. Thus 2H-chromene structures with acceptor substituents in the aromatic ring such as VII and VIII will have the maximal bond length. Systems of the IX type should have a shortened C_{spiro}—O bond and maximal values of the barriers to the A→B reaction in this case.


VII

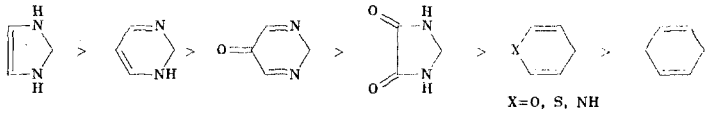

VIII


IX X=O, S, NH

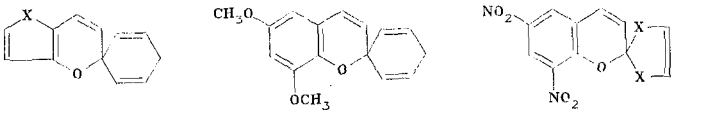
In the case of identical pyran structures the maximal bond length should be observed in spiropyrans that contain the following heterorings:



At the same time, one may assume shortening of the bond lengths in the order



By combining the effects of the heterocyclic and pyran parts of the molecule one can predict spiropyrans with extremal bond lengths:



minimal C_{spiro}—O bonds maximal C_{spiro}—bond

Let us note that lengthening of the C_{spiro}—O bond is observed in the first triplet state, with which the mechanism of the photoreaction is usually associated (see Table 2). It is apparent from an examination of the data in Table 1 that the correlation of the C—O bond length in spiropyrans with their ability to undergo electrocyclic ring opening most likely characterizes the efficiency of the photoreactions but not the efficiency of the thermal reactions, as one should have expected. Our calculations [1] show that the barriers for the thermal reactions range from 90 to 240 kJ/mole, whereas the barriers for the photoreactions range from 30 to 100 kJ/mole, and the structure of the spiropyran in the first triplet state is similar to the structure of the transition state of the ring-opening reaction. This is probably the reason for the fact that the efficiency of a photoreaction can be judged from the structure of the cyclic form. At the same time, the structure of the transition state for thermal reactions differs substantially from the structure of the spiropyran, and this determines the absence of a direct dependence of $R[C_{spiro}—O]$ on the barrier to the thermal reaction for spiropyrans with a short C—O bond.

More detailed results of investigations of the mechanisms of the photoreactions and thermal reactions of substituted 2H-chromenes will be published in one of our future communications.

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QUASI-TAUTOMERISM OF 5-HYDROXY-5-PHENYL-5H-PYRIDO[2,3-b]CHROMENES IN SULFURIC ACID

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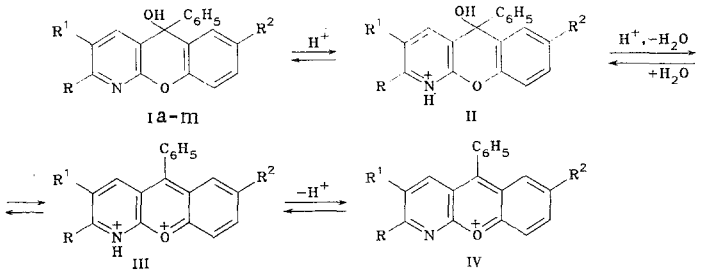
The existence of a quasi-tautomeric equilibrium in solutions of 5-hydroxy-5-phenyl-5H-pyrido[2,3-b]chromenes in sulfuric acid, which was confirmed by a linear dependence of the logarithms of the indicator ratios on acidity function $H_R - H_0$ with a slope close to unity, was established. The pK values of this equilibrium correlate with the σ_p^0 and σ_R^0 substituent constants.

The synthesis and ionization constants of 5-hydroxy-5-phenyl-5H-pyrido[2,3-b]chromene derivatives were described in [1, 2]. It was assumed that upon protonation these compounds undergo stepwise ionization with the successive formation of singly charged ion II and doubly charged pyridinium-chromenylium ion III.



However, a quantitative study of the equilibrium between the protonated forms showed that, although a linear relationship between the logarithms of the indicator ratios and acidity function H_R [3] is observed, the slopes of this relationship differ significantly from unity and range from 0.55 to 0.65. This fact compelled us to reexamine the concept of the investigated equilibrium and to advance the assumption of the existence of the three-component

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