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PHOTOCHROMIC AND THERMOCHROMIC SPIROPYRANS. 11.* CALCULATION OF THE STABILITIES OF THE VALENCE TAUTOMERS OF SPIROPYRANS

B. Ya. Simkin and V. I. Minkin

UDC 541.145'623:547.814

A method was developed for the estimation of the relative stabilities of spirocyclic and merocyanine structures of spiropyrans on the basis of the Pariser—Parr—Pople method in σ,π parametrization with a corresponding estimate of the energy of formation of the spiro node. The results of the calculations are in satisfactory agreement with the experimental data and the results of calculation by the MINDO/3 method.

The photo- and thermocoloration reactions of spiropyrans [2] are due to $A \rightleftarrows B$ valence tautomerization, which is associated with electrocyclic cleavage of the C—O bond in A and is accompanied by the geometrical isomerization of B to the more stable merocyanine quinoneallid form C.

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*See [1] for communication 10.

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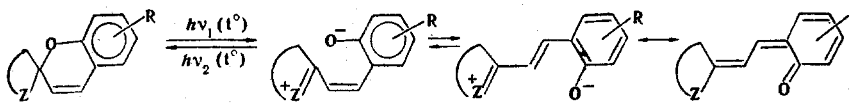


A B C1 C

To understand the mechanism of the photochemical and thermal opening of spiropyrans one must know the position of the singlet and triplet energy levels of the open and closed forms. The positions of the energy levels of the excited states of each individual form can be determined experimentally by using spectroscopic methods. However, to construct the general diagram of the energy levels of tautomers A and C one must have data on their relative stabilities in the ground state. These data can be obtained experimentally only for a limited number of spiropyrans with pronounced thermochromic properties. The problem of the theoretical calculation of the ΔG° values by means of quantum-chemical methods arises in this connection. The methods developed by Dewar, viz., the MINDO/3 method and a variant of the Pariser—Parr—Pople (PPP) method with special σ,π parametrization [3, 4], are currently the most suitable methods for the calculation of the relative stabilities of the molecules in the ground state. Difficulties are encountered in the application of each of these methods to spiropyrans.

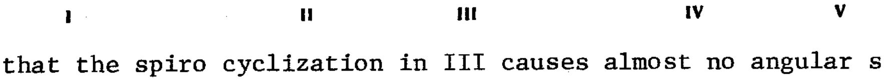
The original program [5] of the MINDO/3 method, an important feature of which is minimization of the total energy with respect to the geometrical parameters of the molecules, was designed for a limited orbital basis and cannot be applied to real spiropyran structures because of the large number of atoms and geometrical parameters. The PPP method was designed for application to completely conjugated systems and can be used in unmodified form only for the calculation of the heats of atomization of conjugated quinoneallid forms B and C. Spiropyran structures A, which contain an sp^3-hybridized carbon atom that unites two perpendicular π systems, cannot be calculated directly by this method.

The task of the present research was to develop a method for the estimation of the relative stabilities of the spirocyclic and merocyanine structures of spiropyrans on the basis of the PPP method in σ,π parametrization with a corresponding estimate of the energy of formation of the spiro node.

1. Computational Method

The application of the PPP method to spiropyran structures of the A type requires an estimate of the effect of spiro conjugation, i.e., of the nonadditive interactions between two mutually perpendicular conjugated fragments of spiropyran molecules. A qualitative theory of spiro conjugation was developed by Simmons and Fukunaga [6] and Hoffmann and co-workers [7]. Quantitative results with respect to the splitting of the orbital levels and the change in the electron distribution in spiro conjugated hydrocarbons were recently obtained by means of theoretical calculations [8-10] and the results of photoelectronic and electron absorption spectroscopy [10, 11]. These results show that spiro conjugation effects are substantial only when the spiro carbon atom links conjugated polyenes (spiro[2.2]pentadiene, spiro[2.4]heptatriene, etc.). The deviations from additivity are slight in saturated spirans, and the calculated energies of the isodesmic reactions involving separation of the rings are close to zero [9].

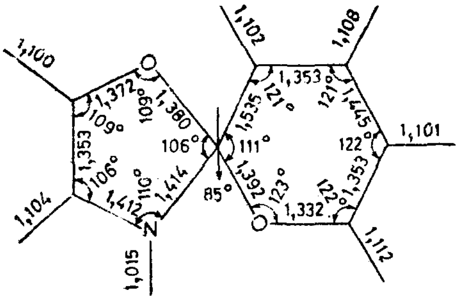
A similar pattern can also be expected for spiropyran compounds of the A type: because of the high electronegativities of the heteroatoms adjacent to the spiro carbon atom, the MO of the fragments intermix only slightly. The electronic spectra of spiropyrans A extremely accurately model the sum of the spectra of the corresponding chromene and dihydro four-ring compound [12, 13]. The energies of separation of the rings of model spirans I and III of the A type calculated by the MINDO/3 method for isodesmic reactions are +2.6 and +3.5 kcal/mole, respectively. It is apparent from the calculated geometrical characteristics of the



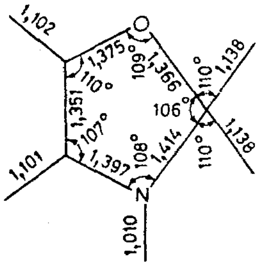
I II III IV V

III-V molecules that the spiro cyclization in III causes almost no angular strain (α_1 = 106°, α_2 = 104°, β_1 = 111°, and β_2 = 109°), which in the case of small spiro rings introduces an appreciable destabilizing effect in the energy of separation of the rings. Thus, the positive energies of separation of the rings are due to the stabilizing effects of branching at the spiro atom (see [9, 14]) and spiro conjugation. The latter effect, although it is somewhat underestimated in the MINDO/3 procedure [8], is consequently extremely small.

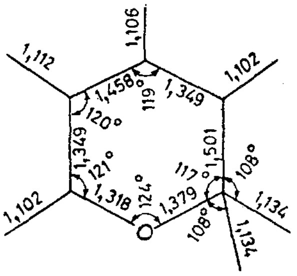
The small degree of spiro conjugation makes it possible to represent the heat of formation (ΔH_f) of spiran form A in the form of the sum of the heats of formation of the components of its fragments. This makes it possible to propose the following method for the estimation of the relative stabilities of the open and closed forms of the spiropyrans. The heat of atomization (ΔH_a) of conjugated structure B is estimated by means of the PPP method in σ,π parametrization, which is well suited for these ends. The heat of atomization of spiran form A is represented in the form of the sum of three terms, viz., the heat of atomization of the conjugated part of the first fragment, the heat of atomization of the conjugated part of the second fragment, and the energy of the spiro node. The energy of the spiro node can be approximated by the sum of the energies of the σ bonds that make up this node. Let us illustrate the proposed method in the case of the calculation of the heats of atomization of quinoline spiropyran VI:



III ΔH_f = -36,1 kcal/mole

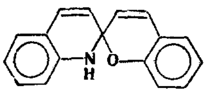


IV ΔH_f = -19,6 kcal/mole

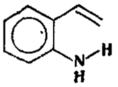


V ΔH_f = -19,3 kcal/mole

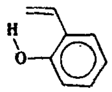
in σ,π parametrization, which is well suited for these ends. The heat of atomization of spiran form A is represented in the form of the sum of three terms, viz., the heat of atomization of the conjugated part of the first fragment, the heat of atomization of the conjugated part of the second fragment, and the energy of the spiro node. The energy of the spiro node can be approximated by the sum of the energies of the σ bonds that make up this node. Let us illustrate the proposed method in the case of the calculation of the heats of atomization of quinoline spiropyran VI:



VI



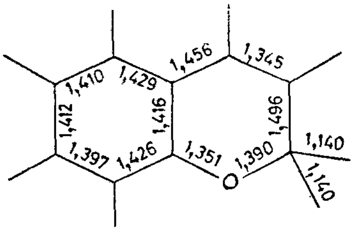
VII



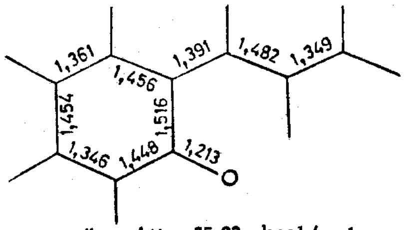
VIII

$$\Delta H_a(\mathrm{VI}) = \Delta H_a(\mathrm{VII}) + \Delta H_a(\mathrm{VIII}) - 2E_{C-C} - E_{C-N} - E_{C-O} + E_{O-H} + E_{N-H}$$

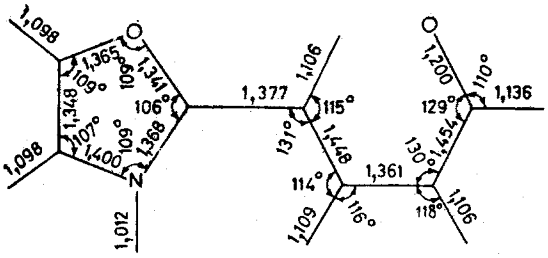
In accordance with [15, 16], the energies of the σ bonds were assumed to be E_{C-C} = 83.48, E_{C-N} = 82.55, E_{C-O} = 92.24, E_{C-H} = 102.03, E_{O-H} = 102.09, and E_{N-H} = 96.64 kcal/mole. The accuracy of this estimate of the energies of the closed forms of the spiropyrans can be verified from a calculation of the relative stabilities of the closed and open forms of an analog of the spiropyran, viz., chromene (IX), by the MINDO/3 method, and via the proposed scheme.



IX ΔH_f = -3,14 kcal/mole



X ΔH$_f$ = 35,03 kcal/mole



XI ΔH$_f$ = -48,1 kcal/mole

The difference in the energies of formation of the closed and open forms calculated by the MINDO/3 method is 38 kcal/mole, whereas similar calculations by our proposed method give 36 kcal/mole. These results, which agree satisfactorily with one another, accurately reflect the experimentally known stability of chromene valence tautomer IX.

At the same time, 2H-pyran structures that do not contain an annelated benzene ring are unstable in the cyclic form. In fact, the heat of formation of spiran III calculated by the MINDO/3 method is 12 kcal/mole higher than that of its dienic tautomer XI.

Calculation by the PPP method via the proposed scheme also currectly reflects the instability of III as compared with XI. The calculated $\Delta\Delta H_a$ value is 9.1 kcal/mole. For comparison, let us point out that calculation of the relative stabilities of valence tautomers III and XI by the MINDO/3 method took 8 h with a BÉSM-6 computer. Only 10 min were required for a similar calculation via the PPM scheme with a BÉSM-4 computer.

2. Results and Discussion

The results of calculations of the relative stabilities of the spirocyclic and open merocyanine forms of a number of spiropyrans are summarized in Table 1. An examination of these data makes it possible to ascertain the effect of heterocyclic and pyran fragments of the molecule on the relative stabilities of the valence tautomers.

Annelation of a benzene ring to the 2H-pyran ring in various positions leads to a shift in the equilibrium to favor the cyclic (Nos. 2 and 3) and open merocyanine (No. 4) forms. Further benzoannelation of the 2H-chromene ring in the most important type of spiropyran structure (No. 2) also may shift the equilibrium in both directions. Thus, for example, 5,5- and 7,8-benzoannelation leads to stabilization of the merocyanine structure as compared with 2,2'-spirobi[2H-chromene] (No. 2), whereas 6,7-annelation additionally stabilizes the spiropyran form. Benzoannelation to a heteroring that is not involved in valence tautomerization does not lead to a change in the relative stability. All of these conclusions can be readily understood from the point of view of the concepts of the effect of the aromatic character of the conjugated system on the state of the tautomeric equilibria possible for it [17].

The $\Delta\Delta H_a$ values of the merocyanine and spiropyran structures do not correlate with the energies of anionic localization (L_α^-) of the cation, which were calculated in [18] and determine the stable structure that develops in the preparation of spiropyrans as a result of cyclization of substituted o-oxidostyryl heterocations. This fact evidently constitutes evidence for kinetic control in the formation of a spiropyran structure.

The few available experimental data on the relative stabilities of the two forms are in satisfactory agreement with the results of the calculations. Thus, for example, the experimental ΔH° value for compound No. 5 is 4.6 kcal/mole, which is in good agreement with the results of the calculation ($\Delta\Delta H_a$ = 6.6 kcal/mole). The agreement between the calculated and experimental values is also satisfactory for spiropyrans 23 and 24 (the experimental values are 6.4 and 5.5 kcal/mole, respectively). The agreement between the calculated and experimental values is poorer in the case of indoline spiropyran 9 ($\Delta\Delta H_a$ = 15 kcal/mole and ΔH° =

TABLE 1. Relative Stabilities of the Spiropyran (A) and Open Merocyanine (B) Forms of Spiropyrans

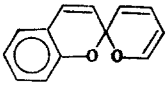
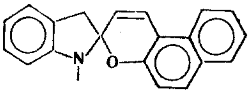
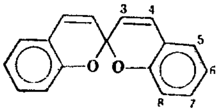
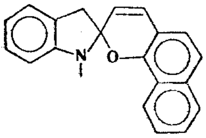
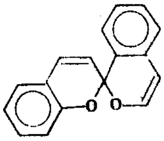
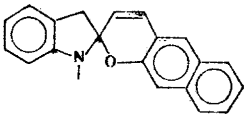
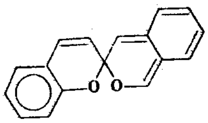
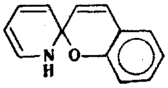
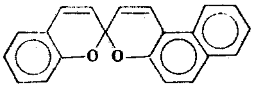
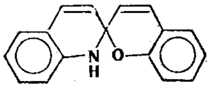
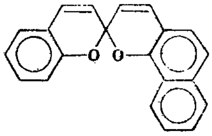
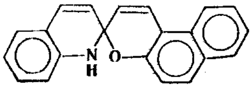
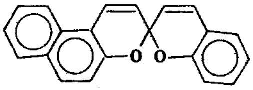
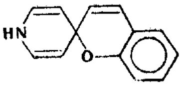
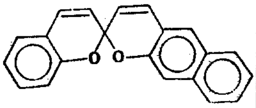
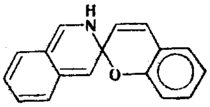
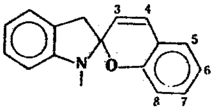
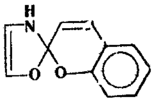
Compound	Form A*	$\Delta\Delta H_a$,† kcal/mole	Compound	Form A	$\Delta\Delta H_a$, kcal/mole
1	2	3	1	2	3
1		−2,2	10		6,0
2		13,8	11		6,0
3		11,3	12		23,1
4		−25,8	13		13,4
5		6,6	14		13,8
6		5,1	15		4,8
7		21,9	16		10,0
8		13,5	17		13,3
9		15,1	18		25,9

TABLE 1. (Cont'd.)

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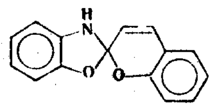
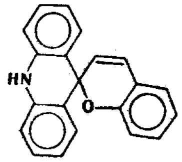
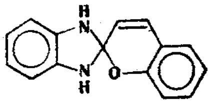
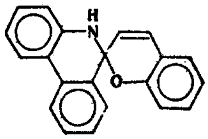
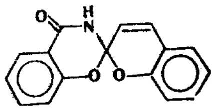
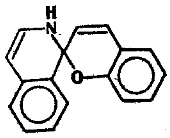
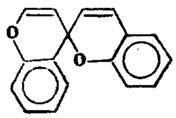
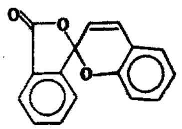
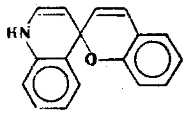
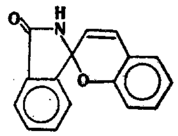
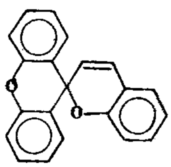
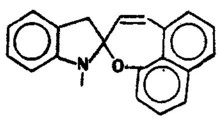
19		26,1	25		10,0
20		32,9	26		14,4
21		27,2	27		14,4
22		10,3	28		15,9
23		10,0	29		16,5
24		10,0	30		46,2

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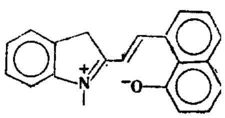
*Opening of the right-hand fragment of the spiropyran is implied in all cases.

†A positive $\Delta\Delta H_a$ value means that the spiropyran form is preferred energetically.

4.4 kcal/mole); however, the qualitative result, viz., the preferableness of the spiropyran form, is correct.

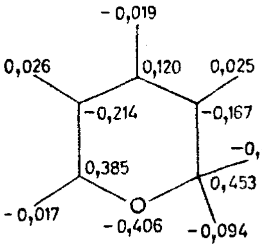
It should be noted that the calculated energies of solvation of the closed and open forms differ by ∿6-8 kcal/mole (the solvation energy is higher for the merocyanine structure). The solvation energies were calculated by the method in [19, 20].

The situation is extremely interesting in the case of spiropyran No. 30. The merocyanine form of this spiropyran is dipolar structure XII, the spectrum of which, according to the results of calculation, should have a long-wave absorption band between the visible and IR regions of the spectrum.



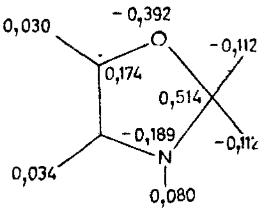
XII

The energies and wavelengths of the first three singlet spectral transitions are, respectively, 0.61 (2049 nm), 2.72 (457 nm), and 2.99 eV (414 nm). The results of calculations of the



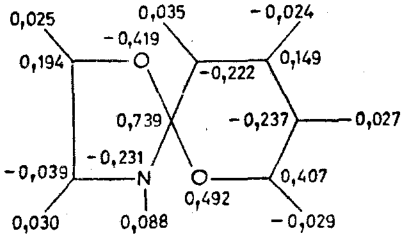
V

$\Sigma q = -0,265$



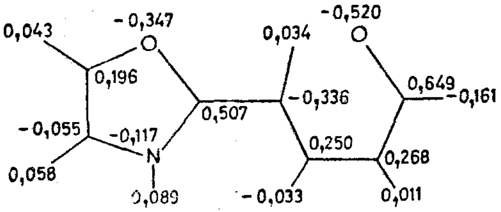
IV

$\Sigma q = -0,290$



III

$\Sigma q = -0,352$ $\Sigma q = -0,387$



XI

relative stabilities of the merocyanine and spiropyran structures constitute evidence for the absolute absence of thermochromism in spiropyrans of this type, since the difference in the energies of the closed and open forms is 46 kcal/mole in favor of the spiropyran structure.

Thus the proposed simple method for the estimation of the relative stabilities of the spirocyclic and merocyanine forms of spiropyrans makes it possible, with good accuracy, to obtain data on their relative stability and its relationship with the structural characteristics of the molecules. It can be used for the construction of diagrams of the energy levels of photochromic spiropyrans. The electron distributions for the III–V and XI structures are presented above. The amount of charge transfer from the oxazole ring to the pyran ring during the formation of the closed form is only 0.1 e (the amount of electron-density transfer can be estimated by calculation of the sum of the charges in the unchanging fragments of the oxazole and pyran rings).

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4-o-CARBORANYLPYRYLIUM PERCHLORATES AND STABLE FREE RADICALS BASED ON THEM

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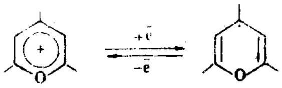
and O. Yu. Okhlobystin

UDC 547.244.813'717:541.515:543.422.27

The corresponding o-carboranylpyrylium perchlorates were obtained from 4H-pyrans of the o-carborane series under the influence of 70% $HClO_4$ in acetic anhydride or 2,2',4,4'-tetramethoxydiphenylammonium perchlorate. The carboranylpyranyl free radicals were studied by EPR spectroscopy, and it was shown that the unpaired electron is localized in the carborane ring.

The EPR spectra of a number of pyranyl free radicals formed in the reduction of 2,4,6-trisubstituted pyrylium cations have been described [1-5]. The accessibility of these radicals promises to make them convenient one-electron reducing agents for organic synthesis, since their extremely facile conversion to pyrylium salts is generally a specific feature of their behavior [4]:



The chemical transformations of this unique class of free radicals have proved to be extremely interesting [4], and from an analysis of their EPR spectra one can conclude that the properties of pyranyl radicals should depend substantially on the nature of the substituents in the starting pyrylium salt. Thus the unpaired electron in the 2,4,6-triphenylpyranyl radical is delocalized over the entire molecule [3], while its tri-tert-butyl analog is a "rigid" C-fixed radical with a strongly shielded reaction center [5]. In this connection, we decided to obtain 4-o-carboranylpyranyl radicals, since the bulky icosahedral system of carborane should create additional possibilities for stabilization through its electron-acceptor properties.

The reduction of the previously described 4-o-carboranylpyrylium hexachloroantimonates [6] did not enable us to obtain sufficiently resolved EPR spectra (evidently because of splittings from the magnetic nuclei of the gegenion). We were unable to replace the anion by the action of 70% $HClO_4$ because of the low solubilities of the hexachloroantimonates.

The necessary pyrylium perchlorates with carborane substituents in the 4 position were obtained from o-carboranylpyrans (I) (Table 1), by the action of 2,2',4,4'-tetramethoxydiphenylammonium perchlorate on them. Pyrylium salts can also be obtained by the usual method,

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