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

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A method was developed for the estimation of the relative stabilities of spirocyclic and merocyanine structures of spiropyrans on the basis of the Pariser–Farr–Pople method in \( \sigma,\pi \) 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\( \rightarrow \)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.

*See [1] for communication 10.
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 AG 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 \( \sigma_3 \pi \) 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 \( \pi \) 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 \( \sigma_3 \pi \) 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 III–V molecules that the spiro cyclization in III causes almost no angular strain (\( \alpha_1 = 106^\circ \), \( \alpha_2 = 104^\circ \), \( \beta_1 = 111^\circ \), and \( \beta_2 = 109^\circ \)), which in the case of small spiro rings introduces an appreciable destabilizing effect in the energy of separation of the rings. Thus, the positive