STRUCTURE, SPECIFIC ORBITAL INTERACTIONS, AND PHOTOCHEMICAL BEHAVIOR OF INDOLINE SPIROPYRANS

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UDC 541.6:541.14:547.754:547.816

The study of the structure of photochromic systems with different types of photochemical transformations [1] has shown that the chemical properties in the excited state are largely a factor of the structural features of these molecules or of their crystals in the ground state. In particular, the photochemical properties of photochromic systems which display photoinitiated acylotropic rearrangement are the result, to a significant extent, of the extension of weakening of the bond broken upon photoexcitation already in the ground state [2]. In our previous work [1, 3], we showed that the Cspiro–O bond broken upon photoexcitation in spiropyrans (SPs) is also extended in the ground state. In this work, a detailed discussion is given for the structural factors which produce the extension of this bond in indoline SPs studied in our laboratory or reported in the literature. The nature of the structural changes in the SP upon photoexcitation and the structural effect on the quantum yield for the photocoloration of these SPs are analyzed taking account of the orbital nature of the excited photochemically active electronic states.

THE MOLECULAR STRUCTURE OF SPIROPYRANS IN THE GROUND STATE

In previously studied SPs (I)-(IV) [3-5], the indoline and benzopyran molecular fragments are approximately orthogonal to each other but are not planar themselves. The indoline fragment of SP molecules has compressed envelope conformation with folding at the N1′...C3′ line of 23-30°. Such a structure of the indoline heterocycle is a consequence of the significantly pyramidal configuration of N1′, which reduces the conjugation of the unshared electron pair (UEP) of N1′ with the benzene ring π-system. Indeed, the length of the N1′-C2′ bond in SPs (I)-(IV) [1.393(5)-1.413(5) Å] is greater than in analogous systems with planar trigonal structure of the nitrogen atom (1.36-1.37 Å), but is the same as the N–Ph bond length (1.39-1.42 Å) in molecules with pyramidal structure of the nitrogen atom (see references in our previous communication [6]). The protrusion of N1′ from the plane passing through C2′, C3′ and the atom of substituent R1′ attached to N1′ is 0.13-0.27 Å in SPs (I)-(IV). This finding indicates considerable sp3 nature of the nitrogen UEP oriented approximately perpendicularly to the plane of these three atoms.

The oxygen unshared electrons pairs are not equivalent [7] and have σ and π character. The σ-UEP is located in the plane of atoms C2OC2a, while the π-UEP is oriented perpendicularly to this plane. In the case of such structure for the SPs, the Cspiro–O bond of the pyran heterocycle is trans to the UEP of N1′, while the Cspiro–N1′ bond of the indoline heterocycle is trans to the π-UEP of the oxygen atom. This structure may lead to specific orbital interactions between the electronegative heteroatoms with the unshared electron pairs of the nitrogen and oxygen atoms bound to tetrahedral carbon (anomeric effect) [8]. This interaction may be described in terms of an n–σ* interaction of the UEP(n) of a heteroatom with the σ*-anti-
bonding orbital of the adjacent polar bond localized mainly on the positive carbon of the spiro unit [9]. Since the electronegativity of the oxygen atom is greater than that of the nitrogen atom, and the energy of the oxygen UEP is lower than the energy of the nitrogen UEP, the antibonding $\sigma^*$ orbital of the C$_{\text{spiro}}$-O bond should be lower in energy than that of the antibonding orbital of the C$_{\text{spiro}}$-N bond, while the nonbonding orbital of the nitrogen atom should be at a higher energy level than the antibonding orbital of the oxygen atom. Thus, the interactions of the n electrons of N with the $\sigma^*$ orbital of the C$_{\text{spiro}}$-O bond should be the predominant interactions in the spiro unit.

The concept of hyperconjugation has recently been used commonly to explain the structural consequences of the anomeric effect in various X-C-Y fragments [10]. As a result of the occupancy of the antibonding orbital of the C$_{\text{spiro}}$-O bond, such an interaction should lead to shortening and strengthening of the C-N bond and extension and weakening of the C$_{\text{spiro}}$-O bond. Indeed, the lengths of the C$_{\text{spiro}}$-N$^\text{N}$ bonds in these SP are in the range from 1.432(4) to 1.453(4) Å and are significantly shorter than normal C$_{\text{sp}}$-N$_{\text{sp}}$ bonds (1.47-1.48 Å) in five-membered heterocycles [11], while the C$_{\text{spiro}}$-O bond lengths are in the range from 1.485(4) to 1.496(5) Å and are significantly greater than for ordinary C-O bonds in six-membered heterocycles (1.41-1.43 Å [11, 12]).

The efficiency of such hyperconjugation should depend considerably on the geometrical orientation of the unshared electron pairs of N$^\text{N}$ and O and of the C$_{\text{spiro}}$-O and C$_{\text{spiro}}$-N$^\text{N}$ bonds, on one hand, and on the electronic state of the nitrogen and oxygen atoms, on the other. In all SP studied, the C$_{\text{spiro}}$-O bond makes an angle of 165-171° with the UEP of N$^\text{N}$ due to the rigid tetrahedral structure of the spiro carbon atom and the identical conformation of the indoline ring. The conformation of the benzopyran fragment in these molecules is more variable. The pyran ring in SPs (I)-(III) is nonplanar and has a flexure of 11-17° at the O...C line and also a flexure which is 3-10° less at the O...C line in the same direction. The conformation of the six-membered heterocycle in SPs is apparently a function of steric factors and packing effects in the crystal and not of substituent electronic effects. Evidence for this conclusion is found in the structure of SP (IV), in which the benzopyran ring in one of the two independent molecules (IVa) is virtually planar, while (IVb) has flexures at the O...C and O...C lines of 15.5° and 5.3°, respectively. The benzopyran ring in SP (I) is bent toward the substituent R$^1$ = CH$_3$, while in SPs (II)-(IVb), it is bent toward the geminal methyl groups. Such structural features of spiropyran may be related to steric interactions of the benzopyran fragment with the R$^1$ substituent, on one hand, and the geminal CH$_3$ groups, on the other. The replacement of the methyl group in SP (I) by a phenyl group (II) and (III) and the shift of the NO$_2$ group from the para to the ortho position of the benzopyran ring leads to an increase in steric repulsion between substituent R$^1$ and the benzopyran fragment which