# STRUCTURE OF THE INTERMEDIATE PARTICLES IN THE RADIOLYSIS OF INDOLINESPIROPYRAN

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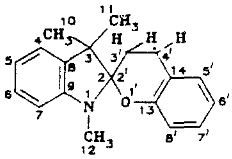
Calculations by the extended Hückel iteration method with self-consistency with respect to the charges were undertaken for the initial molecule, the radical-anion, and the neutral radical formed during protonation of the latter in 1,3,3-trimethylspiro[indoline-2,2'-(2'H)-chromene]. On the basis of the results from the calculations and analysis of the ESR spectrum of the neutral radical it was concluded that the bond between the spiro carbon atom and the oxygen heteroatom of the pyran ring is not broken during the formation of the radical-anion and its subsequent protonation and that the unpaired electron is delocalized in the π system of the benzopyran fragment of the molecule. Protonation in the radical-anion takes place at the carbon atom at position 3'.

Earlier it was established by pulse radiolysis [1, 2] and ESR [3] methods that the radiolysis of ethanol solutions of indolinespiropyrans leads to the formation of their radica anions, which are then protonated in the ethanol matrix and give neutral radicals. The ESR spectrum of the neutral radical of the unsubstituted indolinespiropyran 1,3,3-trimethylspiro-[indoline-2,2'-(2'H)-chromene] (SP) obtained in the solid phase, gave reason to suppose that the structure of the neutral radical corresponds to one of the following two structures [3]:



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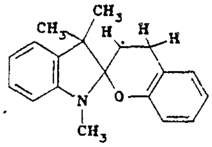

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However, the insufficient resolution of the ESR spectrum obtained in the solid phase did not make it possible to choose between the proposed structures. The aim of the present work was to investigate the structural characteristics of the intermediate products from the radiolysis of the SP, i.e., its radical-anion ($SP^{-\cdot}$) and neutral radical ($SPH^{\cdot}$).

Use of an electrochemical generation method similar to that used in [4] did not make it possible to accumulate the radical-anions in sufficient amounts for recording their ESR spectrum. (the first polarographic reduction wave of the SP, $-E_{1/2}$ = 2.49 V, is irreversible In order to establish the structure of the intermediate particles in the radiolysis of SP, we therefore undertook quantum-chemical calculations for the initial molecule, the radical-anion, and the neutral radical. In the calculations we used the extended Hückel iteration method with self-consistency with respect to the charges (EHIM) [5, 7]. The calculations were made on an EC-1060 computer using the program in [8]. As initial data on the geometry of the molecules we used the results from an x-ray crystallographic analysis of crystals of 1-phenyl-3,3-dimethyl-8]-nitrospiro[indoline-2,2'-(2'H)-chromene] [9]. The valence electron densities at the atoms of the initial molecules of SP and the radicals $SP^{-\cdot}$ and $SPH^{\cdot}$, obtained as a result of the calculation, are given in Table 1. The data for the initial SP molecule agreed satisfactorily with the results from calculation by the CNDO CI method for the ground state of the model molecule of unsubstituted indolinespiropyran [10]; the electron densities show identical tendency in the change from atom to atom, and their values calculated by the EHI method and the CNDO CI method differ by not more than 5%. The energy

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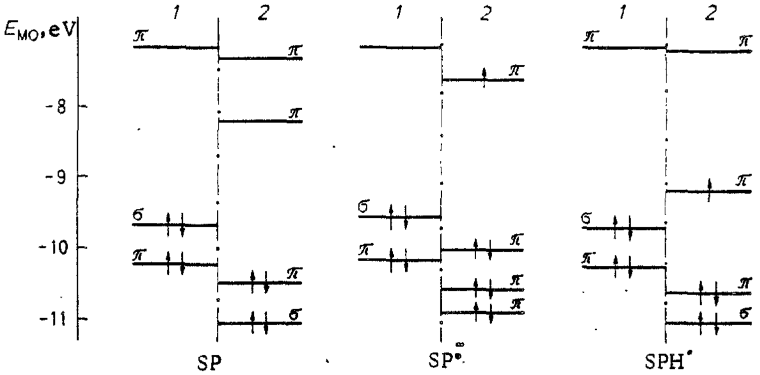

Fig. 1. Diagram of the energy levels of the HOMO and LUMO of 1,3,3-trimethylspiro[indoline-2,2'-(2'H)-chromene] (SP), its radical-anion ($SP^{\overline{\cdot}}$), and its neutral radical ($SPH^{\cdot}$): 1) indoline fragment of molecule; 2) benzopyran fragment.

TABLE 1. Densities of the Valence and Unpaired Electrons at the Atoms of the 1,3,3-Trimethylspiro[indoline-2,2'-(2'H)-chromene] molecule (SP) and the Radicals ($SP^{\overline{\cdot}}$, $SPH^{\cdot}$)

| Atom | Valence electrons | | | Unpaired electron | |
|---|---|---|---|---|---|
| | SP | $SP^{\overline{\cdot}}$ | $SPH^{\cdot}$ | $SP^{\overline{\cdot}}$ | $SPH^{\cdot}$ |
| 1 | 5,175 | 5,185 | 5,179 | | |
| 2 | 3,907 | 3,941 | 3,914 | | |
| 3 | 3,986 | 3,997 | 3,991 | | |
| 4 | 4,079 | 4,082 | 4,080 | | |
| 5 | 4,099 | 4,102 | 4,100 | | |
| 6 | 4,066 | 4,068 | 4,066 | | |
| 7 | 4,087 | 4,089 | 4,088 | | |
| 8 | 4,031 | 4,036 | 4,033 | | |
| 9 | 4,004 | 4,008 | 4,006 | | |
| 10 | 4,225 | 4,232 | 4,230 | | |
| 11 | 4,145 | 4,148 | 4,136 | | |
| 12 | 4,082 | 4,084 | 4,082 | | |
| 1' | 6.266 | 6,309 | 6,266 | 0,027 | 0,085 |
| 2' | 3,907 | 3.941 | 3,914 | 0,000 | 0,000 |
| 3' | 4,040 | 4,143 | 4,050 | 0,274 | 0,040 |
| 4' | 4,047 | 4.132 | 4,049 | 0,052 | 0,423 |
| 5' | 4,059 | 4,125 | 4,079 | 0,083 | 0,111 |
| 6' | 4,070 | 4,123 | 4,083 | 0,028 | 0,000 |
| 7' | 4,060 | 4,141 | 4,083 | 0,204 | 0,138 |
| 8' | 4,056 | 4,110 | 4,069 | 0,025 | 0,000 |
| 13 | 4,035 | 4,029 | 3,981 | 0,065 | 0,076 |
| 14 | 4,025 | 4,115 | 4,047 | 0,157 | 0,013 |

TABLE 2. Changes in the Populations of the Bonds between the Atoms in the Radicals $SP^{\overline{\cdot}}$ and $SPH^{\cdot}$ Compared with Molecule SP

| Bond | $SP^{\overline{\cdot}}$ | $SPH^{\cdot}$ |
|---|---|---|
| 1—2 | −0,007 | 0,006 |
| 2—3 | 0,007 | 0,020 |
| 3—8 | 0,002 | 0,000 |
| 4—8 | 0,000 | 0,000 |
| 4—5 | −0,001 | −0,001 |
| 5—6 | −0,001 | 0,000 |
| 6—7 | 0,000 | 0,000 |
| 7—9 | −0,001 | 0,000 |
| 8—9 | −0,001 | 0,000 |
| 1—9 | 0,004 | 0,001 |
| 1—12 | 0,001 | 0.005 |
| 3—10 | −0,007 | −0,007 |
| 3—11 | 0,002 | 0,001 |
| 1'—2' | 0,415 | 0,000 |
| 2'—3' | −0,022 | −0.036 |
| 3'—4' | −0,131 | −0,377 |
| 4'—14 | 0.069 | 0,124 |
| 5'—14 | −0,089 | −0,062 |
| 5'—6' | 0,029 | 0,024 |
| 6'—7' | −0,060 | −0,025 |
| 7'—8' | −0,064 | −0,015 |
| 8'—13 | 0.036 | 0,016 |
| 13—14 | −0,074 | −0,044 |
| 1'—13 | 0,442 | −0,010 |

levels of the molecular orbitals determined by the EHI method for the initial SP molecules are given in Fig. 1, from which it is seen that the lowest unoccupied orbital is the π-MO of the benzopyran fragment of the SP.

The radical-anion was calculated on the assumption that the C—O bond between the spiro carbon atom and the oxygen atom is not broken, and the possibility of its cleavage during the formation of $SP^{\overline{\cdot}}$ was assessed by comparison of the populations of the bonds between the atoms in the initial molecule SP and in $SP^{\overline{\cdot}}$. Although it is largely qualitative in nature [11], the Mulliken analysis employed in the calculations makes it possible to assess the tendencies for variation of the bond orders. The results from the calculations of the changes in the populations of the bonds between the atoms during the formation of the radical $SP^{\cdot}$ (Table 2) show that the C—O bond between the spiro carbon atom $C_{(2')}$ and the oxygen atom $O_{(1')}$ does not only not become weaker during capture of the additional electron by the SP molecule, but even becomes considerably stronger.

The densities of the valence electrons in the benzopyran fragment of the molecule change significantly during the formation of the radical-anion, while remaining practically unchanged at the atoms of the indoline fragment (Table 1). This gives reason to conclude that the

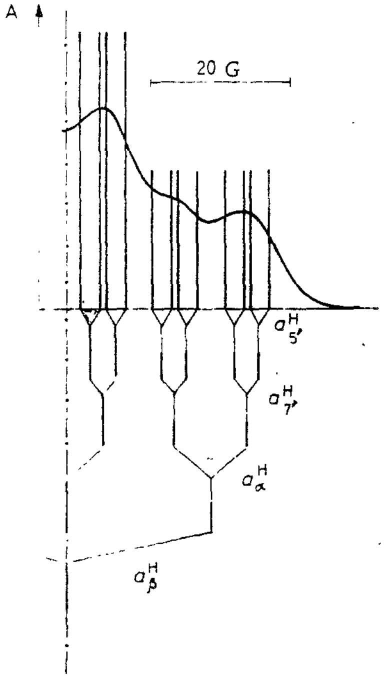

Fig. 2. Diagram of the splitting of the HFS lines and the theoretical ESR spectrum (the absorption curve) of the neutral radical SPH˙.

additional unpaired electron is delocalized in the lowest unoccupied π-MO of the benzopyran fragment of $SP^{\dot{-}}$, as shown diagrammatically in Fig. 1. The results from calculation of the density distribution of the unpaired electron in $SP^{\dot{-}}$ are shown in Table 1, from which it is seen that the maximum density of the unpaired electron occurs at the carbon atom $C_{(3')}$, which is evidently the point of attack during protonation of the radical-anion. During protonation there must be a decrease in the population of the 3'–4' bond, which (as seen from the data in Table 2), is observed even at the stage of the formation of $SP^{\dot{-}}$.

On the basis of the foregoing, from the structure of the radical-anion we calculated the SPH˙ radical on the assumption that its structure corresponds to structure 1, placing the hydrogen atoms at position 3' in accordance with the directions of the bonds of the $sp^3$-hybridized atom. During the formation of SPH˙ with such a structure, the population of the 2'–1' bond does not decrease compared with its population in the initial molecule SP (Table 2). The MO diagram shown in Fig. 1 shows that the MO occupied by the unpaired electron does not extend to the indoline fragment of SPH˙. From the results of the calculation (Table 1) it is seen that the densities of the valence electrons at the atoms of SPH˙ have values closer to the electron densities in the initial molecule SP than the densities of the valence electrons in $SP^{\dot{-}}$. The exception is the carbon atom $C_{(13)}$, which acquires a positive charge in SPH˙, whereas its charge in the initial molecule SP is negative.

From the densities of the unpaired electron in the radical SPH˙ obtained as a result of the calculation (Table 1) we determined the splitting constants of the hyperfine structure (HFS) lines and constructed the theoretical ESR spectrum of the radical SPH˙. To determine the HFS constants at the protons attached to the $sp^2$-hybridized carbon atoms $C_{(4')}$, $C_{(5')}$ and $C_{(7')}$ ( ${}_{\alpha}{}^{H}$, $\alpha_{5'}{}^{H}$, and $\alpha_{7'}{}^{H}$, respectively), we used the McConnell relationship [12], where we assumed that Q = 25 G [13]. We determined the splitting at the protons attached to the carbon atom $C_{(3')}$ ($\alpha_{\beta}{}^{H}$), according to [13] by means of the equation

$$a_{\beta}^{H} = Q^{H}_{CCH_3}\rho_C \cos^2\theta,$$

which holds for the splittings of the HFS lines in the ESR spectrum at the protons of the methyl group attached to a conjugated system. The $QCCH_3{}^H$ and θ values were taken as 58.6 G [13] and 30°, respectively. For the splittings at the α- and β-protons we obtained $\alpha_{\alpha}{}^{H}$ = 10.6 and $\alpha_{\beta}{}^{H}$ = 20.4 G, which are close to the experimental values (10 and 22 G, respectively [3]). The values for the splittings $\alpha_{5'}{}^{H}$ and $\alpha_{7'}{}^{H}$ are 2.8 and 3.5 G, respectively. The last splittings were not observed in the experimental ESR spectrum of the radical SPH˙ [3], and this is probably due to its insufficient degree of resolution in the solid phase. A diagram of the splittings of the HFS lines and the theoretical ESR spectrum (the absorption curve), constructed from the data of the calculation with allowance for the finite width of the HFS lines, are given in Fig. 2.

Comparison of the theoretical spectrum shown in the figure with the experimental ESR spectrum of the radical $SPH^{\cdot}$ [3] makes it possible to state that they are practically identical. Some difference between the theoretical and experimental values of the splitting constants $\alpha_{\alpha}^{H}$ and $\alpha_{\beta}^{H}$ may be due to the inaccuracy of the calculations or to departure of the geometry of $SPH^{\cdot}$ used in the calculations from the actual geometry.

Thus, the data from the calculations on the initial molecule SP and the intermediate particles from its radiolysis in an ethanol matrix, i.e., the radicals $SP^{\bar{\cdot}}$ and $SPH^{\cdot}$, confirm the earlier suggestion [3] that the bond between the spiro carbon atom and the oxygen atom in the pyran ring of the molecule is not broken during the formation of the radical-anion and its subsequent protonation and that the additional unpaired electron is delocalized in the π system of the benzopyran fragment. The results from the calculations also indicate that the protonation of $SP^{\bar{\cdot}}$ takes place at the carbon atom at position 3' with the formation of the radical $SPH^{\cdot}$, the structure of which corresponds to structure (I).

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