9. V. M. Bzhezovskii, G. A. Kalabin, I. A. Aliev, B. A. Trofimov, M. A. Shakhgel'diev, and A. M. Kuliev, Izv. Akad. Nauk SSSR, Ser. Khim., 1999 (1976).
10. V. M. Bzhezovskii, V. A. Pestunovich, G. A. Kalabin, I. A. Aliev, B. A. Trofimov, I. D. Kalikhman, M. A. Shakhgel'diev, A. M. Kuliev, and M. G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., 2004 (1976).
11. B. A. Trofimov, N. I. Golovanova, A. I. Mikhaleva, S. E. Korostova, L. N. Balabanova, and A. N. Vasil'ev, Khim. Geterotsikl. Soedin., No. 7, 915 (1977).
12. B. A. Trofimov, N. I. Golovanova, A. I. Mikhaleva, S. E. Korostova, and A. S. Atavin, Khim. Geterotsikl. Soedin., No. 9, 1225 (1975).
13. B. A. Trofimov, N. I. Golovanova, A. I. Mikhaleva, S. E. Korostova, A. N. Vasil'ev, and L. N. Balabanova, Khim. Geterotsikl. Soedin., No. 7, 910 (1977).

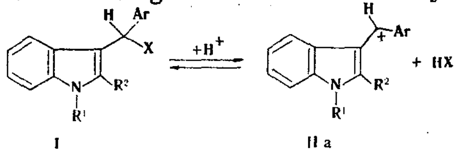
STRUCTURE OF INDOLYLPHENYLMETHYL CATIONS

N. A. Kogan and G. N. Kul'bitskii

UDC 547.759.1:543.422.25

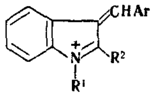
The charge distribution in 1-methyl-2-carboxy-3-indolylphenylmethyl cation (II), which is formed by dissociation of the C−X bond in 1-methyl-2-carboxy-3-(α-X-benzyl)indoles (I) in H_2SO_4 solution, was studied by PMR and ^{13}C NMR spectroscopy. Cation II may have a structure with a positive charge on the benzyl carbon atom (IIa), the nitrogen atom (IIc), or on the α-carbon atom of the indole ring (IIc). Structures IIc and IIa make the major contributions to the II structure; this is confirmed by calculations by the Pariser−Parr−Pople (PPP) method within the σ−π approximation.

The behavior of various indoles in strongly acidic media has demonstrated that alkyl-substituted indoles are protonated in the 3 position to give an indolenine structure with localization of the positive charge on the nitrogen atom [1]. The high probability of a structure with the cationic center in the 2 position of indole has been established by calculations [2]. We have previously investigated the behavior in sulfuric acid solution of 3-(α-chlorobenzyl)indoles, which, in contrast to other alkyl-substituted indoles, form cations through dissociation of the carbon−chlorine bond via the following scheme rather than by the addition of a proton [3]:

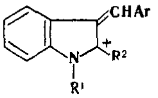


X = OH, Cl; $R^1 = CH_3$; $R^2 = COOH$; Ar = C_6H_5; o-C_6H_4Cl; o-, m-, p-$C_6H_4NO_2$

The existence of two other resonance structures with the charge on the nitrogen atom (IIb) − the indolium cation [4] − and with the charge in the 2 position (IIc) is possible for the 3-indolylphenylmethyl cation (IIa):



IIb



IIc

In view of their insignificant contributions, we will not examine structures with the charge in the benzene ring of indole, which lead to doubly charged ions, and structures with the charge in the benzene ring in the side chain, which lead to quinoid structures.

To estimate the contributions of IIa,b,c to the structure of ionized chlorides I, we used the data from the PMR and ^{13}C NMR spectra and the results of calculations of the charge distribution and bond orders by the Pariser−Parr−Pople (PPP) method within the Dewar π−σ approximation [5] for the IIa cation, where $R^1 = H$, $R^2 = COOH$, and Ar = o-ClC_6H_4.

A multiplet of aromatic protons and a singlet of the NCH_3 group are observed in the PMR spectrum (Fig. 1) of I in D_2SO_4; the signal of the carboxyl proton is not observed because of rapid exchange. The 1H singlet

---

Leningrad Pharmaceutical-Chemistry Institute, Leningrad 197022. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 60-62, January, 1978. Original article submitted March 16, 1977.

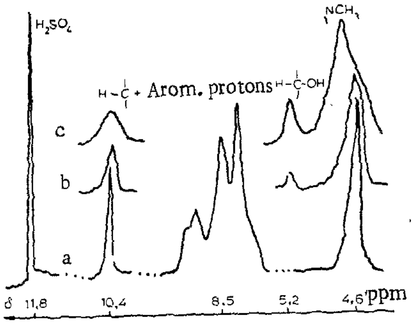


Fig. 1. PMR spectrum of I (X = Cl, $R^1 = CH_3$, and $R^2 = COOH$, and Ar = o-ClC_6H_4) in 100% (a), 80% (b), and 60% (c) D_2SO_4.

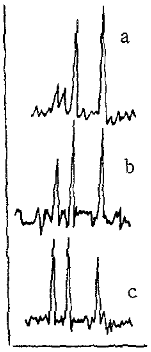


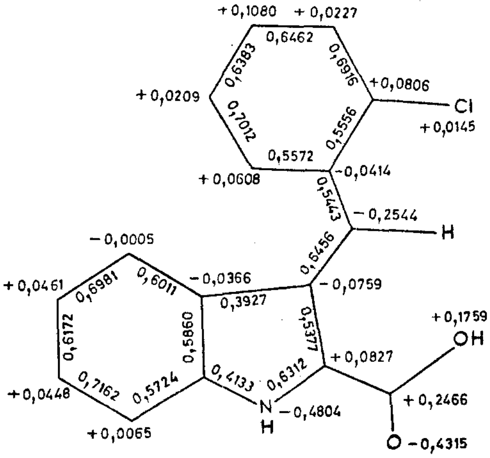
Fig. 2. ^{13}C NMR spectra of I in H_2SO_4: a) without proton decoupling; b) selective monochromatic decoupling; c) total suppression of the $^{13}C-^1H$ spin–spin coupling.

at weak field (δ 10.4 ppm), which belongs to the benzyl proton bonded to the carbonium center of cation IIa, is demonstrative. Its shift to weak field as compared with the signal of the CH_2 group of 1-methyl-2-carboxy-3-(o-chlorobenzyl)indole (I, X = H, $R^1 = CH_3$, $R^2 = COOH$, δ_{CH_2} 3.03 ppm), which is incapable of ionization, is 7.3 ppm. The difference in the position of the signal of the C^+-H group and the signal of the $H-\overset{|}{\underset{|}{C}}-OH$ group of the nonionized carbinol (I, X = OH, $R^1 = CH_3$, $R^2 = COOH$, δ_{CH} 5.1 ppm) is 5.3 ppm. Such significant shifts indicate high positive charge on the benzyl carbon atom.

The singlet of the NCH_3 group (4.6 ppm, 3H) in the IIa cation also undergoes a weak-field shift (Δδ 0.8 ppm) as compared with the signal of the NCH_3 group of uncharged I (X = H). This shift, which is due to the development of charge on the nitrogen atom, is lower in magnitude than in the case of the benzyl proton, as a consequence of the fact that the effect of the charge is transmitted through two bonds. It follows from a comparison with 1,3,3-trimethylindolinium chloride, in the PMR spectrum of which the NCH_3 group resonates at 4.7 ppm [1], that the structure of ionized chloride I is similar to the structures of indolinium salts. The intensity of the signal at 10.4 ppm decreases as a solution of I in D_2SO_4 is diluted with heavy water (D_2O), but a signal at 5.2 ppm corresponding to the benzyl proton in nonionized carbinol I (X = OH) simultaneously appears (Fig. 1).

A fragment of the ^{13}C NMR spectrum of I in H_2SO_4, which contains the signals lying at weak field, is presented in Fig. 2. The weakest-field signal belongs to the carbon atom bonded to one proton, since under conditions without decoupling from the protons it is observed in the form of a doublet of signals (spectrum a) and is evidently the carbonium center of the molecule. To confirm this we used the method of monochromatic selective decoupling from the weak-field proton (1H, 10.4 ppm, Fig. 1), which converts the doublet of signals to a singlet (spectrum b). No changes were observed in the remainder of the spectrum. The signal adjacent to the signal of the benzyl carbon atom is not converted to a multiplet under conditions without suppression of the carbon–proton coupling and evidently belongs to the quaternary α-carbon atom of indole, as might have been expected from [2]. The slight weak-field shift of the ^{13}C signal of the carbonium center as compared with aromatic carbon atoms ($\Delta\delta$ $^{13}C \approx 30$ ppm) attests to considerable delocalization of the positive charge.

The charge distribution was calculated by the PPP method within the Dewar π-σ approximation [4] for the IIa (R^1=H, R^2=COOH, and Ar=o-ClC_6H_4) cation from a program composed by V. A. Kosobutskii. The integrals were calculated from the Mataga–Nishimoto formula [5]. The results of the calculations (see the diagram below) show that the distribution of π-electron density is in agreement with the chemical properties of 3-indolylphenylmethyl cations II, which are intermediates in reactions involving the substitution of the X group in 3-(α-X-alkyl)indoles by nucleophilic agents. It is apparent from the diagram that ~30% of the charge is concentrated on the nitrogen atom and 15% of the charge is concentrated on the benzyl carbon atom, and the remaining charge is distributed over the conjugated system in conformity with formula IIb. The charge on the α-carbon atom of indole is one-third of the charge on the benzyl carbon atom, but strong nucleophilic agents are nevertheless capable of substitution at precisely the 2 position of the indole system [6], which sometimes takes place with decarboxylation [7]. The bond orders in the cation [for example, the benzylidene bond (0.65) and the C=N bond (0.63)] characterize it as cation IIb.



Thus the IIa and IIb structures make major contributions to the set of resonance structures that characterize the behavior of I (X=OH, halogen) in solutions of strong acids.*

EXPERIMENTAL

The ^{13}C NMR spectra (obtained with the natural percentage of the isotope) were recorded under Fourier conditions with a Brucker HX-90 spectrometer at 22.628 MHz. The signal of D_2SO_4 was used as the stabilization signal. The chemical shifts were reckoned from an arbitrary line of the spectrum. The PMR spectrum were recorded with a Varian-100 spectrometer (100 MHz).

LITERATURE CITED

1. R. Hinman and E. Whipple, J. Am. Chem. Soc., 84, 2534 (1962).
2. L. G. Yudin, V. A. Budylin, A. N. Kost, and V. I. Minkin, Dokl. Akad. Nauk SSSR, 176, 1096 (1967).
3. N. A. Kogan, Reakts. Sposobn. Org. Soedin., No. 3, 655 (1975).
4. M. J. S. Dewar, Molecular Orbital Theory of Organic Chemistry, McGraw-Hill (1969).
5. N. Mataga and K. Nishimoto, Z. Phys. Chem., 136, 140 (1957).
6. V. N. Rusinova, Yu. I. Smushkevich, T. A. Kozik, and N. N. Suvorov, Zh. Org. Khim., 8, 1735 (1972).
7. N. A. Kogan, Khim. Geterotsikl. Soedin., No. 6, 857 (1975).

---

*The authors thank Professor V. I. Minkin and V. I. Natanzon for performing the quantum-mechanical calculations.