COMPLEXES OF AROMATIC HYDROCARBONS WITH METAL HALIDES AND HYDROGEN HALIDES

COMMUNICATION 6. DISTRIBUTION OF THE POSITIVE CHARGE IN ARENONIUM IONS*

V.A. Koptyug, É.T. Lippmaa,
A.I. Rezvukhin, and T.I. Pekhk

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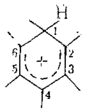
In a consideration of the structure and reactivity of arenonium ions formed as a result of the addition of a proton to aromatic hydrocarbons, the question of the distribution of positive charge in them is of great significance. MacLean and Mackor [2, 3] evaluated the distribution of the positive charge in benzenonium ions (I), using the data of proton magnetic resonance (PMR) spectroscopy on the chemical shifts of the protons of the CH_3 groups occupying the positions in the protonated benzene ring.



(I)

For example, for pentamethylbenzenonium tetrafluoborate, the chemical shifts (in HF) comprise: 7.13 (4-CH_3), 7.31 (2- and 6-CH_3), and 7.59τ (3- and 5-CH_3) [4]. Assuming the influence of the anisotropy of the magnetic susceptibility of the protonated benzene ring on the shielding of the protons of the methyl groups bonded to it to be comparable with the effect observable for the usual unsaturated systems, MacLean and Mackor proposed that the shift of the signal of the i-CH_3 group of the benzenonium ion relative to the normal position of the signals of the CH_3 groups at a C=C bond (~8.40τ) is proportional to the fraction of positive charge on the terminal C_i atom. The distribution of positive charge in the pentadienyl portion of the benzenonium ions found in this way is characterized by an unexpectedly large degree of equalization (+0.22 unit of charge on the C_2 and C_6 atoms, +0.16 unit of charge on the C_3 and C_5 atoms, and +0.25 unit of charge on the C_4 atoms). Calculations performed within the framework of the molecular orbital method [2, 3] show that the positive charge should be localized to a substantially greater degree on the C_2, C_4, and C_6 atoms of the ring.

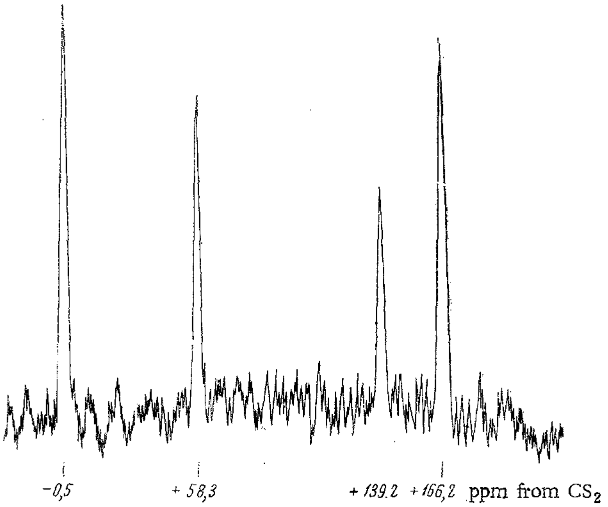


Fig. 1. NMR-C^{13} absorption spectrum of mesitylenonium heptachlorodialuminate, recorded at ~25°C using double $\{H^1\} - C^{13}$ resonance.

The approach used by MacLean and Mackor presupposes that the chemical shift of the protons of the CH_3-C_i fragment of the benzenonium ions is influenced only by the positive charge on the C_i atom; the influence of the electrical fields of the positive charges of the other atoms of the ring (C_j when $j \neq i$) is not taken into consideration. However, the possibility remains that this factor should not be neglected. Actually, if we assume, for example, that the positive charge is distributed only among the C_2, C_4, and C_6 atoms (+0.33 unit of charge each) and estimate the shift of the signals of the protons of the CH_3 groups as a result of the influence of the electrical fields of the charges of these atoms according to the Buckingham-Musher formula [5, 6],

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*For Communication 5, see [1].

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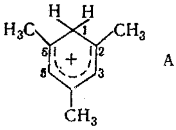
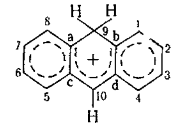
then after averaging over all the conformations due to free rotation of the CH_3 groups around the CH_3-C_i bond, the following results are obtained: for the 2-, 4-, and 6-CH_3 groups, $\Delta\sigma = -1.09$ ppm, while for the 3- and 5-CH_3 groups, $\Delta\sigma = -0.71$ ppm.[†] Thus, the positive charges of the C_2, C_4, and C_6 atoms should produce an extremely appreciable shift of the 3- and 5-CH_3 groups of the benzenonium ions in the direction of weaker fields. Neglecting this circumstance in the analysis of the PMR spectra of benzenonium ions leads to an overestimation of the value of the positive charge on the C_3 and C_5 atoms, and therefore the picture of the distribution of positive charge found according to the PMR spectra may prove unreliable.

Considerably more reliable information on the nature of the distribution of π-electron density in unsaturated systems is given by the NMR-C^{13} spectra [7], since in this case the complicating factors noted above play a considerably more minor role. Taking this circumstance into consideration, we determined the chemical shifts of the carbon atoms of salts of two arenonium ions. The NMR-C^{13} spectra were recorded for the natural content of the isotope C^{13} with the aid of the apparatus described earlier [8, 9]. Salts of the mesitylenonium ion (II), which are liquids at ~20°C, were investigated in the pure form, while the solid salt of the anthracenonium ion (III) was saturated with benzene to convert it to the liquid state. The chemical shifts found according to the NMR-C^{13} spectra, recorded using double $\{H^1\} - C^{13}$ resonance, have the following values (in ppm from CS_2):



$Al_2Cl_7^-$ $(Al_2Br_7^-)$

(II)



$Al_2Cl_7^-$

(III)

C_1	$+139.2$ $(+138.2)$	C_9	$+156$
C_2, C_4, C_6	-0.5 (-0.5)	C_{10}	$+13$
		C_a, C_b	$+40$
C_3, C_5	$+58.3$ $(+57.5)$	C_2, C_7	$+49$ (or $+53$)
2-, 4-, 6-CH_3^*	$+166.2$ $(+165.2)$	C_4, C_5	$+53$ (or $+49$)
		C_1, C_3, C_6, C_8, C_c, C_d[‡].	

Data on the multiplicity of the signals obtained with the aid of weaker monoresonance spectra were also used for the assignment of the signals observed in the double resonance spectra. For example, the signals of heptachlorodialuminate, situated in the double resonance spectrum (Fig. 1) at 166.2, 139.2, 58.3, and 0.5 ppm, are a quartet (J = 130 ± 7 Hz), a triplet (J = 165 ± 7 Hz), and a singlet, respectively, in the monoresonance spectrum. In the case of the anthracenonium ion, in the assignment of the signals of the sp^2-hybrid carbon atoms, the fact that according to molecular orbital calculations the value of the positive charge on the C_i atoms drops in the series $C_{10} > C_a$, $C_b > C_2$, $C_7 \gtrsim C_4$, C_5, etc., and that the chemical shifts should also vary in the same sequence, was also taken into consideration.

In a consideration of the data obtained, attention should first of all be paid to the fact that the chemical shifts of the carbon atoms of the ring CH_2 groups of ions (II) and (III) are close to the shifts of the usual aliphatic CH_2 groups (160-165 ppm. [10]), which confirms the earlier conclusion of [11] of the transition of the carbon atom that has added a proton to the state of sp^3-hybridization. The paramagnetic shift observed for the carbon atoms of the CH_2 groups of the arenonium ions [20-25 ppm for (II) and 5-10 ppm for (III)] is due to the influence of the neighboring, positively charged carbon atoms, transmitted according to an inductive mechanism, and apparently according to a mechanism of hyperconjugation. Evidently this influence is all the stronger, the larger the value of the positive charge on neighboring carbon atoms, i.e., the less the possibility of delocalization of the charge on the remainder of the ion. For this reason the chemical shift of the carbon atoms of the CH_3 groups of the mesitylenonium ion is somewhat less than that of the CH_3 groups of mesitylene (172.2 ppm [12]).

The nature of the distribution of the positive charge in the ring portion of the mesitylenonium ion is detected by a comparison of the chemical shifts of the ring carbon atoms of this ion and of mesitylene. The chemical shift of the nonmethylated carbon atoms of mesitylene is equal to 66.1, while that of the methylated carbon atoms is equal to 56.4 ppm [12]. Thus, the change in the shift under the influence of the positive

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[†] The absolute values of $\Delta\sigma$ may be overestimated, since the value of the microscopic "dielectric constant" was assumed equal to one in the calculation. This, however, may not have a great effect on the ratio of the values of $\Delta\sigma$.

[‡] The signal was concealed by the signal of the solvent, which gives reason for believing the chemical shift is 65 ± 5 ppm.

charge comprises 57 ppm for the C_2, C_4, and C_6 atoms and ~8 ppm for the C_3 and C_5 atoms.* If we neglect the transfer of positive charge to the CH_2 and CH_3 groups and assume that the change in the chemical shift of the C_i atom of the ring is proportional to the fraction of positive charge on this atom [7], then the values of the positive charges on the C_2, C_4, and C_6 atoms prove equal to +0.31,† while on the C_3 and C_5 atoms they are equal to +0.04.† It should be mentioned that the coefficient of proportionality between the change in the chemical shift and value of the positive charge found according to these quantities is equal to 187 ppm /unit of charge, which agrees with the values cited in the literature (160, 168, and 200 ppm/unit of charge [13-15]).

Thus, judging by the NMR-C^{13} spectra, the positive charge on the mesitylenonium ion (II) is concentrated chiefly on the C_2, C_4, and C_6 atoms. The distribution of charge in this way is close to that calculated by the molecular orbital method in the Hückel approximation [2, 3].

In the case of the anthracenonium ion, the side rings participate effectively in the delocalization of the positive charge. This leads to the fact that the chemical shifts of the carbon atoms of the central ring prove to be substantially greater than in the case of the mesitylenonium ion. For anthracene itself, the chemical shifts of the α- and β-carbon atoms are equal to 66.7 ppm., while those of the meso-atoms and junction atoms are 61.5 and 64.5 ppm, respectively (on account of the poor solubility, the spectrum of anthracene was recorded in dimethylformamide at temperatures above 100°C). If we consider that the chemical shifts of the carbon atoms of the anthracenonium ion, the signals of which are masked by the solvent, lie within the range 60-65 ppm, then the sum of the changes in the chemical shifts from anthracene to the anthracenonium ion comprises 160-190 ppm for all the carbon atoms other than the carbon that has added a proton. The expected value of the shift per unit charge (see above) corresponds to this interval. Assuming a coefficient of proportionality between the change in the chemical shift and the value of the positive charge equal to 187 ppm/unit of charge, just as for the benzenonium ions, we obtain the following tentative values for the positive charge on individual carbon atoms of the anthracenonium ion: for the C_{10} atom +0.26 unit of charge, for the C_a and C_b atoms +0.13 unit of charge, for the C_2 and C_7 atoms +0.10 or +0.07 unit of charge, and for the C_4 and C_5 atoms +0.07 or 0.10 unit of charge. The value of the positive charge for the C_{10} atom found in this way is in good agreement with the value obtained in an analysis of the PMR spectra (+0.25 unit of charge [2]), but differs substantially from that predicted by molecular orbital calculations in the Hückel approximation (+0.400 unit of charge [2]). A closer value (+0.276 unit of charge [2]) in this case is given by a calculation performed by the Wheland and Mann method of perturbations.

Our refinement of the distribution of positive charge in arenonium ions, in turn, permits a refinement of the ratio of the contributions of various factors to the proton chemical shifts, which we intend to do in one of our following communications.

EXPERIMENTAL

The procedure for preparation of the salts of arenonium ions used in the work was given in [16, 17]. The NMR-C^{13} spectra were recorded at ~25°C on an instrument with a working frequency of 15.1 MHz, using rapid adiabatic passage under conditions of observation of the dispersion signal using double resonance [8, 9]. In this way, thanks to the disappearance of multiplets in the NMR-C^{13} spectrum and the Overhauser internuclear effect, a sixfold increase in the signal intensity can be achieved. The accuracy of the measurement of the chemical shifts in this case was ±2 ppm. For salts of the mesitylenonium ion, in addition to the dispersion spectra, we also recorded the absorption spectra using development of the frequency and complete uncoupling of the protons, ensuring greater accuracy in the determination of the chemical shifts (±0.5 ppm).

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*It may be assumed that in the transition from an aromatic hydrocarbon to its conjugate acid, the contribution of the effect of anisotropy to the chemical shifts of the ring carbon atoms is practically unchanged. This is indicated by the closeness of the chemical shifts of aromatic (benzene + 65.0 ppm) and olefinic (cyclohexene + 66.3 ppm [7]) carbon atoms.

† $57/(57 \times 3 + 8 \times 2) \approx 0.31$ and $8/(57 \times 3 + 8 \times 2) \approx 0.04$. A consideration of the partial transfer of positive charge to the CH_2 and CH_3 groups leads to a certain decrease in these values, but their ratio is unchanged in this case.

CONCLUSIONS

1. The distribution of π-elecltron density in the mesitylenonium and anthracenonium ions was estimated according to the NMR-C^{13} spectra.

2. In the mesitylenonium ion the charge is concentrated chiefly on the ring carbon atoms corresponding to the ortho- and para-positions with respect to the site of addition of the proton. In the anthracenonium ion, the side rings participate effectively in the delocalization of charge.

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