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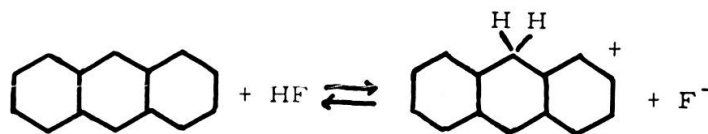
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The influence of localized charges on the magnetic shielding of protons in aromatic carbonium ions

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Aromatic carbonium ions can be obtained by protonation of basic aromatic molecules in strong acids. Anthracene, for instance, dissolves in anhydrous hydrofluoric acid as its proton complex according to the following reversible reaction [1]:



Stable carbonium ions could be prepared from highly basic aromatic molecules when dissolved in very strong acids, such as $\text{HF} + \text{BF}_3$ or $\text{CF}_3\text{COOH} + \text{H}_2\text{O} \cdot \text{BF}_3$.

The comparison between the spectra of an aromatic molecule and its carbonium ion reveals interesting features about the structure of the ion [2]. The spectrum of the aromatic protons in 9, 10-dimethylantracene is an $\text{A}_2 \text{B}_2$ spectrum [3]. The symmetrical form of this spectrum demonstrates the equivalence of the four alpha protons and of the four beta protons. The symmetrical form is lost in the spectrum of the proton complex, and as expected, a new resonance peak of the attached proton is found. The chemical shifts of the methyl-group peaks, one of which displays a doublet structure, are profoundly modified. These changes not only give an unambiguous proof of the accepted structure of the carbonium ion but they also may be used to estimate the magnitudes of the excess positive charges on the various carbon atoms in the carbonium ion, which carries a net positive charge.

The n.m.r. spectra of a great number of aromatic carbonium ions have now been measured [2]. Interesting examples are provided by the spectra of the carbonium ions of methyl-substituted benzenes, in particular those

of the proton complexes of hexamethylbenzene, pentamethylbenzene and mesitylene. In the spectrum of the proton complex of pentamethylbenzene the methyl group resonance is split up into three lines with intensity ratio of 1:2:2. A comparison with the spectrum of the carbonium ion of mesitylene shows that these peaks are caused by the para, ortho and meta protons respectively.

Two major modifications of the magnetic shielding of protons take place when an aromatic molecule is transformed into its proton complex. In the first place excess positive charges are introduced on various carbon atoms in the ring and secondly a conjugated ring current path is interrupted. The first effect causes a decrease in the shielding of the nearby protons whereas the second causes an increase [3].

One would expect that the chemical shift of a substituted methyl group in the absence of the ring current and excess charges is equal to that of a methyl group near an olefinic carbon atom: + 228 c/s from benzene.

In the carbonium ion, however, the resonance peaks of the methyl-group protons are situated at 180, 187 and 198 c/s from benzene, that is they are all displaced to lower field values. If these shifts are effected exclusively by the localized positive charges on the carbon atoms in the complex one calculates a total shift of 220 c/s for a positive charge of one unit on the ring carbon atom. The inferred charge densities on the aromatic carbon atoms with respect to the CH_2 group are: para + 0.25, meta + 0.16 and ortho + 0.21. The Hückel M.O. theory correctly predicts higher charge densities on the ortho and para positions but the charge seems to be much more evenly distributed than predicted by these M.O. calculations. A better correspondence is obtained if the distribution of charge is calculated on the basis of a perturbation method due to Wheland and Mann [4] which leads to a much more even charge distribution.

Full details of measurements on a variety of aromatic molecules will be published elsewhere.

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