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ON VALENCE STATE OF "ALIPHATIC" CARBON ATOM IN ARENONIUM IONS.

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The structure of arenonium ions resulting from proton addition to aromatic hydrocarbons in strongly acidic systems has been attracting the attention of chemists for a long time. Recently it has been proved by means of n.m.r. spectroscopy that the proton is bonded to a definite (the most basic) carbon atom of the aromatic ring giving rise to the formation of "aliphatic" $>C<^{H}_{H}$ or $>C<^{H}_{R}$ groups (1-4). It is believed that the carbon atoms of groups of this kind are sp^3- hybridized, but there is no direct evidence for this. We have attempted to obtain such evidence using the correlation between ^{13}C-H spin spin coupling constant and fractional s- character (α^2) of the ^{13}C hybrid atomic orbital (5-7):

$$J_{^{13}C-H} \approx 500\alpha^2 \text{ c.p.s.}$$

The values of the coupling constants in the case of hydro-

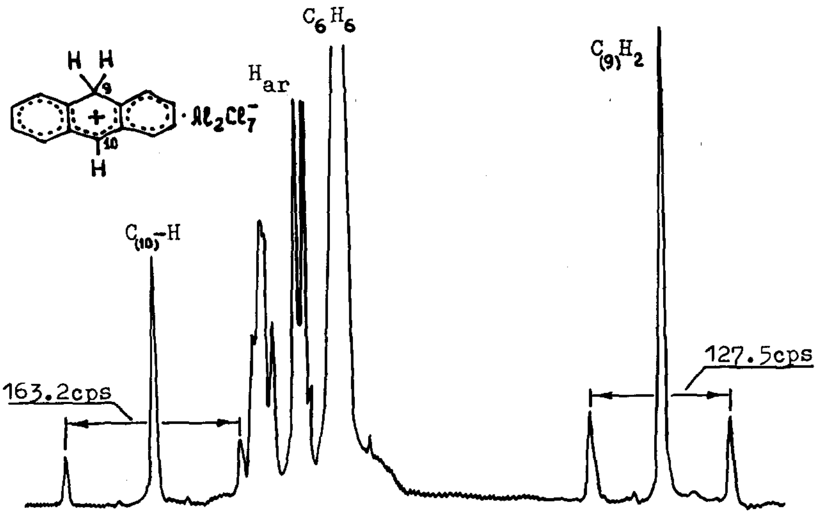

FIG. Proton magnetic resonance spectrum (100 Mc) of 45% benzene solution of anthracenonium-^{13}C heptachlorodialuminate.

carbons are close to 125 and 160 c.p.s. for C_{sp^3}-H (α^2=0.25) and C_{sp^2}-H (α^2=0.33) bonds respectively. The ^{13}C-H coupling constants reported for some cations suggest that $J_{^{13}C-H}$ is being rather slightly increased by positive charge. For example the values of $J_{^{13}C-H}$ (c.p.s.) are equal to: $(CH_3)_3P$ - 127, $(CH_3)_4P^+$- 134; $(CH_3)_3N$ - 131, $(CH_3)_4N^+$- 145; C_6H_6 - 159, $C_7H_7^+$ - 171; $CH_2{=}CH_2$ - 159, $(CH_3)_2CH^+$- 168 (for the CH group) (8-10).

In this paper we'd like to report the results obtained for the anthracenonium ion. The proton magnetic resonance spectrum of 45% benzene solution of anthracenonium heptachlorodialuminate prepared from anthracene and aluminium chloride in the presence of hydrogen chloride (11) consists of two sharp singlets at 5.95 and 1.17τ due to $C_{(9)}H_2$ and $C_{(10)}H$ groups respectively and multiplet of the aromatic protons centered at 2.4τ. The spectrum of such a system prepared from anthracene enriched by 55% of ^{13}C in one meso-position is reproduced in the figure. From this spectrum it follows that the coupling constants $J_{^{13}C_{(9)}-H}$ and $J_{^{13}C_{(10)}-H}$ for the anthracenonium ion are 127.5 and 163.2 c.p.s. respectively. The former coincides with the one obtained earlier for the CH_2 group of diphenylmethane /127c.p.s. (12)/ and the latter is close to the coupling constant observed for the CH group of the diphenylcarbonium ion $(C_6H_5)_2CH^+$ — 164 c.p.s. (10) .

These results prove the addition of proton to a meso-carbon atom of the anthracene molecule to be accompanied by the transition of this atom to the tetrahedral valence state of the sp^3 type. As could be expected the second meso-atom retains the sp^2- hybrid state. The comparison of its coupling constant with that for a meso-carbon atom of the anthracene (156 c.p.s.) once more supports the relative insensitivity of ^{13}C-H spin spin coupling constants to positive charge on the ^{13}C.

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