CARBON-13 NMR SPECTRA AND EXCESS POSITIVE CHARGE

DENSITIES FOR MESITYLENONIUM ION

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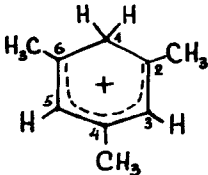Siberian Division, Novosibirsk, USSR

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The data concerning the positive charge distribution in the aro-

matic carbonium ions formed by protonation of substituted benzenes

are very important for understanding the structure and reactivity of

ions of this type. MacLean and Mackor attempted to obtain such infor-

mation for methylbenzenonium ions by proton magnetic resonance spectro-

scopy /1,2/. They discussed the proton chemical shifts of these ions

in terms of localized charges and π- electron ring currents and conclu-

ded that the positive charge is distributed more uniformly (+0.22 elec-

tron charge units on C_2 and C_6, +0.16 units on C_3 and C_5 and +0.2 %

units on C_4), than predicted on the basis of simple molecular orbital

calculations.

The carbon-13 spectra provide a much more direct method for the

measurement of π- electron charge densities and very good linear cor-

relations with carbon-13 chemical shifts were found /3-5/. We have

measured the carbon-13 chemical shifts of 2,4,6-trimethylbenzenonium

(mesitylenonium) ion for two complexes of mesitylene with hydrogen

halides and aluminium halides. The chemical shifts have been measured

at 15.1 Mc and room temperature with natural abundance of carbon-13

nuclei, using adiabatic rapid passage monoresonance spectra and frequen-

cy sweep absorption spectra with total decoupling of all hydrogen nuc-

lei /6/. The time-sharing spectrometer for such experiments was des-

cribed earlier /7/. All chemical shifts are measured relative to car-

bon disulfide with the accuracy of ± 0.5 ppm:

	δ_{CS_2}
C_1	+139.2(+138.2)
C_2, C_4, C_6	-0.5(-0.5)
C_3, C_5	+58.3(+57.5)
2-,4- and 6-CH_3	+166.2(+165.2)

The chemical shift of the methylenic C_1-atom is not very different

from that of alicyclic methylene groups (+166 ppm in cyclohexane).

In fact even much lower values were reported for some special cases /8/.

This confirms the conclusion drawn earlier for anthracenonium ion on

the basis of ^{13}C-H coupling constants, that the attachment of proton

to an aromatic carbon atom is accompanied by the transition of this

atom into hybridization state close to the sp^3- type /9/. The observed

paramagnetic shift (27-28 ppm) may be caused by the positive charges

on the adjacent carbon atoms that diminish the electron density at C_1

through inductive and hyperconjugative mechanisms. The lowering of the

methyl chemical shifts (165-166 ppm for mesitylenonium ion as compa-

red to 172.2 ppm for mesitylene) may be due to the same effect.

The positive charges on the ring carbon atoms can be calculated on the basis of relative shift differences of mesitylenonium ion and mesitylene. The chemical shift of the unsubstituted carbon atoms in mesitylene is +66.1 ppm, while it is +56.4 ppm for the substituted ones. The shift differences are 57 ppm for C_2, C_4 and C_6 and 8 ppm for C_3 and C_5. If one does not take into account the small charge densities on the methyl carbons and on the ring methylene group and one assumes, as it is usually done, linear correlation between excess electronic charges and carbon- 13 chemical shifts, the fractional charges on the sp^2- hybridized carbons can be easily found. The excess positive charges on C_2, C_4 and C_6 are +0.31 units and on C_3 and C_5 +0.04 units leading to 187 ppm per unit charge for the factor of proportionality. The values 160, 168 and 200 ppm per unit charge were reported /3-5/.

Thus it appears, that the π- electron charge density in mesitylenonium ion is distributed very unevenly and the distribution is in fair agreement with the results of simple molecular orbital calculations (cf. /1,2/).

<div align="center">REFERENCES</div>

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