Carbon-13 Nuclear Magnetic Resonance Shifts and Charge Densities in the Triphenylcarbonium Ion

By G. J. RAY, A. K. COLTER, D. G. DAVIS, D. E. WISNOSKY, and R. J. KURLAND*

(*Department of Chemistry and Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pennsylvania* 15213)

THE well-recognized correlation between carbon-13 n.m.r. shifts and charge densities in aromatic compounds[1] may be applied to substituted triphenylcarbonium ions, compounds which are of interest as models for studies of charge delocalization in aromatic systems. Although several theoretical models have been used in calculations of the charge distribution in triphenylcarbonium ion,[2] the use of carbon-13 n.m.r. shifts as an empirical check has been limited by considerations of carbon-13 n.m.r. sensitivity.† However, using advanced instrumental techniques,[3] we have been able to obtain the carbon-13 n.m.r. spectra of a number of substituted triphenyl-carbonium ions, not enriched in carbon-13. We report preliminary results for the unsubstituted triphenylcarbonium ion, for which charge densities at the ring carbons have been derived from carbon-13 n.m.r. shifts of triphenylmethyl cation and [4,4′,4′′-$^2H_1$]triphenylmethyl cations (pH_3 and pD_3), and of the parent carbinols.

Spectra were taken of triphenylmethanol and [4,4′,4′′-$^2H_1$]triphenylmethanol (pH_3-OH and pD_3-OH) as *ca.* 4 M solutions in tetrahydrofuran (THF) and of the corresponding carbonium ions prepared as *ca.* 2 M solutions of the carbinols in chlorosulphonic acid or concentrated sulphuric acid. The slow-passage absorption-mode spectra of pH_3 and pD_3 in chlorosulphonic acid solution are shown in the Figure.

Assignments for the lines are given in Table 1. These assignments have been made on the basis of relative intensity comparisons, a comparison of line positions and intensities for the deuteriated and undeuteriated compounds, and the argument that the *meta*-carbon shift should be least displaced from that of benzene, by analogy with carbon-13 n.m.r. shifts in a series of monosubstituted benzenes.[4]

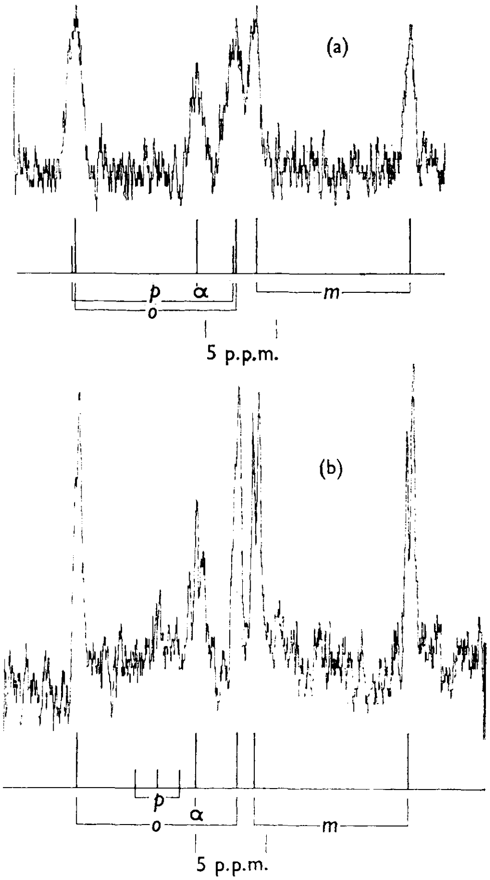

FIGURE. *Carbon-13 n.m.r. spectra of* (a) *triphenylmethyl cation and* (b) [4,4′,4′′-$^2H_1$]*triphenylmethyl cation in chlorosulphonic acid at* ca. 14·1 *kg. and* 30° (ca. 90 *sweeps at* 8 *min. per sweep*). (*The* ^{13}C *line of the central carbon is not shown, being off-scale.*)

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† The carbon-13 n.m.r. shift of the central carbon (enriched in carbon-13) in triphenylcarbonium ion has been reported (G. A. Olah, E. B. Baker, and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1964, **86**, 1265).

TABLE 1

Chemical shift assignments for triphenylcarbinol and triphenylcarbonium ion†

	Central carbon	α-Carbon (1)	*ortho*-Carbon (2,6)	*meta*-Carbon (3,5)	*para*-Carbon (4)
pH_3-OH in THF ..	+111·5±1·0	+43·6±0·5	+64·8±1·0	+64·8±1·0	+64·8±1·0
pD_3-OH in THF ..	+111·5±1·0	+44·2±0·5	+65·0±0·2	+65·8±0·2	+67·0±1·0
pH_3 in H_2SO_4	−18·0±1·0	+53·5±0·6	+50·1±0·6	+62·3±0·6	+50·1±0·6
pH_3 in $ClSO_3H$ ..	−17·0±1·0	+53·0±0·5	+50·3±0·2	+62·5±0·3	+50·3±0·5
pD_3 in $ClSO_3H$	−17·0±1·0	+52·9±0·2	+50·3±0·2	+62·8±0·2	+49·9±0·5

† Spectra were taken using a Varian DP-60, modified for operation in a frequency swept, field-frequency controlled mode, at a field of *ca.* 14·1 kG (ref. 6). Shifts are given in p.p.m. upfield from the carbon-13 line of CS_2; line measurements were taken with respect to CS_2 as an external reference; the precision was determined principally by line widths, which, for these spinning 15 mm. diameter samples, were determined by long-range spin coupling or viscosity effects.

The assignments are also consistent with the magnitude of long-range ^{13}C–H coupling constants which would be expected by comparison with those in benzene.[5]

Charge densities estimated from the difference in shifts between carbinol and carbonium ion are given in Table 2 and compared with theoretical estimates. The Huckel calculations predict no charge delocalization onto the *meta*- or *alpha*-carbons; in this respect, the qualitative correlation between the empirical estimates (from carbon 13 n.m.r. shifts) and those obtained by SCF calculations is better: both indicate negative charge on the alpha-carbon. There is better agreement, however, between the empirical and Huckel estimates of the relative magnitudes of charge at the *ortho*-, *meta*-, and *para*-positions.

TABLE 2

Charge densities for triphenylcarbonium ion[a]

Position	N.m.r.[b]	Huckel[c]	Huckel[d]	SCF[d]
central	+0·185[e]	+0·417	+0·31	+0·25
α (1)	−0·054	0·000	0·00	−0·15
ortho-(2,6) ..	+0·092	+0·065	+0·08	+0·05
meta-(3,5) ..	+0·019	0·000	0·00	+0·06
para-(4)	+0·107	+0·065	+0·08	+0·19

[a] *i.e.*, net positive charge at the particular carbon.

[b] Estimated from the empirical relation $\Delta\sigma$ *ca.* 160 Δq (see ref. 1).

[c] Calculated using the Huckel Molecular Orbital method on the assumption that the plane of the aromatic rings is tilted 30° with respect to the plane formed by the four central carbons (see ref. 6).

[d] (See ref. 2).

[e] Obtained from the charge densities at the ring carbon and from the condition that the total charge on the ion must be unity.

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