The Proton Magnetic Resonance Spectra of Arylcarbonium Ions. Neighboring Group Anisotropies and Charge Distributions[1]

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Abstract: The nmr spectra of a number of arylcarbonium ions in fluorosulfonic acid solution are analyzed with the aid of a computer. The chemical shift parameters obtained are compared with some previously reported. They are interpreted with the aid of a double toroid ring-current model for the anisotropy of neighboring phenyls. They are then discussed with reference to charge distributions as determined by some molecular orbital models.

The proton nmr spectra of arylcarbonium ions have been the subject of both qualitative[3] and quantitative[4] investigations for several years. Among the earliest attempts at quantitative analysis was that of O'Reilly and Leftin[4e] on triphenylcarbonium ion. A considerable dispute over the assignment of chemical shifts and coupling constants in triphenylcarbonium ion[3c,4e] seemed to subside with the publication by Dehl, *et al.*,[4c] of deuterium-labeling studies and a computer-simulated spectrum. It seemed to us that the more sophisticated techniques now available in the rapidly developing field of nmr spectroscopy warranted a reinvestigation of some arylcarbonium ions. Impetus was also provided by the fact that early attempts to interpret the chemical significance of the chemical shifts were based on the wrong chemical shift assignments and an incomplete model for the ring-current effect.[4e]

Table I. Proton Nmr Parameters for Several Arylcarbonium Ions

Compd	Carbonium ion	Chemical shifts, τ values *ortho*	*meta*	*para*	α H or CH_3	Coupling constants, Hz $J(o,m)$	$J(o,p)$	$J(o,m')$	$J(o,o')$	$J(m,p)$	$J(m,m')$
1	$C_6H_5CH_2CH_2C^+(OH)_2$	2.80	2.80	2.80							
2	$C_6H_5C^+(OH)_2{}^{a,c}$	1.73	2.24	1.94		8.2	1.2	0.5	1.2	8.0	1.7
3	$(C_6H_5)_2C^+OH^{a,c}$	1.88	2.17	1.85		8.2	1.2	0.5	1.2	8.0	1.7
4	$C_6H_5C^+(OH)CH_3{}^{a,c}$	1.57	2.22	1.84	6.69	8.2	1.2	0.5	1.2	8.0	1.7
5	$(C_6H_5)_3C^{+a,b}$ (60 MHz)	2.31	2.13	1.76		7.95	1.40	0.33	1.21	7.55	0.89
6	$(C_6H_5)_3C^{+a,b}$ (100 MHz)	2.32	2.14	1.76		8.13	1.20	0.43	1.26	7.54	1.14
7	$(C_6H_5)_2C^+CH_3{}^b$	1.93	2.10	1.68	6.30	8.12	1.05	0.74	1.30	7.37	1.39
8	$(C_6H_5)_2C^+H^{b,c}$	1.54	2.02	1.62	0.19	8.2	1.2	0.5	1.2	7.5	1.7
9	$C_6H_5C^+(CH_3)_2{}^{b-d}$	1.12	1.99	1.37	6.43	8.1	1.0	0.7	1.3	7.4	1.4

[a] In chlorosulfonic acid solution. [b] In fluorosulfonic acid solution. These were similar, but less well resolved, in chlorosulfonic acid.[4a] [c] Coupling constants for these systems, particularly the small ones, can only be regarded as approximate, since resolution was too poor to warrant refinement of the calculations. [d] Spectrum determined at −40°.

In an earlier paper we presented a preliminary analysis of the proton nmr spectra of a number of arylcarbonium ions and suggested that the interpretation previously reported in the literature required some modification.[4a] We here report a detailed analysis of the nmr spectra of several arylcarbonium ions at 60 MHz, including a reanalysis of triphenylcarbonium ion at 60 and 100 MHz. We make an attempt to discuss the observed chemical shifts in terms of realistic models for the geometry, ring-current effect, and charge distribution in these ions.

Experimental Section

Materials. Chlorosulfonic acid was distilled immediately before use; fluorosulfonic acid was distilled over anhydrous potassium fluoride, placed in oven-dried, glass-stoppered bottles, sealed with paraffin, and stored in a drybox. All transfers of fluorosulfonic acid were accomplished in the drybox by pipet. Carbonium ion precursors were the carbinols with the exception of compounds **1** (phenylpropionic acid), **2** (benzoic acid), **3** (benzophenone), **4** (acetophenone), and **7** (1,1-diphenylethylene) in Table I. Solid precursors were commercial samples twice recrystallized and dried under vacuum before use. Liquid samples were distilled and a middle cut was taken. Gas chromatographic analysis in all cases resolved only one component in greater than 99% purity. Phenyldimethylcarbinol was obtained as a crystalline solid, mp 32.5–33.5°, by two sublimations. Nmr samples were made up to 1 to 10% concentration by the addition of a methylene chloride solution of the precursor to vigorously stirred acid at −40°. The acid layer was drawn off for use.

Determination of the Spectra. The proton nmr spectra were determined at 60 and 100 MHz on the Varian A-60 or HA-100 instruments. At low concentrations (1%) the Varian CAT was employed to bring out the spectrum. It was demonstrated that the chemical shifts (relative to tetramethylammonium fluoroborate internal standard taken as τ 6.87[4a]) and general appearance of the spectra were relatively insensitive to concentration (from 1 to 10% for **4**, **7**, and **9** of Table I) and temperature (from −40 to +40°).

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(3) (a) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 2997 (1965); (b) G. A. Olah, *ibid.*, **86**, 932 (1964); (c) R. Dehl, W. R. Vaughan, and R. S. Berry, *J. Org. Chem.*, **24**, 1616 (1959); (d) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, 37, 1402 (1959); (e) C. MacLean, J. H. van der Waals, and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958).

(4) (a) D. G. Farnum, *J. Am. Chem. Soc.*, **86**, 934 (1964); (b) T. Schaeffer and W. G. Schneider, *Can J. Chem.*, **41**, 966 (1963); (c) R. S. Berry, R. Dehl, and W. R. Vaughan, *J. Chem. Phys.*, 34, 1460 (1961); (d) C. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961); (e) D. E. O'Reilly and H. P. Leftin, *J. Phys. Chem.*, **64**, 1555 (1960).

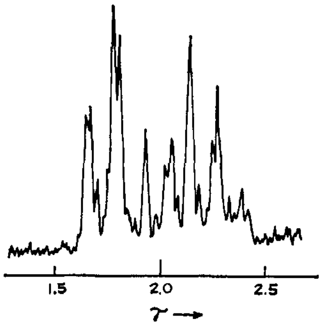

Figure 1. Nmr spectrum (60 MHz) of benzoic acid in chlorosulfonic acid.

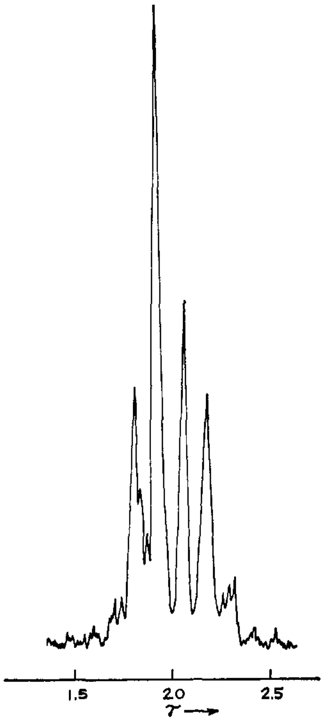

Figure 2. Nmr spectrum (60 MHz) of benzophenone in chlorosulfonic acid.

In those cases which could be determined in both acids, the shifts were nearly the same, but the spectra in fluorosulfonic acid were better resolved (presumably because of the greater fluidity). The structures of the carbonium ions were assured by the reproducibly characteristic nmr patterns, the near identity of the ultraviolet spectra of the diluted solutions of **4** and **9** (Table I) with those reported in the literature,[5] and recovery of the parent alcohol in 60% yield or better by quenching in iced aqueous base in the cases of triphenylcarbinol (**5**), benzhydrol (**8**), benzophenone (**3**), and benzoic acid (**2**). The spectrum of methyldiphenylcarbonium ion (**7**) has appeared in the literature.[4e] Our spectrum was similar in appearance, but better resolved. Spectra were determined on both 500 Hz and 250 Hz nominal scale widths, calibrated with known standards to determine the actual scale widths.

Analysis of the Spectra. Nmr spectra were analyzed with the aid of the nmr simulation computer program, LAOCOON II, devised by Bothner-By.[6] Spectra were computed on a Control Data Corp. 1604 computer, traced on a curve-plotter, and compared with the determined spectra. A line-width factor of 0.8 (approximately equal to width at half-height in Hertz) gave computed spectra of comparable appearance to the experimental ones. Iterations to determine the best fit were performed separately at 60 and 100 MHz for triphenylcarbonium ion. The results at the different frequencies were in close agreement (within 0.5 Hz). To assist in the preliminary choice of parameters 20 spectra with identical approximate coupling constants but differing chemical shifts were computed. An approximate fit to one of these provided the starting point for the interation procedure. In the cases of acetophenone (phenylmethylhydroxycarbonium ion), benzoic acid (phenyldihydroxycarbonium ion), and phenyldimethylcarbonium ion, separation of the peaks was sufficient to assign chemical shifts by inspection after the initial comparison. For benzophenone (diphenylhydroxycarbonium ion) the poorer resolution did not warrant an attempt at a closer assignment than that obtained by estimation from the first comparison. The determined and simulated spectra for the several carbonium ions are compared in Figures 1–8. The chemical shifts and coupling constants are given in Table I. The assignment of the *ortho*, *meta*, and *para* protons rests firmly on the large (7–8 Hz) coupling of the *ortho* proton to *one meta* proton, the large (7–8 Hz) coupling of the *meta* proton to both *ortho* and *para* protons, and the low intensity of the peaks corresponding to the single *para* proton.

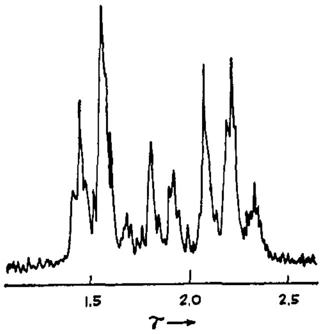

Figure 3. Nmr spectrum (60 MHz) of acetophenone in chlorosulfonic acid.

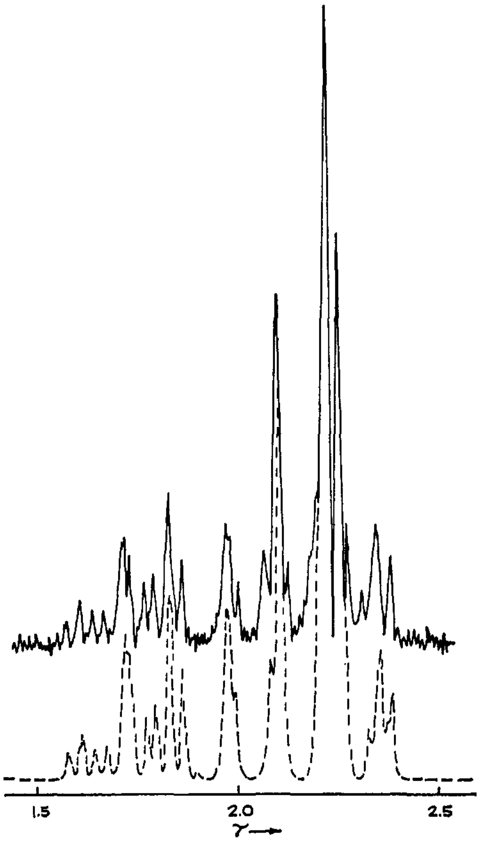

Figure 4. Nmr spectrum (60 MHz) of triphenylcarbinol in fluorosulfonic acid (upper curve) and computer-simulated spectrum (lower curve) using parameter values given in Table I.

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[5] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3044 (1955).

[6] We thank Dr. Bothner-By for providing us with the program deck and instructions for LAOCOON II.

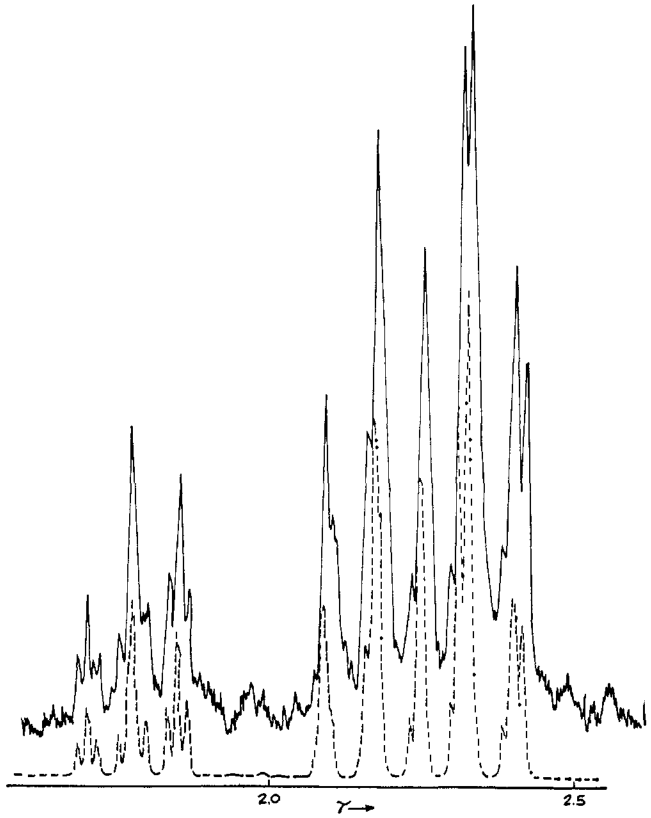

Figure 5. Nmr spectrum (100 MHz) of triphenylcarbinol in fluorosulfonic acid (upper curve) and computer-simulated spectrum (lower curve) using parameter values given in Table I.

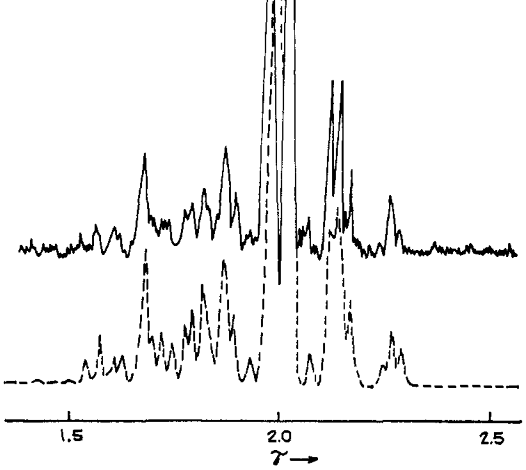

Figure 6. Nmr spectrum (60 MHz) of 1,1-diphenylethylene in fluorosulfonic acid (upper curve) and computer-simulated spectrum (lower curve) using parameter values given in Table I.

There is some variance in the values reported for triphenylcarbonium ion from several sources. These values are compared in Table II. The chemical shifts obtained in this work are in reasonable agreement with those of Schaeffer and Schneider[4b] and Berry, *et al.*,[4c] while coupling constants are quite comparable with those obtained by the latter authors. The variations probably are the result of different solvents and reference standards as well as the difficulty of analyzing the 60-MHz spectrum without the aid of a computer.

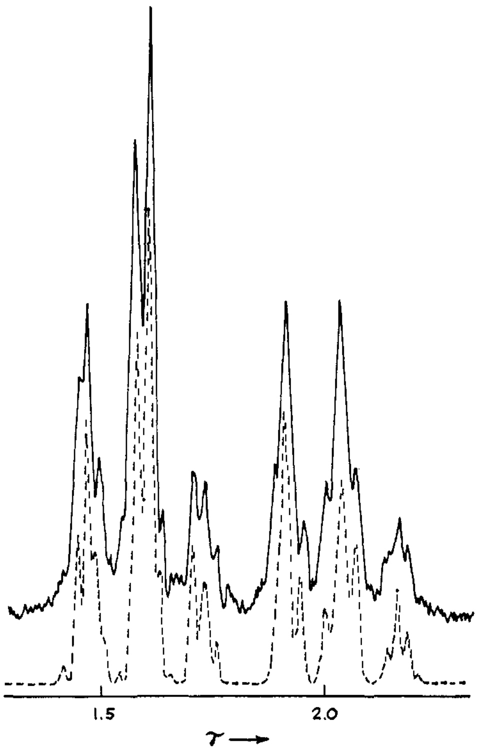

Figure 7. Nmr spectrum (60 MHz) of diphenylcarbinol in chlorosulfonic acid (upper curve) and computer-simulated spectrum (lower curve) using parameter values given in Table I.

Table II. Comparison of Nmr Parameters from Several Sources for Triphenylcarbonium Ions

	Source[a]				
	1	2	3	4	5
τ(*ortho*)	2.38	2.30 (2.45[b])	2.29	2.99	2.32
τ(*meta*)	2.13	2.45 (2.30[b])	2.12	2.49	2.14
τ(*para*)	1.73	1.93	1.76	2.24	1.76
$J(o,m)$[c]			8.2		8.13
$J(o,p)$			1.2		1.20
$J(o,m')$			0.5		0.43
$J(o,o')$			1.2		1.26
$J(m,p)$			8.0		7.54
$J(m,m')$			1.7		1.14

[a] Source code numbers are 1, ref 4b; 2, ref 4e; 3, ref 4c; 4, ref 3b; 5, this work. [b] Alternate assignments. [c] J values given in Hertz.

Discussion

Several general features emerge from the data from nmr analysis of several arylcarbonium ions as given in Table I. The chemical shift value for the phenyl protons of phenylpropionic acid in sulfuric acid solution (τ 2.80) is given as a reference point. As expected, all the arylcarbonium ion chemical shifts fall below this value, and the *p*-proton resonance moves progressively downfield as the electron-releasing ability of the substituents on the α-carbon decreases. This qualitative correlation of the position of the *p*-proton resonance with the electron demands placed on the phenyl by the

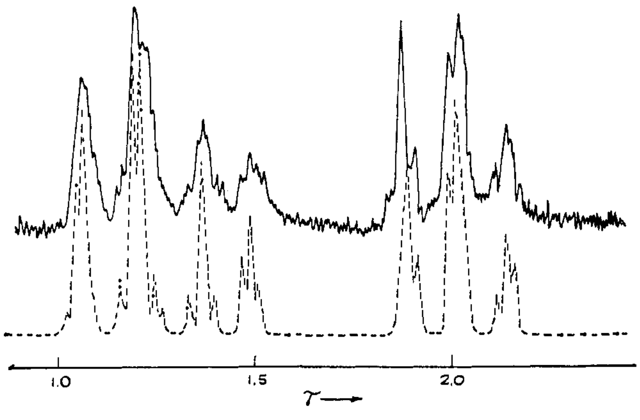

Figure 8. Nmr spectrum (60 MHz) of phenyldimethylcarbinol in fluorosulfonic acid at −40° (upper curve) and computer-simulated spectrum (lower curve) using parameter values given in Table I.

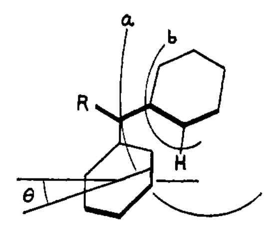

Figure 9. Neighboring ring-current effects in triphenylcarbonium ion: θ = twist angle, a = line of iso shielding, b = line of iso deshielding.

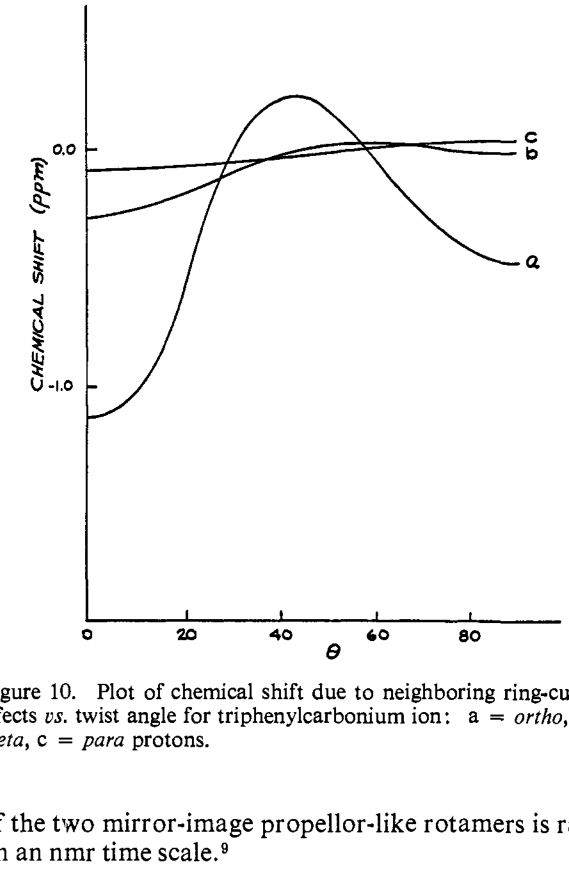

Figure 10. Plot of chemical shift due to neighboring ring-current effects *vs.* twist angle for triphenylcarbonium ion: a = *ortho*, b = *meta*, c = *para* protons.

carbonium ion is expected and has been noted in the literature.[4a] The *o*- and *m*- proton resonances are much less regular and are apparently significantly perturbed by anisotropies of the α substituents.[4a] Thus for the series diphenyl (**8**), hydroxydiphenyl (**3**), methyldiphenyl (**7**), and triphenylcarbonium ion (**6**), the *o*-proton resonances (τ 1.54, 1.88, 1.93, and 2.32) fall progressively upfield, apparently independently of the extent of the positive charge on the phenyl. This order, however, does correlate with the size of the α substituent, and, therefore, with the angle of twist of the phenyls from coplanarity. Increased twisting from coplanarity (up to about 45°) will result in increased *shielding* of the *o*-protons by neighboring phenyl anisotropy as illustrated in Figure 9. For the *meta* chemical shifts (2.02, 2.17, 2.10, and 2.14) the influence of the positive charge and anisotropy might be better balanced; thus the correlation is not expected to be as regular. As an incidental point, all the coupling constants fall within the ranges quoted in the literature for aromatic compounds,[7] in spite of the major perturbation of the positive charge.

In order to examine the quantitative validity of some of the ideas suggested in the previous paragraph, it was necessary to develop a quantitative picture of the neighboring phenyl anisotropy effect as a function of the angle of twist of the phenyls. A model for this effect based upon a modification of the Johnson–Bovey–Waugh–Fessenden[8] double-loop ring-current model has been described in another publication[9] and applied to the di- and triphenylcyclopropenium ions. Figure 10 depicts the neighboring ring-current effect as a function of the angle of twist for triphenylcarbonium ion as calculated using this model (a double doughnut of circulating charge of radius and cross-sectional diameter equal to 1.4 A). The calculation determines the effect of both the near and remote neighbor phenyls on the *o*-, *m*-, and *p*-proton, assuming that all phenyls are twisted the same angle from coplanarity.[9] The effect for a diphenylcarbonium ion should be one-half the values in Figure 10, provided only that interchange of the two mirror-image propellor-like rotamers is rapid on an nmr time scale.[9]

Evaluation of the ring-current effect requires the actual angle of twist of the phenyls in triphenylcarbonium ion in solution, which is not known. Estimates range from 23°[4e] (near the van der Waals approach of the *o*-hydrogens) to 45°,[10] with X-ray analysis of the solid giving 35°.[11] In the absence of any convincing evidence to the contrary we have chosen

Table III. Chemical Shifts of Ring Protons of Several Arylcarbonium Ions Corrected for Neighboring Ring Anisotropies

Compd	Carbonium ion	Chemical shift, τ values *ortho*	*meta*	*para*
2	$C_6H_5C^+(OH)_2$	1.73	2.24	1.94
3	$(C_6H_5)_2C^+OH$ (30° twist)	1.90	2.22	1.88
4	$C_6H_5{}^+C(OH)CH_3$	1.57	2.22	1.84
5	$(C_6H_5)_3C^+$ (45° twist)	2.08	2.14	1.80
7	$(C_6H_5)_2C^+CH_3$ (35° twist)	1.87	2.13	1.71
8	$(C_6H_5)_2C^+H$ (25° twist)	1.69	2.09	1.66
9	$C_6H_5C^+(CH_3)_2$	1.12	1.99	1.37

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(7) J. B. Leane and R. E. Richards, *Trans. Faraday Soc.*, **55**, 707 (1959).

(8) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957); **80**, 6697 (1958); C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(9) D. G. Farnum and C. F. Wilcox, *J. Am. Chem. Soc.*, submitted for publication.

(10) N. C. Deno, P. T. Graves, and G. Saines, *ibid.*, **81**, 5790 (1959).

(11) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Cryst.*, **18**, 437 (1965).

Table IV. Comparison of the Observed Charge Contribution to the Chemical Shift of Phenylcarbonium Ions at Several Twist Angles with That Calculated from Molecular Orbital Models

		Charge contribution to chemical shift[a]							
		Obsd[b]		HMO[c,f]		*d,f*		SCFMO[e,f]	
Species (angle, deg)	Proton	Abs	Rel	Abs	Rel	Abs	Rel	Abs	Rel
Phenyldimethylcarbonium ion (0)	*ortho*	1.60	1.18	2.67	1.10	2.19	1.11	2.36	0.64
	meta	0.77	0.57	1.16	0.48	1.45	0.74	1.95	0.53
	para	1.35	1.0	2.43	1.00	1.97	1.00	3.67	1.00
Diphenylcarbonium ion (25)	*ortho*	1.07	0.93	1.63	1.06				
	meta	0.70	0.61	0.84	0.54				
	para	1.15	1.00	1.54	1.00				
(35)	*ortho*	1.33	1.14	1.50	1.14				
	meta	0.75	0.65	0.78	0.59				
	para	1.17	1.00	1.32	1.00				
(45)	*ortho*	1.38	1.18	1.33	1.29				
	meta	0.78	0.67	0.71	0.68				
	para	1.17	1.00	1.03	1.00				
Triphenylcarbonium ion (25)	*ortho*	0.075	0.08	1.24	0.98				
	meta	0.50	0.52	0.71	0.56				
	para	0.97	1.00	1.27	1.00				
(35)	*ortho*	0.60	0.61	1.22	1.07				
	meta	0.60	0.61	0.69	0.61				
	para	0.98	1.00	1.13	1.00				
(45)	*ortho*	0.73	0.73	1.15	1.23				
	meta	0.65	0.65	0.65	0.69				
	para	1.00	1.00	0.94	1.00				

[a] Column labeled abs gives values in parts per million downfield from the phenyl hydrogens of phenylpropionic acid. Column labeled rel gives values relative to *para* chemical shifts = 1.00. [b] Corrected for the neighboring ring-current effect at the angle in question. [c] Simple Hückel molecular orbitals. [d] Modified ω technique.[15] [e] Self-consistent-field calculations.[16] [f] Chemical shifts are calculated as the sum of the contributions from all carbon atoms using Musher's equations.[12]

to set the twist angles for diphenyl-, dihydroxydiphenyl-, methyldiphenyl-, and triphenylcarbonium ions at 25, 30, 35, and 45°, respectively, corrected the chemical shifts for the determined ring-current effects, and reexamined the thus-obtained order of chemical shifts. The results are shown in Table III. Although the *m*- and *p*-protons now correlate, and the *o*-protons are more nearly in line, the correction is not sufficient to bring complete order to the *o*-proton chemical shifts. We have been unable to find alternative reasonable choices of twist angles which improve the order. It is possible that a residual effect of the α-hydroxyl substituents is causing a downfield shift since the oxygenated cations (**2**, **3**, and **4**) appear at too low field, with the dioxygenated case **2** being particularly low.

With the chemical shifts corrected for neighboring ring-current effects in hand, it was possible to examine their correlation with predicted charge distributions in these ions. Two refinements of earlier work in this field[3,4] were attempted in this investigation. First, earlier efforts had considered only the effect of the positive charge of the directly attached carbon atom. However, Musher has claimed[12] that all nearby positive charges have a significant effect. Therefore, using Musher's equations,[12] we set up a computer program which would calculate the chemical shifts at the *o*-, *m*- and *p*-protons resulting from point charges of specified values at all the carbon atoms in the mono-, di-, and triphenylcarbonium ions. Second, earlier attempts[4] have determined the theoretical charge distribution in di- and triphenylcarbonium ions based upon *planar* molecules rather than realistically twisted ions. We therefore calculated the Hückel charge densities for these ions at twist angles of 25, 35, and 45°.[13] The results of these combined calculations are summarized in Table IV.

Again a qualitative picture can be drawn. Thus, the larger relative[14] downfield chemical shift observed for the *o*-protons of phenyldimethylcarbonium ion is correctly reproduced by both the Hückel and the ω-technique[15] calculations, but not by the SCF[16] method. The moderate chemical shift of the *m*-proton is in accord with all the calculations, in spite of the absence of charge at that position in the Hückel approximation. The relative chemical shifts for a 35° twisted diphenylcarbonium ion are extraordinarily well reproduced by the Hückel model, while much more difficulty is encountered with triphenylcarbonium ion, which shows more dispersal of charge to the *para* position than expected. Unfortunately, calculations by the ω-technique and SCF method for these twisted cations are not yet available for comparison. Since several approximate models have been interposed between the raw data and the numbers being compared in Table IV, it seems wise to be cautious in attempting any more quantitative analysis of the results.

An incidental observation of some interest was made on solutions of the phenyldimethylcarbonium ion in fluorosulfonic acid. These solutions were stable only below −20°, as evidenced by the smooth, reproducible, rapid conversion of their characteristic nmr spectrum above that temperature to a new, well-resolved, and entirely different spectrum illustrated in Figure 11. The irreversible conversion was accompanied by a barely perceptible lightening of the lemon yellow color

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(12) J. I. Musher, *J. Chem. Phys.*, 37, 34 (1962).

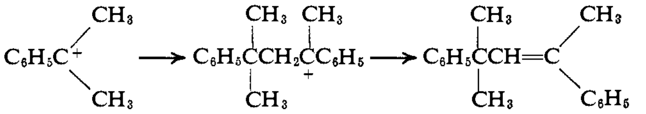
(13) We thank Professor C. F. Wilcox for making a program available to us for these calculations.

(14) The discrepancy between the absolute values and the observed values is not surprising, since the Musher equations contain no correction for the solvent dielectric effect on the charge.

(15) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(16) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 902 (1954).

of the solution. The new species was identified as the dimeric phenylmethyl-(2-phenylisobutyl)carbonium ion (**10**) by isolation of the corresponding olefin (**11**) in good yield by quenching the solution in iced aqueous sodium hydroxide. The olefin was purified by gas chromatography and characterized by its mass spectrum (parent peak, *m/e* 236) and nmr spectrum (τ 2.0–2.9, multiplet, area = 10.0; 4.13, quartet, J = 2 Hz, area ≐ 0.6; 8.02, doublet, J = 2 Hz, area = 2.6; 8.80, singlet, area = 6.0) which left no doubt of its structure. The methyl and methylene resonances of the carbonium ion appeared at τ 6.18 (broad, area *ca.* 2), 6.61 (broad, area *ca.* 3), and 8.47 (sharp, area *ca.* 6).

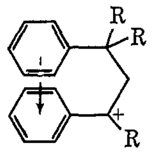


$$C_6H_5\overset{+}{C}(CH_3)_2 \longrightarrow C_6H_5C(CH_3)_2CH_2\overset{+}{C}(CH_3)C_6H_5 \longrightarrow C_6H_5C(CH_3)_2CH{=}C(CH_3)C_6H_5$$

10 **11**

The nmr spectrum of carbonium ion **10** deserves notice. It is entirely different from any which we have encountered in this work in that no phenyl resonance appears at the low-field position usually observed for *o*-protons, nor is there a clear separation between the phenyl conjugated with the carbonium ion center and that attached to the quarternary carbon. A rapid equivalencing of the phenyls by methyl migration (**10a** ⇄ **10b**) cannot account for the results because the methyl resonance signals are sharp and discrete, nor can they be the result of dimeric association, since the spectrum is the same at concentrations from 1 to 10%. We suggest that the unusual nmr spectrum of **10** is accommodated by a folded geometry, as in **10c** (R = CH_3), in which the noncationic phenyl is associated with the cationic phenyl analogously to a charge-transfer complex or a solvation association. A similar explanation, named a "space-polarization effect," has been offered by Williams for the anomalous ultraviolet spectrum of phenyl-β-phenylethylcarbonium ion (**10c**, R = H).[17] The required folded geometry is readily achieved in molecular models.

10a **10b**



10c

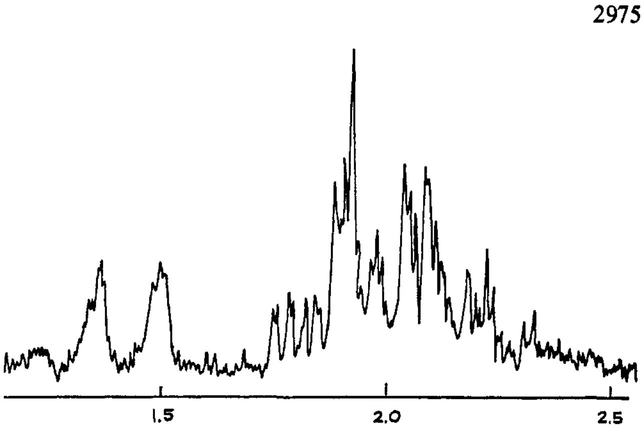


Figure 11. Nmr spectrum (60 MHz) of phenyldimethylcarbonium ion dimer.

In summary, the following conclusions seem justified on the basis of the treatment reported in this paper. (1) The *p*-proton resonance provides a reasonable qualitative measure of the extent of dispersion of positive charge onto the phenyl group of a phenylcarbonium ion. (2) When suitable corrections are made for neighboring ring-current effects and nonplanar geometries, the positive charges calculated by the simple Hückel approximation account for the ring chemical shifts of phenyldimethyl- and diphenylcarbonium ion in an entirely satifactory way. However, triphenylcarbonium ion exhibits somewhat more dispersal of charge to the *para* position than expected. (3) Taken together, the results suggest that the twist angles of the polyphenylcarbonium ions examined are greater than 25°, and perhaps as high as 45° from coplanarity.

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(17) J. F. A. Williams, *Tetrahedron*, **18**, 1487 (1962).

(18) Summer participant in the National Science Foundation Undergraduate Research Participation Program.