Organic and Biological Chemistry

Use of a Model for the Ring-Current Effect in Analysis of the Nuclear Magnetic Resonance Spectra of Di- and Triphenylcyclopropenium Ions[1]

D. G. Farnum[2] and C. F. Wilcox

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received March 4, 1967*

Abstract: The Johnson–Bovey–Waugh–Fessenden double-loop model for the ring-current effect in the nmr spectra of aromatic systems is compared with a slightly less arbitrary double-toroidal shell model. The calculated effect for all points greater than 3 A from the center of the ring is nearly the same for the two models. At closer distances, significant differences sometimes arise. The double-toroidal shell model is used to calculate the ring-current effect in the nmr spectra of di- and triphenylcyclopropenium ions at different angles of twist of the phenyl groups from coplanarity. Comparison with observed spectra gives a self-consistent picture at twist angles from 9.5 to 13.5°. The charge distribution in the ions is discussed briefly.

Models for quantitative calculation of ring-current effects in nmr spectra of aromatic substances have developed from the point dipole[3] through the single current loop to the double current loop.[4,5]

For all of these models, the only quantitative tests have been calculations of the chemical shifts of hydrogens in the plane of the aromatic ring.[8] When they are applied to systems containing hydrogens out of the plane, particularly when the hydrogens are pressed into the π-electron cloud, doubt arises as to even the qualitative accuracy of the predicted chemical shift. The present contribution explores yet another model, the double toroidal shell model, which because of its more distributed current loops might provide a more faithful classical model for the calculation of ring-current effects. The model is used to assist in the analysis of the nmr spectra of di- and triphenylcyclopropenium ions, an analysis which requires the evaluation of the ring-current effect on protons by neighboring rings placed at various twist angles.

The ideal classical model for benzenoid ring currents would use a summation of the infinite set of current loops around the C_6 axis weighted according to the average[9] of the electron density at each ρ and z. One approximation to this ideal would be the ring-current effects arising from the same set of current loops but weighted according to the π-electron density represented by uniformly charged tangent spheres.[10] In this more restricted model the ring currents are summed over the induced currents flowing in toroidal shells of circular cross section ranging out from the simple Johnson–Bovey-like point loops at $\rho = R$, $Z = \pm R/2$ to shells of radius $R/2$ (see Figure 1), where R is the radius of the benzene ring. With a weighting appropriate to the electron distribution of a uniformly charged sphere the relative contribution of each shell (of constant thickness dr) would increase out to a maximum at $r = R/2$ and then drop to zero for shells of larger cross-sectional radius.

Even this simplified double-torus model with a charge distribution given by the average of 12 uniformly charged tangent spheres represents considerable calculational effort. Since the primary interest was to explore the effect of placing hydrogen nuclei close to a ring-current loop a still simpler model was used that retains this feature. The calculation was carried out for a toroidal current shell of circular cross section with an outer radius of $\rho = {}^3/_2R$, an inner radius of $R/2$, and a cross-sectional radius of $r = R/2$. In terms of Figure 1 this corresponds to calculating the magnetic field appropriate to charge flowing in only the outermost pair of shells. A computer program was written for the magnetic field of a single point current loop of arbitrary dimensions.[11] A number, n, of these loops were distributed uniformly on the toroidal surface and the magnetic field arising from the n loops, each containing a current equal to $6e/n$, was calculated at regular dis-

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(2) Fellow of the Alfred P. Sloan Foundation, 1962–1965.

(3) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

(4) 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).

(5) The point-dipole approximation has been reinstated in the form of six point dipoles by Musher.[6] However, it is not clear how this kind of approximation accounts for the in-plane *shielding* observed *within* the ring of systems such as [18] annulene.[7] Our preliminary calculations indicated that, using Musher's value for the magnitude of the point dipoles, the model gave values several times too large for the ring-current effect on the hydrogens of benzene.

(6) J. I. Musher, *J. Chem. Phys.*, **43**, 4081 (1965).

(7) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gami, R. Wolovsky, and A. A. Bothner-by, *J. Am. Chem. Soc.*, **84**, 4307 (1962).

(8) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press Inc., New York, N. Y., 1965, p 140 ff.

(9) In cylindrical coordinates this average would be taken over θ, the angle of rotation about the C_6 axis.

(10) There is no *a priori* reason to expect that a tangent sphere model, so convenient in the calculation of electrostatic effects in π-electronic spectra, has any special significance in a magnetic calculation.

(11) The expressions given in "Handbook of Mathematical Functions," M. Abramowitz and I. A. Stegun, Ed., Dover Publications, Inc., New York, N. Y., 1965, pp 591–592, were used for the complete elliptic integrals K and E.

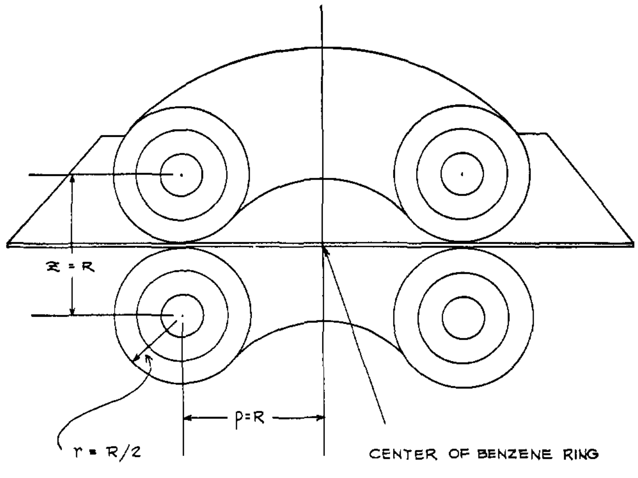

Figure 1. Double torus model for the benzene ring current.

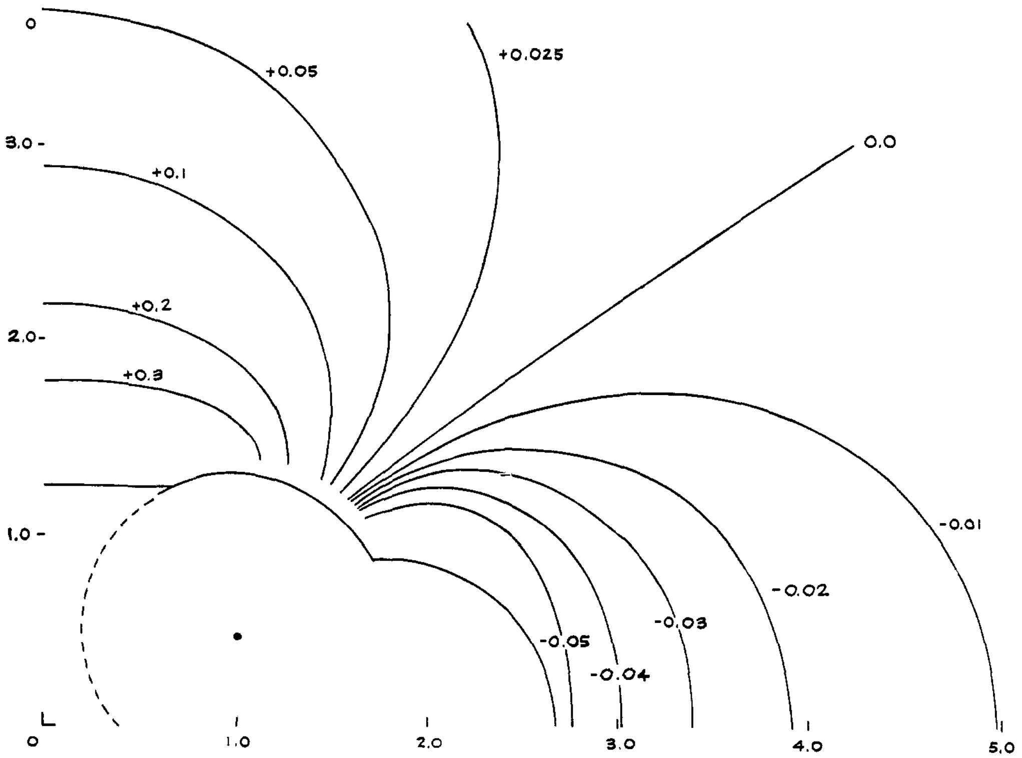

Figure 2. Correction (in ppm) to be added to Johnson–Bovey ring-current effect to give double-torus effect.

tances from the central axis of the loops and at regular heights above the plane. Only points located beyond the van der Waals separation of the benzene ring were considered. This cut-off distance does not include the van der Waals radius of any neighboring atoms and thus covers any normal region of approach. The number of loops, *n*, was increased until no further change in the calculated value of the magnetic shielding was found.[12] The results of this calculation expressed as a correction in parts per million to be added to the Johnson–Bovie double loop model are presented graphically in Figure 2. It can be seen that negative corrections near the plane of the benzene ring are very small and certainly negligible. The positive corrections in the region above the center of the ring are much greater and under circumstances allowing close approach of a hydrogen atom would become significant.[13] This double-toroidal shell model was used in the calculations that follow.

Any reader who contemplates using these corrections should be fully aware that they are derived from a classical model and that it shares with such models the limitation of being only a partial representation of a complete quantum mechanical solution. In general a "refinement" of a classical model does not guarantee that the new model will be a better representation of the actual molecular situation. If it does nothing else, however, the present model does draw attention to the uncertainty of the expected chemical shifts of nuclei in the region immediately above the center of the ring.

The chemical shifts and coupling constants for the nmr spectra of 5% solutions of di- and triphenylcyclopropenium ions in fluorosulfonic acid were determined with the aid of Bothner-By's nmr simulation computer program, LAOCOON II.[14] A comparison of the experimental curves with the best calculated curves is given in Figures 3, 4, and 5. The triphenylcyclopropenium ion was done at both 60 and 100 MHz as a check, and the results agreed within the estimated error.[15] The values of the variables for these calculated spectra are given in Table I. From these values, the τ values for the *para* proton resonances of the di- and triphenylcyclopropenium ions were determined to be 1.92 and 1.93, respectively, and the downfield shift of the *ortho*,

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[12] For the region defined above, the set of 24 loops distributed symmetrically between the upper and lower tangent toruses was found to be sufficient.

[13] It should be pointed out that this double-toroidal shell model does not involve any adjustable parameters other than the initial one inherent in the selection of tangent spheres as a point of departure.

[14] We are indebted to Dr. Bothner-By for a copy of the program deck.

[15] Error was estimated simply by determining how much of a change in the parameter was required to bring about a visually detectable deterioration of the fit.

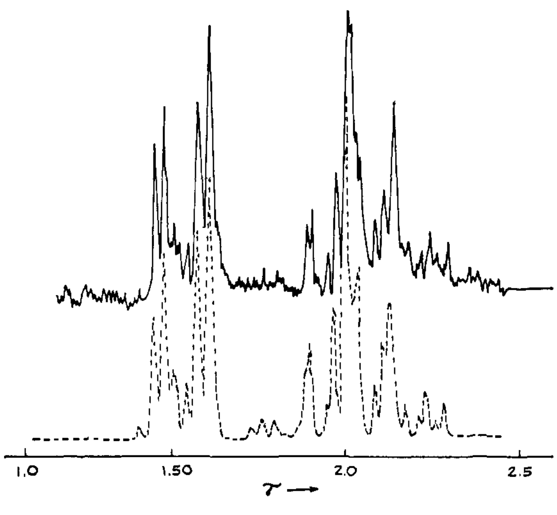

Figure 3. Nmr spectrum (60 MHz) of diphenylcyclopropenium ion in fluorosulfonic acid: upper curve, observed; lower curve, calculated.

meta, and *para* protons from the phenyl protons of phenylpropionic acid was calculated as given in Table I. The coupling constants fall within the range usually observed for aromatic compounds.[16]

Table I. Chemical Shifts and Coupling Constants for Di- and Triphenylcyclopropenium Ions

	Diphenyl 60 MHz	Triphenyl 60 MHz	 100 MHz
	Chemical Shifts, Hz		
ortho-para	22.5 ± 0.3	29.5 ± 0.3	48.6 ± 0.5
meta-para	11.0 ± 0.3	8.0 ± 0.3	12.8 ± 0.5
	Coupling Constants, Hz		
J(*o,m*)	7.70	7.87	7.88
J(*o,p*)	1.38	1.32	1.57
J(*o,m'*)	0.48	0.56	0.31
J(*o,o'*)	1.43	2.09	1.82
J(*m,p*)	7.72	7.49	7.79
J(*m,m'*)	1.55	1.90	1.19
Downfield Shift from Phenylpropionic Acid Phenyl Hydrogens, ppm			
ortho	1.255 ± 0.005	1.362 ± 0.005	
meta	0.697 ± 0.005	0.737 ± 0.005	
para	0.880 ± 0.005	0.870 ± 0.005	

We now wished to correct the observed chemical shifts for the effect of the anisotropy of the neighboring rings. Using the double-toroid model developed above, combined with a program for the calculations of the hydrogen coordinates relative to the center of the neighboring benzene ring as origin, it was possible to calculate the ring-current effect at the *ortho*, *meta*, and *para* positions as a function of the angle of twist of the phenyls from coplanarity.[17] A plot of the results of these calculations for triphenylcyclopropenium ion is given in Figure 6. It should be emphasized that these values include the effects of *both* the near and remote neighbor rings. The values for diphenylcyclopropenium ion were taken as one-half those for triphenylcyclopropenium ion on the assumption that interconversion of the mirror image propellor rotamers would be rapid on an nmr time scale.[19] The chemical shifts from the ring-current effect were then subtracted from the observed downfield shifts to give "corrected chemical shifts" (chemical shifts resulting from all effects other than neighboring phenyl ring currents). These cor-

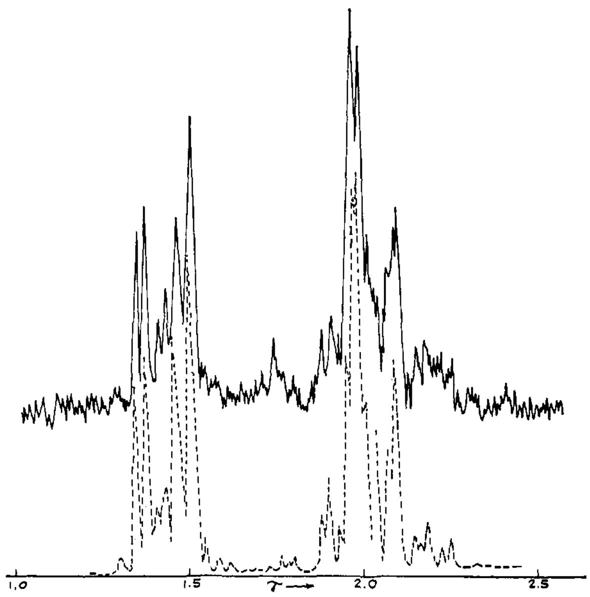

Figure 4. Nmr spectrum (60 MHz) of triphenylcyclopropenium ion in fluorosulfonic acid: upper curve, observed; lower curve, calculated.

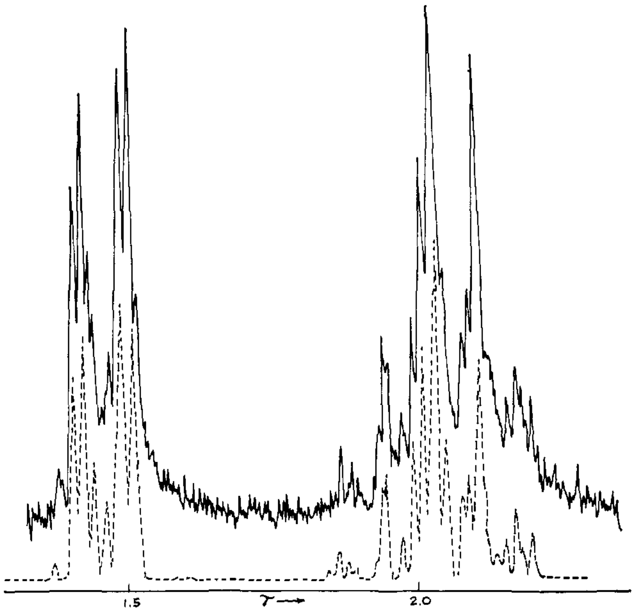

Figure 5. Nmr spectrum (100 MHz) of triphenylcyclopropenium ion in fluorosulfonic acid: upper curve, observed; lower curve, calculated.

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

(17) Although it is by no means sure that the twist angles of all the phenyls are the same in the ion in solution,[18] introduction of the additional variables would render the calculations almost hopeless. We therefore, necessarily, assume that calculations at an average twist angle will approximately reproduce the time average of the values at different twist angles. Similar calculations have been done for biphenyl by R. E. Mayo and J. H. Goldstein, *Mol. Phys.*, 10, 301 (1966).

(18) M. Sundraralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **88**, 198 (1966).

(19) This assumption seems sound both on mechanistic grounds and on the basis of the observation that the nmr spectrum was unchanged from −40 to +40°.

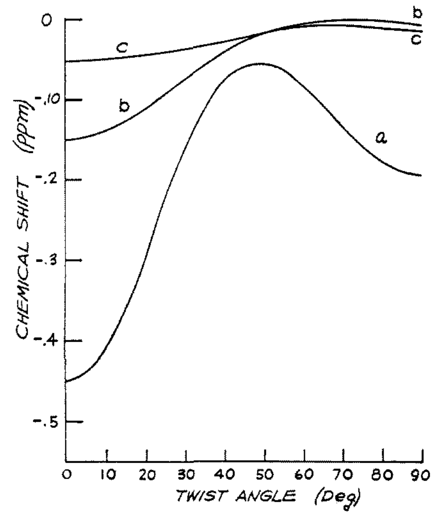

Figure 6. Calculated ring-current effect as a function of the twist angle of the phenyls in triphenylcyclopropenium ion.

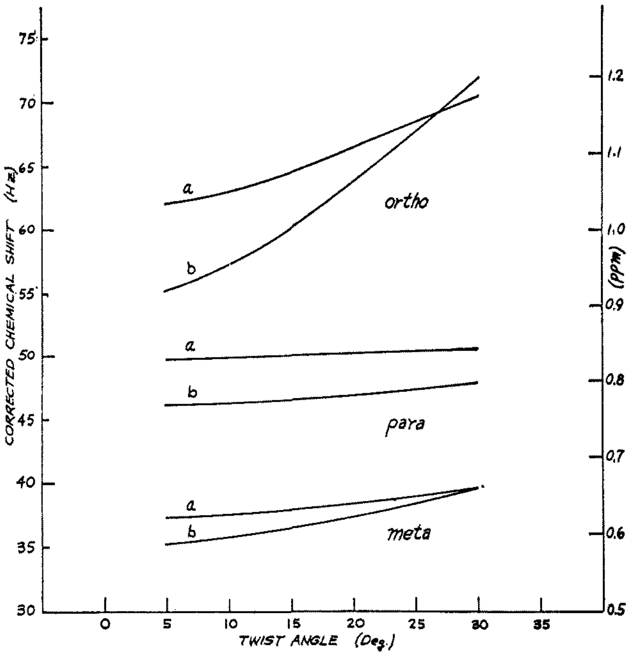

Figure 7. Corrected chemical shifts in (a) diphenyl- and (b) triphenylcyclopropenium ions.

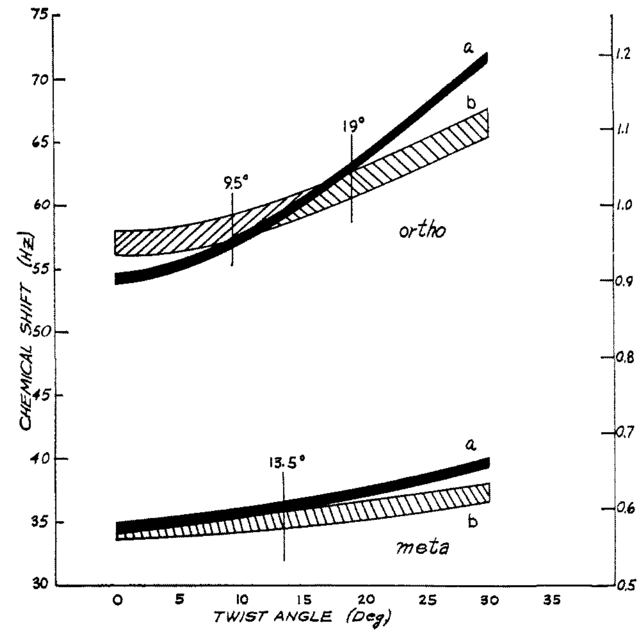

Figure 8. Observed (a) and calculated (b) corrected chemical shifts in triphenylcyclopropenium ion.

rected chemical shifts are plotted as a function of the chosen twist angle in Figure 7.

Although the actual twist angle of the phenyls of these ions in fluorosulfonic acid solution is not known, some simple algebraic manipulations will show that, for a given twist angle, the chemical shifts of the *ortho* and *meta* protons of triphenylcyclopropenium ion can be calculated from the other data and compared with the observed values, thus giving a check on the internal consistency of the data at different twist angles. The assumptions necessary are that the "corrected chemical shift" *ratios* for the two ions are the same, and that the twist angles are the same. The first assumption seems quite reasonable, since the major factor determining the downfield "corrected chemical shifts" is undoubtedly the charge distribution, and the *ortho*:*meta*:*para* charge ratios should be essentially the same for these two closely related ions.[20] The second assumption is an intuitive one which rests less firmly on the suggestion, from an examination of models, that once two phenyls are twisted to avoid one another, the third can slip in at the same angle relatively unmolested.[17] Given these assumptions, we define δ(OT), δ(MT), and δ(PT) as the downfield shifts of the *ortho*, *meta*, and *para* protons of triphenylcyclopropenium ion, and δ(OD), δ(MD), and δ(PD) as the corresponding values for diphenylcyclopropenium ion. The following relationships hold

$$\delta(\mathrm{OT}) = \delta(\mathrm{OD})\frac{\delta(\mathrm{PT})}{\delta(\mathrm{PD})} \qquad (1)$$

and

$$\delta(\mathrm{MT}) = \delta(\mathrm{MD})\frac{\delta(\mathrm{PT})}{\delta(\mathrm{PD})} \qquad (2)$$

Internally consistent values for the twist angle can now be obtained. In Figure 8 the chemical shift values δ(OT) and δ(MT) calculated from eq 1 and 2 as a function of twist angle are compared with the corrected chemical shifts for the *ortho* and *meta* protons of triphenylcyclopropenium ion as a function of the angle of twist. Although the experimental error is large, the only region in which both the *ortho* and *meta* chemical shifts are correctly reproduced is at twist angles from 9.5 to 13.5°. This range may be compared with the average value of 14° obtained by X-ray crystallographic analysis of solid triphenylcyclopropenium perchlorate.[18]

Although it is not yet possible to attempt any quantitative correlations of the nmr spectra of these ions with charge distributions because of the unavailability of calculated distributions for the nonplanar ions, some qualitative points are worth noting. In Table II the "charge contribution" to the chemical shift (actually this is the above-defined "corrected chemical shift") at a twist angle of 10° is calculated. The ratio of this contribution in diphenylcyclopropenium ion to that in triphenylcyclopropenium ion for *ortho*, *meta*, and *para*

(20) We assume that any ring-current effect from the cyclopropenium unit will be relatively small and closely cancel for the two systems.

Table II. Ring-Current and Charge Contributions to the Chemical Shifts of Di- and Triphenylcyclopropenium Ions at a Twist Angle of 10°

	Chemical Shifts, ppm					
	Diphenyl			Triphenyl		
	ortho	*meta*	*para*	*ortho*	*meta*	*para*
Observed	−1.255	−0.697	−0.880	−1.362	−0.737	−0.870
Ring-current contribution	−0.205	−0.070	−0.048	−0.408	−0.140	−0.097
Charge contribution	−1.050	−0.627	−0.832	−0.954	−0.597	−0.773

protons is 1.1, 1.05, and 1.08, respectively, suggesting that from 5 to 10% more positive charge gets onto the phenyls in the diphenyl ion as compared with the triphenyl ion. This rather small difference is in accord with the well-known failure of phenyl groups to contribute significantly to the thermodynamic stability of the cyclopropenium ion.[21] Also interesting in this connection is the very large downfield shift of the *ortho* protons and the proximity of the *meta* and *para* proton resonances to one another. This arrangement is more like that of nitrobenzene[22] than that of the more delocalized phenyldimethylcarbonium ion.[23] In fact, the nmr spectra of nitrobenzene can be virtually superimposed on that of the triphenylcyclopropenium ion. Finally, by the criterion previously suggested in the literature,[23] the appearance of the corrected *para* proton resonance in di- and triphenylcyclopropenium ions at τ 1.97 and 2.03, at higher field than those of diphenylhydroxycarbonium ion (τ 1.85) and phenyldihydroxycarbonium ion (τ 1.94),[23] suggests that the π-electronic demands on the phenyls by the cyclopropenium ion are less than those of monohydroxy- and dihydroxycarbonium ion. This further emphasizes the stability of this closed π-electron system.

Experimental Section

Materials. Triphenylcyclopropenium bromide was prepared by the literature procedure,[24] purified by sublimation, finely powdered, and added directly to stirred fluorosulfonic acid at −40° under a stream of nitrogen. Diphenylcyclopropenium ion was prepared by addition of twice recrystallized, finely powdered bis(diphenylcyclopropenyl) ether[25] to stirred fluorosulfonic acid at −40° under a nitrogen stream.[26] The fluorosulfonic acid used had been distilled over anhydrous potassium fluoride, placed in tightly glass-stoppered bottles, sealed with paraffin, and stored in a drybox. All transfers of fluorosulfonic acid were made in the drybox by pipet.

Methods. Nmr spectra were determined on a Varian A-60 (60 MHz) or HA-100 (10 MHz) instrument at the operating temperature. Spectra determined on the A-60 at −40 and +40° were no different. Spectra recorded on the 500-Hz scale were internally referenced to tetramethylammonium fluoroborate (TMA, τ 6.87),[27] while those recorded on the 250-Hz scale, without an internal reference, were used for nmr simulation. The scale widths were calibrated with a reference standard immediately before or after each determination. All calculations were carried out on a Control Data Corporation 1604 computer.

Acknowledgments. We are grateful for the technical assistance of Dr. Alan Dow, Mrs. Sharon Alderman, Miss Mary Ann Nucci, and Mr. Alfred Hagadorn[28] in the preparation of some of the samples and determination of some of the spectra.

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(21) R. Breslow, H. Hover, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962).

(22) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(23) D. G. Farnum, *J. Am. Chem. Soc.*, **86**, 934 (1964); G. A. Olah, *ibid.*, **86**, 932 (1964).

(24) R. Breslow and H. Chang, *ibid.*, **83**, 2367 (1961).

(25) D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960).

(26) In the presence of air, a deep purple solution often formed which gave a very diffuse nmr spectrum and gave an esr signal.

(27) D. G. Farnum, M. A. T. Heybey, and B. Webster, *J. Am. Chem. Soc.*, **86**, 673 (1964).

(28) Summer participant (1966) in the National Science Foundation Undergraduate Research Participation Program.