Cyclopropa-arenium Cations. Part II.[1] Carbon-13 Nuclear Magnetic Resonance Spectra of 1-Halogenocyclopropabenzenium Cations and their 1,1-Dihalogeno-precursors [1]

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The ^{13}C n.m.r. spectra of 1-fluorocyclopropabenzenium cation (9), 1-chloro-2,5-diphenylcyclopropabenzenium cation (12), 1-fluoro-2,5-diphenylcyclopropabenzenium cation (13), and their 1,1-dihalogeno-precursors have been measured and the chemical shift differences between the neutral and charged species have been used to estimate the positive charge distributions. These empirical charge density distributions are in qualitative agreement with SCC–EH MO calculations for the parent cyclopropabenzenium ion (8). Only a relatively small amount of charge is delocalised into the phenyl substituents of (12) and (13). For (9) and (13) the significant increase in the values of the $^{13}C-^{19}F$ coupling constants and the reduced total downfield shifts of their carbon atoms compared with (12), indicate a substantial withdrawal of charge by back bonding from the fluorine atom.

THE cation derived from cyclopropabenzene (1) was predicted to be a resonance stabilised aromatic cation in 1952 [2] and again, using more sophisticated MO calculations to allow for ring strain effects, in 1973.[3] Until quite recently, the only evidence available to support the existence of cyclopropabenzenium ions was from the electron-impact induced fragmentation $[P - R^1]^+$ of, for example, (1),[4] (2),[5] (3),[6] and (5).[7] However, both the parent cyclopropabenzenium ion (8) and its derivative (12) have now been postulated as reaction intermediates in solution.[4,8]

More recently we reported the first direct observations (n.m.r.) of cyclopropabenzenium cations, 1-chloro-2,5-diphenylcyclopropabenzenium (12) [1] and 1-fluorocyclo-

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[1] Part I, B. Halton, A. D. Woolhouse, H. M. Hügel, and D. P. Kelly, *J.C.S. Chem. Comm.*, 1974, 247.

[2] J. D. Roberts, A. Streitwieser, and C. M. Regan, *J. Amer. Chem. Soc.*, 1952, **74**, 4579.

[3] B. Halton and M. P. Halton, *Tetrahedron*, 1973, **29**, 1717.

[4] P. Müller, *Helv. Chim. Acta*, 1973, **56**, 500.

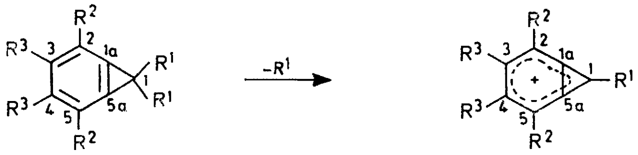
[5] A. Buchs and P. Müller, unpublished data.

[6] H. Dürr and L. Schrader, *Angew. Chem.*, 1969, **81**, 426; *Angew. Chem. Internat. Edn.*, 1969, **8**, 446; *Chem. Ber.*, 1970, **103**, 1334.

[7] B. Halton, *Chem. Rev.*, 1973, **73**, 113.

[8] P. Müller, *J.C.S. Chem. Comm.*, 1973, 895.

propabenzenium (9),[9] prepared by careful ionisation of the corresponding 1,1-dihalogeno-compounds (5) and (2), respectively, in fluorosulphonic acid, and isolation of the unstable hexachloroantimonate of (12).[1] From the



(1)	$R^1 = R^2 = R^3 = H$	(8)
(2)	$R^1 = F; R^2 = R^3 = H$	(9)
(3)	$R^1 = CO_2Me; R^2 = R^3 = Ph$	(10)
(4)	$R^1 = CO_2Me; R^2 = Ph; R^3 = H$	(11)
(5)	$R^1 = Cl; R^2 = Ph; R^3 = H$	(12)
(6)	$R^1 = F; R^2 = Ph; R^3 = H$	(13)
(7)	$R^1 = R^3 = H; R^2 = Ph$	(14)

proton spectrum of (9),[9] it was shown that H(3), H(4) was at lower field (δ 9.20) than H(2), H(5) (δ 8.40) in agreement with the charge density predictions of Halton and Halton.[3] We have now prepared 1-fluoro-2,5-diphenylcyclopropabenzenium cation (13) and in both this ion and (12) [1] H(3),H(4) also occurs at lowest field (δ 9.38 and 9.22,[1] respectively). From the lack of deshielding of the protons of the pendant phenyl rings of (12), we suggested that the amount of charge delocalisation into these rings was small.[1]

TABLE 1

^{13}C N.m.r. parameters for cyclopropabenzenes and cyclopropabenzenium cations [a]

	Compound								
Position	(1) [b]	(2)	(4) [c]	(5)	(6)	(7)	(9)	(12)	(13)
1	18.4	100.3	44.9	60.1	101.6	19.1	148.1	131.2	147.2
1a(5a)	125.4	129.5	128.3	131.6	126.1	127.0	141.1	150.4	134.7
2(5)	114.7	116.0	119.3	130.4	128.6	121.5	119.8	146.4	130.8
3(4)	128.8	134.7	129.4	129.1	132.0	(127.0) [d]	158.3	147.5	148.7
1′(1″)				133.5	133.8	135.8		129.6	128.6
2′(2″)				126.8	126.7	(125.6)		130.5	130.0
3′(3″)				129.1	129.4	128.0		127.8	127.6
4′(4″)				127.9	129.5	(125.6)		133.4	133.0
$^1J_{C(1)F}$		303			300		474.4		461
$^2J_{C(1a)F}$		20			19		2.6		<2
$^3J_{C(2)F}$		1 (175) [e]			1		3.8 (195)		5 [f]
$^4J_{C(3)F}$		2.9 (161)			3		8.3 (170)		9
	$CDCl_3$–CCl_4	$CDCl_3$	$CDCl_3$	THF	THF–$(CD_3)_2CO$	$CDCl_3$	FSO_3H	FSO_3H	FSO_3H

[a] Chemical shifts are ±0.1 p.p.m. from internal Me_4Si for neutral compounds and ±0.1 p.p.m. from external Me_4Si for cations; coupling constants are ±0.5 Hz except for (6) and (13) (±1 Hz). [b] Ref. 15. [c] Ref. 17. [d] Assignments in parentheses may be reversed. [e] Coupling constants in parentheses are the ^{13}C–^1H values. [f] Both the lines at 130.8 and 128.6 showed a small splitting of *ca.* 5 and 7 Hz respectively.

An empirical relationship has been established between π-electron density and ^{13}C chemical shifts in charged aromatic species [10,11] such that $\Delta\delta = 160\Delta q$ where $\Delta\delta$ is the change in chemical shift, and Δq the change in π-electron density, upon ionisation. This relationship has been used successfully to correlate the charge densities in triphenylcyclopropenium [12a] and tetraphenylcyclobutenium [11,13] cations. In order to confirm our suggestion [1] that most of the positive charge resides in the fused ring system of (12), and that the charge density is higher at C(3), C(4) than C(2), C(5),[3] we decided to measure the ^{13}C shifts in these ions and their neutral precursors.

RESULTS AND DISCUSSION

Neutral Compounds.—The ^{13}C spectra were obtained by the Fourier transform technique and the parameters are listed in Table 1. The assignments were made from a consideration of the chemical shifts in model compounds,[14-18] of the magnitude of the ^{13}C–^{19}F coupling constants,[14a,19] of off-resonance spectra, and of relative intensities (and the effect thereon of different spectrometer recycle times *). The shifts for the central ring carbon atoms of 1,1-difluorocyclopropabenzene (2) and 1,1-difluoro-2,5-diphenylcyclopropabenzene (6) can be assigned unambiguously from the magnitude of the ^{13}C–^{19}F coupling constants.[14a,19] A recycle time of 10 s was required before the CF_2 triplet of (6) became clearly

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* Time between successive transmitter pulses.

[9] U. Burger, P. Müller, and L. Zuidema, *Helv. Chim. Acta*, 1974, **57**, 1881.

[10] H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 1961, 468; P. C. Lauterbur, *ibid.*, p. 274.

[11] G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, 1970, **92**, 1430.

[12] (*a*) G. J. Ray, A. K. Colter and, R. J. Kurland, *Chem. Phys. Letters*, 1968, 324; (*b*) G. J. Ray. R. J. Kurland, and A. K. Colter, *Tetrahedron*, 1971, **27**, 735.

[13] A. E. van der Hout-Lodder, J. W. de Haan, L. J. M. van der Ven, and H. M. Buck, *Rec. Trav. chim.*, 1973, **92**, 1040.

[14] (*a*) W. Adcock, B. D. Gupta, T. C. Khar, D. Doddrell, D. Jordan, and W. Kitching, *J. Amer. Chem. Soc.*, 1974, **96**, 1595; (*b*) E. L. Motell, D. Lauer, and G. E. Maciel, *J. Phys. Chem.*, 1973, **77**, 1865.

[15] H. Günther, G. Hikeli, H. Schmickler, and J. Prestien, *Angew. Chem. Internat. Edn.*, 1973, **12**, 762.

[16] D. M. Doddrell and P. R. Wells, *J.C.S. Perkin II*, 1973, 1733.

[17] H. Dürr and H. Kober, personal communication.

[18] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.

[19] J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7107.

visible. The upfield shift of C(2),C(5) compared with C(3),C(4) and the larger value of $J_{^{13}C(2)-H}$ for (2) are in agreement with that observed for cyclopropabenzene (1) itself.[15] This upfield shift of C(2),C(5) and increase in $J_{C(2)-H}$ [and $J_{C(2)-F}$[14a]] with increasing ring strain in the cycloalkabenzenes are not readily rationalised.[15]

The assignments of the quaternary carbon resonances of (5) were made on the basis of relaxation effects. The spectrum of (5), recorded in highly purified tetrahydrofuran due to its rapid decomposition in chloroform or dichloromethane,[20] showed only three quaternary carbon resonances when the recycle time was 2 s (pulse width 30°), one of which (δ 131.6 p.p.m.) was very weak. However, a time of 5 s resulted in a dramatic increase in this weak signal and the appearance of a line at 60.1 p.p.m., the latter being readily assigned to the dichloro-substituted C(1). With this recycle time, the aromatic resonances integrated to *ca.* (low to high field) 1 : 1 : 2+1 : 1 : 2 indicating a nearly equal Overhauser enhancement for these carbons.[21] Since C(1a),C(5a) is furthest away from the nearest proton compared with C(2),C(5) and C(1'),C(1''), it was assigned to the resonance at 131.6 p.p.m. (assuming domination by dipole–dipole relaxation). Carbons 2(5) and 1'(1'') and the protonated carbon atoms were assigned on the basis of the shifts in diphenyl, terphenyl,[18] and terphenic acid. Data for the dihydrogen (7) and bismethoxycarbonyl (4)[17] derivatives are included in Table 1 for comparison purposes.

Carbocations.—Since the ^1H spectra of the ions (9),[9] (12),[1] and (13) show H(3),H(4) at lowest field [(9), δ 9.20;[9] (12) δ 9.22;[1] (13) δ 9.38)], resonances of the proton-bearing carbons at 158.3 (9), 147.5 (12), and 148.7 p.p.m. (13) were readily assigned to C(3),C(4) (Figures 1—3) and confirmed by single frequency decoupling experiments. These chemical shifts are similar to that observed for the tropylium cation (156.1 p.p.m.)[10] and are thus consistent with the formulation of the ions as 1,3-bridged tropylium cations. The remaining two low field quaternary carbon resonances of (12) were assigned to C(1a),C(5a) and C(2),C(5) [in the same relative order as for (5)]. The only other possibility is that one of these lines is due to C(1'),C(1''), but this is unlikely since the corresponding carbons in phenyl cations, where the positive charge is much more localised, resonate at significantly higher field.*

The quaternary carbon resonance at 129.6 p.p.m. and the protonated carbon resonances of (12) were assigned according to well established effects of charge adjacent to phenyl groups. In triphenyl[12b] and dimethylphenylcarbenium[22] ions, tetraphenylcyclobutenium monocation,[13] triphenylcyclopropenium[12a] and diphenylcyclopropenone,[23] *ortho*- and *para*-carbon are always deshielded with respect to *meta*- and *ipso*-carbon. The assignment of C(1') to the line at 129.6 p.p.m. is consistent with these data. The line at 131.2 p.p.m. was therefore assigned to C(1) (the reverse assignment would be inconsistent with the data for other phenyl cations). Of the three quaternary carbon resonances of (13), the one at δ 134.7 p.p.m. showed the smallest splitting and was assigned to C(1a),C(5a) by analogy with (9). Those

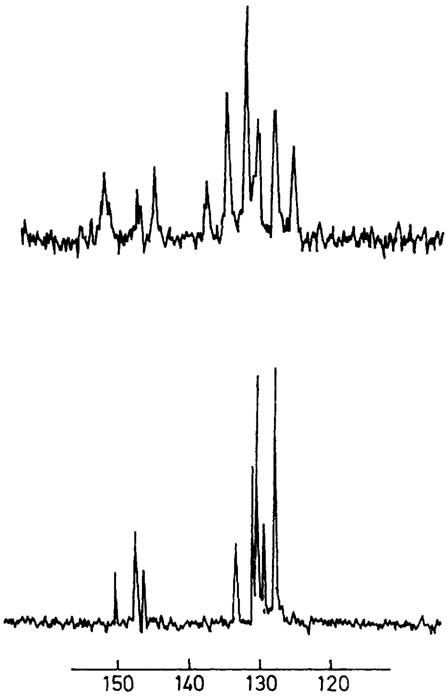

FIGURE 1 ^{13}C Fourier transform n.m.r. spectrum of 1-chloro-2,5-diphenylcyclopropabenzenium cation (12) at 15.08 MHz in FSO_3H at −20°: lower, ^1H noise decoupled; upper, ^1H off-resonance decoupled

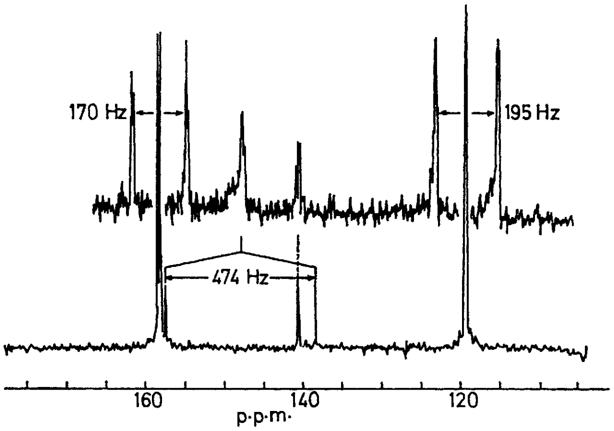

FIGURE 2 ^{13}C Fourier transform n.m.r. spectrum of 1-fluorocyclopropabenzenium cation (9) at 25.2 MHz in FSO_3H at −60°: lower, ^1H noise decoupled; upper, ^{19}F noise decoupled

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* The quaternary *ipso*-carbon resonance in phenyl-substituted cations varies considerably, but within the range from 119.2 (for triphenylcyclopropenium)[12a] to 139.9 p.p.m. (for triphenylcarbenium).[12b]

[20] A. R. Browne, B. Halton, H. M. Hügel, and D. P. Kelly, unpublished data.

[21] A. Allerhand, D. M. Doddrell, and R. Komoroski, *J. Chem. Phys.*, 1971, **55**, 189.

[22] G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, 1973, **95**, 7530.

[23] M. T. W. Hearn and K. T. Potts, *J.C.S. Perkin II*, 1974, 1918.

at δ 130.8 and 128.6 both showed long range coupling with fluorine of *ca.* 5 and 7 Hz respectively. They were assigned to C(2),C(5) and C(1′),C(1″) respectively, which appeared most consistent with the data for the other compounds (Table 1).

In order to attempt a correlation between the change in ^{13}C shift (Δδ) upon ionisation of (5) to (12) and the calculated charge densities,[3] an estimate of the charge contribution to the downfield shift of C(1) (60.1 → 131.2 p.p.m.) is required. Upon ionisation of (5), the shielding at C(1) is influenced by (a) loss of a chlorine atom, (b) rehybridisation, and (c) the presence of some positive charge. An estimate of (a) and (b) can be made from a consideration of the shifts in 1,1-dichloroethane [C(1), δ 69.2] and vinyl chloride [C(1), δ 126.1],[18] a downfield shift of *ca.* 57 p.p.m. This leads to an estimate for C(1) of (12) at 117 p.p.m. (60 + 57) without the influence of any positive charge (and, of course, assuming that there is no change in the diamagnetic screening contributions to the chemical shift upon ionisation) and a value of 14.2 p.p.m. (131.2—117) for the positive charge contribution to ΔδC(1).

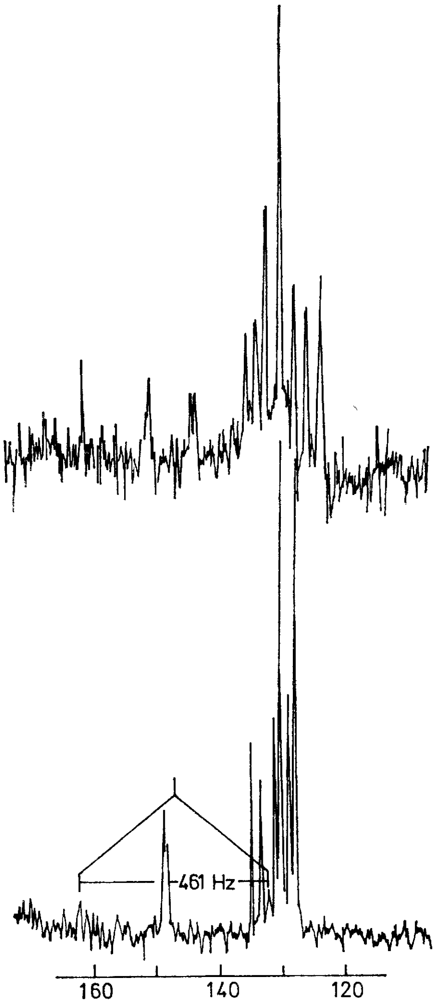

FIGURE 3 ^{13}C Fourier transform n.m.r. spectrum of 1-fluoro-2,5-diphenylcyclopropabenzenium cation (13) at 15.08 MHz in FSO_3H at −20°: lower, ^{1}H noise decoupled; upper, ^{1}H off-resonance decoupled

A similar estimate may be made for C(1) of (9) and (13), although in this case the shift of C(1) in 1,1-difluoroethane is not available.[24] A value of 125 p.p.m. may be estimated from 1,1-dihalogenomethanes and 1,1-dihalogenoethanes,[18,24] and with the value for vinyl fluoride [C(1), δ 148] [24] leads to an expected downfield shift of *ca.* 123 (100.3 + 23) for (9) and 125 p.p.m. for (13) without the effect of any positive charge. The latter is therefore estimated (with the same assumptions as before) as 25 for C(1) of (9) and 23 p.p.m. for C(1) of (13).

Charge Density Distributions.—Ray *et al.* [12b] used the difference between the ^{13}C shifts in *para*-substituted triphenylcarbenium ions and the corresponding triphenylcarbinols to measure the charge density distributions in these ions. The latter were in good agreement with those calculated by the CNDO method. Since the central carbon atoms of the carbinols change hybridisation on formation of the ions, these authors used the chemical shift differences between the cationic carbon of the t-butyl cation [25] and that of the triphenylcarbenium ions to estimate the charge density at the central carbon atoms.

In the case of ions (9), (12), and (13), this approach is not available, and so the charge contribution to the difference in chemical shift has been estimated as outlined in the previous section. The differences in the shifts (Δδ) between the cations (9), (12), and (13) and their precursors (2), (5), and (6) are shown in Table 2, together with the empirical percent charge density (Δ*q*′) and that determined by the SCC–EH MO calculations for the parent ion (8).[3]

While the numerical values of Table 2 are best used in a qualitative sense, it is immediately obvious that the total downfield shifts (ΣΔδ) for these cyclopropabenzenium ions are significantly less than the 160 p.p.m. required by the empirical relationship.[10] This could be due to (a) factors other than π-charge density affecting the chemical shifts, (b) poor estimates of the contribution of charge density to the deshielding of C(1), and/or (c) perturbation of the charge density distribution by the chlorine [(12)] and fluorine [(9) and (13)] atoms. However, in view of the previous successful application of the Spiesecke and Schneider equation to aromatic cations,[11,12b,13] and the fact that anomalously large downfield shifts would be required at C(1) to make up the deficiency in ΣΔδ, we favour factor (c) as that most responsible for the discrepancy.

In a series of alicyclic 1-halogenocarbenium ions, for example, (15) and (17), Olah *et al.*[26] observed that the 1-fluoro-cationic carbons absorb at *higher* field strengths

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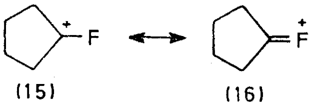
[24] P. D. Ellis, personal communication.

[25] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, 1969, **91**, 5801.

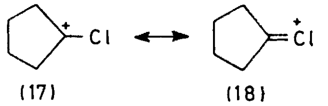
[26] G. A. Olah, G. Liang, and Y. K. Mo, *J. Org. Chem.*, 1974, **39**, 2394.

than those of the corresponding 1-chlorocations. This, and the large values of the $^{13}C-^{19}F$ coupling constants observed, were interpreted as due to a significant contribution from structures of type (16). The back-bonding in (16) would be expected to be more significant than in (18).



(15) (16)

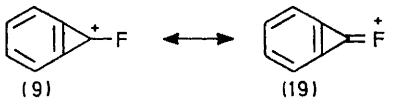
δ(C+) 294($^{1}J_{CF}$439Hz)



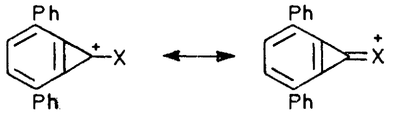
(17) (18)

δ(C+) 316

Our results for (9), (12), and (13) are consistent with the idea of significant contributions from resonance structures (19)—(21) reducing the total downfield shifts of the carbon ring systems [(19) and (21) > (20)]. This is further supported by the very large values of $^{1}J_{CF}$, 474 and 461 Hz, to our knowledge, the largest $^{13}C-^{19}F$ couplings observed. The most significant contribution to the increase in the magnitude of $^{1}J_{CF}$ on ionisation of (2) and (6) can be ascribed to an increase in the *s* electron density at both the carbon and fluorine nuclei due to positive charge. This increase in $|J_{CF}|$ is therefore consistent with a large increase in π-bond character between carbon and fluorine.[18]



(9) (19)



(12) X = Cl (20) X = Cl

(13) X = F (21) X = F

TABLE 2

Calculated and empirical charge density distributions in cyclopropabenzenium cations

	Ion							
	(8)[a]		(9)[b]		(12)[b]		(13)[b]	
Position	Planar	Non-planar[c]	Δδ	Δq′	Δδ	Δq′	Δδ	Δq′
1	28.9	27.9	25.0	15.6	14.2	8.9	23.0	14.4
(1a)5a)	10.5	10.1	11.5	7.2	18.8	11.7	8.6	5.4
2(5)	12.2	12.8	3.8	2.4	16.0	10.0	2.2	1.4
3(4)	12.9	13.1	23.5	14.7	18.4	11.5	16.7	10.4
Ph					12.8[d]	8.0	2.6[d]	1.6
ΣΔδ			102.6		133.4		80.6	

[a] Calculated percent positive charge density from ref. 3. [b] Empirical percentage positive charge density calculated from $\Delta\delta = 1.60\Delta q'$. [c] H(1) out of plane of the ring system (see ref. 3). [d] Total net downfield shifts for all carbons of *both* phenyl substituents.

The suggestion that the fluorine atom perturbs the charge distribution to a greater extent than the chlorine atom, can also be seen from the downfield shifts (Δδ) at each position in (9), (12), and (13). Whereas Δδ is approximately the same for each carbon in (12) [C(1)—(3), Table 2], large variations (2—25 p.p.m.) are observed in (9) and (13).

From the data in Table 2 it may be concluded that 90—97% (based on ΣΔδ) of the charge is in the central rings of (12) and (13) confirming our suggestion from the ^{1}H data for (12), that little charge is delocalised into the phenyl rings. Furthermore, of the charge residing on the bicyclic ring system (ΣΔδ 120.6, 78.0) of (12) and (13), *ca.* 45% is on the three-membered ring system compared to 48—50% calculated for the parent ion (8).[3] The chemical shift data for C(2),C(5) and C(3),C(4) in the three ions are also consistent with higher positive charge at C(3),C(4), as predicted by the MO calculations.[3]

EXPERIMENTAL

Ion Preparation.—*Method A.* 1,1-Dichloro-2,5-diphenylcyclopropabenzene[27] (0.043 g) (or 1,1-difluoro-[28] or 1,1-difluoro-2,5-diphenyl-cyclopropabenzene[8]) was placed in a tube and cooled to −78° under nitrogen and in a dry box. Pre-cooled, freshly distilled fluorosulphonic acid (0.9 cm³) was added dropwise directly to the solid. The resulting greenish yellow suspension was stirred on a vortex mixer and warmed to −40°. At this temperature ionisation occurred to yield an orange solution of 1-chloro-2,5-diphenylcyclopropabenzenium cation (12), ^{1}H n.m.r. δ (−17°) 9.22 (2 H, s), 8.2 (4 H, m), and 7.8 (6 H, m);[1] or 1-fluorocyclopropabenzenium cation (9), ^{1}H n.m.r. δ (−50°) 9.20 (2 H, m) and 8.40 (2 H, m, J_{HF} 9.0 Hz);[9] or 1-fluoro-2,5-diphenylcyclopropabenzenium cation (13), ^{1}H n.m.r. δ (−20°) 9.38 (2 H, s), 8.23 (4 H, m), and 7.85 (6 H, m).

Method B. 1,1-Dichloro-2,5-diphenylcyclopropabenzene[27] (0.084 g) in dichloromethane (4.0 cm³) was cooled under nitrogen and in a dry box, until the solution became cloudy. Antimony pentachloride (0.09 g) was added dropwise with stirring to the cold solution. A bright orange precipitate formed immediately, was removed by vacuum filtration, washed with precooled (−40°) dichloromethane, and dried. The orange solid, 1-chloro-2,5-diphenylcyclo-

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[27] B. Halton and P. J. Milsom, *Chem. Comm.*, 1971, 814.

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propabenzenium hexachloroantimonate, was transferred to an n.m.r. tube and dissolved in precooled chlorosulphonic acid (1.0 cm^3). The ^{1}H n.m.r. spectrum was identical with that obtained by method A.

N.m.r. Measurements.—The natural abundance ^{13}C spectra of (5), (6), (12), and (13) were recorded on a Varian HA-60IL spectrometer, operating at 15.08 MHz and modified with a Digilab frequency synthesiser, deuterium lock system, and pulse amplifier. The pulse programmer and computer interface were home-built and the data acquisition and processing were performed in a DEC PDP-15 computer with 16 k core (for further details see ref. 29). The chemical shifts ($\pm$0.1 p.p.m.) were measured from internal [(5), (6)] or external [(12), (13)] Me_4Si. No bulk susceptibility correction has been made in the case of the external reference. The spectra of compounds (2), (7), and (9) were recorded on a Varian XL-100 FT spectrometer operating at 25.2 MHz. One spectrum of (6) was recorded on a Bruker WH90 spectrometer operating at 22.63 MHz, for which we thank Dr. I. D. Rae and Mr. M. Hughes of Monash University, and that of (7) on an analogous instrument by courtesy of Firmenich S. A. Genève.

We gratefully acknowledge support of this work by the New Zealand Universities Grants Committee, Victoria University, the Australian Research Grants Committee, the Swiss National Science Foundation, and Fonds Phillipe Chuit of the Societé Academique de Genève. We thank Dr. M. T. W. Hearn for a copy of ref. 23 prior to publication.

[5/575 *Received, 24th March,* 1975]

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