Novel Aromatic Systems. 4. Cyclobutadiene Dications[1]

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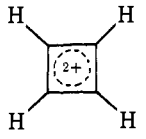
Abstract: The tetraphenyl- (**2**), 1,2-difluoro-3,4-diphenyl- (**6**), 1,2-diphenyl- (**7**), and tetramethylcyclobutadiene (**5**) dications have been prepared under stable ion conditions and studied by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of the phenylated cyclobutadiene dications indicate that the aromatic 2π-electron cyclobutenediylium ring interacts mesomerically with the phenyl rings and accepts a significant amount of π-electron density from them. The degree of conjugative interaction between phenyl substituents and the aromatic cation is shown to be greater in the cyclobutadiene dication system than in the cyclopropenium system. Evidence has also been obtained for the existence of the 1,2-dimethylcyclobutadiene dication, which is quenched in superacidic solution to the related 4-fluorocyclobutenyl cation by the fluoroantimonate counterion. These results are discussed in terms of the relative ability of phenyl and alkyl substituents to contribute to stabilization of cations (dications) in the cyclobutadiene and cyclopropene systems. Further, a rationale is provided for the reversal of the trends observed in these two Hückeloid systems. The question as to whether the NMR spectroscopic observations of cyclobutadiene dications correspond to several species in dynamic equilibrium or to static, nonequilibrating dications has also been systematically investigated and unequivocal evidence for the latter is presented.

Introduction

Simple molecular-orbital theory and Hückel's rule predict that the cyclobutadiene dication **1** should have aromatic character because it is a planar, monocyclic system containing



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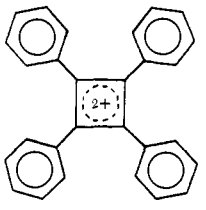
two $[4n + 2\ (n = 0)]$ π electrons.[2,3] In contrast to the four π-electron parent cyclobutadiene, the cyclobutadiene dication is predicted to possess a positive delocalization energy and not be subject to Jahn-Teller distortion forces.[2,3] At the same time considerable charge-charge repulsion arising from the dispersion of two units of positive charge over only four carbon centers and the possible presence of a set of degenerate, vacant, bonding-level molecular orbitals are expected to counteract the stabilizing electronic features of this Hückeloid system and possibly present difficulties in the preparation of stable cyclobutadiene dications.[3d,e] The relative importance of these destabilizing influences might, however, be attenuated in suitably substituted derivatives. The preparation of cyclobutadiene dications thus represents a challenging synthetic problem of considerable interest.

The preparation of the first cyclobutadiene dication, as the tetraphenyl substituted derivative **2,** was claimed by Freedman in 1962 by ionization of 3,4-dibromotetraphenylcyclobutene with stannic chloride.[4] The claim was based primarily on the apparent equivalence of the phenyl groups in the ^{1}H NMR of



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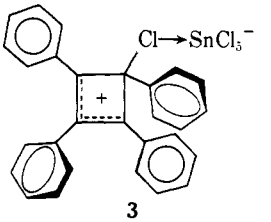
this system. The reported ^{1}H NMR shifts, however, were not consistent with those anticipated of the dication **2.** Subsequent x-ray crystallographic study of the isolated salt indeed showed that only the monocation monodonor-acceptor complex **3** was obtained.[5] Subsequently, Freedman and Young also studied the metathetic reaction of 3,4-dibromotetraphenylcyclobutene



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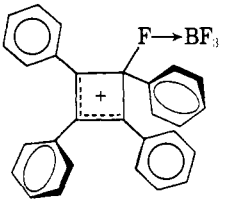
with silver tetrafluoroborate in methylene chloride solution.[6] In the reaction, which may have indeed involved the intermediate dication, 2 mol equiv of silver bromide were eliminated and the ^{19}F NMR spectrum of the solution showed the formation of the tetrafluoroborate anion. Unfortunately, no further spectral characterizations were performed and these reported data alone do not differentiate between the preparation of a rapidly exchanging 4-fluorocyclobutenyl cation-BF_3 system (**4**) and the dication **2.**



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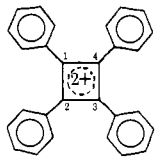
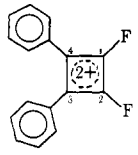
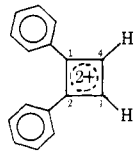
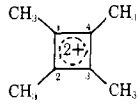
Katz and co-workers have similarly attempted preparation of the tetramethylcyclobutadiene dication (**5**), but were unsuccessful.[7a,b] The preparation of bona fide cyclobutadiene dications has thus remained a challenge.[7c]

In two preliminary communications one of us with Bollinger and White,[1b] and with Mateesen,[1c] respectively, reported the preparation and characterization by ^{1}H and ^{13}C NMR spectroscopy of the tetraphenyl-[1c] and tetramethylcyclobutadiene dications.[1b] We now wish to report in detail our studies on these ions as well as those of the related 1,2-difluoro-3,4-diphenyl- (**6**) and 1,2-diphenylcyclobutadiene dications (**7**). In all cases systematic ^{1}H and ^{13}C NMR spectroscopic studies were carried out which fully establish their structures. In addition, we have obtained evidence for the existence of the 1,2-dimethylcyclobutadiene dication as a transient intermediate which is not stable relative to 4-fluorocyclobutenyl cation formation, and hence provides information on the relative ability of phenyl and alkyl substituents to contribute to cyclobutadiene dication formation.

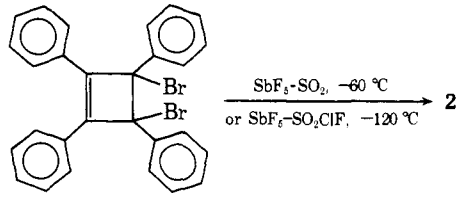
Table I. ^{1}H NMR Parameters for Cyclobutadiene Dications

	Chemical shifts and apparent multiplicities[a]				
		Phenyl			
	Cyclobutenediylium	Meta	Ortho	Para	Methyl
 2		7.87 (t)[c,d,e] 8.40 (t)[b,f]	8.64 (d) 9.14 (d)	8.26 (t) 8.72 (t)	
 6		8.55 (t)[b,g,h]	9.0–9.4 (m)		
 7	10.68 (s)[c,i]	8.6–8.9 (m)	9.2–9.6 (m)		
 5					3.68 (s)[b,e] 4.11 (s)[b,j]

[a] Chemical shifts are in parts per million from external (capillary) Me_4Si. Apparent multiplicities are in parentheses: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. [b] Spectrum recorded on a Varian Associates A56/60 NMR spectrometer. [c] Spectrum recorded on a Varian Associates HA-100 NMR spectrometer. [d] The best fitting NMR parameters of **2** in SbF_5–SO_2 solution at −40 °C were obtained from a computer-simulated spectrum (program, LAOCOON III by A. A. Bothner-By and S. Castellano; computer, CWRU Chi Univac 1108; plotter, CALCOMP 663: δ_o 8.644; δ_p 8.263; δ_m 7.868; $J_{o,m} = J_{o'm'} = 8.05$; $J_{op} = J_{o'p} = 1.15$; $J_{om'} = J_{o'm} = 0.30$; $J_{oo'} = 2.0$; $J_{mp} = J_{m'p} = 7.40$; $J_{mm'} = 0.80$ Hz. [e] In SbF_5–SO_2 solution at −40 °C. [f] In SbF_5–FSO_3H solution at −60 °C. [g] In SbF_5–SO_2ClF solution at −60 °C. [h] Additional couplings are apparent in this resonance; the separations of the main lines of this triplet are approximately 7 Hz. [i] In SbF_5–SO_2ClF solution at −10 °C. [j] In SbF_5–SO_2ClF solution at −50 °C.

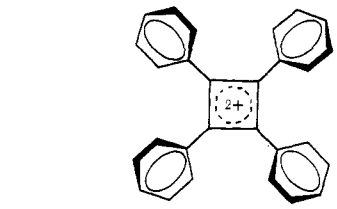
Results and Discussion

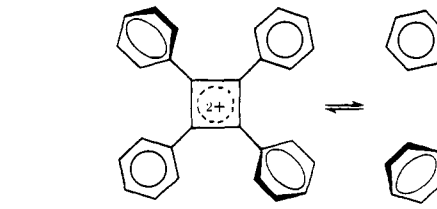
1. Tetraphenylcyclobutadiene Dication. When a suspension of 3,4-dibromotetraphenylcyclobutene[8] in SO_2 was added with vigorous stirring at about −60 °C to a saturated solution of antimony pentafluoride in SO_2, a dark red solution of **2** was obtained. A similar solution may be obtained by ionization of



the dibromide in SbF_5-SO_2ClF at temperatures as low as −120 °C. Methanolysis of an SbF_5-SO_2 solution of **2** in CH_3OH-CH_3ONa at −78 °C resulted in the exclusive isolation of a mixture of *cis*- and *trans*-3,4-dimethoxytetraphenylcyclobutene. The isomeric ratio was 64:36, but the stereochemistry of the products was not assigned.

The ^{1}H NMR spectrum (100 MHz) of **2** in SbF_5-SO_2 solution at −40 °C consists of a doublet at δ 8.64, a triplet at δ 8.26, and a triplet at δ 7.87 of relative area 2:1:2, respectively. These resonances are hence assigned to the ortho, para, and meta protons of the equivalent phenyl rings, respectively (Table I, Figure 1). Because steric repulsions most probably preclude the simultaneous coplanarity of the four phenyl substituents with the cyclobutenediylium ring in **2**,[9] the observed symmetry of the ^{1}H NMR spectrum is most reasonably interpreted as resulting from either a static structure in **2a**, in which all four


2a


2b 2c

phenyl substituents are twisted slightly out of the plane of the four-membered ring, or from a dynamic degenerate system of structures **2b** and **2c**, in which one set of diagonally opposed phenyl substituents is coplanar with the cyclobutenediylium ring, while the remaining set is markedly rotated out of this plane. The highly deshielded para-phenyl protons indicates that a substantial amount of π-electron density is conjugatively delocalized from the phenyl groups into the cyclobutenediylium ring.[10]

The FT ^{13}C NMR spectrum of **2** in SbF_5-SO_2 solution exhibits resonances at δ 173.4 (s), 121.3 (s), 139.1 (d, 160.2), 132.7 (d, 163.4), and 148.6 (d, 172.9), which are assigned to the cyclobutenediylium (C(1,2,3,4)), the ipso-phenyl, ortho-

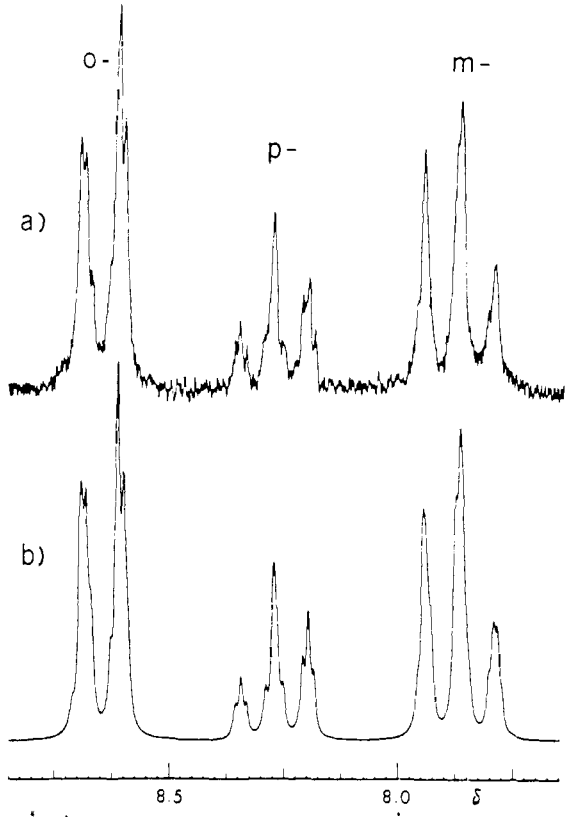


Figure 1. The 100-MHz ^1H NMR spectrum of the tetraphenylcyclobutadiene dication (**2**) in SbF_5–SO_2 solution at −40 °C (a) and the computer-similated spectrum (b) (see Table I, footnote *d*).

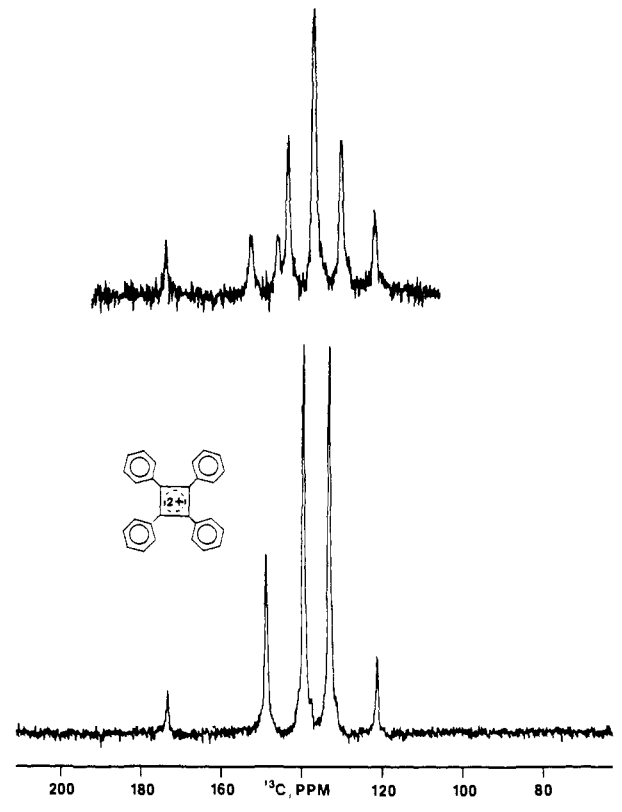
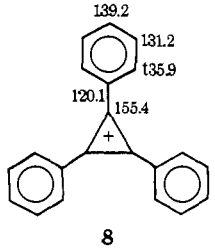


Figure 2. The 25.16-MHz ^{13}C NMR spectrum of the tetraphenylcyclobutadiene dication (**2**) in SbF_5–SO_2 solution at −60 °C. The lower portion is the proton noise-decoupled spectrum and the upper is the fully coupled gyro-gate spectrum.

phenyl, meta-phenyl, and para-phenyl carbons, respectively (Table II, Figure 2). As in the case of the ^1H NMR of **2**, the symmetry of the spectrum indicates the equivalence of the four phenyl rings, but does not allow differentiation to be made as to whether this arises from their simultaneous isochronism or from equilibration of the dynamic degenerate systems **2b** and **2c**.

Carbon-13 NMR shieldings of aromatic systems have been demonstrated to be primarily dependent upon the local π-electron density (ρ) at each carbon nucleus.[2a,10a,11] A least-squares analysis of the data obtained for 2π-, 6π-, and 10π-electron monocyclic aromatics indicates the relationship for these systems to be $\delta_{^{13}C} = -159.5\rho + 288.5$.[12] Utilizing this correlation (Spiesecke–Schneider correlation) the dicationic nature of **2** may be readily demonstrated by comparison of its carbon-13 NMR shieldings with those of the triphenylcyclopropenium cation (**8**).[13] Although differences exist between the cyclobutenediylium and cyclopropenium carbon hybridizations, the observation that the cyclopropenium cation (**9**) shows no large deviation from the Spiesecke–Schneider plot of larger-ring aromatic systems[2a,11a,c,d] strongly suggests that the error introduced into a comparison of the ^{13}C NMR shieldings of **2** with those of **8** arising from these hybridization differences should be minimal. Moreover, the correspondence of the structural array of the atoms in **8** with those in **2** diminishes differences in the ^{13}C NMR shieldings of the two systems arising from neighboring-group effects.[14] Since by symmetry C(1), C(2), and C(3) and their corresponding phenyl substituents in **2** possess 19.5 π electrons, whereas the triphenylcyclopropenium ion possesses 20 π electrons, the Spiesecke–Schneider relationship predicts, in the absence of any other differences, that the total ^{13}C NMR shieldings of C(1), C(2), and C(3) and their phenyl substituents in **2** should exceed the total ^{13}C NMR shieldings of **8** by 79.8 ppm.[12] The observed difference is in the predicted direction and has a magnitude of 114.0 ppm, which is in good agreement with the dicationic formulation of **2**. Moreover, this conclusion is only reinforced by the observation that the *average* ^{13}C NMR shielding observed in the 26π-electron, 28C **2** is δ 141.0, which is in good accord with the *average* ^{13}C NMR shielding of δ 144.3 predicted for **2** by a related Spiesecke–Schneider treatment which correlates *average* π-electron densities to *average* ^{13}C NMR chemical shifts in fully conjugated π systems ($\delta_{^{13}C,av} = -156.8\rho_{av} + 289.9$).[11h]

Studies similar to those of Spiesecke and Schneider[10a,11b] have related the para-carbon ^{13}C NMR shieldings of monosubstituted benzenes to the π-electron density (ρ) at this position with the correlation $\delta_{^{13}C,p} = -166.6\rho + 284.4$.[11f] The resonances of the para-phenyl carbons in **2** at δ 148.6 and their 15.9-ppm deshielding relative to the related meta-phenyl carbon shieldings thus dramatically demonstrate the mesomeric π-electron donation of the phenyl substituents into the cyclobutenediylium ring.[10a,11c,d,f] Moreover, comparison of the para-phenyl carbon ^{13}C NMR shieldings of **2** (δ 148.6) with those of **8** (δ 139.2)[13] indicates that the conjugative electron demand of the cyclobutenediylium ring on phenyl substituents is substantially greater than that of the cyclopropenium ring. This observation is in accord with recent INDO calculations of the two systems[3e,15] and presumably reflects the decreased number of π electrons per ring carbon and concomitant increased coulombic repulsions of the cy-



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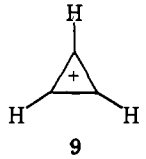

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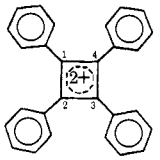
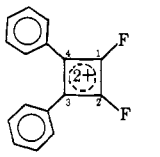
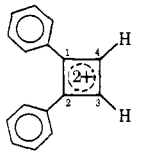
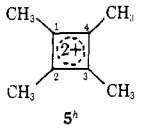
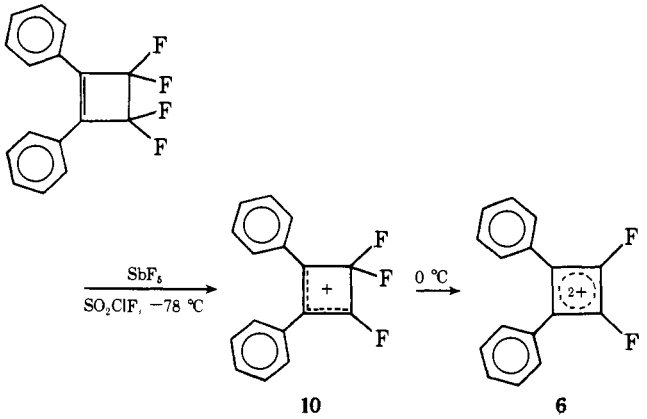
Table II. ^{13}C NMR Parameters for Cyclobutadiene Dications

	Chemical shifts, multiplicities, and coupling constants[a]						
	Cyclobutenediylium		Phenyl				
	C(1,2)	C(3,4)	C_{ipso}	C_o	C_m	C_p	Methyl
 2[b]	173.4 (s)	173.4 (s)	121.3 (s)	139.1 (s) $^1J_{CH}$ = 160.2	132.7 (d) $^1J_{CH}$ = 163.4	148.6 (d) $^1J_{CH}$ = 172.9	
 6[c]	173.8 (d, br) $^1J_{CF}$ = 396.0[d,e]	184.0 (m)[d]	129.3 (m)[d]	143.9 (d) $^1J_{CH}$ = 170.0 148.2 (d) $^1J_{CH}$ = 171.3	136.2 (d) $^1J_{CH}$ = 178.7	165.3 (d) $^1J_{CH}$ = 172.3	
 7[f]	190.9 (s)	182.1 (d) $^1J_{CH}$ = 209.6[e,g]	125.3 (s)	144.5 (d) $^1J_{CH}$ = 174.2 148.2 (d) $^1J_{CH}$ = 166.3	135.3 (d) $^1J_{CH}$ = 172.1	163.0 (d) $^1J_{CH}$ = 171.8	
 5[h]	209.7 (s)	209.7 (s)					18.8 (q) $^1J_{CH}$ = 137.3

[a] Chemical shifts are in parts per million from external (capillary) Me_4Si; coupling constants are in hertz. Multiplicities are given in parentheses. s = singlet, d = doublet, q = quartet, m = multiplet, br = broad. [b] In SbF_5–SO_2 solution at −60 °C. The ^{13}C NMR parameters of **2** reported here are from the FT ^{13}C NMR spectra obtained on the Varian Associates XL-100 NMR spectrometer. Hence the values of these parameters vary slightly from those reported in ref 1c, which were obtained by the INDOR method. [c] In SbF_5–SO_2ClF solution at −60 °C. [d] These resonances are complex multiplets in the ^1H-decoupled ^{13}C NMR spectrum of **6** due to couplings between these ^{13}C's and the two chemically nonequivalent fluorine atoms and correspond to the X parts of ABX spin systems (see F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 2361 (1971) and J. D. Roberts, "An Introduction to the Analysis of Spin–Spin Splitting in Nuclear Magnetic Resonance", W. A. Benjamin, New York, N.Y., 1962, pp 71–85). [e] Although this is the X portion of an ABX spin system, the $^1J_{AX}$ quoted here, which was obtained by subtraction of the frequencies of resonance of the centers of the two multiplets, will be reasonably close to the actual $^1J_{AX}$ since $^1J_{AX} \gg (\nu_A - \nu_B), J_{BX}, J_{AB}$. [f] In SbF_5–SO_2ClF solution at −50 °C. [g] This resonance in the ^1H-coupled ^{13}C NMR of **7** is the X part of an ABX spin system (see references quoted in footnote *d*). [h] In SbF_5–FSO_3H solution at −60 °C. The ^{13}C NMR parameters of **5** reported here are from the FT ^{13}C NMR spectra obtained on the Varian Associates XL-100 NMR spectrometer. Hence the values of these parameters vary slightly from those reported in ref 1b, which were obtained by the INDOR method.

clobutenediylium system relative to the cyclopropenium system.

2. 1,2-Difluoro-3,4-diphenylcyclobutadiene Dication. The addition of a suspension of 1,2-diphenyl-3,3,4,4-tetrafluorocyclobutene[16] in SO_2ClF to an SbF_5–SO_2ClF solution at −78 °C resulted in the formation of the 1,2-diphenyl-3,4,4-trifluorocyclobutenyl cation (**10**, Tables III, IV, and V). Warming this SbF_5–SO_2ClF solution of **10** to 0 °C for approximately 3 min resulted in the quantitative, irreversible conversion of **10** to the 1,2-difluoro-3,4-diphenylcyclobutadiene dication (**6**).



10 **6**

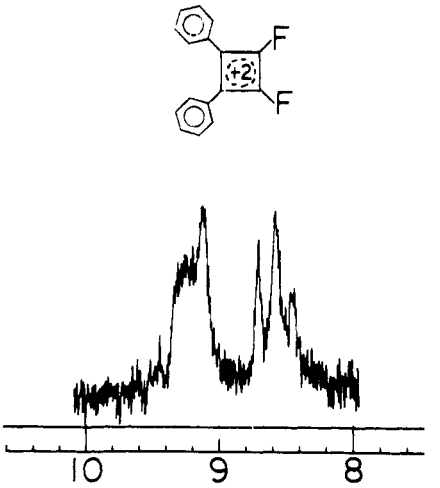
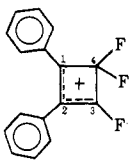
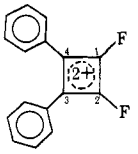
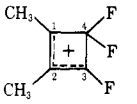
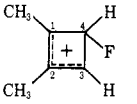
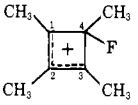


Figure 3. The 60-MHz ^1H NMR spectrum of the 1,2-difluoro-3,4-diphenylcyclobutadiene dication (**6**) in SbF_5–SO_2ClF solution at −60 °C.

The ^1H NMR (60 MHz) of **6** in SbF_5–SO_2ClF solution at −60 °C consists of a triplet with fine structure at δ 8.55 and a complex unresolved multiplet resonance centered at δ 9.2 (Figure 3). Integration of the low- and high-field resonances indicated their relative areas to be in the ratio of 6:4, respec-

Table III. ^{19}F NMR Parameters for Cyclobutadiene Dications and Related Cyclobutenyl Cations

	Chemical shifts, multiplicities, and coupling constants[a]	
	Vinylic fluorine	Fluorine on saturated carbon
 10[b]	26.9 (t, br) $^3J_{FF}$ = 9.0	101.5 (d, br) $^3J_{FF}$ = 9.0
 6[b]	27.0 (s, br)	
 18[c]	−18.9 (t, q) $^3J_{FF}$ = 11.0 $^5J_{FH}$ = 4.0	98.3 (d, q) $^3J_{FF}$ = 11.0 $^5J_{FH}$ = 3.5
 23[d]		154.0 (d, br) $^2J_{FH}$ = 64.0
 32[e]		113.8 (q, q) $^3J_{FH}$ = 19.9 $^5J_{FH}$ = 2.7

[a] Chemical shifts are in parts per million from external (capillary) $CFCl_3$; coupling constants are in hertz. Multiplicities are given in parentheses: s = singlet d = doublet, t = triplet, q = quartet, br = broad. [b] In SbF_5–SO_2ClF solution at −85 °C. [c] In SbF_5–SO_2ClF solution at −60 °C. [d] In SbF_5–SO_2ClF solution at −80 °C. [e] In SO_2 solution at −40 °C.

tively. The triplet at δ 8.55 was thus assigned to the meta-phenyl protons and the complex unresolved multiplet at δ 9.2 was indicated to be the coincident multiplets of the ortho- and para-phenyl protons (Table I).

^1H NMR chemical shifts of the para protons of monosubstituted benzenes have been shown to depend primarily upon the π-electron density (ρ) at the para-carbon nuclei.[10] On this basis, the comparison of the ^1H NMR shifts of the para-phenyl protons of **6** (ca. δ 9.2) with those of the tetraphenylcyclobutadiene dication (δ 8.83) suggests that the conjugative π-electron demand upon the phenyl substituents by the cyclobutenediylium ring is greater in **6** than in **2**. This argument is strengthened by the observation that the ^1H NMR shifts of the meta-phenyl protons, which would not be expected to directly reflect variations in the degree of mesomeric interaction of the phenyl ring, are indeed similar in **6** (δ 8.40) and **2** (δ 8.55).

The FT ^{13}C NMR of **6** in SbF_5–SO_2ClF solution at −60 °C consists of seven resonances at δ 173.8 ($^1J_{CF}$ = 396.0), 184.0 (s), 129.3 (s), 136.2 (d, 178.7), 165.3 (d, 172.3), 143.9 (d, 170.0), and 148.2 (d, 171.3), which are assigned to the fluorinated cyclobutenediylium (C(1,2)), phenylated cyclobutenediylium (C(3,4)), ipso-phenyl, meta-phenyl, para-phenyl, and the magnetically nonequivalent ortho-phenyl carbons, respectively (Table II, Figure 4). The chemical equivalence of the two phenyl substituents in the equilibrium geometry of the 1,2-diphenyl-3,4-difluorocyclobutadiene dication is thus demonstrated, as the observed symmetry in the ^{13}C NMR of **6** is not easily rationalized on any other basis.

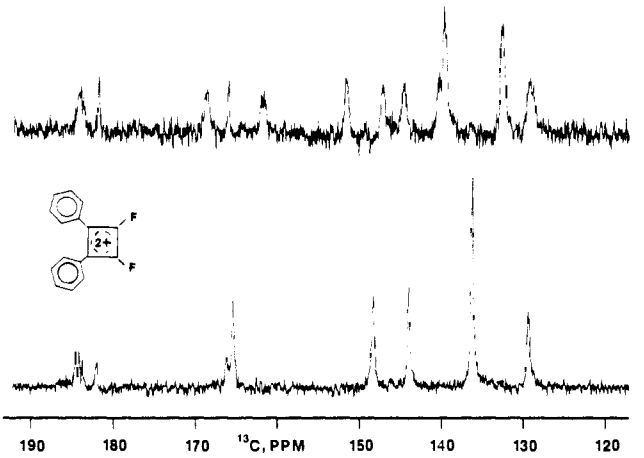
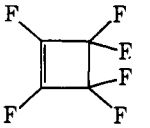


Figure 4. The 25.16-MHz ^{13}C NMR spectrum of the 1,2-difluoro-3,4-diphenylcyclobutadiene dication (**6**) in SbF_5–SO_2ClF solution at −60 °C. The lower portion is the proton noise-decoupled spectrum and the upper is the fully coupled gyro-gate spectrum.

Perhaps the most striking feature of the ^{13}C NMR of **6** is the extent to which the cyclobutadiene dication ring mesomerically interacts with the phenyl substituents in attempting to satiate its electron deficiency.[10a,11c,d,f] The severity of this interaction manifests itself in our observation of the most deshielded para-phenyl carbon resonance of a monosubstituted benzene to date.[17] The observations of two sets of magnetically nonequivalent ortho-phenyl carbons indicates that the π-bond order between the cyclobutenediylium ring and ipso-phenyl carbons has now increased to the point where rotation about these centers is no longer occurring on the NMR time scale.[18,19] It is further informative to compare the para-phenyl carbon ^{13}C NMR shieldings of **6** (δ 165.3) with those of **2** (δ 148.6). Consequently, it is thus deduced that the replacement of two vicinal phenyl groups of **2** with fluorine atoms (**6**) has resulted in an increased π-electron demand by the cyclobutenediylium ring upon the remaining two phenyl groups.[10a,11c,d,f] Thus the phenyl groups are clearly superior to fluorine atoms as π-electron-donor substituents in these systems.

The ^{19}F NMR spectrum (56.4 MHz) of **6** in SbF_5–SO_2ClF solution at −60 °C consists, as expected, of a single broad resonance at $\Phi_{^{19}F}$ + 27.0 (Table III). The broadness of the signal is presumably due to long-range proton–fluorine couplings which are not resolved. Although it is fully appreciated that factors other than electron density contribute to ^{19}F NMR shieldings,[20] a qualitative assessment of the degree of fluorine resonance interaction (i.e., fluorine *n*-electron back-donation) with the π system of the cyclobutenediylium ring in **6** may be gained by comparison of its ^{19}F NMR shielding with that of vinylic fluorines in hexafluorocyclobutene (**11**)[21] and that of the dimethylfluorocarbenium ion (**12**).[22] It thus becomes apparent from the 100+-ppm deshielding of the vinylic fluorine resonances in the dicationic **6** relative to the neutral **11** that mesomeric back-donation of *n* electrons by the fluorines to the cyclobutenediylium ring in **6** is occurring. It is also seen, however, that the electron demand upon the fluorines by the cyclobutenediylium ring in **6**, which, with its phenyl substituents, possesses numerous complementary delocalization opportunities, does not approach that of the carbenium center



11

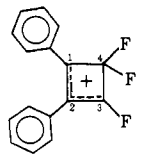
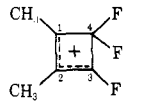
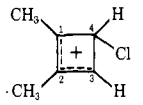
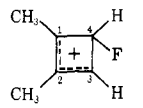
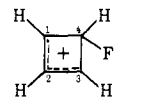
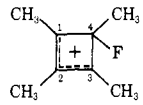
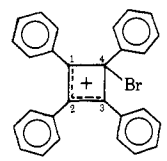
$\Phi_{^{19}F_{vinyl}}$ + 130.4

$(CH_3)_2\overset{+}{C}$—F

12

$\Phi_{^{19}F}$ − 182.0

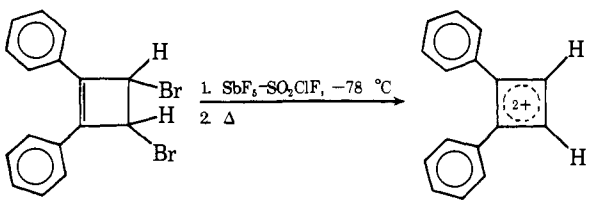
Table IV. ^{1}H NMR Parameters for Cyclobutenyl Cations

	Chemical shifts, multiplicities, and coupling constants[a]			
	C(1) substituent	C(2) substituent	C(3) substituent	C(4) substituent
 10[b]	Ph, 7.9–9.3 (m)	Ph, 7.9–9.3 (m)		
 18[c]	CH_3, 3.87 (d) $^5J_{HF}$ = 4.0	CH_3, 2.87 (t) $^5J_{HF}$ = 3.5		
 19[d]	CH_3, 2.95 (s)	CH_3, 2.83 (d) $^5J_{HH}$ = 3.0	H, 8.18 (s, br)	H, 6.38 (q) $^5J_{HH}$ = 3.0
 23[d]	CH_3, 3.00 (s)	CH_3, ca. 2.9 (m)[e]	H, 8.37 (s, br)	H, 6.55 (d, q) $^2J_{HF}$ = 64.0 $^5J_{HH}$ = 3.5
 26[f]	H, 8.58 (m)	H, 9.8–10.1 (m)[g] $^4J_{HH}$ = 4.0	H, 8.58 (m)	H, 6.92 (d, d) $^2J_{HF}$ = 60.0 $^4J_{HH}$ = 4.0
 32[h]	CH_3, 2.62 (s)	CH_3, 2.30 (d) $^5J_{HF}$ = 2.7	CH_3, 2.62 (s)	CH_3, 1.88 (d) $^3J_{HF}$ = 19.9
 33[i]	Ph, 7.5–8.7 (m)	Ph, 7.5–8.7 (m)	Ph, 7.5–8.7 (m)	Ph, 7.5–8.7 (m)

[a] Chemical shifts are in parts per million from external (capillary) Me_4Si; coupling constants in hertz. Multiplicities are given in parentheses: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. ^{1}H NMR spectra presented here were obtained on Varian Associates A56/60 NMR spectrometer unless specifically denoted otherwise. [b] In SbF_5–SO_2ClF solution at −85 °C. [c] In SbF_5–SO_2ClF solution at −60 °C. [d] In SbF_5–SO_2ClF solution at −80 °C. [e] Chemical shifts and multiplicities were not clearly resolved due to partial coincidence with C(2) methyl substituent resonance. [f] In SbF_5–SO_2ClF solution at ambient temperature. FT 100 MHz spectrum obtained on Varian Associates HA-100 NMR spectrometer equipped with FT-100 Fourier transform accessory. H_3O^+ absorption was utilized as lock reference and resonances were converted to parts per million from external (capillary) Me_4Si utilizing $\delta_{H_3O^+}$ (Me_4Si) = 10.00. [g] Chemical shift and multiplicity were not clearly resolved due to partial coincidence with H_3O^+ resonance. [h] In SO_2 solution at −60 °C. [i] In FSO_3H–SO_2ClF solution at −60 °C.

in **12**. The large $^1J_{C-F}$ in **6** (=396.0 Hz) further evidences the fluorine *n*-electron donation to the π system, as $^1J_{C-F}$'s have been shown in a series of para-substituted fluorobenzenes to increase in magnitude with substitution by substituents with increasing ability to withdraw electron density from the π system.[23]

3. 1,2-Diphenylcyclobutadiene Dication. The disubstituted 1,2-diphenylcyclobutadiene dication (**7**) was prepared by the addition of a suspension of *cis*-3,4-dibromo-1,2-diphenylcyclobutene[24] in SO_2ClF to a solution of SbF_5 in SO_2ClF at −78 °C followed by gentle warming of this solution to approximately −30 °C. **7** is completely stable in this medium after 1 h at −10 °C and 3 weeks at approximately −60 °C.



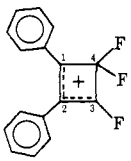
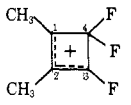
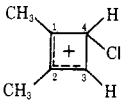
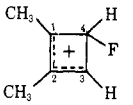
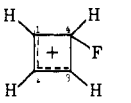
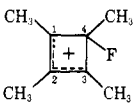
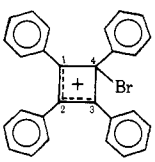
7

The ^{1}H NMR spectra (100 MHz) of **7** in SbF_5–SO_2ClF solution at −10 °C consists of two complex multiplets centered at δ 8.8 and 9.4 and a sharp singlet at δ 10.68 of relative areas 4:6:2, respectively (Figure 5). The multiplets at δ 8.8 and δ 9.4 are hence assigned to the meta- and overlapping ortho- and para-phenyl proton resonances, respectively. The strongly deshielded resonance at δ 10.68, moreover, is unequivocally assigned to the cyclobutenediylium hydrogens (Table I).

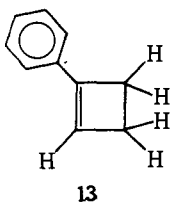
The substantial deshielding of the para-phenyl protons again exemplifies the conjugative release of π-electron density from the phenyl substituents into the electron-deficient four-carbon ring system.[10a,11c,d,f] The proximity in magnitudes of the selective deshielding of the para- relative to the meta-phenyl protons in **6** and **7** implies the similarity of the π-electron donation requirements which are placed upon the phenyl substituents in these two systems.[10a,11c,d,f]

It is informative to compare the ^{1}H NMR shieldings of the cyclobutenediylium protons (δ 10.68) in **7** with that of the vi-

Table V. ^{13}C NMR Parameters for Cyclobutenyl Cations

	Chemical shifts, multiplicities, and coupling constants[a]								
	Cyclobutenyl				C(1) substituent				
	C(1)	C(2)	C(3)	C(4)	CH_3	C_{ipso}	C_o	C_m	C_p
 10[b]	199.9 (d, t)[c] $^3J_{CF}$ = 35.8 $^2J_{CF}$ = 23.2	153.4 (s, br)[c]	185.4 (d, t) $^1J_{CF}$ = 422.1 $^2J_{CF}$ = 27.0	117.9 (t, d) $^1J_{CF}$ = 283.2 $^2J_{CF}$ = 19.4		127.7 (d) $^4J_{CF}$ = 12.2	140.3 (d) $^1J_{CH}$[d] 142.6 (d) $^1J_{CH}$	133.3 (d)* $^1J_{CH}$[d]	154.1 (d) $^1J_{CH}$ = 165.4
 18[f]	242.6 (d, t)[f] $^3J_{CF}$ = 38.0 $^2J_{CF}$ = 28.1	168.1 (s, br)[f]	206.3 (d, t) $^1J_{CF}$ = 449.3 $^2J_{CF}$ = 25.2	117.2 (t, br) $^1J_{CF}$ = 289.7	20.6 (q) $^1J_{CH}$ = 138.5				
 19[g]	164.6 (s)[h]	184.8 (s)[h]	141.4 (d) $^1J_{CH}$ = 207.3	62.0 (d) $^1J_{CH}$ = 215.9	13.3 (q)* $^1J_{CH}$ = 136.4				
 23[g]	159.0 (d)[i] $^2J_{CF}$ = 9.5	181.3 (d)[i] $^3J_{CF}$ = 15.2	136.6 (d, d) $^2J_{CF}$ = 12.0 $^1J_{CH}$ = 208.5	85.3 (d, d) $^1J_{CF}$ = 243.0 $^1J_{CH}$ = 222.7	11.4 (q)* $^1J_{CH}$ = 133.3				
 26[e]	136.7 (d, d) $^2J_{CF}$ = 10.4 $^1J_{CH}$[j]	173.8 (d, d) $^3J_{CF}$ = 16.6 $^1J_{CH}$[j]	136.7 (d, d) $^2J_{CF}$ = 10.4 $^1J_{CH}$[j]	86.8 (d, d) $^1J_{CF}$ = 253.1 $^1J_{CH}$[j]					
 32[g]	181.4 (d) $^2J_{CF}$ = 13.4	175.5 (d) $^3J_{CF}$ = 15.6	181.4 (d) $^2J_{CF}$ = 13.4	96.4 (d) $^1J_{CF}$ = 228.9	13.0 (q) $^1J_{CH}$[j]				
 33[f]	190.0 (s)	152.2 (s)	190.0 (s)	65.2 (s)		127.0 (s)	138.5 (d) $^1J_{CH}$[j]	131.5 (d) $^1J_{CH}$[j]	144.8 (d) $^1J_{CH}$[j]

[a] Chemical shifts are in parts per million from external (capillary) Me_4Si; coupling constants in hertz. Multiplicities are given in parentheses: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. Assignments of resonances denoted with asterisks could be interchangeable as no specific labeling experiments were carried out. [b] In SbF_5–SO_2ClF solution at −85 °C. [c] The assignment of C(1) and C(2) to the resonances at δ 199.9 and 153.4, respectively, were based upon the similarity of the long-range carbon–fluorine coupling observed in the resonance at δ 199.9 with that observed in the resonance of C(3). The resonance at δ 153.4 did not display any resolved coupling and had a $\nu_{1/2}$ = 18 Hz. These assignments, moreover, are in accord with our previous studies (ref 7d) in which it was found that cyclobutenyl cations substituted at C(1) and C(3) with good π donors possess charge distributions similar to those of allyl cations. [d] $^1J_{CH}$'s of these resonances were not resolved due to their partial coincidence in the ^1H-coupled ^{13}C NMR. [e] In SbF_5–SO_2ClF solution at −60°C. [f] The assignments of C(1) and C(2) to the resonances at δ 242.6 and 168.1, respectively, were based upon the similarity of the long-range coupling observed in the resonance at δ



13

nylic proton (δ 6.20) in 1-phenylcyclobutene (**13**).[25] Although local diamagnetic shielding inequality is clearly not the only factor responsible for the disparity in these ^1H NMR shieldings, the large magnitude of their difference (4.48 ppm) undoubtedly reflects the localization of considerable amounts of positive charge at C(3) and C(4) in the dicationic **7**.[26]

The FT ^{13}C NMR or the 1,2-diphenylcyclobutadiene dication displays seven resonances at δ 190.9 (s), 182.1 (d, 209.6), 125.3 (s), 135.3 (d, 172.1), 163.0 (171.8), 144.5 (d, 174.2), and 148.2 (d, 166.3), which are assigned to the phenylated cyclobutenediylium (C(1,2)), protiated cyclobutenediylium (C(3,4)), ipso-phenyl, meta-phenyl, para-phenyl, and magnetically nonequivalent ortho-phenyl carbons, respectively (Table II, Figure 6). The dicationic nature of **6** becomes evident with the observation that the *average* ^{13}C NMR shielding of this species is δ 153.0, which is in excellent accord with that of δ 152.7 predicted by a modified Spiesecke–Schneider treatment for a completely conjugated 14π-electron, 16C system,[11h]

Inspection of the ^{13}C NMR spectra of **6** and **7** reveals the structural and electronic similarities of the two systems. Indeed the almost coincidental, highly deshielded para-phenyl carbon shieldings in **7** (δ 163.0) and **6** (δ 165.3) indicate the similar high level of mesomeric interaction of the phenyl substituents with the cyclobutadiene dication ring in the two systems.[10a,11c,d,f] The presence of a nonequivalent pair of ortho-

Table V (*Continued*)

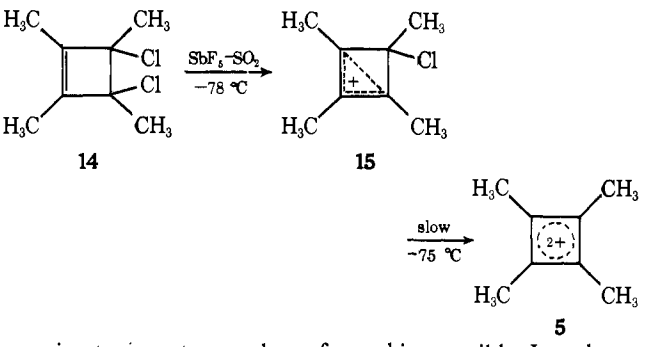
Chemical shifts, multiplicities, and coupling constants[a]											
C(2) substituent					C(3) substituent					C(4) substituent	
CH_3	C_{ipso}	C_o	C_m	C_p	CH_3	C_{ipso}	C_o	C_m	C_p	CH_3	C_{Ph}
	121.1 (s)	130.6 (d)* $^1J_{CH}$[d]	129.3 (d)* $^1J_{CH}$[d]	135.7 (d) $^1J_{CH}$[d]							
7.2 (q) $^1J_{CH}$ = 137.1											
11.9 (q)* $^1J_{CH}$ = 133.2											
12.1 (q)* $^1J_{CH}$ = 135.1											
9.9 (q) $^1J_{CH}$[j]					13.0 (q) $^1J_{CH}$[j]					20.0 (q, d) $^2J_{CF}$ = 27.8 $^1J_{CH}$[j]	
	m					127.0 (s)	138.5 (d) $^1J_{CH}$[j]	131.5 (d) $^1J_{CH}$[j]	144.8 (d) $^1J_{CH}$[j]		*m*

242.6 with that observed in the resonance of C(3). The resonance at δ 168.1 did not display any resolved couplings and had a $v_{1/2}$ = 24 Hz. These assignments are, moreover, in accord with our previous studies (ref 7d) in which it was found that cyclobutenyl cations substituted at C(1) and C(3) with good π donors possess a charge distribution similar to those of allyl cations. [g] In SbF_5–SO_2ClF at −80°C. [h] Assignments of C(1) and C(2) to resonances at δ 164.6 and 184.8, respectively, were based upon similar assignments of C(1) and C(2) in 23 (see footnote *i*). [i] Assignments of C(1) and C(2) to resonances at δ 159.0 and 181.3, respectively, were based upon comparisons of the long-range carbon–fluorine couplings observed in these resonances with those observed in C(1) and C(2) of **26** and **32**. [j] Multiplicities of these resonances were obtained from off-resonance ^{1}H-decoupled experiment, [k] In SO_2 solution at −60°C. [l] In FSO_3H–SO_2ClF solution at −60°C. [m] The aromatic resonances not assigned belong to the following set: 127.6 (d), 128.1, 128.6 (d), 130.3, 130.7, 131.3, 132.3 (d), 133.8 (s).

phenyl carbon resonances in **6** and **7**, the chemical shifts of which show a definite correspondence in the two systems, further implicates the analogous trends of π-density distribution in the two dications.[18]

4. Tetramethylcyclobutadiene Dication. Since the work of Breslow[27] on cyclopropenium cations indicated that alkyl groups give this aromatic cation more thermodynamic stability than aryl groups (the kinetic stability might, however, be decreased), it was logical to attempt the preparation of the tetramethylcyclobutadiene dication (**5**).

When *trans*-3,4-dichlorotetramethylcyclobutene (**14**)[28] was added to SbF_5–SO_2 at −78 °C, a very pale yellow solution was obtained whose ^{1}H NMR spectrum was identical with that previously reported by Katz[7a,b,d] for ion **15** in SO_2 solution. After several minutes at −75 °C, a single new absorption appeared as a sharp singlet at δ 3.68 (Table I). The rate of appearance of the species giving this singlet increased with increasing temperature and was formed irreversibly. In order to generate a maximum concentration of **5** in SO_2 the temperature was maintained at or below −65 °C because at higher temperatures absorptions characteristic of **15** disappeared, but were not proportionally replaced by the single line of **5**. About



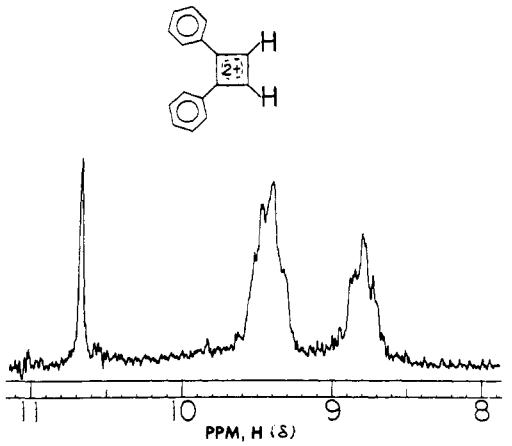


Figure 5. The 100-MHz ^{1}H NMR spectrum of the 1,2-diphenylcyclobutadiene dication (**7**) in SbF_5-SO_2ClF solution at −10 °C. The H_3O^+ resonance at δ 10.10 has been deleted for clarity.

60% **15** could be converted to **5** before appreciable decomposition took place at −65 °C.

Solutions of ion **15** are completely stable in FSO_3H-SO_2 solution at −78 °C for at least 2 weeks. Solutions of **5** in SbF_5-SO_2 show a maximum concentration of **5** at −78 °C after approximately 24 h, and thereafter decomposition takes place to another species whose structure we have been yet unable to determine. Solutions of **5** in 1:1 FSO_3H-SbF_5 in SO_2 are more than 80% decomposed after 6 h at −78 °C.

The preparation of the tetramethylcyclobutadiene dication can also be accomplished by the addition of SbF_5 in SO_2ClF to a FSO_3H-SO_2ClF solution of **15** at −78 °C. The treatment of **14** with SbF_5 in SO_2ClF solution at −78 °C gave **5** directly and the intermediacy of **15** was not detected by ^{1}H NMR spectroscopy under these conditions. The tetramethylcyclobutadiene dication showed considerable stability in SbF_5-SO_2ClF solution, as no detectable (by ^{1}H NMR spectroscopy) decomposition of **5** occurred in this medium after 24 h at −78 °C or 15 min at −40 °C. These disparities in behavior which exist between the SbF_5-SO_2Cl and SbF_5-SO_2 systems are presumably the result of the higher acidity of the former relative to the latter solutions.[29]

The FT ^{13}C NMR spectrum of the tetramethylcyclobutadiene dication in SbF_5-FSO_3H-SO_2ClF solution at −60 °C consists of two resonances at δ 18.8 (q, 137.3) and 209.7 (s) which are thus assigned to the methyl and cyclobutenediylium (C(1,2,3,4)) carbons, respectively (Table II). Although the presence of methyl substituent effects in **5** precludes a quantitative interpretation of the π-electron density residing at the cyclobutenediylium carbons from their ^{13}C NMR shieldings,[14,30] comparison of their ^{13}C NMR shieldings (δ 209.7) with that predicted by the Spiesecke-Schneider relationship for the unsubstituted cyclobutadiene dication (δ 208.8)[12] certainly support the formulation of **5** as a dicationic species delocalizing approximately two π electrons over a four-carbon atom periphery.

The methanolysis of an SbF_5-SO_2 solution of **5** CH_3OH-CH_3ONa solution at −78 °C gave a 78% yield of a mixture of *cis*- and *trans*-3,4-dimethoxytetramethylcyclobutene.[31] The isomer distribution in this experiment was found to be in the ratio of 55:45, respectively. Control experiments were conducted in which **15** was solvolyzed under identical conditions and **14** in CH_3OH-CH_3ONa solution at ambient temperature. In these cases the total yields of *cis*- and *trans*-3,4-dimethoxytetramethylcyclobutene were similar to that obtained for the methanolysis of **5**, but the distributions were determined to be in the ratio of 15:85 and 3:97, respectively. These quenching experiments hence reflect the structural and electronic identity of **5**.

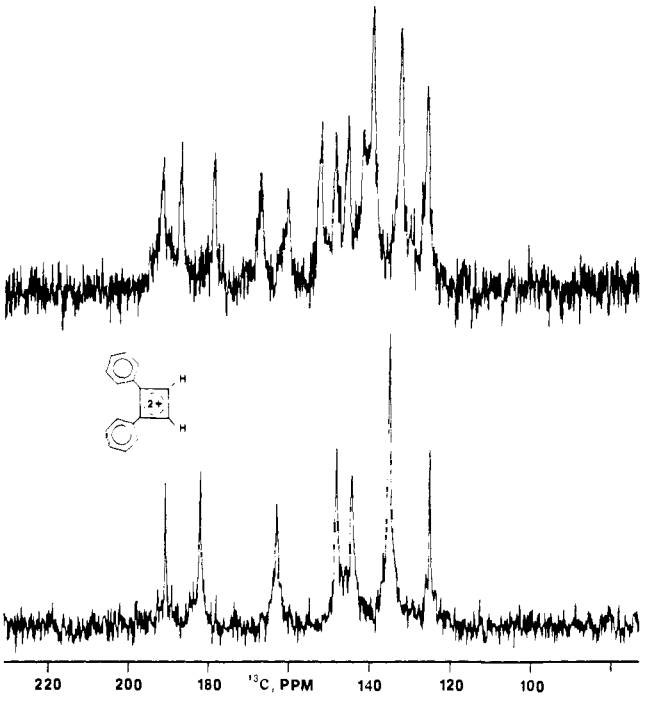
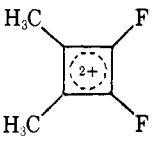


Figure 6. The 25.16-MHz ^{13}C NMR spectrum of the 1,2-diphenylcyclobutadiene dication (**7**) in SbF_5-SO_2ClF solution at −50 °C. The lower portion is the proton noise-decoupled spectrum and the upper is the fully coupled gyro-gate spectrum.

5. Attempted Preparations of the 1,2-Difluoro-3,4-dimethylcyclobutadiene Dication, the 1,2-Dimethylcyclobutadiene Dication, and the Parent Cyclobutadiene Dication. Since, as previously mentioned, Breslow's investigations of cyclopropenium ions indicated that alkyl substituents impart more thermodynamic stability to the 2π-electron, 3C aromatic cation system than do aryl substituents,[27] our preparation of the 1,2-difluoro-3,4-diphenylcyclobutadiene dication (**5**) and 1,2-diphenylcyclobutadiene dication (**6**) suggested the possibility of preparing the 1,2-difluoro-3,4-dimethylcyclobutadiene dication (**16**) and the 1,2-dimethylcyclobutadiene dication (**17**)



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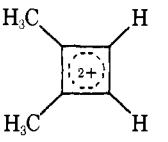

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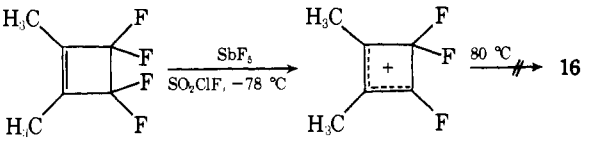
from ionization of the appropriate precursors under similar conditions. The addition of 1,2-dimethyl-3,3,4,4-tetrafluorocyclobutene[16b] to an excess of SbF_5 in SO_2ClF solution at −78 °C resulted in a solution whose ^{1}H, ^{13}C, and ^{19}F NMR spectra corresponded to that of the 1,2-dimethyl-3,3,4-trifluorocyclobutenyl cation (**18**, Tables III, IV, and V). Heating the



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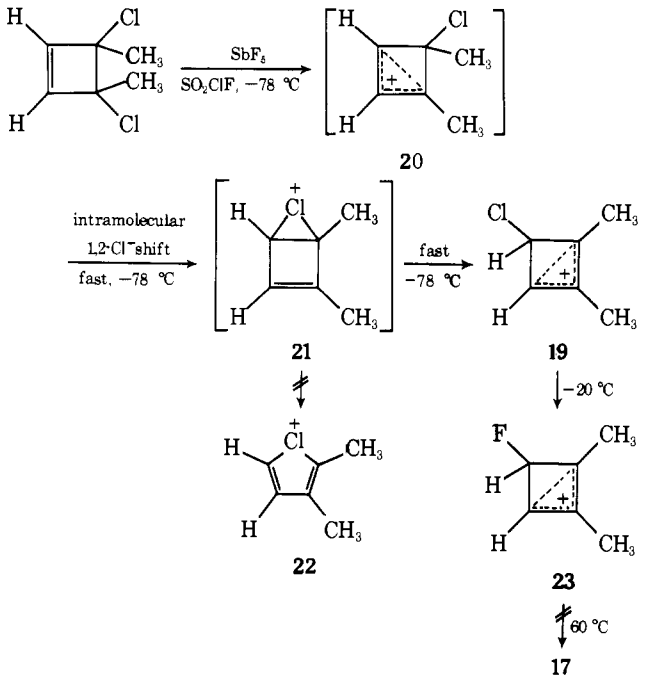
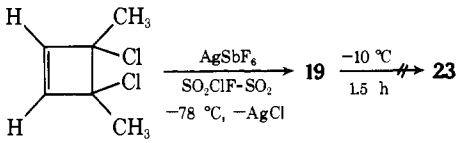
solution of **18** slowly to 80 °C did not result in any change of the observed ^{1}H NMR spectrum and thus demonstrated that further ionization of **18** to the dication **16** had not occurred.

In a similar experiment the dissolution of *trans*-3,4-dichloro-3,4-dimethylcyclobutene[32] into an SbF_5-SO_2ClF solution at −78 °C resulted in the formation of the 4-chloro-1,2-dimethylcyclobutenyl cation (**19**, Tables IV and V). **19** presumably results from the initial formation of the 4-chloro-1,4-dimethylcyclobutenyl cation (**20**), which at this

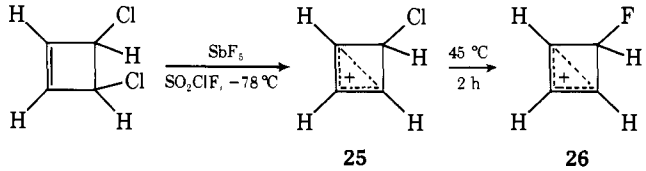


temperature undergoes a rapid *intramolecular* 1,2-chloride shift.[33] No leakage from the assumed intermediate chloronium ion **21** to the potentially aromatic chlorophenium ion **22** was detected.[34] Warming a solution of **19** to −20 °C results in the formation of the 4-fluoro-1,2-dimethylcyclobutenyl cation (**23**, Tables III, IV, and V). The fluorination of **20** to give **23** may proceed by an addition-elimination mechanism in which fluoride ion is released by the hexafluoroantimonate gegenion[36] to **19** to give a neutral cyclobutene (i.e., **24**) which then reionizes at the carbon-chlorine bond to give **23** (Scheme I, mechanism A, R = CH_3). Alternatively, **23** may result from the antimony pentafluoride induced cleavage of the carbon-chlorine bond in **19** to give either an incipient or free cyclobutadiene dication, which is concertedly or subsequently quenched with fluoride-ion donation by the gegenion[36] (Scheme I, mechanism B, R = CH_3). The former possibility was tested in a control experiment in which **19** was prepared in the absence of antimony pentafluoride, but in the presence of the hexafluoroantimonate anion by the metathetic reaction of *trans*-3,4-dichloro-3,4-dimethylcyclobutene[32] with silver hexafluoroantimonate in SO_2ClF-SO_2 solution at −78 °C. Subsequent reaction of this solution of **19** for 1.5 h at −10 °C resulted in no detectable conversion of **19** to **23**. Since **19** in the

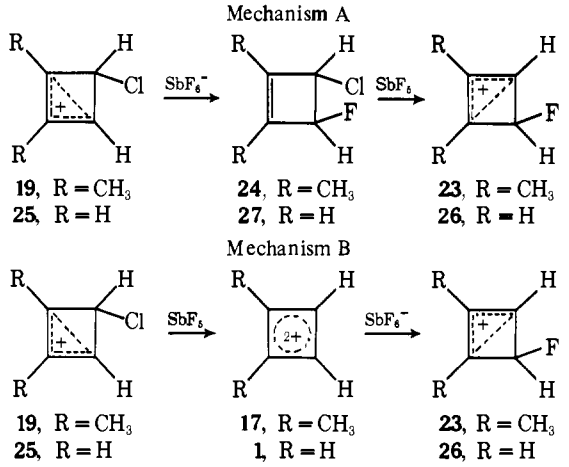


SbF_5-SO_2ClF-SbF_6^- system[36] was almost completely converted to **23** after 20 min at −20 °C, mechanism A is thus improbable as an operative pathway under these conditions.

A similar halogen-exchange phenomenon is observed when a solution of the parent 4-chlorocyclobutenyl cation (**25**)[7d] is reacted in SbF_5-SO_2ClF solution. In this case, however, considerably more severe conditions (45 °C, 2 h) are required to effect the conversion of **25** to the 4-fluorocyclobutenyl cation (**26**, Tables IV and V): no conversion of **25** to **26** can be de-



Scheme I

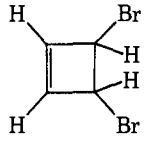


tected by ^1H NMR spectroscopy under conditions in which the conversion of **19** to **23** is essentially complete. One may therefore conclude that the activation energy required for halogen-exchange process **25** → **26** is significantly higher than in the case of the transformation **19** → **23**. Again, the conversion of **25** to **26** may proceed by mechanism A or B as shown in Scheme I. It is informative to examine the hypothetical energy diagrams for the conversion of **19** → **23** and **25** → **26** via each of the two possible mechanistic routes. As a starting point, first consider the relative π energies of the cyclobutenyl cations **19** and **25**. Since the transformation of **25** into **19** corresponds to the replacement of two hydrogens on the allylic fragment of **25** with two methyl substituents, **25** may be estimated to be approximately 11 kcal mol^{-1} higher on the energy profile than **19**.[38] The stabilizing effect of the two methyl substituents bound to the unsaturated linkage (i.e., **24**) relative to the hydrogenated derivative (i.e., **27**) in a neutral cyclobutene is anticipated to be attenuated from the value in the cationic derivatives and may be estimated to have a magnitude of 6 kcal mol^{-1}.[40] Thus the conversion of **19** to **24** may be estimated to be approximately 5 kcal mol^{-1} more endothermic than the conversion of **25** to **27**. A part of this difference should be reflected upon comparison of the activation barriers of the two processes.[43] Thus the activation barrier for the conversion of **19** → **24** is predicted to be higher than that of the conversion **25** → **27**.[43] Utilizing similar arguments and assuming that the stabilizing influence of the methyl substituents relative to hydrogen is enhanced upon the transformation of a cyclobutenyl cation to a cyclobutadiene dication (either incipient or free), the activation energy required for the reaction **19** → **17** is anticipated to be lower than that for the reaction **25** → **1**.[43] It thus becomes apparent that, whereas the relative magnitudes of the experimentally determined energy barriers for the conversion of **19** to **23** and **25** to **26** are inconsistent with the predictions of the Hammond postulate[43] if one assumes that the conversion of **19** to **23** occurs through a neutral cyclobutene intermediate (Scheme I, mechanism A), they are in accord with the predictions if one accepts the intermediacy of an incipient or free cyclobutadiene dication (Scheme I, mechanism B). Thus all the available information suggests that, whereas the cyclobutadiene dication **17** may be generated under so-called stable-ion conditions as a transient intermediate, it may not be observed under these conditions as a long-lived species because it is not the thermodynamically most-stable species of the system.

We therefore conclude that, whereas alkyl substituents provide more of a thermodynamic driving force for the ionization of an appropriate neutral cyclopropene precursor to the related cyclopropenium ion than do aryl substituents, this trend is reversed in the case of the transformation of a 4-halocyclobutenyl cation to the related cyclobutadiene dication. This

reversal of substituent effects in these two systems presumably results because the increased π-electron deficiency and coulombic repulsions of the cyclobutadiene dication relative to the cyclopropenium system enhances the importance of the relative π-donor abilities of the substituents. The greater mesomeric electron demand placed upon the phenyl substituents in the cyclobutadiene dication relative to the cyclopropenium system, as reflected in a comparison of their ^{13}C NMR spectra, certainly bears out this conclusion.

Unsuccessful attempts to prepare the parent (unsubstituted) cyclobutadiene dication have reinforced our conclusions of the expected elusive nature of this species. Heating **26** in SbF_5–SO_2ClF to 75 °C only resulted in the decomposition of this species with no indication for the formation of **1**. Similarly, attempted preparation of **1** from *trans*-3,4-dibromocyclobutene (**28**),[44,45] *cis*-3,4-diiodocyclobutene (**29**),[45] 3-cyclobutene-*cis*-1,2-dicarboxylic anhydride (**30**),[46] and the cyclic carbonate of 3-cyclobutene-*cis*-1,2-diol (**31**)[47] precursors in a variety of superacid systems gave no evidence for the formation of **1**.



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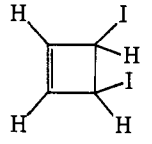

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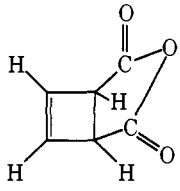

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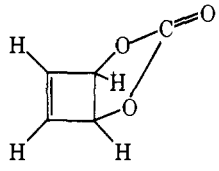

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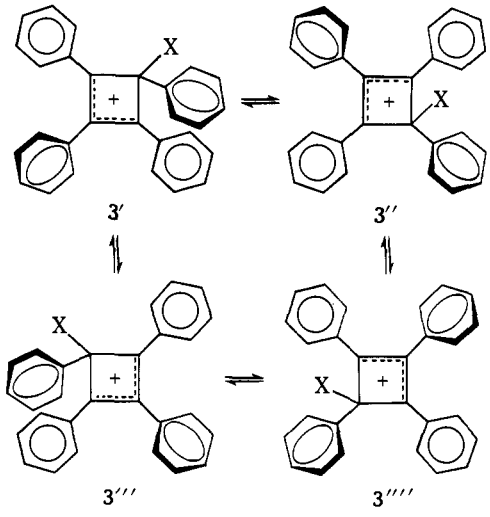
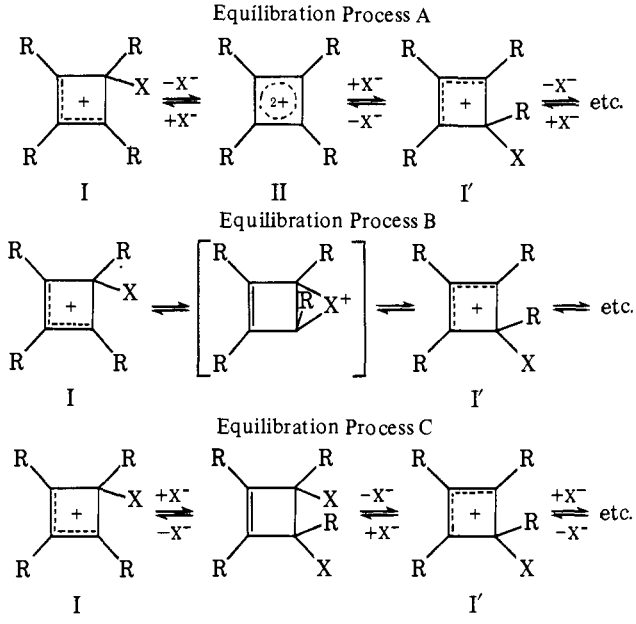
6. Question of Rapid Equilibration Vs. Static Cyclobutadiene Dications. As mentioned in the introduction, the first report[4] of a NMR spectroscopic observation of a cyclobutadiene dication, namely, the tetraphenyl derivative **2**, was later demonstrated to correspond to a rapidly equilibrating set of 4-halocyclobutenyl cations **3′**–**3′′′′**.[5] This early erroneous report has led some authors[48] to doubt the feasibility of preparation and NMR spectroscopic observation of cyclobutadiene dications even under superacidic stable-ion conditions.



3′ **3″** **3‴** **3⁗**

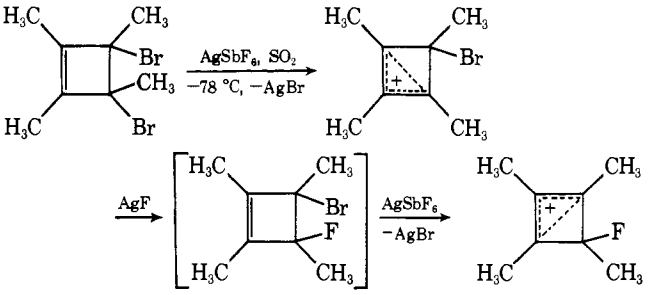
This background and expressed skepticism has suggested the necessity of providing conclusive evidence that our NMR spectral assignments in the studied systems correspond to bona fide cyclobutadiene dications. To this effect it is necessary to demonstrate that possible equilibration processes which, if

Scheme II



sufficiently rapid on the NMR time scale, would result in the observation of NMR spectra of the same symmetry as that required for the cyclobutadiene dication are slow on the NMR time scale under the conditions that the spectrum attributed to the cyclobutadiene dication is obtained.[19] The equilibration processes for which this must be demonstrated are depicted in Scheme II. Equilibration process A is that of a dynamic equilibrium between cyclobutenyl cations and cyclobutadiene dications. If this equilibration is rapid on the NMR time scale, an observed resonance would possess a chemical shift which corresponds to the weighted average of the chemical shifts of all nuclei which contribute to this resonance.[19] It is apparent that if either the cyclobutenyl cation or cyclobutadiene dication is favored in the equilibrium by more than approximately 1.4 kcal mol^{-1} (one equilibrium constant), the positions of the observed resonances will virtually correspond to those of a set of equilibrating cyclobutenyl cations (I, I′, etc) or to those of a static cyclobutadiene dication II, respectively.[19] Similarly, the rapid equilibration of a set of structurally degenerate cyclobutenyl cations (Scheme II, equilibration process B) would result in the observation of a NMR spectrum with identical symmetry with that required of a cyclobutadiene dication.[19] It is obvious, however, that in this case an observed resonance position must be derived from the weighted average of the chemical shifts in the static cyclobutenyl cation that become equivalent upon equilibration.[19] Equilibration process C is analogous to equilibration process A in that the averaging phenomena arise from the presence of a dynamic equilibrium between nondegenerate species.[19] Since in process C, however, the cyclobutenyl cations do not equilibrate through a cyclobutadiene dication, but rather through a neutral cyclobutene, the lowest field observed NMR shieldings which could arise would be those corresponding to a rapidly equilibrating set of cyclobutenyl cations.[19]

The demonstration that these possible equilibration processes depicted in Scheme II, if present, are slow under the conditions in which the ^1H and ^{13}C NMR spectra of the tetramethylcyclobutadiene dication (**5**) were obtained was achieved in the following manner. Addition of *cis*-3,4-dibromotetramethylcyclobutene[49] to a SO_2 suspension of silver fluoride and silver hexafluoroantimonate at −78 °C followed by gentle warming of the solution to −20 °C resulted in the formation of the 4-fluorotetramethylcyclobutenyl cation (**32**), presumably through the depicted reaction sequence. The bromide ion was efficiently removed from the liquid phase



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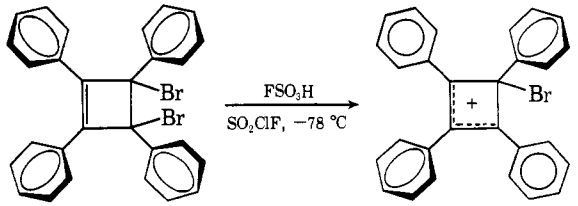
through its precipitation as silver bromide. The ^{19}F, ^{1}H, and ^{13}C NMR spectra parameters of **32** are summarized in Tables III, IV, and V, respectively. The symmetry and coupling interactions displayed in these NMR spectra clearly indicate that the equilibration processes shown in Scheme II are slow on the NMR time scale under the conditions in which these spectra were obtained.[19] To the resultant solution of **32** was then added an excess of SbF_5, also in SO_2 solution, at −78 °C. Allowing this solution of **32** to rise to −60 °C resulted in the slow, irreversible conversion of **32** to the tetramethylcyclobutadiene dication (**5**).

$$\mathbf{32} \xrightarrow[-60\ ^\circ C,\ slow]{SbF_5\text{-}SO_2} \mathbf{5}$$

This transformation of **32** → **5** was monitored by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. The complete conversion of **32** → **5** under these conditions required several hours and NMR spectra displaying several relative concentrations of **32** and **5** were recorded. The coexistence of **32** and **5** in the same solution as "static" species in their ^{1}H and ^{13}C NMR spectra clearly demonstrates that equilibration processes A-C (Scheme II) are not occurring on the NMR time scale under the experimental conditions.[19] In addition, comparison of the ^{13}C NMR shieldings of **32** with those attributable to **5** reveals that even the occurrence of equilibration process B or C could not give rise to the observed ^{13}C NMR spectrum which we assign to **5**. These studies thus conclusively demonstrate that we have prepared and obtained the NMR spectra of the "static" bona fide tetramethylcyclobutadiene dication.

We have also carried out a detailed study to determine the contribution of the equilibration process A-C to the NMR spectra which we assign to the tetraphenylcyclobutadiene dication (**2**). The addition of 3,4-dibromotetraphenylcyclobutene[8] to a FSO_3H-SO_2ClF solution at −78 °C resulted in a solution whose ^{1}H and ^{13}C NMR spectra (Tables IV and V, respectively) indicated the formation of the 4-bromotetraphenylcyclobutenyl cation (**33**). The symmetry of the NMR



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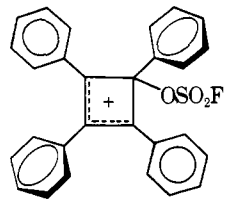
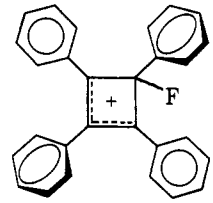
spectra of **33** under these conditions show that equilibration process A-C must be slow on the NMR time scale.[19] When SbF_5 in SO_2ClF at −78 °C was added to the FSO_3H-SO_2ClF of **33** at −78 °C and the resulting solution was allowed to warm to −60 °C, it was possible to monitor the slow, irreversible conversion of **33** to **2** in this system by ^{1}H and ^{13}C NMR spectroscopy.

$$\mathbf{33} \xrightarrow[SO_2,\ -60\ ^\circ C,\ slow]{SbF_5\text{-}FSO_3H} \mathbf{2}$$

Thus the achievement of coexistence of **33** and **2** in the same solution as "static", nonexchanging species rigorously excludes the participation of **33** in the equilibration processes of Scheme II on the NMR time scale.[19] The possibility of these equilibrations proceeding through the cyclobutenyl cations **34** and **35**, which could conceivably be formed in situ, however, warrants further consideration. Equilibration by process B and C



34



35

involving **34** and **35** can be excluded, because, although spectra averaged by these processes could give the symmetry of the spectra observed, the averaged ^{13}C NMR shieldings resulting from such processes would obviously be considerably more shielded than those experimentally obtained. Although the possible involvement of **34** and **35** in equilibration process A may not be conclusively eliminated, the magnitude of the difference between the observed ^{13}C NMR shieldings and those which would be derived from a set of equilibrating cyclobutenyl cations indicates that, if the dynamic equilibrium is involved at all, the population level of the cyclobutadiene dication in the equilibrium must greatly exceed that of the cyclobutenyl cation.

Experimental Section

Materials. 3,4-Dibromotetraphenylcyclobutene,[8] 1,2-diphenyl-3,3,4,4-tetrafluorocyclobutene,[16] *cis*-3,4-dibromo-1,2-diphenylcyclobutene,[24] *cis*-3,4-dibromotetramethylcyclobutene,[49] *trans*-3,4-dichlorotetramethylcyclobutene (**14**),[28] *trans*-3,4-dichloro-3,4-dimethylcyclobutene,[32] 1,2-dimethyl-3,3,4,4-tetrafluorocyclobutene,[16b] *cis*-3,4-dichlorocyclobutene,[50] 3-cyclobutene-*cis*-1,2-dicarboxylic anhydride (**30**),[46] and the cyclic carbonate of 3-cyclobutene-*cis*-1,2-diol (**31**)[47] were prepared according to literature procedures. *trans*-3,4-Dibromocyclobutene (**28**) and *cis*-3,4-diiodocyclobutene (**29**) were kindly provided by Professor R. Pettit (University of Texas). Fluorosulfuric acid was doubly distilled and antimony pentafluoride triply distilled before use. FSO_3H-SbF_5 refers to a 1:1 molar solution of these two reagents unless specified otherwise.

Preparation of Ions. 4-Bromotetraphenylcyclobutenyl Cation (33). To 0.87 g (8.7 mmol) of FSO_3H dissolved in approximately 2 ml of SO_2ClF at −78 °C was added dropwise, with vigorous Vortex stirring, a slurry of 0.41 g (0.79 mmol) of 3,4-dibromotetraphenylcyclobutene in SO_2ClF at −78 °C. The resultant solution was transferred immediately to a precooled NMR tube for direct study. No decomposition was observed in the ^{1}H NMR of this solution after 5 min at 0 °C.

Tetraphenylcyclobutadiene Dication (2). To the above described FSO_3H-SO_2ClF solution of **33** at −78 °C was added rapidly, with vigorous Vortex stirring, 0.30 g (1.4 mmol) of SbF_5 dissolved in SO_2ClF at −78 °C. Reaction of the solution at −60 °C resulted in the observable, irreversible conversion of **33** to **2**.

2 was also prepared directly, without the observation of the intermediacy of **33**, by the addition of a slurry of 3,4-dibromotetraphenylcyclobutene in SO_2 (SO_2ClF) to an approximately tenfold molar excess of SbF_5 or SbF_5-FSO_3H in SO_2 (SO_2ClF) solution. It should be noted, however, that when 3,4-dibromotetraphenylcyclobutene was ionized directly in SbF_5-SO_2ClF solution at −78 °C, in addition to **2**, some unidentified by-products were also produced. The formation of these by-products was not apparent when **2** was prepared according to the alternative methods described above.

Methanolysis of an SbF_5-SO_2 solution of **2** in CH_3OH-CH_3ONa at −78 °C resulted in the exclusive isolation of a mixture of *cis*- and *trans*-3,4-dimethoxytetraphenylcyclobutenes. The ^{1}H NMR spectrum (60 MHz, $CDCl_3$, internal Me_4Si) of the isomeric mixture consists of two methoxy proton singlet resonances at δ 3.33 and 3.42 of relative area 64:36, respectively, and the complex aromatic proton multiplets at δ 7.0-7.7. The stereochemical assignment of the isolated products was not attempted.

1,2-Diphenyl-3,4,4-trifluorocyclobutenyl Cation (10). To 2.37 g

(10.9 mmol) of SbF_5 dissolved in approximately 2 ml of SO_2ClF at −78 °C was added dropwise, with vigorous Vortex stirring, a slurry of 0.27 g (0.97 mmol) of 1,2-diphenyl-3,3,4,4-tetrafluorocyclobutene in SO_2ClF at −78 °C. The resultant solution was transferred immediately to a precooled NMR tube for direct study.

1,2-Difluoro-3,4-diphenylcyclobutadiene Dication (6). When the above described SbF_5–SO_2ClF solution of **10** was warmed to approximately 0 °C the slow, irreversible ionization of **10** to **6** occurred. The conversion of **10** to **6** was complete after several minutes reaction of this solution at approximately 0 °C.

1,2-Diphenylcyclobutadiene Dication (7). To 2.60 g (12.0 mmol) of SbF_5 dissolved in approximately 2 ml of SO_2ClF at −78 °C was added dropwise, with vigorous Vortex stirring, a slurry of 0.20 g (0.55 mmol) of *cis*-3,4-dibromo-1,2-diphenylcyclobutene in SO_2ClF at −78 °C. After reaction of this resultant solution at approximately −30 °C for several minutes, the solution was recooled to −78 °C and transferred to a precooled NMR tube for direct study. **7** was completely stable in SbF_5–SO_2ClF solution after 1 h at −10 °C and 3 weeks at approximately −60 °C.

4-Fluorotetramethylcyclobutenyl Cation (32). To a suspension of 1.65 g of $AgSbF_6$ (4.80 mmol) and 0.25 g of AgF (2.0 mmol) in approximately 2 ml of SO_2 at −78 °C was added, with vigorous Vortex stirring, a slurry of 0.54 g (2.0 mmol) of *cis*-3,4-dibromotetramethylcyclobutene in SO_2 at −78 °C. The resultant solution was warmed slowly with stirring to approximately −20 °C, and then recooled to −78 °C. The resultant solution of **32** was then pipetted off from excess $AgSbF_6$ and precipitated AgBr and transferred to a precooled NMR tube for direct study. The ^1H and ^{13}C NMR spectra of this solution also indicated the presence of minor amounts of unidentified impurities.

Tetramethylcyclobutadiene Dication (5). To the above solution of **32** at −78 °C was added rapidly, with vigorous Vortex stirring, 0.87 g (4.0 mmol) of SbF_5 in SO_2 solution at −78 °C. The irreversible conversion of **32** to **5** was observed by ^1H and ^{13}C NMR spectroscopy upon warming this solution to −60 °C.

5 was also prepared by the addition, with efficient stirring, of an SO_2 (SO_2ClF) slurry of *trans*-3,4-dichlorotetramethylcyclobutene (**14**) at −78 °C to an approximately tenfold molar excess of SbF_5 or SbF_5–FSO_3H in approximately 2 ml of SO_2 (SO_2ClF) at −78 °C. When the dichloride **14** was ionized in SO_2 superacid solutions, the intermediacy of the 4-chlorotetramethylcyclobutenyl cation (**15**) could be detected by ^1H and ^{13}C NMR spectroscopy. In order to generate a maximum concentration of **5** in SO_2 superacid solutions the temperature of the ionization was maintained (due to decomposition) at or below −65 °C because at higher temperatures ^1H NMR absorptions characteristic of **15** disappeared, but were not proportionately replaced by the single line of **5**. About 60% **15** could be converted to **5** in SbF_5–SO_2 solution before appreciable decomposition took place at −65 °C. Solutions of **15** in SbF_5–SO_2 showed a maximum concentration of **5** after approximately 24 hours and thereafter decomposition took place to a yet unidentified species.

When **14** is ionized in SO_2ClF superacid solutions at −78 °C the intermediacy of the cyclobutenyl cation **15** was not detected and **5** was observed directly. **5** was considerably more stable in this medium. For example, **5** showed no decomposition in SbF_5–SO_2ClF solution after 24 hours at −78 °C or 15 min at −40 °C.

The methanolysis of an SbF_5–SO_2 solution of **5** in CH_3OH–CH_3ONa solution at −78 °C gave a 78% yield of a mixture of *cis*- and *trans*-3,4-dimethoxytetramethylcyclobutene,[31] which were determined by ^1H NMR to be in the ratio of 55:45, respectively. Control experiments were conducted in which **15** was solvolyzed under identical conditions and **14** in CH_3OH–CH_3ONa solution at ambient temperature. In these cases the total yields of the *cis*- and *trans*-3,4-dimethoxytetramethylcyclobutene were similar to that obtained for the methanolysis of **5**, but the distributions were determined to be in the ratio of 15:85 and 3:97, respectively. Methanolysis of SO_2ClF–SbF_5 solutions of **5** were performed at −90 °C since these reactions are considerably more vigorous than the quenching of SO_2 solutions, and the yields of the dimethyl ethers in these cases varied between 55 and 60%. Identification of the products isolated in the quenching experiments were based upon their ^1H NMR spectra, which were identical with those reported in the literature[31] for *cis*- and *trans*-3,4-dimethoxytetramethylcyclobutene.

1,2-Dimethyl-3,3,4-trifluorocyclobutenyl Cation (18). To an approximately tenfold molar excess of SbF_5 dissolved in approximately 2 ml of SO_2ClF at −78 °C was added dropwise, with vigorous Vortex stirring, a SO_2ClF solution of 1,2-dimethyl-3,3,4,4-tetrafluorocyclobutene at −78 °C. The resultant solution of **18** was transferred to a precooled NMR tube which was subsequently sealed. **18** was completely stable in this medium upon heating to 80 °C for approximately 5 min.

4-Chloro-1,2-dimethylcyclobutenyl Cation (19). (a) In SbF_5–SO_2ClF Solution. To 3.57 g (16.5 mmol) of SbF_5 dissolved in approximately 2 ml of SO_2ClF at −78 °C was added dropwise, with vigorous Vortex stirring, a slurry of 0.23 g (1.5 mmol) of 3,4-dichloro-3,4-dimethylcyclobutene in SO_2ClF at −78 °C. The resultant solution of **19** was transferred immediately to a precooled NMR tube, which was subsequently sealed.

(b) In $AgSbF_6$–SO_2ClF–SO_2 Solution. To 0.27 g (0.79 mmol) of $AgSbF_6$ suspended in solution composed of approximately 2 ml of SO_2ClF and 2 ml of SO_2 at −78 °C was added, with vigorous Vortex stirring, 0.05 g (0.3 mmol) of 3,4-dichloro-3,4-dimethylcyclobutene in SO_2ClF at −78 °C. The resultant solution was then heated at approximately 0 °C with vigorous stirring until the solution of **19** was concentrated to a total volume of approximately 2 ml. The solution was recooled to −78 °C, pipetted off from the excess $AgSbF_6$ and precipitated AgBr, and transferred to a precooled NMR tube for direct study. No decomposition of **19** nor formation of **23** could be detected by ^1H NMR spectroscopy upon reaction of this solution at −10 °C for 1.5 h.

4-Fluoro-1,2-dimethylcyclobutenyl Cation (23). Reaction of the above described SbF_5–SO_2ClF solution of **19** at approximately −20 °C for 20 min resulted in almost complete conversion of **19** to **23**. Upon heating this solution slowly to 40 °C, decomposition of **23** occurred with no evidence for the formation of the 1,2-dimethylcyclobutadiene dication.

4-Chlorocyclobutenyl Cation (25). To 3.45 g (15.9 mmol) of SbF_5 dissolved in approximately 3 ml of SO_2ClF at −78 °C was added, with vigorous Vortex stirring, 0.20 g (1.6 mmol) of *cis*-3,4-dichlorocyclobutene in SO_2ClF at −78 °C. This resultant solution of **25** was transferred immediately to an NMR tube, which was subsequently sealed. No decomposition of **25** was detected by ^1H NMR spectroscopy upon reaction of this solution for 3 h at 0 °C.

4-Fluorocyclobutenyl Cation (26). After reaction of the above described SbF_5–SO_2ClF solution of **25** for 2 h at 45 °C the conversion of **25** to **26** was essentially complete. Heating this resultant solution to 75 °C resulted only in the decomposition of **26**, with no evidence for the formation of **1**.

Nuclear Magnetic Resonance Spectroscopy. (a) Proton Nuclear Magnetic Resonance Spectra. ^1H NMR spectra were obtained on Varian Associates Model A56/60 and HA-100 NMR spectrometers. The FT ^1H NMR spectrum of the 4-fluorocyclobutenyl cation (**26**) was obtained on the latter instrument equipped with a FT-100 Fourier transform accessory (V-4357 pulsing and control unit). Field/frequency regulation was maintained by the homonuclear lock system of the spectrometer. The free induction signal derived after each pulse was digitized and accumulated in a Varian 620/l computer (8K). Fourier transform of the accumulated free induction signal gave the frequency spectrum.[51] Both instruments were equipped with variable temperature accessories, and proton chemical shifts are referenced to external (capillary) Me_4Si.

(b) Fluorine Nuclear Magnetic Resonance Spectra. ^{19}F NMR spectra were obtained on a Varian Associates Model A56/60 NMR spectrometer equipped with a variable temperature accessory. Fluorine chemical shifts are referenced to external (capillary) $CFCl_3$.

(c) Carbon Nuclear Magnetic Resonance Spectra. ^{13}C NMR spectra were obtained by the Fourier transform method on a Varian Associates model XL-100 NMR spectrometer equipped with a broad-band proton decoupler and variable-temperature probe. The complete details of the instrumentation and techniques employed have been described previously.[52] ^{13}C NMR chemical shifts were measured from external (capillary) Me_4Si. Proton–carbon coupling constants were measured directly from spectra recorded in the gyro-gate mode of operation.

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fessor R. Pettit (University of Texas) for samples of *trans*-3,4-dibromocyclobutene and *cis*-3,4-diiodocyclobutene, and Professor P. D. Bartlett (Harvard University) for a sample of 1,2-diphenyl-3,3,4,4-tetrafluorocyclobutene.

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A + B → C + D

ΔH_f (kcal mol^{-1}, MINDO/3)[39] =

A	B	C	D
21	228	33	208

$\Delta\Delta H_f$ (MINDO/3) = 8 kcal mol^{-1}

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Tertiary 2-Benzonorbornenyl Cations[1]

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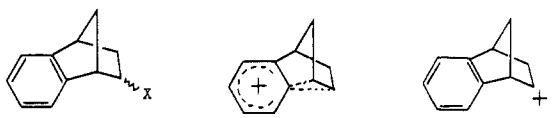
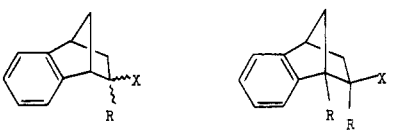
Abstract: The tertiary 2-methyl-, 2-ethyl-, and 1,2-dimethyl-2-benzonorbornenyl cations were prepared under stable ion conditions and characterized by ^1H and ^{13}C NMR spectroscopy. All three ions display very similar charge delocalization pattern of the benzo ring in their NMR spectra. The 2-methyl- and 2-ethyl-2-benzonorbornenyl cations are shown to be static unsymmetrical carbenium ions with less benzonortricyclyl-like nature than the parent secondary 2-benzonorbornenyl cations; while the 1,2-dimethyl-2-benzonorbornenyl cation is a symmetrical carbenium ion undergoing rapid 1,2 Wagner–Meerwein shift. The 2-ethyl-2-benzonorbornenyl cation undergoes ring expansion reaction upon heating to give the 2-methyl-2-benzobicyclo[3.2.1]octenyl cation. Although charge delocalization into the benzo ring in both 2-benzonorbornenyl and 2-benzobicyclo[3.2.1]octenyl cations is substantial, the interaction between C(1)–C(11) σ bond and the empty p orbital at C(2) in the former is much stronger than that of the C(1)–C(12) σ bond and the empty p orbital at C(2) in the latter.

The importance of phenyl-ring participation in the solvolysis of secondary benzonorbornenyl derivatives (**1**) has been clearly demonstrated.[2] The solvolytic reactions generally have been considered to involve assisted ionization for *exo*-2-benzonorbornenyl derivatives to give symmetrically bridged nonclassical ions **2**, rather than unsymmetrical classical ions **3**. Ambiguous interpretations have been given of the solvolysis



1 2 3

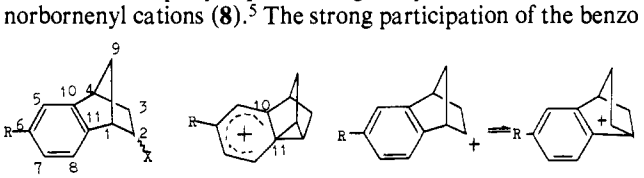
of tertiary benzonorbornenyl derivatives (**4**).[3] Goering et al.[4] have recently been able to show that solvolysis of optically active tertiary 2-benzonorbornenyl derivatives (**5**) gave exclusively optically active products and thus concluded that the reactions involved the unsymmetrical carbenium ions, rather than nonclassical ions.



4 5

R= CH_3 or C_6H_5 R= CH_3

In earlier work we have shown that the ionization of secondary 2-benzonorbornenyl derivatives (**6**) under stable ion conditions gives symmetrical benzonortricyclyl cations (**7**) rather than rapidly equilibrating unsymmetrical 2-benzonorbornenyl cations (**8**).[5] The strong participation of the benzo ring into the developing empty p orbital at C(2) thus results in formation of sterically constrained tricyclic carbenium ions of ethylenebenzenium ion type,[6] clearly indicated by the observation of the aliphatic spiro carbon absorption (C(11)) in their ^1C NMR spectra.



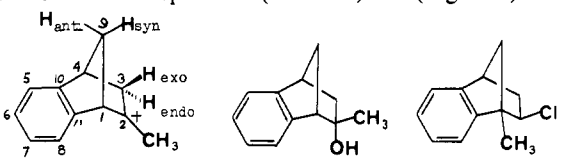
6 7 8

R = H, CH_3, Cl, OCH_3

In continuation of our studies, we now report our investigation of the structure of tertiary 2-benzonorbornenyl cations under stable ion conditions, showing that they are either static or rapidly equilibrating carbenium ions with expected charge delocalization into the benzo ring, but with rather limited contribution from benzonortricyclyl structures.

Results and Discussion

Preparation of 2-Benzonorbornenyl Cations. 2-Methyl-2-benzonorbornenyl cation (**9**) was prepared by careful ionization of 2-methyl-*endo*-2-benzonorbornenol (**10**)[7] or 1-methyl-*exo*-2-chlorobenzonorbornene (**11**) with SbF_5–SO_2ClF at −78 °C. The ^1H NMR spectrum (60 MHz) of **9** (Figure 1) consists



9 10 11

of a sharp singlet at δ 3.08 (3 H); a multiplet centered at δ 3.20 (2 H); a broad singlet at δ 3.84 (1 H); a multiplet centered at δ 4.10 (2 H); a broad singlet at δ 6.08 (1 H); and aromatic multiplets extending from δ 7.70 to 8.46 (4 H). The proton noise-decoupled FT ^{13}C NMR spectrum (Figure 1) of **9** at −85 °C shows *12* carbon resonances, clearly indicating that the ion is unsymmetrical. The ^1H and ^{13}C NMR spectroscopic data are summarized in Table I along with their assignments. Assignments for carbon shifts were made with the aid of the proton coupled ^{13}C NMR spectrum. There are three singlet carbon resonances at $\delta_{^{13}C}$ 199.1, 177.2, and 104.5, which are assigned to C(2), C(10), and C(11), respectively. The two doublets at $\delta_{^{13}C}$ 80.8 ($J_{^{13}C-H}$ = 180.4 Hz) and 41.6 ($J_{^{13}C-H}$ = 158.7 Hz) are assigned to the two bridgehead positions C(1) and C(4), respectively. The two doublet of doublets centered