Cyclopropyl/Phenylcyclopropenyl Cations: Studies in Stabilization

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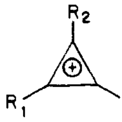
Abstract: Tricyclopropylcyclopropenium ($Cy_3C_3^+$) and 1,2-dicyclopropyl-3-phenylcyclopropenium ($Cy_2PhC_3^+$) ions have been synthesized by additions of cyclopropylchlorocarbene or phenylfluorocarbene, respectively, to dicyclopropylacetylene. X-ray crystal structures indicate orthogonality of all cyclopropyl and cyclopropenium residues; the phenyl moiety in $Cy_2PhC_3^+$ is coplanar with the cyclopropenium group. pK_{R^+} determinations give 7.09 for $Cy_2PhC_3^+$ and 9.4 for $Cy_3C_3^+$. Together with literature data for $Ph_3C_3^+$ and $CyPh_2C_3^+$, the new data show that each Cy for Ph exchange in the cyclopropyl/phenylcyclopropenium ion series is worth a gain of ~2 pK units on the pK_{R^+} scale. Molecular orbital calculations rationalize the relative stabilities of these cations in terms of differential donor–acceptor interactions.

Breslow's synthesis and study of the triphenylcyclopropenyl cation **1a** ($Ph_3C_3^+$) helped verify the predictive power of simple molecular orbital theory for nonbenzenoid aromatic molecules.[1] Since this pioneering work, many aryl-, alkyl-, and heteroatomic-substituted derivatives of this simplest aromatic system have been prepared.[2] A particular goal has been the correlation of structure and thermodynamic stability, with the latter usually measured as pK_{R^+}. The varieties of cyclopropenyl cations have included, inter alia, the parent (unsubstituted) ion[3] and its alkyl,[4-6] aryl,[1,7] halo,[8] and dialkylamino[2d,5] derivatives. A reasonably comprehensive list appears in Okamoto's study of the comparative stabilities of cyclopropenyl and cycloheptatrienyl cations.[9]



1a, $R_1 = R_2 = R_3 = Ph$ ($Ph_3C_3^+$)
1b, $R_1 = R_2 = Ph$; $R_3 = c\text{-}C_3H_5$ ($CyPh_2C_3^+$)
1c, $R_1 = Ph$; $R_2 = R_3 = c\text{-}C_3H_5$ ($Cy_2PhC_3^+$)
1d, $R_1 = R_2 = R_3 = c\text{-}C_3H_5$ ($Cy_3C_3^+$)

In 1973, Kerber and Hsu prepared the cyclopropyldiphenylcyclopropenyl cation **1b** ($CyPh_2C_3^+$) and demonstrated that cyclopropyl was superior to phenyl as a cyclopropenium ion stabilizing substituent.[5] Comparison of the pK_{R^+} values for $Ph_3C_3^+$ (3.1)[4] and $CyPh_2C_3^+$ (5.04)[5,10] indicated an approximately 2.0 pK_{R^+} unit stabilization by the cyclopropyl substituent. If we assume *additivity* of substituent effects on cyclopropenyl cation stability, as found in the stepwise conversion of $Ph_3C_3^+$ to the tri-*p*-anisylcyclopropenium cation,[1b] then we would predict $pK_{R^+} \sim 9$ for the tricyclopropylcyclopropenium ion **1d** ($Cy_3C_3^+$), making this species the most stable all-hydrocarbon cyclopropenyl cation.

Kerber and Hsu were unable to prepare $Cy_3C_3^+$ by the reaction of cyclopropylmagnesium bromide with dicyclopropylcyclopropenone.[5] Subsequently, however, our development of the intermolecular chemistry of cyclopropylchlorocarbene[11] pointed the way to a simple synthesis of $Cy_3C_3^+$ based upon addition of the carbene to dicyclopropylacetylene. This approach succeeded, and was reported simultaneously from Okamoto's laboratory[12] and our own.[13] Gratifyingly, the pK_{R^+} of $Cy_3C_3^+$ did fall in the anticipated range.[12,13]

In this full report, we detail the synthesis of $Cy_3C_3^+$ as well as that of the heretofore-missing member of the cyclopropyl/phenylcyclopropenyl cation series, $Cy_2PhC_3^+$ (**1c**). Also included are pK_{R^+} values and X-ray crystal structures for $Cy_2PhC_3^+$ and $Cy_3C_3^+$ as well as ab initio molecular orbital calculations of model phenyl- and cyclopropyl-substituted cyclopropenyl cations. Taken together, these results now permit a comprehensive discussion of structure and stability in this unusually stable series of hydrocarbon cations.

Results

Synthesis. $Cy_3C_3^+Cl^-$ was prepared by the addition of cyclopropylchlorocarbene[11] to dicyclopropylacetylene[14] (eq 1). In our initial synthesis,[13] about 2 mmol of cyclopropylchlorodiazirine[15] was photolyzed at 20 °C until ~28% decomposition, as judged by manometric determination of the evolved nitrogen. The precipitated, white $Cy_3C_3^+Cl^-$ was filtered under dry nitrogen, triturated with ether, and reprecipitated from cold, dry acetonitrile solution by the addition of ether. This procedure afforded ~70 mg of $Cy_3C_3^+Cl^-$ (~60% yield, based on decomposed diazirine).

(1)

Continuation of the photolysis to greater extents of decomposition led to yellowing of the product. In more recent preparations, we have lowered the reaction temperature to 5–10 °C, extended the photolysis time to 1 h, harvested the product, transferred the reaction solution to a fresh photolysis vessel, diluted with additional dicyclopropylacetylene, and repeated the photolysis/harvest procedure twice. In this way, about 140 mg of $Cy_3C_3^+Cl^-$ could

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(1) (a) Breslow, R. *J. Am. Chem. Soc.* **1957**, *79*, 5318. (b) Breslow, R.; Chang, H. W. *Ibid.* **1961**, *83*, 2367.

(2) (a) Krebs, A. W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 10. (b) Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53. (c) D'yakonov, I. A.; Kostikov, R. R. *Russ. Chem. Rev.* (*Engl. Transl.*) **1967**, *36*, 557. (d) Yoshida, Z-I. *Top. Curr. Chem.* **1973**, *40*, 47.

(3) Breslow, R.; Groves, J. T.; Ryan, G. *J. Am. Chem. Soc.* **1967**, *89*, 5048. Breslow, R.; Groves, J. T. *Ibid.* **1970**, *92*, 984.

(4) Breslow, R.; Höver, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168.

(5) Kerber, R. C.; Hsu, C.-M. *J. Am. Chem. Soc.* **1973**, *95*, 3239.

(6) Ciabattoni, J.; Nathan, E. C., III. *Tetrahedron Lett.* **1969**, 4997.

(7) Breslow, R.; Lockhart, J.; Chang, H. W. *J. Am. Chem. Soc.* **1961**, *83*, 2375.

(8) Tobey, S. W.; West, R. J. *J. Am. Chem. Soc.* **1964**, *86*, 1459.

(9) Okamoto, K.; Takeuchi, K.; Komatsu, K.; Kubota, Y.; Ohara, R.; Arima, M.; Takahashi, K.; Waki, Y.; Shirai, S. *Tetrahedron* **1983**, *39*, 4011.

(10) Unless otherwise indicated, cited pK_{R^+} values were determined in 50 vol % aqueous acetonitrile.

(11) Moss, R. A.; Fantina, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 6788.

(12) Komatsu, K.; Tomioka, I.; Okamato, K. *Tetrahedron Lett.* **1980**, *21*, 947.

(13) Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1980**, *21*, 1221.

(14) Köbrich, G.; Merkel, D.; Thiem, K. W. *Chem. Ber.* **1972**, *105*, 1683.

(15) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

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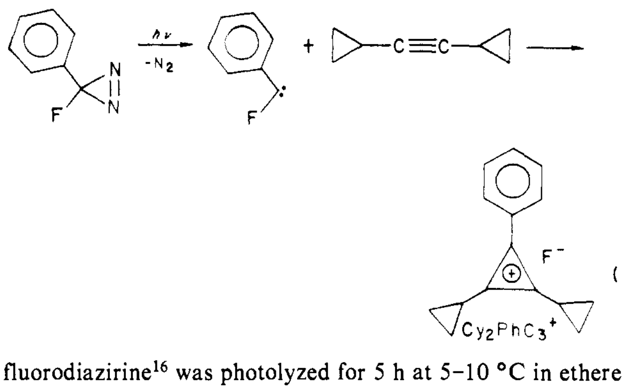
be prepared in a typical run; see Experimental Section.

Analytically pure $Cy_3C_3^+Cl^-$, mp 89–90 °C, is insoluble in hexane, benzene, ether, and carbon tetrachloride, somewhat more soluble in chloroform, and soluble in acetone, acetonitrile, dimethyl sulfoxide, and water. This solubility pattern is consistent with an ionic species. $Cy_3C_3^+Cl^-$ is moderately hygroscopic and slowly yellows upon storage at ambient temperature. The chloride salt could be readily transformed into the tetrafluoroborate or hexafluoroantimonate by treatment of $Cy_3C_3^+Cl^-$ in acetonitrile with 1 equiv of $AgBF_4$ or $AgSbF_6$.

$Cy_3C_3^+Cl^-$ showed λ_{max} 210 nm (ϵ 22 900, H_2O, pH 3.7) and ν_{max} 1425 cm^{-1} (KBr). The latter band is the most intense in the IR spectrum and may be associated with the cyclopropenium ring.[2b,4,5] NMR spectra of $Cy_3C_3^+$ will be presented below.

$Cy_2PhC_3^+F^-$ (**1c**) was prepared by the addition of phenylfluorocarbene to dicyclopropylacetylene (eq 2). Thus phenyl-



(2)

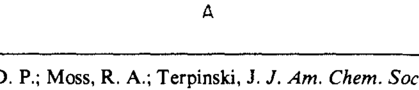
fluorodiazirine[16] was photolyzed for 5 h at 5–10 °C in ethereal dicyclopropylacetylene. Crystals of $Cy_2PhC_3^+F^-$ were harvested by filtration each hour, giving a total yield of 33%, based on the initial diazirine.

$Cy_2PhC_3^+F^-$, mp 79–81 °C, is insoluble in hexane, ether, and carbon tetrachloride, but soluble in acetonitrile, nitromethane, dimethyl sulfoxide, acetone, methanol, ethanol, and water. The solubility pattern is again consistent with an ionic species. The fluoride salt is hygroscopic and yellows noticeably after 3 h of storage at ambient temperature.

$Cy_2PhC_3^+F^-$ showed λ_{max} (EtOH) 265 nm (phenyl) and end absorption below 225 nm. The IR spectrum (KBr) revealed a very strong cyclopropenium absorption at 1420 cm^{-1}. NMR spectra are described below.

The fluoride salt was readily converted to the tetrafluoroborate by treatment with boron trifluoride etherate in nitromethane. $Cy_2PhC_3^+BF_4^-$ was recrystallized from ether, mp 123–125 °C, and was analytically pure. Its IR spectrum (KBr) showed very strong bands at 1420 (cyclopropenium) and 1060 (BF_4^-) cm^{-1}.

NMR Spectra. In the 20-MHz ^{13}C NMR spectra of $Cy_3C_3^+BF_4^-$ (−50 °C, acetone-d_6) and $Cy_2PhC_3^+F^-$ (25 °C, D_2O), we observe similar chemical shifts for the α-cyclopropyl, β-cyclopropyl, and cyclopropenyl carbon atoms: **1d**(Me_4Si) δ 8.65 (α), 15.79 (β), 169.2 (cyclopropenium); **1c** (Me_4Si) δ 9.68 (α), 16.57 (β), 156.4 (Ph-C^+), and 169.4 (Cy-C^+).[17] The greater deshielding of the β relative to the α carbons is consistent with significant positive charge specifically imposed on the β cyclopropyl carbons of these cations, a feature previously noticed by Okamoto.[12] It is in accord both with simple hyperconjugative explanations for the stabilization of the cyclopropenium ion by the cyclopropyl group, viz. A, and with results of molecular orbital calculations (see below).



A

Table I. pK_{R^+} Values of Cyclopropyl/Phenylcyclopropenium Ions[a]

cation	substituents	anion	pK_{R^+}	ref
1a	Ph_3	Br^-	3.1	4
1a	Ph_3	BF_4^-	3.4	5
1b	$CyPh_2$	BF_4^-	5.04	5
1c	Cy_2Ph	BF_4^-, F^-	7.09	this work
1d	Cy_3	Cl^-	9.4	13, this work
1d	Cy_3	BF_4^-	10.0	12

[a] Data are for potentiometric titrations in 50% aqueous acetonitrile.

The 400-MHz proton NMR spectra (25 °C, acetone-d_6) of $Cy_3C_3^+BF_4^-$ (**1d**) and $Cy_2PhC_3^+BF_4^-$ (**1c**) feature two β-cyclopropyl proton multiplets centered at δ 1.54 (**1d**) and 1.88 (**1c**) ("pentuplets" with further fine splitting) and 1.77 (**1d**) and 1.97 (**1c**) ("sextuplets" with further fine splitting). We also observe 7-line α-proton signals at δ 2.65 (**1d**) and 3.01 (**1c**). Double resonance experiments with **1d** afford J = 8 and 5 Hz for couplings between H_α and the lower-field or higher-field β protons, respectively. On the basis that cis-vicinal proton–proton coupling is stronger than trans-vicinal coupling in cyclopropanes,[18] we assign the δ 1.77 multiplet of **1d** to the cis (with respect to H_α) β protons and the δ 1.54 multiplet to the trans β protons. The chemical shifts parallel the magnitudes of the fractional positive charges imposed on the protons, as inferred from molecular orbital calculations (see below).

The 20-MHz ^{13}C and 400-MHz proton NMR spectra of $Cy_3C_3^+BF_4^-$ and $Cy_2PhC_3^+BF_4^-$ were each determined at 25 and −50 °C. No temperature-dependent phenomena were observed for either nucleus with either cation over this temperature range. This behavior is consistent with rapid rotation of the cyclopropyl groups on the NMR time scale and with calculated (see below) C–C rotational barriers of ≤8 kcal/mol.

pK_{R^+}. The pK_{R^+} values of $Cy_2PhC_3^+$ and $Cy_3C_3^+$ were determined titrimetrically in 1:1 acetonitrile/0.1 N aqueous NaOH.[5] The cyclopropenium ion solutions were titrated, under a nitrogen atmosphere, against a glass electrode using standardized (0.023–0.035 N) aqueous NaOH.[4] With $Cy_2PhC_3^+$, the observed dependence of pH on the volume of titrant described a classical titration curve whose midpoint was taken as the pK_{R^+}. The results of four titrations on two lots of $Cy_2PhC_3^+BF_4^-$ and one lot of $Cy_2PhC_3^+F^-$ were 7.13, 7.15, 7.07, and 7.00, affording pK_{R^+} = 7.09 ± 0.05_4.

The high pK_{R^+} value of the $Cy_3C_3^+$ cation prevented us from obtaining a classical, sigmoidal titration curve for this ion. We therefore calculated theoretical titration curves for each experiment, varying the pK_{R^+} assigned to the ion until the sums of the squares of the differences between the observed and calculated pH values were minimized at each volume of titrant. The pK_{R^+} corresponding to the best minimization was taken as the actual value. Three runs carried out in 1980[13] gave the pK_{R^+} of $Cy_3C_3^+Cl^-$ as 9.4 ± 0.3_3; a redetermination now gave 9.47. Okamoto et al. reported 10.0 ± 0.3 for a potentiometric titration of the fluoroborate salt in 50% aqueous acetonitrile.[12]

Table I collects pK_{R^+} data for the four cyclopropyl/phenylcyclopropenium ions **1a**–**d**. From these data, it is apparent that each cyclopropyl for phenyl substitution stabilizes the cyclopropenium cation. To a first approximation, the expression of this stability enhancement is about 2 pK units for each cyclopropyl/phenyl exchange. Comparing only the fluoroborate salts in Table I, there appears to be a progression in the enhancement associated with each succeeding substituent exchange: 1.6 units for $Ph_3C_3^+$ to $CyPh_2C_3^+$, 2.1 units for the next exchange, and 2.9 units for $Cy_2PhC_3^+$ to $Cy_3C_3^+$. However, given the known and probable errors in the pK_{R^+} values (±0.3 unit), this trend should probably not be taken literally.

Crystal Structure Determinations. Clear, needle-like crystals of $Cy_3C_3^+SbF_6^-$ were obtained from acetonitrile/ether. A single crystal was cleaved perpendicular to the long axis and mounted

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(16) Cox, D. P.; Moss, R. A.; Terpinski, J. *J. Am. Chem. Soc.* **1983**, *105*, 6513. Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *Ibid.* **1985**, *107*, 2743.

(17) The Ph carbons of **1c** appear at δ 119.84 (ipso), 131.1 (m), 135.4 (o), and 138.0 (p).

(18) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969, p 286 ff.

Table II. Crystal and Refinement Data

item	$Cy_3C_3^+SbF_6^-$	$Cy_2PhC_3^+BF_4^-$
formula	$SbF_6C_{12}H_{15}$	$F_4C_{15}BH_{15}$
mol wt	349.99	282.09
a, Å	22.158 (1)	9.071 (2)
b, Å	8.599 (2)	18.820 (3)
c, Å	7.619 (1)	9.379 (2)
α, deg	90	90
β, deg	90	117.91 (2)
γ, deg	90	90
V, Å^3	1451.7 (5)	1415 (1)
space group	$Pnma$	$P2_1/n$
Z	4	4
d_{calcd}, g/cm^3	1.807	1.324
d_{obsd}, g/cm^3	1.81 (1)	1.31 (1)
λ (Mo Kα), Å	0.71073	0.71073
monochromator	graphite crystal	graphite crystal
diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
data collection method	θ–2θ	θ–2θ
2θ limit, deg	50	45
temp, K	297 (1)	297 (1)
scan range, deg	$1.0 + 0.35 \tan \theta$	$0.9 + 0.30 \tan \theta$
weighting scheme	$w = 4F_o^2/\sigma^2(F_o^2)^a$	$w = 4F_o^2/\sigma^2(F_o^2)^a$
no. of std reflns	3	3
variation in std intens	±4%	±0.3%
crystal size, mm	0.12 × 0.12 × 0.4	0.13 × 0.3 × 0.4
no. of unique data collected	1367	1841
no. of data used in refinement	$830[F_o^2 \geqslant 3\sigma(F_3^2)]$	$1148[F_o^2 \geqslant 2\sigma(F_o^2)]$
data: parameter ratio	6.5	4.9
final G.O.F.^{b}	1.39	1.93
final $R_F{}^c$	0.041	0.062
final $R_{wF}{}^d$	0.049	0.067
highest peak in final difference map, e$^-$/Å^3	0.48	0.37
final largest shift/esd	<0.01	<0.01

^{a} $\sigma(F_o^2) = [S^2(C + R^2B) + 0.04F_o^2]^{1/2}/Lp$ where S is the scan rate, C is the total integrated peak count, R is the ratio of scan to background counting time, B is the total background count, and 0.04 is a factor used to downweight intense reflections. ^{b} Error in an observation of unit weight, equal to $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO = number of observations and NV = number of variables in the least-squares refinement. ^{c} $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. ^{d} $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

inside a capillary tube, which was then sealed. Crystals of $Cy_2PhC_3^+BF_4^-$ were obtained from methanol/ether as clear plates and were also mounted inside a capillary tube for X-ray study.

Details of the data collection process and structure solution are given in Table II. Systematic absences were determined from diffractometer examination of the reciprocal lattices. For $Cy_2PhC_3^+$, this led unambiguously to space group $P2_1/n$. For $Cy_3C_3^+$, as described below, the choice between $Pnma$ and $Pna2_1$ was difficult. Intensities were corrected for Lorentz, polarization, absorption (empirical), and decay effects.

The structures were solved by direct methods using the program MULTAN 82[19] and refined on F by using full-matrix least-squares techniques.[20] Neutral atom scattering factors were used, and anomalous dispersion corrections were applied to the scattering factors of all non-hydrogen atoms. For $Cy_3C_3^+$, because $Z = 4$, an initial attempt was made to solve the structure in space group $Pn2_1a$, a nonstandard form of $Pna2_1$. In this space group, the solution with the highest combined figure of merit revealed the Sb and six light atoms; the remaining non-hydrogen atoms were located from successive difference maps. However, attempts to refine all atoms led to oscillating parameters, nonpositive definite temperature factors, and correlation coefficients as high as 0.92. Similar difficulties in space group $Pn2_1a$ have been observed with other cyclopropenium and cyclopropene structures; e.g., 1,2,3-tris(dimethylamino)cyclopropenium perchlorate[21] and *cis*-cyclopropylbis(dioxopiperazine).[22] Consequently, as with these structures, refinement was carried out in $Pnma$, where the cation and anion both have m symmetry.

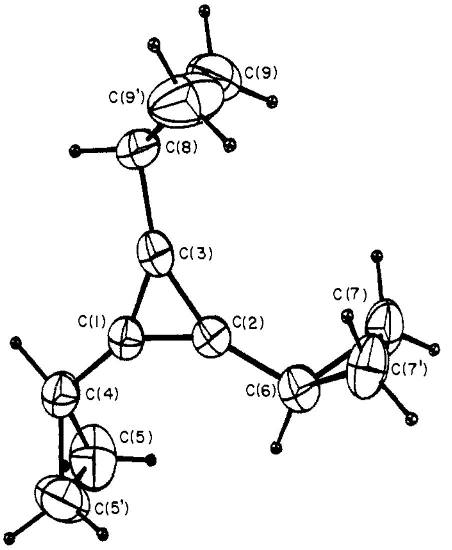

Figure 1. ORTEP view of the tricyclopropylcyclopropenium cation, $Cy_3C_3^+$, showing the atom numbering scheme. Primed and unprimed atoms are related by the mirror plane operation.

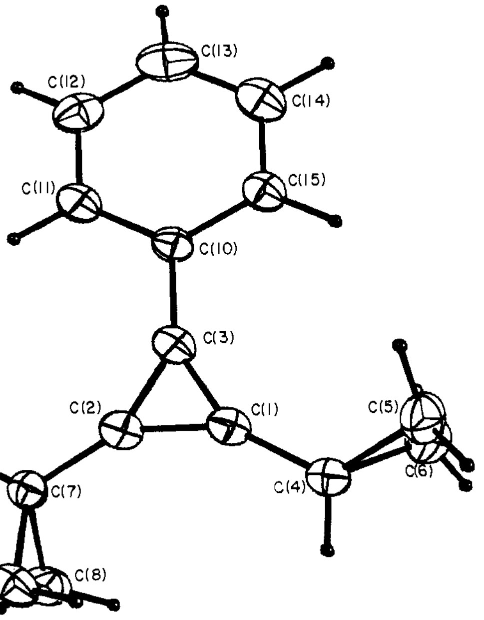

Figure 2. ORTEP view of the 1,2-dicyclopropyl-3-phenylcyclopropenium cation, $Cy_2PhC_3^+$, showing the atom numbering scheme.

At isotropic convergence, H atom coordinates were calculated by assuming idealized bond geometry and a C–H bond distance of 0.95 Å.[23] Temperature factors were set according to $B_H = B_n + 1$, where n is the atom bonded to H. H atom parameters were not refined. Anisotropic refinement converged with $R_F = 0.041$ and $R_{wF} = 0.049$. Although the refinement proceeded smoothly, relatively large thermal parameters and coordinate esd's were observed, particularly for the cyclopropane carbons not constrained to lie on mirror planes in $Pnma$.

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[19] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN 82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Universities of York, England and Louvain, Belgium, 1982.

[20] The Enraf–Nonius Structure Determination Package, Enraf–Nonius, Delft, Holland (1983) was used for data collection, processing, and structure solution.

[21] Ku, A. T.; Sundaralingam, M. *J. Am. Chem. Soc.* **1972**, *94*, 1688.

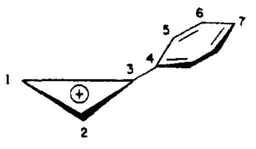
[22] Hempel, A.; Camerman, N.; Camerman, A. *J. Am. Chem. Soc.* **1982**, *104*, 3456.

[23] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

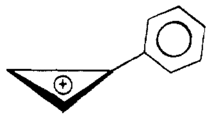
In the case of $Cy_2PhC_3^+$, the MULTAN solution set with the highest combined figure of merit revealed the 20 non-hydrogen atoms as the highest peaks on an E map prepared by using 253 reflections with $E > 1.53$. At isotropic convergence, all H atoms except three of the phenyl H atoms were located on a difference Fourier map and were added to the model. The remaining three H atoms were added at calculated positions. H atom coordinates were refined, whereas temperature factors were fixed as described above for $Cy_3C_3^+$. Fractional atomic coordinates, selected bond distances and angles, observed and calculated structure factors, and anisotropic thermal parameters for both cyclopropenium salts are contained in the supplementary material.

ORTEP drawings of $Cy_3C_3^+SbF_6^-$ and $Cy_2PhC_3^+BF_4^-$ appear in Figures 1 and 2, respectively. The anions are omitted for simplicity. All cyclopropyl/cyclopropenium dihedral angles are within ±1.5° of orthogonality. In $Cy_2PhC_3^+$, the phenyl/cyclopropenium dihedral angle is close to 0° (actually 2.8°), so that the two rings are effectively coplanar. Further discussion of the crystal structures appears below.

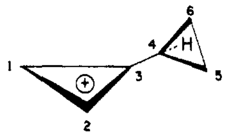
Computations. To help characterize the substituent effects exerted by cyclopropyl and phenyl groups on the cyclopropenium ion, we carried out ab initio molecular orbital calculations on a DEC VAX 11/780 computer with the GAUSSIAN 82 series of electronic structure programs.[24a] Geometries of the phenylcyclopropenium (**2**) and cyclopropylcyclopropenium (**3**) model ions and their neutral parent cyclopropenes were completely optimized,[24b] subject only to overall symmetry constraints (C_{2v} for **2**, C_s for **3** and the neutral species), by using restricted Hartree–Fock (HF) single determinant theory[24c] and the split-valence 3-21G basis set (HF/3-21G//3-21G).[24d] For comparison purposes, the geometries of cyclopropene (C_{2v}), cyclopropane (D_{3h}), and benzene (D_{6h}) were also optimized.



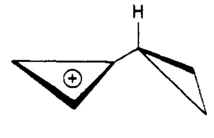
2a (coplanar)



2b (perpendicular)



3a (bisected)



3b (perpendicular)

Energy refinements were then obtained from single-point calculations on **2** and **3** using the extended 6-31G* basis set, including d-functions on C (HF/6-31G*//3-21G).[24e] The wave functions were subjected to the conventional Mulliken population analysis.[24f] Gross orbital and net atomic charges cited in the text represent values obtained with the minimal STO-3G basis set (HF/STO-3G//3-21G),[24g] because it was found that the use of the split-valence basis sets gave rise to seemingly unrealistic populations in some instances.[25]

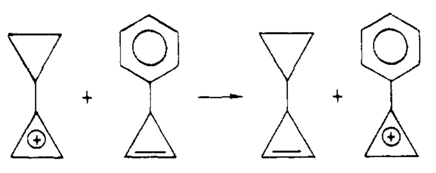
Calculated geometries for the individual ring constituents of **2** and **3** agree well with the measured parameters of actual molecules. For the cyclopropenium ion, the calculated C–C bond length is 1.361 Å, in close agreement with the average C–C bond distances found in $Cy_3C_3^+$ [1.37 (3) Å] and $Cy_2PhC_3^+$ [1.359 (8) Å]; see below. The calculated structure of benzene (C–C = 1.385 Å and C–H = 1.072 Å) agrees with the experimentally determined (microwave) structure (C–C = 1.397 Å and C–H = 1.084 Å).[26] Finally, for cyclopropane, our calculations give C–C = 1.513 Å, C–H = 1.072 Å, and ∠HCH = 114.9°. Microwave and Raman experiments give 1.514 Å, 1.080 Å, and 116°, respectively, for these parameters.[27]

Thus, the structures of the individual rings are well-reproduced by calculations with the 3-21G basis set. It is known that d-functions in the basis set are important for accurate descriptions of the bonding and energetics of strained cyclic systems,[28] but it has also been shown that substituent effects can be reliably calculated without such polarization functions.[28b] Thus, the small split-valence s,p basis set appears fully adequate for our structural studies.

Discussion

General Comments. The major results and implications of this study are clear. Cyclopropyl substituents strongly stabilize cyclopropenium ions, more strongly in fact than phenyl substituents. The tricyclopropylcyclopropenium ion, $Cy_3C_3^+$, is the most stable all-hydrocarbon cyclopropenium ion known, with pK_{R^+} in the range 9.4–10.0 (Table I). In contrast, the pK_{R^+} values of trimethylcyclopropenium (7.4)[6] and triphenylcyclopropenium (3.1–3.4)[4,5] are lower.

The effects of phenyl or cyclopropyl substituents on cyclopropenyl cation stability, as measured by pK_{R^+}, appear to be nearly additive (Table I), with each Cy for Ph exchange worth about 2 pK_{R^+} units. This is generally in keeping with calculated results. For example, with optimized geometries for the "best" conformations (bisected for all species except **2a**), the isodesmic reaction eq 3 is *endothermic* by 1.3 kcal/mol (HF/3-21G//3-21G).



3a **2a** (3)

Assuming that the preference is not inherent in the neutral species of eq 3, this result accords with a greater cyclopropenium ion stabilizing effect of cyclopropyl over phenyl.[29] The origin of this effect may simply be that the major electron donation from cyclopropyl comes from an orbital that is not particularly strong in binding the cyclopropyl skeleton, whereas electron donation from phenyl decreases the aromatic stabilization of the phenyl ring. The amount of charge transferred to the ion is *larger* in **2a** than in **3a**, but the charge *transferred* in this case does not parallel the stability of the *entire* ionic molecule. Further details of the calculations are discussed below.

One of the reasons for the regular increase in pK_R^+ of the cyclopropenium ions **1a–1d** that attends each Cy for Ph exchange may be that in **1b–1d**, Cy and Ph are relatively free to assume their optimal geometries for the electronic stabilization of adjacent electron deficient p orbitals. This appears to be true in the solid state, as determined by X-ray analysis, and presumably would also be so in solution. Thus, although in **1a**, $Ph_3C_3^+ClO_4^-$, the phenyl groups are propeller-like and make angles of 7.6°, 12.1°, and 21.2° with respect to the cyclopropenium plane,[30] the Ph/C_3^+

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[24] (a) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon Chemistry Publication Unit, Pittsburgh, PA, 1983. (b) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. Z-matrices and total energies for the optimized geometries are available upon request from one of us (K.K.-J.). (c) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69. (d) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (e) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (f) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343. (g) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 2191.

[25] For example, the 3-21G basis set "predicts" that in **3** substantial charge (>0.2 e⁻) is donated across the C_3C_4 linkage from the cyclopropenium ion to the cyclopropane unit. For problems with Mulliken populations of three-membered rings, see e.g.: Deakyne, C. A.; Allen, L. C.; Craig, N. C. *J. Am. Chem. Soc.* **1977**, *99*, 3895.

[26] Langseth, A.; Stoicheff, B. P. *Can. J. Phys.* **1956**, *34*, 350.

[27] Jones, W. J.; Stoicheff, B. P. *Can. J. Phys.* **1969**, *42*, 2259.

[28] (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217. (b) Rohmer, M.-M.; Roos, B. *J. Am. Chem. Soc.* **1975**, *97*, 2025.

[29] It is known independently, from σ_R^+ values, that cyclopropyl is a better resonance donator than phenyl toward a directly conjugated vacant p orbital; cf.: Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119, especially pp 202–215. Indeed, tricyclopropylmethyl cation ($pK_{R^+} = -2.3$) is much more stable than triphenylmethyl cation ($pK_{R^+} = -6.6$): Deno, N. C.; Richey, H. G., Jr.; Liu, J. S.; Lincoln, D. N.; Turner, J. O. *J. Am. Chem. Soc.* **1965**, *87*, 4533.

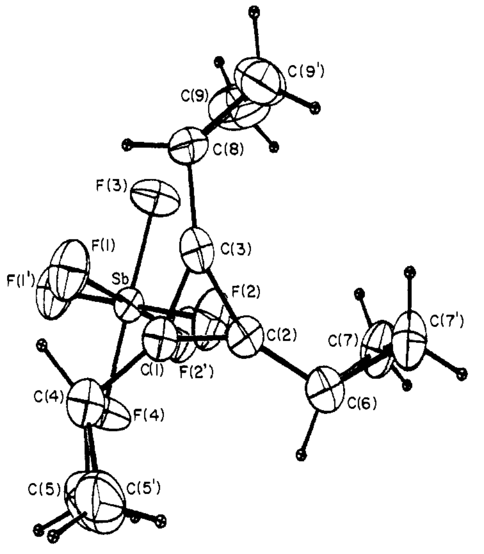
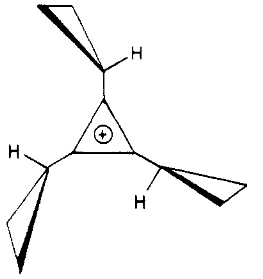


Figure 3. ORTEP view of the tricyclopropylcyclopropenium hexafluoroantimonate unit. The shortest interionic contacts are F(2)···C(2), 3.048 (3) Å, F(2)···C(3), 3.174 (2) Å, and F(2)···C(1), 3.375 (5) Å.

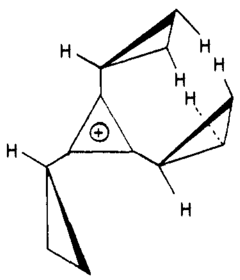
dihedral angle is reduced to 2.8° in $Cy_2PhC_3^+$ (see Figure 2). Here, steric interactions between the ortho protons of adjacent Ph groups in $Ph_3C_3^+$ are absent, and the Ph group assumes the preferred coplanar arrangement with C_3^+. Calculations for **2a** and **2b** give the adiabatic barrier to rotation around the C_3^+–Ph bond as 11.7 kcal/mol at the HF/6-31G*//3-21G level (12.6 kcal/mol at the HF/3-21G//3-21G level).

At the same time, as shown in Figure 2, the Cy groups of $Cy_2PhC_3^+$ are effectively orthogonal to the C_3^+ unit, i.e., in the preferred bisected conformation for Cy stabilization of an adjacent vacant p orbital.[31] This is also true in $Cy_3C_3^+$ (Figure 1) where calculations for **3a** ⇌ **3b** give the adiabatic barrier to rotation about the Cy–C_3^+ bond as 7.3 kcal/mol at the HF/6-31G*//3-21G level (8.9 kcal/mol at the HF/3-21G//3-21G level).[32]

One interesting structural note is that with $Cy_3C_3^+$, two rotameric isomers are possible if Cy groups are held orthogonal to the cyclopropenium ring. These are illustrated in structures **1d**$_{\text{sym}}$ and **1d**$_{\text{unsym}}$, which represent top views of the isomers. A priori, one would imagine that the propeller-like **1d**$_{\text{sym}}$ structure would be preferred because it avoids the pair of H–H steric interactions of the cyclopropyl protons anticipated for **1d**$_{\text{unsym}}$. Surprisingly, in the solid state, X-ray studies reveal **1d**$_{\text{unsym}}$ to be the conformation adopted by $Cy_3C_3^+$ (see Figure 1). As discussed below, and illustrated in Figure 3, this peculiarity may be a result of the packing in the $Cy_3C_3^+SbF_6^-$ crystal and the need to create a "pocket" for the large SbF_6^- anion so that it can most closely approach the C_3^+ ring. The preferred conformation of $Cy_3C_3^+$ in *solution* is unknown.



1d$_{\text{sym}}$



1d$_{\text{unsym}}$

X-ray Structures. The crystal structures of $Cy_3C_3^+SbF_6^-$ and $Cy_2PhC_3^+BF_4^-$ are represented in Figures 1 and 2, respectively, which also show the atom numbering schemes. Crystal and refinement data appear in Table II; selected bond distances and angles appear in the supplementary material.

In the $Cy_3C_3^+SbF_6^-$ structure, the cation has mirror symmetry; consequently, the three Cy groups are perpendicular to the C_3^+ ring. As indicated above, the Cy groups are *not* arranged in the propeller-like fashion that could be obtained by rotating the C(8)–C(9)–C(9') Cy group 180° about the C(3)–C(8) bond to give a cation of approximate C_{3h} symmetry (i.e., **1d**$_{\text{sym}}$). In $Cy_2PhC_3^+BF_4^-$, the Cy groups are very nearly perpendicular to the C_3^+ plane [dihedral angles: C(1)–C(3)/C(4)–C(6), 88.8°; C(1)–C(3)/C(7)–C(9), 91.5°], whereas the Ph and C_3^+ planes are very nearly coplanar.

Within the C_3^+ units, average C–C bond distances [1.37 (3) Å for $Cy_3C_3^+$, 1.359 (8) Å for $Cy_2PhC_3^+$] lie within experimental error of each other and of those reported for the C_3^+ groups in $(Me_2N)_3C_3^+ClO_4^-$ [1.363 (7) Å][21] and $Ph_3C_3^+ClO_4^-$ [1.373 (5) Å].[30] There appears to be no large effect of substituents on bond lengths within the C_3^+ units of highly substituted cyclopropenium ions.

In contrast, bond alternations anticipated in the Cy substituents are clearly seen. For example, in $Cy_2PhC_3^+$, the vicinal cyclopropyl bond lengths [1.514 (5), 1.515 (6), 1.511 (6), and 1.511 (6) Å] are equivalent within experimental error, as are the distal bond lengths [1.444 (6) and 1.455 (6) Å], but the vicinal bonds are all ~0.06 Å longer than the distal bonds. Large substituent-induced asymmetries have previously been observed for cyclopropyl rings,[33] and the effect has been analyzed in detail by Allen.[34] A brief molecular orbital analysis of these effects appears below for model ion **3a**.

In $Cy_3C_3^+SbF_6^-$, the cations and anions are arranged in ··· $Cy_3C_3^+$···SbF_6^-··· chains along *b*, similar to those reported for other structures containing C_3^+ rings.[21,30] As shown in Figure 3, there are several short interionic contacts between the SbF_6^- and the C_3^+ ring; these contacts stabilize the structure coulombically. Figure 3 illustrates that the SbF_6^- anion sits in a "pocket" formed by the C_3^+ atoms and atoms C_4 and C_8 of the Cy groups that face *away* from each other (cf., **1d**$_{\text{unsym}}$). The anion could not approach the C_3^+ groups as closely if the cation had the pseudo C_{3h} propeller-like conformation of **1d**$_{\text{sym}}$.

Finally, we note that the packing in $Cy_2PhC_3^+BF_4^-$ differs from the sandwich arrangement observed for the three other C_3^+-containing structures. It consists of interpenetrating ···ABAB··· layers that alternate along the [10$\bar{1}$] direction. The A layers contain cations arranged centrosymmetrically in a head-to-tail fashion reminiscent of the packing of certain dye cations,[35] whereas the B layers contain the BF_4^- anions and the cyclopropyl rings of the cations. These cyclopropyl groups link the A and B layers. The shortest cation–anion contacts occur between F atoms and the cyclopropyl H atoms [F(4)···H(C61), 2.38(4) Å; F(2)···H(C52), 2.47(4) Å].

Molecular Orbital Calculations. Some findings from the ab initio calculations carried out in accord with the procedures described under Results are discussed here.

Phenylcyclopropenium Cation (2a or 2b, $PhH_2C_3^+$). The major stabilizing interaction for $PhH_2C_3^+$ in coplanar conformation **2a** is of the donor–acceptor $\pi \rightarrow \pi^*$ type. The (HF/STO-3G//3-21G) coefficients for the π-HOMO of benzene (e_{1g} symmetry in D_{6h}, $a_2 + b_1$ in C_{2v}) and the π^*-LUMO of cyclopropenium (e_2'' in D_{3h}, $a_2 + b_1$ in C_{2v}) appear below. Two pairs of orbital interactions are feasible, but the dominant interaction will involve

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(30) Sundaralingam, M.; Jensen, L. H. *J. Am. Chem. Soc.* **1966**, *88*, 198.

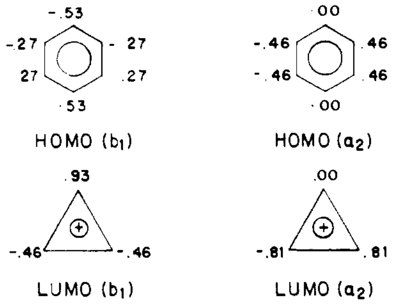
(31) Van Dine, G. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1966**, *88*, 2321. Schleyer, P. v. R.; Buss, V. *ibid.* **1969**, *91*, 5880 and references cited there.

(32) As indicated above, a barrier of this size, although large enough to insure that >>99% of the $Cy_3C_3^+$ molecules maintain their Cy substituents in the bisected conformation at any given time, is still insufficiently great to freeze out Cy–C_3^+ rotation on the NMR time scale within the investigated temperature limits.

(33) Bethell, D.; Chadwick, D. J.; Harding, M. M.; Maling, G. Q. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1677.

(34) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 81.

(35) Potenza, J. A.; Toby, B. H.; Bird, G. R.; Lalancette, R. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 1291.

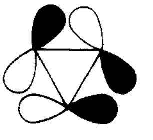


the orbitals of b_1 symmetry. Only these orbitals have coefficients on the linking carbons, and judging from the large coefficients, significant HOMO–LUMO mixing and π electron transfer is predicted. Thus, whereas the π-charge on each carbon in the cyclopropenium ion is 0.67 e⁻, we calculate (in **2a**) π-charges of 0.75 e⁻ on $C_1(C_2)$ and 0.70 e⁻ on C_3; i.e., 0.19 e⁻ has been donated from the phenyl group. Additionally, considerable polarization occurs in the phenyl ring with excess π-charge accumulating on C_4 (0.15 e⁻). Carbons C_5 (0.10 e⁻) and C_7 (0.14 e⁻) are the sole π-donor atoms in **2a**.

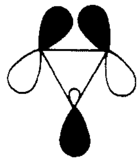
The calculated C–C bond lengths of **2a** are in accord with the coefficient patterns of the interacting HOMO(phenyl)–LUMO(cyclopropenium) pair. For example, relative to the cyclopropenium ion, the C_1–C_2 bond in **2a** is shortened by 0.021 Å to 1.340 Å and the C_2–C_3 (C_1–C_3) bond is lengthened by a similar amount (0.023 Å) to 1.384 Å.[36] The C_3–C_4 linkage is calculated to be very short (1.407 Å) and in the range of aromatic C(sp²)–C(sp²) bond lengths, reflecting the mixing of the cyclopropenium LUMO into the phenyl HOMO in a bonding fashion across the C_3–C_4 link, thus lending partial double bond character to this bond (cf. resonance structures A, above).

In the perpendicular conformation of $PhH_2C_3^+$, **2b**, the direct conjugation between the π-systems is "turned off", and essentially no charge is transferred to the ion. Structural changes are minor, except that the C_3–C_4 bond length (1.454 Å) is calculated to increase by nearly 0.05 Å relative to **2a**, indicative of the loss of the π-bond character in this linkage that is present in **2a** but not in **2b**.

Cyclopropylcyclopropenium Cation (3a or 3b, $CyH_2C_3^+$). The dominant charge-stabilizing effect in **3** is of σ(cyclopropyl) → π*(cyclopropenium) character. This type of hyperconjugation can be exceptionally strong when the interacting units are properly oriented.[31] Cyclopropane possesses a high-lying set of σ-MO's (e′ in D_{3h}, a + a″ in C_s) of very diffuse nature and high in 2p-character. This set of "Walsh orbitals" is sketched below.

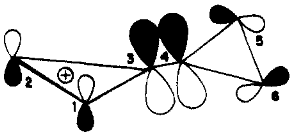


HOMO (a")



HOMO (a')

When ion **3** is in the bisected conformation, **3a**, the HOMO (a″) transforms locally as a π-orbital and can interact strongly with the same LUMO (π*) orbital of the cyclopropenium ion that interacts with the phenyl HOMO (b_1) in **2a**. This interaction is sketched in **4**.



4

The total charge transfer in **3a** is not as large as it is in **2a**. The average increase on C_1 and C_2 amounts to 0.08 e⁻, and no increase is calculated for C_3. Electronic charge is donated both by cyclopropyl carbons and protons. Relative to cyclopropane, the loss of e⁻ is 0.03 from the α carbon (C_4), whereas e⁻ loss from each β carbon is 0.05. The slightly greater positive charge thus imposed on the β carbons appears to be reflected in the ^{13}C NMR chemical shifts ($\delta C_\beta > \delta C_\alpha$), as discussed above. Additionally, each cyclopropyl proton carries more positive charge than it does in cyclopropane, with the largest charge on the C_α-proton (+0.07), followed by the cis C_β-protons (+0.06) and then the trans C_β-protons (+0.04). Qualitatively, this ordering of charge magnitudes parallels the ¹H NMR chemical shifts of the cyclopropyl protons of **1d**; see above.

Geometrical distortions in the cyclopropenium ring of **3a** are similar to those calculated for model ion **2a**. Relative to the parent cyclopropenium ion, C_1–C_2 of **3a** is shortened by 0.019 Å to 1.342 Å, and the average C_1–C_3 and C_2–C_3 increase is 0.020 Å. Following the nodal pattern of the a″ donor orbital, the vicinal C_4–C_5 (=C_4–C_6) bond length increases, relative to cyclopropane, by 0.046 Å to 1.559 Å in **3a**, whereas the distal C_5–C_6 bond is shortened by a similar amount to 1.472 Å. The calculated asymmetry in these bond lengths (0.09 Å) is slightly larger than the experimentally observed difference (~0.06 Å in **1c**) but in the same direction. Surprisingly, the C_3–C_4 bond length of **3a** is calculated at the same value (1.407 Å) as C_3–C_4 of **2a**, indicating not only substantial 2s-character in the σ part of this linkage but also effective π-type interaction between C_3 and C_4 in **3a**.

In the perpendicular conformation, **3b**, inter-ring hyperconjugation is no longer possible, and we find only small structural deformations (~0.005–0.010 Å) in either three-membered ring. The changes are in the same direction as those calculated for conformation **3a**. The C_3–C_4 bond length increases by 0.04 Å in **3b**, relative to **3a**, a smaller increase than the corresponding change in **2a** → **2b** (0.05 Å), in keeping with the smaller rotational barrier for **3a** → **3b** (7.3 kcal/mol vs. 11.7 kcal/mol in **2a** → **2b**).

Experimental Section

General. IR and UV spectra were recorded on Perkin-Elmer Model 137 and Cary Model 17D spectrometers, respectively. NMR spectra were determined on Varian T-60, FT-80, or XL-400 instruments (¹H), whereas ^{13}C spectra were obtained on a Varian CFT-20 spectrometer. Melting points are uncorrected. Elemental analyses were carried out by Robertson Laboratory, Florham Park, NJ.

X-ray analysis employed an Enraf-Nonius CAD-4 diffractometer. For other X-ray data, see Table II. pK_{R^+} measurements were made according to the procedure described by Kerber;[5] see Table I and the Results section.

Tricyclopropylcyclopropenium Chloride ($Cy_3C_3^+Cl^-$, 1d). 3-Chloro-3-cyclopropyldiazirine was prepared according to the method of Graham[15] (see also Moss and Fantina[11]): a solution of 25 g of NaCl in 175 mL of commercial "pool chlorine" (Miracle Maid Co., ~12% hypochlorite) was quickly added to a cooled (0 °C) magnetically stirred solution containing 1.8 g (15 mmol) of cyclopropylamidine hydrochloride[37] and 5.8 g of LiCl in 70 mL of Me_2SO. The receiving solution was contained in a 2-L, round-bottom, three-neck flask that was connected to a series of traps and evacuated to 0.5–2.0 mmHg by a vacuum pump. The diazirine was produced rapidly during the addition, was carried out of the generating flask, through a U-trap filled with NaOH pellets, then through an empty trap cooled to −25 °C, and was finally condensed in a trap containing ~2 mL of dicyclopropylacetylene[14] cooled to −78 °C. The diazirine generation reaction was complete in 8–15 min.

The contents of the trap were transferred to a screw-top Pyrex Carius tube with the aid of 0.5 mL of the acetylene. The tube was sealed, cooled to 5–10 °C, and irradiated with a focussed Osram 200-W XE mercury lamp for 1 h. During irradiation, white solid deposited on the walls and bottom of the tube. After 1 h, the liquid portion of the contents of tube 1 was transferred to a second tube and diluted with 0.5 mL of dicyclopropylacetylene. Tube 2 was sealed and subjected to irradiation (as above), while tube 1 (and its contained solid) was stored over dry ice. After 1 h of irradiation, tube 2 was manipulated as described above for

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(36) Additionally, we find a substantial increase of 0.016 Å for the C_4–C_5 bond length of **2a**, relative to benzene, whereas the C_5–C_6 bond decreases by 0.010 Å to 1.375 Å; only a small increase (0.005 Å) is calculated for the C_5–C_6 bond.

(37) The amidine salt (mp 124–128 °C) was prepared in 60% yield from cyclopropyl cyanide (Aldrich) by using the method of Dox, A. W.; Whitmore, F. C. *Org. Synth.* **1941**, *Collect Vol. I*, 5.

tube 1. A third irradiation, involving (a new) tube 3, was carried out.

Finally, the white solids deposited in tubes 1–3 were washed out with cold anhydrous Et_2O (drybox), triturated several times with additional ether, and then recrystallized from CH_3CN/Et_2O. The final $Cy_3C_3^+Cl^-$, 140 mg, was dried under vacuum. The yield is ~60%, based on decomposed diazirine (see Results).

For $Cy_3C_3^+Cl^-$, we observed mp 89–90 °C; IR (KBr) 3080 (m), 3010 (s), 1425 (s), 1400 (sh), 1330 (m), 1060 (s), 1040 (s), 900 (s), 875 (sh) cm^{-1}. The UV and NMR spectra are discussed in the Results.

Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.0; H, 7.77; Cl, 18.2. Found: C, 74.1; H, 7.82; Cl, 18.0.

Other $Cy_3C_3^+$ Salts. Fluoroborate. $Cy_3C_3^+Cl^-$ (70 mg, 0.36 mmol) was dissolved in 5 mL of dry CH_3CN. To this solution was added 70 mg (0.36 mmol) of $AgBF_4$ in 5 mL of CH_3CN. An immediate precipitate of AgCl formed and was filtered. The filtrate was stripped of solvent on the rotary evaporator and the white residue was recrystallized from CH_3CN/Et_2O to give 70 mg (0.285 mmol, 79%) of $Cy_3C_3^+BF_4^-$, mp 137–140 °C (lit.[12] mp 141–142 °C). NMR spectra are discussed under Results.

Hexafluoroantimonate. $Cy_3C_3^+SbF_6^-$ was prepared in 74% yield from the chloride salt exactly as described for the fluoroborate, except that $AgSbF_6$ was used in place of $AgBF_4$: mp 213–215 °C; IR (KBr) 3070 (w), 3010 (w), 1445 (s), 1330 (m), 1300 (s), 1060 (s), 1030 (m), 1010 (m), 910 (s), 740 (m), 640 (s) cm^{-1}. The density of crystalline $Cy_3C_3^+SbF_6^-$ was 1.81 g/cm³ as determined by the flotation method in a $CHBr_3/CCl_4/n\text{-}C_6H_{14}$ mixture. The X-ray crystal structure is presented under Results; cf. Table II and Figures 1 and 3.

1,2-Dicyclopropyl-3-phenylcyclopropenium Fluoride ($Cy_2PhC_3^+F^-$, 1c). 3-Fluoro-3-phenyldiazirine[16] (408 mg, 3.0 mmol) and 2.23 g (21 mmol) of dicyclopropylacetylene[14] were dissolved in 5 mL of anhydrous ether and photolyzed, with magnetic stirring, in a Pyrex tube at 5–10 °C for 5 h. The focused Osram 200-W XE mercury lamp was used. White precipitate (later yellow) was collected by filtration at the end of each hour. A total of 214 mg (33%) of $Cy_2PhC_3^+F^-$ was obtained, washed several times with dry ether, and dried under vacuum. The salt did not recrystallize well from CH_3CN/Et_2O and had to be stored over dry ice to avoid decomposition. We observed mp 79–81 °C; IR (KBr), 3375 (s), 3010 (m), 2975 (m), 1585 (m), 1490 (m), 1450 (m), 1420 (s), 900 (s), 700 (m), 740 (m), 680 (m) cm^{-1}. NMR and UV spectra are discussed under Results.

Fluoroborate Salt. To a solution of 120 mg (0.56 mmol) of $Cy_2PhC_3^+F^-$ in 10 mL of nitromethane freshly distilled from CaH_2 was added a solution of 3 mL of freshly distilled BF_3–ether in 10 mL of nitromethane. The reaction solution was protected from moisture and stirred magnetically for 1.5 h at ice-bath temperature. Solvents were removed under vacuum, and the residual white solid was dissolved in dry acetone and reprecipitated by the addition of ether. We obtained 120 mg (0.43 mmol, 77%) of $Cy_2PhC_3^+BF_4^-$ as white crystals: mp 123–125 °C; d = 1.31 g/cm³ (flotation in $n\text{-}C_6H_{14}/CCl_4$); IR (KBr) 3400 (s), 3050 (m), 1595 (s,sh), 1470 (s), 1430 (s), 1340 (m), 1315 (m), 1060 (s,br), 900 (s), 865 (m), 775 (m), 680 (m) cm^{-1}. The NMR spectra and X-ray crystal structure (Table II, Figure 2) are discussed under Results.

Anal. Calcd for $C_{15}H_{15}BF_4$: C, 63.8; H, 5.36; F, 26.96. Found: C, 64.1; H, 5.44; F, 26.1.[38]

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Registry No. **1c**·F^-, 99310-18-6; **1c**·BF_4^-, 99310-20-0; **1d**·Cl^-, 75094-00-7; **1d**·BF_4^-, 75359-38-5; **1d**·SbF_6^-, 99310-21-1; **2**, 26811-00-7; **3**, 99310-17-5; dicyclopropylacetylene, 27998-49-8; cyclopropylamidine hydrochloride, 57297-29-7; 3-chloro-3-cyclopropyldiazirine, 4222-24-6; 3-fluoro-3-phenyldiazirine, 87282-19-7.

Supplementary Material Available: Listings of fractional atomic coordinates, bond distances and angles, anisotropic thermal parameters, and structure factor amplitudes for $Cy_2PhC_3^+BF_4^-$ and $Cy_3C_3^+SbF_6^-$ (20 pages). Ordering information is given on any current masthead page.

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[38] The presence of boron may interfere with the fluorine analysis. The structure is secured by the X-ray analysis, however.

Selective Removal of Electron-Accepting *p*-Toluene- and Naphthalenesulfonyl Protecting Groups for Amino Function via Photoinduced Donor–Acceptor Ion Pairs with Electron-Donating Aromatics

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Abstract: When *N*-tosylamines (**3a**, **3b**, **7**, **17a**, **17b**, **21**, **23**) in aqueous ethanol were irradiated with a high-pressure mercury lamp in the presence of an electron-donating aromatic such as 1,2- (**6**) and 1,4-dimethoxybenzenes (**10**) and 1,5-dimethoxynaphthalene (**14**) and a reductant (sodium borohydride, ascorbic acid, ammonia borane, hydrazine), a photochemical detosylation proceeded quite easily to give the corresponding amines (**4a**, **4b**, **8**, **18a**, **18b**, **22**, **24**) in the high yields. On irradiation in the presence of **10** and sodium borohydride, *N*-(naphthalenesulfonyl)phenethylamine (**19**) also gave **4a**. Mechanistic studies based on fluorescence quenching, quantum yield measurement, and free energy change calculation show that this photoreaction involves an electron transfer from an electron-donating aromatic to an electron-accepting sulfonamide. A preliminary application for the synthesis of lysine peptides was also described.

Since the concept of exciplex and electron transfer was introduced into organic photochemistry a number of new reactions have been reported mainly from the mechanistic point of view.[2] However, a few reactions involving the exciplex or the electron transfer in excited donor–acceptor pairs are generally useful in synthetic organic chemistry.[3] The synthesis of various heterocycles

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[2] Gordon, W.; Ware, W. "The Exciplex"; Academic Press: New York, 1975.

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