plane of the porphinato core is 0.24 Å, a value smaller than that typically observed in five-coordinate zinc porphyrinates.[10] This smaller zinc displacement is probably the result of the interaction of one monomeric unit with its cofacial partner (see below). As noted previously, the effect of π-complexation[11] or π–π dimer formation[12] on the metal atom position with respect to the porphyrin plane is somewhat equivalent to that of a weakly interacting sixth ligand. The effect of $[\mathrm{Zn(OEP^{\bullet})(OH_2)}]_2(\mathrm{ClO_4})_2$ is relatively large and is the presumed consequence of the extremely strong dimerization. It is presumably the effects of dimer formation that also lead to the relatively short $\mathrm{Zn–N_p}$ bonds that are close to the 2.037-Å value found for four-coordinate Zn porphyrinates[13] rather than the 2.067 Å found[10] for the five-coordinate Zn(P)L complexes.

In the solid state, $[\mathrm{Zn(OEP^{\bullet})(OH_2)}]_2(\mathrm{ClO_4})_2$ is a cofacial π–π dimer with several significant and novel features. First, the two porphyrin rings in the dimer interact in an exceptionally strong manner with an interplanar separation between the two porphyrin planes of 3.31 Å. Perhaps not surpisingly, the crystalline material is diamagnetic.[14] Second, the absence of any lateral shift between the two cofacial porphyrin rings is unprecedented.[15] Previously characterized, extremely tight π–π dimeric interactions between two rings exhibit lateral shifts of about 1.5 Å or larger.[16] The absence of ring slip is illustrated in Figure 2 which shows a view down the crystallographic 2-fold axis of one unit and clearly shows the overall high symmetry of the dimer. The *dimer* has crystallographically required D_2-222 symmetry but additionally conforms to the higher idealized symmetry of D_{2d}. Third, despite the strong interaction between rings, the rings are essentially planar as seen in Figure 3. Fourth, the pattern of bond distances in the inner 16-membered ring of the porphyrin core are inconsistent with a completely delocalized system. Rather, there are two unusually distinct sets of $\mathrm{C_a–N}$ and $\mathrm{C_a–C_m}$ bond distances.[17] Within each class, the two kinds of bond lengths differ by about 0.04 Å. The position of the sets of short bonds in the dimer are indicated in Figure 2 by the broken bonds. It is clearly seen that all short bonds are within overlapped pyrrole rings. This apparent localization of bonding[18] is presumably due to the effects of dimerization whose tightness and spin coupling suggests a new kind of interaction, best described as a new type of nonclassical bond. Indeed, the large enthalpy of dimerization (−17 kcal/mol), significant spectral changes upon dimerization,[4c] and complete loss of paramagnetism from the radical are consistent with the notion of forming a new compound. Interestingly, it can be noted that similar spectral changes have been seen upon dimerization (in solution) of the $[\mathrm{Mg(OEP^{\bullet})}]^+$ radical cation.[4b,19]

The question of whether this unprecedented departure from complete delocalization in porphyrin derivatives is a general feature of tightly bonded π-cation dimers is under active investigation. In any event, these bond length changes present an interesting and challenging theoretical problem. We can note that the alternating bond distances do not result simply from bringing two porphyrin rings extremely close together. A similar inter-ring separation and ring orientation is found in the $[\mathrm{Ru(OEP)}]_2$ dimer[20] held together by the short Ru=Ru double bond, but no bond length alternation in the core is observed.

Acknowledgment. We thank the National Institutes of Health for support of this research through Grants GM-38401 (W.R.S.) and GM-23851 (C.A.R.).

Supplementary Material Available: Figure 1S, infrared spectrum, Table IS, complete atomic coordinates, Tables IIS and IIIS, complete tables of bond distances and angles for $[\mathrm{Zn(OEP^{\bullet})(OH_2)}]_2(\mathrm{ClO_4})_2$, Table IVS, anisotropic thermal parameters, and Table VS, magnetic data (7 pages); listing of observed and calculated structure factors (×10) (13 pages). Ordering information is given on any current masthead page.

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(14) The raw magnetic susceptibility data are given in the Supplementary Material and show the presence of less than 1% paramagnetic impurity.

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(17) A complete listing of individual bond distances and angles in the $[\mathrm{Zn(OEP^{\bullet})(OH_2)}]\mathrm{ClO_4}$ molecule are available as Supplementary Material.

(18) This localization may be reflected in the doubling of peaks in the IR spectrum. (See spectrum in Supplementary Material.)

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Evidence for a 1,2-Fluoride Shift in a Gaseous Cation

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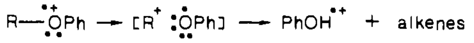
Bond heterolysis of a gaseous ion to form an ion–molecule complex (exemplified by the species in brackets shown in reaction 1) has been described as a gas-phase analogue of solvolysis.[1]



$$\mathrm{R{-}\overset{\bullet +}{\underset{\bullet\bullet}{O}}Ph \longrightarrow [R^{+}\ {:}\overset{\bullet}{\underset{\bullet\bullet}{O}}Ph] \longrightarrow PhOH^{\bullet +} + alkenes} \qquad (1)$$

Conversion of a covalent bond in the precursor ion to an electrostatic bond in the complex is often accompanied by rearrangement of the cation moiety $\mathrm{R^+}$, as revealed by the structures of the recovered alkenes. This communication reports the migratory aptitude of a fluorine relative to a methyl in the Wagner–Meerwein rearrangement schematically depicted in reaction 2. We have measured this using the electron bombardment flow (EBFlow) technique[2] to collect neutral products of reaction 1 where ROPh is 2-fluoro-2-methyl-1-phenoxypropane. Our results provide evidence for intramolecular fluorine transfer via a bridged fluoronium ion.

Experimental evidence for bridged fluoronium ions is surprisingly scant. Unlike the corresponding chloronium and bromonium ions,[3] whose stability in both gas phase and solution are well attested, neither fluoriranium (three-member ring) nor any larger cyclic ions have been unambiguously shown to exist (not even as transition states). In 1983 Ciommer and Schwarz reported experimental results consistent with the intermediacy of the simplest symmetrical case, ion **1**, in the gas phase.[4] Their isotopic scrambling data, though, could be equally well explained in terms of structure **2**, an ion–molecule complex between a symmetrically bridged vinyl cation (the most stable $\mathrm{C_2H_3^+}$ geometry[5]) and hydrogen fluoride. Since ion–molecule complexes between vinylic cations and hydrogen fluoride correspond to local minima on SCF potential energy surfaces,[6] such an option cannot be dismissed out of hand.

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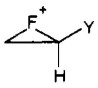
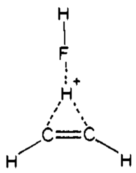
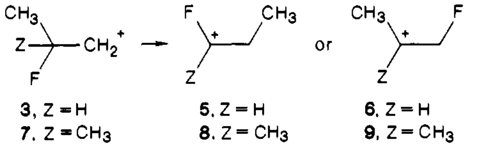


1, Y = H
4, Y = CH_3



2

Ab initio calculations[7] starting from the primary ion structure **3** imply that there are at least two barrier-free pathways to rearrangement. One pathway goes to the bridged ion **4** with unequal C–F bond lengths, which corresponds to a local minimum on the 3-21G SCF potential energy surface.[6] The other pathway proceeds via methyl shift to **5**. With a larger basis set (6-31G**) SCF

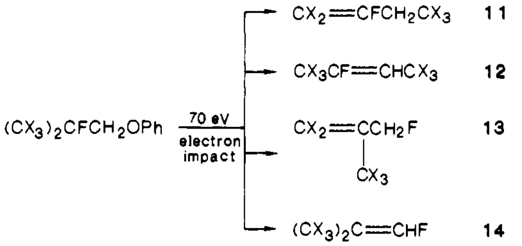


(2)

calculations predict that bridged ion **4** is not a minimum and has no barrier to further rearrangement to ion **6**. Calculated SCF energies are summarized in Table I: **6** is 13 kJ mol^{-1} (3 kcal mol^{-1}) higher than **5** at 6-31G**, suggesting that the two stable isomeric cations are not vastly different in their stabilities.

It turns out to be complicated to assess experimentally the proportions of **5** and **6** from rearrangement of **3**. We have therefore investigated a more highly branched system. SCF calculations on ions **8** and **9** show that they, too, are not vastly different in stability, with calculated SCF electronic energies given in Table I. When corrected for a 5 kJ mol^{-1} difference in zero-point energies (based on normal modes calculations at 3-21G) we estimate that **9** has a heat of formation approximately 20 kJ mol^{-1} (5 kcal mol^{-1}) higher than that of **8**.

We have examined the recovered alkenes from 70 eV electron bombardment of phenyl ether **10a** at 2 × 10^{-4} Torr, as represented by reaction 3. In the mass spectrum, reaction 1 accounts for 40% of the total ionization. In the EBFlow, compounds **11–14** are the only C_4H_7F structural isomers recovered, as shown by 282 MHz ^{19}F NMR of the radiolysis mixture. No evidence is seen for the formation of 1-(fluoromethyl)cyclopropane (**15**)[8] which must therefore represent less than 3% of the C_4H_7F yield. These results confirm that the molecular ion of **10** decomposes via ion–molecule complexes containing **8** or **9**, regardless of whether **7** is a discrete intermediate. The normalized yield of C_4H_7F product is 2 μmol A^{-1} s^{-1}, and the recovered isomer ratios are summarized in Table II. Alkene structures **11** and **12** result from deprotonation of ion **8**, while **13** and **14** correspond to ion **9**. Since there is a small amount (5% of the PhOH$^{•+}$ intensity) of free $C_4H_8F^+$ in the mass spectrum of **10a**, it is conceivable that a fraction of these neutral products might result from the deprotonation of the free ion rather than via reaction 1. In any event, the recovery of **13** and **14** signals that a fluoride shift has taken place.



(3)

Table I. Electronic Energies (in Atomic Units) for Monofluorinated Carbocations (6-31G**//6-31G**)[a]

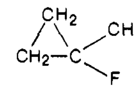
formula	ion	SCF energy (au)
$C_3H_6F^+$	**5**	-216.25711[b]
$C_3H_6F^+$	**6** (E)	-216.21930[b]
$C_3H_6F^+$	**6** (Z)	-216.22224[b]
$C_4H_8F^+$	**8** (Z)	-255.29901
$C_4H_8F^+$	**9**	-255.28975

[a] All structures were first optimized at 3-21G with no constraints and found to have carbons and fluorine coplanar. Optimizations at 6-31G** were then performed with planar skeletons. [b] Stams, D. A.; Thomas, T. D.; MacLaren, D. C.; Ji, D.; Morton, T. H., submitted for publication.

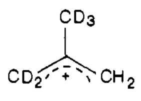
Table II. Isomer Distribution from 70 eV EBFlow Radiolyses of **10a** (d_0) and **10b** (d_6) Based on Integration of ^{19}F NMR Signals (Corrected for Differences in T_1 Relaxation Times)[a]

	d_0	SD	d_6	SD	t
12/11	0.90	0.036	1.28	0.043	12.3[b]
(E)-**12**/(Z)-**12**	0.57	0.020	0.63	0.017	4.30[b]
14/13	0.93	0.20	1.48	0.015	4.75[c]
(**11** + **12**)/(**13** + **14**)	3.40	0.13	4.13	0.65	1.91[d]

[a] From unpaired t-tests with the designated degrees of freedom (df) isotope effects are found to be significant for the first three ratios but not for the last one. [b] df = 5, $p < 0.01$. [c] df = 4, $p < 0.01$. [d] df = 4, not significantly different ($p > 0.1$) for d_0 and d_6.



15



16

EBFlow radiolysis of the hexadeuterio analogue **10b** yields the correspondingly deuterated fluoroalkenes. The isomer ratios, summarized in Table II, predict that the ratio of PhOH$^{•+}$ to PhOD$^{•+}$ from decomposition of **10b** via reaction 1 ought to be 1.32 (SD = 0.04). From the peak intensities in the 70 eV mass spectrum (after correction for ^{13}C natural abundances) we observe a ratio of 1.31 (standard deviation = 0.04), in good agreement with our predicted value.

From neutral product ratios in Table II we infer that the migratory aptitude of a methyl group is only two times greater than that of the fluorine (when corrected for the 2:1 statistics in favor of methyl migration). If we compare the ratio **12a**:**11a** with **12b**:**11b** we infer that the primary deuterium kinetic isotope effect for deprotonation of the acidic methyl of ion **8** in the second step of reaction 1 is k_H/k_D = 1.42 (SD = 0.07). The measured ratios of **13**:**14** in the two sets of experiments yield an isotope effect of 1.59 (SD = 0.05) for deprotonation of **9**. These values are to be compared with k_H/k_D = 1.3 for deprotonation of *tert*-amyl cation in the ion–molecule complex formed by electron bombardment of neopentyl phenyl ether.[1] There is also a statistically significant deuterium isotope effect on the E:Z ratio of **12** from ion **8**.

We place great emphasis on the recovery of **13b** and **14b** instead of other possible isotopic analogues. A major question that has arisen in previous reports of putative intramolecular fluoride migrations is whether alternative pathways are responsible for observed rearrangements.[9] In some cases elimination of hydrogen fluoride followed by readdition can explain reported experimental results in solution,[10] just as structure **2** might account for previous gas-phase results.

In the ion–molecule complex from **10**, elimination of hydrogen fluoride from the cationic fragment would produce methallyl cation. In the case of the deuterated analogue **10b**, any methallyl

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[7] Computations performed on a Cray X-MP/48 using the program GAUSSIAN 82 by Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavchari, K.; Whiteside, R. A.; Schlegel, H. B.; Fleuder, E. M.; Pople, J. A. Department of Chemistry, Carnegie-Mellon University: Pittsburgh, PA.

[8] An authentic sample of **15** was prepared by a Simmons–Smith reaction [Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057–2058] of 2-fluoropropene (PCR): ^{1}H NMR (acetone-d_6) = δ 1.55 (dt, 19.2 Hz, 0.75 Hz, 3 H), 0.92 (m, 19.8, 7.9 Hz, 0.75 Hz, 2 H), 0.52 (m, 8.9 Hz, 7.9 Hz, 6.7 Hz, 2 H); ^{19}F NMR (acetone-d_6, $CFCl_3$ external reference) -172.9 ppm, (qtt, 19.2, 19.8, 8.9 Hz); mass spectrum (70 eV) 74 (23), 73 (12), 59 (100), 53 (29).

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[10] Peterson, P. E.; Bopp, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 1283–1284.

cation produced would have structure **16**, which possesses chemically equivalent, charge-bearing CH_2 and CD_2 groups. Therefore the intermediacy of methallyl cation (either free or in an ion-molecule complex) ought to yield products in which deuterium and fluorine are attached to the same carbon approximately half the time. From ^{19}F NMR studies of authentic samples, we find that methallyl fluoride with a $-CD_2F$ isotopic label is shifted 1 ppm away from a sample with a $-CH_2F$. A shift of similar magnitude is expected for the related label distributions in **14**. Scrutiny of the NMR of the EBFlow reaction product mixture (both undecoupled and with ^2H-noise decoupling) shows that no other label distributions are seen above base line and that they cannot be more than 8% of **13b** or **14b**. We therefore conclude that the EBFlow data provide the first unambiguous demonstration of an intramolecular fluoride shift.

Acknowledgment. This work was supported by NSF Grant CHE88-02086. Ab initio computations were performed at the San Diego Supercomputing Center.

Precursors to the Cyclo[*n*]carbons: [4*n* + 2]- and [4*n*]Annulenes with Unusual Stabilities

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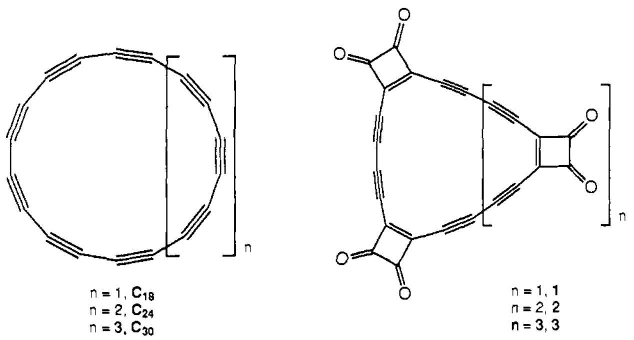
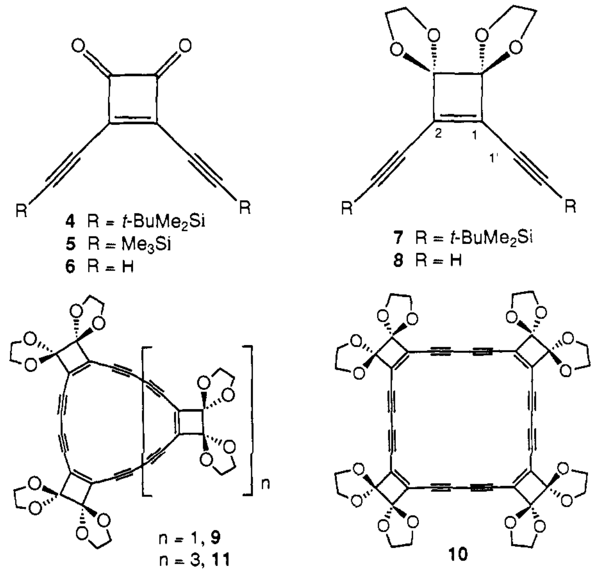
Recently, all-carbon molecules C_n have become the subject of an increasing number of studies.[1] Compounds of sizes ranging from C_2 to C_{200} have been detected in the supersonic beams generated by the laser vaporization of graphite. Theoretical investigations have been useful in assigning structures to these all-carbon molecules.[2] For the unambiguous determination of the structure of a single-sized all-carbon molecule, however, its total chemical synthesis from a well-characterized precursor is required.[3] We describe here the unusual properties of cyclobutenoannulenes, precursors to cyclic C_{18}, C_{24}, and C_{30}. These all-carbon molecules are members of the class of the *cyclo*[*n*]*carbons* in which *n* carbon atoms are connected to form monocyclic ring structures. A special relative stability has been predicted for the larger closed-shell cycles ($n \geq 10$) with $4n + 2$ atoms, e.g., cyclo[18]carbon.[4]

Our strategy to the cyclo[*n*]carbons C_{18}, C_{24}, and C_{30} involves the preparation of the dehydro[*n*]annulenes **1–3** fused to 3-cyclobutene-1,2-diones. Starting from **1–3**, the residual acetylenic bonds should be formed by irradiation or flash vacuum pyrolysis under carbon monoxide extrusion.[5,6]

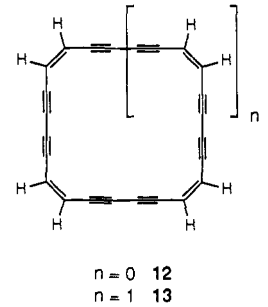
For the synthesis of the 1,2-dione **6**, a direct precursor to **1–3**, the soluble copper(I) acetylide of *tert*-butyldimethylsilylacetylene was reacted with 3,4-dichloro-3-cyclobutene-1,2-dione (THF, 20 °C, 15 min) to afford **4** in 57% yield.[7,8] Similarly, the 1,2-dione **5** was prepared in 27% yield from trimethylsilylacetylene. Unfortunately, all attempts to deprotect **4** or **5** to give **6** led exclusively to polymeric material. Therefore, a route to **1–3** via carbonyl-protected derivatives of **6** was pursued.



Scheme I



Scheme II



Scheme III

For the preparation of bis(ketal) **7**, compound **4** was heated in 1,2-bis(trimethylsilyloxy)ethane in the presence of 1 equiv of trimethylsilyltriflate (80 °C, 6 h, 76%).[9] Deprotection of the acetylenic groups in **7** (catalytic tetrabutylammonium fluoride, THF, H_2O, 20 °C, 30 min, 95%) gave the ene-diyne **8** as a stable solid. While the coupling of **8** under Eglinton–Glaser conditions[10] produced only polymers, Hay coupling[11] (O_2, CuCl·*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine, acetone, 20 °C, [**8**] = 0.01 M) gave three cyclic products, the pale yellow trimer **9** (3.8%), the orange-red tetramer **10** (5.1%), and the bright yellow pentamer **11** (0.8%). While the hexadehydro[18]annulene **12**[12,13] and the

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