expected that oxidation to the sulfoxide and/or sulfone to enhance leaving and complexing ability[13] would facilitate such processes, particularly in the presence of the neighboring ring oxygen lone pair of electrons. These expectations were fully realized and led to a number of new and highly effective transformations as shown in Scheme II. Thus, treatment of either sulfoxide **3** or sulfone **4**[14] with $BF_3 \cdot Et_2O$ (1.0 equiv) in the presence of excess Et_3SiH (5.0 equiv) in CH_2Cl_2 at 0 °C (2 h) led in excellent yield (>90%) to the 4,5-trans tricyclic system **5**.[15] Trimethylaluminum ($AlMe_3$, 2.0 equiv) reacted with either **3** or **4**[15] with equal ease and effectiveness (CH_2Cl_2 0–25 °C, 2 h) to afford compound **7**[16] in 92% yield. The observed retention of stereochemistry in these reactions implicates oxonium species B (Chart I) as an intermediate. Molecular models demonstrate severe nonbonding interactions of the incoming nucleophile with 8β-H and 9-Me, as well as torsional strain[17] with 3β-H and 5-H in the transition state leading to the 4,5-cis oxocene by β-attack on B. In contrast, α-attack may proceed via a significantly less congested transition state leading to the observed 4,5-trans product.[18] Interestingly, DIBAL, a stronger hydride donor, reacted rapidly (−78 °C, 15 min) with sulfone **4** to afford a mixture of **5** and its cis isomer **6**[15] in ca. 1:1 ratio (90% yield), presumably by a dual pathway involving direct S_N2-type displacement of the SO_2Et group or attack on a tight ion pair (inversion) and via oxonium species B (retention).

The versatility and usefulness of this technology was tested in a number of more demanding situations involving polycyclic systems of higher rigidity such as the one depicted in Chart I.[19] Thus the oxocene-containing system **8** was constructed from the corresponding hydroxyl dithioketal[8] (retrosynthetically derived by opening the ring at the dotted line, Chart I) according to the above procedure and in high yield. Whereas formation of **2** was complete in less than 5 min at 0 °C (20 min without silica),[10] the cyclization leading to **8** required 30 min (2 h without silica)[10] indicating a more highly strained eight-membered ring transition state for the later system as anticipated. Finally, oxidation (2.2 equiv, mCPBA) followed by in situ reduction ($Et_2SiH–BF_3$) resulted in compound **9** in excellent yield (see Chart I).[15]

The chemistry described above sets the stage for the construction of the complex naturally occurring brevetoxins and simple structural analogues of them for neurobiological investigations. It may also prove useful in other areas of organic synthesis including glycoside and medium- and large-ring construction.[20]

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Supplementary Material Available: Listing of ^1H NMR data for compounds **1**, **2**, and **5–13**, ^{13}C NMR data for compounds **2** and **5**, experimental section for compounds **2**, **4**, and **5–7**, and X-ray crystallographic analysis data for **4** (11 pages). Ordering information is given on any current masthead page.

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(14) This transformation is more conveniently carried out directly from sulfide **2** without isolation of the intermediates **3** and/or **4** in one pot and with equal efficiency.

(15) Stereochemical assignments were made on the basis of ^1H decoupling and NOE studies. The trans compounds **5**, **9**, **11**,[19] and **13** exhibited a *J* value for H-4,5 of ca. 9.2 Hz while the corresponding value for the cis compound **6** was 3.7 Hz.

(16) The syn relationship of the C-4 methyl and the C-10 proton was assigned on the basis of NOE experiments. Thus, irradiation of the C-4 methyl (δ 1.22, C_6D_6, 50.3 MHz) resulted in a 30% enhancement of the C-10 proton signal (δ 3.91).

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(19) For the construction of a number of other related systems (**10–13**), see the supplementary material.

(20) All new compounds exhibited satisfactory spectral and analytical and/or exact mass data. Yields refer to spectroscopically and chromatographically homogeneous materials.

Stability of Buckminsterfullerene and Related Carbon Clusters

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Under appropriate collisional conditions the mass spectrum of carbon fragments produced by laser vaporization of graphite is dominated by C_{60} and (to a lesser extent) C_{70} clusters.[1] The discoverers of this phenomenon have noted that the carbon valence requirements can be satisfied in closed, hollow structures. For C_{60} they suggest an icosahedral soccerball network, which they call buckminsterfullerene and we abbreviate as BF.[2] Experimental support has come from studies with lanthanum-impregnated graphite.[1b] The resulting mass spectra show intense $C_{60}La$ peaks, but no C_nLa_2 or C_nLa_3 peaks. Subsequent experiments have demonstrated the inertness of C_{60} and, indeed, other large C_{2n} clusters under NO attack.[1c]

We report here the results of quantum calculations which were prompted by the experiments cited above and other earlier work.[3] Our purpose has been to test the intrinsic stability of BF and related polyhedral species and to compare their stability with that of planar graphite fragments. The latter have the advantage of being strain free, but suffer from dangling valences on their perimeters. We also make comparisons with linear carbon chains.

Preliminary Hückel level results are shown in the central columns of Table I. Like BF the other polyhedra included in the table have closed-shell Hückel wave functions and multiple Kekulé structures. Note that *all* have resonance energies that are comparable with graphite[4] and 50–70% greater than that of benzene.[5] Note also, however, that in contrast to graphite, the bond orders of the polyhedra exhibit considerable variation from bond to bond, suggesting a parallel variation in bond length.

In order to account realistically for angle strain, we carried out MNDO[6,7] calculations, with full geometry optimization. This method has been shown to be reliable (ΔH_f per C good to ~1 kcal/mol) for hydrocarbons containing five- and six-membered rings. A highly pertinent and satisfactory test is provided by corannulene ($C_{20}H_{10}$),[8] which consists of five six-membered rings fused about a pentagon (i.e., one sector of BF): all calculated angles are within 2° of X-ray values, and the bond lengths are correctly ordered, with a 0.01-Å mean error.

For large planar fragments, we employed Benson's empirical group equivalents[9] (accurate to better than 0.5 kcal/mol per C for unstrained aromatic systems).[10]

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Table I. Properties of Aromatic Carbon Atom Clusters

C_n species			Hückel MO		MNDO	
n	symm	ring types[a]	E_{res}[b]	p_{cc}[c]	ΔH_f[d]	r_{cc}[e]
24[f]	O_h	$6^8/4^6$	0.496	0.404, 0.686	34.0	1.502, 1.386
40[g]	D_{5d}	$6^{10}/5^{12}$	0.528	0.405-0.633	22.5	1.522-1.382
50[h]	D_{5h}	$6^{15}/5^{12}$	0.539	0.382-0.624	18.4	1.486-1.389
60[i]	I_h	$6^{20}/5^{12}$	0.553	0.476, 0.602	14.5	1.474, 1.400
60[j]			0.475	(0.52 ± 0.01)[k]	(19 ± 1)[l]	
60[m]	D_{6h}	$6^{20}/5^{12}$	0.542	0.393-0.691	18.3	1.493-1.370
70[h]	D_{5h}	$6^{25}/5^{12}$	0.554	0.470-0.596	13.5	1.49-1.39
q			0.574[n]	0.525[n]	(1.5)[o]	(1.421)[p]

[a] Superscripts indicate number of each polygon type. [b] Ethylene-based resonance energy per C in units of the resonance integral β. [c] Nearest-neighbor π-type bond orders (unique values or ranges). [d] MNDO[6,7] ΔH_f at 298 K (kcal/mol per C atom). [e] Nearest-neighbor values in Å, listed analogously to bond orders. [f] Truncated octahedron. [g] Formed from BF by deleting 10 hexagons from an equatorial belt. [h] C_{50} and C_{70} are formed from BF by rotating one hemisphere $2\pi/10$ radians relative to the other and then removing or adding an equatorial belt of 10 C atoms. [i] Buckminsterfullerene. [j] Finite graphite sheet: planar, polyaromatic C_{60} cluster with a minimal number (i.e., 20) of dangling bonds. [k] Mean for interior bonds. [l] Based on data in ref 9a for $C_{60}H_{20}$ and 101 ± 3 kcal for the mean CH bond energy (from the process, benzene → o-benzyne + 2H).[9a,13] [m] Graphitene.[5] [n] Reference 4. [o] Reference 9a. [p] Reference 14. [q] Infinite graphite sheet.

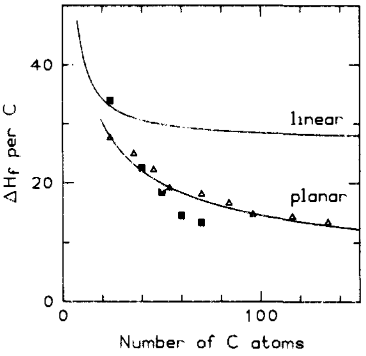

Figure 1. ΔH_f (per C atom) for various polyhedral, planar (graphite-like), and linear (C_{2n} triplet states) carbon clusters. Based, respectively, on MNDO results (solid squares; see Table I), empirical estimates (footnote 1, Table I), and UHF MNDO results. The linear results for n = 2-18 were extrapolated to larger n (limiting ΔH_f = 27.0 kcal/mol/C). Each planar cluster (triangles) has the minimal number m of "edge" atoms and is obtained by dehydrogenating the corresponding C_nH_m molecule. Use of $m = (6n)^{1/2}$ gives the exact stoichiometry for n = 6, 24, 54, ... (i.e., concentric "shells" about a benzene nucleus) and provides a smooth approximation (solid curve) for the general pattern.

Our principal results are as follows:

(1) BF is intrinsically stable. Its normal mode frequencies are all real and range from 186 to 1217 cm^{-1}. Included is a totally symmetric "double-bond" stretching mode at 1179 cm^{-1}, intermediate between that of benzene (990 cm^{-1}) and ethylene (1623 cm^{-1}).[11] The "double bonds" are those shared by hexagonal rings. These are shorter by 0.07 Å than the pentagonal edge bonds. This shortening is consistent with the Hückel prediction. (Hückel bond orders did not yield good predictions for relative bond lengths in other clusters, but these were well correlated with MNDO bond orders.)

(2) The graphitene form of C_{60} suggested by Haymet[5] is considerably less stable than the icosahedral form.

(3) Spheroidal C_{70} appears to be somewhat more stable than C_{60}, so that the greater abundance observed experimentally for C_{60} may reflect either kinetic conditions during cluster generation or the influence of the mass spectrometric detection method.

(4) The crossover (Figure 1) in energy preference from planar to polyhedral clusters occurs near n = 40. Since planar fragments with their unsatisfied valences are likely to be highly reactive, it is understandable that mass peaks with $n < 40$ diminish when NO is added to the reaction system.[1c]

(5) The MNDO ionization potentials for C_{50}, C_{60}, and C_{70} are 8.6, 9.1, and 8.7, respectively. Even when reduced by an estimated ~1-eV correction, they remain at variance with an early reported threshold of ≲5.0 eV for single photon ionization.[3a] However, they seem compatible with more recent[12] upper (7.9 eV) and lower (6.4 eV) bounds.

(6) The MNDO MO's in BF separate cleanly into π (≳97% radial 2p) and σ(2s and tangential 2p) types, and 21 of the 30 occupied π levels lie at the top of the occupied manifold. Thus, despite the obvious angle strain, it is reasonable to think of BF in conventional aromatic terms.

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Chemistry of Dioxiranes. 4. Oxygen Atom Insertion into Carbon-Hydrogen Bonds by Dimethyldioxirane[1]

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We have recently reported[2] that we have discovered a method of producing solutions of pure methyldioxiranes. This discovery has permitted us to record the spectroscopic properties of dimethyldioxirane (**1**), as well as to carry a number of very efficient O atom transfer reactions with a variety of substrates including olefins, polycyclic aromatic hydrocarbons, sulfides, tertiary amines, aldehydes, and triphenylphosphine. These reactions usually take place very rapidly and under extremely mild conditions with the oxidized product being obtained, usually in very high yield, as a

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