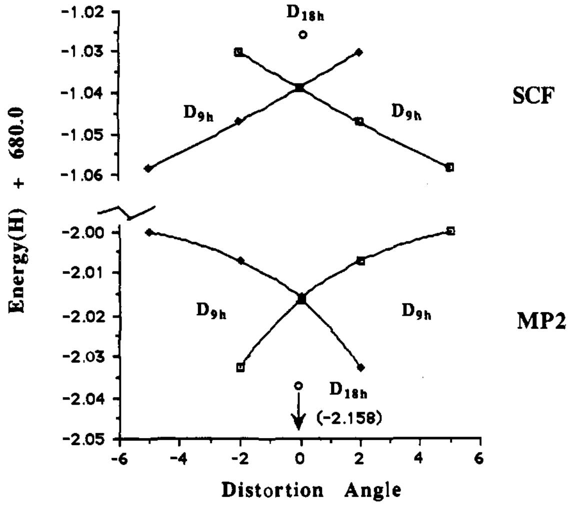

Figure 1. SCF and MP2 energies (in atomic units) of the cumulenic form plotted against the distortion of the bond angle (in degrees) relative to the D_{18h} form with bond angles of 160°. The bond distances were kept at 1.277 Å. This plot shows the symmetry-breaking solution. (The minima in the SCF curves are observed at distortions of ±15°.)

function (exponent 0.55) yielding 324 contracted basis functions. The geometry of **2** was optimized at the MP2 level of theory, correlating 36 valence electrons (the 1s core electrons and the σ-bonds were not correlated), while **1** and **3** were optimized at the SCF level since an optimization at the MP2 level would lead to structure **2**. All-valence MP2 energies were then calculated by using an ANO[5] (13s8p4d2f)/[5s4p3d2f] basis set with a total of 828 contracted functions. Optimized geometry parameters are listed in Table I and relative energies in Table II. All calculations were performed with the direct SCF[6] and direct MP2[7] formalism, using the program DISCO.[8]

D_{9h} symmetry was imposed in all calculations. During optimization of the D_{18h}-symmetric form **2**, a symmetry-broken solution (the wave function possessing only D_{9h} symmetry) was also obtained at the SCF level. This is clearly an artifact of the SCF approximation, as the MP2 energy for the symmetric solution is several electronvolts below the symmetry-broken one (cf. Figure 1). However, since SCF orbitals have to be used for an MP2 calculations, there is no way to obtain a potential energy curve corresponding to the most stable solution at the MP2 level. The SCF calculation for that solution would correspond to an excited electronic state, and the MP2 calculation would collapse.

In summary, calculations at the SCF level give results very similar to those of previous theoretical work, even with much larger basis sets. The symmetric, cumulene-like form **2** lowers its energy by more than 1 eV by distorting the angles to create two nonequivalent types of C atoms (form **3**). By alternating the bond distances, the polyacetylenic form **1** becomes stabilized with respect to **2** by more than 2 eV. No other forms of distortions were considered, and there is certainly the possibility that other distortions not considered here would lower the energy even further. At the correlated level, however, our calculations show that **2** (the cumulenic form) has the lowest energy among the structures considered. Apparently, electron correlation plays a critical role in determining the ground-state conformer of this system.

Acknowledgment. The Minnesota Supercomputer Institute and the National Science Foundation provided support for this work. All calculations reported here were performed on the CRAY-2 computer at the University of Minnesota Supercomputer Center.

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Two Different Fullerenes Have the Same Cyclic Voltammetry

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The recent success in the preparation of the fullerenes C_{60} and C_{70}[1-3] and the confirmation[4] of the theoretical prediction[5] that the former is a relatively electronegative molecule prompted us to do a comparative study of the cyclic voltammetry (CV) of these two new carbon clusters to determine the effect of structure on redox properties.

Samples of the pure fullerenes C_{60} and C_{70} were obtained as described previously for the purification of analytical quantities.[3] The first ^{13}C NMR spectrum of pure C_{70} is shown in Figure 1. The two compounds were used without special precautions, other than the usual oxygen removal from solvent–electrolyte systems prior to electrochemical cycling. The typical voltammogram shown in Figure 2 was recorded with a commercial BAS 100A apparatus. Table I shows the solvent and scan rate effect on the position of the voltammetric waves. The values are relative to Ag/AgCl with internal ferrocene for calibration.

We discovered three interesting features:

1. Both fullerenes have essentially the same CV behavior.
2. There are *three* observable reversible reduction waves and not two, as claimed earlier.[4] The third wave ($E = -1.25$ V) is chemically reversible in CH_2Cl_2 only on cycling at rates above 1 V s^{-1}. In agreement with Haufler,[4] we observed no oxidation waves even in benzonitrile.
3. There is a dramatic solvent effect on the reduction potentials; E_1 is lowered by ~0.2 eV but E_2 remains unchanged in THF, when compared to other solvents. Since three of the solvents (CH_2Cl_2, THF, and ODCB) have essentially the same dielectric constant and that of PhCN is much higher, the solvent effect may be related to the Gutmann solvent donicity number (DN),[6,7] rather than the solvent polarity.

We were surprised to observe identical behavior for both fullerenes. Intuitively, C_{60}'s high electron affinity and ionization

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(3) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.*, in press. The soluble extract (400 mg) of the soot resulting from resistive heating of graphite was adsorbed on 100 g of alumina and chromatographed on neutral alumina (activity I; column dimensions: 8 × 60 cm). Hexane/toluene (95:5 v/v) elution afforded 250 mg of pure C_{60}. Increasing the polarity to hexane/toluene (80:20 v/v) gave 50 mg of pure C_{70}. The purity of C_{60} was established by comparison with previously reported spectral data.[1,2] New characterization data are as follows: UV–vis$_{C_{60}}$ [hexanes, 300 K, 2.47×10^{-6} and 1.235×10^{-5} M, λ_{max} (log ϵ)] 211 (5.17), 227 sh (4.91), 256 (5.24), 328 (4.71), 357 sh (4.08), 368 sh (3.91), 376 sh (3.75), 390 (3.52), 395 sh (3.30), 403 (3.48), 407 (3.28), 492 sh (2.72), 540 (2.85), 568 (2.78), 590 (2.86), 598 (2.87), 620 (2.60); UV–vis$_{C_{70}}$ [hexanes, 300 K, 1.706×10^{-5} M, λ_{max} (log ϵ)] 214 (5.05), 235 (5.06), 249 sh (4.95), 268 sh (4.78), 313 (4.23), 330 (4.38), 359 (4.29), 377 (4.45), 468 (4.16), 542 (3.78), 590 sh (3.47), 599 sh (3.38), 609 (3.32), 623 sh (3.09), 635 sh (3.13), 646 sh (2.80); ^{13}C NMR (see Figure 1).

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Table I

compd	scan rate, mV/s	ODCB[a] (V)[d]			THF (V)[d]			CH_2Cl_2 (V)[d]			PhCN (V)[d]		
		E_1	E_2	E_3	E_1	E_2	E_3	E_1	E_2	E_3	E_1	E_2	E_3
C_{60}	100 (Ag/AgCl)	−0.40	−0.76	−1.25	−0.21	−0.81	−1.39	−0.33	−0.73	−1.22	−0.33	−0.76	−1.25
	1000 (Ag/AgCl)	−0.41	−0.81	−1.27	−0.18	−0.81	−1.40	−0.39	−0.78	−1.25	−0.33	−0.78	
C_{70}	100 (Ag/AgCl)	−0.41	−0.78		−0.18	−0.74	−1.28	−0.38	−0.76	−1.17	−0.33[b]	−0.74[b]	
	1000 (Ag/AgCl)	−0.32[b]	−0.77[b]	−1.23[b]	−0.19	−0.78	−1.29	−0.35	−0.74	−1.17			
Fc[c]	100 (Ag/AgCl)		+0.67			+0.67			+0.59			+0.58	

[a] ODCB = *o*-dichlorobenzene. [b] Scan rate = 25 mV/s. [c] Fc = ferrocene. [d] E_1, E_2, and E_3 are half-cell potentials; e.g., $E_1 = {}^1/_2(E^p{}_{1red} + E^p{}_{1ox})$.

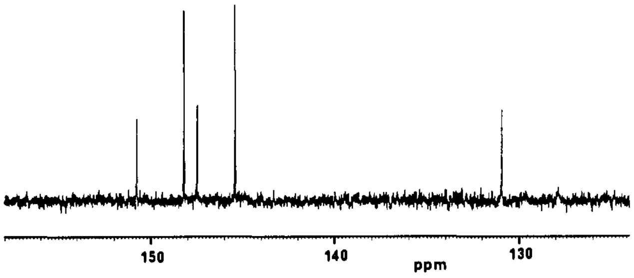


Figure 1. ^{13}C NMR spectrum of a solution of C_{70} in 1,1,2,2-tetrachloroethane-d_2 (6800 scans).

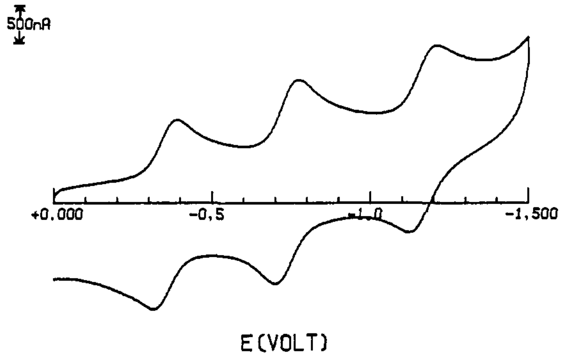
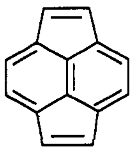


Figure 2. Cyclic voltammogram of fullerene C_{70} in CH_2Cl_2 with 0.1 M $Bu_4N^+BF_4^-$ at ambient temperature. Working and counter electrodes were Pt, the reference electrode was Ag/AgCl, and the scan rate was 1000 mV/s (entry 4 in Table I).

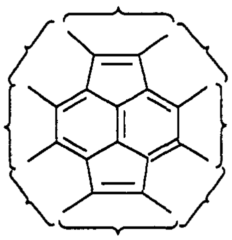
potential could be ascribed to two factors:[8]

a. Negatively charged carbon atoms resulting from electron capture would have more sp^3 character and would have longer bond lengths to their neighbors and hence decrease the strain energy of the cluster; conversely, positively charged members of the cage resulting from electron loss would have more sp^2 character and would have shorter bond lengths to their neighbors and hence increase the strain energy of the cage.

b. If one could consider C_{60} a spherical "superbenzopyracylene", the cage would be expected to be electronegative because pyracylene has a relatively high electron affinity and its LUMO is a NBMO.[9]



Pyracylene



"C_{60}"

On the other hand, C_{70} is more strained than C_{60}[10] and it has fewer pyracylene bonds.[11,12] For reason a, above, the larger strain relief would tend to increase C_{70}'s electron affinity relative to C_{60} but the fewer pyracylene bonds would have the opposite effect. It is possible that both effects operate and cancel each other to produce the observed results.

In conclusion, we discovered that pure C_{60} and pure C_{70} exhibit the same first reduction wave potentials in four different solvents of disparate solvent properties. A reversible reduction potential of only −0.21 V vs Ag/AgCl was found in THF, indicating that the radical anion salts of these fullerenes should be preparable in that solvent. Our results are in agreement with theoretical calculations for C_{60} but not for C_{70}. According to theoretical calculations,[11] the latter would be expected to have a value of $E_1{}^{1/2}$ closer to 0 relative to Ag/AgCl. We interpret our observations in terms of relief of strain[13] and pyracylene-type electronic character of the fullerenes.

Acknowledgment. We thank the National Science Foundation for support through Grants DMR-88-20933, CHE89-08323 (F.W.), and CHEM-89-21133 (F.D. and R.L.W.).

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[8] Haddon, R. C. (see ref 5, above), has stated that C_{60} fullerene is an aromatic compound, but no reference is made to the Hückel rule. The C_{60} would be a "4*n*" system, and addition of two electrons would make this a (4*n* + 2)π aromatic dianion.

[9] Trost, B. M.; Bright, G. M.; Frihart, C.; Brittelli, D. *J. Am. Chem. Soc.* **1971**, *93*, 737.

[10] From mass spectrometric measurements, it was determined that C_{70} is 8 kcal/mol less stable than C_{60}: Sharma, D. K., et al., in preparation.

[11] Haddon et al. (Haddon, R. C.; Brus, L. E.; Raghavacharty, K. *Chem. Phys. Lett.* **1986**, *131*, 165) reported that C_{70} has a LUMO of ~0 × β.

[12] If the Hückel rule would apply (see ref 8, above), then C_{70} would be a (4*n* + 2)π aromatic molecule.

[13] Dr. R. C. Haddon has pointed out that what we have termed strain may be the same as his interpretation of bonding in the fullerenes in terms of *rehybridization* (Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243). The higher s character of the bonding system ($s^{0.093}p$) makes it more electronegative.

Formation of Reversed Vesicles

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There is a symmetry among most amphiphilic self-organizing structures in regard to the distribution of polar and nonpolar components. Normal and reversed micelles and normal and reversed hexagonal liquid crystals, as well as normal and reversed O/W and W/O macro- and microemulsions and bicontinuous phases, are documented examples of this symmetrical pattern. One notable exception is vesicles. Normal vesicles or liposomes possessing closed hydrocarbon shells separating well-defined aqueous interior and exterior phases were first described in 1964.[1,2] These first vesicles were prepared by dispersing phospholipid lamellar liquid crystals in water. Since then many other amphiphiles with

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