The final three examples in Table I illustrate the general utility of titanium enolates in aldol reactions of substrates possessing commonly utilized chiral auxiliaries. Comparative data is provided for the titanium- and boron-mediated aldol reactions of these substrates.[10a,11,12] Entry K is notable in that TMEDA improves the selectivity of this addition for the "nonchelate" product. In each of these reactions, there is no evidence of chelate control in spite of the opportunity for such regulation. The aldehyde stoichiometry was also found to be crucial to the success of these reactions. In most cases (entries A–K, O), only 1.0–1.2 equiv of aldehyde is required for complete consumption of starting material. However, in the case of one substrate (entries J and K), 2 equiv of aldehyde is necessary for complete conversion. With the sultam chiral auxiliary (entries O and P), 5 equiv of aldehyde is required for complete conversion for both the titanium and boron aldol reactions as has been advertised by Oppolzer.[12]

The preceding studies highlight the unexpected stereoselectivity of chlorotitanium enolate aldol bond constructions which offer a practical alternative to the use of other metalloids such as boron to achieve comparable stereocontrol.

Acknowledgment. Support has been provided by the NIH, the NSF, and Merck. The NIH BRS Shared Instrumentation Grant Program (1-S10-RR04870) and the NSF (CHE88-14019) are acknowledged for providing NMR facilities. Postdoctoral fellowships for D.L.R. (American Cancer Society) and F.U. (NATO) are gratefully acknowledged.

Supplementary Material Available: Experimental procedures and spectral data for all new compounds (6 pages). Ordering information is given on any current masthead page.

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(10) Related transition structures have been proposed by others as well: (a) Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *J. Am. Chem. Soc.* **1981**, *103*, 1566–1568. (b) Reference 4a. (c) Reference 10. (d) Enders, D.; Lohray, B. B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 581–583. Variations in the proposed models occur in the disposition of the pendant enolate stereogenic center.

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The [18] All-Carbon Molecule: Cumulene or Polyacetylene?

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Received September 24, 1990

A large number of recent experimental[1] and theoretical[2] studies on carbon clusters have mainly focused on their electronic and molecular structures. Small and medium-sized carbon clusters are generally assumed to have linear or monocyclic structures, whereas the larger ones are assumed to be three-dimensional. Recently, the synthesis of the all-carbon molecule C_{18} from an organic precursor was reported.[3] An attempt was also made to determine its electronic and molecular structure by using small-basis ab initio calculations. The SCF results with a 3-21G basis suggest that the cyclic form with alternating bond lengths (acetylenic structure **1**) is the ground-state conformer. Its energy was found to be 53.8 and 37.6 kcal/mol lower than that of other cyclic forms, i.e., the cumulenic structure **2** (perfect D_{18h} symmetry) and the distorted-cumulenic structure **3** (D_{9h} with alternating bond angles), respectively. (The three cyclic forms are all more stable than the linear geometry by several electronvolts.) This prediction is somewhat surprising since the molecule is a $(4n + 2)$ π-electron system, and a structure allowing for the maximum delocalization of the π electrons (i.e., structure **2**) would be expected to be the most stable form.

Table I. Optimized Geometry Parameters of Three Ring Structures: Acetylenic **1**, Cumulenic **2**, and Distorted Cumulenic **3**[a]

structure	symmetry	bond length, Å	bond angle, deg
1	D_{9h}	1.375, 1.194	160
2	D_{18h}	1.277	160
3	D_{9h}	1.277	175, 145

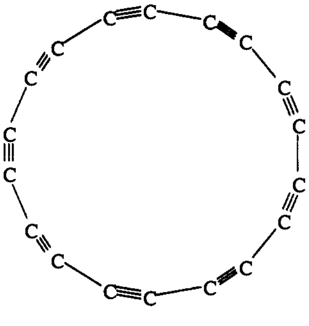
[a] The optimization was made at the MP2 level of theory for **2** and at the SCF level of theory for **1** and **3**, using the [4s3p1d] basis set.

Table II. Energies (kcal/mol) of Alternative Monocyclic Forms of C_{18} Relative to Structure **2**

		relative energy	
basis set	method	1	3
[4s3p1d]	SCF	−68.7	−33.5
[4s3p1d]	36-MP2[a]	54.6	108.8
[5s4p3d2f]	SCF	−71.5	
[5s4p3d2f]	72-MP2[b]	85.7	

[a] Thirty-six valence electrons were correlated. [b] Seventy-two valence electrons were correlated.

Here, large-basis ab initio SCF and MP2 calculations on the three ring structures **1–3** are reported. Geometries were optimized by using a (9s5p)/[4s3p] basis set[4] augmented with a single d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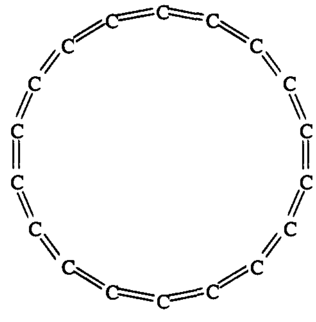
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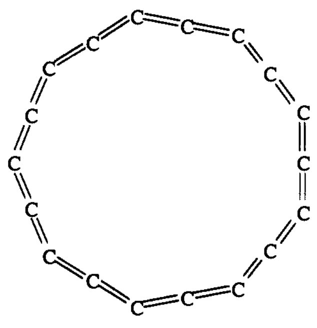
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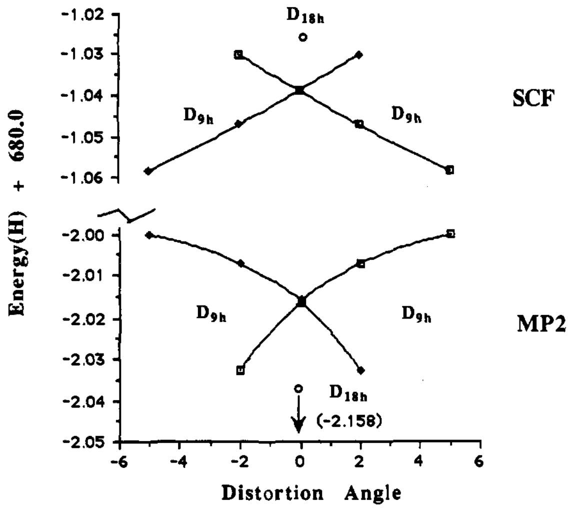

Figure 1. SCF and MP2 energies (in atomic units) of the cumulenic form plotted against the distortion of the bond angle (in degrees) relative to the D_{18h} form with bond angles of 160°. The bond distances were kept at 1.277 Å. This plot shows the symmetry-breaking solution. (The minima in the SCF curves 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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Received November 14, 1990

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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