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C_{18} Is a Polyyne

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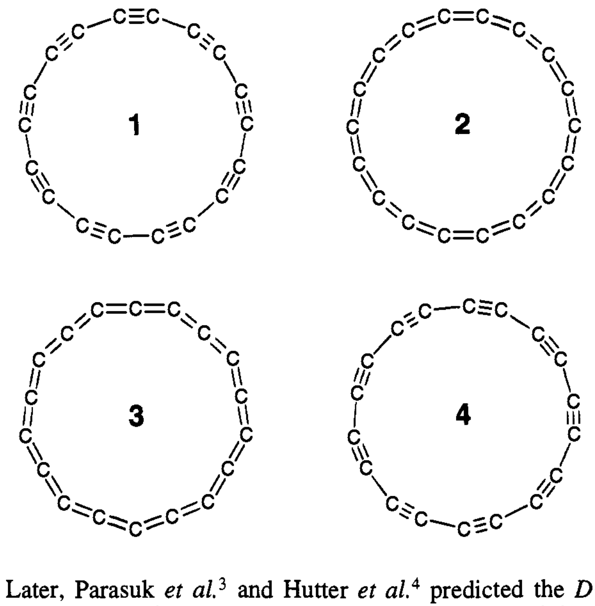
Cyclic carbon clusters have stimulated much attention during the past years, both experimentally[1,2] and theoretically.[1,3,4] There is now growing evidence that cyclocarbons play a decisive role in the formation of fullerenes.[5−7] Numerous theoretical efforts notwithstanding, a consensus on the bonding in monocyclic carbon clusters C_n ($n = 10-20$) is still lacking.[8] We present theoretical arguments and computational evidence that monocyclic C_{18} has a flattened circular polyyne structure. The tendency for bond alternation in the C_n systems is greater than that in C_nH_n systems. Previous calculations on this system led to erroneous conclusions about structures. Our studies also show that density functional theory (DFT) errs consistently in the prediction of energies for isomeric cumulenic and acetylenic structures.[9] Nevertheless, the combination of RHF and DFT calculations provides firm conclusions about structural trends in the potentially doubly-aromatic cyclocarbons, C_{10}, C_{14}, and C_{18}.

In 1989, Diederich *et al.* reported the synthesis of an organic precursor of cyclo[18]carbon.[1] Laser flash decomposition and mass spectrometric analysis gave evidence for formation of C_{18}. Logical structures include (Chart 1) the circular D_{9h} polyyne **1**, the D_{18h} cumulene **2**, and the flattened D_{9h} cumulene **3**. The flattened C_{9h} polyyne structure **4** was not considered at that time. With the Hartree−Fock level of theory, **1** was found to be lowest in energy with various basis sets.[1,3] Although small aromatic systems have equal CC bond lengths, larger aromatics have alternating single and double bonds; in polyenes, bond alternation sets in at about $C_{22}H_{22}$.[10−13] Liang and Schaefer already noted the greater tendency of cyclic polyynes than polyenes to adopt the bond-alternant forms.[14,15] This tendency can be rationalized by the greater stability of acetylenes as compared to allenes.

Chart 1



Later, Parasuk *et al.*[3] and Hutter *et al.*[4] predicted the D_{18h} symmetric cumulenic structure **2** to be the energy minimum based on MP2 and DFT calculations, respectively. We now report evidence that the flattened polyacetylenic structure **4** is the actual minimum structure for C_{18} and conclude that bond alternation sets in at about C_{14}.

HF/6-31G* calculations[16] predict that **1** is most stable; cumulene **2** is 68.4 kcal/mol less stable. Bond angle alternation reduces the energy of **3** to 32 kcal/mol above that of **1**. In order to check the validity of Almlöf's MBPT approach,[3] we tested the stability of the single-determinant HF wave functions;[17] Møller−Plesset energies based on RHF wave functions which are unstable with respect to UHF wave functions are invalid.[18] We find that all cyclic C_{18} geometries **1−4** display a RHF → UHF instability. Thus, the MP energies obtained by Parasuk *et al.*[3] for **1** and **3** are meaningless. It was noted earlier by Watts and Bartlett in their study of monocyclic C_{10} that second- and fourth-order MBPT is erroneous for such systems.[19]

In addition, all the geometries **1−3** show at least one imaginary frequency, and they cannot qualify as energy minima. In all cases the modes associated with these frequencies are of a ring-flattening type, *i.e.*, alternate atoms move toward and away from the ring centroid. Optimization with reduced symmetry led to the polyacetylenic C_{9h} structure **4**, with two different bond angles (156.7° and 163.3°); **4** is an energy minimum, 0.3 kcal/mol lower in energy than the D_{9h} **1**.

While inclusion of electron correlation effects is important for the quantitative assessment of the relative energies of isomers of C_{18} and related carbon clusters, it is not currently possible to perform definitive calculations using the necessary post-HF methodology on a CASSCF wave function for a system as large as C_{18}. DFT methods including correlation functionals[20] provide the only current possibility of studying such systems with a high level of accuracy. Recent DFT studies of C_n ($2 \leq n \leq 18$) by Hutter *et al.* predicted the fully symmetric structure **2** to be the energy minimum for C_{18}, in spite of the fact that their calculations showed that it was a saddle point.[4] However, using the nonlocal B-LYP exchange-correlation functional and the

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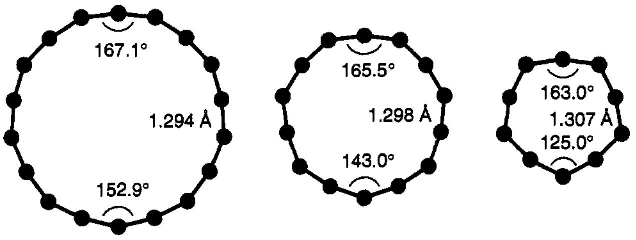

Figure 1. Optimized DFT Structures for C_{18}, C_{14} and C_{10}.

Table 1. Geometries and Relative Energies for C_{10}, C_{14} and C_{18}[a]

	RHF (B-LYP)		rel E (kcal/mol)	
C_n isomer	bond lengths (Å)	bond angles (deg)	RHF	B-LYP
C_{10} cumulene D_{10h}	1.276 (1.301)	144 (144)	+33.1	+5.5
C_{10} polyacetylene D_{5h}	1.215, 1.361	144	+25.5	
C_{10} cumulene D_{5h}	1.290 (1.307)	119.4 (125.0), 168.6 (163.0)	0	0
C_{14} cumulene D_{14h}	1.272 (1.296)	154.3 (154.3)	+39.1	+2.8
C_{14} cumulene D_{7h}	1.283 (1.298)	135.1 (143.0), 173.5 (165.5)	+8.5	0
C_{14} polyacetylene D_{7h}	1.201, 1.378	154.3	+3.0	
C_{14} polyacetylene C_{7h}	1.217, 1.360	140.0, 168.6	0	
C_{18} polyacetylene D_{9h} (**1**)	1.198, 1.380 1.232, 1.347	160 160	+0.3	+53.0[b] +20.1[b]
C_{18} cumulene D_{18h} (**2**)	1.271 (1.294)	160 (160)	+68.7	+2.4
C_{18} cumulene D_{9h} (**3**)	1.280 (1.294)	144.4 (152.9), 175.6 (167.1)	+32.4	0
C_{18} polyacetylene C_{9h} (**4**)	1.198, 1.379 1.232, 1.347	156.7, 163.3 156.7, 163.3	0	+50.8[b] +18.4[b]

[a] All calculations were performed using the 6-31G* basis set. [b] Single-point energy calculation.

6-31G* basis set,[21] we have found the cumulenic D_{9h} isomer, **3**, to be the energy minimum. The D_{18h} structure, **2**, is 2.4 kcal/mol higher in energy. The same result is obtained by B-LYP/6-31G* for two other $(4n + 2)$ π-electron clusters, C_{10} and C_{14}: the D_{5h} and D_{7h} symmetric cumulenic structures (see Figure 1) are minima on the potential energy surface, while the D_{10h} and D_{14h} symmetric cumulenic isomers are 5.5 and 2.8 kcal/mol, respectively, higher in energy. This is also in contradiction to the results by Hutter *et al.*, who found the D_{14h} isomer (1.289 Å, 154.3°) as the minimum for C_{14} with the Becke–Perdew functional and a TZ+d basis set.

Surprisingly, polyacetylenic structures of the $(4n + 2)$ π-electron clusters are not stationary points using DFT methods. In order to estimate the DFT energies of the acetylenic isomers, single-point energy calculations for polyacetylenic C_{18} geometries at HF equilibrium geometries or with bond lengths estimated from normal DFT geometries[4] were performed (Table 1). DFT predicts the C_{18} polyyne structures to be about 20 kcal/mol above the cumulenic.

However, DFT at all levels in Table 2 predicts incorrectly the relative energies of acetylenes and cumulenes. DFT methods predict allene to be lower in energy than 1-propyne. This is contrary to experimental data; propyne is thermodynamically more stable by 1.7 kcal/mol.[23,24] The errors in DFT methods accumulate in larger polyyne–cumulene systems. As shown in Table 2, thermodynamic group equivalents predict that 1,3-pentadiyne is more stable than the isomeric cumulene, 1,2,3,4-pentatetraene, by 15.7 kcal/mol.[23] RHF/6-31G* calculations reproduce the thermodynamic energy order very well.

Table 2. Relative Energies (kcal/mol) of Acetylene and Cumulene Model Compounds

	E(allene) − E(propyne)	E(pentatetraene) − E(1,3-pentadiyne)
LSDA/3-21G	−2.1	+1.1
B-LYP/6-31G*	−4.1	−1.0
Becke3-LYP/6-31G*	−2.8	+2.1
Becke3-LYP/(7111/411/1)[a]	−2.0	+2.9
RHF/6-31G*	+2.0	+14.6
experimental $\Delta H_f°$	+1.7	+15.9[b]

[a] Reference 22. [b] Estimated from thermochemical group equivalents.[23]

DFT errs in favor of allenic structures by about 6 kcal/mol per C≡C—C → C=C=C transformation. In C_{18}, a very large error, as much as 9 × 6 = 54 kcal/mol in favor of the cumulenic structure, **3**, is expected with DFT calculations. A linear extrapolation should be very approximate; nevertheless, when the DFT preference of 18 kcal/mol for **3** is corrected by 54 kcal/mol, DFT predicts **4** to be more stable by 36 kcal/mol, close to the value of 32 kcal/mol predicted by RHF calculations (Table 1). There is clear evidence for the greater stability of **4**.

Structures **1**–**3** are not minima, but are transition states for various isomerization processes. When monocyclic C_{18}, **4**, is detected spectroscopically, the carbons will all become equivalent by a "rounding" process via transition state **1**, with E_a of 0.3–1.8 kcal/mol, while the bond shift isomerization via transition state **3** will occur only around room temperature (E_a ~ 20 kcal/mol).

While RHF calculations may favor bond-alternant structures unduly,[13] the RHF results for the $(4n + 2)$ π-electron clusters C_{10}, C_{14}, and C_{18} predict the expected tendency toward greater bond localization with increasing ring size: C_{10} is predicted to be cumulenic D_{5h}, which is in accordance with highest-level post-HF calculations.[14,19] C_{14} is the borderline case; the polyacetylenic structure is slightly favored by RHF calculations, but the cumulenic and polyynic will be very close in energy. For C_{18}, the RHF calculations and corrected DFT calculations agree that the polyyne structure **4** is highly favored.

Our calculations show the following trends in cyclocarbon structures. (1) All $4n + 2$ systems favor the "flattened" bond angle alternating structures.[14,25] (2) The cumulenic $D_{(n/2)h}$ structures are lowest in energy for small C_n clusters, but as the value of n increases, the energy of the polyynic $C_{(n/2)h}$ structure drops below that of the cumulene. For the molecules studied here, C_{10} has a cumulenic D_{5h} structure, the energies of cumulenic D_{7h} and polyynic C_{7h} are nearly degenerate, and C_{18} is a flattened circular polyyne of C_{9h} symmetry.

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