

Theoretical Prediction of the Dimerization Energy of C₆₀

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The structures of three possible C₆₀ dimers with intact cages have been calculated at the semiempirical (MNDO/AM-1, PM-3) and ab initio density functional theory (DFT) levels. At the DFT level, both local (LDFT) and non-local (NLDFT) calculations have been performed. The dimers are formed by the 1,2-, 1,4- and 1,2+1,4-cycloaddition of a cyclohexatrienyl unit of each C₆₀. The energies of the dimers relative to that of the most stable 1,2-C₆₀ dimer are 74.0 kcal/mol (AM-1), 75.2 kcal/mol (PM-3), 69.7 kcal/mol (LDFT) and 76.2 kcal/mol (NLDFT) for the 1,4-C₆₀ dimer, and 93.0 kcal/mol (AM-1), 87.0 kcal/mol (PM-3), 69.8 kcal/mol (LDFT) and 69.5 kcal/mol (NLDFT) for the 1,2+1,4-C₆₀ dimer. The dimerization reaction to form the C₆₀ dimers from C₆₀ is calculated to be weakly endothermic only for the formation of 1,2-(C₆₀)₂, and for the others, the reaction is predicted to be strongly endothermic. This result suggests that 1,2-cycloaddition is the most plausible scheme for the dimerization and polymerization of C₆₀ molecules, if the cages remain intact.

1. INTRODUCTION

In part due to the large number of reaction sites, the chemistry of fullerenes can be quite complex. We believe that results from computational studies should prove to be useful for understanding the factors that control the regiochemistry of addition to the exterior of the carbon framework. We have performed such studies on all isomers of dihydrogenated C₆₀ (C₆₀H₂)^{1a} with the MNDO/PM-3 method. That study showed that only two addition schemes are likely to occur with low energies; 1,2- and 1,4-addition to a cyclohexatrienyl unit in C₆₀. In addition, we have performed calculations on C₆₀ derivatives of 1,2- and 1,4-C₆₀X₂'s with X = H, F, Cl, Br and I at the local density functional (LDFT) level^{1b}. The energies of the 1,4-isomer relative to the 1,2-isomer are 6.8, 6.6, 2.5, -0.5 and -9.0 kcal/mol for X = H, F, Cl, Br and I, respectively, showing that the balance between the steric effect present in 1,2-isomer and the electronic effect present in 1,4-isomer plays an important role in the addition chemistry to C₆₀.

On the basis of these results, we have calculated the structures of dimers of C₆₀ as well as the energetics of dimerization as an aid for designing polymers containing C₆₀. The C₁₂₀'s that we describe below have a dumbbell shape as we studied dimers formed by 1,2- or 1,4-addition because these should be the lowest

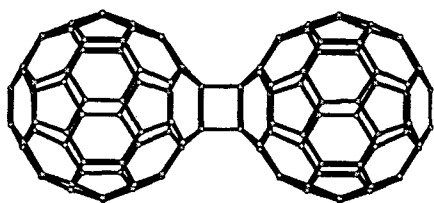
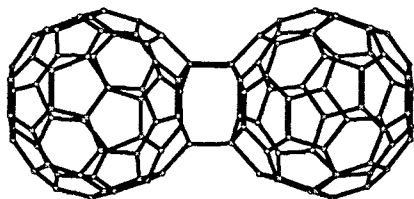
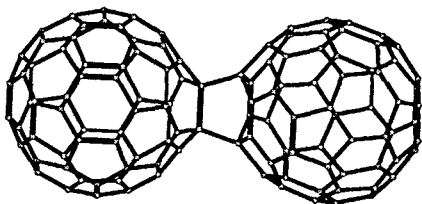
energy additions if the nature of C₆₀ cage is not disrupted. Three of the four structures that we investigated are shown in Figure 1. For 1,2-(C₆₀)₂, there is only one isomer (*D*_{2h} symmetry), whereas for 1,4-(C₆₀)₂, there are two possible isomers (*C*_{2v} or *C*_{2h} symmetry). As the results are essentially identical, we discuss only the *C*_{2v} isomer below. We also calculated the isomer formed by 1,2+1,4-addition (1,2+1,4-(C₆₀)₂) having *C*_s symmetry.

2. CALCULATIONS

It is not yet possible to use ab initio molecular orbital methods with a reasonable basis set to calculate the electronic structures of large molecules with low symmetry such as the (C₆₀)₂ isomers now under consideration, especially if a geometry optimization is to be done. Thus, we performed optimizations with a semiempirical method and used the MNDO Hamiltonian^{2a}) with the AM-1^{2b}) and PM-3^{2c}) parameterizations. The program system MOPAC^{2d}) was used for these calculations. Geometries were optimized with no constraint of symmetry, and an SCF energy convergence criterion of 10⁻⁸ kcal/mol was applied.

We have also performed density functional theory (DFT³) calculations with local (LDFT) and nonlocal (NLDFT) approximations at the MNDO/AM-1 final geometries. The LDFT and NLDFT calculations were done with the program systems DMol⁴) and DGauss⁵). DMol uses the

von Barth and Hedin potential⁶) for LDFT calculations, and uses the Lee, Yang and Parr⁷) non-local correction for the correlation energy and the Becke non-local correction⁸) for the exchange energy for the NLDFDFT calculations. DGauss uses the Vosko-Wilk-Nusair potential⁹) for LDFT calculations and the non-local exchange potential of Becke⁸) and the correlation potential of Perdew¹⁰) for the NLDFDFT calculations. The basis sets used in the DMol calculations are double numerical (DN) basis sets unless noted below. Double-zeta valence basis sets (DZV) on C are used in the DGauss calculations. For all of the calculations, a CRAY-YMP computer or an Alliant FX-2800 computer was used.

Figure 1(a) 1,2-(C₆₀)₂Figure 1(b) C_{2v}-1,2-(C₆₀)₂Figure 1(c) 1,2+1,4-(C₆₀)₂

3. RESULTS AND DISCUSSIONS

Before describing the results on the C₆₀ dimers, we first calculated energies of model reactions of (1) and (2). The results are shown in Table I.

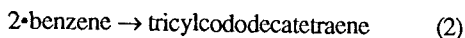
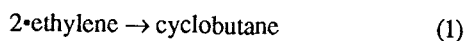


Table I. Dimerization Energies of Ethylene and Benzene in kcal/mol.

Method	ethylene ^a	benzene			
		1,2 (<i>anti</i>)	1,2 (<i>syn</i>)	1,4	1,2+1,4
AM-1	-34.0	26.9	30.0	38.2	27.6
PM-3	-37.0	21.0	24.1	38.8	24.3
LDFT/DN	-37.5	38.5	41.6	48.8	28.9
NLDFDFT/DN	-6.8	56.4	66.0	85.1	60.3
NLDFDFT/DZV	-17.8 ^b	58.5	62.2	77.2	54.8

^a expt :-18.0 (ref 12). ^b Thermodynamic corrections are applied.

For all of the reactions, the semiempirical values are in qualitative agreement with the LDFT values. The LDFT reaction energies tend to be more endothermic or less exothermic as compared to the semiempirical values. For reaction (1), we obtained electronic energy differences of -25.6 kcal/mol at the non-local level with the DZV basis set augmented with polarization functions on C and -20.7 kcal/mol with the DZV basis set. Including a thermodynamic correction (-4RT) and a correction for zero-point effects ($\Delta ZPE = 5.3$ kcal/mol¹¹), we obtain for reaction (1) $\Delta H(298 \text{ K}) = -22.7$ kcal/mol (DZVP) and -17.8 kcal/mol (DZV). These are in reasonably good agreement with the experimental value¹²). We also calculated the value of ΔE for reaction (2) with a polarized DN basis set at the NLDFDFT level. This gives -13.7 kcal/mol, which too endothermic as compared to experiment by ~7 kcal/mol. At the NLDFDFT/DN level, the reaction is even more endothermic as compared to experiment with a value of -6.8 kcal/mol.

Dimerization of two benzenes is substantially endothermic, reflecting the loss of two benzene resonance energies of ~36 kcal/mol¹³). Including non-local corrections makes the reaction energies more endothermic. There is a larger difference between the *anti* and *syn* structures for 1,2-(benzene)₂ at the NLDFDFT/DN level. The addition of non-local effects also changes the relative energies for the various benzene dimers. The most stable dimer is the 1,2-dimer (*anti*) followed by the 1,2+1,4-dimer and the 1,2-dimer (*syn*). The least stable dimer is the 1,4-dimer at the NLDFDFT/DN basis set level. The NLDFDFT/DZV calculation shows that the 1,2+1,4-benzene dimer is more stable than the *anti*-1,2-benzene dimer.

From these results, it is clear that non-local corrections are needed to properly describe the dimerization energies of these systems. We thus calculated the dimerization energies for C_{60} including non-local effects with the DZV Gaussian basis set. These calculations include correlation effects self-consistently in a basis set with 1080 functions. The relative energies of the C_{60} dimers and the dimerization energies (reaction (3)) are shown in Table II and III, respectively, together with the results obtained at the semiempirical levels as well as the LDFT level.



For both parameterizations of the MNDO method, the calculated relative energies are in good agreement with respect to each other. 1,2- $(C_{60})_2$ is predicted to be the most stable isomer, and the 1,4- $(C_{60})_2$ isomer is more stable than 1,2+1,4- $(C_{60})_2$. The relative energy of 1,4- $(C_{60})_2$ at the LDFT/DZV level is slightly smaller than the AM-1 and PM-3 values. The LDFT/DZV relative value for the 1,2+1,4- $(C_{60})_2$ isomer is comparable to that of the 1,4- $(C_{60})_2$ isomer. Thus, the LDFT value is 20 kcal/mol lower than the AM-1 and PM-3 values. Inclusion of non-local corrections does not lead to any substantial changes in the relative energies of the three isomers except that the 1,2+1,4-isomer becomes 6-7 kcal/mol more stable as compared to 1,4-isomer.

Table II. Relative Energies of the C_{60} dimers in kcal/mol

	1,2	C_{2v} -1,4	C_{2h} -1,4	1,2+1,4
AM-1	0.0	74.0	74.1	93.0
PM-3	0.0	75.2	75.3	87.0
LDFT/DN ^a	0.0	69.7		69.8
LDFT/DZV ^a	0.0	68.7		66.2
NLDFT/DZV ^a	0.0	77.6		69.5

^a Calculated at AM-1 optimized geometries.

The results in Table III show that the use of a Gaussian basis set makes reaction (3) which forms the 1,2-isomer less exothermic by 9 kcal/mol as compared to using a numerical basis set. This difference holds true roughly for the other isomers. Inclusion of non-local effects as discussed above for reactions (1) and (2) will make reaction (3) more endothermic (or less

exothermic). For dimerization of ethylene to form cyclobutane, the inclusion of non-local effects is on the order of 20-25 kcal/mol. For 1,2-dimerization of C_{60} , the effect is 24 kcal/mol, which makes the reaction endothermic by 8 kcal/mol at the DZV/NLDF level. However, we note that the numerical basis set would suggest a less endothermic process which leads us to conclude that the reaction is somewhat endothermic, on the order of 5 ± 5 kcal/mol for formation of the 1,2-isomer. The other isomers will not be formed as the reaction is clearly too endothermic. These results show that only 1,2-addition will occur in the polymerization of C_{60} , if the cages remain intact. Recently, the presence of the 1,2-cycloaddition products has been suggested in experimental observations¹⁴⁾, consistent with our theoretical results.

Table III. Dimerization Energies of C_{60} in kcal/mol.

	1,2	C_{2v} -1,4	1,2+1,4
AM-1	-33.0	41.0	60.0
PM-3	-36.9	38.3	50.1
LDFT/DN ^a	-24.2	45.5	45.6
LDFT/DZV ^a	-15.5	53.2	50.7
NLDFT/DZV ^a	8.5	86.1	78.0

^a Calculated at the AM-1 optimized geometries.

What kind of behavior does the dimerization of C_{60} to form the 1,2-isomer have? The reaction is less exothermic than the ethylene dimerization by ~30 kcal/mol but more exothermic than the benzene dimerization process by about 50 kcal/mol. Thus, the dimerization of C_{60} is intermediate between ethylene dimerization and benzene dimerization. This is consistent with the presence of some resonance stabilization in the C_{60} hexatriene rings. However, we do note that it is closer to ethylene dimerization than to benzene dimerization.

4. CONCLUSIONS

Three possible C_{60} dimers with intact cages have been calculated at the MNDO/AM-1, PM-3 and LDF levels. The calculations predict that 1,2- $(C_{60})_2$ is more stable than 1,4- and 1,2+1,4- $(C_{60})_2$ by 70-90 kcal/mol. The dimerization reaction to form the C_{60} dimers is calculated to be slightly endothermic only for the formation of

1,2-(C₆₀)₂, whereas for the other two isomers, the reaction is predicted to be substantially endothermic. This result suggests that 1,2-cycloaddition is the most plausible scheme for the dimerization and polymerization of C₆₀ molecules, if the cages remain intact. Comparison of the reaction energies for the dimerization of C₆₀ to those for ethylene and benzene indicate that the double bonds in C₆₀ can be regarded as being intermediate between these two types of double bonds.

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