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C_{60} Topological Isomers: Other Carbon Allotropes

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The structure and stability of nonlinear carbyne carbon clusters was estimated on the basis of ab initio quantum mechanical calculations. The catenane (catecarbynes), cyclic (cycarbynes), and knotted (knocarbynes) structures of closed polycarbon chains containing 60 carbon atoms are described. Comparison of the calculated ^{13}C NMR spectra with that of C_{60} fullerene provides a basis for experimental identification of C_{60} topological isomers in the mixture.

1. Introduction

The discovery of fullerenes[1] was a milestone in the understanding of possible new allotropic forms of polycarbon systems. Nevertheless, the confirmation of the existence of fullerenes did not contribute too much to the explanation of the complex spectra emitted by interstellar dust. The small carbon molecules (up to C_8) were identified by using mass spectrometry in the early 50s,[2−4] and even much larger molecules were studied theoretically.[5,6] Now, the spectroscopy of small carbon clusters is a field of increasing interest,[7−9] and interaction of medium-size cyclic carbyne molecules with lanthanium was recently observed[10] and studied theoretically.[11−14] Recently, we reported[15] on the possibility of the existence of another stable carbon allotrope, like cyclic 0^1_1 C_{60} cycarbynes and knotted 3_1 C_{60} knocarbynes (trefoil) (structures **1c** and **1d** in Figure 1, respectively; names are preceded by a numerical symbol defining a topological type of knotted or linked structure[16]). However, other carbyne topological isomers of C_{60} buckminsterfullerene (structure **1e** in Figure 1) are also possible. Till now various topological (carbon) isomers were described in terms of mathematical chemistry.[17−26]

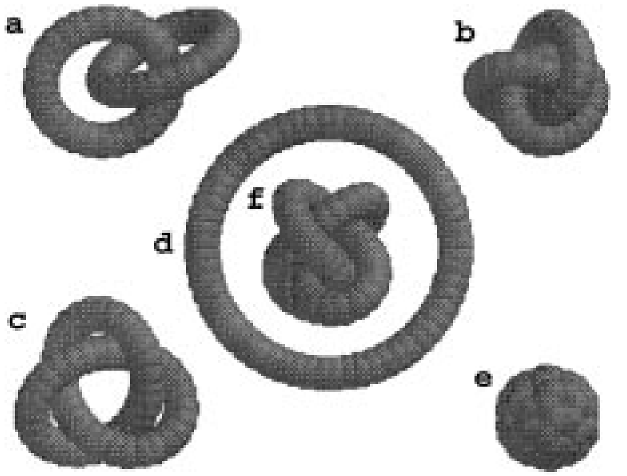

Figure 1. Space filling model of 2^2_1 ($C_{30}C_{30}$) catecarbyne (**1a**), 6^3_2 ($C_{20}C_{20}C_{20}$) catecarbyne (**1b**), 3_1 C_{60} knocarbyne (trefoil) (**1c**), C_{60} cycarbyne (**1d**), C_{60} fullerene (**1e**), and 4_1 C_{60} knocarbyne (figure-eight structure) (**1f**).

2. Methods

The present ab initio calculations were carried out with the Gaussian 94[27] system of programs executed on an SGI supercomputer. A full optimization of all the C_{60} molecules was done at the HF/3-21G//HF/3-21G level. Additionally, the single-point calculations were done at the MP2/3-21G//HF/3-21G, HF/DZP-HB//HF/3-21G, and MP2/3-21G//HF/3-21G levels (where DZP-HB denotes the double-ζ DZP-CGTO basis of Hansen and Bouman[28] composed of carbon atoms of (721/221/1) AO contracted to [3s3p1d]). The theoretical ^{13}C NMR chemical shifts were calculated using the CHF-GIAO approach[29] based on the HF/DZP-HB single-point calculations for the HF/3-21G optimized structures of C_{60} molecules. The double-ζ basis set[28] as used here has already been shown to be efficient for chemical-shift calculations.[30−33]

3. Results and Discussion

The results of ab initio quantum mechanical calculations performed at different theoretical levels are presented in Table 1. Along with one-electron properties we calculated also the ^{13}C NMR chemical shifts as well as the IR spectra.

Here, we explored with quantum chemical methods the C_{60} catecarbynes that can be formed by linking (interlocking and threading) of the C_{30} and C_{20} carbon rings. Both the 2_1 catecarbyne ($C_{30}C_{30}$) and 6^3_2 catecarbyne ($C_{20}C_{20}C_{20}$) structures might exist under special conditions.

It is interesting that in the case of the 2_1 C_{60} catecarbyne ($C_{30}C_{30}$) (structure **1a** in Figure 1) the interlocking of the two C_{30} rings requires only a very small energy investment when compared to the separated C_{30} subunits. The repulsion increases significantly for the 6^3_2 catecarbyne ($C_{20}C_{20}C_{20}$) (structure **1b** in Figure 1) but is expected to decline for the 6^3_2 ($C_{30}C_{30}C_{30}$), 6^3_2 ($C_{40}C_{40}C_{40}$), and higher analogues. The counterpoise correction for BSSE is presented in Table 2. However, on the basis of thermodynamics only, it would seem that in reality the observation of the C_{60} carbyne topological isomers is unlikely, but it is well-known that diamond under normal conditions is thermodynamically unstable.[34]

Data presented in Table 3 clearly indicate the NMR spectral features that can be used to distinguish and identify the hypothetical carbon allotropes experimentally. The C_{60} fullerene, C_{60} cycarbyne, and in effect 2^2_1 ($C_{30}C_{30}$) catecarbyne yield only one NMR signal, whereas for the 3_1 C_{60} knocarbyne 10 signals

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TABLE 1: Total Energies (in hartrees) and Stabilization Energies[a] (in kcal/mol) for the Carbyne Topological Isomers Calculated at the Different Theoretical Levels

molecule	HF/DZP-HB//HF/3-21G[b]	HF/3-21G//HF/321-G	MP2/3-21G//HF/3-21G
C_{60} cycarbyne	−2270.635 773 (0.00)	−2257.793 040 (0.00)	−2263.029 874 (0.00)
2^2_1 ($C_{30}C_{30}$) catecarbyne	−2270.522 860 (70.85)	−2257.674 325 (74.49)	−2262.944 437 (53.61)
3_1 C_{60} knocarbyne (trefoil)	−2270.481 319 (96.92)	−2257.636 039 (98.52)	−2262.934 791 (59.67)
4_1 C_{60} knocarbyne (figure-eight)	−2270.335206 (188.61)	−2257.490 355 (189.94)	−2262.839 371 (119.54)
6^3_2 ($C_{20}C_{20}C_{20}$) catecarbyne	−2270.176 907 (287.94)	−2257.348 919 (278.69)	−2262.774 661 (160.148)
C_{60} fullerene	−2272.193 593 (−963.77)	−2259.047 674 (−787.29)	−2264.386 983 (−851.60)
C_{30} cycarbyne	−1135.261 457 (0.03)[c]	−1128.837 162 (0.00)[c]	−1131.471 385 (−1.05)[c]
C_{20} cycarbyne	−756.779 082 (100.61)[d]	−752.493 639 (82.83)[d]	−754.264 717 (12.23)[d]

[a] Stabization energies given in parentheses are calculated relative to the C_{60} cycarbyne. [b] For basis set used see ref 16. [c] $E(C_{30}C_{30}) - 2E(C_{30})$. [d] $E(C_{20}C_{20}C_{20}) - 3E(C_{20})$.

TABLE 2: Counterpoise Correction for Basis Set Superposition Error for Two Catecarbyne Molecules

molecule	ΔE[a]	CP_1[b]	CP_2[c]
MP2/3-21G//HF/3-21G			
2^2_1 ($C_{30}C_{30}$) catecarbyne	−1.05	−0.95	−1.05
6^3_2 ($C_{20}C_{20}C_{20}$) catecarbyne	12.23	46.43	46.51
HF/3-21G//HF/3-21G			
2^2_1 ($C_{30}C_{30}$) catecarbyne	0.00	−1.64	−1.09
6^3_2 ($C_{20}C_{20}C_{20}$) catecarbyne	82.83	98.87	106.20

[a] $\Delta E = E_{AB} - (E_A + E_B)$ or $\Delta E = E_{ABC} - (E_A + E_B + E_c)$. In hartrees. [b] $CP_1 = E_{AB} - (E^*_A + E^*_B)$ or $CP_1 = E_{ABC} - (E^*_A + E^*_B + E^*_c)$, where E^* stands for calculations in the basis of the whole system. In hartrees. [c] $CP_2 = \Delta E - (E^*_A + E^*_B - (E^{**}_A + E^{**}_B))$ or $CP_2 = \Delta E - (E^*_A + E^*_B + E^*_C - (E^{**}_A + E^{**}_B + E^{**}_C))$, where E^{**} stands for single-point calculations of the C_{20} (or C_{30}) subunit in its own basis only for geometry deformed in the whole system. In hartrees.

TABLE 3: ^{13}C NMR[a] Chemical Shifts (in ppm) Calculated for the C_{60} Carbon Topological Isomers at the HF/DZP-HB//HF/3-21G Level

molecule	no. equal signals	chemical shift[a]
2^2_1 ($C_{30}C_{30}$) catecarbyne	1	102.96
6^3_2 ($C_{20}C_{20}C_{20}$) catecarbyne	60	152.69−99.80
3_1 C_{60} knocarbyne	10	126.84, 125.53, 120.16, 119.92, 111.81, 104.13, 101.64, 89.08, 87.44, 81.92
4_1 C_{60} knocarbyne	30 (doublets)	146.60−64.65
4_1 C_{64} knocarbyne	16	140.45, 140.17, 133.36, 130.86, 128.53, 125.92, 110.09, 110.08, 105.56, 102.84, 94.59, 82.24, 76.92, 72.61, 66.55, 63.07
C_{60} cycarbyne	1	86.02
C_{60} fullerene	1	169.42

[a] For the method, see ref 7. [b] Chemical shifts are calculated against the ^{13}C atoms of TMS (shielding constant is 201.05 ppm).

of equal intensity should be observed. The 4_1 C_{60} knocarbyne (a figure-eight structure (structure **1f** in Figure 1)) has no symmetry, but in fact, the calculated spectrum consists of 30 NMR doublets; however, the C_{64} figure-eight structure belongs to the S_4 group of symmetry. Therefore, 16 signals of equal intensity are expected (Table 3) and for the 6^3_2 ($C_{20}C_{20}C_{20}$) catecarbyne we found 60 different signals in a large spectral range (Table 3). The level of complexity of the IR spectrum[15] is also a key to a solution of the fullerene cyclic, knotted, and catenane structures.

As in the case of fullerenes, both the topological isomeric C_{60} carbon structures and their heteroanalogues might have unusual properties.[15]

4. Conclusion

The topological knotted structures are known for complex biological systems.[35−53] Therefore, further quantum chemical investigations on hypothetical topological structures of simpler chemical molecules need to be explored.

Results of our calculations clearly show that these structures are really possible. The conversion between moderately different thermodynamic endpoints requires overcoming high-energy barriers due to the necessity of C−C bond breaking. On the other hand, the calculated NMR spectra can be helpful for interpretation of future experimental measurements.

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