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C_{78} IPR fullerenes: Computed B3LYP/6-31G*//HF/3-21G temperature-dependent relative concentrations

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Abstract. The five isolated-pentagon-rule (IPR) satisfying isomers of C_{78}, labeled 1–5, or according to symmetry as D_3, C_{2v}, C'_{2v}, D_{3h}, and D'_{3h}, are computed. The cage geometries are optimized at the *ab initio* HF level with the standard 3-21G basis set (HF/3-21G). The separation energetics is then computed using the B3LYP density-functional treatment in the standard 6-31G* basis set (B3LYP/6-31G*//HF/3-21G). Harmonic vibrational frequencies are calculated by the SAM1 semiempirical method. The computed energies, structural and vibrational data are employed in the construction of isomeric partition functions and evaluation of the relative Gibbs free energies. The results are converted into relative concentrations for a wide temperature interval. The C'_{2v} structure is the most populated throughout while the D_{3h} species is negligible at all temperatures. The agreement between theory and experiment is reasonable, though some aspects are still to be clarified.

PACS. 82.60.Hc Chemical equilibria and equilibrium constants – 82.30.Qt Isomerization and rearrangement – 61.48.+c Fullerenes and fullerene-related materials – 31.15.Ar Ab initio calculations – 31.15.Ew Density-functional theory

1 Introduction

There are just five isolated-pentagon-rule (IPR) satisfying isomers of C_{78}, labeled 1–5 according to [1] and in this order they exhibit the D_3, C_{2v}, C_{2v}, D_{3h}, and D_{3h} symmetries. The two C_{2v} species exhibit [2] qualitatively different ^{13}C NMR patterns, however, the two D_{3h} species have the same pattern, five strong and three weak lines. In the past, a different numbering scheme was introduced [3] followed for example in [4]. Diederich *et al.* [2] used modified symmetry labels D_3, C_{2v}, C'_{2v}, D_{3h}, and D'_{3h}, ordered in the sequence 1–5 according to the new numbering system [1]. The C_{2v} species is also labeled as C_{2v}(I) in [4,5].

In experiments, at first only two isomers were observed by Diederich *et al.* [2], with D_3 and C_{2v} symmetry in a ratio 1:5. Later on, Kikuchi *et al.* [6] reported three isomers of C_{78} with the symmetries D_3, C_{2v}, and C'_{2v} in a ratio 2:2:5. Taylor *et al.* [7] also reported three structures, C_{2v}, D_3, and C'_{2v} in a ratio 5.2:3:1.8 (though there is a difference from the previous report [2] in the location of one NMR peak for D_3). NMR spectra of ^{3}He in C_{78} reported by Saunders *et al.* [8] qualitatively agree with the previous findings.

In contrast to this relative abundance of observations, the isomeric ratios were computed only at semiempirical level (MNDO, AM1, and PM3) [4] and the agreement with experiments has been only partial. This situation has prompted the present higher-level calculations.

2 Computations

The geometry optimizations started with the new semiempirical method SAM1, developed [9] to overcome some drawbacks of previous methods. This part of the computations was carried out with the AMPAC program package [10]. The geometry optimizations were performed with no symmetry constraints in Cartesian coordinates and with analytically constructed energy gradients. For the SAM1 optimized geometries, the harmonic vibrational analysis was carried out by a numerical differentiation of the analytical energy gradient.

The SAM1 geometries were further re-optimized at the *ab initio* HF level with the standard 3-21G basis set (HF/3-21G). The separation energetics was moreover refined at two higher levels of theory, though performed for the HF/3-21G optimized geometries. One of them was the *ab initio* HF approach with the standard 4-31G basis set (HF/4-31G//HF/3-21G), the other was the B3LYP

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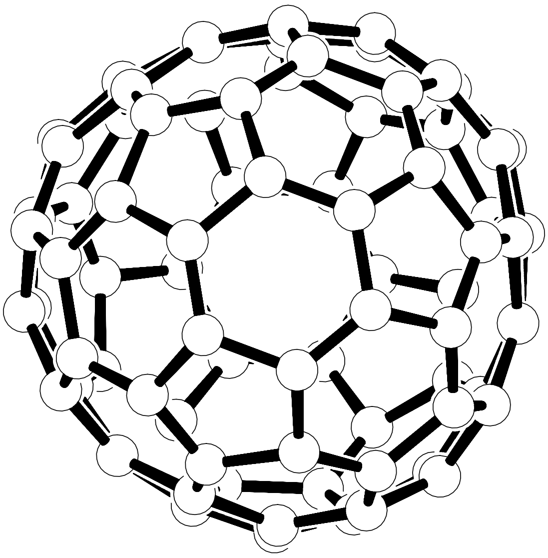

Fig. 1. The HF/3-21G optimized structure of the D_3 isomer.

density-functional treatment in the standard 6-31G* basis set (B3LYP/6-31G*//HF/3-21G). All the *ab initio* calculations were carried out with the Gaussian program package [11].

The computed energy, structural and vibrational data are employed in the construction of isomeric partition functions and evaluation of the relative Gibbs free energies. The rotational-vibrational partition functions are of the rigid rotator and harmonic oscillator quality, and no frequency scaling is considered. Relative concentrations (mole fractions) x_i of n isomers can be expressed through the partition functions q_i and the ground-state energy $\Delta H^{\circ}_{0,i}$ by a compact formula

$$x_i = \frac{q_i \exp\left(-\Delta H^{\circ}_{0,i}/(RT)\right)}{\sum_{j=1}^{n} q_j \exp\left(-\Delta H^{\circ}_{0,j}/(RT)\right)},$$

where R is the gas constant and T is the absolute temperature. The symmetries of the optimized cages represent an important issue and they were determined by a new procedure which treats precision of the computed coordinates as a variable parameter [12]. Chirality contribution was also considered, for the D_3 enantiomeric pair its partition function was doubled.

3 Results and discussion

Table 1 presents the computed energetics for the C_{78} IPR set (see Figures 1–5). The C_{2v} isomer labeled 3 is always the system ground state and species 4 is always the highest in energy. Otherwise, the results from the selected computations are not that consistent. In particular, in three cases the ground state isomer is followed by isomer 2, however, in the B3LYP/6-31G*//HF/3-21G treatment isomer 5 is the second lowest structure in energy.

The relative energies themselves cannot always predict relative stabilities in an isomeric system at high temperatures as stability interchanges induced by temperature are possible [12]. In other words, we deal with a significant enthalpy-entropy interplay related to considerably high temperatures used in fullerene synthesis. In our treatment the Gibbs free energy terms are converted into more convenient relative concentrations.

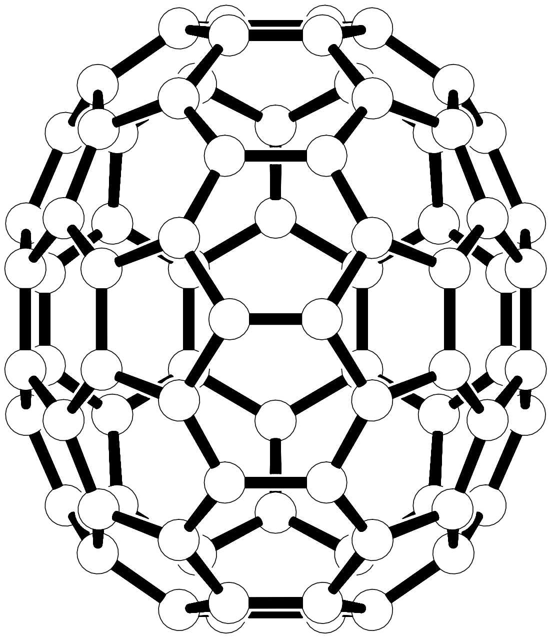

Fig. 2. The HF/3-21G optimized structure of the C_{2v} isomer.

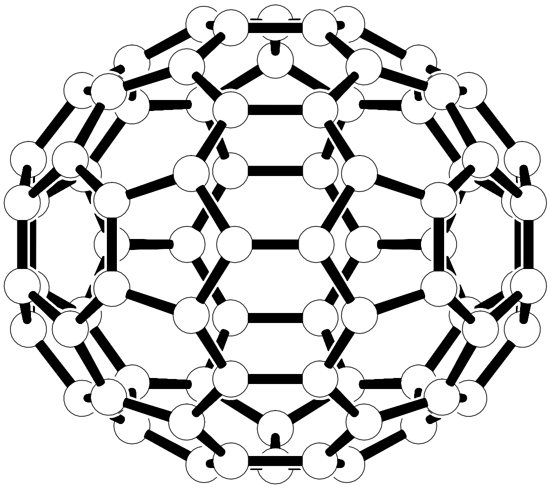

Fig. 3. The HF/3-21G optimized structure of the C'_{2v} isomer.

Figure 6 presents the development of the relative concentrations x_i in the C_{78} IPR set for a wide temperature interval based on the HF/3-21G rotational, SAM1 vibrational, and B3LYP/6-31G*//HF/3-21G energy data. At very low temperatures, of course, the ground-state structure has to be prevailing. In fact, the C'_{2v} isomer 3 remains the most populated species throughout. There is actually only one relative stability interchange, close to 1500 K. The D_{3h} isomer 4 is negligible at all temperatures. The three experimental studies [2,6,7] of C_{78} are not really consistent. Diederich *et al.* [2] report only two

Table 1. The relative energies^a of the IPR structures of C_{78} in kJ/mol.

Label	SAM1	HF/3-21G	HF/4-31G	B3LYP/6-31G*
1, D_3	31.16	17.11	30.84	40.87
2, C_{2v}	20.54	0.71	10.73	26.96
3, C'_{2v}	0.00	0.00	0.00	0.00
4, D_{3h}	89.61	53.40	75.29	102.67
5, D'_{3h}	26.26	46.32	38.78	20.13

$^a \Delta H^\circ_{f,298,r}$ for SAM1

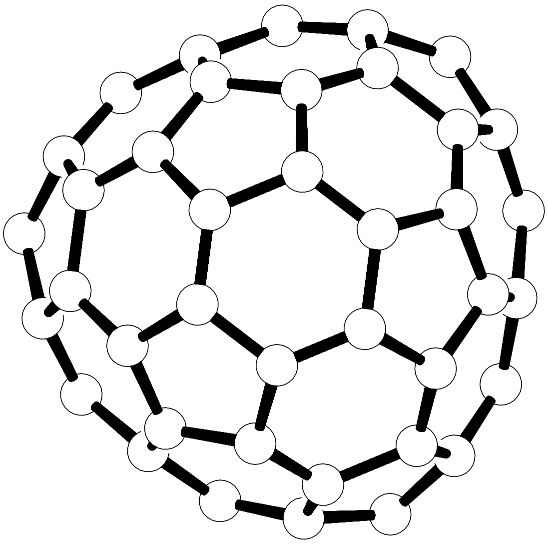

Fig. 4. The HF/3-21G optimized structure of the D_{3h} isomer.

isomers while the other two works [6,7] observed three structures. What comes as the major component in one paper [6], is only the third most populated species in the other study [7]. The present calculations agree reasonably well with findings of Kikuchi *et al.* [6], structures 1, 2, and 3 (D_3, C_{2v}, and C'_{2v}) in a ratio 2:2:5.

The achieved theory-experiment correspondence is encouraging, though still more computations on energetics and vibrations are needed to clarify possible sources of only partial agreement. The presence of isomer 5 has never been observed, though computations suggest it as a possible minor component, even more populated than isomer 1. A latter isolation of a missing minor fullerene isomer, predicted by computations, is possible, as has recently happened [12–14] with C_{80}.

Our treatment presupposes inter-isomeric equilibrium. It is difficult to guess a degree to which this presumption is satisfied in each particular experiment. Experiments of Wakabayashi *et al.* [15] indicate that such an equilibrium requires sufficiently high pressures of He. Moreover, there may be some yet unknown catalytic effects [16] involved.

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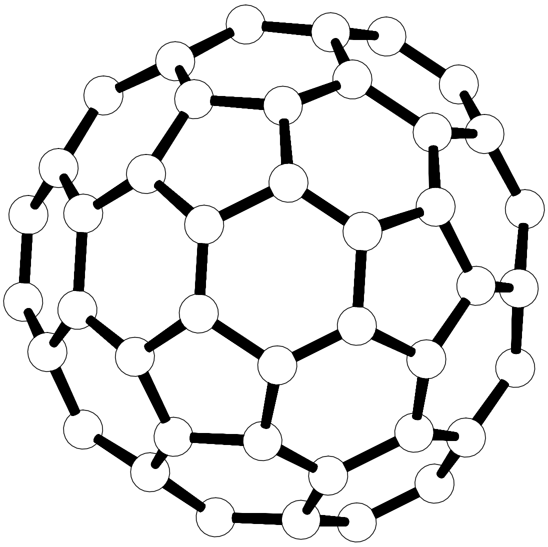

Fig. 5. The HF/3-21G optimized structure of the D'_{3h} isomer.

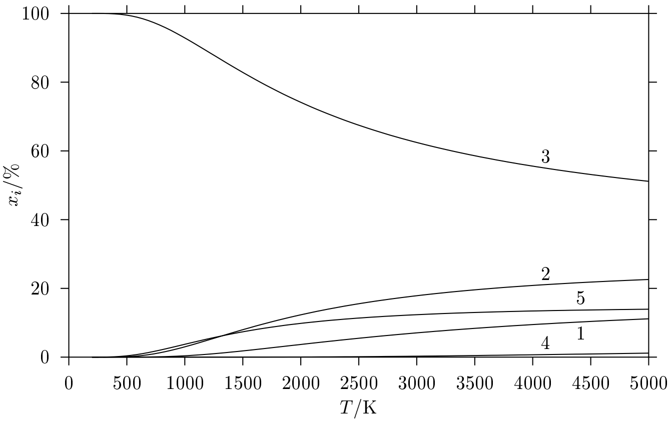

Fig. 6. The temperature dependence of the relative concentrations of the C_{78} IPR isomers.

Note added in proof

Yamamoto [17] has recently reported an isolation of the fourth isomer of C_{78}, namely a D'_{3h} species. This species is labeled by 5 in Figure 6 and thus, it is indeed computed as the third most stable at high temperatures (even the second most populated at moderate temperatures).

References

1. P.W. Fowler, D.E. Manolopoulos, *An Atlas of Fullerenes* (Clarendon Press, Oxford, 1995).
2. F. Diederich, R.L. Whetten, C. Thilgen, R. Ettl, I. Chao, M.M. Alvarez, Science **254**, 1768 (1991).

3. P.W. Fowler, R.C. Batten, D.E. Manolopoulos, J. Chem. Soc., Faraday Trans. **87**, 3103 (1991).
4. Z. Slanina, J.-P. François, D. Bakowies, W. Thiel, J. Mol. Struct. (Theochem) **279**, 213 (1993).
5. D. Bakowies, A. Geleßus, W. Thiel, Chem. Phys. Lett. **197**, 324 (1992).
6. K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, Y. Achiba, Nature **357**, 142 (1992).
7. R. Taylor, G.J. Langley, A.G. Avent, T.J.S. Dennis, H.W. Kroto, D.R.M. Walton, J. Chem. Soc., Perkin Trans. **2**, 1029 (1993).
8. M. Saunders, R.J. Cross, H.A. Jiménez-Vázquez, R. Shimshi, A. Khong, Science **271**, 1693 (1996).
9. M.J.S. Dewar, C. Jie, J. Yu, Tetrahedron **49**, 5003 (1993).
10. *AMPAC 6.0* (Semichem, Shavnee KS, 1997).
11. M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, *Gaussian 94, Revision D.4* (Gaussian, Inc., Pittsburgh PA, 1995).
12. M.-L. Sun, Z. Slanina, S.-L. Lee, F. Uhlík, L. Adamowicz, Chem. Phys. Lett. **246**, 66 (1995).
13. F.H. Hennrich, R.H. Michel, A. Fischer, S. Richard-Schneider, S. Gilb, M.M. Kappes, D. Fuchs, M. Bürk, K. Kobayashi, S. Nagase, Angew. Chem., Int. Ed. Engl. **35**, 1732 (1996).
14. C.-R. Wang, T. Sugai, T. Kai, T. Tomiyama, H. Shinohara, J. Chem. Soc., Chem. Commun. No. 7, 557 (2000).
15. T. Wakabayashi, K. Kikuchi, S. Suzuki, H. Shiromaru, Y. Achiba, J. Phys. Chem. **98**, 3090 (1994).
16. Z. Slanina, X. Zhao, F. Uhlík, M. Ozawa, E. Ōsawa, J. Organomet. Chem. **599**, 57 (2000).
17. K. Yamamoto, Abstract No. 1489, *The 200th ECS Meeting*, ECS, San Francisco, 2001.