

Theoretical studies on relative stabilities of C₇₀ fullerene dimers

Xiang Zhao^{a,*}, Zdenek Slanina^b, and Hitoshi Goto^a

- a. Laboratory of Theoretical/Computational Chemistry, Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Toyohashi 441-8580, Japan
- b. Department of Theoretical Studies, Institute for Molecular Science, Okazaki 444-8585, Japan

ABSTRACT

Five stable fullerene dimers (C₇₀)₂ with [2+2] bridges between hexagon-hexagon bonds, which are experimentally characterized very recently, have been investigated by several semi-empirical MO approaches and *ab initio* Hartree-Fock self-consistent field calculation and hybrid density functional theory treatment. Energy difference among the five isomers is predicted to be quite small, where two of them seem to be isoenergetic. The computed B3LYP/6-31G temperature-dependent relative concentrations indicate the two lower energy isomers to be the most thermodynamically populated one with a ratio of 1:1 over a wide temperature area. This finding agrees reasonably well with the recently reported experimental observations.

Keywords: fullerene dimer, *ab initio* method, density-functional theory, entropy-enthalpy interplay

INTRODUCTION

A great deal of considerable interest has been

paid to fullerene dimers^[1,2] since the discovery of C₆₀^[3]. Recently, several experimental and theoretical investigations on (C₆₀)₂, (C₇₀)₂ and even (C₅₉N)₂ have been reported^[4-7], which seem to be important to elucidate the unique physical properties of fullerene polymeric materials. Very recently, Shinohara *et al.*^[8] reported the first experimental synthesis and characterizations of five [2+2] structural isomers of fullerene dimers (C₇₀)₂. They also reported the five separated isomers in a relative production ratio of 0.8/1.0/0.5/0.5/0.2. Although the relative isomeric mixtures in experiment are not yet clear before the individual structures are assigned, such an experimental effort obviously leads to the corresponding theoretical study. In the present report this fullerene dimer system is addressed with quantum-chemical calculations.

COMPUTATIONS

According to the previous calculations by Fowler *et al.*^[6], all 15 lower energy (C₇₀)₂ dimer structures were considered and pre-optimized with several semi-empirical MO methods (i.e. PM3, AM1, and MNDO). It is found, in

agreement with previous results, that five energetically reasonable isomers indeed exist dominantly over the rest of isomers. The five low-energy structures are labeled same as previous code combined with its symmetry – **cis**: C_{2v} , **trans**: C_{2h} , **abc**: C_1 , **c1**: C_{2h} , and **c2**: C_{2v} . In order to promote the energetic accuracy, the five isomers are further subjected to the fully geometry optimizations at the HF/6-31G and B3LYP/6-31G levels of theory, with the Gaussian 98 program package [9]. The harmonic vibrational analyses are carried out on the five isomers at both AM1 and PM3 levels in order to evaluate their relative concentrations at high temperatures using both enthalpy and entropy terms.

Relative concentrations (mole fractions) x_i of m isomers can be expressed through the partition functions q_i and the enthalpies at the absolute zero temperature or the ground-state energies $\Delta H_{0,i}^p$ by a compact formula [10]:

$$x_i = \frac{q_i \exp[-\Delta H_{0,i}^o / (RT)]}{\sum_{j=1}^m q_j \exp[-\Delta H_{0,j}^o / (RT)]}$$

where R is the gas constant and T the absolute temperature. Since PM3 energetic results show some contradictions to other applied methods, the rotational-vibrational partition functions are constructed from the AM1 calculated structural and vibrational data under the rigid rotator and harmonic oscillator approximation. Chirality's contribution, frequently ignored, is included accordingly. Finally, temperature-dependent relative stabilities under thermodynamic equilibrium can be evaluated as a key output (mole fractions in the isomeric mixture) for comparisons with the available experimental

observations.

Table 1: The relative energies (kJ/mol) of five $(C_{70})_2$ dimers

isomer:sym.	B3LYP	HF	AM1	PM3	MNDO
abc : C_1	9.34	5.69	1.37	-0.27	4.48
c1 : C_{2h}	20.16	11.37	2.81	-0.47	9.06
c2 : C_{2v}	20.88	12.02	2.95	-0.33	9.23
cis : C_{2v}	0.28	0.21	0.04	0.04	0.04
trans : C_{2h}	0.0	0.0	0.0	0.0	0.0

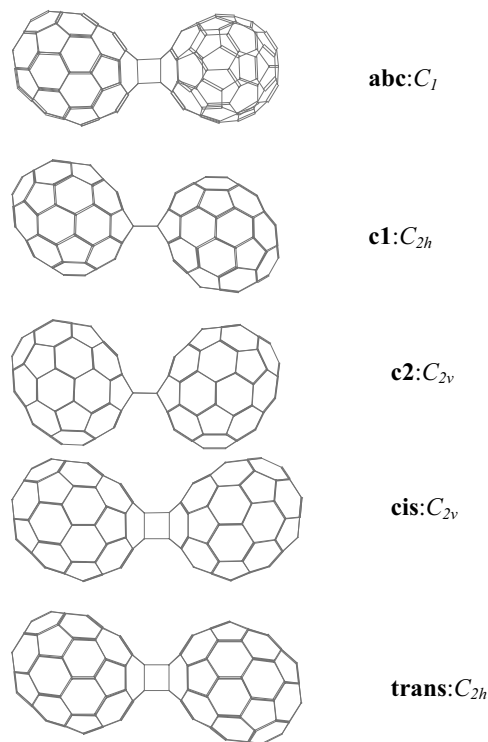


Fig. 1: Five stable isomers of $(C_{70})_2$ dimers

RESULTS AND DISCUSSION

Table 1 presents the computed energetics for the five stable fullerene dimers $(C_{70})_2$ with [2+2] bridges between hexagon-hexagon bonds (see Figure 1). The structure **trans**: C_{2h} is predicted as

the lowest energy species in the dimeric system only with exception of PM method. Based on the AM1, MNDO, HF/6-31G, and B3LYP/6-31G energetic results, it is clear that the energy difference among the five isomers is rather small and two dimeric structures (**trans**: C_{2h} and **cis**: C_{2v}) are almost isoenergetic (only 0.28 kJ/mol at B3LYP level).

The relative energetics themselves cannot always predict relative stabilities in an isomeric system at high temperatures as stability interchanges induced by a significant enthalpy-entropy interplay. In our treatment the Gibbs free energy contributions are taken into account to predict the general relative stabilities within higher temperatures.

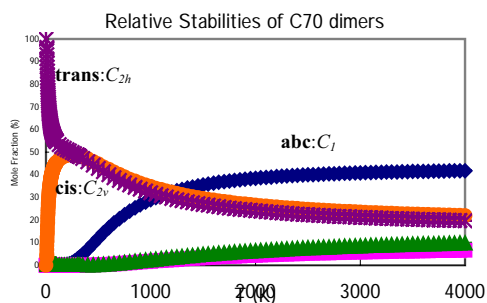


Fig. 2: Relative stabilities of C_{70} dimers

Figure 2 presents the development of the relative concentrations x_i in the five lower energy dimeric system for a wide temperature interval based on the B3LYP/6-31G energetics and the AM1 rotational/vibrational data. At very low temperatures, of course, the **trans**: C_{2h} structure has to be prevailing. When temperatures increase, the population of the **cis**: C_{2v} structure jumps very rapidly and the first relative stability interchange

in this dimeric system should happen around the room temperature (300K) between the **trans**: C_{2h} and the **cis**: C_{2v} structures. As temperatures further increase, the third dimer **abc**: C_1 becomes much more important and finally the most thermodynamically stable species over the temperature of 1250K. Two other dimers (**c1**: C_{2h} , and **c2**: C_{2v}) show some relatively small but non-negligible populations at higher temperatures.

Interestingly enough, at a selected temperature of 2000K for instance, the computed B3LYP/6-31G concentration ratio of the five dimers (**cis**: C_{2v} / **trans**: C_{2h} / **abc**: C_1 / **c2**: C_{2v} / **c1**: C_{2h}) shows about 0.7/0.7/1.0/0.2/0.2 of the relative abundances. This result agrees reasonably well with the experimental observation of Shinohara et al. [8], where the production ratio of the five dimers is given with 0.8/1.0/0.5/0.5/0.2.

The achieved theory-experiment correspondence is certainly encouraging, though still more advanced computations on energetics and vibrations are needed to clarify possible sources of some disagreement. Further efforts and improvement [11] are still ongoing.

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* Corresponding Author. Fax: +81-532-485588.
Email: zhao_cochem2.tutkie.tut.ac.jp