

**GEOMETRICAL AND THERMODYNAMIC
APPROACHES TO THE RELATIVE STABILITIES
OF FULLERENE ISOMERS**

Zdenek Slanina,^{a,d} Filip Uhlík,^b Shyi-Long Lee^c and Eiji Ōsawa^d

^aInstitute of Chemistry, Academia Sinica

Nankang, Taipei 11529, Taiwan - R.O.C.

^bDepartment of Physical and Macromolecular Chemistry, School of Science

Charles University, CZ-128 43 Prague 2, Czech Republic

^cDepartment of Chemistry, National Chung-Cheng University

Ming-Hsiung, Chia-Yi 621, Taiwan - R.O.C.

^dDepartment of Knowledge-Based Information Engineering

Toyohashi University of Technology, Toyohashi 441-8580, Japan

Abstract. Three possible stability measures are considered for fullerene cages: the Wiener index, a sphericity quotient, and molar fractions derived from quantum chemical calculations combined with partitions functions. The treatments are studied as possible measures of the relative-stability order for the isolated-pentagon-rule (IPR) isomers of higher fullerenes. The treatments are illustrated on the C_{78} , C_{80} , C_{86} , and C_{88} IPR sets. The full computational treatment can be reduced to topological/geometrical evaluations only in some specific cases.

INTRODUCTION

Applications of graph theory to chemical problems represent one of the oldest parts of theoretical chemistry. The first comprehensive survey of the techniques from chemical point of view was published in 1976 under the editorship of A. T. Balaban [1]. Chemical enumerations go back to Cayley who enumerated [2,3] certain types of trees already in the middle of the nineteenth century. Fullerenes [4] and their derivatives [5] have also been subjected to vigorous enumerations.

Apparent stability of C_{60} and some higher fullerenes represents a challenging theoretical problem [4,5]. Two types of relative stabilities can be considered, either for carbon cages with different or with the same number of carbon atoms. Not too many theoretical results have been reported on the former topic. It has been however pointed out [6-10] that the relative-stability schemes for clusters of different dimensions are not only temperature but also pressure dependent. Moreover, the schemes can in fact be sometimes sensitive to pressure considerably. Generally speaking, chemical theory has not yet suggested a practical stability quotient in order to measure stabilities of fullerenes of different dimensions. Designing such a quotient is not an easy task, as, most probably, formation of fullerenes is controlled by a complicated kinetics, with relevant processes not only in gas but also in condensed phase.

The fullerene relative-stability problem can however be considerably simplified if we select just a particular fullerene C_n , keeping the carbon contents n constant, and treating the relative stabilities of various fullerene isomers with the given composition C_n . In fact, experimental knowledge on higher fullerenes is rather extensive - over thirty stable species have been reported [11-13] with n from 60 to 96. The number itself of all isomeric cages built from pentagons and hexagons is rather high - for example C_{60} allows [4] for 1812 fullerene isomers (3532 if enantiomeric pairs are considered as two distinct fullerenes). This number of structures can however be drastically reduced using so called isolated-pentagon-rule (IPR) concept [4]. The empirical rule claims that higher fullerene cages, with all 12 pentagons exclusively surrounded by hexagons, are especially stable. The IPR concept has been computationally tested [14] for example on the C_{76} isomeric family. The rule has widely been accepted in both experimental and theoretical studies of higher fullerenes (though, exceptions are known [15,16]).

The smallest possible IPR structure is the well-known buckminsterfullerene, and together with C_{70} it is a unique structure. The smallest fullerene with more than one IPR structure is C_{76} , however, therefrom the number of the IPR isomers increases quite rapidly as demonstrated [17] in enumerations with the spiral algorithm. For $n = 100$ we already meet [4] 450 IPR isomers (862 if enantiomers are respected). Such an isomeric set could hardly be handled by quantitative quantum-chemical methods. Clearly enough, much simpler and more transparent approaches are needed.

Observations have frequently indicated [11-13] a coexistence of several isomers for higher fullerenes. In fact, there are several fullerene-isomeric mixtures with a considerable experiment-theory agreement, for example: C_{78} (e.g. [18-21]), C_{82} (e.g., [22-26]), and C_{84} (e.g. [27-31]). More recently, computations [32-35] on C_{80} have been experimentally confirmed [36,37], too. At present, we have continued our computational studies with still higher fullerenes [38]. Thus, we have created a bank of quantum-chemical fullerene data and thus, we can try to search for quotients that correlate with them in order to use selected quotients in relatively reliable predictions for n well beyond 100.

METHODS

The Wiener index [40] is a rather natural choice for our probatory correlation tests. The carbon atoms in fullerenes are always distorted from an ideal sp^2 hybridization; this distortion can be measured by the surface curvature. For example, buckminsterfullerene itself exhibits a constant curvature. Other stable fullerenes exhibit quasi-spherical shapes. On the other hand, structures with abrupt changes of their curvature (which happens for example if two pentagons are connected) are likely to have a high energy, i.e. low stability. The abrupt changes in the curvature cause a deformed, elongated rather than spherical shape. Instead of treating the terms of curvature or quasi-sphericity, we can also use a measure of the structural compactness, and the Wiener index in particular.

The Wiener index is defined [39,40] as the sum of topological distances between all pairs of vertices in a molecular graph. Traditionally, it has been evaluated from the adjacency matrix of the corresponding graph. As we link the evaluations to quantum-chemical outputs, it is convenient that the adjacency matrix itself can be readily deduced from the Cartesian coordinates of the atoms, resulting from a quantum chemical geometry optimization. The quality of the optimized geometry is of course not important (unless connectivity pattern is changed during the optimization) as the Wiener index is a topological invariant. The energetics used in our correlations with the Wiener index originated in our previous semiempirical or non-empirical quantum chemical-calculations. The semiempirical methods primarily yield the heat of formation at room temperature, and the term could directly be used. However, in order to keep consistency with related *ab initio* calculations, the semiempirical data should be reduced to the absolute zero temperature and the vibrational zero-point energy

then extracted, yielding the terms of relative potential energy (i.e., the primary output of *ab initio* calculations).

In addition to the topological measure of structural compactness, we also consider a geometrical quotient of sphericity. We have been using a best-sphere approach for the purpose. If we have a set of N points, we can fit a sphere (radius r_0) that is the best in the sense of the least-square technique. If R_i denotes the distance of the i -th point from the center of the sphere, then we require that the sum of the squares of the differences:

$$\Delta = \sum_{i=1}^N (R_i - r_0)^2 \quad (1)$$

reaches a minimal value. From this requirement, the radius of the best sphere and the position of its center is obtained. A quality of the fit can be, for example, measured by a reduced quotient:

$$\delta = \frac{\sqrt{\Delta}}{N} \quad (2)$$

The reduced sphericity quotient δ can be computed for various quantum-chemically optimized structures and is thus method-dependent.

While the previous two approaches clearly represent simplified evaluations, the third technique considered here represents a rigorous treatment (at least within equilibrium thermodynamics). The quantum-chemically computed energy, structural and vibrational data are combined for construction of the isomeric partition functions q_i . The latter terms are used for production of the relative Gibbs free energies and thus also relative concentrations. The rotational-vibrational partition functions q_i are of the rigid rotator and harmonic oscillator quality at present, and no frequency scaling is considered. Relative concentrations (mole fractions) x_i of m isomers can be expressed through the partition functions q_i and the ground-state energy $\Delta H_{0,i}^0$ by the following compact formula:

$$x_i = \frac{q_i \exp[-\Delta H_{0,i}^0 / (RT)]}{\sum_{j=1}^m q_j \exp[-\Delta H_{0,j}^0 / (RT)]} \quad (3)$$

where R is the gas constant and T the absolute temperature. The partition functions require

not only the harmonic vibrational frequencies and moments of inertia but also symmetry numbers and chirality factors.

RESULTS AND DISCUSSION

Let us start with the IPR isomeric set of C_{80} . There are just seven [4] IPR isomers for C_{80} . The relative potential-energy changes are derived from our SAM1 (Semi-Ab-Initio Model 1) calculations [35,38]. The ground state structure has a D_{5d} symmetry, being closely followed by a structure with a D_2 symmetry. Figure 1 shows a fair correlation between the Wiener indices and the SAM1 computed energies. This finding itself is encouraging, however, the C_{80} relative stabilities are only partly controlled by energetics while the complete picture (and a full agreement with experiments [36,37]) emerges [35,38] after inclusion of entropy.

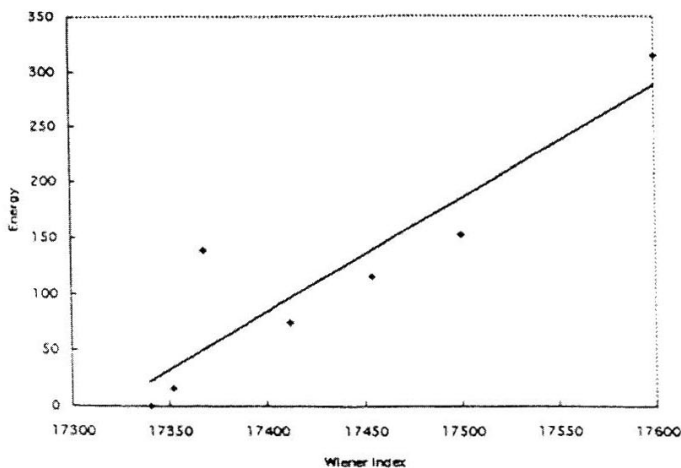


FIGURE 1. The Wiener indices correlated with the SAM1 C_{80} energies.

Figure 2 deals with the Hartree-Fock *ab initio* HF/3-21G energetics [41] of the IPR isomers of C_{88} (there are [4] already 35 IPR isomers for C_{88}). Here, the correlation with the Wiener indices is already less satisfactory, and actually suggests that one cannot expect a general applicability of the tool to relative stabilities of fullerenes.

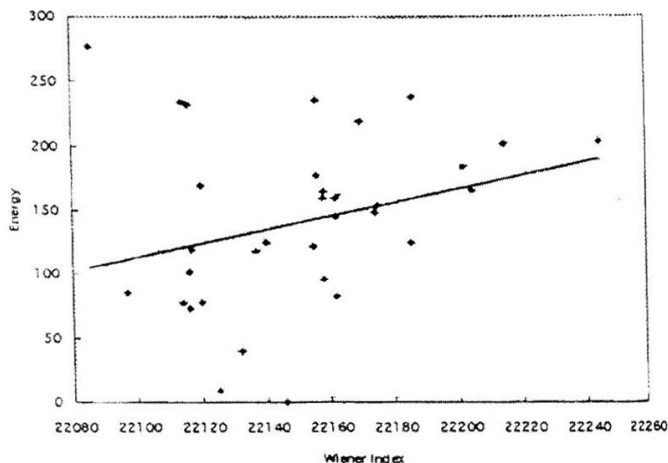


FIGURE 2. C_{88} HF/3-21 G energies and Wiener indices.

Although the HOMO-LUMO gap has sometimes been suggested as a possible alternative stability measure for fullerenes, there are also examples where this term fails [38]. Figure 3 plots the Hartree-Fock *ab initio* HF/3-21G HOMO-LUMO gaps [41] of the IPR isomers of C_{88} against the Wiener indices. In this particular case, the correlation works better than in the case of relative potential energies, however, the opposite is true in the C_{80} IPR set. In overall, the results suggest only partial applicability of the Wiener indices to the relative stabilities of the IPR isomers of fullerenes.

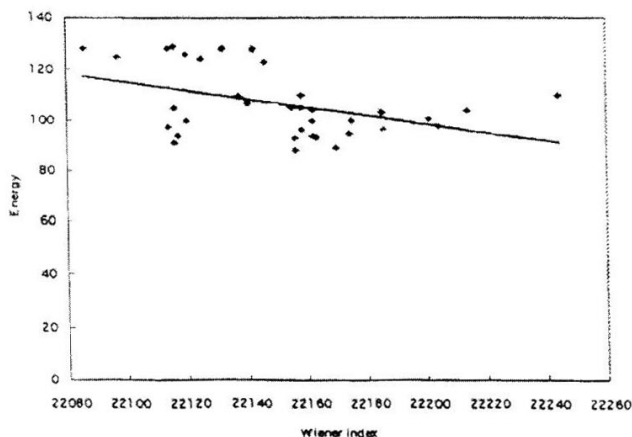


FIGURE 3. C₈₈ HF/3-21G HOMO-LUMO gaps

Let us turn now our interest to the reduced sphericity quotient δ . We shall illustrate its performance on the set of C₈₆ IPR isomers. There are [4] nineteen topologically different C₈₆ IPR structures. Achiba *et al.* have concluded [11,13] from ¹³C NMR spectra presence of just two isomers in their C₈₆ sample, C₂ and C₅ (the abundance of the isomers was about 4:1). A representative production temperature for their sample is however not known. Our SAM1 computations [41,42] around a temperature of 1500 K basically agree with the observation, though at higher temperatures it would predict coexistence of more than two isomers. Figure 4 surveys the correlations of energetics against the reduced sphericity quotient δ for the semiempirical AM1, SAM1 and the Hartree-Fock *ab initio* HF/STO-3G, HF/3-21G, and HF/4-31G treatments. Although the correlations are not particularly high, it is always true that the lowest energy structure also exhibits the best sphericity quotient δ . We could find the same feature also for C₈₈, C₉₀, and C₉₂. On the other hand, the relationships breaks for the C₈₀ IPR set where the lowest energy structure actually exhibits the worst sphericity quotient δ .

There is however a key feature frequently present in the IPR isomeric sets - interchanges of relative stabilities of some species with a temperature change. Obviously, the two previous topological/geometrical treatments cannot predict such a crucial thermodynamic

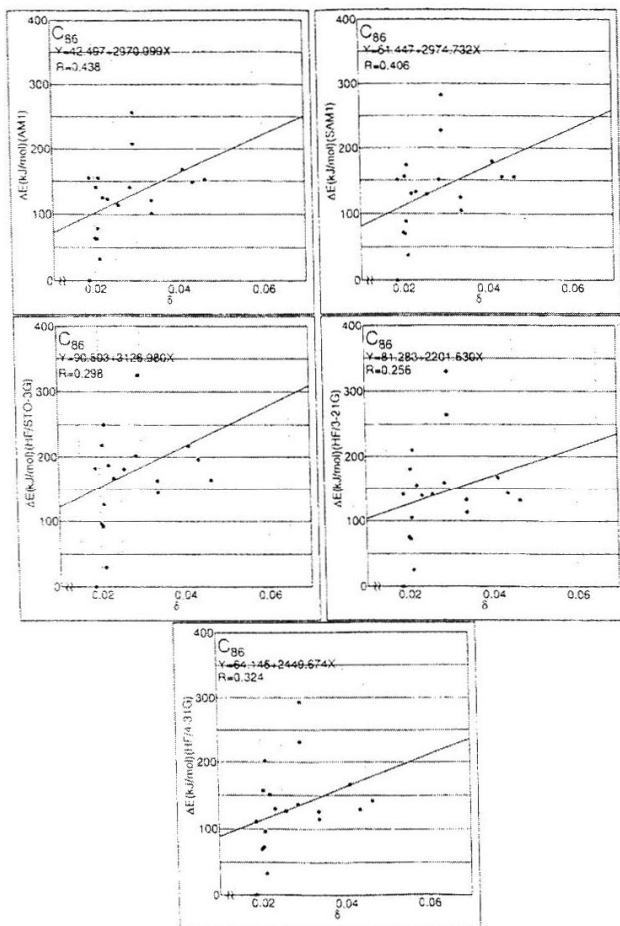


FIGURE 4. C_{86} energies against the reduced sphericity quotient δ

event. The interchange can be, for example, well seen [35,38] in the C_{80} IPR set. We can also discuss the feature on the C_{78} IPR set. In fact, there are [4] just five IPR isomers for C_{78} . They are labeled 1-5 and in this order they exhibit [4] the D_3 , C_{2v} , C'_{2v} , D_{3h} , and D_{3h} symmetries (Figure 5). However, Diederich *et al.* [18] used modified symmetry labels: D_3 , C_{2v} , C'_{2v} , D_{3h} , and D'_{3h} (ordered in the sequence 1-5 according to the numbering system [4]). At first, only two isomers were observed [18]: D_3 and C_{2v} symmetry in a ratio 1:5. Later on, Kikuchi *et al.* [19] however reported three isomers of C_{78} with the symmetries D_3 , C_{2v} , and C'_{2v} and in a ratio 2:2:5. Finally, Taylor *et al.* [43] also report three structures - C_{2v} , D_3 , and C'_{2v} with a ratio 5.2:3:1.8.

We have performed so far the highest-level calculations on the C_{78} IPR isomers - the B3LYP density-functional treatment with the standard 6-31G* basis set in the HF/3-21G optimized geometries (B3LYP/6-31G*//HF/3-21G). The C_{2v} isomer labeled by 3 is the system ground state, and species 4 is the highest in potential energy (Figure 5). Isomer 5 is the second lowest structure in the B3LYP/6-31G*//HF/3-21G treatment. Clearly enough, the relative potential energies themselves cannot always predict relative stabilities in an isomeric system at high temperatures. Indeed, if we apply the partition-function based treatment (3), a relative stability interchange can be observed (though not as dramatic as [35,38] in the C_{80} IPR set).

Figure 6 presents the B3LYP/6-31G*//HF/3-21G computed development of the relative concentrations x_i in the C_{78} IPR set for a wide temperature interval. At very low temperatures the ground-state structure has of course to be prevailing. In fact, the isomer coded by 3 (C'_{2v}) remains the most populated species throughout. There is then one relative stability interchange, close to 1500 K. The D_{3h} isomer 4 is negligible at any temperature. However, the three experimental studies [18,19,43] of C_{78} are not really consistent. Diederich *et al.* [18] report only two isomers while the other two works [19,43] observed three structures. However, what comes as the major component in one paper [18], is only the third most populated species in the other study [43]. If experiments are in a conflict, computations can agree at most with one of them. The results of Figure 6 agree reasonably well with Kikuchi *et al.*'s finding [19] of structures 1, 2, and 3 (D_3 , C_{2v} , and C'_{2v}) in a ratio 2:2:5. Although the achieved theory-experiment correspondency is encouraging, still some more computations on energetics and vibrations are needed to clarify possible sources of the only partial agreement.

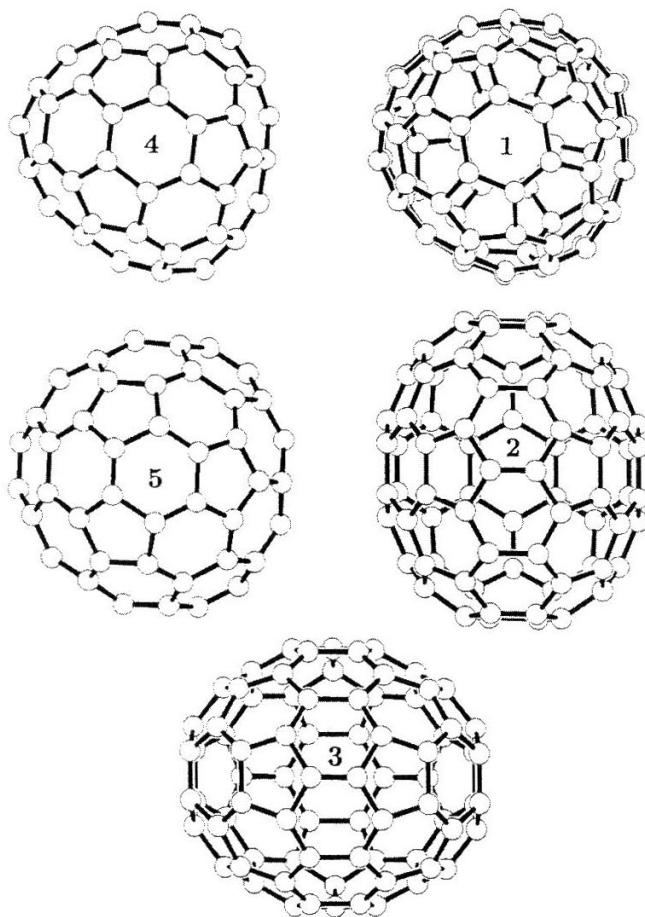


FIGURE 5. The HF/3-21G optimized IPR structures of C₇₈.

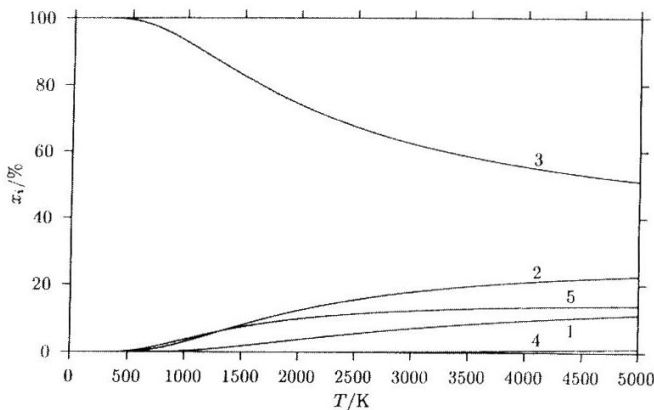


FIGURE 6. The B3LYP/6-31G*//HF/3-21G relative concentrations x_i for C_{76} IPR isomers.

CONCLUSIONS

Our attempts to correlate fullerene relative stabilities with topological/geometrical quotients suggest that the Wiener indices are less suitable for the purpose than the direct geometrical measure of cage sphericity. However, neither of the two treatments can grasp the full physical nature of the system thermodynamic behavior. An exhaustive description of the relative thermodynamic stabilities of fullerene isomers can be achieved only with the computationally demanding partition-function based treatment.

ACKNOWLEDGEMENTS

The reported research has in part been supported by the National Science Council, Taiwan, Republic of China, the Japan Science and Technology Corporation (JST), and the Ministry of Education, Science and Culture in Japan. The authors also thank the National Center for High-Performance Computing in Hsinchu, Taiwan, Republic of China, for computer time.

REFERENCES AND NOTES

- [1] A. T. Balaban, Ed., *Chemical Applications of Graph Theory*, Academic Press, London, 1976.
- [2] A. Cayley, *Phil. Mag.* (4), **1857**, 13, 172-176.
- [3] A. Cayley, *Phil. Mag.* (5), **1877**, 3, 34-35.
- [4] P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon Press, Oxford, 1995.
- [5] Z. Slanina, S.-L. Lee, and C.-H. Yu, *Rev. Comput. Chem.*, **1996**, 8, 1-62.
- [6] Z. Slanina, J. M. Rudziński, and E. Ōsawa, *Carbon*, **1987**, 25, 747-750.
- [7] Z. Slanina, J. M. Rudziński, and E. Ōsawa, *Collect. Czech. Chem. Commun.*, **1987**, 52, 2381-2838.
- [8] J. M. Rudziński, Z. Slanina, M. Togasi, and E. Ōsawa, T. Iizuka, *Thermochim. Acta*, **1988**, 125, 155-162.
- [9] Z. Slanina, J. M. Rudziński, M. Togasi, and E. Ōsawa, *Thermochim. Acta*, **1989**, 140, 87-95.
- [10] Z. Slanina, J. M. Rudziński, and E. Ōsawa, *Z. Phys. D*, **1991**, 19, 431-433.
- [11] Y. Achiba, K. Kikuchi, Y. Aihara, T. Wakabayashi, Y. Miyake, and M. Kainosho, Trends in Large Fullerenes: Are They Balls or Tubes. In *The Chemical Physics of Fullerenes 10 (and 5) Years Later*, Ed.: W. Andreoni, Kluwer Academic Publishers, Dordrecht, 1996, pp. 139-147.
- [12] R. Mitsumoto, H. Oji, I. Mori, Y. Yamamoto, K. Asato, Y. Ouchi, H. Shinohara, K. Seki, K. Umishita, S. Hino, S. Nagase, K. Kikuchi, and Y. Achiba, *J. Phys. IV*, **1997**, 7, C2-525 - C2-526.
- [13] Y. Achiba, Y. Miyake, H. Ishiwatari, M. Kainosho, and K. Kikuchi, NMR Characterization of Higher Fullerenes up to C₉₄. In *MRS Boston 1998 Fall Meeting*, MRS, Pittsburgh, 1998, Abstract S2.2.
- [14] S. J. Austin, P. W. Fowler, G. Orlandi, D. E. Manolopoulos, and F. Zerbetto, *Chem. Phys. Lett.*, **1994**, 226, 219-225.
- [15] Z. Slanina, S.-L. Lee, K. Kobayashi, and S. Nagase, *J. Mol. Struct. (THEOCHEM)*, **1994**, 312, 175-178.

- [16] K. Kobayashi, S. Nagase, M. Yoshida, and E. Ōsawa, *J. Am. Chem. Soc.*, **1997**, *119*, 12693-12694.
- [17] D. E. Manolopoulos and P. W. Fowler, *J. Chem. Phys.*, **1992**, *96*, 7603-7614.
- [18] F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, I. Chao, and M. M. Alvarez, *Science*, **1991**, *254*, 1768-1770.
- [19] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, *Nature*, **1992**, *357*, 142-145.
- [20] D. Bakowies, A. Geleßus, and W. Thiel, *Chem. Phys. Lett.*, **1992**, *197*, 324-329.
- [21] Z. Slanina, J.-P. François, D. Bakowies, and W. Thiel, *J. Mol. Struct. (THEOCHEM)*, **1993**, *279*, 213-216.
- [22] K. Kikuchi, N. Nakahara, T. Wakabayashi, M. Honda, H. Matsumiya, T. Moriwaki, S. Suzuki, H. Shiromaru, K. Saito, K. Yamauchi, I. Ikemoto, and Y. Achiba, *Chem. Phys. Lett.*, **1992**, *188*, 177-180.
- [23] S. Nagase, K. Kobayashi, T. Kato, and Y. Achiba, *Chem. Phys. Lett.*, **1993**, *201*, 475-480.
- [24] G. Orlandi, F. Zerbetto, and P. W. Fowler, *J. Phys. Chem.*, **1993**, *97*, 13575-13579.
- [25] S. Nagase and K. Kobayashi, *Chem. Phys. Lett.*, **1993**, *214*, 57-63.
- [26] Z. Slanina, S.-L. Lee, K. Kobayashi, and S. Nagase, *J. Mol. Struct. (THEOCHEM)*, **1995**, *339*, 89-93.
- [27] F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. C. Khemani, and A. Koch, *Science*, **1991**, *252*, 548-551.
- [28] R. D. Beck, P. S. John, M. M. Alvarez, F. Diederich, R. L. Whetten, *J. Phys. Chem.*, **1991**, *95*, 8402-8409.
- [29] K. Kikuchi, N. Nakahara, M. Honda, S. Suzuki, K. Saito, H. Shiromaru, K. Yamauchi, I. Ikemoto, T. Kuramochi, S. Hino, Y. Achiba, *Chem. Lett.*, **1991**, 1607-1610.
- [30] K. Raghavachari and C. M. Rohlfing, *J. Phys. Chem.*, **1991**, *95*, 5768-5773.
- [31] Z. Slanina, J.-P. François, M. Kolb, D. Bakowies, and W. Thiel, *Fullerene Sci. Technol.*, **1993**, *1*, 221-230.
- [32] S. J. Woo, E. Kim, and Y. H. Lee, *Phys. Rev. B*, **1993**, *47*, 6721-6727.
- [33] K. Nakao, N. Kurita, and M. Fujita, *Phys. Rev. B*, **1994**, *49*, 11415-11420.
- [34] K. Kobayashi, S. Nagase, and T. Akasaka, *Chem. Phys. Lett.*, **1995**, *245*, 230-236.

- [35] M.-L. Sun, Z. Slanina, S.-L. Lee, F. Uhlík, and L. Adamowicz, *Chem. Phys. Lett.*, **1995**, *246*, 66-72.
- [36] F. H. Hennrich, R. H. Michel, A. Fischer, S. Richard-Schneider, S. Gilb, M. M. Kappes, D. Fuchs, M. Bürk, K. Kobayashi and S. Nagase, *Angew. Chem., Int. Ed. Engl.*, **1996**, *35*, 1732-1734.
- [37] C.-R. Wang, T. Sugai, T. Kai, T. Tomiyama, and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, **2000**, 557-558.
- [38] Z. Slanina, X. Zhao, and E. Ōsawa, *Advan. Strain. Inter. Org. Mol.*, **1999**, *7*, 185-235.
- [39] H. Wiener, *J. Am. Chem. Soc.*, **1947**, *69*, 17-20.
- [40] H. Hosoya, *Bull. Chem. Soc. Jpn.*, **1971**, *44*, 2332-2339.
- [41] Z. Slanina, S.-L. Lee, and L. Adamowicz, *Int. J. Quantum. Chem.*, **1997**, *63*, 529-535.
- [42] Z. Slanina, S.-L. Lee, M. Yoshida, and E. Ōsawa, *Chem. Phys.* **1996**, *209*, 13-18.
- [43] R. Taylor, G. J. Langley, A. G. Avent, T. J. S. Dennis, H. W. Kroto, and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 1029-1036.