— TPI-MINN-92-21-T —

13

Theoretical Physics Institute
University of Minnesota

TPI-MINN-92/21-T

Relative Stability of C_{78} Isomers

X.-Q. Wang

Theoretical Physics Institute, University of Minnesota,
116 Church Street S.E., Minneapolis, Minnesota 55455
and Center for Theoretical Studies of Physical Systems,
Clark Atlanta University, Atlanta, Georgia 30314

C. Z. Wang, B. L. Zhang, and K. M. Ho

Ames Laboratory– U.S. Department of Energy, Department of
Physics and Astronomy, Iowa State University, Ames, Iowa 50011

The structural and electronic properties of the five C_{78} isolated-pentagon isomers are studied using all-electron local-density functional calculations with complete geometry optimization. The results are compared with available experimental data, and suggest that kinetic factors play an important role in the formation of large fullerenes.

PACS numbers: 31.20.Sy, 36.40.+d, 33.10.-n

Recently, there has been tremendous progress in the understanding of fullerenes–intriguing cage-like molecules of carbon atoms. Their physical and chemical properties have been the subject of much attention. While the experimental fullerene extract is dominated by C_{60} and C_{70}, larger fullerenes such as C_{76}, C_{78}, and C_{84}, have also been isolated [1-5]. Experimental analysis by ^{13}C nuclear magnetic resonance (NMR) spectroscopy has been very useful in clarifying the structural properties of these molecules. Consistent with theoretical predictions, the ground-state geometries of C_{60}, C_{70}, and C_{76} have been characterized to possess I_h, D_{5h}, and helical-D_2 symmetries [1,6,7], respectively. A useful guideline for determining candidates for the ground-state geometries of fullerenes is to search for cage structures composed of pentagons and hexagons, without any adjacent pentagons. This empirical isolated-pentagon rule, arising from necessity of reducing the surface stress of the cage, provides a practical way to predict the ground-state structure. In fact, for C_{60} and C_{70}, each has only one isolated-pentagon isomer which corresponds to the ground-state configuration. For C_{76}, the chiral-D_2 structure is one of the two possible isolated-pentagon isomers [1,8].

For C_{78}, there are five topologically distinct isolated-pentagon isomers [9], two with C_{2v} symmetry, one with D_3, and the other two with D_{3h}, as shown in Fig. 1. Using Hückel theory, Fowler, Batten and Manolopoulos [9] predicted that the closed-shell D'_{3h} isomer of Fig. 1(e) should be the most stable geometry. However, empirical tight-binding calculation by Zhang, Wang, and Ho [10] and modified neglect of differential overlap (MNDO) calculation by Raghavachari [11] revealed that the D'_{3h} isomer is in fact energetically rather unfavorable. Recently, the structure of C_{78} has been studied using NMR technique by two different groups [4,5]. As a step towards a complete understanding of the structural and electronic properties of C_{78} isomers, we have performed first-principles local-density-functional calculations for all five isolated-pentagon isomers mentioned above. Our calculations show that the C'_{2v} isomer has the lowest energy, and the ordering in binding energies for the remaining isomers is D_{3h}, C_{2v}, D_3, and D'_{3h}. The results are compared with the available experimental data.

The present calculation was carried out using first-principles density-functional methods for molecules with analytical energy gradients [12]. The Hedin-Lundqvist form [13] was used for the exchange-correlation energy of the electron within the local-density-approximation (LDA). We used a double-numerical basis set in the calculation. This scheme has been previously tested for C_{60} and C_{70} [14], and has been applied to C_{84} [14] for which two isomers, one with D_2 and another with D_{2d} symmetries, were predicted to be most stable, consistent with recent experimental observation [5].

Our search for the optimized structures of the five C_{78} isomers was performed in three steps: (*i*) construction of the topological network using a 'face-dual' network generating scheme proposed by Zhang, Wang, and Ho [10], (*ii*) simulated annealing optimization with tight-binding molecular-dynamics (TBMD) without symmetry constraints, and finally, (*iii*) conjugate-gradient minimization of the resultant structures using first-principles LDA calculations. The optimized structures have carbon-carbon bond lengths ranging from 1.364 to 1.458 Å, 1.359 to 1.459 Å, 1.363 to 1.475 Å, 1.371 to 1.458 Å, and 1.343 to 1.454 Å for the five isomers shown in Figs. 1(a)-1(e), respectively. To provide detailed information on the structural properties of the isomers, we present in Fig. 2 the calculated radial distribution function $J(r)$. As seen in Fig. 2, the radial distribution functions for the five isomers are similar except for a peak in the radial distribution of the D_3 isomer near 5.8 Å which is not present for the other isomers.

The results for the binding energies and the gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the five C_{78} isomers are summarized in Table I, along with the corresponding results of TBMD [10] for comparison. Our calculation shows that the C'_{2v} isomer shown in Fig. 1(a) is energetically most favorable. The D_{3h}, C_{2v}, D_3, and D'_{3h} isomers shown in Figs. 1(b)-1(e) have binding energies per molecule of about 0.14, 0.19, 0.33, and 1.11 eV, respectively, higher than that of the ground-state C'_{2v} isomer.

There is an interesting correlation between the binding energy and the distribution of pentagons in the large fullerenes isomers. In our previous study of C_{84} [14], we have noted that the lower energy isomers tend to have less cap configurations (i.e. the configuration in which a hexagon is surrounded by three non-adjacent pentagons). This tendency is also observed here for the C_{78} isomers. In the lower energy C'_{2v} and D_{3h} isomers, only two cap configurations are found for each isomer. While in the higher-energy D_3 and D'_{3h} isomers, the pentagons are confined in the pole regions, leading to as many as eight cap configurations for each isomer. The C_{2v} isomer of Fig. 1(c) has six cap configurations and its energy is intermediate between the other four isomers. This correlation indicates a tendency to distribute the pentagons as far apart as possible in order to minimize the local stress.

Experimental studies of the structure of C_{78} isomers have been reported by Diederich *et al.* [4] and by Kikuchi *et al.* [5]. These two experimental groups obtained different products under slightly different synthesis conditions. Diederich *et al.* [4] observed a mixture of the C_{2v} and D_3 isomers forming in a ratio of 5:1, while Kikuchi *et al.* [5] found a mixture consisting of the C'_{2v}, C_{2v}, and D_3 isomers in a ratio of 5:2:2. Our results are consistent with the observation by Kikuchi *et al.* [5] that the C'_{2v} isomer shown in Fig. 1(a) is the most abundant isomer. However, it should be noted that apart from the D'_{3h} isomer, all the other four isomers are quite close in energy and thus kinetic factors may play a role in determining the relative abundance of the various isomers. It is interesting to note that the D_{3h} isomer, which is the second best in energy among the five isomers, has not been observed in both experiments. This seems to suggest that a complete explanation of experimental results has to consider the details of the kinetics and mechanism of fullerene formation in addition to the energetics. In a systematic study of structures and stabilities of carbon fullerenes in the range C_{20} to C_{94} using tight-binding calculations, Zhang *et al.* [15] observed that the most abundant fullerene isomers usually have both relatively low energy and relatively large HOMO-LUMO gap. It is expected that, in general, isomers with smaller HOMO-LUMO gaps tend to be more chemical reactive. We note that the D_{3h} isomer has a relatively small HOMO-LUMO gap, and so does the ground-state C'_{2v} isomer. Thus, chemical reactions in the formation and extraction process may provide a clue to understand the discrepancies in the two experiments, and the fact that the D_{3h} isomer was not found in both experiments.

It is worth pointing out that the HOMO-LUMO gap is also directly related to the particle-hole excitations and the many-body correlation effects. The discussion of many-body effects which can not be handled by the conventional calculation methods based upon one-electron pictures (e.g., LDA and tight-binding) is beyond the scope of this paper. We hope to pursue this issue in a separate study.

Another piece of useful information concerning the molecule is its electronic density-of-states (DOS), which can be probed by photoemission and inverse photoemission experiments. In Fig. 3, our results for the electronic DOS of the five isomers are plotted. This should provide useful information for future experimental studies. It should be noticed that the DOS for the five isomers is pretty similar, but a double peak exists for D_{3h} below the HOMO. This may be a distinctive feature worth more experimental attention.

In summary, we have performed first-principles local-density functional calculations of the electronic and geometric properties of all isolated-pentagon isomers of C_{78}. The resulting picture indicates that kinetic factors in the fullerene formation process may have a crucial influence on the yield of the various isomers in the product.

X-Q.W. would like to thank D. Bessis, C. E. Campbell, A. Z. Maezane, Y. H. Mariam, and C. R. Handy for useful discussions. Ames Laboratory is operated for the U. S. Department of Energy by Iowa State University under contract No. W-7405-ENG-82. This work was supported in part by the Director for Energy Research, Office of Basic Energy Science and Minnesota Supercomputer Institute. The Center for Theoretical Studies of Physical Systems at the Clark Atlanta University is founded by the National Science Foundation.

References

[1] R. Ettl, I. Chao, F. Diederich, and R. L. Whetten, Nature (London) **353** (1991) 149.

[2] 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 **252** (1991) 548.

[3] 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., **188** (1992) 177.

[4] F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, T. Chao, and M. M. Alvarez, Science **254** (1992) 1768.

[5] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, Nature (London) **357** (1992) 142.

[6] R. Taylor, J. R. Hare, A. K. Abdule-Sada, and H. J. Kroto, J. Chem. Soc., Chem. Commun. **20** (1990) 1423.

[7] R. D. Johson, G. Meijer, and D. S. Bethune, J. Am. Chem. Soc. **112** (1990) 8983.

[8] D. E. Manolopoulos, J. Chem. Soc. Faraday Commun. **87** (1991) 2861.

[9] P. W. Fowler, R. C. Batten, and D. E. Manolopoulos, J. Chem. Soc. Faraday Commun. **87** (1991) 3103.

[10] B. L. Zhang, C. Z. Wang, and K. M. Ho, Chem. Phys Lett., **193** (1992) 225.

[11] K. Raghavachari, private communications.

[12] All the LDA calculations reported in this work were performed using DMol, Biosym Technologies, Inc., San Diego CA, 1991.

[13] L. Hedin and B. I. Lundqvist, J. Phys. C **4** (1971) 2064; U. von Barth and L. Hedin, J. Phys. C **5** (1972) 1629.

[14] X. Q. Wang, C. Z. Wang, B. L. Zhang, and K. M. Ho, Phys. Rev. Lett. **69** (1992) 69.

[15] B. L. Zhang, C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B (Rapid Communications), in press.

Figure Captions

FIG. 1. Optimized equilibrium geometry of (a) C'_{2v}, (b) D_{3h}, (c) C_{2v}, (d) D_3, and (e) D'_{3h} C_{78} isomers. These notations were used in Refs. [4,5].

FIG. 2. Radial-distribution functions for the five C_{78} isomers. Here, $J(r)$ is defined such that $J(r)dr$ gives the average number of atoms whose distance from a given atom is between r and $r + dr$.

FIG. 3. Molecular energy levels of the five C_{78} isomers and the associated density of states per cluster obtained by the Lorentzian broadening (0.25 eV) of the discrete energy levels. Zero is defined as the energy position of HOMO.

Table 1: Binding energies per atom (in eV), HOMO-LUMO gaps (in eV), and the number of distinct NMR lines for C_{60} and five C_{78} molecules. $E_{\rm TB}$ and $E_{\rm LDA}$ are binding energies calculated using TBMD and LDA, respectively. $\Delta_{\rm LDA}$ and $\Delta_{\rm TB}$ are HOMO-LUMO gaps calculated using LDA and TBMD, respectively.

Molecule	Symmetry	$E_{\rm TB}$	$E_{\rm LDA}$	$\Delta_{\rm LDA}$	$\Delta_{\rm TB}$	NMR
C_{60}	I_h	-8.0084	-8.0803	1.714	1.610	1
C_{78}	C'_{2v}	-8.0645	-8.1402	0.746	0.493	22
	D_{3h}	-8.0633	-8.1383	0.562	0.353	8
	C_{2v}	-8.0609	-8.1377	1.123	0.545	21
	D_3	-8.0604	-8.1359	0.775	0.443	13
	D'_{3h}	-8.0528	-8.1259	1.668	1.373	8

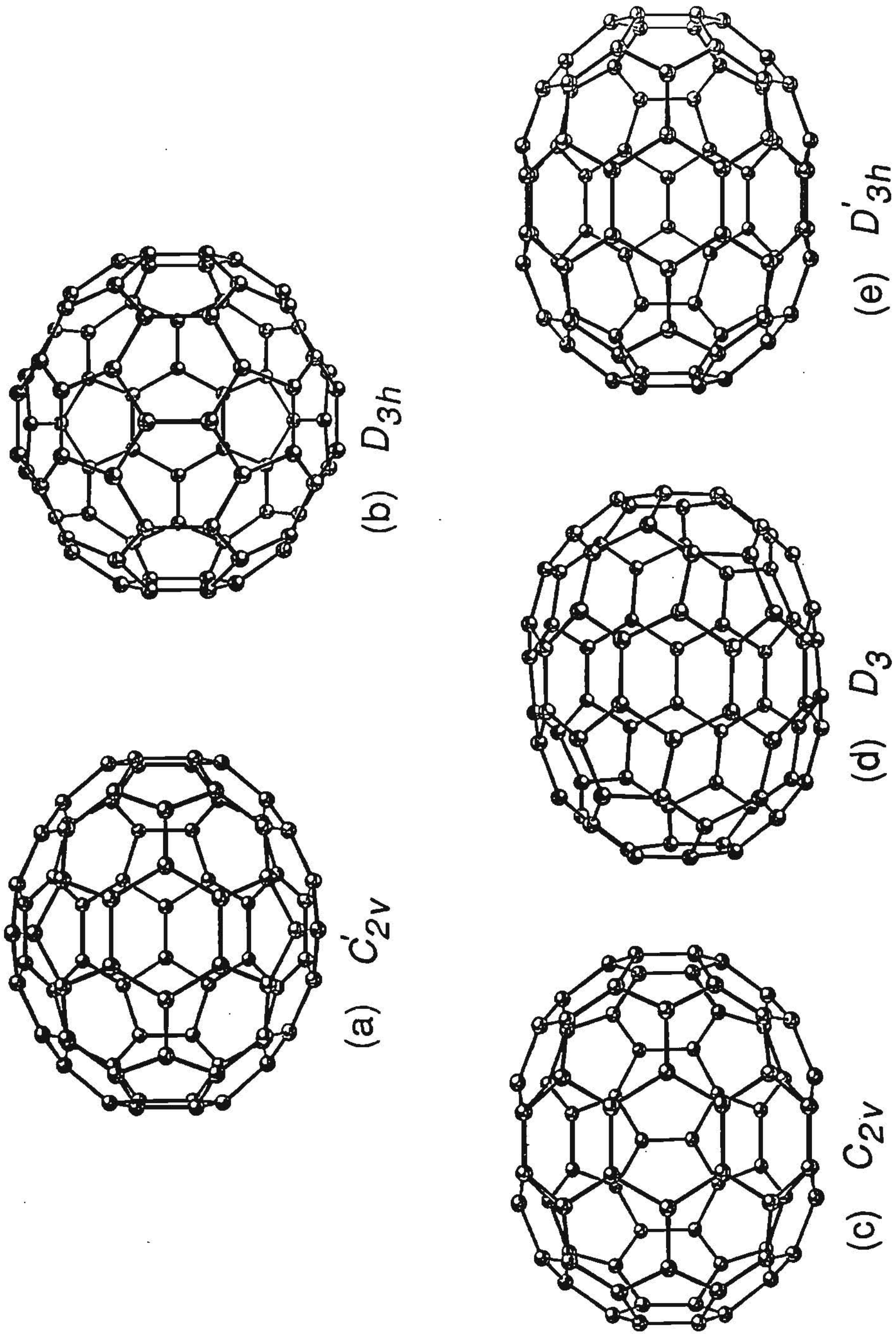

Figure 2

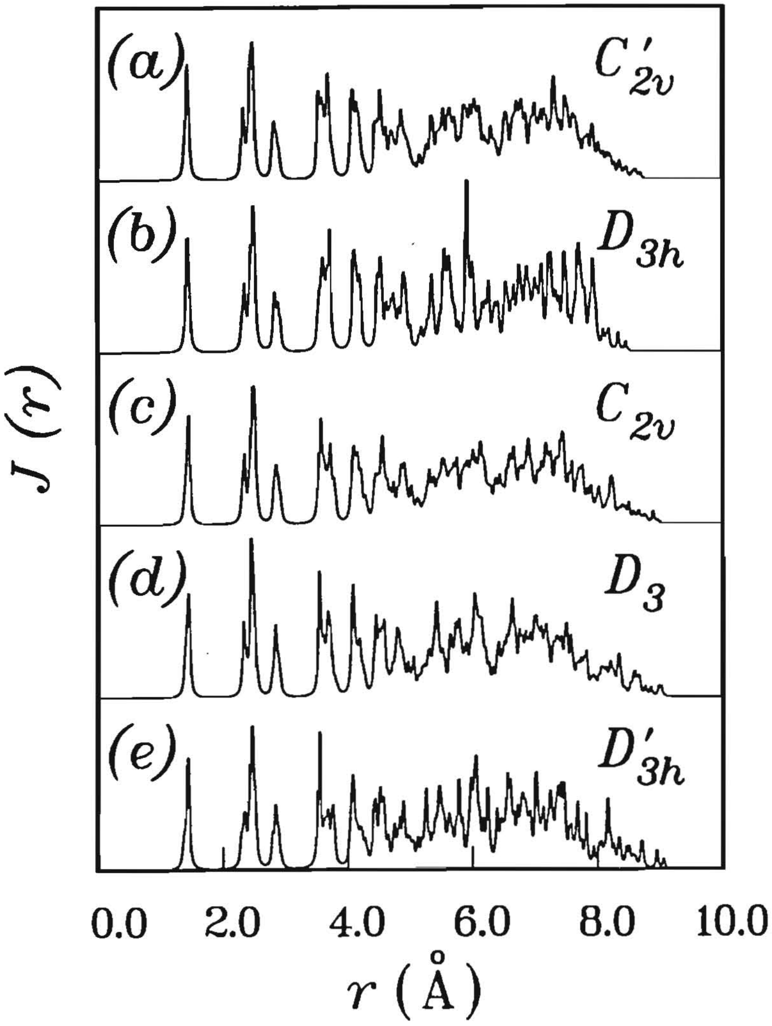

Figure 3