PREDICTION OF STABLE STRUCTURES OF FULLERENES BY ENERGY CALCULATIONS

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Heats of formation for various plausible structures of four higher fullerenes (C_{76}, C_{78}, C_{82} and C_{84}) were calculated with semi-empirical molecular orbital method AM1. The symmetries of the calculated most stable isomers agree with the results obtained from experimental measurements. The calculations of C_{76} and C_{84} show that the most stable isomers satisfy the IPR rule, and the calculations of C_{84} isomers show that seven-membered rings destabilize the fullerene structures.

1. INTRODUCTION

Carbon clusters (fullerenes) have been the focus of many experimental and theoretical studies since Kroto et al. reported the existence of C_{60} clusters in laser vaporized products of graphite in 1985. Recently Kratschmer et al. reported that carbon clusters are produced in large quantity in the evaporation of graphite. The major species are C_{60} and C_{70} clusters, and small amounts of higher fullerenes (C_{76}, C_{78}, and larger) are also produced. The structures of C_{60} and C_{70} fullerenes were extensively studied by experimental and theoretical methods. On the other hand, information on higher fullerenes is still quite limited. The crude but effective Huckel method was applied to estimate resonance energies of a few plausible structures of C_{84}. Unfortunately this method, however, cannot evaluate strain (stretching and bending strain energy). Recently Bakowies and Thiel reported MNDO calculation of 30 carbon clusters (C20-C540). Raghaxachari and Rohlfing reported MNDO and HF/3-21G level ab initio MO calculations of C_{60}, C_{70} and C_{84}. Negri et al. reported the relative stability and vibrational frequencies of D_{6h} and T_d C_{84} calculated with QCFF/PI method. However they considered only two or three isomers of C_{84} in their work. Here we report the calculations of heats of formation for various plausible structures of higher fullerenes with semi-empirical molecular orbital method AM1.

2. COMPUTATIONAL TECHNIQUE

Heats of formation with AM1 were calculated using MOPAC program version 6.01. Geometries of isomers were fully optimized using the geometry optimization routine in the program.

A large number of geometrical isomers of higher fullerenes can be considered. However, it is not possible to calculate the energies of all isomers. C_{60} has only five- and six-membered rings, and all the five-membered rings in C_{60} are isolated. This is an empirically known rule as "isolated pentagon rule (IPR)". Higher fullerenes, which have only five- and six- membered rings and whose five-membered rings are isolated, were considered here. In addition some other isomers which do not satisfy IPR were also considered.

3. RESULTS AND DISCUSSION

3.1 C_{76}

NMR measurement shows that C_{76} has D_2 symmetry. The energies of six isomers including two IPR isomers were calculated here. The optimized structures of those isomers are shown in Fig. 1. The calculated heats of formation are given in Table 1. The most stable isomer F satisfies IPR, and its symmetry is D_2, which agrees with the experimental observation by NMR.

3.2 C_{78}

Chromatography separation data show that C_{78} is the mixture of three isomers. Two of them have C_{2v} symmetry and another has D_3 symmetry. The dominant isomer has C_{2v} symmetry. The energies of five IPR isomers were calculated here. The optimized structures of those isomers are shown in Fig. 1. The calculated heats of formation are given in Table 1. The most stable isomer E has C_{2v} symmetry, and the three lowest energy isomers have C_{2v}, C_{2v} and D_3 symmetry, which agree with the experimental observation by NMR.

3.3 C_{82}

Experimental measurements show that C_{82} is the mixture of three isomers, and the dominant isomer has C_2 symmetry. The energies of seven IPR isomers were calculated here. The optimized structures of those isomers are shown in Fig. 1. The calculated heats of formation are given in Table 1. The most stable isomer C has C_2 symmetry, which agrees with the experimental measurement.

3.4 C_{84}

Experimental measurement shows that C_{84} is the mixture of two isomers, which have D_2 and D_{2d} symmetries. The energies of eight IPR isomers and six non-IPR isomers were calculated here. Two of the non-IPR isomers have a few seven-membered rings. The optimized structures of those isomers are shown in Fig. 1. The calculated heats of formation are given in Table 1. The most stable two isomers G and K have D_{2d} and D_2 symmetries, which agree with the experimental measurement.

4. CONCLUSION

The energies of various plausible isomers of higher fullerenes were

(a) C_{76} A   B   C   D   E   F

(b) C_{78} A   B   C   D   E

(c) C_{82} A   B   C   D   E   F   G

(d) C_{84} A   B   C   D   E   F   G

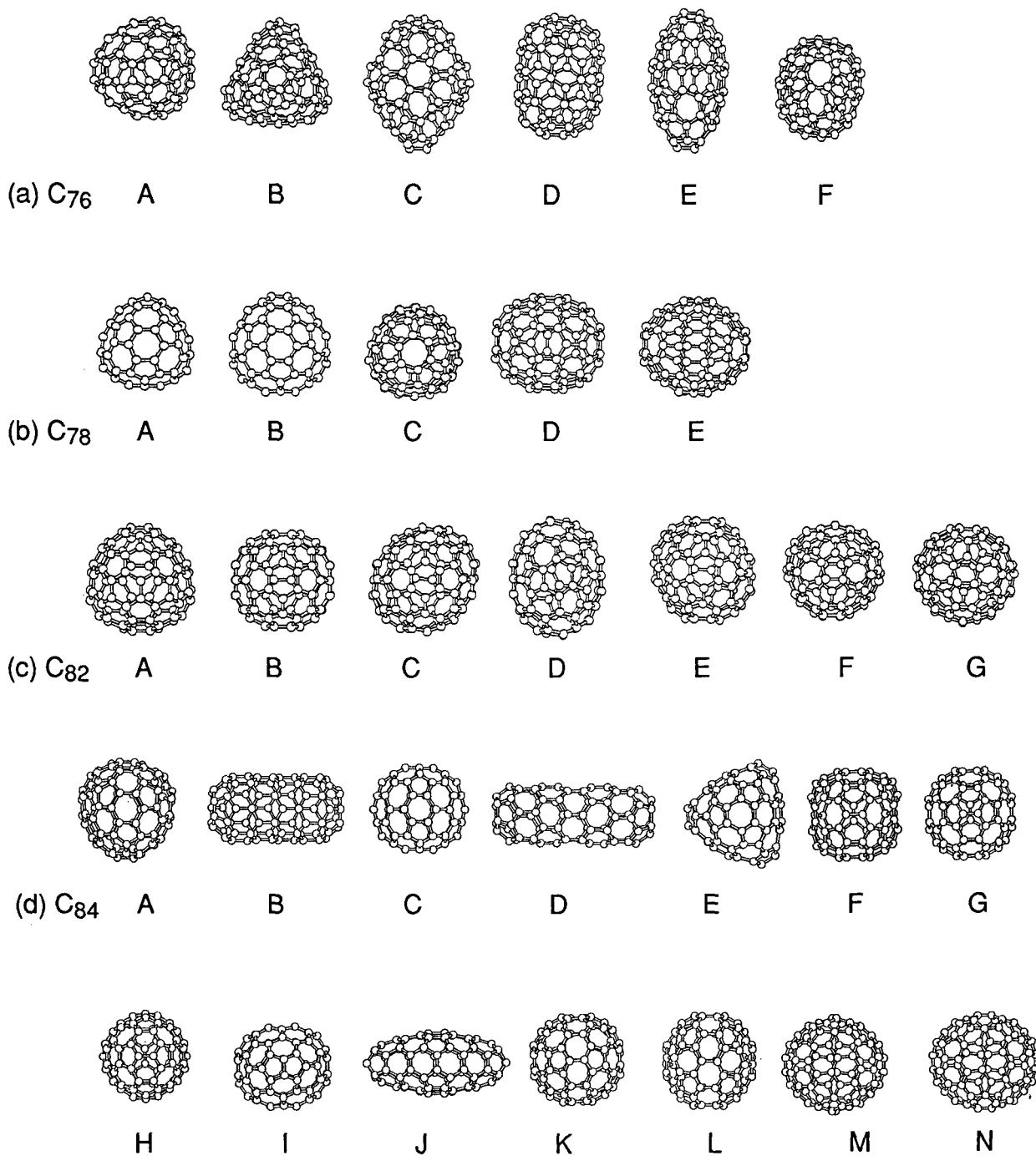H   I   J   K   L   M   N

Fig. 1   Optimized structures of various isomers of higher fullerenes

Table 1 Heats of formation of higher fullerenes calculated with AM1

Fullerene	Isomer	Symmetry	Heat of formation (kca/mol)	IPR/7MR*
C_{76}	A	T_d	1147	IPR
	B	T	1483	
	C	D_2	1409	
	D	D_2	1227	
	E	D_2	1323	
	F	D_2	1122	IPR
C_{78}	A	D_{3h}	1165	IPR
	B	D_{3h}	1148	IPR
	C	D_3	1140	IPR
	D	C_{2v}	1138	IPR
	E	C_{2v}	1133	IPR
C_{82}	A	C_{3v}	1204	IPR
	B	C_{3v}	1189	IPR
	C	C_2	1161	IPR
	D	C_2	1165	IPR
	E	C_2	1173	IPR
	F	C_s	1167	IPR
	G	C_s	1168	IPR
C_{84}	A	T_d	1196	IPR
	B	D_7	1541	7MR
	C	D_{6h}	1173	IPR
	D	D_{6h}	1664	
	E	D_{3h}	1309	
	F	D_{3h}	1505	7MR
	G	D_{2d}	1165	IPR
	H	D_{2d}	1186	IPR
	I	D_{2h}	1243	
	J	D_{2h}	1449	
	K	D_2	1166	IPR
	L	D_2	1191	IPR
	M	D_2	1184	IPR
	N	D_2	1217	IPR

* IPR : satisfies the isolated pentagon rule.
7MR : contains seven-membered rings.

calculated with semi-empirical molecular orbital method AM1. The symmetries of the calculated most stable isomers agree with those determined from experimental measurements. The calculations of C_{76} and C_{84} show that the most stable isomers satisfy the IPR rule. The calculation of C_{84} also show that seven-membered rings destabilize the fullerene structure.