Relative stabilities of octabromo[60]fullerene isomers: limitations and semi-empirical methods

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Application of semi-empirical molecular orbital methods to brominated fullerenes $C_{60}Br_8$ finds 19 isomers within ±25 kJ mol^{-1} of the experimental C_{2v} structure, demonstrating the need for caution in using these methods as tools in fullerene structural chemistry.

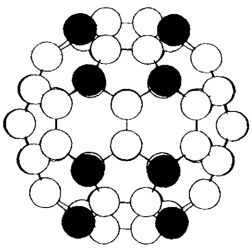
In order to investigate the stabilities and geometries of fullerenes and their addition compounds, frequent recourse is made to approximate methods such as Hückel theory,[1] molecular mechanics,[2,3] and semi-empirical molecular-orbital calculations.[4–7] These methods are likely to remain in use for some time to come since full *ab initio* treatment of all isomers at a level sufficient to ensure accuracy—already costly for optimisation of a single fullerene cage—is ruled out by the sheer size of the problem. There are 1 456 598 distinct fullerene structural isomers C_n in the range $20 \leqslant n \leqslant 100$, for example,[8] and clearly some qualitative filters must be applied to bring the problem within the practical range of even semi-empirical methods. The isolated pentagon rule[9] is one such filter, reducing the number of structures to 1267 in the same range.

The unique structures of fullerenes (polyhedral trivalent cages with only pentagonal and hexagonal faces) might be expected to lead to problems[3] when using semi-empirical methods, since none of the popular MNDO,[10] AM[11] or PM3[12] parameterisations included fullerenes in their 'basis set' of molecules. Often, however, these problems do not materialise. For example, a study[13] of the 24 isolated pentagon isomers of C_{84} using all three semi-empirical parameterisations as well as the *ab initio* method (split-valence SCF) gave the same two isomers (D_2 and D_{2d}) as the most stable with exactly the same energy difference (0.4 kcal mol^{-1}) between them in all four methods. Another parameterised method, the QCFF/PI method of Warshel and Karplus[14] is remarkably successful in calculation of vibrational frequencies in fullerene cages.[15–17]

Addition of hydrogen or halogen atoms to the fullerene cage adds a further dimension to the challenge. A single formula such as $C_{60}Br_8$, even with a fixed carbon topology, encompasses no less than 21 330 558 distinct structural isomers.[18] Nature apparently selects just one of these under the conditions of the synthesis of this compound.[19] A number of studies of halogenated fullerenes have been carried out using semi-empirical methods, yielding plausible conclusions about isomer preference.[5,6] It was therefore surprising to read[7] that AM1 calculations predicted a C_s isomer to be considerably more stable than the experimentally characterised C_{2v} isomer of $C_{60}Br_8$, a claim which prompted the present study. Whilst the particular result in ref. 7 is incorrect, it is true that all three parameterisations MNDO, AM1 and PM3 favour a class of low-symmetry isomers of $C_{60}Br_8$ over the experimental structure. The conclusions to be drawn from this are discussed below.

The energetics of addition of the first two atoms to the C_{60} cage was studied by Dixon *et al.*[6] who compared the energetics of 1,2-addition across a hexagon junction with 1,4-addition in a hexagon in C_{60} for hydrogen, fluorine, chlorine, bromine and iodine using the AM1 parameterisation. The AM1 results were also tested against more sophisticated LDF calculations at the same geometries, showing that with chlorine the latter method reverses the AM1 preference, making the 1,2- preferred over the 1,4-addition; with bromine both methods agree on making 1,4-addition just preferred. However the maximum discrepancy between AM1 and LDF energy differences was only 12 kJ mol^{-1}. These authors went on to propose structures for more highly halogenated compounds, basing their choices on either 1,2- or 1,4-pairings of addends within relatively high point group symmetry. The experimentally determined structures of $C_{60}Br_6$, $C_{60}Br_8$ and $C_{60}Cl_6$ belong to groups C_s, C_{2v} and C_s respectively,[19,20] and so do not support any assumption of a link between high symmetry and stability.

Peel and Rothwell[7] investigated energies of the experimentally characterised[19,21] isomers of the three bromo compounds, $C_{60}Br_6$, $C_{60}Br_8$ and $C_{60}Br_{24}$, within the AM1 model and found all three to be stable to dissociation: $C_{60}Br_{2n} \longrightarrow C_{60} + nBr_2$, but with the lowest stabilisation per bromine addend for the octabromo compound, **1** (carbon atoms bearing bromine are designated by filled circles). Ascribing this to an extraordinary stability of the Br_6 pattern in $C_{60}Br_6$, in which five bromine atoms are *exo* to a pentagon and one lies within it, these authors experimented with an alternative isomer, **2**, of $C_{60}Br_8$ in which the stable Br_6 pattern was supplemented by a 1,4 pair of bromine atoms in a separate hexagon, and found this to be more stable than **1** by 68 kJ mol^{-1}. If correct, this calls into question the validity of the semi-empirical approach, for there is no reason to doubt the experimental characterisation.



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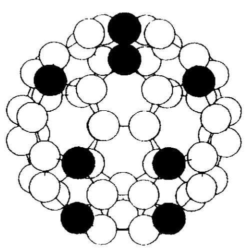

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Standard heats of formation were calculated for various isomers of $C_{60}Br_8$ using MNDO, AM1 and PM3 parameterisations (MOPAC Version 6.00[22]) and they are listed in Table 1. We find the C_{2v} isomer to have a heat of formation (AM1) of 3780 kJ mol^{-1}, rather than the 3859 kJ mol^{-1} given in ref. 7. Our AM1 results for **2** are in agreement. It is possible that the higher figure for **1** refers to an incorrect structure or to a special point on the potential surface that is not at the global minimum. The authors of ref. 7 do not state whether their progressive relaxation approach used the fast but possibly

Table 1 Standard heats of formation (kJ mol^{-1}) of some bromofullerenes calculated using MOPAC 6.00[a]

Compound	a	b	Symmetry group	MNDO	AM1	PM3
$C_{60}Br_6$			C_s	3306	3826	3100
	45	57	C_1	3206	3765	3037
	47	59	C_1	3206	3765	3037
	51	59	C_1	3206	3765	3037
	50	60	C_1	3206	3765	3037
	48	58	C_1	3207	3766	3037
	43	46	C_s	3210	3770	3043
	46	49	C_1	3210	3770	3043
	49	52	C_1	3211	3771	3044
	24	27	C_s	3216	3774	3050
	28	31	C_1	3217	3776	3051
	32	35	C_1	3219	3778	3052
	30	47	C_1	3224	3782	3051
	33	51	C_1	3224	3782	3051
	29	48	C_1	3225	3781	3051
	34	50	C_1	3225	3783	3051
	26	44	C_1	3230	3784	3052
	30	33	C_1	3234	3789	3053
	34	37	C_s (**2**)	3236	3791	3054
	26	29	C_1	3242	3793	3055
$C_{60}Br_8$			C_{2v} (**1**)	3217	3780	3081

[a] Our $C_{60}Br_8$ structures are defined by the numbering in the Schlegel diagram (Fig. 1) where the six fixed bromine atoms occupy positions 1, 6, 9, 12, 15 and 18 in accordance with the proposed[19] systematic name for $C_{60}Br_6$, and the other two occupy positions a and b. **1** is the experimental structure[19] for $C_{60}Br_8$ and **2** is the alternative proposed by Peel and Rothwell.[7] A third proposal by Dixon *et al.*[6] corresponds to an energy (AM1) of 3795 kJ mol^{-1} and has four isolated 1,4 pairs of Br atoms.

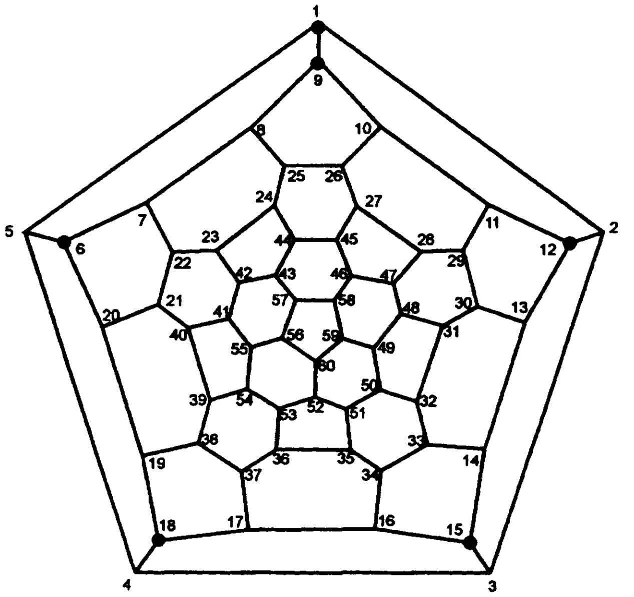

Fig. 1 Schlegel diagram of C_{60}, showing bromination sites for $C_{60}Br_6$ (black circles) and the $C_{60}Br_8$ isomers treated in this study (see Table 1)

unreliable BFGS method or the generally more stable eigenvector following technique[23] in their geometry optimisation. We have found it useful in MOPAC calculations on fullerene cages to define internal coordinates to enforce the correct symmetry; deviations between electronic and structure symmetry are then easily observed.

MNDO and AM1 parameterisations therefore agree in finding C_{2v} **1** to be more stable by 10–20 kJ mol^{-1} than C_s **2**. It is worth noting that the PM3 parameterisation does in fact predict the 'wrong' isomer of $C_{60}Br_8$ to be stable; Dixon *et al.*[6] have traced the poor performance of PM3 to an unphysical minimum in the interaction energy of non-bonded heavy halogen atoms, which causes the method to favour 1,2-addition.

Although our calculations have rectified the original anomaly, they raise a new difficulty. The difference in stability is of the expected sign but is still rather small. In view of this it seemed useful to explore the isomers based on $C_{60}Br_6$ + Br_2 more fully. Taking the reasoning of ref. 7 a little further, if the Br_6 addition pattern is especially stable (which remains true even with the revised AM1 energies) and 1,4-addition is favoured for addition of Br_2, then any isomer in which 1,4-addition has taken place at a distance from the Br_6 core is also likely to be stable. Systematic generation of all possible isomers in which two Br atoms are added 1,4 across a hexagon to $C_{60}Br_6$ without generating any further 1,2 adjacencies leads to three C_s and 16 distinct C_1 isomers. Computed heats of formation are given for optimised geometries of all 19 isomers in Table 1 and a key to the structures is given in Fig. 1.

Within this extended set of isomers, there are now 11 more stable than **1** at the AM1 and 9 at the MNDO levels. The PM3 parameterisation, which is known to be biased,[6] predicts all 19 to be more stable than the experimental isomer. The spread of energies relative to **1** is small (only ± 15 kJ mol^{-1} in AM1) but the results show internal consistency in that MNDO and AM1 energies fall into five more or less distinct sets according to the topological distance between the Br_6 and Br_2 groups, the most stable arrangements involving addition to the antipodal pentagon.

Given the narrow spread of energies and the inherent uncertainties of the methods, it is clear that none of the parameterisations can be said to make an unambigious prediction for the most stable isomer of $C_{60}Br_8$. Insofar as the experimental conditions (heating $C_{60}Br_6$ in benzene gives C_{2v} $C_{60}Br_8$) indicate thermodynamic stability for the latter, the predictions of higher stability for almost a dozen other isomers must be doubtful. The very small energy differences amongst $C_{60}Br_8$ isomers are however consistent with the mobility of Br atoms that is implied by the difference in addition patterns for $C_{60}Br_6$ and $C_{60}Br_8$. Given the large number of isomers of $C_{60}Br_8$ that could have been treated in this study (6 764 C_2, 10 027 C_s and 21 313 194 C_1 structures,[18] for example) it is unlikely that MNDO/AM1/PM3 unaided by experimental or other input could ever be expected to pick out the best of all possible isomers from what must be an almost continuous distribution of energies. Where methods such as these are much more useful is in distinguishing between candidates that satisfy all experimental contraints and are widely separated in energy. A recent successful example[24] is the identification of a structure for $C_{70}Cl_{10}$ that is consistent with the ^{13}C NMR evidence and is predicted to be 73 kJ mol^{-1} more stable than its nearest rival in the set of all isomers that exclude double bonds from pentagons.

References

1 P. W. Fowler, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1945.
2 B. L. Zhang, C. Z. Wang and K. M. Ho, *Chem. Phys. Lett.*, 1992, **193**, 225.
3 R. L. Murry, J. R. Colt and G. E. Scuseria, *J. Phys. Chem.*, 1993, **97**, 4954.
4 S. J. Austin, P. W. Fowler, G. Orlandi, D. E. Manolopoulos and F. Zerbetto, *Chem. Phys. Lett.*, 1994, **226**, 219.
5 D. A. Dixon, N. Matsuzawa, T. Fukunaga and F. N. Tebbe, *J. Phys. Chem.*, 1992, **96**, 6107.
6 N. Matsuzawa, T. Fukunaga and D. A. Dixon, *J. Phys. Chem.*, 1992, **96**, 10747.
7 J. B. Peel and R. G. Rothwell, *Aust. J. Chem.*, 1994, **47**, 131.
8 P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Oxford University Press, Oxford, 1995.

9 H. W. Kroto, *Nature*, 1987, **329**, 529; T. G. Schmalz, W. A. Seitz, D. J. Klein and G. E. Hite, *J. Am. Chem. Soc.*, 1988, **110**, 1113.
10 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.
11 M. J. S. Dewar, E. G. Zoebisch, E. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
12 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209, 221.
13 D. Bakowies, M. Kolb, W. Thiel, S. Richard, R. Ahlrichs and M. M. Kappes, *Chem. Phys. Lett.*, 1992, **200**, 411.
14 A. Warshel and M. Karplus, *J. Am. Chem. Soc.*, 1972, **94**, 5612.
15 F. Negri, G. Orlandi and F. Zerbetto, *Chem. Phys. Lett.*, 1992, **189**, 495.
16 F. Negri, G. Orlandi and F. Zerbetto, *Chem. Phys. Lett.*, 1992, **192**, 303.
17 G. Orlandi, F. Zerbetto and P. W. Fowler, *J. Phys. Chem.*, 1993, **97**, 13575.
18 S. Fujita, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 3215.
19 P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *Nature*, 1992, **357**, 479.
20 P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1993, 1230.
21 F. N. Tebbe, R. L. Harlow, D. B. Chase, D. L. Thorn, G. C. Campbell, J. C. Calabrese, N. Herron, R. J. Young and E. Wassermann, *Science*, 1992, **96**, 822.
22 M. B. Coolidge and J. J. P. Stewart, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO, 80840, USA, 1990.
23 J. Baker, *J. Comput. Chem.*, 1986, **7**, 385.
24 S. J. Austin, P. W. Fowler, J. P. B. Sandall, P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Koto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1027.

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