

MOLECULAR MECHANICS (MM3) STUDY OF THE STRUCTURES AND ENERGETICS OF CORANNULENE ($C_{20}H_{10}$), CYCLOPENTACORANNULENE ($C_{22}H_{12}$) AND THE HEMI-SPHERICAL $C_{30}H_{10}$

RUIFENG LIU, XUEFENG ZHOU AND NORMAN L. ALLINGER*

Computational Center for Molecular Structure and Design, Department of Chemistry, University of Georgia, Athens, Georgia 30602, U.S.A.

Molecular mechanics (MM3) calculations were carried out on the title compounds. Comparison between the MM3 results and those of semi-empirical and *ab initio* calculations and experiment indicates that the MM3 results are at least as good as results of much more expensive calculations. The MM3 calculations predict that unlike corannulene and cyclopentacorannulene, the transition state of the bowl-to-bowl inversion of the related $C_{30}H_{10}$ is non-planar, and the activation barrier is too high for this motion to occur.

The discovery of the stability of buckminsterfullerene^{1,2} and the fact that it can be prepared in macroscopic quantities³ generated much interest in the structures and chemistry of fused polycyclic carbon rings.⁴⁻⁸ Of particular interest are the curvature and flexibility of small carbon clusters. The carbon framework of corannulene (1), which can be considered to represent the polar cap of buckminsterfullerene, is surprisingly flexible. The bowl-to-bowl inversion takes place more than 200 000 times per second at room temperature!^{4,5} The inversion barrier of corannulenyl-dimethylcarbinol, which can be considered close to that of corannulene itself, was deduced from a temperature dependent NMR study to have $\Delta G^\ddagger = 10.2 \pm 0.2 \text{ kcal mol}^{-1}$ (1 kcal = 4.184 kJ); indeed, a recent experimental study determined the inversion barrier of corannulene to be $11-12 \text{ kcal mol}^{-1}$.⁹ These are in agreement with the barrier of corannulene calculated by *ab initio* 3-21G ($10.3 \text{ kcal mol}^{-1}$),¹⁰ and local density functional (LDF) ($11.0 \text{ kcal mol}^{-1}$)⁵ methods. However, the barrier calculated by the *ab initio* 6-31G* Hartree-Fock method, $8.8 \text{ kcal mol}^{-1}$,¹⁰ is lower.

It is expected that the larger members of the similar structures (C_nH_{10}) ($n = 3-5$) will be more rigid. Both experiment and theoretical calculations have been proposed to investigate the structure and inversion barrier of $C_{30}H_{10}$ (3).¹¹ However, presumably owing to the size of the molecule and the complicated fused-ring structure, there has been no previous report of any such

studies. In a recent experimental study of the rigidity of the corannulene carbon framework, Abdourazak *et al.*¹² successfully synthesized cyclopentacorannulene (2), and on the basis of a dynamics study they concluded that the lower limit of the bowl-to-bowl inversion barrier of 2 is *ca* 26 kcal mol^{-1} , suggesting that the bowl-shaped geometry of corannulene is effectively 'locked' by the additional five-membered ring, but no experimental structure is yet available.

During the past 20 years, molecular mechanics has become a powerful method for studying molecular structure and energetics.¹³ However, molecular mechanics results on these molecules and the larger fullerenes are often not reported but only used as starting points for the much more expensive *ab initio* or semi-empirical calculations. In this paper, we present results of our MM3 calculations on the structures and energetics of the title compounds, and show that the MM3 method is at least as reliable as the *ab initio* and semi-empirical methods for these molecules.

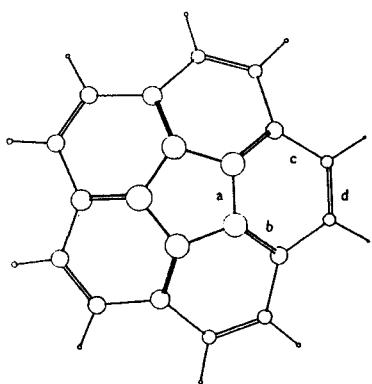
Our calculations used the MM3(92) program* and

* The MM3 force field is described in detail by Allinger *et al.*¹⁴ The MM3 program is available to all users from Technical Utilization, 235 Glen Village Court, Powell, OH 43065, and to commercial users only from Tripos, 1699 South Hanley Road, St Louis, MO 63144, and to academic users only from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405. The current version is available to run on most types of computers, and interested parties should contact one of the distributors directly.

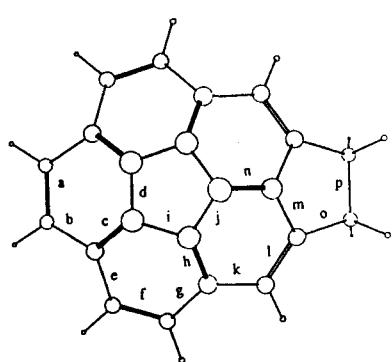
Received 14 February 1994

Revised 19 April 1994

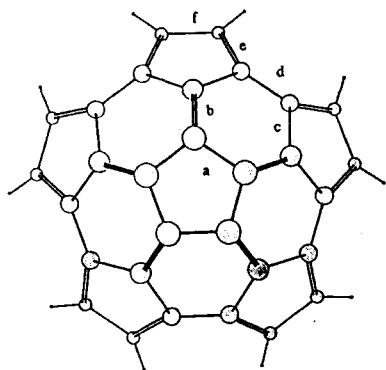
* Author for correspondence.



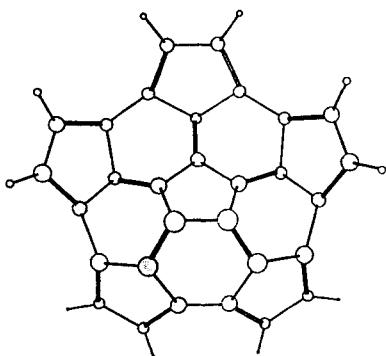
1



2



3



4

the standard procedure, that is, the conjugated pi systems were treated by semi-empirical variable electron SCF (VESCF) theory,¹⁵ and the force field parameters were adjusted according to the calculated bond orders. The calculated MM3 CC distances of the equilibrium structures are shown in Table 1. The available experimental¹⁶ and *ab initio*¹⁰ results on corannulene are also included for comparison. As is shown, the MM3 CC distances for corannulene are in better agreement with experiment than the much more expensive *ab initio* STO-3G and 6-31G* results. The out-of-plane angle between the plane of the five-membered ring and the edge of the inner portion of the six-membered rings, which describes the deviation of the carbon skeleton from planarity, is calculated to be 25.4°, in good agree-

ment with the experimental¹⁶ and *ab initio* 6-31G* values, 26.8° and 25.5°, respectively. The same angle in C₃₀H₁₀ is calculated to be 34.9°, indicating more substantial curvature than in corannulene. The MM3 heats of formation are 120.4, 126.1 and 278.5 kcal mol⁻¹ for corannulene, cyclopentacorannulene and C₃₀H₁₀, respectively. There have been no experimental reports of the heats of formation of these molecules. For corannulene itself, the heat of formation was predicted by Schulman and co-workers,¹⁰ using the group equivalent scheme of Ibrahim and Schleyer¹⁷ and the *ab initio* STO-3G and 6-31G* energies, to be 123.4 (STO-3G) and 116.8 (6-31G*) kcal mol⁻¹. As was shown in the studies of many classes of compounds,¹⁸ this combined *ab initio* energy and

Table 1. Calculated and experimental CC bond lengths

Compound	Bond ^b	Length (Å)			
		MM3	STO-3G ^c	6-31G* ^c	Exptl ^d
$C_{20}H_{10}$ (1)	a	1.421	1.423	1.413	1.413
	b	1.373	1.361	1.361	1.391
	c	1.450	1.462	1.451	1.440
	d	1.389	1.363	1.370	1.402
$C_{22}H_{12}$ (2)	a	1.386			
	b	1.449			
	c	1.377			
	d	1.427			
	e	1.477			
	f	1.386			
	g	1.449			
	h	1.386			
	i	1.425			
	j	1.424			
	k	1.465			
	l	1.384			
	m	1.428			
	n	1.367			
$C_{30}H_{10}$ (3)	o	1.524			
	p	1.587			
	a	1.443			
	b	1.385			
	c	1.442			
	d	1.381			
	e	1.474			
	f	1.366			

^a MM3 bond lengths are r_g , the *ab initio* bond lengths are r_e and the x-ray bond lengths are r_x .

^b Labeling of bonds is given on the structures.

^c Ref. 10.

^d Ref. 16.

group equivalent scheme is about as reliable as good experimental measurements, and the agreement between the MM3 heat of formation and those of Schulman and co-workers suggests that all are approximately correct. The reliability of the MM3 prediction is also supported by a recent study¹⁹ of the heat of formation of C_{60} , in which the MM3 heat of formation per carbon atom, 9.6 kcal mol⁻¹, is in much better agreement with the measured result, 9.1 kcal mol⁻¹, than those of AM1 (16.2), MNDO (14.5) or *ab initio* 6-31G*//STO-3G (11.2 kcal mol⁻¹) calculations.

Previous AM1 calculations have concluded that the planar structure of corannulene is the transition state for the bowl-to-bowl inversion.⁵ In agreement with the AM1 result, MM3 vibrational analysis of the planar corannulene also indicates one imaginary frequency (106i cm⁻¹), corresponding to the inversion of the bowl structure. The MM3 energy difference between the transition and equilibrium structures is 14.7 kcal mol⁻¹, which is in fair agreement with the experimental result,

11–12 kcal mol⁻¹. The AM1 calculation gave a higher barrier of 16.9 kcal mol⁻¹.⁵

The MM3 calculations on the planar cyclopenta-corannulene ($C_{22}H_{12}$) structure indicate that it is also the transition state (one imaginary frequency at 121i cm⁻¹) for the bowl-to-bowl inversion. This is in agreement with the AM1 results of Abdourazak *et al.*¹² The MM3 energy barrier for the inversion is 32.1 kcal mol⁻¹, which is lower than the AM1 value, 39 kcal mol⁻¹. As the AM1 calculations overestimate the inversion barrier of corannulene by about 5 kcal mol⁻¹, if a similar overestimation by AM1 for cyclopentacorannulene occurs, the MM3 and AM1 results are consistent with one another.

For the half-bowl-shaped $C_{30}H_{10}$, the MM3 calculation indicates that the planar D_{5h} structure is not a transition state, as there are three imaginary frequencies, one at 179i cm⁻¹ and a doubly degenerate pair at 53i cm⁻¹. This is in agreement with our expectation, as the perimeter of the C_{30} framework is too small and would invoke too high a strain to force all the carbon atoms to be simultaneously coplanar. The transition structure was located by geometry relaxation along the degenerate imaginary modes. It was found to be 49.1 kcal mol⁻¹ lower than the planar structure, and to have a single imaginary frequency of 147i cm⁻¹. This transition structure is shown (4). If one assumes the perimeter of the C_{30} framework to be roughly on a plane, the transition structure can be visualized as half of the molecule above the plane and half under it. The MM3 energy difference between the transition state and the ground state structures is 161.5 kcal mol⁻¹, indicating that the $C_{30}H_{10}$ molecule is very resistant to the bowl-to-bowl inversion. In fact, with such a high energy barrier, the carbon framework would be expected to break rather than pass through the transition state.

The Cartesian coordinates of all the MM3 structures are given in the supplemental material. These represent good starting geometries for further high-level theoretical studies.

We also checked to see what MM2 would show us about the structure of corannulene, since it normally gives fairly good results with conjugated or aromatic hydrocarbon systems. Indeed, the structure found was very similar to that found by MM3. The molecule is bowl shaped in the ground state, and the planar form represents a barrier 8 kcal mol⁻¹ higher than the ground state. [A reviewer indicated that in his hands MM2 gave a planar configuration for corannulene. We checked this specifically with MM2(91), which is the current version of MM2, which is available from the Quantum Chemistry Program Exchange (see earlier footnote). It is perhaps worth a comment here because this problem frequently comes up, and it may occur from either of two reasons. First, there are many imitations of MM2 in wide use today. Some are better than others, but most give inaccurate results for some calculations. We

can only speak for the authentic version of MM2. If one uses some other variant of MM2, not provided by us, any defects in the program must be taken up with the provider of that program. Second, it should also be noted that geometry optimizations are just that, they are not necessarily energy minimizations. If one begins the calculation with a planar structure, one is on a transition state, and there are no forces acting to deform the molecule from planarity. Accordingly, one will normally obtain a planar structure after the geometry optimization. If one wants to obtain a minimum energy structure, one must start at least slightly off the planar conformation, so that there will be forces acting to deform the system into the correct non-planar conformation. So-called 'energy minimizations' as commonly carried out in molecular mechanics are usually 'geometry optimizations,' and this is usually, but not necessarily, the same thing. The results quoted to us by the reviewer are surely a result of one or the other of these errors; either he used a defective imitation of MM2 instead of the actual program, or he used too poor a starting geometry. The actual MM2 results are almost the same as the MM3 results.]

Supplementary Tables S1–S6, containing the Cartesian coordinates of the MM3 equilibrium and transition structures for corannulene, cyclopentacorannulene and the half-ball-shaped $C_{30}H_{10}$, are available as supplementary material directly from the authors.

ACKNOWLEDGEMENT

This work was supported by the US National Science Foundation grant CHE-9222655.

REFERENCES

1. E. A. Rohlfsing, D. M. Cox and A. Kaldor, *J. Chem. Phys.* **81**, 3322 (1984).

2. H. W. Kroto, J. P. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature (London)* **318**, 162 (1985).
3. W. Kratschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature (London)* **347**, 354 (1990).
4. L. T. Scott, M. M. Hashemi and M. S. Bratcher, *J. Am. Chem. Soc.* **114**, 1920 (1992).
5. A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldridge and J. S. Siegel, *J. Am. Chem. Soc.* **114**, 1921 (1992).
6. K. Yamamoto, Y. Saitho, D. Lwaki and T. Ooka, *Angew. Chem.* **103**, 1202 (1991).
7. D. N. Leath and J. A. Reiss, *Aust. J. Chem.* **32**, 361 (1979).
8. T.-M. Chang, A. Naim, S. N. Ahmed, G. Goodloe and P. B. Shevlin, *J. Am. Chem. Soc.* **114**, 7603 (1992).
9. A. Sygula and P. W. Rabideau, to be published; cited in Ref. 12.
10. R. C. Peck, J. M. Schulman and R. L. Disch, *J. Phys. Chem.* **94**, 6637 (1990); J. M. Schulman, R. C. Peck and R. L. Disch, *J. Am. Chem. Soc.* **111**, 5675 (1989).
11. J. S. Siegel and L. T. Scott, cited by R. M. Baum, *Chem. Eng. News* **70**, 16 March, 27 (1992).
12. A. H. Abdourazak, A. Sygula and P. W. Rabideau, *J. Am. Chem. Soc.* **115**, 3010 (1993).
13. (a) U. Burkert and N. L. Allinger, *Molecular Mechanics*. American Chemical Society, Washington, DC (1982); (b) N. L. Allinger, Y. H. Yuh and J.-H. Lii, *J. Am. Chem. Soc.* **111**, 8551, 8566, 8576 (1989), and references cited therein.
14. N. L. Allinger, Y. H. Yuh and J.-H. Lii, *J. Am. Chem. Soc.* **111**, 8551 (1989), and subsequent papers.
15. N. L. Allinger, F. Li, L. Yan and J. C. Tai, *J. Comput. Chem.* **11**, 868 (1990), and references cited therein.
16. J. C. Hanson and C. E. Nordman, *Acta Crystallogr., Sect. B* **32**, 1147 (1976).
17. M. R. Ibrahim and P. v. R. Schleyer, *J. Comput. Chem.* **6**, 157 (1985).
18. N. L. Allinger, L. R. Schmitz, I. Motoc, C. Bender and J. K. Labanowski, *J. Phys. Org. Chem.* **3**, 732 (1990); N. L. Allinger, L. R. Schmitz, I. Motoc, C. Bender and J. K. Labanowski, *J. Am. Chem. Soc.* **114**, 2880; (1992); N. L. Allinger, L. R. Schmitz, I. Motoc, C. Bender and J. K. Labanowski, *J. Comput. Chem.* **13**, 838 (1992); L. R. Schmitz, I. Motoc, C. Bender, J. K. Labanowski and N. L. Allinger, *J. Phys. Org. Chem.* **5**, 225 (1992).
19. H.-D. Beckhaus, C. Ruchardt, M. Kao, F. Diederich and C. S. Foote, *Angew. Chem., Int. Ed. Engl.* **31**, 63 (1992).