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X-ray Quality Geometries of Geodesic Polyarenes from Theoretical Calculations: What Levels of Theory Are Reliable?

Marina A. Petrukhina,*,[†] Kristian W. Andreini,[†]
James Mack,[‡] and Lawrence T. Scott*,[§]

Department of Chemistry, University at Albany, State University of New York, Albany, New York 12222-0100, Department of Chemistry, University of Cincinnati, PO Box 210172, Cincinnati, Ohio 45221-0172, and Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02167-3860

marina@albany.edu; lawrence.scott@bc.edu

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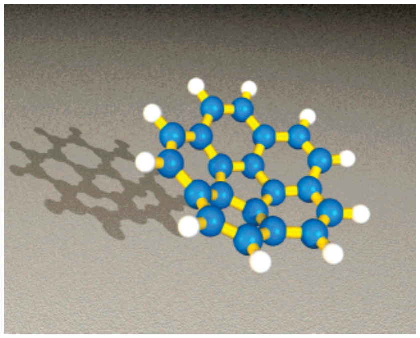

Computational methods for calculating molecular geometries have not been well calibrated heretofore against X-ray data for bowl-shaped polycyclic aromatic hydrocarbons (PAHs). The analysis presented here capitalizes on a rare opportunity provided by corannulene to account explicitly for molecular distortions from crystal packing forces. Within the error limits of an extensive X-ray data set, B3LYP/6-31G* calculations were found to correctly reproduce all of the experimental bond distances and bond angles. The reliability and shortcomings of geometry calculations at other levels of theory are enumerated.

Bond lengths and bond angles predicted for the lowest energy geometry of a molecule by computer modeling at one level of theory virtually never coincide precisely with those calculated by geometry optimizations performed on the same molecule at other levels of theory (e.g., molecular mechanics, semiempirical, ab initio, density functional molecular orbital methods, etc.). To decide which calculations can be trusted for a given class of molecules, therefore, chemists often turn to X-ray crystal structures as experimental calibration points, and those theories that fail to reproduce the experimental structure within acceptable error limits get branded as “unreliable.”

One problem with using X-ray crystal structures as the definitive geometry standard is the inescapable effect of crystal packing forces, which can distort molecules, often significantly, away from the true optimum geometries they would adopt in the absence of external influences (see below). Thus, some portion of the blame for discrepancies between calculated geometries and X-ray crystal structures must be attributed to these bothersome distortions, rather than to intrinsic inadequacies of the various theoretical methods, which deal with isolated molecules.

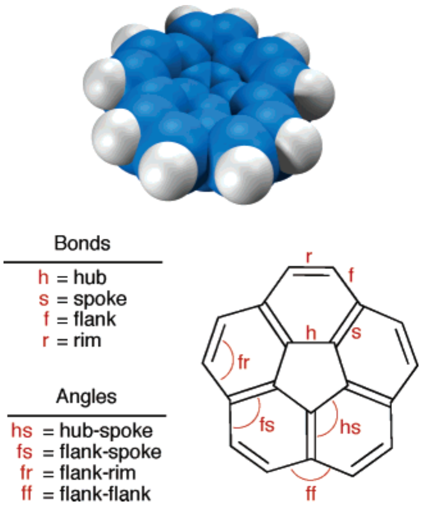

FIGURE 1. Corannulene (**1**). Top: space-filling model of the bowl. Bottom: labels used for the four types of CC bonds and for the four types of CCC bond angles.

Corannulene (**1**) provides an excellent case in point. Gas-phase microwave spectroscopy[1] and every level of theory that we have examined indicate that the minimum energy geometry of this $C_{20}H_{10}$ geodesic polyarene has C_{5v} symmetry (Figure 1). Such high symmetry reduces the number of independent CC bond distances in corannulene from 25 down to only 4 (Figure 1) and the number of independent CCC bond angles from 40 down also to just 4 (Figure 1), not counting the internal CCC bond angle of the central five-membered ring, which C_{5v} symmetry fixes as that of a regular pentagon (i.e., exactly 108°). In the crystal, on the other hand, two independent molecules of corannulene occupy the unit cell in an orientation that causes all molecular symmetry to be lost (Figure 2).[2] As a consequence, every one of the 50 CC bonds in the molecular pair is unique and unrelated by symmetry to all of the other CC bonds in both molecules. Thus, instead of providing just one experimental bond distance for the “hub” CC bond, for example, the X-ray analysis of a single crystal of corannulene yields *ten independent experimental measurements* for the “hub” CC bond. Ten independent values are also obtained for both the “spoke” CC bond distance and the “rim” CC bond distance; *twenty* independent measurements are obtained for the “flank” CC bonds. For the same reason, the X-ray analysis gives 10 independent measurements for both the “flank−flank” and the “hub−hub” CCC bond angles and

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[†] University at Albany, SUNY.
[‡] University of Cincinnati.
[§] Boston College.

[1] Lovas, F. J.; McMahon, R. J.; Grabow, J.; Schnell, M.; Mack, J.; Scott, L. T.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **2005**, *127*, 4345−4349.

[2] Hanson, J. C.; Nordman, C. E. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1147−1153.

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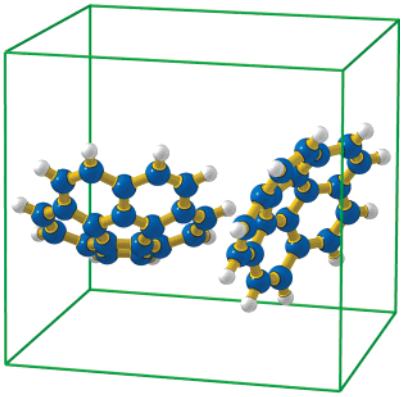

FIGURE 2. Orientation of the two independent corannulene molecules in the unit cell of the crystal.

20 independent measurements for each of the other CCC bond angle types. Some bond angles vary over a range of more than 1.2° as a result of distortions imposed by crystal-packing forces (see below).

When viewed in an opportunistic light, these data give a splendid quantitative picture of the magnitude of crystal packing force distortions and, consequently, a rare chance to compare calculated geometries to an X-ray crystal structure *with packing force distortions explicitly taken into account*. Recognizing this attractive opportunity, we redetermined the X-ray crystal structure of corannulene using modern equipment.[3] To enlarge the data set, we performed the X-ray structural analysis at two different temperatures (−100 and −183 °C) and thereby doubled the number of experimental values for every bond distance and bond angle. It should be noted that the quality of our new data ($R = 0.040$) significantly exceeds that reported in 1976 by Hanson and Nordman in their original X-ray analysis of corannulene ($R = 0.069$ at 20 °C and 0.074 at −70 °C).[2,3] Table 1 summarizes the CC bond distance and CCC bond angle data obtained from our two new X-ray crystal structures and also shows the range of values observed for each. More complete tables can be found in the Supporting Information.

A few words are in order here about the ranges of values seen in the experimentally determined geometric parameters. At the 99.7% confidence level, one can consider two bond distances to be statistically nonequivalent if the difference between them lies outside the "six σ limit" (i.e., $\pm 3\sigma$ for each measurement).[4] For example, the observed difference between the longest and the shortest bond distances measured for the hub CC bonds is 0.0063 Å and that difference lies within the six σ limit for these crystallographic experiments. Thus, the 10 hub CC bond distances measured are indistinguishable, within the limits of experimental error. The ranges of distance values for the other three types of CC bonds likewise all fall within the six σ limit. By contrast, the ranges of values for the four types of CCC bond angles all fall outside the six σ limit, so the largest difference in bond angles within each type must be considered statistically significant. Molecular distortions from crystal packing forces are clearly quite real.

Figure 3 graphically illustrates the extent of agreement between the geometric parameters calculated at numerous levels of theory[5] and the experimentally measured bond distances and bond angles listed in Table 1. Predicted values of the geometric parameters that fall within three σ of at least one experimentally determined value are considered to be indistinguishable from the X-ray data. Several conclusions are immediately obvious from Figure 3.

B3LYP/6-31G calculations perfectly reproduce the X-ray structure of corannulene, within the error limits of the X-ray analysis.* This level of theory has become one of the mostly widely used for serious calculations and proves to be completely reliable when tested against the 120 experimental values in this geodesic polyarene data set. The inclusion of polarization functions on hydrogens (B3LYP/6-31G**) has virtually no effect; however, B3LYP/6-311G* calculations give parameters that all fall within 2σ of the experimental values. The other density functional methods examined reproduce the bond angles well, but they all miss one or more of the bond distances.

AM1 and PM3, the two most widely used semiempirical methods, perform almost as well as the more time consuming B3LYP methods listed above, although both slightly overestimate the length of the hub CC bond (AM1 by 0.0163 Å and PM3 by 0.0097 Å). The older MNDO method is totally unreliable; it overestimates every bond distances and gets only one bond angle within three σ of any experimentally determined value.

All of the Hartree−Fock methods underestimate the length of the two bonds that have the greatest double bond character; the error is more pronounced for the spoke bond (too short by 0.0104−0.0117 Å) than for the rim bond (too short by 0.0011−0.0083 Å). Surprisingly, the use of relatively large basis sets (e.g., HF/6-311+G**) results in no significant improvement over the results obtained with the lowest split level basis set (HF/3-21G). All of the Hartree−Fock calculations that use split level

TABLE 1. Geometric Parameters Obtained from Two New X-ray Crystal Structures of Corannulene (1)

	bond distances[a] (Å)				bond angles[a] (deg)			
	hub	spoke	flank	rim	hub−spoke	flank−spoke	flank−rim	flank−flank
avg (X-ray 1)[b]	1.4137(17)	1.3779(16)	1.4438(18)	1.3800(19)	122.91(20)	114.32(24)	122.02(17)	130.07(36)
avg (X-ray 2)[c]	1.4151(16)	1.3790(14)	1.4464(16)	1.3831(15)	122.92(23)	114.39(22)	121.95(17)	129.94(35)
maximum[d]	1.4172(15)	1.3814(15)	1.4498(17)	1.3865(18)	123.27(11)	114.70(11)	122.31(12)	130.69(12)
minimum[d]	1.4109(16)	1.3758(16)	1.4409(19)	1.3770(20)	122.49(10)	113.90(11)	121.56(11)	129.45(10)
difference (Δ)[e]	0.0063	0.0056	0.0089	0.0095	0.78	0.80	0.75	1.24

[a] See Figure 1 for definitions of bond types and bond angle types. The average CC distances and the average CCC angles are reported for each set of bonds and angles of the same type, respectively (standard deviations in the last two decimal places are shown in parentheses). [b] X-ray 1 determined at −100 °C.[3] [c] X-ray 2 determined at −183 °C.[3] [d] The maximum and minimum values reported correspond to the extreme values found for each bond type and for each bond angle type in the combined data sets from both X-ray crystal structures. [e] Difference (Δ) = (maximum) − (minimum).

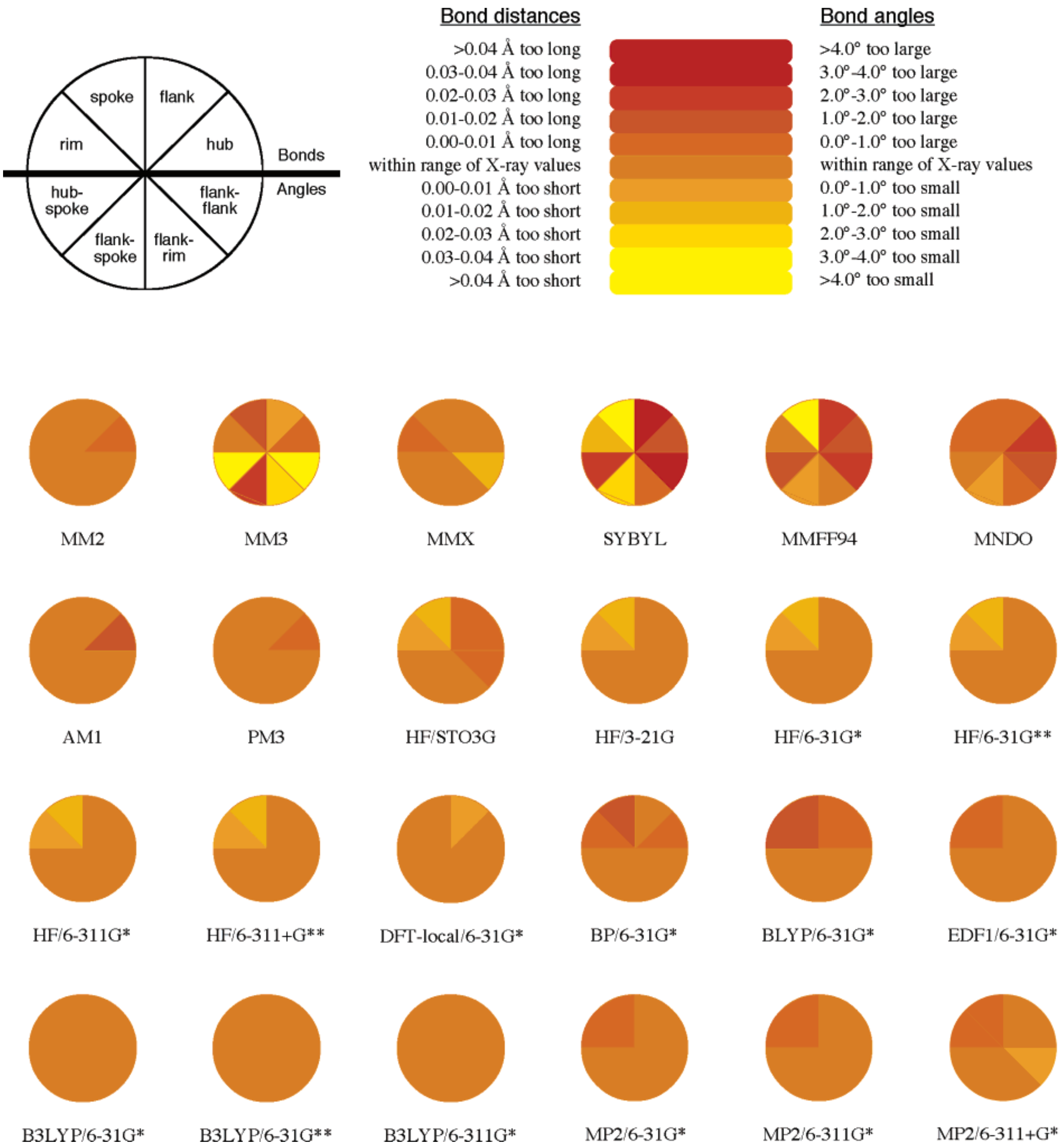

FIGURE 3. Graphical depictions of the extent to which the geometric parameters calculated at numerous levels of theory[5] agree with the experimentally measured bond distances and bond angles listed in Table 1. Predicted values of the geometric parameters that fall within three σ of one or more of the experimentally determined values are considered to be indistinguishable from the X-ray data.

basis sets (3-21G, 6-31G*, 6-31G**, 6-311G*, and 6-311+G**) do well on the other two bond distances and on all the bond angles. The old minimal basis set method (HF/STO3G) does a poor job on five of the eight structural parameters and must be considered unreliable.

MP2 corrections for electron correlation lengthen the two bonds that have the greatest double bond character so much that the calculated values still fall outside the range of the X-ray data, but now on the high side. This discrepancy persists even with the largest basis set examined (MP2/6-311+G**), and this time-consuming calculation did not even get all of the bond angles right. For every basis set checked, therefore, B3LYP calcula-

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(3) The original X-ray crystal structure of corannulene[2] was performed using crystals grown from solution. For the new X-ray crystal structures reported here, crystals were grown by subliming corannulene at 175 °C. See the Supporting Information for complete crystallographic tables and details.

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(5) Geometry optimizations were performed using the programs packaged in Spartan '02 (Linux version, 2002; Wavefunction, Inc., Irvine, CA 92612), with the following exceptions: MM2 calculations were performed using the program in Chem-3D (v 5.0, 1999; CambridgeSoft Corp., Cambridge, MA 02140); MM3 and MMX calculations were performed using the program in PCModel (v 8.0 for Linux, 2002; Serena Software, Bloomington, IN 47402). Default termination thresholds were used in all cases.

tions proved superior to both Hartree–Fock and MP2 calculations.

Of the molecular mechanics methods examined, the MMX force field in PCModel and the MM2 force field in Chem-3D perform pretty well; however, the 1976 X-ray structure of corannulene may well have been used to develop these force fields (i.e., corannulene may have been one of the "training compounds" used for the program). The other molecular mechanics methods (MM3, SYBYL, and MMFF94) are completely unreliable for calculating geometries of geodesic polyarenes.

Prior to the dawn of the fullerene era, corannulene (**1**) stood alone as the only bowl-shaped polycyclic aromatic hydrocarbon (PAH) that had ever been synthesized.[6] The discovery of fullerenes in 1985,[7] however, triggered a rush among synthetic organic chemists to develop new methods for the preparation of curved networks of trigonal carbon atoms,[8] and that movement eventually led to a rational chemical synthesis of C_{60}.[9] Today, geodesic polyarenes whose ring systems map onto that of C_{60} comprise a family of more than two dozen members, and new representatives are being added every year.[10] The currently known "fullerene fragments" range in size from $C_{20}H_{10}$ (corannulene, **1**) to $C_{42}H_{14}$ (indeno[1,2,3-*cd*]circumtrindene[11]), but few have been structurally characterized by X-ray crystallography.[12] The geometric features of most bowl-shaped C_{60} subunits have not been available, therefore, except from theoretical calculations,[13] and their reliability has been uncertain, since computational methods were uncalibrated, until now, for PAHs characterized by curved topologies.[14]

In this paper, we have reported a critical assessment of the computational methods used most often for molecular modeling of polycyclic aromatic hydrocarbons and have identified those that perfectly reproduce the geometry of a representative geodesic polyarene, within the limits of precision of two new high quality X-ray crystal structures ($R = 0.040$), in a treatment that *explicitly takes into account the magnitude of molecular distortions from crystal packing forces*. We have also identified the other commonly used computational methods that come close to achieving this level of agreement between theory and experiment and have reported which methods predict bond distances and/or bond angles that deviate substantially from those obtained experimentally. The experimental data set employed consists of 120 independent bond distances and bond angles. Data from X-ray structures of other geodesic polyarenes were intentionally omitted from the analysis, because they do not allow molecular distortions from crystal packing forces to be factored out so thoroughly.

Our findings provide a benchmark on the reliability and shortcomings of various theoretical methods for predicting the geometries of geodesic polyarenes. We hope these results will prove useful to others who are interested in compounds that belong to this intriguing and rapidly expanding family.

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Supporting Information Available: Tables of all calculated bond distances and bond angles; X-ray data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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