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[7]Circulene: A Remarkably Floppy Polycyclic Aromatic C₂₈H₁₄ Isomer

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The stationary point geometries for the high-symmetry planar transition state (D_{7h}) and the low-symmetry (C_2) equilibrium form of the [7]circulene molecule were fully optimized at the self-consistent-field (SCF) level of theory with the STO-3G minimal, double-zeta (DZ), and double-zeta plus polarization (DZP) basis sets. The energy difference between the planar and nonplanar structures is about 8 kcal/mol. The vibrational spectrum of the molecule was also considered theoretically. The most interesting feature of the vibrational spectrum is the presence of the very low-frequency ($4i\text{ cm}^{-1}$) mode which belongs to the B symmetry corrugating vibration. The theoretical results are compared to very recent experiments on the bowl-to-bowl inversion in [5]circulene (corannulene) and related compounds.

I. Introduction

In the family of polycyclic aromatic compounds produced by the fusion of benzene rings, [7]circulene (C₂₈H₁₄) is the first that exhibits a saddle-shaped nonplanar structure. The lower homologues corannulene ([5]circulene) and coronene^{1,2} ([6]circulene) have bowl-like (C_{5v}) and planar (D_{6h}) structures, respectively.^{3,4} The main factor that determines the structure of corannulene and [7]circulene is apparently the compromise between aromaticity and the structural strain due to the deviation of the CCC angles from the optimum value of 120°. From geometrical considerations it was predicted by Dopfer and Wynberg⁵ that the molecule that consists of five fused benzene rings should have a bowl-like structure and that with seven benzene rings should be corrugated. In 1983, [7]circulene was prepared by Yamamoto, Harada, Nakazaki, Nakao, Kai, Harada, and Kasai,⁶ and subsequent X-ray analysis by Yamamoto, Harada, Okamoto, Chikamatsu, Nakazaki, Kai, Nakao, Tanaka, Harada, and Kasai has confirmed earlier predictions of this molecule being nonplanar.⁷

Very recently, a communication appeared describing the bowl-to-bowl inversion in the closely related [5]circulene molecule, corannulene. Scott, Hashemi, and Bratcher¹⁹ concluded from their NMR measurements that the barrier for bowl-to-bowl inversion is $\Delta G^\ddagger = 10.2 \pm 0.2$ kcal/mol. Scott further states "unless this barrier has a significant negative ΔS^\ddagger component, the corannulene ring system must invert more than 200,000 times per second at room temperature!" In a companion experimental communication, Borchardt, Fuchicello, Kilway, Baldrige, and Siegel²⁰ report bowl-to-bowl activation energies of 6–9 kcal/mol for two molecules closely related to [5]circulene. Clearly, all three experiments yield planar-equilibrium barriers close to the 8.5 kcal/mol predicted here for [7]circulene. In their closing sentence Borchardt and co-workers state "this demonstrates the flexible nature of these bowls, a property one can relate to the analogous carbon fragments leading up to buckminsterfullerene."

There are only a few theoretical studies of the molecules in this fascinating family, mostly performed at the semiempirical level.^{8–11} Self-consistent-field (SCF) wave functions have been determined for coronene using a 3-21G basis set at the geometry given by the experimental molecular crystal structure.¹⁰ The first ab initio optimized structures of corannulene and coronene were obtained at the SCF level of theory using an STO-3G minimum basis. At these geometries the 3-21G and 6-31G SCF total energies were also reported by Schulman, Peck, and Disch.¹¹ No such

computations have been carried out on the larger [7]circulene molecule, despite the fact that the electronic structure of this molecule is of interest as a unique representative of the circulene family, with a structure of low symmetry.

II. Theoretical Details

The Turbomole ab initio direct-SCF computer program package¹² as implemented on the IBM RS/6000, DECstation 3100, and HP Apollo 9000 Series 700 workstations was used in this research. The first basis set employed was the STO-3G minimum basis set of Hehre, Stewart, and Pople.¹³ A double-zeta (DZ) basis set, constructed as C (9s5p/4s2p) and H (4s/2s) by Huzinaga and Dunning,^{14,15} was also used. A double-zeta plus polarization (DZP) basis set was finally constructed with additional pure d functions of orbital exponent $\alpha_C = 0.75$ on each carbon and p functions of orbital exponent $\alpha_H = 0.75$ on each hydrogen. The STO-3G set for the C₂₈H₁₄ molecule contains 154 basis functions, the DZ basis set 308 functions, and the DZP basis set 490 basis functions. Although the [7]circulene studies are not unusually large in terms of number of basis functions, the lower symmetry (C_2) in fact makes the work highly computation intensive.

There are 60 totally symmetric internal coordinates (or 60 vibrational normal modes belonging to the totally symmetric irreducible representation) for the C_2 C₂₈H₁₄ molecule, and it was a challenge to construct a full and nonredundant set of internal coordinates for geometry optimization.¹⁶ We have used a rather straightforward approach by introducing 15 C–C and 7 C–H stretches, 14 C–C–C and 7 C–C–H bend coordinates, 10 torsional coordinates describing rotations around C–C bonds, and 7 C–H out-of-plane coordinates. However, this set (and we suspect any other set of internal coordinates based on traditional¹⁶ separation of stretching, bending, and torsional coordinates) was nonideal for the highly networked [7]circulene molecule. Recently, Pulay, Liu, and Zhou¹⁷ have reported work on the natural internal coordinates, which may be better suited to the geometry optimization of molecules such as [7]circulene with highly interconnected cyclic substructures.

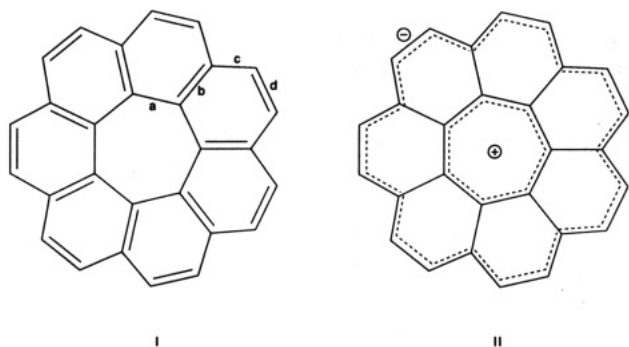
In order to facilitate a more direct comparison with the X-ray experimental data of Yamamoto et al.⁷ on the nonplanar form of [7]circulene, we have reported the "arithmetic average of the absolute deviations from the least squares plane" passing through the six carbon atoms of individual benzene rings. Generally speaking, and supposing that there is an arbitrary set of atoms, we may define a "least squares plane" passing through this set of atoms as one that minimizes the sum of the square of the distances from each atom to the said plane.¹⁸ Having found the

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TABLE I: Theoretical Stationary Point Geometrical Parameters (Bond Lengths in Å and Bond Angles in deg) and Total Energies (in hartrees) for the Planar Form of [7]Circulene

	STO-3G SCF	DZ SCF	DZP SCF
total energy	-1055.50179	-1068.19553	-1068.64477
equilibrium geometry			
CC (type a)	1.495	1.491	1.486
CC (type b)	1.418	1.432	1.424
CC (type c)	1.428	1.420	1.418
CC (type d)	1.321	1.331	1.326
CH	1.080	1.070	1.075
CC'H	118.4	118.7	118.8

CHART I



least squares planes for two adjacent benzene rings (hydrogen atoms not included in the present procedure), one may also determine the dihedral angle between the two planes as a measure of the tilt between the carbon frameworks of the two adjacent benzene rings, as Yamamoto et al.⁷ did. The procedure of finding the least squares planes certainly smears out detailed geometrical information on each atom but nonetheless may yield useful insight (as an addendum to the traditional structure) into the overall geometrical features of large (and specifically sheetlike) molecules such as [7]circulene.

III. Results and Discussion

The geometry of the [7]circulene molecule was optimized within D_{7h} and C_2 symmetries. The theoretical total energies and optimized stationary point geometries for the planar form of [7]circulene are shown in Table I. There are four types of CC bonds in the planar form of [7]circulene, respectively labeled a, b, c, and d. These are identical to the designations used by Yamamoto et al.;⁷ see Chart I. All the CH bonds are symmetry equivalent. There is also one independent bond angle governing the swiveling of the hydrogen atoms. This angle is indicated in Table I as the CC'H entry, where C and C' are the two carbon atoms at the two ends of the type-c CC bonds. For the planar form, these constitute a complete and nonredundant set of symmetry-independent internal coordinates. The presence of a degenerate pair of imaginary vibrational frequencies (STO-3G SCF level) for the planar structure indicates that this form corresponds to a higher order stationary point on the potential energy surface than a genuine transition state.

As may be observed from Table I, the optimized stationary point geometry undergoes an appreciable change from STO-3G SCF to DZ SCF, in that the lengths of the type-b and type-c CC bonds changes order. The DZP SCF bond lengths are smaller than the DZ SCF counterparts as expected. One notes that type-b CC bonds are longer than the type-c bonds (by 0.012 Å at the DZ SCF and 0.006 Å at the DZP SCF level of theory, respectively).

A typical single carbon-carbon bond in a paraffin (saturated hydrocarbon) molecule is 1.541 ± 0.003 Å. In the immediate vicinity of double bonds, the typical single carbon-carbon bond is 1.53 ± 0.01 Å, a typical carbon-carbon bond in aromatic

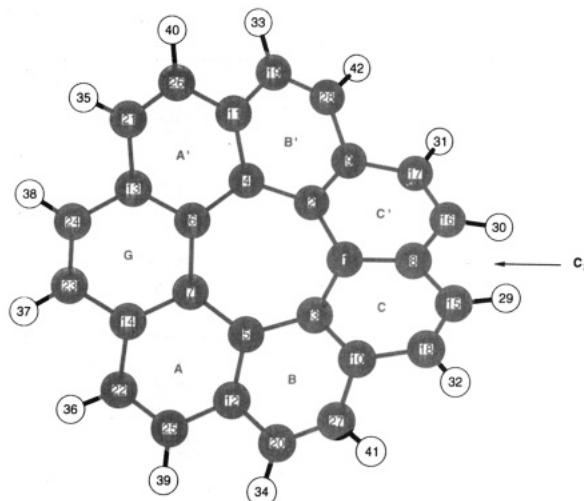


Figure 1. The C_2 symmetry, nonplanar form of [7]circulene ($C_{28}H_{14}$). The atomic labeling scheme is consistent with Table II. The seven benzene rings are designated A, A'; B, B'; C, C'; and G, consistent with Table III. The C_2 symmetry element is indicated.

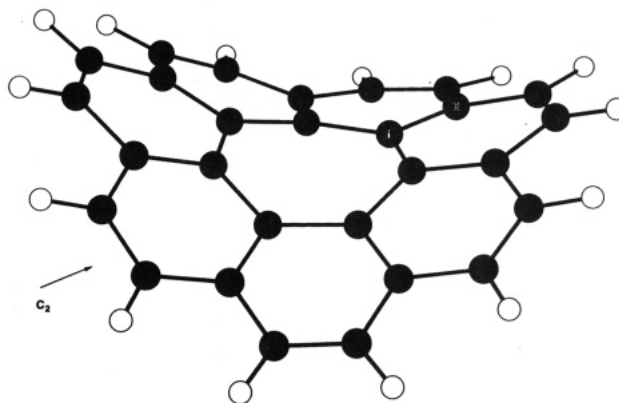


Figure 2. A perspective view of the saddle shape of the C_2 symmetry, nonplanar form of [7]circulene. The C_2 symmetry element passes through the carbon atoms 1 and 8.

compounds is 1.395 ± 0.003 Å, and a typical simple double carbon-carbon bond is 1.337 ± 0.006 Å. In the Kekulé localized form (I) the type-b and type-d bonds should be double and type-a and type-c bonds should be single. On the other hand, in the delocalized resonance form (II) the type-b CC bonds should be closer to single and type-a, type-c, and type-d bonds closer to double. In other words, if the localized Kekulé form (I) dominates, type-b and type-d CC bonds should be shorter than type-a and type-c CC bonds. If the delocalized form (II) dominates, the type-b CC bonds should be longer than the type-a, type-c, and type-d CC bonds. From the theoretical bond lengths in Table I, one may conclude that (i) the two resonance forms in Chart I are not entirely adequate,⁹ which is also borne out qualitatively by the results of Mulliken population analyses,¹² (ii) the outermost seven CC bonds are very close to a typical double bond, and (iii) on account of the type-b and type-c CC bond lengths at the DZ and DZP SCF levels, the delocalized resonance form (II) is somewhat more dominating. Finally, the delocalized form (II) requires that the carbon atoms are in one plane, while the localized Kekulé form (I) should not prefer the global planar form over the global nonplanar form to the same extent. Therefore, in the nonplanar form one should expect to find that the delocalized form (I) dominates. One consequence of this may be that, among other things, one should also expect to find that the type-b CC bonds is shorter than type-c CC bonds in the nonplanar form.

The theoretical total energies, optimized equilibrium bond lengths, and bond angles for the nonplanar form [7]circulene are

TABLE II: Theoretical Equilibrium Bond Lengths (in Å), Bond Angles (in deg), and Total Energies (in hartrees) for the Nonplanar (C_2) Form of [7]Circulene (A Comparison to Low-Temperature X-ray Analysis Is Presented in Table III)

	STO-3G SCF	DZ SCF	DZP SCF	expt ^a
total energy	-1055.51671	-1068.20807	-1068.65833	
$\Delta E_c,^b$ kcal/mol	-9.4	-7.9	-8.5	
equilibrium geometry				
C(1)-C(2)	1.476	1.471	1.467	~1.461
C(2)-C(4)	1.479	1.474	1.469	
C(4)-C(6)	1.473	1.468	1.462	
C(6)-C(7)	1.481	1.475	1.471	
C(1)-C(8)	1.408	1.420	1.412	~1.430
C(2)-C(9)	1.405	1.418	1.410	
C(4)-C(11)	1.408	1.420	1.412	
C(6)-C(13)	1.406	1.419	1.411	
C(8)-C(16)	1.432	1.424	1.422	~1.422
C(9)-C(17)	1.434	1.425	1.423	
C(9)-C(28)	1.435	1.427	1.425	
C(11)-C(19)	1.434	1.426	1.424	
C(11)-C(26)	1.431	1.423	1.421	
C(13)-C(21)	1.432	1.423	1.421	
C(13)-C(24)	1.435	1.427	1.425	
C(16)-C(17)	1.331	1.343	1.337	~1.344
C(19)-C(28)	1.330	1.342	1.336	
C(21)-C(26)	1.331	1.343	1.338	
C(23)-C(24)	1.330	1.342	1.336	
C-H	1.081	1.072	1.077	
C(2)-C(1)-C(3)	127.4	127.5	127.4	
C(1)-C(2)-C(4)	125.5	125.7	125.5	
C(2)-C(4)-C(6)	127.0	127.1	127.0	
C(4)-C(6)-C(7)	126.2	126.3	126.2	
C(1)-C(8)-C(16)	122.6	122.5	122.5	
C(2)-C(9)-C(28)	122.9	122.9	122.9	
C(2)-C(9)-C(17)	122.8	122.8	122.8	
C(4)-C(11)-C(19)	122.7	122.6	122.6	
C(2)-C(11)-C(26)	122.5	122.5	122.5	
C(6)-C(13)-C(21)	122.6	122.6	122.6	
C(6)-C(13)-C(24)	122.9	122.8	122.8	
C(8)-C(16)-C(17)	119.8	119.9	119.8	
C(16)-C(17)-C(9)	119.2	119.2	119.1	
C(9)-C(28)-C(19)	119.2	119.3	119.2	
C(28)-C(19)-C(11)	119.7	119.8	119.8	
C(11)-C(26)-C(21)	119.7	119.7	119.6	
C(26)-C(21)-C(13)	119.4	119.4	119.3	
C(13)-C(24)-C(23)	119.5	119.6	119.5	
C(16)-C(8)-C(15)	114.9	115.0	115.0	
C(17)-C(9)-C(28)	113.7	113.8	113.7	
C(19)-C(11)-C(26)	114.7	114.7	114.7	
C(21)-C(13)-C(24)	114.1	114.2	114.2	
C(8)-C(1)-C(2)	116.3	116.3	116.3	
C(9)-C(2)-C(1)	117.0	117.0	117.0	
C(9)-C(2)-C(4)	116.8	116.7	116.8	
C(11)-C(4)-C(6)	116.7	116.6	116.7	
C(13)-C(6)-C(4)	117.0	116.9	117.0	
C(13)-C(6)-C(7)	116.4	116.4	116.4	
C(8)-C(16)-H(30)	118.2	118.6	118.6	
C(9)-C(17)-H(31)	118.4	118.8	118.9	
C(9)-C(28)-H(42)	118.3	118.8	118.9	
C(11)-C(19)-H(33)	118.1	118.6	118.6	
C(11)-C(26)-H(40)	118.3	118.7	118.8	
C(13)-C(21)-H(35)	118.4	118.8	118.9	
C(13)-C(24)-H(38)	118.2	118.6	118.7	

^a Yamamoto, K.; Harada, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M.; Kai, Y.; Nakao, T.; Tanaka, M.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 3578. These authors did not report individual CC bond lengths; cited here are the averages in each type. ^b Relative to the planar form of [7]circulene.

shown in Table II. Also listed are the energies of the nonplanar form relative to the planar form. The planar and nonplanar forms are both electronically closed shell, and this may be used to explain in part the fact the theoretical relative energies with different basis sets remain quite constant. Detailed presentation of torsional angles is omitted (but see Table III). A labeling of the atoms for the nonplanar C_2 form is shown in Figure 1 and is consistent with the labels used in Table II. The numerical label runs from 1 to 42, different from the one used by Yamamoto et al.⁷ A perspective view of the molecular saddle shape is given in Figure

2. In both of the illustrations, the C_2 rotation axis is indicated. For the nonplanar form of [7]circulene, the bonds and bond angles, which are degenerate in the planar form, become split. Nevertheless, a rough classification of these internal coordinates is still useful. Yamamoto et al.⁷ did not present detailed bond lengths for the four types of CC bonds in the nonplanar form, but only a range and an average. For the type-a CC (first four in Table II), type-c CC (seven entries in the third group in Table II), and type-d CC (last four CC in Table II) bonds, the agreement between our results and Yamamoto et al.'s X-ray experiment is satis-

TABLE III: A Comparison of Theoretical and Low-Temperature X-ray^a Experimental Geometrical Parameters for the Nonplanar [7]Circulene

	STO-3G SCF	DZ SCF	DZP SCF	expt ^a
torsional angles ^b				
C(6)–C(7)–C(5)–C(3)	–7.0	–6.8	–7.0	–6.3
C(7)–C(5)–C(3)–C(1)	–28.8	–27.9	–28.7	–31.9
C(5)–C(3)–C(1)–C(2)	19.8	19.2	19.8	21.5
C(3)–C(1)–C(2)–C(4)	19.8	19.2	19.8	21.5
C(1)–C(2)–C(4)–C(6)	–28.8	–27.9	–28.7	–31.9
C(2)–C(4)–C(6)–C(7)	–7.0	–6.8	–7.0	–6.3
C(4)–C(6)–C(7)–C(5)	32.0	31.0	31.9	33.1
dihedral angles ^c				
A–B	15.1	15.0	15.3	16.4
B–C	20.8	20.3	20.9	23.1
C–C'	13.3	13.4	13.6	16.0
A–G	18.5	18.1	18.6	19.6
mean atomic dev ^d				
A	0.055	0.056	0.056	0.063
B	0.060	0.059	0.061	0.065
C	0.055	0.055	0.055	0.060
G	0.058	0.057	0.058	0.065

^a Yamamoto, K.; Harada, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M.; Kai, Y.; Nakao, T.; Tanaka, M.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 3578. Only the parameters pertaining to the shape of the molecule are considered in this table. Bond lengths are presented in Table II. ^b Around the CC bonds in the central seven-membered ring, in degrees. ^c Theoretical dihedral angles are between the "least squares" planes which fit the six carbon atoms of benzene rings involved. The values are in degrees. ^d Theoretical values are arithmetically averaged absolute deviations of the six carbon atoms from the "least squares" plane, in angstroms.

factory.⁷ However, there is a disagreement between theory and experiment on type-b CC bond lengths, the difference being on the order of 0.02 Å, the theoretical distances being shorter. Intuition would appear to suggest that the shorter type-b CC bonds are consistent with the global nonplanar feature of the geometry.

In Table III we have made a more direct comparison between our theoretical results and the X-ray analysis of Yamamoto et al.⁷ In observing the differences between the theoretical and X-ray experimental results, one may keep in mind that our theoretical results are for the equilibrium geometry (lowest point

on the potential energy surface). The X-ray results necessarily involve thermal averages due to vibrations. In the upper part of Table III, the torsional angles around each CC bond in the inner seven-membered ring are presented. Due to the presence of the C_2 symmetry axis, only four such torsional angles are symmetry independent. Firstly, one may observe that the torsional angles are quite insensitive to the change in basis sets. This suggests that it may be reasonable to apply the STO-3G basis set to much larger hydrocarbons. One may also conclude that the agreement between theory and the experimental crystal structure is very satisfactory. In the middle section of Table III, "dihedral angles" between adjacent benzene rings are presented. The seven benzene rings are designated A, A'; B, B'; C, C'; and G, following Yamamoto et al.⁷ Inasmuch as the benzene rings are not perfectly planar, there is really no unique measure of the tilt between any adjacent pairs. One measure may be the average of the two torsional angles around the CC bond common to the adjacent benzene rings. Another is the dihedral angle between two "least squares" planes which pass through the adjacent benzene rings (hydrogen atoms excluded). We have adopted the latter, as apparently did Yamamoto et al.⁷ Here the agreement between theory and experiment is again quite satisfactory, but there seems to be a more systematic difference: theoretical dihedral angles are uniformly smaller, or the theoretical geometry is systematically more planar. The third part of Table III presents the "arithmetic average of the absolute deviations" of carbon atoms with respect to individual "least squares planes". Again the agreement seems to be satisfactory, although there is a systematic difference in that the theoretical structures are more nearly planar.

The theoretical harmonic vibrational frequencies evaluated with the minimum STO-3G basis set are shown in Table IV. The most striking feature among the theoretical result is the presence of the very low-frequency mode of B symmetry. Since the estimated energy difference between the planar and C_2 forms is rather small (8.5 kcal/mol, Table II), one may expect that the totally symmetric out-of-plane motion should correspond to a low frequency. Indeed, this symmetric vibration has frequency 78 cm⁻¹. However, the lowest frequency belongs to the asymmetric (with respect to the 2-fold axis) vibration, which apparently corresponds to a continuous wave running through the molecule. The symmetry of this vibration explains why (even at room

TABLE IV: Theoretical STO-3G SCF Harmonic Vibrational Frequencies (in cm⁻¹) for the Planar D_{7h} and Nonplanar C_2 Stationary Points of the [7]Circulene Molecule

C_2 sym	D_{7h}	C_2	C_2 sym	D_{7h}	C_2	C_2 sym	D_{7h}	C_2
7A + 7B	3763–3730	3750–3720	B	1327	1343	B	811	795
A	2050	2006	A + B	1295	1304	A + B	756	746
A + B	2037	1998	A + B	1283	1293	A + B	738	729
A + B	1997	1971	A	1202	1203	B	708	715
A + B	1926	1914	B	1202	1201	B	644	649
B	1821	1815	A + B	1197	1198	A	617	637
A + B	1806	1797	B	1190	1191	B	617	633
A + B	1797	1792	A	1190	1192	A	598	579
B	1773	1752	A	1187	1185	B	598	567
A	1773	1756	A + B	1152	1178	B	564	536
A + B	1683	1675	A	1151	1163	A	564	537
B	1601	1607	B	1052	1067	A	554	576
A	1601	1605	A	1052	1064	A + B	523	535
B	1582	1594	B	1051	1058	A + B	481	488
A	1582	1596	B	1036	1026	A	462	487
A	1571	1585	A + B	1022	1014	A + B	424	436
B	1571	1579	A + B	991	984	B	344	370
A + B	1557	1555	A	982	984	A	344	321
A	1555	1550	B	982	981	B	321	328
A + B	1478	1475	B	938	933	A	321	330
B	1447	1439	A	938	934	B	310	324
B	1406	1383	A + B	926	927	A	310	325
A	1406	1387	A + B	888	877	B	198	157
A + B	1398	1382	A + B	863	868	A + B	194	227
A + B	1396	1381	B	825	807	A + B	70	125
A	1395	1384	A	825	803	A	62i	78
A	1327	1348	A	811	794	B	62i	4i

temperature) X-ray studies decisively determine the C_2 symmetry of the molecule. This vibration, due to the very rigid frame of the molecule, effects only marginally the molecular geometry and therefore may be considered a pseudorotational degree of freedom.

The force field (second-order derivatives of the total energy with respect to the symmetrized internal coordinates) of the molecule in internal coordinates is of interest. The CH stretch and CCH bend diagonal terms have their usual values of about 7.6 and 1.4 mdyn/Å, respectively. Comparatively "normal" are the CC stretching diagonal terms; their values are in the 10–29 mdyn/Å range. Similarly, the CC stretch–CC stretch off-diagonal force constants are relatively normal, i.e., no larger in absolute value than 6 mdyn/Å. However, some of the off-diagonal terms describing stretch–bend interactions are surprising in that they have absolute values slightly larger than the corresponding diagonal stretching terms. The diagonal CCC deformation force constants are quite remarkable; the smallest are about 30 mdyn/Å. There are some diagonal force constants as large as 268 mdyn/Å. The off-diagonal terms (CCC deformation–CCC deformation) are of the same order of magnitude. The torsional force constants are smaller, although some of them go up to 13 mdyn/Å. Consequently, it is difficult to provide an assignment of the theoretical vibrational spectrum in terms of independent CC stretchings, bendings, and torsions. For example, the CCC bending coordinates have significant contributions to vibrations with frequencies as high as 2000 cm^{-1} !

IV. Concluding Remarks

The [7]circulene molecule is very floppy, with a barrier of only 8.5 kcal/mol (DZP SCF) between the planar D_{7h} structure and the C_2 equilibrium geometry. For as many atoms to move so far with an energy difference this small is quite remarkable. This floppiness in combination with the relatively rigid benzene rings leads to the appearance of a very low-frequency (close to zero) vibration that may be characterized as a pseudorotation.

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References and Notes

- (1) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730.
- (2) Scholl, R.; Meyer, K. *Chem. Ber.* **1932**, *65*, 902.
- (3) Hanson, J. C.; Nordman, C. E. *Acta Crystallog. B* **1976**, *32*, 1147.
- (4) Robertson, J. M.; White, J. G. *J. Chem. Soc. London* **1945**, 607.
- (5) Dopfer, J. H.; Wynberg, H. *J. Org. Chem.* **1975**, *40*, 1975.
- (6) Yamamoto, K.; Harada, T.; Nakazaki, M.; Nakao, T.; Kai, Y.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 7171.
- (7) Yamamoto, K.; Harada, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M.; Kai, Y.; Nakao, T.; Tanaka, M.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 3578.
- (8) Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975.
- (9) Gleicher, G. J. *Tetrahedron* **1967**, *23*, 4257.
- (10) Price, S. L. *Chem. Phys. Lett.* **1985**, *114*, 359.
- (11) Schulman, J. M.; Peck, R. C.; Disch, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5675.
- (12) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.
- (13) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
- (14) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
- (15) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
- (16) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550.
- (17) Pulay, P.; Liu, R.; Zhou, X. Submitted for publication.
- (18) In practice, it is most expeditious to work with the normal form of a plane in three-dimensional space, $ax + by + cz - p = 0$, with $a = \cos \alpha$, $b = \cos \beta$, $c = \cos \gamma$, and $a^2 + b^2 + c^2 = 1$. The atoms have Cartesian coordinates (x_i, y_i, z_i) , $i = 1, 2, \dots, n$, with squared distance to the least squares plane $d_i^2 = (ax_i + by_i + cz_i - p)^2$. The sum of the squared distances may be denoted by Δ . The problem of finding the "least squares plane" is thus one of minimizing Δ with the constraint on a , b , and c , using Lagrange's method of undetermined multipliers. In order to facilitate the use of Lagrange's method, it is useful to shift the center of mass of the set of atoms to the origin (thus for the least squares plane we assume $p = 0$). The resulting equation is a 3×3 eigenvalue problem, with the eigenvector corresponding to the lowest eigenvalue giving the a , b , and c of the least squares plane.
- (19) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920.
- (20) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921.