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Gas-Phase Molecular Structure of Corannulene, $C_{20}H_{10}$. An Electron-Diffraction Study Augmented by ab Initio and Normal Coordinate Calculations

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The molecular structure of corannulene has been investigated by gas-phase electron diffraction with help from ab initio calculations at the B3LYP/6−31(d) level and normal coordinate analysis. The structure is closely similar to both that found in the crystal and that predicted from the molecular orbital calculation, but the carbon skeleton differs significantly from a C_{20} fragment of C_{60}. The molecule of C_{5v} symmetry is skull-cap shaped with five six-membered rings fused to the central five-membered ring and to each other. However, unlike C_{60} in which the corresponding hexagons are planar, the outermost pairs of carbon atoms with their hydrogens are bent out, tending to flatten the molecule. The bond lengths (r_g/Å) with uncertainties of 2σ for the four different types of C−C bonds in corannulene are, beginning with that held jointly by the pentagon and hexagon and proceeding around the hexagon, $C_1{-}C_2 = 1.414(6)$, $C_1{-}C_6 = 1.414(20)$, $C_6{-}C_7 = 1.447(16)$, and $C_7{-}C_8 = 1.380(16)$. The average C−C bond is about 0.022 Å shorter than in C_{60}. The structure is discussed.

Introduction

Corannulene was first synthesized over 30 years ago,[1] but it has only been in recent times that investigation of the properties of this interesting material has been possible due to the development of efficient preparatory methods.[2] A molecule of corannulene, $C_{20}H_{10}$, may be viewed as the upper one-third of a C_{60} molecule with the valences of the basal atoms saturated by hydrogen atoms: it is thus a sort of “skull-cap” or shallow, bowl-like molecule with C_{5v} symmetry (Figure 1). The corannulene skeleton has intrinsic interest as a fragment of the famous fullerene molecules, and the entire molecule has special interest because it inverts rapidly in solution (*ca* 200 kHz) at room temperature.[3] This motion is arrested in the crystal[4] where the molecule is clearly quite stiff, and the plane of the five-member ring is nearly 0.9 Å out of the plane of the 10 carbons (C_7, C_8, C_{10}, etc.) at the top of the bowl. It is also interesting that what appears to be only a small addition to the skeleton—replacement of the hydrogens on C_8 and C_{10} with a $-C(H){=}C(H)-$ or a $-C(H_2)\text{-}C(H_2)-$ group—essentially reduces the inversion rate to zero at room temperature.[5] This reflects the enforced “pyramidalization” of the carbon atoms over those of corannulene itself and hence leads to greater rigidity of the skeleton.

Although the X-ray work[4] leaves no doubt about the details of the corannulene structure in the crystal, the gas-phase structure, heretofore unknown, seemed worth investigating. Crystal- and gas-phase structures sometimes differ significantly, but apart from that, evidence about the inversion process is missing from the X-ray results. From past experience with similarly inverting systems (ammonia is the classic example), we did not expect our gas-phase electron-diffraction (GED) investigation to offer any direct evidence about the inversion dynamics, such as a distribution of molecules along the inversion coordinate, but it was possible that some conclusions about the dynamics might be drawn from measurements of vibrational amplitudes.

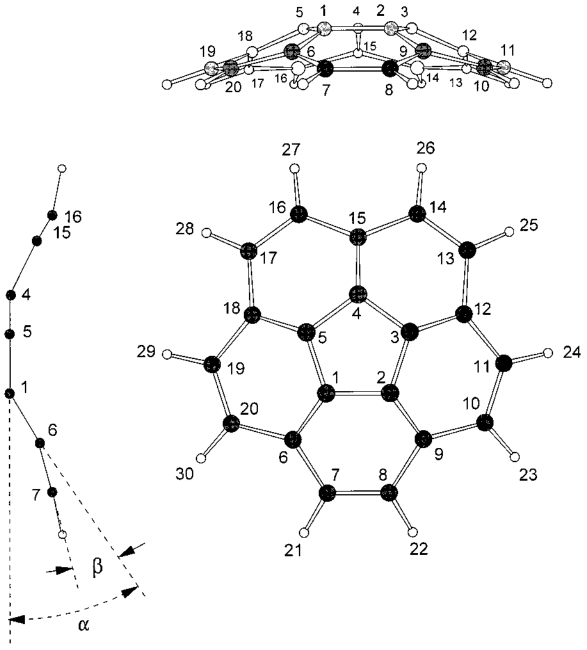

Figure 1. Diagrams of corannulene showing the atom numbering and the “pyramidalization” of the molecule. α is the dihedral angle between the five-membered ring and the adjacent half of the attached six-membered ring, i.e., ∠(5,1,2);(6,1,2). β is the dihedral angle between the two halves of the six-membered ring, i.e., ∠(6,1,2);(6,7,8).

Experimental Section

A corannulene sample was prepared at Boston College by the method previously described[2] and about 250 mg sent to Oregon State for the diffraction experiments. The sample was

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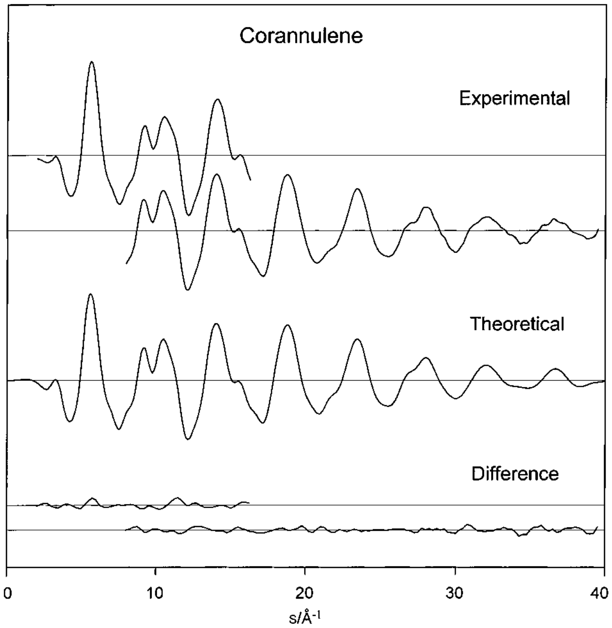


Figure 2. Intensity curves for corannulene. The difference curve is experimental minus theoretical.

volatilized from the high-temperature oven fitted with a needle valve used in our C_{60} and C_{70} work.[6,7] The oven temperature required to obtain sufficient vapor pressure for diffraction photographs was 302−303 °C. Other experimental conditions were an r^3 sector, Kodak electron image plates developed in D19 diluted 1:1, nominal camera distances of 75 cm (LC) and 30 cm (MC), a 60 kV accelerating potential, exposure times of 30−60 s (LC) and 120−200 s (MC), and an ambient background pressure during exposure of 2×10^{-6} Torr. One plate from each camera distance was selected for analysis. Three microphotometric traces of each plate were made while the plates were being rotated around the axis of the rings. The digital information resulting from these traces was averaged to give two data sets which were handled in the usual way[8,9] to yield scattered intensities over the ranges $2.00 \leq s/\text{Å}^{-1} \leq 16.25$ (LC) and $8.00 \leq s/\text{Å}^{-1} \leq 39.50$ (MC) in intervals $\Delta s/\text{Å}^{-1} = 0.25$. The electron-scattering factors and phases used in these and other calculations were taken from tables.[10] Intensity curves of these data are shown in Figure 2; the data are available as Supporting Information. The corresponding experimental radial distribution curve is shown in Figure 3; it was calculated from a composite of the intensity sets multiplied by $(Z_C^2/A_C^2)\exp(-0.0025)s^2$, where $A = s^2F$ and F is the magnitude of the complex electron-scattering amplitude. The experimental distribution of distances is consistent with the expected bowl-shaped molecule, and incompatible with planarity.

Structure Analysis

Molecular Orbital Calculations. A corannulene molecule of C_{5v} symmetry has four nonequivalent carbon−carbon bonds which would be expected to have similar values. This and other similarities among the remaining interatomic distances ensure that the interesting structural details cannot be determined from the GED data alone. As is now nearly routine in GED work, we used results from ab initio molecular orbital calculations[11] to derive certain structural constraints, and to obtain other data such as vibrational force constants. These calculations were performed at the levels HF/3-21G, HF/6-31G*, and B3LYP/6-31G*, giving the results summarized in Table 1.

Normal Coordinate Calculations. As is well-known, the effects of thermal averaging, or “shrinkage”,[12] lead to average interatomic distances that in many cases are not consistent with real structures. Corannulene, where the number of different distances is greater than the number of structure-defining parameters, is such a case. Although the inconsistencies were expected to be small—the order of thousandths of an angstrom—they were also expected to be large enough to introduce additional uncertainty into the values of some parameters obtained from our electron-diffraction analysis unless corrections were applied. These corrections are obtained from normal coordinate calculations.

Our calculations were done with the program ASYM40[13] which in an updated version allows the symmetrization of Cartesian force constants obtained from ab initio calculations. We used constants from the B3LYP/6-31G* calculation mentioned in the preceding section; the force constants from the other calculations did not differ enough to give significantly different distance corrections. The symmetry coordinates for a molecule of C_{5v} symmetry divide into four groups: a_1, a_2, e_1, and e_2. Although the choice of these coordinates has no effect on the values derived for the corrections themselves, nor on

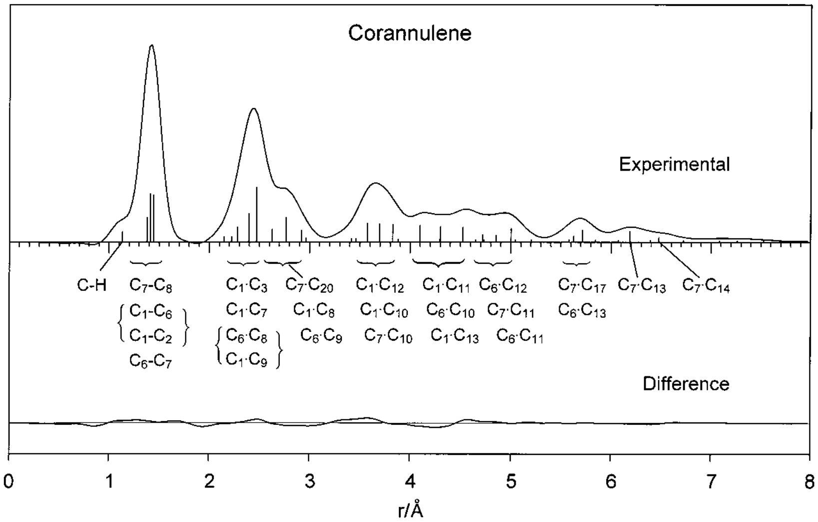


Figure 3. Radial distribution curves for corannulene. The vertical bars indicate all interatomic distances except H···H. Except for the C−H bond, only carbon−carbon distances are labeled. When two distances are approximately the same (indicated by the pairs in braces), the bars have been combined. Lengths of the bars indicate relative weights of the terms.

TABLE 1: Ab Initio Results from Optimizations of the Corannulene Structure[a]

	bond lengths/Å				out-of plane angles/deg		
	HF/3-21G	HF/6-31G*	B3LYP/6-31G*		HF/3-21G	HF/6-31G*	B3LYP/6-31G*
$r(\mathrm{CH})$	1.073	1.076	1.088	∠(7,21);(6,7,8)	-4.5	-4.1	-4.8
$r(\mathrm{C_1C_2})$	1.415	1.412	1.417	∠(1,6);(5,1,2)	-22.7	-21.1	-22.0
$r(\mathrm{C_1C_6})$	1.359	1.361	1.385	∠(6,1);(20,6,7)	-12.2	-12.1	-12.5
$r(\mathrm{C_6C_7})$	1.449	1.450	1.448				
$r(\mathrm{C_7C_8})$	1.368	1.370	1.390				

	bond angles/deg				torsion angles/deg		
	HF/3-21G	HF/6-31G*	B3LYP/6-31G*		HF/3-21G	HF/6-31G*	B3LYP/6-31G*
$\angle(\mathrm{C_6C_7H_{21}})$	119.2	119.5	119.4	$\angle(\mathrm{C_6C_1C_2C_9})$	0.0	0.0	0.0
$\angle(\mathrm{C_8C_7H_{21}})$	118.9	118.4	118.3	$\angle(\mathrm{C_1C_2C_9C_8})$	-9.9	-9.2	-9.5
$\angle(\mathrm{C_2C_1C_6})$	122.8	123.2	123.0	$\angle(\mathrm{C_2C_9C_8C_7})$	9.8	9.0	9.4
$\angle(\mathrm{C_1C_6C_7})$	114.7	114.1	114.2	$\angle(\mathrm{C_9C_8C_7C_6})$	0.0	0.0	0.0
$\angle(\mathrm{C_6C_7C_8})$	121.7	122.0	122.0	$\angle(\mathrm{C_8C_7C_6C_1})$	-9.8	-9.0	-9.4
$\angle(\mathrm{C_{20}C_6C_7})$	129.3	130.6	130.3	$\angle(\mathrm{C_7C_6C_1C_2})$	9.9	9.2	9.5
				$\angle(\mathrm{C_1C_6C_7H_{21}})$	175.4	175.7	176.1

	HF/3-21G	HF/6-31G*	B3LYP/6-31G*
energy/E_h	−758.908 176 0	−763.189 2878	−768.149 327 5

[a] Atom numbering from Figure 1.

TABLE 2: Symmetry Coordinates for the Five-Member Ring of Corannulene[a]

a_1	$S_2 = 1/\sqrt{5}\,(r_{12} + r_{23} + r_{34} + r_{45} + r_{51})$
e_1(a)	$S_{19} = 1/\sqrt{\mathrm{n}}^{b}\,(r_{12} + \alpha\, r_{23} + \beta\, r_{34} + \beta\, r_{45} + \alpha\, r_{51})$
e_2(a)	$S_{35} = 1/\sqrt{\mathrm{n}}^{b}\,(r_{12} + \beta\, r_{23} + \alpha\, r_{34} + \alpha\, r_{45} + \beta\, r_{51})$
	$S_{42} = 1/\sqrt{n}^{b}\,(\varphi_{345} + \beta\varphi_{451} + \alpha\varphi_{512} + \alpha\varphi_{123} + \beta\varphi_{234})$
	$S_{47} = 1/\sqrt{n}^{b}\,(-\delta\tau_{1234} + \gamma\tau_{2345} - \gamma\tau_{3451} + \delta\tau_{4512})$
e_1(b)	$S_{53} = 1/\sqrt{n}^{b}\,(\gamma r_{23} + \delta\, r_{34} - \delta\, r_{45} - \gamma\, r_{51})$
e_2(b)	$S_{69} = 1/\sqrt{n}^{b}\,(\delta r_{23} - \gamma r_{34} + \gamma r_{45} - \delta r_{51})$
	$S_{76} = 1/\sqrt{n}^{b}\,(\delta\,\varphi_{451} - \gamma\varphi_{512} + \gamma\varphi_{123} - \delta\varphi_{234})$
	$S_{81} = 1/\sqrt{n}^{b}\,(\tau_{5123} + \beta\tau_{1234} + \alpha\tau_{2345} + \alpha\tau_{3451} + \beta\tau_{4512})$

[a] $\alpha = \cos 2\pi/5$, $\beta = \cos 4\pi/5$, $\gamma = \sin 2\pi/5$, $\delta = \sin 4\pi/5$, r = bond distance, φ = bond angle, τ = torsion angle. [b] n = sum of squares of coefficients.

other quantities such as calculated mean amplitudes of vibration, the choice does determine the values of the symmetry force constants. Because of the large number of internal coordinates, it is possible to construct many different combinations of the simple stretch, bend, out-of-plane, and torsional motions that obey the symmetry requirements. However, for certain combinations, especially those connected with bending and out-of-plane coordinates, many elements of the symmetrized **F**-matrix can obtain very large values that are inconsistent with experience. Our final choice has avoided much of this, but there are still fairly large values for several of the interaction constants that are clearly connnected with the fused ring structure of the molecule. Our set of symmetry coordinates is defined in Table S1 of the Supporting Information in terms of the internal coordinates listed in Table S2. Together with the geometry and Cartesian force constants provided by the B3LYP/6-31G* optimization, these symmetry coordinates yielded the force constants and wavenumbers seen in Table S3. Table 2 provides an example of the use of Tables S1 and S2 to generate the symmetry coordinates.

Model Specification. The corannulene molecule was assumed to have C_{5v} symmetry and accordingly its structure is defined by the values of nine parameters. These were chosen as the bond lengths $r(\mathrm{C{-}H})$ and $r(\mathrm{C_1{-}C_2})$; the bond-length differences $r(\mathrm{C_1{-}C_6}) - r(\mathrm{C_1{-}C_2})$ and $r(\mathrm{C_6{-}C_7}) - r(\mathrm{C_1{-}C_2})$; the bond angle $\angle(\mathrm{C_{20}{-}C_6{-}C_7})$; the angle between the $\mathrm{C_1{-}C_6}$ bond vector and the plane of the five-member ring, ∠(1,6);(5,1,2); the angle between the $\mathrm{C_6{-}C_1}$ bond vector and the plane defined by atoms $\mathrm{C_{20}}$, $\mathrm{C_6}$, and $\mathrm{C_7}$, ∠(6,1);(20,6,7); the angle between the projection of a carbon−hydrogen bond onto the plane defined by the adjacent carbon−carbon bonds and the bisector of the angle made by those bonds, $\angle(\mathrm{CH})_{\mathrm{prj}};(\mathrm{CCC})_{\mathrm{bsct}}$; and the angle between a carbon−hydrogen bond and the plane defined by the adjacent carbon−carbon bonds, ∠(7,21);(6,7,8). There are 390 different distances exclusive of H••H in the molecule (H•••H terms were ignored), but the multiplicities of five and 10 reduce this number to 44, each of which has an associated amplitude of vibration. These were collected into eight groups for ultimate refinement; within each group, group-member amplitudes were set to reflect differences obtained from the ASYM40 calculations.

Structure Refinements. The structure refinements were carried out in the usual way[14] by a least-squares fitting of a theoretical intensity curve simultaneously to the two experimental curves. It was found that the two angle parameters defining the positions of the hydrogen atoms, $\angle(\mathrm{CH})_{\mathrm{prj}};(\mathrm{CCC})_{\mathrm{bsct}}$ and ∠(7,21);(6,7,8), were determined with such large uncertainties that the values had no significance. They were assigned values obtained from the ab initio calculations. Results for two models are presented in Tables 3 and 4. Model A is based on the parameters defined in r_α space and thus represents a set of distances consistent with the restrictions of C_{5v} symmetry; it is the preferred model. Model B lacks the distance corrections $r_a - r_\alpha$ and is, strictly speaking, not consistent with C_{5v} symmetry. Comparison of the results for the two models shows, however, that the differences are very small. Table 5 is the correlation matrix for the parameters of Model A.

Discussion

A comparison of the structure of corannulene in the gas, its average structure in the crystal,[4] and the theoretical structure (B3LYP/6-31G*) is given in Table 3. The X-ray values are averages derived from each of the two crystallographically independent molecules. Differences between the two values for corresponding pairs of parameters are presumably due to the different packing forces for each molecule arising from their different structural environments. These parameter differences are small (those for carbon−carbon bond lengths and bond angles seem to be less than 0.02 Å and 1°), and similar to the differences between the gas-phase values and the crystal values averaged over both molecules (respectively 0.015 Å, 0.2° and

TABLE 3: Experimental (r_α,$\angle_\alpha$) and Theoretical (r_e,$\angle_e$) Parameter Values for Corannulene[a]

	this work (303 °C)		X-ray (20 °C)[b]		
	model A[d]	model B	molecule 1	molecule 2	theory[c]
structure-defining parameters					
$r(\mathrm{C{-}H})$	1.112 (17)	1.130 (17)	0.99 (3)	1.05 (2)	1.0878
$r(\mathrm{C_1{-}C_2})$	1.410 (6)	1.412 (7)	1.419 (2)	1.402 (7)	1.4167
$r(\mathrm{C_1{-}C_6}) - r(\mathrm{C_1{-}C_2})$	−0.002 (24)	0.003 (26)	−0.025	0.008	−0.0319
$r(\mathrm{C_6{-}C_7}) - r(\mathrm{C_1{-}C_2})$	0.031 (14)	0.032 (16)	0.024	0.025	0.0313
$\angle(\mathrm{C_{20}{-}C_6{-}C_7})$	131.5 (23)	131.6 (25)	129.8 (3)	130.5 (5)	130.3
$\angle(1,6);(5,1,2)$[e]	24.4 (21)	24.8 (22)	22.4 (3)[f]		22.0
$\angle(6,1);(20,6,7)$[e]	−8.8 (84)	−8.1 (92)	−11.6[f]		−12.5
$\angle(\mathrm{CH})_{\mathrm{prj}};(\mathrm{CCC})_{\mathrm{bsct}}$ [g]	[0.5]	[0.5]			0.5
$\angle(7,21);(6,7,8)$[e]	[−4.8]	[−4.8]			−4.8
other parameters					
$\langle r(\mathrm{C{-}C})\rangle$	1.414 (2)	1.418 (2)	1.417	1.419	1.417
$\angle(\mathrm{C_2{-}C_1{-}C_6})$	122.4 (6)	122.3 (6)	122.9 (1)	123.1 (3)	123.0
$\angle(\mathrm{C_1{-}C_6{-}C_7})$	113.9 (6)	113.9 (7)	114.4 (2)	114.2 (4)	114.2
$\angle(\mathrm{C_6{-}C_7{-}C_8})$	122.4 (4)	122.4 (4)	121.9 (2)	122.1 (3)	122.0
$\angle(\mathrm{C_6{-}C_7{-}H_{21}})$	119.2 (2)	119.2 (2)	119 (2)	113 (4)	119.4
$\angle(\mathrm{C_8{-}C_7{-}H_{21}})$	118.2 (2)	118.2 (2)	118 (2)	124 (4)	118.3
$\angle(5,1,2);(6,1,2)$[h] $= \angle\alpha$	29.3 (23)	29.7 (25)	27.0 (3)	26.0 (3)	26.5
$\angle(6,1,2);(6,7,8)$[h] $= \angle\beta$	13.8 (56)	14.5 (61)	10.3 (3)	10.0 (2)	10.2
$\angle(6,7,8);(21,7,8)$[h]	[−5.4]	[−5.4]	6 (1)	9 (2)	−5.4
R[i]	0.0832	0.0834	0.069		

[a] Distances in angströms, angles in degrees. Uncertainties are estimated 2σ (this work) and σ (X-ray). [b] Reference 4. Values are averages from two crystallographically independent molecules. [c] B3LYP/6-31G*. [d] Preferred model, C_{5v} symmetry. [e] Out-of-plane angle between the indicated bond and plane. [f] Average from both molecules. [g] In the group C−C(H)-C, the angle between the bisector of the C−C−C angle and the projection of the C−H bond onto the C−C−C plane. [h] Interplanar angles; see Figure 1. [i] Quality of fit factor: $R = [\sum_i w_i\Delta_i^2/\sum_i I_i(\mathrm{obsd})^2]^{1/2}$; $\Delta_i = I_i(\mathrm{obsd}) - I_i(\mathrm{calcd})$ with $I_i = s_i I_m(s_i)$.

TABLE 4: Distances (r/Å) and Amplitudes of Vibration (l/Å) for Corannulene

	model A (preferred)					model B			B3LYP/6-31G*	
	r_α [a]	r_g [b]	r_a [c]	l[d]		r_a [c]	l[d]		r_e [e]	l
$\mathrm{C{-}H}$	1.112	1.136 (17)	1.132	0.070 (16)		1.130 (17)	0.069 (15)		1.088	0.076
$\mathrm{C_1{-}C_2}$	1.410	1.414 (6)	1.412	0.053	(6)	1.412 (7)	0.053	(7)	1.417	0.047
$\mathrm{C_1{-}C_6}$	1.408	1.414 (20)	1.412	0.051		1.414 (22)	0.051		1.385	0.045
$\mathrm{C_6{-}C_7}$	1.441	1.447 (16)	1.445	0.057		1.443 (17)	0.057		1.448	0.051
$\mathrm{C_7{-}C_8}$	1.374	1.380 (16)	1.378	0.052		1.375 (17)	0.052		1.390	0.046
$\mathrm{C_6 \cdot H_{21}}$	2.207	2.227 (23)	2.221	0.113	(43)	2.225 (23)	0.115	(45)	2.197	0.102
$\mathrm{C_8 \cdot H_{21}}$	2.137	2.154 (20)	2.148	0.112		2.153 (20)	0.114		2.133	0.101
$\mathrm{C_1 \cdot C_3}$	2.281	2.285 (10)	2.283	0.056	(6)	2.284 (11)	0.057	(6)	2.292	0.056
$\mathrm{C_1 \cdot C_7}$	2.388	2.395 (8)	2.393	0.061		2.496 (9)	0.062		2.379	0.061
$\mathrm{C_1 \cdot C_9}$	2.469	2.476 (10)	2.474	0.074		2.475 (10)	0.075		2.462	0.074
$\mathrm{C_6 \cdot C_8}$	2.466	2.472 (9)	2.471	0.069		2.470 (9)	0.070		2.482	0.069
$\mathrm{C_7 \cdot C_{20}}$	2.627	2.631 (12)	2.630	0.061		2.634 (13)	0.062		2.628	0.061
$\mathrm{C_1 \cdot C_8}$	2.764	2.770 (5)	2.769	0.061		2.771 (6)	0.062		2.762	0.061
$\mathrm{C_6 \cdot C_9}$	2.917	2.922 (11)	2.920	0.073		2.922 (11)	0.074		2.926	0.073
$\mathrm{C_1 \cdot C_{12}}$	3.571	3.575 (9)	3.573	0.084	(14)	3.578 (10)	0.085	(15)	3.574	0.069
$\mathrm{C_1 \cdot C_{10}}$	3.692	3.696 (8)	3.694	0.089		3.701 (8)	0.090		3.695	0.074
$\mathrm{C_7 \cdot C_{10}}$	3.824	3.828 (10)	3.826	0.083		3.832 (11)	0.084		3.840	0.068
$\mathrm{C_1 \cdot C_{11}}$	4.095	4.098 (7)	4.096	0.082	(12)	4.103 (7)	0.081	(11)	4.103	0.075
$\mathrm{C_6 \cdot C_{10}}$	4.299	4.303 (12)	4.301	0.092		4.307 (12)	0.091		4.313	0.085
$\mathrm{C_1 \cdot C_{13}}$	4.524	4.528 (9)	4.526	0.096		4.534 (9)	0.095		4.534	0.089
$\mathrm{C_6 \cdot C_{12}}$	4.720	4.723 (18)	4.721	0.093		4.727 (18)	0.092		4.734	0.086
$\mathrm{C_7 \cdot C_{11}}$	4.849	4.852 (19)	4.850	0.104		4.858 (20)	0.103		4.876	0.097
$\mathrm{C_6 \cdot C_{11}}$	4.997	5.003 (12)	5.001	0.087		5.005 (12)	0.086		5.108	0.080
$\mathrm{C_7 \cdot C_{17}}$	5.624	5.629 (14)	5.628	0.095	(17)	5.636 (15)	0.095	(17)	5.642	0.085
$\mathrm{C_6 \cdot C_{13}}$	5.712	5.715 (13)	5.713	0.117		5.722 (13)	0.117		5.733	0.107
$\mathrm{C_7 \cdot C_{13}}$	6.188	6.190 (17)	6.188	0.120		6.201 (17)	0.120		6.213	0.110
$\mathrm{C_7 \cdot C_{14}}$	6.473	6.477 (18)	6.475	0.114		6.486 (19)	0.114		6.500	0.104
$\mathrm{C_7 \cdot H_{30}}$	2.955	2.971 (17)	2.965	0.139	(54)	2.970 (17)	0.144	(60)	2.940	0.097
$\mathrm{C_1 \cdot H_{21}}$	3.405	3.420 (20)	3.414	0.141		3.431 (20)	0.146		3.374	0.099
$\mathrm{C_6 \cdot H_{22}}$	3.456	3.468 (21)	3.461	0.151		3.477 (21)	0.156		3.452	0.109
$\mathrm{C_1 \cdot H_{22}}$	3.875	3.885 (20)	3.880	0.146		3.901 (20)	0.151		3.849	0.104
$\mathrm{C_7 \cdot H_{23}}$	4.290	4.299 (22)	4.294	0.152		4.308 (24)	0.157		4.288	0.110
$\mathrm{C_1 \cdot H_{23}}$	4.639	4.655 (18)	4.650	0.141		4.665 (17)	0.146		4.618	0.099
$\mathrm{C_7 \cdot H_{29}}$	4.729	4.740 (20)	4.733	0.181		4.753 (21)	0.186		4.723	0.139
$\mathrm{C_6 \cdot H_{23}}$	5.041	5.050 (16)	5.044	0.165		5.063 (16)	0.170		5.035	0.123
$\mathrm{C_1 \cdot H_{24}}$	5.201	5.208 (19)	5.202	0.181		5.229 (19)	0.186		5.184	0.139
$\mathrm{C_1 \cdot H_{25}}$	5.574	5.587 (19)	5.581	0.191		5.603 (19)	0.196		5.558	0.149
$\mathrm{C_7 \cdot H_{24}}$	5.839	5.849 (30)	5.844	0.166		5.865 (32)	0.171		5.842	0.124
$\mathrm{C_6 \cdot H_{24}}$	6.071	6.077 (21)	6.071	0.199		6.098 (21)	0.204		6.068	0.157
$\mathrm{C_7 \cdot H_{28}}$	6.390	6.396 (27)	6.390	0.193		6.417 (29)	0.198		6.384	0.151
$\mathrm{C_6 \cdot H_{25}}$	6.721	6.728 (21)	6.723	0.188		6.749 (21)	0.193		6.717	0.146
$\mathrm{C_7 \cdot H_{25}}$	7.081	7.089 (32)	7.083	0.203		7.110 (35)	0.207		7.081	0.160
$\mathrm{C_7 \cdot H_{27}}$	7.252	7.264 (31)	7.261	0.163		7.283 (33)	0.168		7.250	0.121
$\mathrm{C_7 \cdot H_{26}}$	7.512	7.534 (33)	7.529	0.188		7.549 (36)	0.193		7.517	0.146

[a] Distance between average nuclear positions. [b] Thermal average distance: $r_g = r_a + \langle\Delta r\rangle$. [c] Electron-diffraction distance parameter: $r_a = r_g - l^2/r$. [d] Uncertainties in parentheses are estimated 2σ. [e] Equilibrium distance.

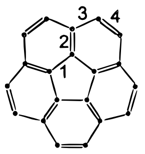
TABLE 5: Correlation Matrix (×100) for Parameters of Model A[a]

	parameter[b]	$\sigma_{LS} \times 100$[c]	r_1	r_2	r_3	r_4	$\angle_5$	$\angle_6$	$\angle_7$	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}
1	$r(C-H)$	0.61	100														
2	$r(C_1-C_2)$	0.22	10	100													
3	$r(C_1-C_6) - r(C_1-C_2)$	0.89	−15	−72	100												
4	$r(C_6-C_7) - r(C_1-C_2)$	0.53	19	<1	−59	100											
5	$\angle(C_{20}-C_6-C_7)$	86.7	−17	−46	91	−79	100										
6	$\angle(1,6);(5,1,2)$[d]	76.6	15	37	−86	77	−91	100									
7	$\angle(6,1);(20,6,7)$[d]	311.	−17	−47	84	−78	95	−93	100								
8	$l(C_7-H_{21})$	0.54	1	13	−21	14	−19	18	−15	100							
9	$l(C_1-C_2)$	0.22	−21	−39	66	−83	76	−68	82	−14	100						
10	$l(C_6-H_{21})$	1.53	−3	−62	43	7	26	−20	26	−4	14	100					
11	$l(C_1-C_3)$	0.20	13	−23	−2	57	−25	10	−23	−1	−45	37	100				
12	$l(C_1-C_{12})$	0.48	8	23	−15	2	−14	12	−17	<1	−8	−17	−1	100			
13	$l(C_1-C_{11})$	0.41	−5	−6	6	−6	3	−8	6	−2	9	<1	1	−8	100		
14	$l(C_7-C_{17})$	0.59	−3	−6	7	−1	6	−6	7	−2	5	3	5	<1	3	100	
15	$l(C_7-C_{30})$	1.96	8	−1	−23	26	−26	22	−16	8	−11	−2	10	32	13	3	100

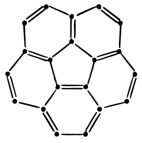
[a] Preferred model (C_{5v} symmetry). [b] For atom numbering, see Figure 1. [c] Standard deviations from least-squares fitting; distances (r) and amplitudes (l) in angströms, angles (∠) in degrees. [d] See text for description of parameters.

0.6° for bond lengths, bond angles, and dihedral angles). The implication is that the packing forces are small. The theoretical values also agree well with the experimental ones. More detailed comparisons are difficult because of uncertainty about systematic deficiencies in the theoretical level used for the calculations, and because the electron-diffraction, X-ray, and theoretical results in principle concern different distance types from samples at quite different temperatures. We regard the agreement among the structural results from these different methods as excellent.

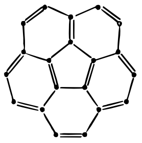
There are four different types of carbon−carbon bonds in corannulene, and one may attempt to understand their relative lengths in terms of classical resonance structures.[15] The three Kekule-type structures are shown in the following scheme. Structure **1** has a multiplicity of one, but both **2** and **3** each represent five equivalent resonance structures. Taking into account these multiplicities, one finds the fraction of double-bond character for bonds 1, 2, 3, and 4 to be respectively 0.27, 0.46, 0.27, and 0.73; in other words, the shortest bond is predicted to be 4 (C_7-C_8) and the longest 3 (C_6-C_7) or 1 (C_1-C_2), with 2 (C_1-C_6) in between. As Table 4 shows, the experimental lengths of three of these bonds agree with the prediction of 4 as the shortest, 3 as the longest, and 2 intermediate. However, 1 is out of line with prediction. Although the experimental uncertainties diminish the reliability of these bond-length comparisons, it remains both pleasing and mildly surprising that the relative values of the bond lengths even in this nonplanar molecule predicted by the old concept of resonance among Kekule structures is in reasonable agreement with observation.



1



2



3

It was pointed out earlier that the carbon skeletons of corannulene and a 20-atom fragment of the C_{60} molecule containing a five-membered ring have the same atomic arrangement. However, instead of the four carbon−carbon bond types in corannulene, there are only two in the corresponding fragment of C_{60}. The lengths of those bonds with similar environments in the two molecules are those within the five-membered ring, C_1-C_2, and those leading from it, C_1-C_6. Of the bonds within the ring, those in corannulene are significantly shorter (ca. 0.04 Å) than those in C_{60}, whereas those leading from the ring are slightly longer (ca. 0.01 Å). The average bond length in C_{60} is 1.436 Å, about 0.024 Å longer than the average of the *similar* bonds in corannulene. The reason for these differences may lie in the interplanar angles which, to the extent that they differ from zero, reduce the π-bonding and strain the molecular skeletons. The following simple ideas account qualitatively for the relative lengths of the bonds in corannulene. The angle in C_{60} corresponding to α (Figure 1) is −37.4° (−24.3° in corannulene), whereas β is 0° (13.6° in corannulene). These values suggest the strain is less from $\angle\alpha$ in corannulene, which should lead to shorter bonds in the five-membered ring of this molecule. On the other hand, the strain is greater from $\angle\beta$ (the flap angle of the six-membered ring) in corannulene than in C_{60}, which should lead to longer "spokes" in the former through the lesser conjugation. In corannulene itself the strain from $\angle\beta$ should also lengthen the C_6-C_7 bond and concentrate the π overlap in the C_7-C_8 bond, making the former longer and the latter shorter.

Although corannulene inverts at 200 kHz,[3] as expected there is no evidence of inversion in the diffraction data. In our models such evidence would consist of abnormally large amplitudes of vibration caused by "pseudoconformers", or molecules with altered shapes, distributed along the inversion coordinate. The absence of this evidence implies a high barrier to inversion which localizes most of the molecules in the region of the potential minima.

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Supporting Information Available: Tables of the coefficients of internal coordinates comprising symmetry coordinates for corannulene, the definitions of internal coordinates comprising the symmetry coordinates, the symmetry force constants and wavenumbers calculated at the B3LYP/6-31G* level, and the molecular intensity data. This material is available free of charge via the Internet at http://pubs.acs.org.

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