

# Gas-Phase Molecular Structure of Decachlorocorannulene, C<sub>20</sub>Cl<sub>10</sub>. An Electron-Diffraction Study Augmented by *ab Initio*, DFT, and Normal Coordinate Calculations

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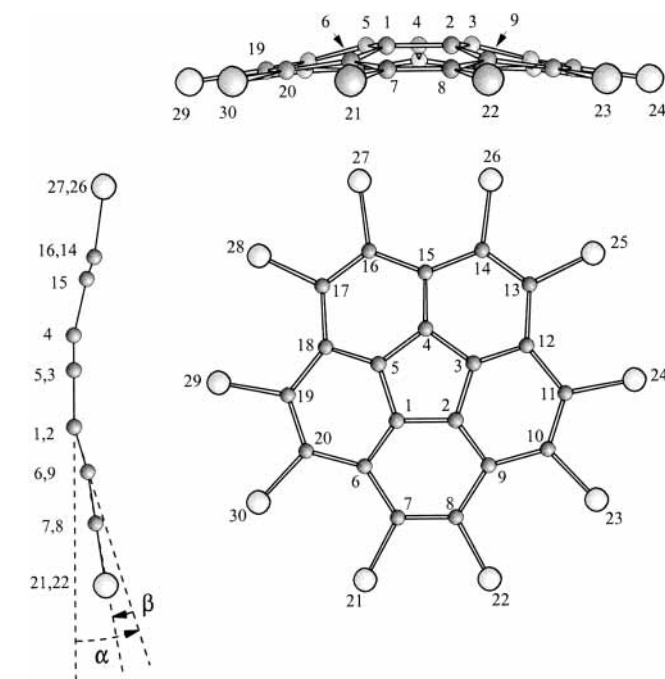
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The molecular structure of decachlorocorannulene has been investigated by gas-phase electron diffraction with help from quantum chemical calculations at the HF and B3LYP level with several basis sets and from normal coordinate analysis. The structure is in excellent agreement with the prediction from the B3LYP/6-311G\* calculation. The molecule of C<sub>5v</sub> symmetry is bowl-shaped with five six-membered rings fused to the central five-membered ring and to each other. The bowl is flatter than the similar corannulene molecule and is consistent with the lower inversion barrier predicted from calculations. The bond lengths ( $r_g/\text{Å}$ ) with uncertainties of  $2\sigma$  for the four different types of C–C bonds are C<sub>1</sub>–C<sub>2</sub> (in the C<sub>5</sub> ring, or “hub”) = 1.421(17), C<sub>1</sub>–C<sub>6</sub> (spokes from the hub) = 1.383(23), C<sub>6</sub>–C<sub>7</sub> (flanking bonds from ends of spokes) = 1.472(18), and C<sub>7</sub>–C<sub>8</sub> (the rim bonds) = 1.410(27). The C–Cl bond length is 1.732(5) Å.

## Introduction

This research comprises a part of our program of work on the structures of fullerenes and their derivatives and on molecules with carbon skeletons comprising fullerene fragments. These have so far included C<sub>60</sub>,<sup>1</sup> C<sub>70</sub>,<sup>2</sup> and corannulene (C<sub>20</sub>H<sub>10</sub>, hereafter CA).<sup>3</sup> CA may be viewed as the upper one-third of a C<sub>60</sub> molecule with the valences of the outermost atoms saturated by H atoms. The molecule is shaped like a shallow bowl with C<sub>5v</sub> symmetry (Figures 1 and 2) and has a number of interesting properties. These include a rapid inversion rate of ca. 200 kHz at room temperature in solution<sup>4</sup> that is arrested in the solid.<sup>5</sup> It is also arrested in solution by certain substitutions, e.g., by –CH=CH–, of hydrogens on *peri*-oriented CH rim atoms.<sup>6</sup> In this case, the result is a fused cyclopentene ring which increases the “pyramidalization” of all carbon atoms, stiffens the skeleton, and thus raises the inversion barrier.

Some interesting symmetrical derivatives of CA are known. *sym*-pentamethylcorannulene and decamethylcorannulene have been synthesized and quantum chemical calculations carried out at several levels of theory with a variety of basis sets.<sup>7</sup> The calculations predict the bowl shape of decamethylcorannulene to be significantly flatter, and the inversion barrier to be much less, than those of either *sym*-pentamethylcorannulene or CA itself. The predicted flattening is apparently in response to steric repulsion across the *peri* positions, which tends to destabilize the bowl shape relative to the flat conformation. Some bond length changes are also predicted: the flank (C<sub>6</sub>–C<sub>7</sub>) and the rim (C<sub>7</sub>–C<sub>8</sub>) bonds are both longer and the hub (C<sub>1</sub>–C<sub>2</sub>) bond shorter than in CA. The bond length of the spokes (C<sub>1</sub>–C<sub>6</sub>) is about the same. Experimental work on the structures of these molecules seems not to exist.



**Figure 1.** Diagrams of the decachlorocorannulene structure with atom numbering. Corannulene is similar.

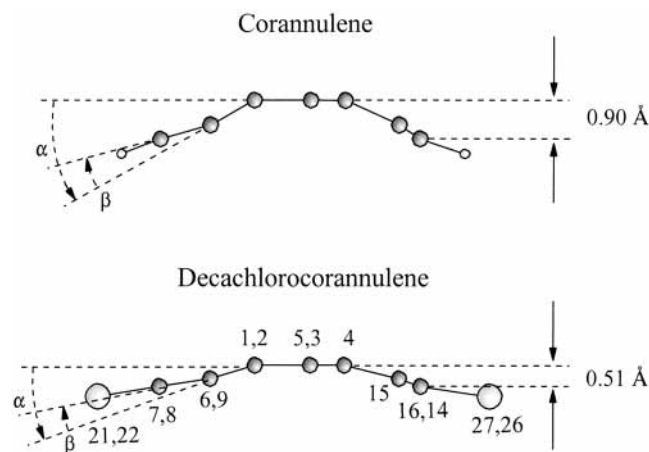
Decachlorocorannulene (hereafter DCA) was first synthesized in 1994 from corannulene by Scott and Cheng<sup>8,9</sup> using the Ballester method for perchlorination of polycyclic aromatic hydrocarbons.<sup>10</sup> Siegal and co-workers have subsequently reported that the same method also works to convert 1,10-dichlorocorannulene to DCA.<sup>7,11</sup> Under suitable conditions, the 10 chlorine atoms can all be replaced with either thioethers<sup>10</sup> or methyl groups.<sup>12,13</sup> Several nonspecific preparations of DCA have recently been reported by Zheng et al.<sup>12–15</sup> but so far these have not been developed into practical syntheses.

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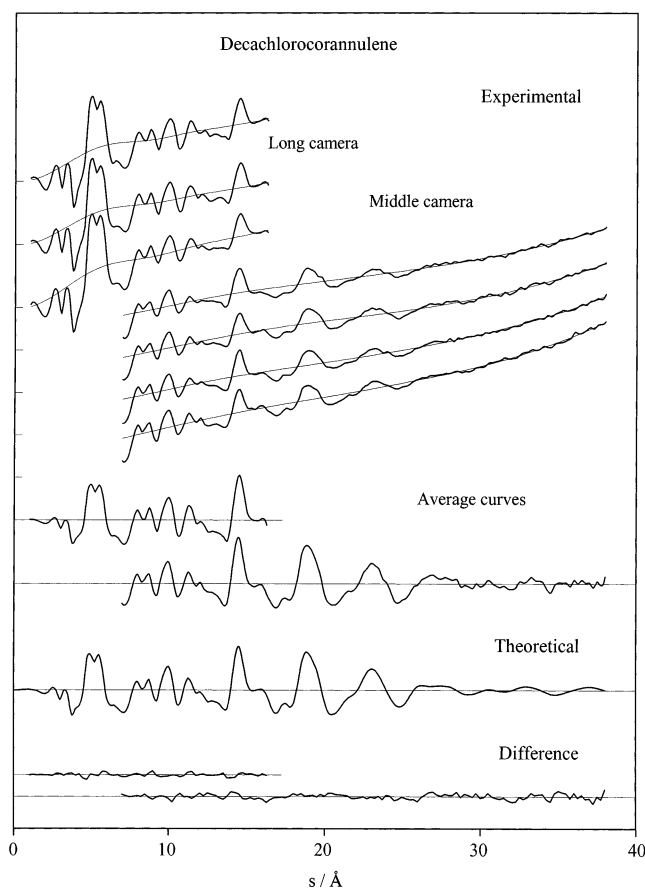
**Figure 2.** Diagrams of the corannulene and decachlorocorannulene structures showing a comparison of the flatness of the molecules. For corannulene, the angles  $\alpha$  and  $\beta$  are  $-29.3 \pm 2.3^\circ$  and  $+13.8 \pm 5.6^\circ$  and for decachlorocorannulene  $-16.6 \pm 3.5^\circ$  and  $+7.9 \pm 2.1^\circ$ .

The first ab initio molecular orbital calculations on DCA appeared in 1998.<sup>16</sup> Zheng et al. reported a mass spectrometric technique for detecting DCA in 1999,<sup>17</sup> but there has apparently not yet been a structure determination of this molecule in either the gaseous or the solid state. DCA is a good candidate for a gas-phase electron-diffraction (GED) investigation, which has added importance because of the lack of direct structure measurements on the other symmetrically substituted corannulenes. The following is an account of our investigation.

### Experimental Section

**Preparation of DCA.** A significantly improved experimental procedure for the direct chlorination of corannulene to form DCA was used for the current study and is found in the Supplementary Information.

**Electron Diffraction.** A 260 mg sample of DCA, which had a brown-yellow color, was sent to Oregon State for the GED experiments. The sample was volatilized from the high-temperature oven fitted with a needle valve used in our CA,<sup>3</sup> C<sub>60</sub>,<sup>1</sup> and C<sub>70</sub><sup>2</sup> work. Several groups of diffraction experiments were done over a period of several months when it became apparent that the early patterns held evidence of substantial amounts of an impurity. For example, the radial distribution curves calculated from the first groups of diffraction patterns did not show the expected prominent peak corresponding to a C–Cl bond. Investigation revealed that the suspected impurity was likely diphenyl ether which had been used as a solvent during the preparation.<sup>18</sup> Because the electron-diffraction experiment required volatilization of the solid sample, we reasoned that it could serve as a crude purification-via-fractionation method. The diffraction data eventually used in the structure analysis were obtained as follows. The sample, expected to be relatively involatile below about 400 °C, was placed in the oven and gradually heated to 200 °C with the needle valve open. Evidence for escaping vapor was obtained by closing and opening this valve, which resulted in small pressure changes in the main chamber. Heating with the needle valve open was then continued at 250 °C for 40 min. The next day the sample was slowly heated to 360 °C during which the main chamber pressure at first increased from  $3.0 \times 10^{-6}$  to  $9.0 \times 10^{-6}$  Torr and, after 6 min, began to decrease. The sample was then slowly heated to 450 °C. Two films of the diffraction pattern were made at this nozzle temperature, and a third was made at 473 °C, all at the “long camera” (LC) distance. Four middle camera (MC)



**Figure 3.** Intensity curves for decachlorocorannulene. Data from individual plates are shown magnified 10 times with respect to the backgrounds on which they are superimposed. The average curves are from the long and middle distances with backgrounds removed. The theoretical curve is for model A. The difference curve is experimental minus theoretical.

films were next recorded at a nozzle temperature of 479 °C. The sector opening, accelerating potential, films, and camera distances were similar to those described for CA.<sup>3</sup> Exposure times were 180–210 s (LC) and 240–360 s (MC); ambient background pressure during exposure was about  $1.0\text{--}1.4 \times 10^{-6}$  Torr, and the ranges of scattered intensities were  $1.00 \leq s/\text{Å}^{-1} \leq 16.25$  (LC) and  $7.00 \leq s/\text{Å}^{-1} \leq 38.00$  (MC) at a data interval  $\Delta s/\text{Å}^{-1} = 0.25$ . Intensity curves of these data are shown in Figure 3; the data are available as Supporting Information. The corresponding experimental radial distribution curve is shown in Figure 4. The leveling-damping factor was  $(Z_{\text{C}}Z_{\text{Cl}}/A_{\text{C}}A_{\text{Cl}}) \exp(-0.0025)s^2$ . As with CA itself, the distance distribution is consistent with the expected bowl-shaped molecule and incompatible with planarity.

### Structure Analysis

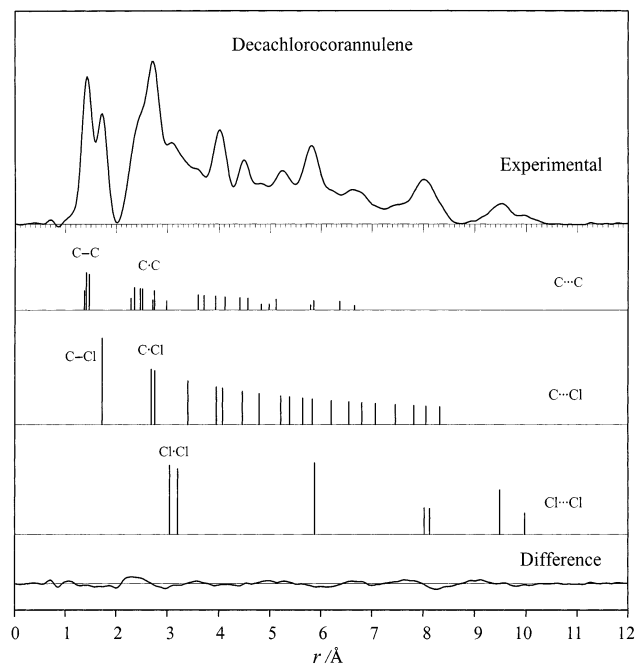
**Molecular Orbital Calculations.** It is now routine in most GED work to carry out quantum chemical calculations. Results from these calculations are mainly used to estimate values for parameters, both geometrical and vibrational, that cannot be measured. The quantum chemical calculations were done with the Gaussian 98 program set<sup>19</sup> assuming  $C_{5v}$  symmetry for the molecule,<sup>20</sup> at the levels HF/3-21G, HF/6-31G\*, HF/6-311G\*, B3LYP/6-31G\*, and B3LYP/6-311G\*. The results are summarized in Table 1 where the results for CA are also listed for comparison.

**Normal Coordinate Calculations.** The reasons for carrying out normal coordinate calculations are several and have been

**TABLE 1: Theoretical Results from Structure Optimizations of Decachlorocorannulene and Corannulene<sup>a,b</sup>**

	decachlorocorannulene					corannulene		
	HF/3-21G	HF/6-31G*	HF/6-311G*	B3LYP/6-31G*	B3LYP/6-311G*	HF/3-21G	HF/6-31G*	B3LYP/6-31G*
	Bond Lengths/Å							
$r(\text{C}_1\text{C}_2)$	1.401	1.403	1.403	1.406	1.406	1.415	1.412	1.417
$r(\text{C}_1\text{C}_6)$	1.350	1.352	1.350	1.377	1.375	1.359	1.361	1.385
$r(\text{C}_6\text{C}_7)$	1.455	1.464	1.464	1.459	1.457	1.449	1.450	1.448
$r(\text{C}_7\text{C}_8)$	1.371	1.385	1.383	1.414	1.409	1.368	1.370	1.390
$r(\text{CX})$	1.797	1.729	1.730	1.741	1.741	1.073	1.076	1.088
	Bond Angles/deg							
$\angle(\text{C}_2\text{C}_1\text{C}_6)$	124.9	125.2	125.2	125.1	124.9	122.8	123.2	123.0
$\angle(\text{C}_1\text{C}_6\text{C}_7)$	112.0	112.0	112.0	111.9	112.1	114.7	114.1	114.2
$\angle(\text{C}_6\text{C}_7\text{C}_8)$	122.8	122.5	122.5	122.7	122.6	121.7	122.0	122.0
$\angle(\text{C}_6\text{C}_7\text{X}_{21})$	119.2	119.4	119.4	119.6	119.7	119.2	119.5	119.4
$\angle(\text{C}_8\text{C}_7\text{X}_{21})$	118.0	118.1	118.0	117.7	117.7	118.9	118.4	118.3
$\angle(\text{C}_{20}\text{C}_6\text{C}_7)$	135.9	135.9	135.8	136.0	135.6	129.3	130.6	130.3
	Out-of-Plane Angles/deg							
$\angle(1,6);(5,1,2)$	-13.3	-11.5	-11.4	-12.0	-13.0	-22.7	-21.1	-22.0
$\angle(6,1);(20,6,7)$	-5.9	-4.9	-5.1	-5.5	-6.0	-12.2	-12.1	-12.5
$\angle(7,21);(6,7,8)$	-0.8	-0.2	-0.1	-0.5	-0.4	-4.5	-4.1	-4.8
	Torsion Angles/deg							
$\angle(\text{C}_6\text{C}_1\text{C}_2\text{C}_9)$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\angle(\text{C}_1\text{C}_2\text{C}_9\text{C}_8)$	-7.1	-6.3	-6.1	-6.4	-6.8	-9.9	-9.2	-9.5
$\angle(\text{C}_2\text{C}_9\text{C}_8\text{C}_7)$	7.0	6.1	5.9	6.2	6.6	9.8	9.0	9.4
$\angle(\text{C}_9\text{C}_8\text{C}_7\text{C}_6)$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\angle(\text{C}_8\text{C}_7\text{C}_6\text{C}_1)$	-7.0	-6.1	-5.9	-6.2	-6.6	-9.8	-9.0	-9.4
$\angle(\text{C}_7\text{C}_6\text{C}_1\text{C}_2)$	7.1	6.3	6.1	6.4	6.8	9.9	9.2	9.5
$\angle(\text{C}_1\text{C}_6\text{C}_7\text{X}_{21})$	174.0	174.1	174.2	174.4	173.8	175.4	175.7	176.1

<sup>a</sup> Atom numbering from Figure 1. <sup>b</sup> Energies/ $E_h$  for decachlorocorannulene: HF/3-21G, -5325.9223916; HF/6-31G\*, -5352.0676580; HF/6-311G\*, -5352.4291556; B3LYP/6-31G\*, -5364.0175996; B3LYP/6-311G\*, -5364.4375729. For corannulene: HF/3-21G, -758.9081760; HF/6-31G\*, -763.1892878; B3LYP/6-31G\*, -768.1493275.



**Figure 4.** Radial distribution curve for decachlorocorannulene. Vertical bars show positions of interatomic distances, and their lengths are proportional to the weights of the terms. The labels indicate bonds and distances separated by one bond angle. The damping factor  $B$  was equal to  $\exp(-0.0025s^2)$ .

described in our CA article.<sup>3</sup> In summary, an important part of such calculations concerns an estimation of the effects of vibrational averaging, known as “shrinkage”,<sup>21</sup> which operates to give average interatomic distances from GED that are not quite consistent with real structures. The inconsistencies are normally small (thousandths of an angstrom) but, if ignored,

are still large enough to contribute additional uncertainty to the measured values of some parameters.

Implicit in the theory for calculation of distance corrections ( $\Delta r = r_g - r_\alpha$ ) to remove the inconsistencies is the assumption of a harmonic force field under which the atoms perform only small oscillations about their equilibrium positions. For relatively stiff hydrocarbon molecules such as CA itself, this is a good approximation. However, for DCA, there are eight vibrational modes, six of  $E$  symmetry and one each of  $A_1$  and  $A_2$  symmetry, that are predicted by the B3LYP/6-311G\* calculation to have wavenumbers less than  $100\text{ cm}^{-1}$ . Because large-amplitude displacements of the participating atoms are possible for these modes, the reliability of the corrections calculated for them by the harmonic approximation is uncertain. Of the eight modes, all of the  $E$  as well as the  $A_2$  involve out-of-plane motions of the chlorine atoms, whereas the remaining one is the  $A_1$  inversion of the bowl. The existence of these modes plays a role in the design of models on which to base the structure refinements. These models are described in the next section.

Our calculations of the distance corrections were done with the program ASYM40<sup>22</sup> which allows the symmetrization of Cartesian force constants obtained from ab initio calculations. We used force constants from the B3LYP/6-311G\* calculation; the force constants from the other calculations did not give significantly different corrections. The symmetry coordinates were the same as those used for CA<sup>3</sup> and are 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/6-311G\* optimization, these symmetry coordinates yielded the force constants and wavenumbers seen in Table S3.

**Model Specification.** The most important questions for the formulation of a DCA model for refinement is whether large-amplitude motion is present and, if so, whether its magnitude is great enough to require special methods, such as use of

**TABLE 2: Experimental and Theoretical Parameter Values for Decachlorocorannulene and Corannulene<sup>a</sup>**

	decachlorocorannulene				corannulene	
	model A <sup>b</sup> $r_{\alpha}; \angle_{\alpha}$	model B <sup>c</sup> $r_{\alpha}; \angle_{\alpha}$	model C <sup>d</sup> $r_{\alpha}; \angle_{\alpha}$	theor <sup>f</sup> $r_{\epsilon}; \angle_{\epsilon}$	model A <sup>b</sup> $r_{\alpha}; \angle_{\alpha}$	theor <sup>e</sup> $r_{\epsilon}; \angle_{\epsilon}$
Structure-Defining						
$r(\text{C}-\text{Cl}/\text{H})$	1.729 (5)	1.730 (5)	1.727 (5)	1.741	1.112 (17)	1.088
$r(\text{C}_1-\text{C}_2)$	1.419 (17)	1.418 (17)	1.420 (18)	1.406	1.410 (6)	1.417
$r(\text{C}_1-\text{C}_6) - r(\text{C}_1-\text{C}_2)$	-0.037 (35)	-0.030 (36)	-0.030 (38)	-0.031	-0.002 (24)	-0.032
$r(\text{C}_6-\text{C}_7) - r(\text{C}_1-\text{C}_2)$	0.050 (19)	0.050 (20)	0.026 (28)	0.051	0.031 (14)	0.031
$\angle \text{C}_{20}-\text{C}_6-\text{C}_7$	135.0 (13)	135.0 (14)	135.4 (13)	135.6	131.5 (23)	130.3
$\angle (1,6);(5,1,2)^g$	-13.7 (29)	-15.2 (26)	-16.0 (27)	-13.0	24.4 (21)	22.0
$\angle (6,1);(20,6,7)^g$	[-6.0]	[-6.0]	[-6.0]	-6.0	-8.8 (84)	-12.5
$\angle(\text{C}-\text{Cl})_{\text{proj}};(\text{CCC})_{\text{bsct}}^h$	0.6 (8)	0.2 (7)	0.9 (11)	1.0	[0.5]	0.5
$\angle(7,21);(6,7,8)^i$	[-0.4]	[-0.4]	[-0.4]	-0.4	[-4.8]	-4.8
Other Parameters						
$\langle r(\text{C}-\text{C}) \rangle$	1.429 (3)	1.430 (3)	1.425 (3)	1.421	1.414 (2)	1.417
$\angle(\text{C}_2-\text{C}_1-\text{C}_6)$	124.3 (5)	124.1 (5)	124.4 (5)	124.9	122.4 (6)	123.0
$\angle(\text{C}_1-\text{C}_6-\text{C}_7)$	111.9 (7)	111.9 (7)	112.2 (6)	112.1	113.9 (6)	114.2
$\angle(\text{C}_6-\text{C}_7-\text{C}_8)$	122.2 (6)	122.2 (6)	122.8 (5)	122.6	122.4 (4)	122.0
$\angle(\text{C}_6-\text{C}_7-\text{Cl}_{21})$	118.8 (9)	118.7 (9)	119.5 (12)	119.7	119.2 (2)	119.4
$\angle(\text{C}_8-\text{C}_7-\text{Cl}_{21})$	117.8 (7)	118.0 (6)	117.7 (10)	117.7	118.2 (2)	118.3
$\angle(5,1,2);(6,1,2)^j = \angle\alpha$	-16.7 (35)	-18.6 (31)	-19.5 (32)	-15.9	-29.3 (23)	-26.5
$\angle(6,1,2);(6,7,8)^j = \angle\beta$	8.1 (21)	9.2 (19)	9.8 (19)	7.5	13.8 (56)	10.2
$\angle(6,7,8);(21,7,8)^j$	-0.45 (6)	-0.45 (3)	-0.45 (2)	-0.41	[-5.4]	-5.4
$X^j$	0.06 (9)	0.07 (9)	0.08 (8)			
$R^k$	0.165	0.172	0.173		0.083	

<sup>a</sup> Distances are in angstroms, and angles are in degrees. Uncertainties are estimated  $2\sigma$ . <sup>b</sup> Preferred model;  $C_{5v}$  symmetry with  $r_{\alpha} \rightarrow r_{\alpha}$  corrections minus effects of  $S_{50,50}$ . <sup>c</sup> With all  $r_{\alpha} \rightarrow r_{\alpha}$  corrections included. <sup>d</sup> No  $r_{\alpha} \rightarrow r_{\alpha}$  corrections. <sup>e</sup> B3LYP/6-311G\*. <sup>f</sup> B3LYP/6-31G\*. <sup>g</sup> Out-of-plane angle between the indicated bond and plane. <sup>h</sup> In the group C-C(Cl)-C, the angle between the bisector of the C-C-C angle and the projection of the C-Cl bond onto the C-C-C plane. <sup>i</sup> Interplanar angle; see Figures 1 and 2. <sup>j</sup> Mole fraction impurity. <sup>k</sup> Quality of fit factor:  $R = [\sum w_i \Delta_i^2 / \sum (I_i(\text{obsd})^2)]^{1/2}$ ;  $\Delta_i = I_i(\text{obsd}) - I_i(\text{calcd})$  with  $I_i = s_i I_m(s_i)$ .

curvilinear coordinates, for its representation. As to the first question, there is little or no evidence for large-amplitude motion in the experimental radial distribution curve because the peaks corresponding to the affected distances are not abnormally broad. However, the theoretical results for some of the atomic displacements are indicative of large-amplitude motion because they include larger than normal shrinkages, i.e., large differences between calculated values of  $r_g$ , the average distance between two atoms, and  $r_{\alpha}$ , the distance between the average positions of the two atoms. Analysis of the displacements reveals that the differences  $r_g - r_{\alpha}$  for the Cl $\cdots$ Cl terms are generally larger than those for C $\cdots$ C and C $\cdots$ Cl, but one in particular, that for adjacent chlorine atoms at a distance of 3.3 Å, is 0.13 Å, about twice as large as any other. This and other distance differences are mostly due to out-of-plane vibrations and torsions about the ClC-CCl bonds which contribute heavily to seven of the eight lowest-frequency normal modes. Notably, a similar analysis of the bowl-inversion mode at 55 cm<sup>-1</sup>, which more than any other might be thought to require representation with curvilinear coordinates, shows much smaller atomic displacements and thus no indication of large-amplitude bowl-inversion motion. This point is explored further in the Discussion section.

Given that large-amplitude motion involving the chlorine atoms is present, the second question posed above—whether its magnitude is great enough to require special treatment—remained to be investigated. Large-amplitude motion is most often encountered in simple systems where rotation around a single bond converts one conformer into another. It is handled by viewing the system as a collection of pseudoconformers distributed at selected points along the rotational coordinate in amounts determined by Boltzmann weighting defined by a torsional potential, i.e.,  $\exp[-V(\phi)/RT]$ .<sup>23</sup> It is evident that the construction of a similar model of the motion in DCA with seven large-amplitude coordinates is a practical impossibility. The answer to the second question then hinges on whether the

harmonic approximation for the large-amplitude motion leads to a distorted picture of the molecular structure, particularly that of the carbon skeleton. This was investigated by refinements of three models that differ only in the size of the distance corrections  $r_g - r_{\alpha}$ ; for reasons given in the discussion section, the results speak directly to the adequacy of the harmonic approximation for treatment of the molecular vibrations in DCA. The first model (A) was defined in  $r_{\alpha}$  space with the set of distance corrections calculated from the theoretical harmonic force field discussed above with one exception: the force constant  $F_{50,50}$  was arbitrarily increased to 100 aJ/Å<sup>2</sup> because the symmetry coordinate  $S_{50,50}$ , which comprises one combination of ClC-CCl torsions, makes up most of the normal coordinate with the lowest wavenumber (24 cm<sup>-1</sup>). When  $S_{50,50}$  is stiffened by this increase in the value of  $F_{50,50}$ , the  $r_g - r_{\alpha}$  differences for the C-Cl, C $\cdots$ Cl, and Cl $\cdots$ Cl terms are reduced about 50%. Model B was defined similarly but with  $F_{50,50}$  equal to the calculated value, and model C was defined in  $r_{\alpha}$  space, i.e., with no distance corrections. The geometries of all models were specified by the values of nine parameters consistent with an assumption of  $C_{5v}$  symmetry for the DCA molecule as indicated by our theoretical calculations.<sup>20</sup> The parameters were the same as those for CA<sup>3</sup> with hydrogen atoms replaced by chlorines. They were the bond lengths  $r(\text{C}-\text{Cl})$  and  $r(\text{C}_1-\text{C}_2)$ ; the bond-length differences  $r(\text{C}_1-\text{C}_6) - r(\text{C}_1-\text{C}_2)$  and  $r(\text{C}_6-\text{C}_7) - r(\text{C}_1-\text{C}_2)$ ; the bond angle  $\angle(\text{C}_{20}-\text{C}_6-\text{C}_7)$ ; the oop (out-of-plane) angle between the C<sub>1</sub>-C<sub>6</sub> bond vector and the plane of the five-member ring,  $\angle(1,6);(5,1,2)$ ; the oop angle between the C<sub>6</sub>-C<sub>1</sub> bond vector and the plane defined by atoms C<sub>20</sub>, C<sub>6</sub>, and C<sub>7</sub>,  $\angle(6,1);(20,6,7)$ ; the angle between the projection of a carbon-chlorine bond onto the plane defined by the adjacent carbon-carbon bonds and the bisector of the angle made by those bonds,  $\angle(\text{CCl})_{\text{proj}};(\text{CCC})_{\text{bsct}}$ ; and the oop angle between a carbon-chlorine bond and the plane defined by the adjacent carbon-carbon bonds,  $\angle(7,21);(6,7,8)$ .

TABLE 3: Distances ( $r/\text{\AA}$ ) and Amplitudes of Vibration ( $l/\text{\AA}$ ) for Decachlorocorannulene

	model A <sup>a</sup> (preferred)				model C <sup>a</sup>		theory	
	$r_{\alpha}^b$	$r_g^c$	$r_a^d$	$l$	$r_a^d$	$l$	$r_e^e$	$l_e$
C <sub>1</sub> –C <sub>2</sub>	1.414	1.421 (17)	1.419	0.052	1.420 (18)	0.060	1.406	0.049
C <sub>1</sub> –C <sub>6</sub>	1.373	1.383 (23)	1.382	0.050	1.390 (25)	0.057	1.374	0.046
C <sub>6</sub> –C <sub>7</sub>	1.465	1.472 (18)	1.469	0.058	1.447 (22)	0.066	1.457	0.055
C <sub>7</sub> –C <sub>8</sub>	1.400	1.410 (27)	1.408	0.055	1.423 (34)	0.062	1.409	0.051
C <sub>1</sub> •C <sub>3</sub>	2.289	2.295 (27)	2.293	0.069	2.298 (30)	0.067	2.275	0.058
C <sub>1</sub> •C <sub>7</sub>	2.353	2.365 (15)	2.363	0.077	2.354 (16)	0.074	2.349	0.066
C <sub>1</sub> •C <sub>9</sub>	2.470	2.479 (15)	2.477	0.073	2.486 (16)	0.070	2.465	0.062
C <sub>6</sub> •C <sub>8</sub>	2.514	2.522 (11)	2.520	0.078	2.520 (13)	0.076	2.514	0.067
C <sub>7</sub> •C <sub>20</sub>	2.712	2.717 (36)	2.714	0.086	2.677 (46)	0.084	2.698	0.075
C <sub>1</sub> •C <sub>8</sub>	2.742	2.753 (11)	2.750	0.084	2.750 (12)	0.082	2.738	0.073
C <sub>6</sub> •C <sub>9</sub>	2.982	2.989 (20)	2.987	0.086	2.990 (19)	0.083	2.980	0.075
C <sub>1</sub> •C <sub>12</sub>	3.595	3.602 (20)	3.601	0.077	3.612 (22)	0.096	3.586	0.067
C <sub>1</sub> •C <sub>10</sub>	3.705	3.714 (16)	3.712	0.082	3.703 (16)	0.101	3.693	0.072
C <sub>7</sub> •C <sub>10</sub>	3.932	3.937 (19)	3.935	0.093	3.919 (21)	0.112	3.926	0.083
C <sub>1</sub> •C <sub>11</sub>	4.115	4.123 (14)	4.121	0.089	4.121 (14)	0.098	4.104	0.077
C <sub>6</sub> •C <sub>10</sub>	4.405	4.412 (23)	4.409	0.097	4.393 (26)	0.105	4.397	0.084
C <sub>1</sub> •C <sub>13</sub>	4.557	4.564 (20)	4.563	0.088	4.559 (20)	0.097	4.542	0.076
C <sub>6</sub> •C <sub>12</sub>	4.825	4.831 (32)	4.829	0.093	4.839 (31)	0.102	4.822	0.081
C <sub>7</sub> •C <sub>11</sub>	4.977	4.982 (22)	4.980	0.102	4.979 (24)	0.111	4.978	0.090
C <sub>6</sub> •C <sub>11</sub>	5.115	5.120 (22)	5.118	0.101	5.117 (23)	0.109	5.111	0.088
C <sub>7</sub> •C <sub>17</sub>	5.788	5.793 (38)	5.791	0.109	5.755 (46)	0.119	5.775	0.095
C <sub>6</sub> •C <sub>13</sub>	5.852	5.857 (27)	5.855	0.104	5.847 (28)	0.115	5.845	0.091
C <sub>7</sub> •C <sub>13</sub>	6.362	6.366 (31)	6.364	0.112	6.340 (35)	0.122	6.353	0.098
C <sub>7</sub> •C <sub>14</sub>	6.654	6.657 (31)	6.655	0.114	6.634 (34)	0.124	6.646	0.100
C <sub>7</sub> –Cl <sub>21</sub>	1.699	1.732 (5)	1.729	0.064 (6)	1.727 (5)	0.064 (6)	1.741	0.060
C <sub>6</sub> •Cl <sub>21</sub>	2.732	2.759 (13)	2.756	0.093	2.746 (15)	0.093	2.769	0.083
C <sub>8</sub> •Cl <sub>21</sub>	2.661	2.694 (17)	2.692	0.086	2.700 (21)	0.086	2.701	0.076
C <sub>7</sub> •Cl <sub>30</sub>	3.385	3.407 (23)	3.402	0.131	3.379 (30)	0.145	3.408	0.116
Cl <sub>21</sub> •Cl <sub>22</sub>	2.996	3.051 (22)	3.045	0.134	3.027 (36)	0.148	3.027	0.120
Cl <sub>21</sub> •Cl <sub>30</sub>	3.161	3.209 (27)	3.201	0.161	3.149 (42)	0.175	3.180	0.147
C <sub>1</sub> •Cl <sub>21</sub>	3.932	3.959 (17)	3.956	0.091	3.964 (18)	0.085	3.973	0.082
C <sub>6</sub> •Cl <sub>22</sub>	4.050	4.074 (10)	4.072	0.090	4.073 (12)	0.085	4.085	0.082
C <sub>1</sub> •Cl <sub>22</sub>	4.438	4.463 (11)	4.461	0.087 (17)	4.473 (11)	0.083 (17)	4.476	0.084
C <sub>7</sub> •Cl <sub>23</sub>	4.776	4.793 (21)	4.789	0.134 (37)	4.793 (26)	0.130 (38)	4.809	0.122
C <sub>1</sub> •Cl <sub>23</sub>	5.189	5.210 (12)	5.208	0.101	5.220 (14)	0.111	5.222	0.092
C <sub>7</sub> •Cl <sub>29</sub>	5.367	5.384 (27)	5.382	0.113	5.370 (34)	0.122	5.394	0.103
C <sub>6</sub> •Cl <sub>23</sub>	5.626	5.643 (20)	5.639	0.131	5.642 (23)	0.126	5.659	0.113
C <sub>1</sub> •Cl <sub>24</sub>	5.813	5.831 (15)	5.829	0.105	5.848 (15)	0.100	5.844	0.087
Cl <sub>21</sub> •Cl <sub>23</sub>	5.856	5.881 (22)	5.875	0.192 (51)	5.874 (24)	0.190 (54)	5.903	0.151
C <sub>1</sub> •Cl <sub>25</sub>	6.185	6.203 (18)	6.201	0.108	6.219 (20)	0.113	6.215	0.090
C <sub>7</sub> •Cl <sub>24</sub>	6.538	6.552 (23)	6.549	0.126	6.562 (25)	0.131	6.576	0.108
C <sub>6</sub> •Cl <sub>24</sub>	6.790	6.805 (24)	6.802	0.130	6.817 (24)	0.179	6.828	0.102
C <sub>7</sub> •Cl <sub>28</sub>	7.060	7.072 (34)	7.069	0.154	7.052 (41)	0.203	7.087	0.126
C <sub>6</sub> •Cl <sub>25</sub>	7.452	7.464 (28)	7.461	0.140 (55)	7.476 (29)	0.148 (64)	7.490	0.111
C <sub>7</sub> •Cl <sub>25</sub>	7.813	7.824 (30)	7.821	0.153	7.822 (33)	0.155	7.849	0.125
C <sub>7</sub> •Cl <sub>27</sub>	8.047	8.057 (34)	8.054	0.144	8.050 (39)	0.146	8.080	0.117
C <sub>7</sub> •Cl <sub>26</sub>	8.317	8.326 (33)	8.324	0.148	8.324 (36)	0.150	8.353	0.121
Cl <sub>21</sub> •Cl <sub>24</sub>	8.009	8.026 (30)	8.022	0.164	8.047 (35)	0.166	8.078	0.137
Cl <sub>21</sub> •Cl <sub>28</sub>	8.111	8.129 (36)	8.125	0.193	8.123 (45)	0.194	8.173	0.165
Cl <sub>21</sub> •Cl <sub>25</sub>	9.476	9.489 (36)	9.486	0.188 (51)	9.505 (39)	0.185 (53)	9.552	0.149
Cl <sub>21</sub> •Cl <sub>26</sub>	9.963	9.973 (37)	9.970	0.192 (115)	9.994 (41)	0.180 (103)	10.043	0.150

<sup>a</sup> Quantities in parentheses are estimated  $2\sigma$ , and those in braces were refined as groups. <sup>b</sup> Distance between average nuclear positions. <sup>c</sup> Thermal average distance:  $r_g = r_{\alpha} + \langle \Delta r \rangle$ . <sup>d</sup> Electron-diffraction distance parameter:  $r_a = r_g - l^2/r$ . <sup>e</sup> Equilibrium distance.

There are 51 numerically different interatomic distances in the DCA molecule, each of which has an associated amplitude of vibration. Some of these amplitudes were refined independently, and others were refined in groups within which the amplitudes of the component distances were given values consistent with their differences as calculated from ASYM40. Altogether, 20 amplitude parameters were refined. Although we had taken care to remove the residual diphenyl ether present in our DCA sample, it was thought necessary to allow for the possible presence of residual amounts via a refinable mole-fraction parameter. The molecular structure of diphenyl ether was taken from the literature<sup>24</sup> and included all inter- and

intraring distances between heavy atoms and all non-torsion-sensitive hydrogen- to heavy-atom distances.

**Refinement Results.** The structure refinements were carried out in the usual way<sup>25–27</sup> by a least-squares fitting of a theoretical intensity curve simultaneously to the two curves obtained as averages of the LC and MC experimental curves. Initial tests showed that certain parameters, particularly the oop angles  $\angle(1,6);(5,1,2)$  and  $\angle(7,21);(6,7,8)$ , obtained such large uncertainties as to make their values meaningless. A series of test refinements was then done with these angles fixed at selected values over large ranges. The other parameter values were virtually unchanged throughout these tests. For our final

**TABLE 4: Correlation Matrix for Selected Parameters of Model A for Decachlorocorannulene**

	parameter <sup>a</sup>	$\sigma_{LS}^b$	$r_1$	$r_2$	$r_3$	$r_4$	$\angle_5$	$\angle_6$	$\angle_7$	$l_8$	$l_9$	$l_{10}$	$l_{11}$	$X$
1	$r(\text{C}-\text{Cl})$	0.15	100											
2	$r(\text{C}_1-\text{C}_2)$	0.58	4	100										
3	$r(\text{C}_1-\text{C}_6) - r(\text{C}_1-\text{C}_2)$	1.2	5	-85	100									
4	$r(\text{C}_6-\text{C}_7) - r(\text{C}_1-\text{C}_2)$	0.67	-17	-51	18	100								
5	$\angle_{\text{C}_{20}-\text{C}_6-\text{C}_7}$	46.	11	16	4	-6	100							
6	$\angle(1-6);(5,1,2)$	102.	-15	-3	-25	29	50	100						
7	$\angle(\text{C}-\text{Cl})_{\text{prj}};(\text{CCC})_{\text{bsct}}$	28.	-4	-31	31	-36	-53	-26	100					
8	$l(\text{C}_1-\text{C}_2)$	0.51	8	-41	69	-46	3	-27	57	100				
9	$l(\text{C}_1-\text{C}_3)$	0.40	5	12	-11	-6	-24	-15	11	1	100			
10	$l(\text{C}_7-\text{Cl}_{21})$	0.18	-5	-9	-8	26	-16	6	-3	-14	3	100		
11	$l(\text{C}_6-\text{Cl}_{21})$	0.32	4	-23	13	-5	17	37	-3	22	-25	21	100	
12	$X^c$	4.4	8	-6	-25	53	-27	3	-25	-63	-11	43	4	100

<sup>a</sup> See footnotes to Table 2 for definitions. <sup>b</sup> Standard deviation ( $\times 100$ ) from least squares. Distances ( $r$ ) and amplitudes ( $l$ ) are in angstroms, and angles ( $\angle$ ) are in degrees. <sup>c</sup> Mole fraction impurity.

refinements, the angles were assigned the theoretical (B3LYP/6311G\*) values.

Results of the final refinements are presented in Table 2 and show that the three models yield very similar values for the structure-defining parameters and the various related bond and oop angles; indeed, the differences between the models are statistically insignificant. For this reason, the choice of a “best” model is quite arbitrary. We choose model A as offering a reasonable compromise for the effects of the six low-frequency vibrational modes. A listing of distance and amplitude values for this model is given in Table 3. Table 4 is the correlation matrix for the more important parameters of the model; the complete correlation matrix is found in the Supporting Information.

## Discussion

Because the results for the amount of impurity in the final refinements are 6% ( $2\sigma = 9\%$ ) and because the scattering power of the presumed impurity molecule is only about 14% as much as that from a DCA molecule, the impurity contributes less than 1% of the total scattered intensity. At this amount, the effect of impurity on the measurements of the DCA structure is insignificant. However, to remove any doubt, we carried out two refinements of the structure with the amount of impurity fixed at  $6 + \sigma\%$  and  $6 + 2\sigma\%$ . The changes from the parameter values of any of the models in Table 2 were at most a small fraction of one standard deviation. We conclude that the possible presence of sample impurity has no effect on our results for the DCA structure.

The three models adopted for representation of the DCA structure are all based on the assumption that the harmonic (small amplitude) approximation for the internal molecular vibrations does not have a significant effect on the important parameter values for the structure. A test of validity for the approximation is contained in the parameter values obtained from the models, each of which has built into it a different set of distance corrections  $r_a - r_{\alpha}$ . For example, if the harmonic vibration approximation were to be a poor one, the evidence would be found in significant differences between the parameter values for models B and C, which are respectively designed to take into account, and to ignore, the effects of harmonic vibrational averaging. However, each of these models yields essentially the same refined values for the thermal average  $r_a$  distances and  $\angle_a$  angles. Further, to the extent that the approximation might be less than ideal, one would expect the largest differences between the models to lie in parameters involving chlorine atoms because the large-amplitude motion primarily affects these atoms. As Table 2 shows, however, the

C–Cl bond distance and the C–C–Cl bond angles from models B and C respectively differ by only 0.003 Å and 0.8°, each less than their uncertainties. The differences between the values involving only carbon atoms is generally considerably smaller.

It was mentioned earlier that quantum mechanical calculations in GED work are useful for providing values of unmeasurable structural parameters, which to the extent of their reliability then improve the accuracy of the structure determination. Evidence for this reliability is contained in the results from the calculations summarized in Table 1. Although similarities in the values for the various types of angles conform to general experience, it is nevertheless surprising how little variation is found across the large range of theoretical level and basis set. For example, for DCA, the HF and B3LYP values for the bond, oop, and torsion angles respectively vary less than 0.3°, 1.0°, and 0.6° from their averages, and if the HF/3-21G results are ignored, these are 0.2°, 0.8°, and 0.5°. Prediction of the bond distances across the two theoretical levels is not quite so consistent, but within each level, the consistency is good, and for the two B3LYP sets, the maximum difference for any distance parameter is only 0.005 Å. Among the listed calculations, we consider the B3LYP/6-311G\* as the most reliable for comparison with the experimental geometry. The best comparison between the experimental parameter values and the theoretical ( $r_{\alpha}$ ) ones is the experimental  $r_{\alpha}$  for all carbon–carbon terms, but for terms involving chlorine atoms, where the effects of the low-frequency torsions tend to be concentrated, the  $r_a$  value is preferred. It should be mentioned that the quality of fit obtained in this study is somewhat poorer than usual, and thus the experimental uncertainties are larger. The reason is that the need for maintaining as low a sample temperature as possible in order to avoid decomposition led to more lightly exposed films and a lower signal-to-noise ratio. This may be seen most easily in the MC experimental curves of Figure 3 for the region  $s > 30 \text{ \AA}^{-1}$ . Despite these difficulties, the agreement between the experimental and theoretical structures is good.

A question of interest in the corannulenes is the barrier to inversion, which is defined as the energy difference between a planar structure of  $D_{5h}$  symmetry and a nonplanar structure with  $C_{5v}$  symmetry. The inversion barrier for CA is predicted to be 9.1 (HF), 10.2 (B3LYP), and 12.3 kcal/mol (MP2) with a 6-311G\*\* basis set.<sup>28</sup> The predicted inversion barriers for sym-pentamethylcorannulene and decamethylcorannulene are respectively 8.7 and 2.2 kcal/mol at the B3LYP/cc-pVDZ level of theory,<sup>7</sup> and those for DCA are 1.36, 0.77, and 1.21 kcal/mol respectively from HF/3-21G, HF/6-311G\*, and B3LYP/6-311G\* calculations (this work). Although these calculations are not strictly comparable because of differing basis sets, it is reason-

able to conclude that the barrier for DCA is much smaller than for CA itself and smaller even than that for decamethylcorannulene. The DCA values have relevance to the question of inversion of the bowl and whether the models based on the harmonic-vibration approximation for the carbon-carbon terms are flawed. Comparison of the C...C distances across the ring predicted by the B3LYP/6-311G\* calculations for the presumed transition state of *D*<sub>5h</sub> symmetry and the lowest energy structure of *C*<sub>5v</sub> symmetry shows that the largest difference, *r*(C<sub>6</sub>...C<sub>14</sub>), is only about 0.05 Å. Because most of the molecules, i.e., about 80%, are found at the minimum of the inversion potential, it is clear that a model based on a large-amplitude approximation for the inversion would lead to essentially the same parameter values for the structure.

The angles  $\alpha$  and  $\beta$  for CA, respectively  $-29.3^\circ$  and  $13.8^\circ$ , and for model A of DCA,  $-16.7^\circ$  and  $8.1^\circ$ , show that DCA is considerably flatter than CA itself and are intuitively consistent with a lower inversion barrier in DCA. A comparison of the flatness of the two molecules is seen in Figure 2. The quantum chemical results for these molecules seen in Table 2 indicate some significant differences in the bond lengths that are generally in agreement with experiment. The bond lengths in DCA are individually longer than their counterparts in CA.<sup>3</sup> They may be explained in terms of oop angle strain related to the flatness of the molecule together with inductive effects of the chlorine atom. Applying the arguments invoked to account for the CA bond lengths relative to those in C<sub>60</sub>,<sup>1</sup> one predicts the angle strain represented by  $\angle\alpha$  (greatest in C<sub>60</sub>, least in DCA) to make the C<sub>1</sub>-C<sub>2</sub>, C<sub>1</sub>-C<sub>6</sub>, and C<sub>7</sub>-C<sub>8</sub> bonds shorter than in CA and the C<sub>6</sub>-C<sub>7</sub> bond longer. In addition, one expects the inductive effect of the chlorine atom to withdraw electrons from the  $\pi$  system and thus to lengthen the bonds relative to CA, particularly those nearest the substituent, C<sub>6</sub>-C<sub>7</sub> and C<sub>7</sub>-C<sub>8</sub>. A reasonable balancing of these effects leads to the prediction that bonds C<sub>6</sub>-C<sub>7</sub> and C<sub>7</sub>-C<sub>8</sub> should be longer, and bonds C<sub>1</sub>-C<sub>2</sub> and C<sub>1</sub>-C<sub>6</sub> shorter, in DCA than in CA. The prediction fits the observation except for C<sub>1</sub>-C<sub>2</sub>, which is longer, although not significantly so, by 0.008 Å in DCA.

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**Supporting Information Available:** Tables of the complete correlation matrix for the parameters of model A, the coefficients of internal coordinates comprising symmetry coordinates for DCA, the definitions of internal coordinates comprising the symmetry coordinates, the symmetry force constants and wavenumbers calculated at the B3LYP/6-311G\* level, and the molecular intensity data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Hedberg, K.; Hedberg, L.; Bethune, D. S.; Brown, C. A.; Dorn, H. C.; Johnson, R. J.; de Vries, M. *Science* **1991**, *254*, 410.
- (2) Hedberg, K.; Hedberg, L.; Bühl, M.; Bethune, D. S.; Brown, C. A.; Johnson, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 5314.
- (3) Hedberg, L.; Hedberg, K.; Cheng, P.; Scott, L. T. *J. Phys. Chem. A* **2000**, *104*, 7689.
- (4) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920.
- (5) Hanson, J. C.; Nordman, C. E. *Acta Crystallogr.* **1976**, *B32*, 1147.
- (6) Sygula, A.; Abdourazak, A. H.; Rabideau, P. W. *J. Am. Chem. Soc.* **1996**, *118*, 339.
- (7) Seiders, T. J.; Baldrige, K. K.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7439.
- (8) Cheng, P.-C.; Scott, L. T. *Abstracts of Papers*; 208th National Meeting of the American Chemical Society; American Chemical Society: Washington, DC, 1994.
- (9) Cheng, P.-C. Ph. D. Dissertation, Boston College, Boston, MA, 1996.
- (10) Ballester, M. *Adv. Phys. Org. Chem.* **1989**, *25*, 267.
- (11) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804.
- (12) Huang, R.; Huang, W.; Wang, Y.; Tang, Z.; Zheng, L. *J. Am. Chem. Soc.* **1997**, *119*, 5954.
- (13) Huang, R.-B.; Xie, S.-Y.; Tang, Z.-C.; Wang, Y.-H.; Huang, W.-J.; Chen, H.; Zheng, L.-S. *J. Cluster Sci.* **1999**, *10*, 383.
- (14) Xie, S.-Y.; Huang, R.-B.; Ding, J.; Yu, L. J.; Wang, Y.-H.; Zheng, L.-S. *J. Phys. Chem. A* **2000**, *104*, 7161.
- (15) Xie, S.-Y.; Deng, S. L.; Huang, R.-B.; Yu, L. J.; Zheng, L. S. *Chem. Phys. Lett.* **2001**, *343*, 458.
- (16) Lin, M.; Wang, Y.; Huang, W.; Huang, R.; Zeng, L. *Fullerene Sci. Technol.* **1998**, *6*, 1111.
- (17) Ding, J.; Xie, S.-Y.; Yu, L.-J.; Huang, R.-B.; Zheng, L.-S. *Gaodeng Xuexiao Huaxue Xuebao* **1999**, *20*, 1936.
- (18) Interestingly, a purity check via combustion analysis showed no evidence of impurity. However, diphenyl ether has a significantly higher vapor pressure than decachlorocorannulene, and most likely, it was vaporized out of the sample before the analysis began.
- (19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (20) A few tests were made starting from models of *C*<sub>3</sub> symmetry. In every case, the final structure had *C*<sub>5v</sub> symmetry.
- (21) Almendinger, A.; Bastiansen, O.; Trættestad, M. *Acta Chem. Scand.* **1959**, *12*, 1699. Morino, Y.; Nakamura, J.; Moore, P. W. *J. Chem. Phys.* **1962**, *36*, 1050.
- (22) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **2000**, *203*, 82.
- (23) For a good example of the method, see: Danielson, D. D.; Patton, J. V.; Hedberg, K. *J. Am. Chem. Soc.* **1977**, *99*, 6484.
- (24) Naumov, V. A.; Ziatdinova, R. N.; Naumov, A. V.; Hagen, K. *Russ. J. Gen. Chem. Eng. Trans.* **2000**, *70*, 273-277.
- (25) Hedberg, K.; Iwasaki, M. *Acta Crystallogr.* **1964**, *17*, 529.
- (26) Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.
- (27) Hedberg, L. *Abstracts*, Fifth Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, 1974; p 37.
- (28) Biedermann, P. U.; Pogodin, S.; Agranat, I. *J. Org. Chem.* **1999**, *64*, 3655.