

The Crystal and Molecular Structure of Corannulene, C₂₀H₁₀

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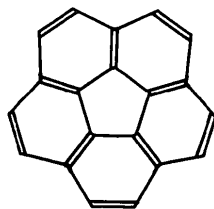
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Dibenzo[*ghi,mno*]fluoranthene, or corannulene, C₂₀H₁₀, is a highly strained hexacyclic hydrocarbon composed of five benzene rings fused into an annulus of fivefold symmetry. The compound crystallizes in space group $P2_1/c$ with $Z=8$ and cell dimensions $a=13.260$ (7), $b=11.859$ (4), $c=16.520$ (7) Å, $\beta=102.69$ (5)° at 20°C, and $a=13.233$ (15), $b=11.785$ (15), $c=16.432$ (15) Å, $\beta=102.55$ (7)° at -70°C. Data were obtained by densitometry of doubly integrated oscillation photographs at 20°C, and by diffractometer techniques at -70°C. The structure was solved by a Patterson search procedure. Refinement by block-diagonal least squares brought the final R value to 0.069 for 2013 data observed at 20°C and to 0.074 for 2137 data observed at -70°C. The molecules are cupped with an average dihedral angle of 20.4° between least-squares planes defined by the five- and six-membered rings. Averages of chemically equivalent bond distances (corrected for foreshortening due to molecular libration) from two crystallographically independent molecules and two independent sets of data are 1.413 (3) Å for the five bonds in the central ring, 1.391 (4) Å for the five 'spokes', 1.440 (2) Å for the ten peripheral bonds adjacent to the 'spokes', and 1.402 (5) Å for the five outermost peripheral bonds.

Introduction

Barth & Lawton (1966) synthesized the compound dibenzo[*ghi,mno*]fluoranthene (I) and assigned it the trivial name corannulene. The molecular geometry is of considerable interest, because it provides information about the required compromise between strain and aromaticity (Barth & Lawton, 1971). Gleicher (1967) performed self-consistent field M. O. calculations and strain energy calculations for the corannulene molecule. The results indicated a non-planar molecule with appreciable aromatic character.



(I)

Experimental

Crystals of corannulene, prepared by sublimation under reduced pressure, were kindly supplied by R. G. Lawton of the University of Michigan.

The lattice parameters at 20°C were determined as an average of results from least-squares refinement (Burnham, 1964) of diffractometer 2θ data, and from measurement of spacings on precession photographs.

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The low-temperature lattice parameters were determined from precession photographs which were double exposures of low-temperature and room-temperature nets on the same film.

Crystal data

C₂₀H₁₀, M.W. 250.30, monoclinic, space group $P2_1/c$, $Z=8$; μ for Cu $K\alpha$ ($\lambda=1.5418$) = 5.8 cm⁻¹; $a=13.260$ (7), $b=11.859$ (4), $c=16.520$ (7) Å, $\beta=102.69$ (5)°, $V=2534.3$ Å³, $D_x=1.31$ g cm⁻³ at 20°C; $a=13.233$ (15), $b=11.785$ (15), $c=16.432$ (15) Å, $\beta=102.55$ (17)°, $V=2501.4$ Å³, $D_x=1.33$ g cm⁻³ at -70°C.

The first set of data was collected at room temperature on a doubly integrating oscillation camera (Nordman & Patterson, 1957), using Ni-filtered (0.06 mm) Cu $K\alpha$ radiation. The integrated intensities were obtained as peak heights on densitometer tracings. The reflections in each layer line were indexed by fitting a computer-generated template containing all calculated reflection positions for the oscillation range in question. Data were collected about the a and c axes. The crystal, which was used for both settings, was a prism of dimensions 0.4 × 0.4 × 0.3 mm. The approximately 8000 individual intensity measurements were scaled together (Nordman, 1960; Schilling, 1968) yielding averaged intensities for 2025 independent reflections. Approximately 1600 reflections inside the sphere defined by the outermost observed reflections were too weak to measure. The observed reflections comprise approximately 35% of the reflections within the Cu $K\alpha$ limiting sphere. This low coverage reflects the relatively strong thermal motion in the crystal.

In an attempt to increase the amount of observed

data, a second set was collected at -70°C on an automatic Weissenberg-type diffractometer. The crystal, mounted in a Lindemann glass capillary, was cooled by a stream of cold nitrogen gas, which was obtained by boiling liquid nitrogen in a Dewar and transferring the gas to the crystal through an insulated delivery tube. The temperature, measured with a copper-constantan thermocouple mounted at the end of the gas delivery tube, about 6 mm from the crystal, was maintained at $-70 \pm 5^{\circ}\text{C}$. To reduce the amount of moisture around the crystal, and to prevent ice formation, a stream of dry nitrogen gas was directed to flow concentric to the cold gas, and the entire diffractometer was enclosed in a plastic bag. Even with these precautions some ice unavoidably formed on the crystal.

Low-temperature data for the Hkl ($H=0$ to 11) nets were collected from a crystal of dimensions $0.3 \times 0.3 \times 0.2$ mm mounted on the a axis. The $\text{Cu } K\alpha$ radiation was monochromatized by means of Ni-Co balanced filters and pulse height analysis. A fixed counter, moving crystal technique with variable step scans was used (Hanson & Nordman, 1975). In this technique a scan range, whose width depended on the expected peak width, was calculated for each reflection. Furthermore, each scan range was divided into 10 equal parts, whose accumulated counts were individually recorded on the output tape. With crystal scan ranges from 2.5 to 6.0° , several of the partial scans represented readings of the background on each side of the peak. The assignment of 'peak' and 'background' scan steps, and evaluation of the integral under the peak was done by a separate data reduction program (Hanson, 1969). The number of reflections with intensities greater than 2σ was 2288. During the subsequent refinement 139 weak reflections were rejected because they were suspected of resulting from ice on the crystal, as indicated by abnormal peak shapes. Also, reflections with low counter settings were removed, if the step scan data indicated that the scan range was insufficient.

There was no cross net scaling of the diffractometer data. However, a check for scale factor dependence with level was made by scaling partial nets of room-temperature diffractometer data to the scaled set of room-temperature film data. The absence of a trend of scale factor with level indicated that no level-by-level rescaling of the low-temperature diffractometer data was required.

Determination and refinement of the structure

The partial knowledge of the molecular geometry of corannulene made it appear advantageous to solve the structure by Patterson search techniques (Nordman, 1966; Schilling, 1968, 1970a; Nordman & Schilling, 1970).

A Wilson treatment was used to obtain an overall isotropic thermal parameter and scale factor. These were used to calculate the coefficients of a 'point atom' Patterson function, which was used in all searches.

The orientation of the molecule relative to a crystal-fixed Cartesian system was determined in terms of the Euler angles A , B and C which, when used to rotate the intramolecular vectors, gave the best fit to the Patterson function. In the initial orientation searches, only those vectors were used which are insensitive to the degree of cupping of the molecule, in order to minimize the effect of this unknown parameter. These are the vectors between atoms *within* the concentric rings of C(1)-C(5), C(6)-C(10), C(11)-C(20) (Fig. 2c). The two highest peaks in the search were subsequently found to correspond to the orientations of the two independent molecules in the asymmetric unit.

Once the promising orientations of the molecules were determined, a series of local Patterson searches in these orientations using vectors sensitive to the cupping were performed. The dihedral angle between the five- and six-membered rings was varied in generating the vectors for these searches. The sensitive vectors are those *between* the concentric rings described above. The value of the dihedral angle determined in these searches was subsequently found to be within 1° of the correct, average dihedral angle, as determined from the final refined coordinates. This model was used in the subsequent translation searches.

In the original translation searches the assumed molecular orientation was that corresponding to the highest peak in the orientation search map. The translation search serves to determine the location of a group in a known orientation by a superposition of vectors between this group and its symmetry-related mates in the Patterson function. The y coordinate of the molecule was determined with a one-dimensional translation search, where the search vectors were those between the molecule and its c glide-related mate. The correct location was easily found. The x and z coordinates of the molecule were determined by a two-dimensional translation search using vectors between the molecule and its 2_1 screw axis mate. The highest peak in this search was subsequently verified to be correct.

Based on the coordinates of one molecule as determined above, a weighted difference electron density map was calculated, and the coordinates of part of the second independent molecule were found. The rest of the molecule was found in subsequent maps.

The coordinates and isotropic thermal parameters were first refined by diagonal least squares. The hydrogen atoms were found in difference electron density maps. Additional refinement was done with isotropic thermal parameters for the hydrogen atoms and anisotropic thermal parameters for carbon atoms using the block-diagonal mode of the CLS least-squares program (Schilling, 1970b). During the refinement, 12 reflections which were expected to be most affected by secondary extinction were rejected (Zachariasen, 1967). The thermal parameters of several hydrogen atoms became very large at this stage. It was then decided that the hydrogen thermal parameters should be held at a fixed value for each molecule, and determined from

Table 1. *Fractional atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$) of the carbon atoms*

The estimated standard deviation, given in parentheses, refers to the last significant place. The thermal parameters β_{ij} are those of the temperature factor $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$.

Molecule 1 at 20°C

| | <i>x</i> | <i>y</i> | <i>z</i> | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|-----------|----------|----------|--------------|--------------|--------------|--------------|--------------|--------------|
| C(1) | 1598 (4) | 3148 (4) | 3104 (3) | 69 (4) | 82 (4) | 31 (2) | 8 (3) | 18 (2) | -9 (2) |
| C(2) | 2397 (4) | 2672 (4) | 3727 (3) | 52 (3) | 79 (4) | 46 (2) | 13 (3) | 16 (2) | -16 (3) |
| C(3) | 1929 (4) | 1944 (4) | 4212 (3) | 67 (4) | 64 (4) | 37 (2) | 16 (3) | 10 (2) | -6 (2) |
| C(4) | 846 (4) | 1962 (4) | 3890 (3) | 67 (4) | 58 (4) | 38 (2) | 0 (3) | 14 (2) | -14 (2) |
| C(5) | 652 (4) | 2705 (4) | 3210 (3) | 65 (4) | 72 (4) | 31 (2) | 7 (3) | 7 (2) | -13 (2) |
| C(6) | 1680 (4) | 4180 (5) | 2739 (3) | 79 (4) | 116 (5) | 34 (2) | 4 (4) | 31 (3) | -3 (3) |
| C(7) | 3310 (4) | 3220 (5) | 4031 (4) | 60 (4) | 116 (6) | 56 (3) | 23 (4) | 22 (3) | -10 (3) |
| C(8) | 2360 (4) | 1710 (4) | 5030 (3) | 70 (4) | 75 (4) | 50 (3) | 22 (3) | 5 (2) | 3 (3) |
| C(9) | 128 (4) | 1743 (4) | 4364 (3) | 74 (4) | 65 (4) | 42 (2) | -8 (3) | 19 (2) | -11 (2) |
| C(10) | -277 (4) | 3269 (4) | 2949 (3) | 62 (4) | 99 (5) | 34 (2) | 9 (3) | -3 (2) | -16 (2) |
| C(11) | 2708 (5) | 4662 (5) | 2934 (4) | 90 (5) | 122 (6) | 66 (3) | 6 (4) | 44 (3) | 14 (3) |
| C(12) | 3495 (4) | 4195 (5) | 3571 (4) | 82 (4) | 126 (6) | 76 (4) | 1 (4) | 50 (3) | 0 (4) |
| C(13) | 3842 (4) | 2843 (5) | 4844 (4) | 54 (4) | 123 (6) | 74 (3) | 10 (4) | 5 (3) | -15 (4) |
| C(14) | 3379 (4) | 2123 (5) | 5318 (4) | 73 (4) | 123 (6) | 62 (3) | 26 (4) | -2 (3) | 0 (3) |
| C(15) | 1615 (5) | 1292 (5) | 5496 (3) | 120 (5) | 86 (5) | 43 (3) | 8 (4) | 11 (3) | 3 (3) |
| C(16) | 572 (4) | 1323 (5) | 5177 (3) | 104 (5) | 82 (5) | 49 (3) | -13 (4) | 23 (3) | 0 (3) |
| C(17) | -887 (4) | 2181 (5) | 4017 (4) | 71 (4) | 95 (5) | 61 (3) | -20 (4) | 19 (3) | -26 (3) |
| C(18) | -1078 (4) | 2911 (5) | 3344 (4) | 55 (4) | 120 (6) | 58 (3) | -7 (4) | 12 (3) | -24 (3) |
| C(19) | -224 (4) | 4257 (5) | 2469 (3) | 84 (4) | 115 (6) | 35 (2) | 15 (4) | -2 (3) | 2 (3) |
| C(20) | 715 (5) | 4695 (5) | 2370 (3) | 114 (5) | 104 (6) | 36 (2) | 26 (4) | 13 (3) | 7 (3) |

Molecule 2 at 20°C

| | <i>x</i> | <i>y</i> | <i>z</i> | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|----------|----------|----------|--------------|--------------|--------------|--------------|--------------|--------------|
| C(1) | 7179 (4) | 4045 (5) | 4804 (3) | 57 (4) | 107 (5) | 49 (3) | 15 (3) | 19 (2) | -14 (3) |
| C(2) | 6973 (4) | 4688 (4) | 4081 (4) | 72 (4) | 55 (4) | 79 (3) | 10 (3) | 42 (3) | -1 (3) |
| C(3) | 6278 (4) | 4108 (5) | 3467 (3) | 52 (3) | 129 (6) | 47 (2) | 36 (4) | 22 (2) | 16 (3) |
| C(4) | 6048 (4) | 3080 (4) | 3827 (4) | 44 (3) | 84 (5) | 68 (3) | -0 (3) | 17 (2) | -6 (3) |
| C(5) | 6596 (4) | 3063 (4) | 4640 (3) | 60 (4) | 104 (5) | 50 (3) | 19 (3) | 26 (2) | 19 (3) |
| C(6) | 8093 (4) | 4111 (5) | 5407 (4) | 85 (4) | 134 (6) | 57 (3) | 1 (4) | 27 (3) | -34 (3) |
| C(7) | 7684 (5) | 5492 (4) | 3909 (4) | 99 (5) | 63 (5) | 87 (4) | 20 (4) | 36 (4) | -0 (3) |
| C(8) | 6221 (4) | 4255 (5) | 2613 (4) | 63 (4) | 128 (6) | 77 (4) | 33 (4) | 11 (3) | 19 (4) |
| C(9) | 5735 (4) | 2118 (5) | 3353 (4) | 57 (4) | 122 (6) | 82 (4) | -6 (4) | 10 (3) | 6 (4) |
| C(10) | 6888 (4) | 2064 (5) | 5093 (4) | 74 (4) | 125 (4) | 69 (3) | 4 (4) | 38 (3) | 9 (4) |
| C(11) | 8754 (5) | 5014 (6) | 5308 (4) | 87 (5) | 145 (7) | 86 (4) | -12 (4) | 33 (4) | -57 (4) |
| C(12) | 8533 (5) | 5691 (5) | 4560 (4) | 82 (5) | 95 (6) | 104 (4) | -18 (4) | 21 (4) | -42 (4) |
| C(13) | 7502 (5) | 5772 (5) | 3043 (4) | 112 (6) | 89 (6) | 89 (6) | 26 (4) | 39 (4) | 25 (4) |
| C(14) | 6801 (5) | 5185 (6) | 2425 (4) | 91 (5) | 139 (7) | 80 (4) | 39 (5) | 34 (4) | 44 (4) |
| C(15) | 5768 (5) | 3311 (6) | 2123 (4) | 69 (4) | 164 (8) | 70 (4) | 19 (4) | 5 (3) | 1 (4) |
| C(16) | 5521 (4) | 2296 (6) | 2469 (4) | 60 (4) | 166 (8) | 76 (4) | 10 (4) | -4 (3) | -27 (4) |
| C(17) | 5877 (5) | 1109 (6) | 3828 (5) | 81 (5) | 106 (6) | 110 (5) | -18 (4) | 22 (4) | -8 (4) |
| C(18) | 6417 (5) | 1093 (5) | 4667 (5) | 86 (5) | 97 (6) | 104 (4) | 2 (4) | 33 (4) | 15 (4) |
| C(19) | 7710 (5) | 2167 (6) | 5787 (4) | 90 (5) | 166 (8) | 55 (3) | 33 (5) | 27 (3) | 15 (4) |
| C(20) | 8318 (5) | 3173 (6) | 5939 (4) | 100 (5) | 178 (8) | 46 (3) | 30 (5) | 23 (3) | -0 (4) |

Molecule 1 at -70°C

| | <i>x</i> | <i>y</i> | <i>z</i> | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|-----------|----------|----------|--------------|--------------|--------------|--------------|--------------|--------------|
| C(1) | 1602 (4) | 3145 (4) | 3110 (3) | 76 (4) | 70 (4) | 22 (2) | 15 (3) | 11 (2) | -4 (2) |
| C(2) | 2408 (4) | 2681 (4) | 3732 (3) | 63 (4) | 69 (4) | 36 (2) | 9 (3) | 15 (2) | -10 (3) |
| C(3) | 1926 (4) | 1943 (4) | 4210 (3) | 74 (5) | 48 (4) | 35 (2) | 11 (3) | 11 (2) | -9 (2) |
| C(4) | 854 (4) | 1958 (4) | 3892 (3) | 83 (5) | 46 (4) | 27 (2) | 2 (3) | 8 (2) | -10 (2) |
| C(5) | 653 (4) | 2712 (4) | 3207 (3) | 69 (4) | 65 (4) | 22 (2) | 8 (3) | 4 (2) | -12 (2) |
| C(6) | 1692 (5) | 4191 (5) | 2746 (3) | 99 (5) | 89 (5) | 27 (2) | 8 (4) | 29 (2) | -1 (3) |
| C(7) | 3309 (5) | 3216 (5) | 4032 (4) | 70 (5) | 80 (5) | 46 (3) | 13 (4) | 15 (3) | -4 (3) |
| C(8) | 2346 (5) | 1721 (4) | 5034 (3) | 76 (5) | 60 (4) | 32 (2) | 14 (3) | 2 (2) | 1 (2) |
| C(9) | 119 (5) | 1737 (4) | 4374 (3) | 84 (5) | 51 (4) | 35 (2) | -10 (3) | 12 (3) | -14 (2) |
| C(10) | -278 (5) | 3278 (5) | 2957 (3) | 77 (5) | 72 (4) | 27 (2) | 3 (3) | -4 (2) | -12 (2) |
| C(11) | 2725 (5) | 4678 (5) | 2949 (4) | 105 (6) | 87 (5) | 45 (3) | 3 (4) | 36 (3) | 2 (3) |
| C(12) | 3495 (5) | 4210 (5) | 3568 (4) | 79 (5) | 87 (5) | 59 (3) | -5 (4) | 31 (3) | -12 (3) |
| C(13) | 3849 (5) | 2832 (6) | 4854 (4) | 55 (5) | 110 (6) | 57 (3) | 14 (4) | -8 (3) | -13 (4) |
| C(14) | 3376 (5) | 2122 (5) | 5327 (4) | 86 (5) | 96 (6) | 45 (3) | 31 (4) | -6 (3) | 4 (3) |
| C(15) | 1616 (6) | 1295 (4) | 5513 (3) | 126 (6) | 54 (4) | 32 (2) | 9 (4) | 4 (3) | 2 (2) |
| C(16) | 569 (5) | 1323 (4) | 5193 (3) | 128 (6) | 51 (4) | 38 (3) | -12 (4) | 24 (3) | -2 (2) |
| C(17) | -895 (5) | 2188 (5) | 4031 (4) | 71 (5) | 67 (4) | 53 (3) | -14 (4) | 18 (3) | -24 (3) |
| C(18) | -1080 (5) | 2923 (5) | 3354 (4) | 68 (5) | 82 (5) | 44 (2) | 2 (4) | 4 (2) | -22 (3) |
| C(19) | -205 (5) | 4300 (5) | 2472 (3) | 87 (5) | 86 (5) | 28 (2) | 28 (4) | -4 (2) | -7 (3) |
| C(20) | 727 (5) | 4725 (5) | 2377 (3) | 104 (6) | 83 (5) | 28 (2) | 16 (4) | 4 (3) | 4 (3) |

Table 1 (*cont.*)Molecule 2 at -70°C

| | <i>x</i> | <i>y</i> | <i>z</i> | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|----------|----------|----------|--------------|--------------|--------------|--------------|--------------|--------------|
| C(1) | 7163 (5) | 4033 (5) | 4816 (3) | 78 (5) | 75 (5) | 42 (3) | 10 (4) | 21 (3) | -8 (3) |
| C(2) | 6974 (5) | 4712 (4) | 4084 (3) | 73 (5) | 53 (4) | 50 (3) | 10 (3) | 25 (3) | -0 (3) |
| C(3) | 6252 (5) | 4109 (5) | 3468 (3) | 80 (5) | 76 (5) | 37 (2) | 23 (4) | 17 (2) | 12 (3) |
| C(4) | 6006 (4) | 3069 (5) | 3824 (3) | 59 (4) | 70 (4) | 47 (2) | 4 (3) | 12 (2) | 2 (3) |
| C(5) | 6576 (5) | 3045 (5) | 4652 (3) | 88 (5) | 70 (4) | 38 (2) | 16 (4) | 21 (3) | 6 (3) |
| C(6) | 8067 (5) | 4100 (5) | 5418 (3) | 101 (6) | 83 (5) | 39 (2) | -6 (4) | 18 (3) | -16 (3) |
| C(7) | 7666 (5) | 5484 (4) | 3905 (4) | 100 (6) | 47 (4) | 61 (3) | 20 (4) | 24 (3) | -4 (3) |
| C(8) | 6219 (5) | 4246 (6) | 2626 (4) | 83 (5) | 105 (6) | 43 (3) | 31 (4) | 9 (3) | 14 (3) |
| C(9) | 5711 (5) | 2106 (6) | 3348 (4) | 73 (5) | 90 (5) | 61 (3) | -9 (4) | 4 (3) | -3 (3) |
| C(10) | 6859 (5) | 2041 (5) | 5088 (4) | 97 (6) | 83 (5) | 50 (3) | 11 (4) | 29 (3) | 15 (3) |
| C(11) | 8738 (6) | 5015 (6) | 5307 (4) | 103 (6) | 93 (6) | 61 (3) | 3 (4) | 20 (3) | -40 (4) |
| C(12) | 8532 (6) | 5673 (5) | 4581 (4) | 97 (6) | 65 (5) | 71 (4) | -11 (4) | 18 (3) | -26 (3) |
| C(13) | 7500 (6) | 5791 (5) | 3038 (4) | 112 (6) | 63 (5) | 70 (4) | 22 (4) | 39 (4) | 24 (3) |
| C(14) | 6801 (5) | 5201 (6) | 2432 (4) | 95 (6) | 111 (6) | 54 (3) | 38 (5) | 29 (3) | 35 (4) |
| C(15) | 5738 (6) | 3315 (7) | 2125 (4) | 85 (6) | 156 (8) | 41 (3) | 16 (5) | -9 (3) | 4 (4) |
| C(16) | 5498 (5) | 2308 (6) | 2456 (4) | 71 (5) | 115 (6) | 62 (3) | 5 (5) | -2 (3) | -20 (4) |
| C(17) | 5847 (6) | 1083 (5) | 3822 (5) | 90 (6) | 70 (5) | 83 (4) | -17 (4) | 12 (4) | -2 (4) |
| C(18) | 6389 (5) | 1057 (5) | 4658 (5) | 86 (6) | 65 (5) | 79 (4) | -5 (4) | 24 (4) | 12 (4) |
| C(19) | 7701 (6) | 2144 (6) | 5798 (4) | 116 (6) | 96 (6) | 44 (3) | 24 (5) | 18 (3) | 17 (3) |
| C(20) | 8292 (6) | 3128 (6) | 5947 (4) | 119 (7) | 125 (7) | 35 (3) | 28 (5) | 15 (3) | -1 (3) |

Table 2. Fractional coordinates ($\times 10^3$) of the hydrogen atoms

| | Molecule 1, 20°C | | | Molecule 2, 20°C | | | Molecule 1, -70°C | | | Molecule 2, -70°C | | |
|-------|--------------------------------|----------|----------|--------------------------------|----------|----------|---------------------------------|----------|----------|---------------------------------|----------|----------|
| | <i>x</i> | <i>y</i> | <i>z</i> | <i>x</i> | <i>y</i> | <i>z</i> | <i>x</i> | <i>y</i> | <i>z</i> | <i>x</i> | <i>y</i> | <i>z</i> |
| H(11) | 278 (4) | 531 (4) | 262 (3) | 947 (4) | 524 (5) | 565 (4) | 291 (5) | 548 (5) | 268 (4) | 950 (5) | 507 (6) | 574 (4) |
| H(12) | 423 (4) | 466 (5) | 376 (3) | 911 (4) | 619 (5) | 450 (4) | 409 (4) | 463 (5) | 373 (4) | 908 (5) | 614 (6) | 456 (4) |
| H(13) | 448 (4) | 311 (4) | 515 (3) | 805 (4) | 634 (5) | 313 (4) | 447 (5) | 323 (5) | 515 (4) | 807 (5) | 639 (6) | 287 (4) |
| H(14) | 373 (4) | 193 (4) | 587 (3) | 678 (4) | 534 (5) | 178 (4) | 377 (5) | 189 (5) | 583 (4) | 678 (5) | 536 (6) | 185 (4) |
| H(15) | 200 (4) | 114 (5) | 605 (3) | 584 (4) | 373 (5) | 155 (4) | 199 (4) | 107 (5) | 613 (4) | 561 (5) | 358 (6) | 156 (4) |
| H(16) | 8 (4) | 113 (5) | 558 (3) | 520 (4) | 160 (5) | 214 (4) | 12 (5) | 105 (5) | 555 (4) | 519 (5) | 159 (6) | 221 (4) |
| H(17) | -136 (4) | 208 (4) | 428 (3) | 557 (4) | 40 (5) | 357 (4) | -147 (5) | 201 (5) | 436 (4) | 560 (5) | 44 (6) | 365 (4) |
| H(18) | -179 (4) | 310 (4) | 324 (3) | 657 (4) | 31 (5) | 499 (3) | -184 (5) | 316 (5) | 323 (4) | 654 (5) | 27 (6) | 488 (4) |
| H(19) | -82 (4) | 466 (5) | 218 (3) | 797 (4) | 131 (5) | 613 (4) | -85 (5) | 470 (5) | 227 (4) | 810 (5) | 139 (6) | 616 (4) |
| H(20) | 72 (4) | 553 (5) | 203 (3) | 904 (4) | 313 (5) | 635 (4) | 92 (4) | 543 (5) | 202 (4) | 884 (5) | 305 (6) | 638 (4) |

the carbon thermal parameters, by radial extrapolation in a manner similar to a scheme used by Boyko & Vaughan (1964). The values 7.5 and 9.0 \AA^2 were used for molecules 1 and 2 respectively.

The quantity $\sum w(|F_o| - k|F_c|)^2$ was minimized with $\sqrt{w} = 16.5/F_o$ if $F_o > 16.5 e$, and $w = 1$ otherwise. The atomic scattering factors for carbon and hydrogen were those of Hoerni & Ibers (1954), and Stewart, Davidson & Simpson (1965), respectively. The final *R* value was 0.069 for 2013 observed reflections.* The final parameters are given in Table 1.

The space and thermal parameters of the room-temperature structure were used as the starting point for refinement of the low-temperature data. The final stages of this refinement were the same as for the room-temperature data refinement, except that the isotropic thermal parameters of the hydrogens were determined to be 6.0 and 7.2 \AA^2 , and fixed at these values. Twelve

reflections suspected of being affected by secondary extinction were not included. The final *R* value for 2137 observed reflections was 0.074.* The final parameters are given in Tables 1 and 2.

Analysis of thermal motion

The thermal ellipsoid plot given in Fig. 1 shows that the largest component of the atomic thermal motion is tangential to the perimeter of the molecule. Also, the amplitude of the thermal motion increases with increasing distance of the atom from the center of the molecule. The implied rigid-body molecular motion is borne out by a thermal motion analysis in terms of the T, L, and S rigid-body motion tensors (Schomaker & Trueblood, 1968). The eigenvalues of the libration tensor **L** are given in Table 3. The largest amplitudes of libration are about the fivefold axis in each molecule. As expected, the amplitudes are smaller at the lower temperature. The r.m.s. differences, $\langle (\Delta U_{ij})^2 \rangle^{1/2}$, between the calculated and the observed atomic thermal parameters are small compared to the r.m.s. values, $\langle U_{ij}^2 \rangle^{1/2}$, of the atomic thermal parameters themselves, showing that the model accounts for most

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31400 (28 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

of the thermal motion. The libration tensors were used to calculate libration-corrected interatomic distances. The libration corrections ranged from 0.005 to 0.008 Å.

Table 3. Rigid-body thermal motion parameters

| Eigenvalues of the libration tensor | Molecule 1 | | Molecule 2 | |
|---|------------|--------|------------|-----------------------|
| | 20°C | -70°C | 20°C | -70°C |
| L(1) | 4.1° | 3.9° | 4.9° | 4.4° |
| L(2) | 3.7 | 3.0 | 3.8 | 3.2 |
| L(3) | 3.6 | 2.4 | 3.0 | 2.7 |
| $\langle(\Delta U_{ij})^2\rangle^{1/2}$ | 0.0041 | 0.0036 | 0.0073 | 0.0044 Å ² |
| $\langle U_{ij}^2\rangle^{1/2}$ | 0.048 | 0.033 | 0.062 | 0.051 Å ² |

Molecular symmetry and distortion

There are many independent estimates of a given angle or distance in the corannulene molecule. First, there are two crystallographically independent molecules in the unit cell, and two independent sets of experimental data. Second, the molecule must nearly possess C_{5v} symmetry. In order to test for deviations from C_{5v} symmetry, two sets of long intramolecular distances have been calculated for each of the two independent molecules, and displayed graphically in Fig. 2. The two sets of distances shown in each figure are the five 'rim-to-rim' distances, which most nearly represent the 'diameter' of the carbon skeleton, and the ten somewhat shorter 'spoke-to-rim' distances also ex-

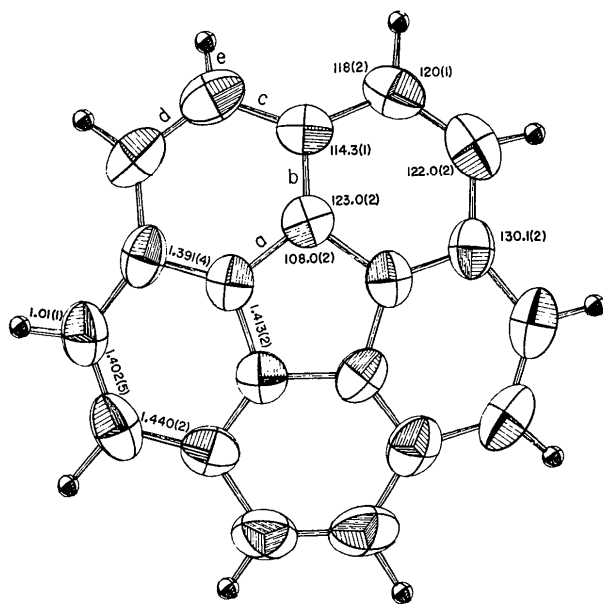


Fig. 1. ORTEP plot (Johnson, 1965) of the corannulene molecule viewed along the fivefold molecular axis. The 50% equiprobability ellipsoids represent, for molecule 1 at 20°C, the thermal motion of all atoms except the hydrogens, which are represented by spheres of radius 0.1 Å. Bond lengths (Å) and angles (°) are the overall averages for chemically equivalent bonds and angles.

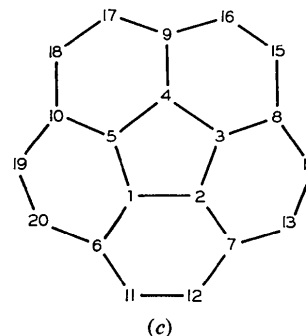
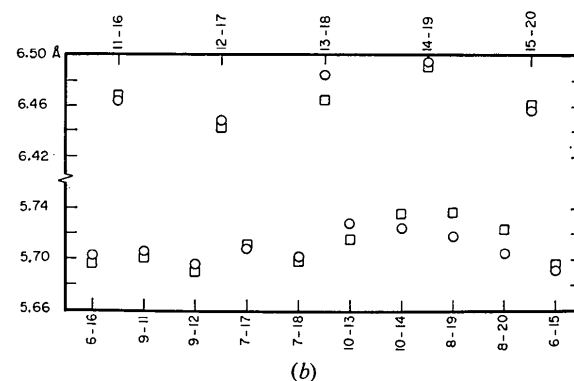
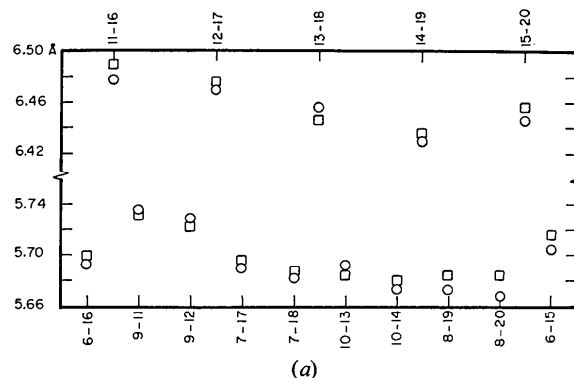


Fig. 2. Directional variation of the molecular diameter in (a) molecule 1, and (b) molecule 2. For each molecule two sets of long interatomic distances (Å), identified by atom numbers given in (c), are plotted in counterclockwise sequence to display the slight ellipticity of the molecules. Squares and circles designate, respectively, the 20°C and the -70°C results.

tending across the molecule. The distances within each group would be equal if the symmetry were strictly C_{5v} . In Fig. 2(a) the 15 distances in molecule 1 are plotted in order of their angular orientation about the fivefold axis of the molecule. It is clear that there is a directional variation of the 'diameter' of molecule 1; the effect is seen to be the same for both sets of distances and at both temperatures. The average standard deviation of these distances is 0.01 Å, thus the variation spans a range of about 5σ . The results for molecule 2 (Fig. 2b) also show a significant, although somewhat less clear-cut variation.

It is possible to account for the slight ellipticity of the molecules in terms of the molecular packing, shown in Fig. 3. Those atoms lying on the compressed sides of the molecules tend to be involved in the shortest intermolecular contacts. For example, the shortest C...C distance, 3.42 Å, is between C(8) of molecule 1 and C(12) of molecule 2; both of these atoms lie at or near the points of minimum diameter in their respective molecules.

Although the above distortions amount to variations of up to 0.05 Å in the approximately 6 Å 'diameter' of the carbon skeleton, it is reasonable to assume that the effect of these packing distortions on individual bond angles and, particularly, bond lengths, is very small. Furthermore, these effects among chemically equivalent bond lengths and angles are likely to be positive and negative to an approximately equal degree. On this basis the average value of all chemically equivalent bond lengths and angles may be taken as the best estimate of the parameter in question in the undistorted molecule. These averages and their standard deviations are given in Fig. 1. Values of bond distances and angles averaged within the individual molecules are given in Table 4.

Table 4. Summary of average distances and angles for corannulene

Bond designations are as in Fig. 1, atom numbers as in Fig. 2(c). A dihedral angle designated $i-j-k-l$ denotes the angle between the two planes defined by the atoms i, j, k and j, k, l , respectively. The numbers given in parentheses are the standard deviations of the respective means.

| | Temper- ature | Mol- ecule 1 | Mol- ecule 2 | Overall average |
|------------------------|------------------|-----------------|-----------------|--------------------|
| Bond distances (corr.) | | | | |
| <i>a</i> | 20° | 1.419 (3) Å | 1.402 (7) Å | 1.413 (3) Å |
| | -70 | 1.413 (4) | 1.419 (6) | |
| <i>b</i> | 20 | 1.384 (3) | 1.410 (5) | 1.391 (4) |
| | -70 | 1.383 (10) | 1.387 (4) | |
| <i>c</i> | 20 | 1.443 (4) | 1.427 (5) | 1.440 (2) |
| | -70 | 1.448 (5) | 1.440 (2) | |
| <i>d</i> | 20 | 1.398 (8) | 1.427 (9) | 1.402 (5) |
| | -70 | 1.385 (4) | 1.397 (6) | |
| <i>e</i> | 20 | 0.99 (3) | 1.05 (2) | 1.01 (1) |
| | -70 | 1.00 (3) | 1.00 (2) | |

Table 4 (cont.)

| | | | | |
|-----------------|-----|------------|------------|------------|
| Bond angles | | | | |
| <i>aa</i> | 20° | 108.0 (2)° | 108.0 (5)° | 108.0 (2)° |
| | -70 | 108.0 (6) | 108.0 (5) | |
| <i>cd</i> | 20 | 121.9 (2) | 122.1 (3) | 122.0 (1) |
| | -70 | 121.9 (2) | 122.1 (2) | |
| <i>ab</i> | 20 | 122.9 (1) | 123.1 (3) | 123.0 (1) |
| | -70 | 122.8 (2) | 123.0 (2) | |
| <i>bc</i> | 20 | 114.4 (2) | 114.2 (4) | 114.3 (1) |
| | -70 | 114.5 (2) | 114.2 (4) | |
| <i>cc</i> | 20 | 129.8 (3) | 130.5 (5) | 130.1 (2) |
| | -70 | 129.6 (3) | 130.6 (6) | |
| <i>de</i> | 20 | 118 (2) | 124 (4) | 120 (1) |
| | -70 | 119 (2) | 118 (2) | |
| <i>ce</i> | 20 | 119 (2) | 113 (4) | 118 (1) |
| | -70 | 118 (2) | 119 (3) | |
| Dihedral angles | | | | |
| 5-1-2-7 | 20° | 153.0 (3)° | 154.0 (3)° | 153.2 (2)° |
| | -70 | 152.7 (3) | 153.2 (4) | |
| 6-1-2-5 | 20 | 153.0 (3) | 154.0 (1) | 153.2 (2) |
| | -70 | 152.7 (2) | 153.2 (4) | |
| 11-6-7-1 | 20 | 169.7 (3) | 170.0 (2) | 169.6 (2) |
| | -70 | 169.6 (3) | 169.3 (4) | |
| 1-6-7-12 | 20 | 169.7 (3) | 170.0 (3) | 169.6 (2) |
| | -70 | 169.6 (3) | 169.3 (4) | |
| 5-1-6-11 | 20 | 159.7 (2) | 159.3 (3) | 158.9 (2) |
| | -70 | 158.4 (2) | 159.2 (3) | |
| 2-1-6-5 | 20 | 149.1 (5) | 150.1 (3) | 149.3 (3) |
| | -70 | 148.7 (5) | 149.3 (8) | |
| 11-1-6-20 | 20 | 168.3 (3) | 168.4 (4) | 168.5 (2) |
| | -70 | 168.2 (5) | 169.3 (6) | |
| 19-20-6-11 | 20 | 157.0 (4) | 157.0 (5) | 156.8 (2) |
| | -70 | 156.4 (3) | 157.1 (3) | |
| 19-20-6-1 | 20 | 9.5 (3) | 9.1 (4) | 9.5 (2) |
| | -70 | 9.6 (4) | 9.8 (5) | |
| H(11)-11-12-7 | 20 | 174 (1) | 171 (2) | 173 (1) |
| | -70 | 174 (1) | 171 (2) | |
| 6-11-12-H(11) | 20 | 174 (1) | 171 (2) | 173 (1) |
| | -70 | 174 (1) | 171 (2) | |

Discussion

Least-squares planes were calculated through the three sets of atoms C(1) to C(5), C(6) to C(10), and C(11) to C(20) for molecules 1 and 2 and at both temperatures. The largest r.m.s. deviation of atoms from their plane is 0.024 Å. The average separations between the planes are given in Fig. 4, which shows a side view of the strongly cupped molecule. The average angle between

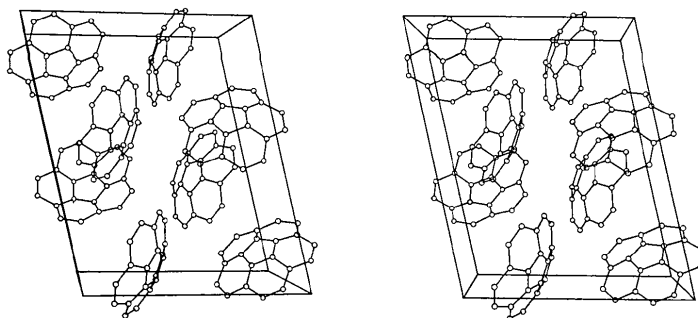


Fig. 3. A stereoscopic view (Johnson, 1965) of the corannulene structure viewed approximately along the *b* axis, with the *a* axis horizontal. Hydrogen atoms have been omitted.

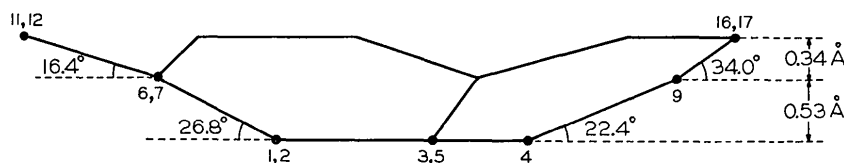


Fig. 4. The idealized carbon skeleton of the corannulene molecule viewed perpendicular to a molecular mirror plane. Where two atom numbers are given, the atoms coincide in the projection. Atom numbers refer to Fig. 2(c).

least-squares planes defined by atoms C(11) to C(20) and the mean planes of the six-membered rings is 20.4° . The average dihedral angle between the five- and the inner portion of the six-membered rings is $26.8 (2)^\circ$. The outer portion of the six-membered ring then bends back from the inner portion of the six-membered ring with an average dihedral angle of $10.4 (2)^\circ$. The hydrogen atoms are bent up from the plane of the outer portion of the six-membered ring by $7 (2)^\circ$. This angle, whose difference from zero is marginally significant, may arise from packing forces producing an additional cupping of the cone of C-H bonds. The 'spokes' bend up from the five-membered ring with an angle of $22.4 (3)^\circ$. The angle between the spoke and the plane of the two adjacent spoke-to-rim bonds is 11.6° ; the plane is bent upward, as shown in Fig. 4. This non-coplanarity of the three bonds joining at the outer end of the spoke, and the 10.4° bend of the six-membered rings about their tangential diameter may be viewed as a compromise which minimizes both effects. If either angle were zero, the other would necessarily be larger.

For a number of planar aromatic hydrocarbons the bond distances predicted from rather simple quantum mechanical calculations compare favorably with the experimental values (Dewar & Gleicher, 1965; Fawcett & Trotter, 1966). For coronene, the planar 'analogue' of corannulene, Fawcett & Trotter (1966) find r.m.s. differences between measured and calculated bond distances amounting to 0.018 and 0.013 \AA for the V.B. and M.O. methods, respectively.

Gleicher (1967), who correctly predicted the non-planar structure of corannulene, also calculated bond distances for two assumed geometries, planar and cupped. In the latter model an angle of 38° was assumed between the five- and six-membered rings. The calculated bond lengths for bonds *a*, *b*, *c* and *d* (Fig. 1) are rather similar for the two models, namely 1.437 , 1.399 , 1.433 and 1.371 \AA for the planar, 1.430 , 1.408 , 1.430 and 1.374 \AA for the bowl-shaped model. The calculated distances *b* and *c* are in reasonably good agreement with experiment (Fig. 1), but *a* and *d* are not. The comparison suggests that those bonds, *a* and *b*, which are under compression, are calculated too long, while the peripheral bonds *c* and *d*, which are under tension, are calculated too short.

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