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The Crystal Structure of 3,4-Benzocyclodeca-1,5-diyne, $C_{14}H_{12}$

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3,4-Benzocyclodeca-1,5-diyne was formed during an attempted synthesis of a planar 10π-electron system. $C_{14}H_{12}$ is tetragonal with $a = 7{\cdot}891\,(1)$, $c = 17{\cdot}108\,(1)$ Å, space group $P4_32_12$, $Z = 4$. The structure was solved by trial and error and refined to a final $R = 8{\cdot}6\%$ for 260 counter reflexions. The precision of the structure is limited by disorder involving the four sp^3 hybridized C atoms.

Introduction

A novel attempt to prepare a new 10π-electron aromatic hydrocarbon was described by Darby, Kim, Salaün, Shelton, Takada & Masamune (1971). The final step of the reaction scheme produced 1,2,3,4-tetrahydroanthracene and, in 30% yield, a new hydrocarbon with the molecular formula $C_{14}H_{12}$. The spectroscopic properties of the compound were consistent with two possible structures (Fig. 1).

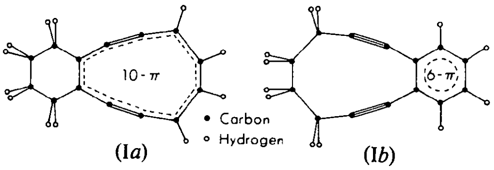

Fig. 1. The desired 10π-electron system (I*a*) and a rearrangement product (I*b*).

The X-ray diffraction study described in this paper was undertaken to resolve this question of gross stereochemistry and, if the structure was found to be (I*a*), to determine precise bond lengths for the new aromatic system.

Experimental

Colourless tetragonal-bipyramidal crystals were kindly supplied by Dr S. Masamune. The crystals are unstable in air and samples were sealed in Lindemann glass capillaries with a nitrogen atmosphere. The crystals supplied had faces of the form {113}, but were too large for diffraction studies and repeated attempts to grow smaller ones failed. The crystals did not cleave cleanly, but shattered to give irregular fragments; however, some fragments were found that were suitable for a diffraction study.

Preliminary photographs led to the assignment of the crystal class as tetragonal, and the diffraction conditions ($00l$, $l = 4n$; $h00$, $h = 2n$) are consistent with the space group $P4_12_12$ or the enantiomorphous $P4_32_12$. Since the anomalous-dispersion effects are too small to distinguish between these, an arbitrary assignment of the latter was made. A fresh crystal $0{\cdot}025 \times 0{\cdot}020 \times 0{\cdot}025$ cm was taken and mounted about **a**. A least-squares refinement of 2θ values for 13 reflexions centred on a Picker four-circle manual diffractometer (no monochromator, λ Cu $K\alpha_1 = 1{\cdot}54051$ Å) gave $a = 7{\cdot}891\,(1)$, $c = 17{\cdot}108\,(1)$ Å at 22°C.

The observed density ($1{\cdot}12$) was in good agreement with the calculated value of $1{\cdot}12$ g cm^{-3} for $Z = 4$. The molecules are therefore required to lie on a twofold axis. The agreement between the observed and calculated densities is probably somewhat fortuitous as the density was measured by flotation in KI solution and the crystals decomposed in less than 10 min under these conditions. The noncentrosymmetric high-symmetry space group and the high loss of data expected from examination of the photographs suggested that if (I*a*) proved to be correct, the room-temperature study would not supply parameters of a quality that would be considered suitable for theoretical considerations. Nevertheless, the room-temperature structure was pursued because of the lack of an available cryostat for an immediate low-temperature study. In the event that (I*a*) was confirmed, a low-temperature study was planned since it would warrant the considerable effort required.

Cu $K\alpha$ radiation was used in the data collection and the intensities of 517 independent reflexions with $2\theta \leq 120°$ were measured. A graphite monochromator [(002) plane] was used with a take-off angle of 2°. One-minute scans through 2° were employed, the area under the peak being integrated, and the backgrounds either side of the peaks ($B1$ and $B2$) were measured for

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20 s in the stationary positions. On the assumption that the background was linear, the data were reduced to $|F|$ and σF (Doedens & Ibers, 1967). A value of $p = 0{\cdot}03$ was used in $\sigma F = [P + t^2(B1 + B2) + p^2 I]^{1/2}$. The criterion for observation was $I \geq 3\sigma(I)$; 260 reflexions satisfied this condition and were used in further calculations.

Six standard reflexions were measured every 3 h and showed no significant decrease. No absorption corrections were applied [μ(Cu $K\alpha$) = 5 cm^{-1}].

Solution and refinement of the structure

The structure was solved by trial and error. The reflexions 004 and 113 had very large $|F|$'s (004 was the larger, but quadruply weighted). Since the molecule was thought to be approximately planar [be it (I*a*) or (I*b*)] and known to lie along the twofold axis, the magnitude of the 113 reflexion was consistent with a coincidence of one of the molecular planes with the crystal (113) plane, the crystal habit adding weight to this consideration, *i.e.* the molecules lie on the twofold axis and are inclined at about 45° to **c**. Structure factor calculations for the 004 reflexions were consistent with this angular orientation for either model.

The two models have very similar shapes and are approximately planar, with only 2 out of 14 C atoms likely to show any large deviation from the mean plane. Several models of varying shape for the ten-membered ring were constructed, placed on graph paper and the fractional coordinates for each model found in an arbitrary position along the diagonal.

A short program was devised by one of us (RAS) for this, and the structure factors of a limited number of reflexions and associated R values were calculated on the basis of the input model. Scattering factors for C were from Cromer & Mann (1968), those for H from Mason & Robertson (1966). The fractional coordinates in x and y were then increased by 0·01 for each atom and the calculations repeated until the model had travelled half the length of the diagonal. On reaching this point the model was returned to the starting position, tilted through 5° with respect to **c** and the calculations repeated. One of these models gave rise to a clearly defined minimum with a tilt of 50° with respect to **c**. Examination of the structure factor expressions showed that reflexions with l odd were affected in both sign and magnitude by the sense of tilt, whereas those with l even were unaffected. Two structure factor calculations on the full data set were made with both senses of tilt investigated. One model gave $R = 40$ and the other $R = 50\%$. The model which gave the better fit was retained.

Refinement of this model with isotropic atoms and the inclusion of H atoms in calculated positions reduced R to 12% and showed (I*b*) to be correct. C(1)—C(1′) was only 1·4 and C(1)—C(2) 1·67 Å; all other bond lengths were reasonable for this stage of refinement. The thermal parameters of C(1) were unreasonably large. In an attempt to find out why, five more least-squares cycles with all atoms anisotropic were calculated, reducing R to 10%. U_{33} for C(1) was very large and required further investigation. A difference map phased on C(2)—C(7) was calculated and examined. A contour of the section containing C(1) and C(1′) indicated disorder. Two well-resolved positions for C(1) occur and are called C(*p*) and C(*a*) for predominant and alternate respectively (Hanson, 1965). The nature of the disorder is in the conformation of the C(2)—C(*p*)—C(*p*′)—C(2′) twist, 25% or so of the atoms having the opposite conformation (Fig. 2).

Since C(*a*) and C(*a*′) are approximately equidistant from C(*p*), then C(*p*) would be expected to shift approximately along the C(*p*)—C(*p*′) vector, accounting for the anomalous bond lengths involving C(*p*). The unusual thermal parameters of C(*p*) and C(*p*′) can also be explained by the attempts of the ordered model to express the unexplained areas of high electron density.

The lack of data and parameter correlations make it difficult to refine the disorder model by least squares. The disorder was assumed to involve only C(*p*) and C(*p*′) and, subsequently, the associated H atoms. C(2) and C(2′) might be expected to be affected, but the more reasonable temperature factors of C(2) in the

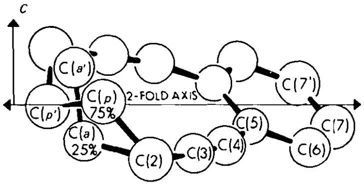

Fig. 2. The nature of the disorder involving the predominant atoms C(*p*) and C(*p*′) and the alternate atoms C(*a*) and C(*a*′).

Table 1. *Results of isotropic refinement with different occupancy values for* C(*a*)

Occupancy for C(*a*) (%)	10	20	25	30	40
R (%)	13·4	10·9	10·7	10·8	11·7
U for C(1) (Å^2)	0·116	0·110	0·091	0·082	0·075
U for C(1*d*) (Å^2)	—0·097	0·060	0·079	0·111	0·132

previous stages of refinement suggested that any deviations were small and would be impossible to resolve. C(a) was fixed such that C(2)–C(a) and C(a)–C(a') were 1·54 Å and the mid-point of C(a)–C(a') was coincident with the mid-point of C(p)–C(p'). C(p) and C(a) were constrained to have fixed occupancy factors and only their temperature factors were allowed to vary. Isotropic refinement of the structure was then attempted with 10, 20, 25, 30 and 40% occupancy for C(a). After each refinement C(a) was shifted manually so that the geometrical restraints outlined above held. Table 1 lists some of the resulting values.

The 25% occupancy model was taken to be the most likely and may be justified with Hamilton's (1965) test. H atom positions were recalculated and included in subsequent structure factor calculations. The H atoms attached to C(p) were called H(1) and H(2), those attached to C(a) were called H(3) and H(4), the 75% occupied and 25% occupied H atoms on C(2) were called H(5)–H(6) and H(7)–H(8) respectively, and those attached to C(6) and C(7) were called H(9) and H(10) respectively. Thermal parameters for these H atoms were set at 10% greater than the C atoms to which they were attached, but their parameters were not refined. The small data set with high σ's forced the maintenance of isotropic temperature factors. Three cycles of least squares reduced R to 8·6%. Refinement was considered complete with (maximum shifts/σ) $<$ 0·1.

Major crystallographic programmes used include *MIXG*2 by D. P. Shoemaker, *PMMO* by M. J. Bennett, *FORDAP* by A. Zalkin, a local modification of *SFLS*-5 by C. T. Prewitt, *MGEOM* by J. S. Wood, *ORFFE*-2 by W. Busing and H. A. Levy, *ORTEP* by C. Johnson, and other local programs.

The final coordinates are listed in Table 2.*

Table 2. *Fractional coordinates* ($\times 10^4$) *and isotropic thermal parameters*

The temperature factor is in the form $\exp[-2\pi^2 U(\sin\theta/\lambda)^2]$.

	x	y	z	U (Å^2)
C(a)	1174	915	−442	0·053 (6)
C(p)	1674 (15)	230 (17)	−33 (9)	0·080 (7)
C(2)	2953 (15)	317 (15)	−665 (6)	0·081 (5)
C(3)	4079 (13)	1811 (13)	−601 (5)	0·074 (4)
C(4)	4902 (12)	3018 (13)	−498 (5)	0·075 (4)
C(5)	5578 (11)	4609 (11)	−267 (4)	0·065 (4)
C(6)	7143 (13)	5229 (13)	−516 (5)	0·084 (4)
C(7)	7708 (13)	6812 (13)	−262 (6)	0·098 (5)
H(1)	2390	460	560	0·090
H(2)	1120	940	60	0·090
H(3)	290	10	−630	0·060
H(4)	930	2070	−720	0·060
H(5)	3699	−790	−700	0·090
H(6)	2260	400	−1210	0·090
H(7)	3380	−670	−330	0·090
H(8)	2950	−110	−1270	0·090
H(9)	7880	4450	−870	0·095
H(10)	8830	7270	500	0·110

Results and conclusions

The analysis shows that the structure is (Ib) (3,4-benzocyclodeca-1,5-diyne). The disorder limits the precision of the determination and we cannot exclude the possibility that the disorder is even more complicated and that the crystals contain, for example, a small percentage of (Ia). The C skeleton is shown in Fig. 3 with pertinent distances and angles.

A detailed discussion of the geometry is limited by the systematic errors which must be present. The observed bond lengths agree with the usual values for hydrocarbons (Mason & Robertson, 1966). C(2) through C(7) inclusive are planar within experimental error (Table 3).

Strain within the ten-membered ring leads to significant deviations from the normal values for the bond angles. The particular pattern of deviations of the bond angles is somewhat unexpected in that one angle involving the acetylenic link is considerably more distorted

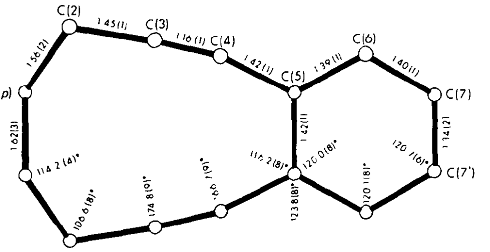

Fig. 3. The C skeleton of 3,4-benzocyclodeca-1,5-diyne with pertinent distances and angles.

Table 3. *Deviations of atoms from the plane defined by C(2)–C(7) and their twofold related atoms with respect to a Cartesian coordinate system*

$$0{\cdot}445x - 0{\cdot}445y + 0{\cdot}777z - 3{\cdot}5111 = 0.$$

	Deviation		Deviation
C(2)	0·044 Å	C(6)	−0·013 Å
C(3)	−0·004	C(7)	−0·034
C(4)	−0·002	C(p)	−0·496
C(5)	−0·016	C(a)	0·533

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32184 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

from 180° than the other [166·7 for C(3)–C(4)–C(5) compared to 174·8° for C(2)–C(3)–C(4)]. This is surprising in that by moving C(3) further from the twofold axis these two angles would become more similar and C(1)–C(2)–C(3) would increase towards 109·5°, the tetrahedral angle. We have no explanation for this feature of the structure.

Table 4. *Intermolecular distances*

Predominant–predominant

	Symmetry position	
H(2)···H(10)	$x-1, y-1, z$	2·48 Å
H(1)···H(9)	$y, x-1, -z$	2·65
H(1)···H(5)	$\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{4}+z$	2·64
C(4)···H(6)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$	2·87
C(5)···H(6)	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{4}-z$	2·91
C(6)···H(5)	$1+y, x, -z$	2·90

Predominant–alternate

	Symmetry position	
H(3)···H(10)	$x-1, y-1, z$	2·46 Å
H(7)···H(9)	$y, x, -1-z$	2·49
H(8)···H(1)	$\frac{1}{2}-y, \frac{1}{2}+x, z-1$	2·60
H(4)···H(5)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$	2·52
C(4)···H(3)	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{4}-z$	2·83
C(5)···H(3)	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{4}-z$	2·84
C(6)···H(7)	$1+y, x, -z$	2·68
C(6)···H(3)	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{4}-z$	3·01
C(*p*)···C(4)	$\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{4}-z$	3·61
C(*p*)···C(5)	$\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{4}-z$	3·52
C(*p*)···C(6)	$\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{4}-z$	3·75

Table 4 shows important intermolecular contacts, with those dependent on the conformation grouped together. The alternate–alternate distances are not reported as there are no unusually short distances, other than those between alternate positions and positions unchanged by the conformation, *i.e.* not involved in the disorder. These positions are reported for the predominant–predominant case. An examination of these contacts shows only one disruptive feature associated with the disorder: the C(6)–H(7) contact of 2·68 Å which is considerably less than the van der Waals contact sum of 2·90 Å. This is presumably the major contributor to the preference for a C(*p*)–C(*p*′) bond approximately perpendicular to the fourfold screw axis.

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Insecticides. I. The Crystal Structure and Absolute Configuration of (–)-1-(*o*-Chlorophenyl)-1-(*p*-chlorophenyl)-2,2,2-trichloroethane, (–)-*o*,*p*′-DDT

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(–)-1-(*o*-Chlorophenyl)-1-(*p*-chlorophenyl)-2,2,2-trichloroethane or (–)-*o*,*p*′-DDT, $C_{14}H_9Cl_5$, is orthorhombic, $P2_12_12_1$, $a = 11{\cdot}419$ (2), $b = 17{\cdot}635$ (3), $c = 7{\cdot}501$ (1) Å, $Z = 4$, $\rho_o = 1{\cdot}53$, $\rho_c = 1{\cdot}54$ g cm^{-3}. The structure was solved by direct methods and refined to $R = 5{\cdot}6\%$ for 942 counter reflexions. The more oestrogenically active (–) isomer is shown to be the *R* form.

Introduction

The crystal structure of racemic (±)-*o*,*p*′-DDT was reported by Delacy & Kennard (1972); it crystallizes in the triclinic class with two independent molecules per asymmetric unit and the molecular structures of these two independent molecules are very similar, suggesting a dominance of intramolecular forces. Recently McBlain & Wolfe (1975) and McBlain, Currie & Wolfe (1976) have reported a method of resolving the isomers.

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