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The Synthesis and Structure of 5,6,6aα,6bβ,7,8,12bβ,12cα-Octahydrodibenzo[*a*,*i*]biphenylene, the Major Photodimer from 1,2-Dihydronaphthalene

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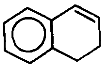
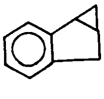
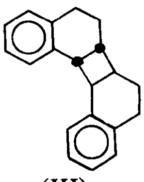
The photodimer 5,6,6aα,6bβ,7,8,12bβ,12cα-octahydrodibenzo[*a*,*i*]biphenylene is obtained as the major product from the benzophenone-sensitized photolysis of 1,2-dihydronaphthalene. The preparation, purification, and spectral data of the compound are described. Crystals of the compound are orthorhombic, space group *Pbca*. The cell dimensions are: a = 14·638 (5), b = 11·09 (1), c = 17·536 (8) Å (at −160 °C). The structure was determined by direct methods and refined with least-squares calculations based on 2704 data collected at −160 °C. The final R value is 0·047. The molecule has approximately twofold symmetry. The central cyclobutane ring is planar and has one elongated bond of 1·579 (2) Å.

Introduction

The dimerization of 1,2-dihydronaphthalene (I) has been extensively investigated. Because of the structural similarity to styrene, previous investigations of (I) involved treatment with acid (Hertzler, Eisenbraun & Flanagan, 1969) and base (Eisenbraun, Ansell, Dobbs, Harris, Hertzler, Ruehle, Burks & van der Helm, 1976). More recently, interest has been directed to the photolysis of (I). In dilute solution, benzobicyclo[3.1.0]hex-2-ene (II) is formed (Kleinhuis, Wijting & Havinga, 1971), whereas irradiation of (I) in hexane at 238–300 nm gives polymer (Salisbury, 1971). However, irradiation of (I) in the presence of benzophenone affords dimer (III) (Krauch, Metzner & Schenck, 1963; Dekker & Dekker, 1973, 1975). We report a single-crystal X-ray analysis which confirms structure (III) as the photodimer. In addition, we report techniques leading to improved yields of photodimer (III).


(I)


(II)


(III)

Since it is known that perhydrobiphenylene is epimerized through photolysis (Salomon & Kochi, 1973), we considered that (III) might also be epimerizable. However, we found no evidence for epimerization with their conditions.

Experimental

Crystallographic data

Suitable crystals for single-crystal X-ray diffraction of (III) were grown from a petroleum spirit solution. The crystals appeared as clear plates elongated in the **b** direction. Preliminary studies indicated the crystals were orthorhombic, space group *Pbca*. Least-squares cell dimensions were obtained from a least-squares fit of the $+2\theta$ and -2θ values of 40 reflections measured at a temperature of −160 °C with Cu $K\alpha_1$ radiation (λ = 1·54051 Å). Crystallographic data (Table 1) and integrated X-ray intensity data were collected at −160 °C [cooling was by a stream of cold nitrogen gas and a concentric outer room-temperature stream (Post, Schwartz & Fankuchen, 1951; van Bolhuis, 1971)] with a Nonius CAD-4 automatic diffractometer. The temperature variation was less than 3°. The 2704 intensity data, comprising all unique reflections with $2\theta \leq 140°$ were collected from a crystal having dimensions 0·47 × 0·55 × 0·69 mm. The data were collected with Ni-filtered Cu $K\bar{\alpha}$ radiation and θ–2θ scan techniques. The θ scan width was calculated as $(1 \cdot 0 + 0 \cdot 1 \tan \theta)°$. The maximum scan time was 50 s with $\frac{2}{3}$ of the time spent while scanning the peak and $\frac{1}{6}$ on each of the left and right backgrounds. The scan time was less than 50 s for those intensities where a value of 40 000 for I could be attained with a faster scan speed than normal. 93 reflections were considered indistinguishable from the background, having $I < 1 \cdot 4\sigma(I)$. These reflections were assigned an intensity equal to $\sigma(I)$ for the purposes of least-squares refinement. A standard reflection was monitored after every 25 measurements.

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The intensities of the monitored reflections for the entire data collection varied less than 2·5%, while most were within a 1% range. Lorentz and polarization corrections were applied to the data but no absorption corrections were made.

Preparation of 5,6,6a*α*,6b*β*,7,8,12b*β*,12c*α*-*octahydrodibenzo*[*a,i*]*biphenylene*

A 70 g (0·53 mol) sample of (I) and 5 g (0·027 mol) of benzophenone were dissolved in benzene. The final volume was 250 ml. This solution was added to a quartz photochemical tube and then irradiated at 26 °C for 48 h with a Hanovia 450 W, medium-pressure mercury lamp enclosed in a Pyrex filter. The homogeneous solution was concentrated under reduced pressure with a rotary evaporator. The concentrate was distilled (Kugelrohr apparatus) at 145–175 °C (0·3 mm) to give an oil which crystallized from 95% ethanol to afford 42 g (0·16 mol) of white crystals of (III), m.p. 70–71 °C. The filtrate was concentrated, dissolved in an ether–isohexane mixture, and then eluted through a 2·5 × 10 cm column of basic alumina (Merck, activity 1). Concentration of this solute gave an additional 18·6 g of (III), m.p. 70–72 °C, for an overall yield of 82%. The mass spectrum (70 eV) showed a parent ion at *m/e* 260. The PMR spectrum is consistent with that previously reported (Dekker & Dekker, 1973).

Effect of solvent on dimerization of (I)

Samples of (I) in quartz tubes were prepared as follows: one tube contained 10 g (0·077 mol) of (I) and 1·0 g of benzophenone; the other three tubes received a 50% solution (v/v) containing 5·0 g (0·38 mol) of (I), an equal volume of the appropriate solvent and 0·5 g of benzophenone. The tube contents were thoroughly mixed and then sealed under nitrogen with Neoprene stoppers. These tubes were placed in a 432 W Rayonet photochemical reactor, model RPR 100, and irradiataed at room temperature for 42 h at 350 nm. The yields are summarized in Table 2.

Table 1. *Crystallographic data*

Formula: $C_{20}H_{20}$
FW 260·18
Space group: *Pbca*
Systematic absences
$0kl,\ k = 2n + 1$
$h0l,\ l = 2n + 1$
$hk0,\ h = 2n + 1$
$h00,\ h = 2n + 1$
$0k0,\ k = 2n + 1$
$00l,\ l = 2n + 1$
$a = 14{\cdot}638\ (5)$ Å
$b = 11{\cdot}09\ (1)$
$c = 17{\cdot}536\ (8)$
$V = 2847$ Å^3
$Z = 8$
$F(000) = 140$
$D_c = 1{\cdot}214$ g cm^{-3}

Attempted epimerization of (III)

A solution of 0·5 g photodimer (III) in 20 ml of acetone was placed in a quartz tube capped with a Neoprene stopper. The solution was irradiated at room temperature for 72 h in a Rayonet photochemical reactor model RPR 100, at 350 nm. The tube was opened and the acetone was evaporated from the mixture. The resulting residue was recrystallized and the white crystals were shown to be unchanged by mixture melting point. A GC analysis of the mother liquor showed (III) accompanied by <1% of (I). No new peaks were observed.

Structure determination and refinement

The structure was solved with data collected at room temperature. Disorder in the molecular structure led to the subsequent data collection and refinement at low temperature. The overall temperature factor and scale were determined by Wilson's (1942) method. The normalized structure factors, $|E|$, were calculated and a statistical test of their distribution confirmed the centrosymmetry of the space group.

The structure was solved by application of the symbolic addition procedure (Zachariasen, 1952; Karle & Karle, 1966) to the room-temperature data. The phases for 360 normalized structure factors having $E \geq 1{\cdot}5$ were used in generating an E map from which the positions of all 20 C atoms in the molecule were located. After a few cycles of least-squares refinement, all H atoms were located by a comparison of their positions calculated on the basis of geometric considerations with the peaks appearing in a calculated difference Fourier map. For the room-temperature data, the presence of disorder in the molecular structure of atoms C(6) and C(7) and neighboring atoms was also noted in this difference Fourier map.

The initial structure factor calculation based on low-temperature data used the final positional parameters

Table 2. *Effect of solvent on dimerization*

1,2-Dihydronaphthalene (mol)	Solvent	Benzophenone (mol)	Amount of (III) produced (mol)	Dimeric product (% yield)
0·077	Neat	0·0055	0·012	32
0·038	Benzene	0·0028	0·017	86
0·038	*n*-Hexane	0·0028	0·012	62
0·038	Cyclohexane	0·0028	0·015	80

Table 3. *Positional parameters of all non-hydrogen atoms* (×10⁵)

x, *y* and *z* are expressed in fractions of the edges *a*, *b* and *c*. Standard deviations for the last digit are in parentheses.

	x	*y*	*z*
C(1)	15142 (8)	33331 (11)	8486 (7)
C(2)	11462 (8)	25015 (12)	13560 (7)
C(3)	16713 (9)	15333 (11)	16003 (7)
C(4)	25567 (9)	14026 (11)	13369 (7)
C(4a)	29313 (8)	22184 (10)	8146 (6)
C(5)	38856 (8)	20492 (11)	5064 (7)
C(6)	43657 (8)	32616 (12)	3775 (7)
C(6a)	38182 (8)	40799 (11)	−1483 (7)
C(6b)	36792 (8)	36228 (11)	−9796 (7)
C(7)	40280 (8)	44104 (11)	−16270 (7)
C(8)	35159 (8)	56146 (11)	−16750 (7)
C(8a)	24968 (8)	54322 (11)	−17457 (6)
C(9)	19599 (9)	62028 (11)	−21897 (7)
C(10)	10183 (9)	60624 (11)	−22275 (7)
C(11)	5972 (8)	51398 (11)	−18208 (6)
C(12)	11268 (8)	43435 (11)	−13974 (7)
C(12a)	20761 (8)	44771 (11)	−13535 (6)
C(12b)	26254 (8)	36309 (10)	−8661 (6)
C(12c)	27647 (8)	40645 (10)	−164 (6)
C(12d)	24040 (8)	32021 (10)	5702 (6)

Table 4. *Hydrogen atom parameters*

	x (×10⁴)	*y* (×10⁴)	*z* (×10⁴)	*B* (Å²)
H(1)	1135 (11)	4001 (14)	691 (9)	2·0 (3)
H(2)	506 (10)	2582 (14)	1542 (8)	1·9 (3)
H(3)	1427 (11)	959 (13)	1960 (9)	2·2 (3)
H(4)	2942 (10)	682 (14)	1512 (9)	2·0 (3)
H(51)	4226 (11)	1512 (14)	871 (9)	2·4 (3)
H(52)	3874 (11)	1553 (14)	−2 (9)	2·6 (3)
H(61)	4455 (12)	3707 (14)	904 (9)	2·7 (4)
H(62)	4982 (12)	3111 (14)	162 (9)	2·4 (3)
H(6a)	4056 (10)	4931 (15)	−138 (9)	2·4 (3)
H(6b)	3940 (10)	2774 (13)	−1032 (8)	1·8 (3)
H(71)	4714 (10)	4569 (13)	−1545 (9)	2·0 (3)
H(72)	3965 (11)	3945 (12)	−2135 (9)	2·0 (3)
H(81)	3663 (11)	6093 (14)	−1212 (10)	2·2 (3)
H(82)	3719 (11)	6091 (13)	−2134 (10)	2·4 (3)
H(9)	2249 (10)	6861 (13)	−2499 (8)	2·0 (3)
H(10)	652 (11)	6620 (14)	−2547 (9)	2·4 (3)
H(11)	−75 (11)	5060 (13)	−1845 (9)	2·3 (3)
H(12)	833 (11)	3679 (13)	−1132 (10)	2·4 (3)
H(12b)	2353 (10)	2835 (15)	−876 (8)	2·3 (3)
H(12c)	2495 (10)	4886 (14)	64 (8)	1·5 (3)

from the room-temperature structure determination, giving an R ($=\Sigma||kF_o| - |F_c||/|kF_o|$) of 0·34. After several further cycles of least-squares refinement, the parameter shifts were less than ⅔ of the corresponding standard deviations for all C and H atoms, and the refinement was terminated. All C atoms were included in the refinement with anisotropic temperature factors. All H atoms were included in the refinement with isotropic temperature factors. A final difference Fourier map was calculated in which all electron densities were between −0·2 and 0·2 e Å^{-3} except for regions of negative electron densities from −0·3 to −0·4 e Å^{-3} which appeared at the center of the benzene rings. No trace of disorder was observed in the final difference Fourier map.

All least-squares refinements were carried out by the block-diagonal least-squares program of Ahmed (1966). The unweighted R based on the final parameters (Tables 3 and 4) was 0·047 for all data. The e.o.f. was 1·70. Each amplitude was assigned a weight based on an experimental weighting scheme which has been described previously (van der Helm, Ealick & Burks, 1975). The average value of $w_F\Delta F^2$ did not show significant variation with either $|F_o|$ or $\sin^2\theta/\lambda$ in the structure factor analysis, thus validating the weighting scheme which was used. The quantity minimized in the refinement was $\Sigma\, w_F(|kF_o| - |F_c|)^2$.*

The atomic scattering factors for C were taken from *International Tables for X-ray Crystallography* (1962). The scattering factors for H were those of Stewart, Davidson & Simpson (1965).

Results and discussion

As shown in Fig. 1, the molecule consists of five carbon rings fused together with a cyclobutane ring as the central ring. Cotton & Frenz (1974) have reviewed the literature concerning structures of compounds containing cyclobutane rings. From Fig. 1 the *cis* fusion of the cyclohexene rings to the central cyclobutane ring and the *anti* conformation of the fused rings are quite evident.

Fig. 1 also shows that the molecule has nearly perfect, but noncrystallographic, twofold symmetry, with the rotation axis passing through the middle of bonds C(12b)–C(12c) and C(6a)–C(6b). All related bond distances and bond angles are equal, in pairs, within three standard deviations (Figs. 2 and 3). The two C–C bonds in the cyclobutane ring which form the bridges between the two naphthalene moieties, C(12b)–C(12c) and C(6b)–C(6a), are not related to each other by the twofold symmetry and differ significantly (10σ) in distance. The C(12b)–C(12c) bond is significantly longer [1·579 (2) Å] than a normal C–C single bond. The average bond distance in the cyclobutane ring in fused-ring systems is 1·551 (3) Å (Cotton & Frenz, 1974). In the present compound this average is 1·563 Å, indicating more strain than in previously determined organically fused cyclobutanes. Most of the strain is located in the C(12b)–C(12c) bond. The significance of this observation is supported by the facile cleavage of the elongated bond during reduction of (III) with lithium or sodium in liquid ammonia giving 1,1′,2,2′,3,3′,4,4′-octahydro-2,2′-

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32975 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

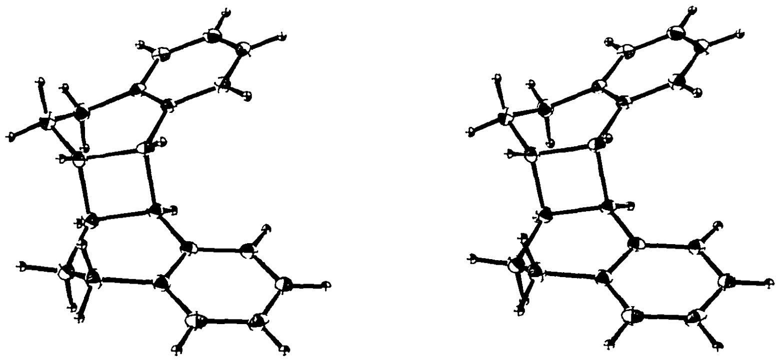

Fig. 1. A stereoview (Johnson, 1965) of the molecule.

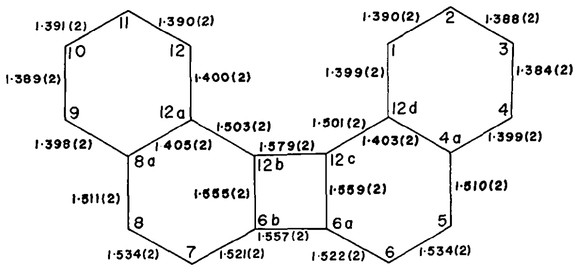

Fig. 2. Bond distances (Å).

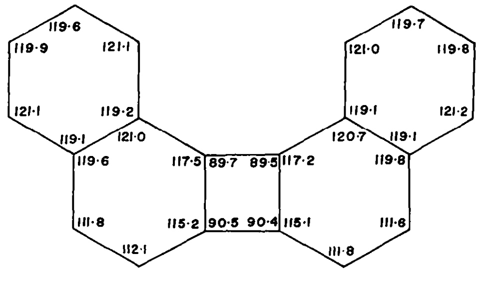

Fig. 3. Bond-angles (°). Standard deviation for all angles is 0·1°.

binaphthyl (Ruehle, Dobbs, Ansell, van der Helm & Eisenbraun, 1977).

The largest deviations from twofold symmetry are observed for the torsion angles which are given in Table 5. The fusion forces the cyclohexene rings into a distorted half-boat conformation. A further description of this conformation is obtained from the least-squares planes calculated through the planar parts of the cyclohexene rings (Table 6). The cyclobutane ring is very nearly planar (plane III, Table 6) with a dihedral angle of 178·3°, which is an unexpected result. Of the structures reviewed by Cotton & Frenz (1974) which contain cyclobutane fused to other rings (not involving transition metals), only one compound, a cyclopropane–cyclobutane system, has a nearly planar cyclobutane ring which is not crystallographically required to be planar.

Our structure agrees with that proposed by Dekker & Dekker (1975) for the product obtained from the photodimerization of dihydronaphthalene. Their assignment resulted from PMR interpretation of (III) and its oxidation products.

Irradiation of (I) in ethanol (Dekker & Dekker, 1973) suffers from the fact that a heterogeneous system

Table 5. *Torsion angles*

The *cis* conformation is taken as 0°. Angles represent the right-handed rotation, in degrees, needed to obtain the conformation observed in the structure.

Cyclohexene rings			
I		II	
C(6a)C(12c)C(12d)C(4a)	−18·9	C(8a)C(12a)C(12b)C(6b)	−16·2
C(12c)C(12d)C(4a)C(5)	+2·3	C(8)C(8a)C(12a)C(12b)	−0·2
C(12d)C(4a)C(5)C(6)	+35·5	C(7)C(8)C(8a)C(12a)	+36·2
C(4a)C(5)C(6)C(6a)	−56·2	C(6b)C(7)C(8)C(8a)	−55·5
C(5)C(6)C(6a)C(12c)	+40·3	C(12b)C(6b)C(7)C(8)	+39·9
C(6)C(6a)C(12c)C(12d)	−3·7	C(12a)C(12b)C(6b)C(7)	−4·9
Cyclobutane ring			
C(6a)C(6b)C(12b)C(12c)	−1·3	C(12b)C(12c)C(6a)C(6b)	−1·3
C(6b)C(12b)C(12c)C(6a)	+1·3	C(12c)C(6a)C(6b)C(12b)	+1·3

Table 6. *Least-squares planes*

The expression for the planes is $Ax + By + Cz = D$, where x, y and z are fractional coordinates and D is in Å.

	A	*B*	*C*	*D*
Plane I	5·429	6·310	12·869	4·050
Plane II	2·131	−6·608	−13·849	−0·641
Plane III	0·673	−10·526	5·464	−4·110

ΔI		ΔII		ΔIII	
*C(12c)	−0·005 Å	*C(8a)	0·001 Å	*C(12c)	0·009 Å
C(6a)	0·407	*C(12a)	−0·001	*C(6a)	−0·009
*C(12d)	0·010	*C(12b)	0·000	*C(12b)	−0·009
*C(4a)	−0·010	C(6b)	0·388	*C(6b)	0·009
C(6)	0·865	C(7)	0·838		
*C(5)	0·005	*C(8)	−0·000		

* Atom positions included in plane.

is formed; they report 25% yield of dimeric product. We therefore investigated the solvent effect on the photolysis of (I) with benzophenone as a sensitizer, and found benzene to be the preferred solvent with 86% yield. These reactions are remarkably free from polymerization. The results appear in Table 2. Crystal formation renders photolysis in the absence of solvent unsatisfactory.

It has been reported (Salomon & Kochi, 1973) that epimerization of perhydrobiphenylene may take place during irradiation in acetone solution. We irradiated a dilute solution (acetone) of photodimer (III) at 350 nm for 72 h and analysis of the products from this epimerization attempt gave unchanged starting material with some cleavage of (III) to (I).

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