

The Crystal Structure of 6b,8a-Dihydrocyclobut[*a*]acenaphthylene, C₁₄H₁₀

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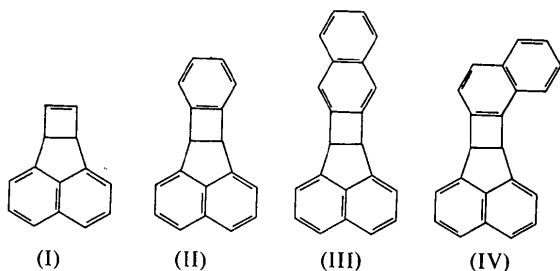
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6b,8a-Dihydrocyclobut[*a*]acenaphthylene is orthorhombic, space group *Pnma*, with $a=7.960(6)$, $b=13.825(6)$, $c=8.349(6)$ Å, $Z=4$. Least-squares refinement with 851 reflexions [with $I>3\sigma(I)$] gave $R=0.041$ for 88 parameters. The molecule is bent about the long bond, $1.592(3)$ Å, of the cyclobutene ring, the dihedral angle being $115.04(15)^\circ$. The short bond of the cyclobutene ring is found to be only $1.307(4)$ Å; however on refinement with only high-order data the distance increases to $1.337(6)$ Å, the apparent shortening being attributed to the effect of the bonding electrons. For cyclobut[*a*]acenaphthylene there is a correlation between the length of the unsaturated bond in the cyclobutene ring and the magnitude of the coupling constant J_{HH} between the two non-aromatic protons.

Introduction

The cyclobut[*a*]acenaphthylenes are the precursors of pleiadenes and have been studied both spectroscopically and theoretically by Kolc & Michl (1973), whose NMR studies show that there seems to be a very interesting correlation between the length of the unsaturated bond in the cyclobutene ring and the magnitude of the coupling constant J_{HH} between the two non-aromatic protons. The structures of cyclobut[*a*]acenaphthylene (I), 6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (II) (Hazell & Hazell, 1976) and 6b,12b-dihydronaphtho[2,3-*j*]cyclobut[*a*]acenaphthylene (III) (Hazell & Weigelt, 1976) have been determined and the correlation is confirmed.



Crystal data

C₁₄H₁₀, $M=178.2$. Orthorhombic, $a=7.960(6)$, $b=13.825(6)$, $c=8.349(6)$ Å, $U=918.8$ Å³, $Z=4$, $D_c=1.29$ g cm⁻³. Space group *Pnma*. $\mu(\text{Mo } K\alpha)=0.68$ cm⁻¹. The crystals are tabular on (010) and are bounded by {101}.

Experimental

The crystals were kindly provided by Josef Michl.

A crystal, $0.02 \times 0.11 \times 0.04$ cm, was sealed in a Lindeman glass capillary to prevent sublimation. It was mounted along b and intensities $I(hkl)$, $h=0$ to 11, were measured with a computer-steered Supper dif-

fractometer (Kryger, 1975). Monochromatic Mo $K\alpha$ radiation was used with a scintillation counter and a pulse-height analyser. 1388 independent reflexions were measured of which 853 had $I>3\sigma(I)$, according to counting statistics. No correction was applied for absorption.

Determination and refinement of the structure

The structure was determined by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971). H atom positions were obtained by geometry. Least-squares refinement of atomic coordinates, thermal parameters (anisotropic for C, isotropic for H), a scale factor and an isotropic extinction coefficient, g , gave $R=0.041$ and $R_w=0.051$ for 88 parameters and 851 reflexions (020 and 011 were omitted). Another refinement, carried out with only the high-order data ($\sin \theta/\lambda > 0.5$), gave $R=0.046$ and $R_w=0.048$ for the same number of parameters and 441 reflexions. The values obtained for g were 1.94×10^{-7} and 5.0×10^{-8} assuming \bar{i} to be unity; the minimum values of $F_o/F_o(\text{corr})$ were 0.96 and 1.0.

Atomic coordinates and thermal parameters are listed in Table 1.*

The thermal motion of the atoms was analysed (Schomaker & Trueblood, 1968). T, L, and S with their standard deviations are given in Table 2. The values of L were used to correct the bond lengths for thermal motion.

Bond lengths and selected short intramolecular distances are given in Table 3, angles in Table 4. The atomic numbering and the bond labelling are in accordance with Fig. 1. Short intermolecular distances are given in Table 5.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31601 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates and thermal parameters*

For carbon atoms the coordinates are multiplied by 10^4 , for hydrogen atoms by 10^3 . All thermal parameters are in $\text{\AA}^2 \times 10^{-4}$. The first set of parameters is from the refinement with all the data, the second from the refinement with $\sin \theta/\lambda > 0.5$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(1)	6779 (2)	7971 (1)	4325 (2)	332 (6)	551 (10)	511 (10)	-55 (6)	29 (7)	-4 (9)
C(2)	5123 (2)	8071 (1)	3421 (2)	371 (6)	453 (9)	393 (8)	-25 (6)	33 (6)	48 (8)
C(3)	3624 (2)	8352 (1)	4429 (2)	340 (5)	417 (8)	335 (7)	16 (6)	-39 (6)	14 (7)
C(4)	2981 (2)	9223 (1)	4886 (2)	457 (7)	427 (9)	466 (10)	40 (7)	-67 (7)	16 (8)
C(5)	1575 (2)	9239 (1)	5932 (2)	538 (8)	503 (11)	485 (10)	179 (8)	-53 (8)	-90 (8)
C(6)	835 (2)	8417 (1)	6488 (2)	410 (6)	672 (12)	381 (9)	112 (8)	25 (7)	-62 (9)
C(7)	1456 (2)	7500	6032 (3)	317 (8)	553 (15)	308 (11)	0	-3 (8)	0
C(8)	2852 (2)	7500	4996 (3)	298 (7)	408 (11)	301 (10)	0	-41 (7)	0
H(1)	750 (2)	847 (1)	475 (2)	622 (58)					
H(2)	519 (2)	840 (1)	234 (3)	515 (49)					
H(4)	347 (2)	982 (1)	449 (2)	625 (57)					
H(5)	118 (2)	987 (1)	625 (2)	520 (49)					
H(6)	-9 (3)	846 (1)	718 (3)	685 (60)					
C(1)	6779 (2)	7982 (2)	4325 (3)	284 (6)	493 (13)	483 (12)	-49 (7)	23 (7)	2 (11)
C(2)	5123 (2)	8074 (2)	3418 (2)	313 (7)	409 (10)	337 (9)	-20 (6)	33 (6)	48 (7)
C(3)	3624 (2)	8353 (2)	4424 (2)	293 (6)	352 (9)	317 (8)	12 (6)	-18 (6)	15 (7)
C(4)	2992 (2)	9230 (2)	4883 (3)	427 (8)	351 (13)	424 (11)	52 (7)	-47 (7)	10 (8)
C(5)	1575 (3)	9249 (2)	5934 (3)	498 (10)	479 (15)	420 (11)	177 (9)	-25 (8)	-80 (8)
C(6)	827 (2)	8417 (2)	6494 (3)	381 (8)	598 (15)	360 (10)	113 (8)	36 (7)	-66 (10)
C(7)	1454 (3)	7500	6036 (3)	297 (9)	528 (17)	277 (11)	0	203 (8)	0
C(8)	2853 (2)	7500	4990 (3)	263 (8)	349 (13)	268 (10)	0	-28 (7)	0
H(1)	744 (8)	837 (6)	474 (8)	501 (110)					
H(2)	517 (8)	830 (7)	262 (13)	620 (134)					
H(4)	338 (8)	976 (7)	464 (10)	585 (130)					
H(5)	125 (7)	982 (5)	606 (7)	352 (94)					
H(6)	-12 (10)	838 (7)	712 (12)	514 (165)					

Table 2. *T, L, and S relative to an orthogonal axial system with A parallel to a and C parallel to c**

T is in $\text{\AA}^2 \times 10^{-4}$, L in $(^\circ)^2$, and S in $(^\circ) \text{\AA} \times 10^{-3}$. T', L', and S' are the values from the refinement with high-order data. The r.m.s. Δ [$\Delta = U_{ij}(\text{obs}) - U_{ij}(\text{cal})$] are 0.0014 and 0.0011. For the symmetric matrices only the upper triangle of cross terms is given.

	<i>M</i> ₁₁	<i>M</i> ₂₂	<i>M</i> ₃₃	<i>M</i> ₁₂	<i>M</i> ₁₃	<i>M</i> ₂₁	<i>M</i> ₂₃	<i>M</i> ₃₁	<i>M</i> ₃₂
T	309 (6)	391 (6)	289 (9)	0	-24 (7)		0		
T'	270 (4)	338 (4)	261 (6)	0	-10 (4)		0		
L	10.1 (7)	7.4 (6)	10.3 (5)	0	2.0 (5)		0		
L'	8.8 (5)	7.1 (4)	10.2 (3)	0	2.1 (4)		0		
S	0	0	0	5 (15)	0	10 (12)	-51 (10)	0	-114 (10)
S'	0	0	0	-2 (10)	0	41 (9)	-47 (7)	0	-115 (7)

Table 3. *Bond distances, l, and the values, l_{corr}, corrected for thermal motion (l' and l'_{corr} are the corresponding values from the refinement with only those reflexions for which $\sin \theta/\lambda > 0.5$)*

		<i>l</i>	<i>l</i> _{corr}	<i>l</i> '	<i>l</i> ' _{corr}
<i>j</i>	C(1)-C(1')	1.303 (4)	1.307	1.333 (6)	1.337
<i>h</i>	C(1)-C(2)	1.525 (2)	1.528	1.526 (2)	1.529
<i>i</i>	C(2)-C(2')	1.578 (3)	1.583	1.587 (4)	1.591
<i>g</i>	C(2)-C(3)	1.511 (2)	1.516	1.509 (2)	1.514
<i>a</i>	C(3)-C(4)	1.363 (2)	1.367	1.367 (3)	1.371
<i>f</i>	C(3)-C(8)	1.410 (2)	1.414	1.411 (2)	1.415
<i>b</i>	C(4)-C(5)	1.420 (3)	1.425	1.429 (3)	1.433
<i>c</i>	C(5)-C(6)	1.361 (3)	1.365	1.378 (4)	1.382
<i>d</i>	C(6)-C(7)	1.413 (2)	1.417	1.415 (3)	1.419
<i>e</i>	C(7)-C(8)	1.409 (3)	1.413	1.416 (3)	1.420
<i>k</i>	C(1)-H(1)	0.96 (2)	0.96	0.83 (8)	0.83
<i>l</i>	C(2)-H(2)	1.01 (2)	1.02	0.74 (11)	0.74
<i>m</i>	C(4)-H(4)	0.97 (2)	0.97	0.82 (10)	0.82
<i>n</i>	C(5)-H(5)	0.96 (2)	0.96	0.83 (7)	0.83
<i>o</i>	C(6)-H(6)	0.94 (2)	0.94	0.92 (10)	0.92

Computational details

Calculations were carried out on RC4000 and CDC6400 computers with the following programs: data reduction (Kryger, 1975), averaging of symmetry-related reflexions, *DSORTH*, State University of New York at Buffalo; Fourier syntheses, *JIMDAP*, A. Zalkin; full-matrix least-squares refinement, *LINUS* (Busing, Martin & Levy, 1962; Coppens & Hamilton, 1970); distances and angles, *ORFFE* (Busing, Martin & Levy, 1964); drawings, *ORTEP* (Johnson, 1965); energy minimization, *STRAIN* (Hazell, 1976).

The quantity minimized was $r = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$ where $w = \{[\sigma(F_o^2) + 1.03F_o^2]^{1/2} - |F_o|\}^{-2}$. The scattering factors were those of Cromer & Mann (1968) for C and of Stewart, Davidson & Simpson (1965) for H. *R* and *R_w* are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

Discussion

The molecule consists of two approximately planar fragments and is bent about the long bond of the cyclobutene ring, C(2)–C(2'), with a dihedral angle of 115.04 (15)°. Refinement with all intensities [$I > 3\sigma(I)$] gave C(1)–C(1') of only 1.307 (4) Å for the short bond of the cyclobutene ring, significantly shorter than the distance obtained by microwave spectroscopy, 1.342 (4) Å (Bak, Led, Nygaard, Rastrup-Andersen & Sørensen, 1969), for cyclobutene itself and also shorter than the accepted value, 1.335 Å (Lide, 1962), for an ethylenic double bond. As asphericity of atoms leads

Table 4. Angles θ from the refinement with all the data, θ' from the refinement with only high-order data, θ_{cal} values calculated from the bond lengths from the high-order refinement and varying the angles so as to minimize the strain energy

		θ	θ'	θ_{cal}
ab	C(3)–C(4)–C(5)	118.8 (2)°	118.7 (2)°	118.8°
bc	C(4)–C(5)–C(6)	122.5 (2)	122.3 (2)	122.0
cd	C(5)–C(6)–C(7)	120.4 (2)	120.3 (2)	120.6
de	C(6)–C(7)–C(8)	116.2 (1)	116.4 (1)	116.1
ef	C(3)–C(8)–C(7)	123.4 (1)	123.3 (1)	123.4
af	C(4)–C(3)–C(8)	118.7 (1)	119.1 (1)	119.1
dd	C(6)–C(7)–C(6')	127.6 (2)	127.3 (2)	127.8
ff	C(3)–C(8)–C(3')	113.3 (2)	113.4 (2)	113.1
ag	C(2)–C(3)–C(4)	132.8 (2)	132.4 (2)	132.2
fg	C(2)–C(3)–C(8)	108.4 (1)	108.4 (2)	108.7
gh	C(1)–C(2)–C(3)	115.5 (2)	115.4 (2)	117.9
gi	C(2')–C(2)–C(3)	104.9 (1)	104.8 (1)	104.7
hi	C(1)–C(2)–C(2')	84.8 (1)	85.2 (1)	85.2
hj	C(1')–C(1)–C(2)	95.2 (1)	94.8 (1)	94.8
Dihedral angle		115.0 (2)	115.0 (2)	117.6
jk	C(1')–C(1)–H(1)	135.3 (1.1)	130.5 (4.7)	133.9
hk	C(2)–C(1)–H(1)	129.5 (1.1)	134.6 (4.6)	131.3
hl	C(1)–C(2)–H(2)	115.9 (1.0)	116.1 (5.1)	115.1
il	C(2')–C(2)–H(2)	116.4 (1.0)	115.6 (7.2)	114.9
gl	C(3)–C(2)–H(2)	115.1 (1.0)	115.5 (5.5)	114.7
am	C(3)–C(4)–H(4)	120.6 (1.1)	125.5 (5.1)	121.4
bm	C(5)–C(4)–H(4)	120.6 (1.1)	115.8 (5.2)	119.9
bn	C(4)–C(5)–H(5)	116.3 (1.0)	110.2 (4.0)	118.4
cn	C(6)–C(5)–H(5)	121.2 (1.0)	127.3 (3.9)	119.6
co	C(5)–C(6)–H(6)	119.8 (1.2)	126.6 (6.2)	120.0
do	C(7)–C(6)–H(6)	119.8 (1.2)	113.0 (6.2)	119.5

to systematic errors in bond lengths, the effect being particularly large for aromatic hydrocarbons where

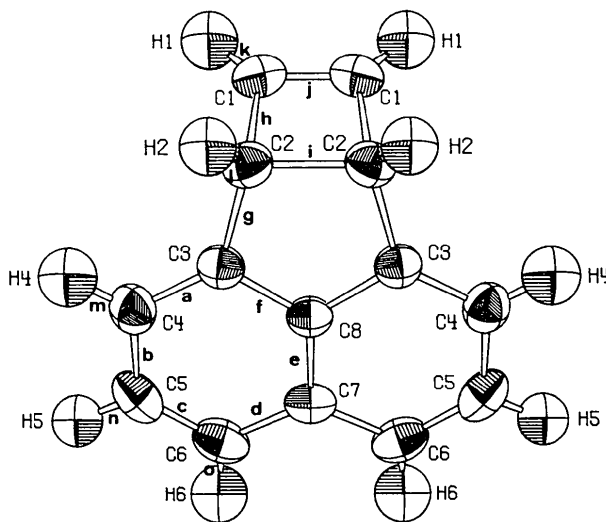


Fig. 1. The molecule showing the numbering of the atoms and the labelling of the bonds.

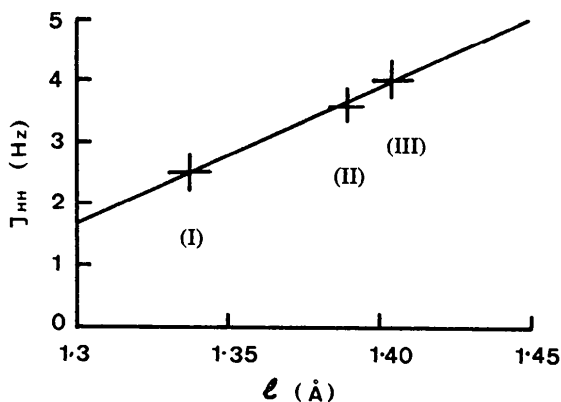


Fig. 2. The coupling constants, J_{HH} , vs the length, l , of the unsaturated bond of the cyclobutene ring. The vertical error bars represent the errors in J_{HH} , the horizontal bars are $\pm\sigma(l)$.

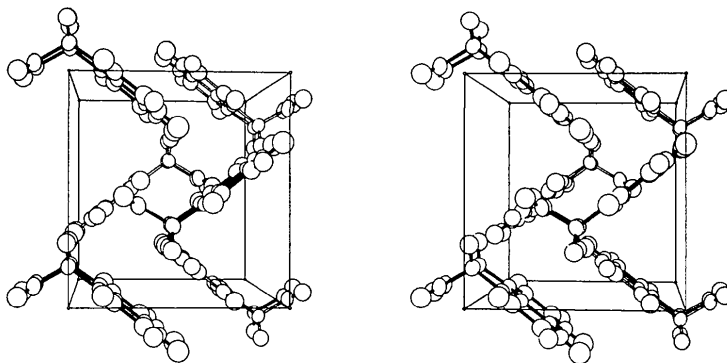


Fig. 3. A stereoscopic view of the cell contents as seen down $[0\bar{1}0]$, a is across the page, c down the page. The molecules at $y = \frac{1}{2}$ are shown with black bonds.

Table 5. *Close approaches between molecules, H...H distances less than 2.85 Å, C...H less than 3.1 Å, and C...C less than 3.75 Å*

Symmetry code			
(i)	$\frac{1}{2} + x,$	$y,$	$\frac{1}{2} - z;$
(iii)	$\frac{1}{2} + x,$	$y,$	$1\frac{1}{2} - z;$
(v)	$\frac{1}{2} + x,$	$1\frac{1}{2} - y,$	$1\frac{1}{2} - z;$
(vii)	$\frac{1}{2} - x,$	$2 - y,$	$-\frac{1}{2} + z;$
(ii)	$-x,$	$2 - y,$	$1 - z$
(iv)	$1 + x,$	$y,$	z
(vi)	$1 - x,$	$2 - y,$	$1 - z$
(viii)	$\frac{1}{2} - x,$	$2 - y,$	$\frac{1}{2} + z$
H(1)–H(4 ^{iv})	2.568 (34)	C(1)–C(3 ⁱ)	3.501 (3)
H(4)–H(4 ^{iv})	2.632 (42)	C(1)–C(2 ⁱ)	3.516 (3)
H(1)–H(5 ^{iv})	2.671 (32)	C(5)–C(5 ⁱⁱ)	3.625 (4)
H(4)–H(5 ⁱⁱⁱ)	2.750 (29)	C(1)–C(6 ⁱⁱⁱ)	3.629 (4)
H(1)–H(2 ⁱ)	2.764 (32)	C(2)–C(8 ⁱ)	3.671 (4)
H(2)–H(5 ⁱⁱⁱ)	2.788 (31)	C(2)–C(3 ⁱ)	3.684 (3)
H(5)–H(5 ^{iv})	2.840 (39)	C(1)–C(6 ^{iv})	3.750 (3)
C(3)–H(6 ^v)	3.017 (27)		

there is a very short bond between two long ones (*cf.* pyrene: Hazell, Larsen & Lehmann, 1972; phenanthrene: Kay, Okaya & Cox, 1971), refinement was also carried out with only reflexions for which $\sin \theta/\lambda > 0.5$. C(1)–C(1') obtained from the high-order refinement was 1.337 (6) Å in good agreement with the expected value. The difference, 0.030 Å, is extremely large but is smaller than the value predicted, 0.037 Å, from the empirical relationship obtained for pyrene. In the following discussion distances and angles from the high-order refinement will be used except where H atoms are involved.

C(1)–C(2) is similar to that for cyclobutene, 1.517 (3) Å, whereas C(2)–C(2') is longer, 1.591 (6) Å compared with 1.566 (3) Å. Long bonds are also found in (II) and (III); in all three compounds the long bond is shared between a four and a five-membered ring.

In Fig. 2 the coupling constants J_{HH} between the two non-aromatic protons [*e.g.* H(2) and H(2') for (I)] are plotted against the length of the unsaturated bond in the cyclobutene ring. There is a linear relationship between the coupling constant and the bond length, $J_{\text{HH}} = -27.71 + 22.59 l$. The bond lengths, l , for (I) to (IV) are very similar to those in the related hydrocarbon, *i.e.* (I) 1.337 (6), ethylene 1.337 (3) Å (Allen & Plyler, 1958); (II) 1.390 (3), benzene 1.395 (4) Å (Cruickshank, 1970); (III) 1.403 (9), naphthalene 1.401 (7) Å (Pawley & Yeats, 1969); (IV) 1.369, by interpolation of the measured coupling constant, 1.372 (5) Å naphthalene.

The bond lengths of the naphthalene fragment are very similar to those of naphthalene itself; the angles are, however, distorted as the molecule deforms to reduce the strain caused by joining a five-membered ring to the naphthalene ring to a minimum. The conformation was calculated using observed bond lengths and varying the angles so as to minimize the sum of the angular deformation energy and the repulsion due to the non-bonded interactions. For the acenaphthylene

ring the maximum difference between observed and calculated angles is 0.5° for CCC angles and 2° for the less accurately determined HCC angles. The agreement for the dihedral angle, and hence also for C(1)–C(2)–C(3) is not so good, but the strain energy is insensitive to variations in the dihedral angle. The calculations correctly predict the large C(6)–C(7)–C(6') angle which is characteristic of acenaphthylene derivatives.

The packing is shown in Fig. 3. The molecules lie on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$ with the acenaphthylene groups parallel to {101}. The periodic bond chain (p.b.c.) vectors (Hartman & Perdok, 1955) [101] and [10 $\bar{1}$] account for the observed morphology. The *F*-face (010) containing both p.b.c. vectors is the most important form, the other faces are {101} which are *S*-faces and contain only one p.b.c. vector.

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