

6b,12b-Dihydronaphtho[2,3-*j*]cyclobut[*a*]acenaphthylene

BY ALAN C. HAZELL AND ÅGE WEIGELT

Department of Inorganic Chemistry, Århus University, DK-8000 Århus C, Denmark

(Received 1 September 1975; accepted 12 September 1975)

Abstract. C₂₂H₁₄, monoclinic, $P2_1/c$; $a=8.56$ (2), $b=10.93$ (2), $c=15.19$ (2) Å, $\beta=98.5$ (2)°, $Z=4$, $D_x=1.29$, $D_c=1.32$ g cm⁻³. Full-matrix least-squares refinement gave $R=0.063$ and $R_w=0.052$ for 255 parameters and 792 significant reflexions ($I>3\sigma$). The molecule is bent about the long bond, 1.601 (10) Å, of the cyclobutene ring, the dihedral angle being 114.9 (7)°. The molecule deviates slightly from symmetry *m*.

Introduction. Kolc & Michl (1973) have prepared a series of cyclobutacenaphthylenes and have studied their photochemistry. We are carrying out structure determinations of several of these compounds to correlate their n.m.r. spectra with their geometries. As well as the title compound (I) the structures of 6b, 10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (II) and of cyclobut[*a*]acenaphthylene (III) (Hazell, 1975) have been determined.

Table 1. Atomic coordinates and thermal parameters

(a) Fractional atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\text{Å}^2 \times 10^{-3}$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	8644 (8)	1015 (5)	5789 (6)	36 (5)	41 (4)	55 (7)	9 (4)	10 (4)	-3 (4)
C(2)	8385 (8)	415 (6)	6572 (6)	33 (5)	47 (4)	55 (7)	1 (4)	16 (5)	8 (4)
C(3)	7334 (10)	-562 (8)	6444 (7)	59 (7)	72 (6)	57 (8)	5 (5)	23 (6)	10 (6)
C(4)	6670 (10)	-934 (6)	5605 (7)	50 (6)	50 (4)	64 (8)	-6 (4)	16 (5)	19 (5)
C(5)	7013 (10)	-332 (6)	4851 (7)	49 (6)	53 (5)	59 (8)	9 (4)	-1 (5)	-19 (5)
C(6)	8000 (9)	653 (6)	4931 (6)	38 (5)	55 (4)	43 (6)	6 (4)	17 (4)	-10 (4)
C(7)	8522 (9)	1514 (6)	4259 (6)	51 (6)	52 (4)	34 (6)	7 (4)	12 (4)	-4 (4)
C(8)	7420 (9)	2585 (6)	4004 (5)	56 (6)	49 (4)	30 (5)	0 (4)	12 (4)	5 (4)
C(9)	6036 (10)	2907 (7)	3512 (6)	67 (7)	56 (5)	20 (5)	-18 (5)	6 (4)	-5 (4)
C(10)	5498 (9)	4137 (6)	3581 (5)	47 (5)	51 (4)	41 (6)	-14 (6)	-1 (4)	7 (4)
C(11)	4070 (10)	4538 (8)	3116 (7)	49 (6)	73 (6)	61 (7)	-11 (5)	-3 (5)	10 (5)
C(12)	3539 (11)	5704 (8)	3212 (7)	51 (7)	70 (6)	83 (8)	20 (5)	6 (6)	28 (6)
C(13)	4482 (12)	6504 (8)	3753 (7)	78 (9)	71 (6)	66 (8)	18 (6)	23 (6)	14 (6)
C(14)	5856 (10)	6157 (7)	4209 (6)	43 (6)	74 (6)	41 (6)	7 (5)	9 (5)	-7 (5)
C(15)	6460 (9)	4955 (6)	4149 (6)	33 (5)	61 (4)	46 (6)	5 (4)	16 (4)	1 (4)
C(16)	7894 (9)	4582 (6)	4641 (6)	47 (6)	47 (4)	54 (6)	-16 (4)	21 (5)	-6 (4)
C(17)	8341 (8)	3425 (6)	4548 (5)	30 (5)	50 (3)	43 (5)	1 (4)	16 (4)	-4 (4)
C(18)	9617 (9)	2469 (6)	4859 (6)	35 (5)	51 (3)	56 (6)	-11 (4)	13 (4)	1 (4)
C(19)	9652 (9)	2027 (6)	5787 (6)	35 (5)	52 (4)	44 (6)	9 (4)	9 (4)	-4 (4)
C(20)	10376 (9)	2475 (7)	6579 (5)	49 (5)	55 (4)	37 (6)	8 (5)	7 (4)	5 (5)
C(21)	10122 (11)	1880 (7)	7365 (7)	56 (7)	73 (5)	45 (7)	12 (5)	-6 (5)	0 (5)
C(22)	9131 (11)	919 (8)	7360 (6)	72 (7)	71 (5)	41 (7)	12 (5)	10 (5)	-2 (6)

(b) Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters, and **T**, **L**, and **S** relative to an orthogonal axial system with *A* parallel to **a** and *C* parallel to **c***. **T** is in $\text{Å}^2 \times 10^{-4}$, **L** in (°)² and **S** in (°) Å $\times 10^{-3}$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	
H(3)	688 (8)	-83 (5)	679 (5)	4.8 (2.9)	$\mathbf{T} = \begin{pmatrix} 308 (28) & 9 (20) & 82 (22) \\ & 498 (21) & -40 (20) \\ & & 349 (25) \end{pmatrix}$
H(4)	573 (6)	-154 (5)	548 (4)	2.2 (1.3)	
H(5)	668 (6)	-55 (4)	431 (4)	1.4 (1.6)	
H(7)	915 (7)	113 (5)	384 (4)	3.3 (2.6)	$\mathbf{L} = \begin{pmatrix} 4.6 (1.0) & -1.9 (1.0) & 1.0 (0.9) \\ & 13.7 (1.7) & -5.7 (1.4) \\ & & 6.8 (1.3) \end{pmatrix}$
H(9)	547 (5)	239 (4)	312 (4)	1.1 (1.4)	
H(11)	345 (6)	393 (4)	277 (4)	1.1 (1.2)	
H(12)	247 (9)	591 (6)	278 (6)	7.5 (2.3)	$\mathbf{S} = \begin{pmatrix} -44 (47) & -16 (28) & -44 (25) \\ -77 (34) & 121 (61) & 43 (40) \\ 16 (27) & -59 (35) & -76 (452^*) \end{pmatrix}$
H(13)	408 (6)	723 (5)	387 (4)	3.1 (1.8)	
H(14)	661 (5)	670 (3)	460 (3)	0.4 (1.1)	
H(16)	848 (8)	525 (5)	496 (5)	6.3 (2.0)	
H(18)	1070 (7)	266 (4)	477 (4)	3.6 (1.7)	
H(20)	1190 (8)	311 (5)	659 (5)	4.6 (2.1)	
H(21)	1064 (9)	221 (7)	793 (6)	8.4 (2.7)	
H(22)	897 (8)	58 (6)	788 (5)	5.5 (2.1)	

* The trace of **S** has been set to zero, e.s.d. of deleted *S*(3,3) is given.

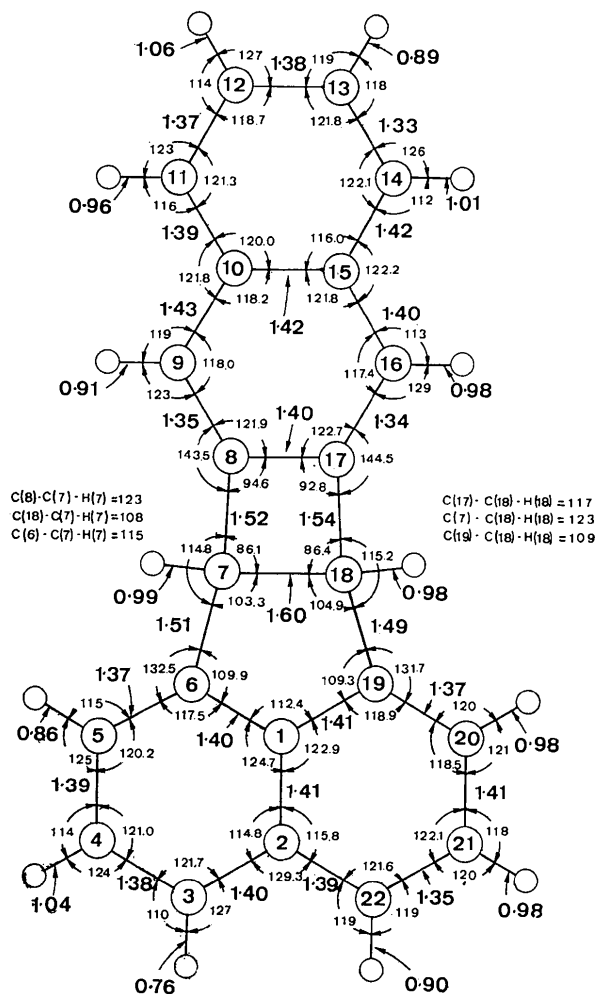


Fig. 1. Bond distances and angles; the mean standard deviations are: $\sigma(\text{C}-\text{C}) = 0.010 \text{ \AA}$, $\sigma(\text{C}-\text{H}) = 0.060 \text{ \AA}$, $\sigma(\text{C}-\text{C}-\text{C}) = 0.6^\circ$, $\sigma(\text{H}-\text{C}-\text{C}) = 4^\circ$. The large circles represent C atoms, the small ones, H atoms; the H atoms are numbered so that, for example, H(5) is the atom bonded to C(5).

Intensities were collected on a computer-controlled Supper diffractometer with graphite-monochromated Mo $K\alpha$ radiation, a scintillation counter and a pulse height analyser. 2095 independent reflexions were measured by the background-peak-background method out to $\sin \theta = 0.5$. The crystal, $0.25 \times 0.6 \times 0.10 \text{ mm}$, was mounted about *b*. No corrections were made for absorption.

The structure was determined with *MULTAN* (Germain, Main & Woolfson, 1971). Coordinates, thermal parameters (anisotropic for C, isotropic for H) and an overall scale factor were refined by full-matrix least-squares calculations (*LINUS*; Coppens & Hamilton, 1970) to give $R = 0.063$ and $R_w = 0.052$ for 255 parameters and 792 significant reflexions* [$I > 3\sigma(I)$]. The weighting scheme was $w = \sigma(F)^{-2}$ where $\sigma(F) = \sqrt{[\sigma_c(F^2) + (1+A)F^2]}$, $\sigma_c(F^2)$ is the standard deviation of F^2 from the counting statistics and A ($= 0.02$) a parameter chosen to make $\langle w\Delta F^2 \rangle$ independent of $|F|$. Reflexions close to the rotation axis were not included in the refinement. The scattering factors used were those of Cromer & Mann (1968) for C and of Stewart, Davidson & Simpson (1965) for H.

Final coordinates and thermal parameters are given in Table 1. The thermal parameters were analysed (Schomaker & Trueblood, 1968) and the atomic coordinates corrected for libration: the corrections ranged from 0.003 – 0.005 \AA . *T*, *L*, and *S* are given in Table 1, the r.m.s. value of Δ , where $\Delta = U_{ij}(\text{obs}) - U_{ij}(\text{calc})$ was 0.0073 \AA^2 , and $\sigma(\Delta)$ was 0.0076 \AA^2 . Bond distances and angles are shown in Fig. 1.

Discussion. The molecule consists of two approximately planar fragments, and is bent about the long bond of the cyclobutene ring, C (7)–C (18), with a

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31366 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

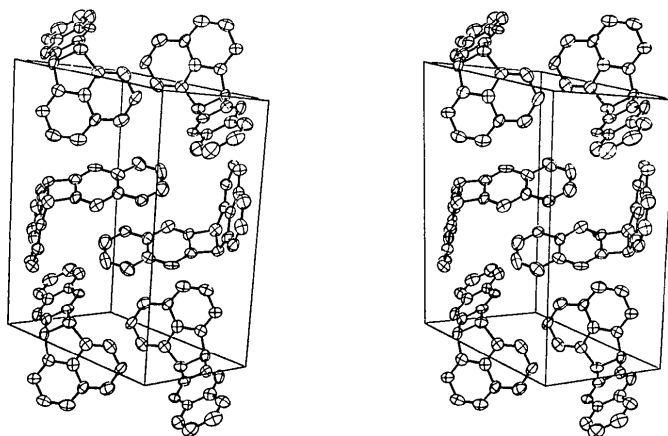


Fig. 2. The unit-cell contents viewed down the [110] axis; *a* is to the right, *b* to the left, *c* points up the page.

dihedral angle of 114.9 (7)°. The C–C distances for the naphthalene fragments are similar to those for naphthalene itself (Pawley & Yeats, 1969); the angles are however distorted as the naphthalene parts are fused to five-membered and to four-membered rings. The distortions due to the five-membered ring are similar to those found in acenaphthene (Ehrlich, 1957), those due to the four-membered ring are smaller as in naphtho[*b*]cyclobutene (Crawford & Marsh, 1973) and in (II).

C (7)–C (18) is very long for a single bond, 1.601 (10) Å; the weakening of the bond is presumably caused by the strain due to the fusion of the four- and five-membered rings. Similar long bonds are found in (II) [1.606 (4)] and (III) [1.591 (6) Å]. The cyclobutene ring is not quite planar, the angle between the planes through C (7), C (8), C (17) and C (7), C (18), C (17) is 177.5 (9)°, so that the molecule as a whole is slightly twisted. We attribute the deformation to packing forces. A stereo view of the unit-cell contents is shown in Fig. 2.

Acta Cryst. (1976). B32, 308

cis-Tetracarbonyl (1,3-tetramethyl-2-*t*-butyltriphosphane-1*P*,3*P*)molybdenum(0)

BY W. S. SHELDRIK

*Gesellschaft für Biotechnologische Forschung m.b.H.,
33 Braunschweig-Stöckheim, Mascheroder Weg 1, Germany (BRD)*

(Received 25 August 1975; accepted 20 September 1975)

Abstract. C₁₂H₂₁O₄P₃Mo, monoclinic, *P*2₁, *a* = 8.432 (11), *b* = 12.751 (14), *c* = 9.243 (6) Å, β = 107.51 (8)°, *M* = 418.16, *Z* = 2, *D*_x = 1.47 g cm⁻³. Considerable distortion from perfect octahedral coordination is observed at Mo with a small P–Mo–P angle of 72.7 (1)°. The four-membered MoPPP chelate ring is non-planar [distances from the least-squares plane: Mo, –0.104; P(1), 0.284; P(2), –0.345; P(3), 0.383 Å] and contains a remarkably small P(1)–P(2)–P(3) angle of 85.0 (1)°. The P–P distances of 2.193 (4) and 2.186 (4) Å are normal.

Introduction. Cell dimensions were determined by a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex *P*2₁ four-circle diffractometer (Mo *K*α, 0.71069 Å). Intensities from a prismatic crystal, elongated *c*, with approximate dimensions 0.16 × 0.19 × 0.42 mm, were collected on the diffractometer with graphite-monochromated Mo *K*α radiation. Measurements were carried out in the θ –2 θ mode (3.0 ≤ 2 θ ≤ 50.0°) at scan speeds varying linearly between 2.93° min⁻¹ (150 c.p.s. and below) and 8.37° min⁻¹ (5000 c.p.s. and above). Scan and background times were equal. Three standard reflexions, monitored at regular

References

- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
 CRAWFORD, J. L. & MARSH, R. E. (1973). *Acta Cryst.* B29, 1238–1241.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
 EHRLICH, H. W. W. (1957). *Acta Cryst.* 10, 699–705.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
 HAZELL, A. C. (1975). Unpublished.
 KOLC, J. & MICHL, J. (1973). *J. Amer. Chem. Soc.* 95, 7391–7401.
 PAWLEY, G. S. & YEATS, E. A. (1969). *Acta Cryst.* B25, 2009–2013.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–76.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

intervals, did not display any significant variations. Lorentz and polarization but no absorption [$\mu(\text{Mo } K\alpha) = 9.4 \text{ cm}^{-1}$] corrections were applied. From the 1886 reflexions recorded (one quadrant of reciprocal space) 1417 were retained for use in the structure analysis, after application of the criterion $F \geq 2.5\sigma(F)$ and averaging, where $\sigma(F)$ is based on the counting statistics.

The structure was solved by conventional Patterson and difference Fourier methods. Refinement with anisotropic temperature factors for all non-hydrogen atoms was by full-matrix least squares, $\sum w\Delta^2$ being minimized. A final difference synthesis revealed possible coordinates for some but not all of the H atoms. In view of the ambiguous nature of this information no attempt was made to include any H atoms in the final cycles. The terminal value of $R_G = [\sum w\Delta^2 / \sum wF_o^2]^{1/2}$ was 0.069, with $R_w = \sum w^{1/2}\Delta / \sum w^{1/2}F_o = 0.054$ and $R = 0.050$. The weights were given by $w = k / [\sigma^2(F_o) + gF_o^2]$ where *k* and *g* refined to 0.6609 and 0.005354 respectively. In the final cycle the largest observed shift/e.s.d. was –0.006. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed. The atom coordinates are listed in Table 1 and the temperature factors in Table 2. The