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The Crystal Structure of Benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene, $C_{18}H_{12}$, an Overcrowded Non-Alternant Hydrocarbon

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Benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene is orthorhombic, space group $Pca2_1$ with $a = 14{\cdot}110\,(4)$, $b = 10{\cdot}883\,(3)$, $c = 7{\cdot}713\,(3)$ Å and $Z = 4$. Refinement of 211 parameters with 1092 reflexions $[I > 2\sigma(I)]$ gave $R = 0{\cdot}036$ and $R_w = 0{\cdot}038$. The molecule is non-planar, torsion angles in the seven-membered ring ranging from 10 to 40°; the localized double bond is on the opposite side of the plane from the benzene ring. Strain induced by the seven-membered ring results in distortion of both bonds and angles of the naphthalene group; the distortions are compared with those found in other strained *peri*-naphthalenes. The molecules pack in such a way as to give maximum London attraction.

Introduction

The structure of benzo[4,5]cyclohepta[1,2,3-*de*]-naphthalene has been determined as part of a study of the geometries of non-alternant hydrocarbons. Whereas the parent compound cyclohepta[*de*]naphthalene (pleiadiene) has been shown by NMR measurements (Wendisch, Hartmann & Heine, 1974) and by X-ray diffraction (Hazell, Hazell & Larsen, 1978) to be almost planar, steric hindrance between H(3) and H(15) is expected to result in the benzo[4,5] derivative being non-planar.

Crystal data

$C_{18}H_{12}$, $M_r = 228{\cdot}3$, orthorhombic, $a = 14{\cdot}110\,(4)$, $b = 10{\cdot}883\,(3)$, $c = 7{\cdot}713\,(3)$ Å, $U = 1184$ Å^3, $Z = 4$, $D_c = 1{\cdot}24$ g cm^{-3}, space group $Pca2_1$, μ(Mo $K\alpha$) = 0·65 cm^{-1}. The bright yellow crystals are elongated along **c** and terminated by {201}; the most prominent face is {010}. Systematic absences are: $0kl$ for l odd and $h0l$ for h odd.

Experimental

The crystals were provided by Richard Pagni.

A crystal, 0·40 × 0·33 × 0·30 mm, was mounted along [201] on a Picker FACS-1 diffractometer and intensities were measured out to $2\theta = 55°$ with monochromatic Mo $K\alpha$ radiation. Data were collected using the ω–2θ step-scanning technique with a step length of 0·04° and scan widths of $3{\cdot}92 + 0{\cdot}692 \tan\theta$ for $2\theta \leq 30°$ and $2{\cdot}0 + 0{\cdot}692 \tan\theta$ for $2\theta > 30°$. 1464 independent reflexions were measured of which 1092 had $I > 2\sigma(I)$ according to counting statistics. No corrections were made for absorption.

Structure determination and refinement

The structure was determined by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971). Least-squares refinement of atomic coordinates, anisotropic

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *for* C, $\times 10^3$ *for* H) *and the deviation* Δ (Å $\times 10^{-3}$) *from the plane through the naphthalene group*

	x	y	z	Δ
C(1)	8533 (2)	2352 (3)	1423 (5)	−50
C(2)	7963 (2)	3410 (2)	1810 (5)	−166
C(3)	6987 (2)	3273 (3)	1820 (6)	15
C(4)	6541 (2)	2200 (3)	1254 (6)	130
C(5)	7064 (2)	1262 (3)	628 (6)	31
C(6)	8064 (2)	1302 (3)	712 (0)	−45
C(7)	8598 (3)	277 (3)	123 (7)	−82
C(8)	9547 (3)	237 (4)	305 (7)	−47
C(9)	10005 (3)	1191 (3)	1170 (7)	98
C(10)	9534 (2)	2237 (3)	1748 (5)	113
C(11)	10086 (2)	3057 (3)	2842 (6)	468
C(12)	9914 (2)	4189 (4)	3398 (6)	393
C(13)	9167 (2)	5047 (3)	2887 (6)	−251
C(14)	8320 (2)	4695 (2)	2040 (6)	−600
C(15)	7746 (2)	5638 (3)	1385 (6)	−1403
C(16)	7952 (3)	6868 (3)	1653 (7)	−1769
C(17)	8746 (3)	7189 (4)	2586 (7)	−1341
C(18)	9336 (3)	6288 (4)	3178 (6)	−601
H(3)	661 (2)	400 (2)	214 (4)	−30
H(4)	584 (2)	212 (3)	132 (5)	−295
H(5)	683 (2)	54 (3)	11 (5)	5
H(7)	823 (2)	−40 (3)	−35 (5)	−80
H(8)	992 (2)	−53 (3)	−10 (5)	−47
H(9)	1065 (2)	113 (2)	138 (4)	199
H(11)	1067 (2)	266 (3)	326 (5)	867
H(12)	1039 (2)	458 (3)	411 (5)	669
H(15)	723 (2)	541 (3)	67 (4)	−1752
H(16)	757 (2)	745 (2)	120 (5)	−2298
H(17)	884 (2)	806 (3)	275 (5)	−1607
H(18)	995 (3)	645 (3)	378 (5)	−318

Table 2. **T** ($Å^2 \times 10^{-4}$), **L** (deg^2) *and* **S** ($deg\ Å \times 10^{-3}$)

The r.m.s. $\delta U = 0{\cdot}0028\ Å^2$. The trace of **S** has been set to zero; the e.s.d. of deleted S_{33} is given.

ij	11	22	33	12	13	23
T_{ij}	435 (10)	587 (8)	355 (15)	−46 (7)	6 (10)	59 (9)
L_{ij}	8·2 (0·5)	13·0 (1·1)	10·0 (0·4)	1·8 (0·5)	−0·3 (0·4)	1·6 (0·6)
S_{ij}	78 (18)	−66 (26)	12 (176)	−162 (16)	−21 (10)	8 (15)
S_{ji}				−36 (24)	41 (10)	122 (12)

thermal parameters for C, isotropic thermal parameters for H, a scale factor and an isotropic extinction coefficient, g, gave a final R of 0·036 ($R_w = 0{\cdot}038$) for 211 parameters.

The value obtained for g was $1{\cdot}18\ (2) \times 10^{-6}$ with $\bar{t}$ assumed to be unity. The minimum value of F_o/F_o(corr) was 0·81.

Atomic coordinates are listed in Table 1.* The thermal motion of the atoms was analysed with the assumption that the molecule could be treated as a rigid body (Schomaker & Trueblood, 1968). **T**, **L**, and **S** are given in Table 2. The value of **L** was used to correct the bond lengths for thermal motion.

Table 3. *Bond lengths* (l) *and the values* (l_c) *corrected for thermal motion, compared with the calculated values* (l_{calc}) (Å)

		l	l_c	l_{calc}
e	C(1)–C(6)	1·430 (4)	1·434	1·416
f	C(1)–C(2)	1·435 (4)	1·440	1·428
f	C(1)–C(10)	1·440 (4)	1·445	1·428
d	C(5)–C(6)	1·414 (4)	1·419	1·425
d	C(6)–C(7)	1·420 (4)	1·425	1·424
a	C(2)–C(3)	1·386 (3)	1·391	1·391
a	C(9)–C(10)	1·391 (4)	1·395	1·392
c	C(4)–C(5)	1·349 (5)	1·354	1·384
c	C(7)–C(8)	1·348 (5)	1·353	1·385
b	C(3)–C(4)	1·396 (4)	1·400	1·416
b	C(8)–C(9)	1·393 (5)	1·397	1·414
g	C(2)–C(14)	1·496 (4)	1·500	1·453
h	C(10)–C(11)	1·454 (4)	1·458	1·449
j	C(12)–C(13)	1·462 (4)	1·467	1·456
i	C(11)–C(12)	1·327 (4)	1·330	1·360
k	C(13)–C(14)	1·414 (4)	1·419	1·411
l	C(14)–C(15)	1·401 (4)	1·406	1·405
m	C(15)–C(16)	1·386 (4)	1·389	1·397
n	C(16)–C(17)	1·376 (5)	1·381	1·402
o	C(17)–C(18)	1·366 (5)	1·370	1·397
p	C(18)–C(13)	1·390 (5)	1·394	1·405
	C(3)–H(3)	0·98 (3)	0·98	
	C(4)–H(4)	0·99 (3)	1·00	
	C(5)–H(5)	0·94 (3)	0·94	
	C(7)–H(7)	0·97 (3)	0·98	
	C(8)–H(8)	1·04 (4)	1·05	
	C(9)–H(9)	0·93 (3)	0·93	
	C(11)–H(11)	0·99 (3)	0·99	
	C(12)–H(12)	0·97 (3)	0·97	
	C(15)–H(15)	0·95 (3)	0·95	
	C(16)–H(16)	0·90 (3)	0·90	
	C(17)–H(17)	0·96 (3)	0·96	
	C(18)–H(18)	1·00 (4)	1·01	

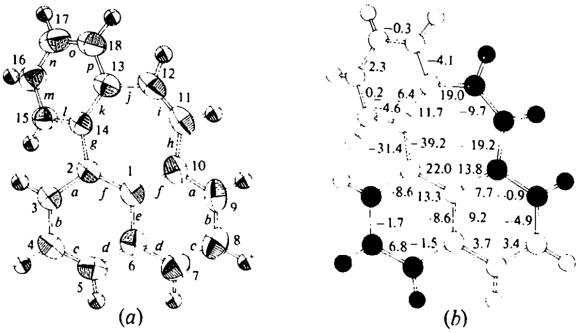

Fig. 1. (*a*) The molecule showing the thermal ellipsoids, the numbering of the atoms and the labelling of the bonds. (*b*) Torsion angles (°), standard deviations are *ca* 0·4°.

Bond lengths are given in Table 3, bond angles in Table 4. Fig. 1(*a*) shows the atomic numbering, Fig. 1(*b*) the torsion angles. Deviations from planarity are given in Table 1 and short intermolecular distances in Table 5.

Computational details

Calculations were carried out on a CDC 6400 computer with the following programs: data processing, *PROFILE*, *DATAP* and *DSORTH* (State University of New York at Buffalo); full-matrix least-squares refinement, *LINUS* (Coppens & Hamilton, 1970); distances and angles, *ORFFE* (Busing, Martin & Levy, 1964); drawings, *ORTEP* (Johnson, 1965).

The quantity minimized was $r = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$ where $w = \{[\sigma(F_o^2) + 1{\cdot}03\ F_o^2]^{1/2} - |F_o|\}^{-2}$. 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 $R_w = r^{1/2}$.

Discussion

The molecule is distinctly non-planar. If it were planar, H(3) and H(15) would be only *ca* 1·5 Å apart. The

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33687 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond angles* (°)

af	C(1)–C(2)–C(3)	118·2 (2)	*gk*	C(2)–C(14)–C(13)	126·3 (3)	C(6)–C(7)–H(7)	116 (2)
af	C(1)–C(10)–C(9)	119·0 (3)	*hi*	C(10)–C(11)–C(12)	131·2 (3)	C(8)–C(7)–H(7)	123 (2)
ab	C(2)–C(3)–C(4)	122·4 (3)	*jk*	C(14)–C(13)–C(12)	124·1 (3)	C(7)–C(8)–H(8)	120 (2)
ab	C(8)–C(9)–C(10)	122·8 (3)	*ij*	C(11)–C(12)–C(13)	129·7 (3)	C(9)–C(8)–H(8)	121 (2)
bc	C(3)–C(4)–C(5)	119·9 (3)	*kp*	C(18)–C(13)–C(14)	118·9 (3)	C(8)–C(9)–H(9)	119 (2)
bc	C(7)–C(8)–C(9)	119·2 (4)	*kl*	C(13)–C(14)–C(15)	117·2 (3)	C(10)–C(9)–H(9)	118 (2)
cd	C(4)–C(5)–C(6)	120·5 (3)	*lm*	C(14)–C(15)–C(16)	122·2 (3)	C(10)–C(11)–H(11)	112 (2)
cd	C(6)–C(7)–C(8)	121·2 (4)	*mn*	C(15)–C(16)–C(17)	119·5 (3)	C(12)–C(11)–H(11)	117 (2)
de	C(1)–C(6)–C(5)	120·3 (3)	*no*	C(16)–C(17)–C(18)	119·3 (3)	C(11)–C(12)–H(12)	118 (2)
de	C(1)–C(6)–C(7)	120·3 (3)	*op*	C(17)–C(18)–C(13)	122·6 (3)	C(13)–C(12)–H(12)	112 (2)
ef	C(6)–C(1)–C(2)	117·5 (2)	*gl*	C(2)–C(14)–C(15)	116·6 (2)	C(14)–C(15)–H(15)	118 (2)
ef	C(6)–C(1)–C(10)	116·8 (3)	*jp*	C(12)–C(13)–C(18)	116·9 (3)	C(16)–C(15)–H(15)	120 (2)
dd	C(5)–C(6)–C(7)	119·4 (3)		C(2)–C(3)–H(3)	117 (2)	C(15)–C(16)–H(16)	120 (2)
ff	C(2)–C(1)–C(10)	125·7 (3)		C(4)–C(3)–H(3)	120 (2)	C(17)–C(16)–H(16)	121 (2)
ag	C(3)–C(2)–C(14)	115·7 (2)		C(3)–C(4)–H(4)	121 (2)	C(16)–C(17)–H(17)	116 (2)
ah	C(9)–C(10)–C(11)	115·6 (3)		C(5)–C(4)–H(4)	120 (2)	C(18)–C(17)–H(17)	125 (2)
fg	C(1)–C(2)–C(14)	125·8 (2)		C(4)–C(5)–H(5)	126 (2)	C(17)–C(18)–H(18)	124 (2)
fh	C(1)–C(10)–C(11)	124·9 (3)		C(6)–C(5)–H(5)	113 (2)	C(13)–C(18)–H(18)	114 (2)

benzene ring is consequently twisted out of the plane of the naphthalene group, the torsion angle C(1)–C(2)–C(14)–C(13) being −39·2 (4)°, giving H(3)–H(5) = 2·16 Å. The seven-membered ring is buckled so that C(11) and C(12) are on the same side of the ring, the largest torsion angles being generally at the weakest bonds. The naphthalene group is also non-planar.

Bond lengths are compared, in Table 3, with theoretical values (Michl, 1978; calculated by method *B* of Muller, Cagniant, Chalvet, Lavalette, Kolc & Michl, 1974). The bond C(11)–C(12) is very short, 1·330 (4) Å; *i.e.* it is essentially a delocalized double bond as would be expected from its reactivity with osmium tetroxide and from the chemical shifts of protons H(11) and H(12) (Muller, Cagniant & Cagniant, 1972). C(2)–C(14) is 1·500 (4) Å which is typical for aryl–aryl bond distances (Table 6); these bond distances do not seem to be influenced by the torsion angle.

Comparison of a number of 1,8-substituted naphthalenes (Hazell, 1978) shows that the distortions of both bonds and angles correlate with α, the mean of the angles C(1)–C(2)–C(14) and C(1)–C(10)–C(11). The distances and angles predicted for $\alpha = 125{\cdot}35°$ found in this study are compared with the mean observed values in Table 7.

The packing is shown in Fig. 2. The molecules are roughly perpendicular to **c** and form stacks which are parallel to **c**. Spectroscopic measurements (Muller *et*

Table 5. *Short intermolecular distances* (Å) (C–C < 3·62, C–H < 3·1, *and* H–H < 2·5 Å)

The mean standard deviations are 0·005 Å for C–C, 0·032 Å for C–H, and 0·045 Å for H–H.

Symmetry code

(i)	$2-x, 1-y, -\frac{1}{2}+z$	(iv)	$1\frac{1}{2}-x, -y, \frac{1}{2}+z$
(ii)	$2-x, -y, \frac{1}{2}+z$	(v)	$-\frac{1}{2}+x, -y, z$
(iii)	$2-x, -y, -\frac{1}{2}+z$	(vi)	$\frac{1}{2}+x, 1-y, z$

C(1)–C(5^{iv})	3·555	C(13)–H(12^{i})	3·008
C(4)–C(6^{iv})	3·618	C(13)–H(15^{iv})	2·937
C(4)–C(11^{iv})	3·615	C(14)–H(12^{i})	3·006
C(8)–C(9^{iii})	3·604	C(14)–H(15^{iv})	3·006
C(10)–C(18^{i})	3·564	C(18)–H(4^{vi})	3·094
C(4)–H(8^{v})	3·097	C(18)–H(15^{iv})	3·075
C(9)–H(8^{ii})	2·964	H(4)–H(8^{v})	2·419
C(10)–H(18^{i})	2·791		

Table 6. *Aryl–aryl bond lengths* (l) *and torsion angles* (τ) *in biphenyl and related compounds*

Compound	l	τ	Reference
Biphenyl (gas)	1·48 Å	45°	(*a*)
Biphenyl (solid)	1·496 (3)	0	(*b*)
4,4′-Dichlorobiphenyl	1·485 (4)	40	(*c*)
peri-Diphenylacenaphthene	1·490 (2)	57	(*d*)
1,8-Diphenylnaphthalene	1·492 (4)	67	(*e*)
p-Terphenyl	1·496 (4)	0	(*f*)
1,4,5,8-Tetraphenylnaphthalene	1·504 (4)	58	(*g*)
This work	1·500 (4)	30	

References: (*a*) Bastiansen (1949), (*b*) Charbonneau & Delugeard (1976), (*c*) Brock, Kuo & Levy (1978), (*d*) Clough, Kung, Marsh & Roberts (1976), (*e*) Ogilvie (1971), (*f*) Evrard, Piret & Van Meerssche (1972), (*g*) Rietveld, Maslen & Clews (1970).

Table 7. *Comparison of the geometry of the naphthalene group with that predicted* (*Hazell*, 1978) *for* $\alpha = 125{\cdot}35°$

	Distances (Å)			Angles (°)	
	Observed	Predicted		Observed	Predicted
a	1·393 (3)	1·384	*ab*	122·6 (2)	122·4
b	1·399 (4)	1·397	*bc*	119·5 (3)	119·5
c	1·354 (4)	1·354	*cd*	120·8 (3)	121·0
d	1·422 (3)	1·415	*de*	120·3 (2)	120·5
e	1·434 (4)	1·437	*ef*	117·2 (3)	117·2
f	1·442 (3)	1·438	*af*	118·6 (3)	119·3
2–10	2·568 (4)	2·564	*dd*	119·4 (3)	119·0
5–7	2·446 (5)	2·439	*ff*	125·7 (3)	126·0

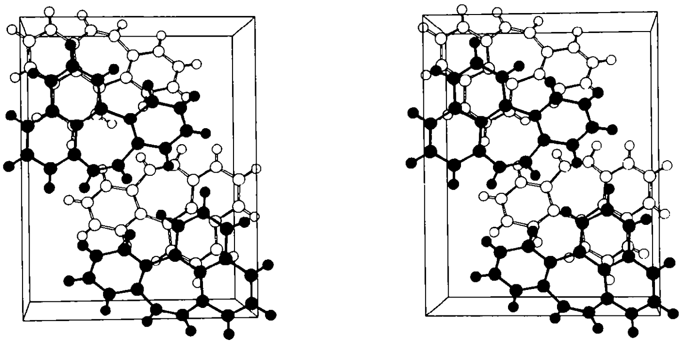

Fig. 2. The unit-cell contents viewed along **c**; **a** is down the page, **b** to the left. Molecules with black bonds are at $z \simeq 0$, those with open bonds at $z \simeq 0{\cdot}5$.

al., 1974) show that the polarization directions for the low-energy transitions are approximately in the C(1)—C(13) direction. This means that the directions of greatest polarizability of the four molecules in the unit cell are almost parallel, an arrangement giving the maximum London attraction forces between the molecules.

References

Bastiansen, O. (1949). *Acta Chem. Scand.* **3**, 408–412.

Brock, C. P., Kuo, M. & Levy, H. E. (1978). *Acta Cryst.* B**34**, 981–985.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

Charbonneau, G.-P. & Delugeard, Y. (1976). *Acta Cryst.* B**32**, 1420–1423.

Clough, R. L., Kung, W. J., Marsh, R. E. & Roberts, J. D. (1976). *J. Org. Chem.* **41**, 3603–3609.

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Evrard, P. G., Piret, P. & Van Meerssche, M. (1972). *Acta Cryst.* B**28**, 497–506.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Hazell, A. C. (1978). *Acta Cryst.* A**34**, S97.

Hazell, A. C., Hazell, R. G. & Larsen, F. K. (1978). In preparation.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Michl, J. (1978). Private communication.

Muller, J. F., Cagniant, D. & Cagniant, P. (1972). *Bull. Soc. Chim. Fr.* pp. 4364–4370.

Muller, J. F., Cagniant, D., Chalvet, O., Lavalette, D., Kolc, J. & Michl, J. (1974). *J. Am. Chem. Soc.* **96**, 5038–5045.

Ogilvie, R. A. (1971). PhD thesis, Massachusetts Institute of Technology.

Rietveld, H. M., Maslen, E. N. & Clews, C. J. B. (1970). *Acta Cryst.* B**26**, 693–706.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Wendisch, D., Hartmann, W. & Heine, H. G. (1974). *Tetrahedron*, **30**, 295–299.