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1,8-Naphthotricyclo[4.1.0.0^{2,7}]heptene

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Abstract. $C_{14}H_{10}$. Orthorhombic, *Iba*2, $a = 17{\cdot}424$, $b = 13{\cdot}948$, $c = 8{\cdot}003$ Å, $D_c = 1{\cdot}22$ g cm^{-3}, $Z = 8$. Full-matrix least-squares refinement gave $R = 0{\cdot}062$ and $R_w = 0{\cdot}060$ for 92 parameters and 439 significant reflexions $[I > 2\sigma(I)]$.

Introduction. The structures of 1,8-naphthotricyclo-[4.1.0.0^{2,7}]heptene and its valence isomers 6b,8a-dihydrocyclobut[*a*]acenaphthylene (Hazell, 1976) and pleiadiene are being determined as part of a study of strained aromatic hydrocarbons.

The naphthotricycloheptene was prepared by the method of Pagni & Watson (1973) who kindly provided the crystals. The compound crystallizes from ligroin as colourless prisms elongated along [011] and bounded by (100) and (010), the prominent face being (100).

Intensities were collected on a computer-controlled Supper diffractometer with graphite-monochromated Mo *Kα* radiation, a scintillation counter and a pulse-height analyser. 784 independent reflexions were measured by the background-peak-background method out to $\sin\theta = 0{\cdot}4$. The crystal, $1{\cdot}0 \times 0{\cdot}5 \times 0{\cdot}2$ mm, was sealed in a capillary tube to prevent sublimation, and mounted about **c**. No corrections were made for absorption.

The structure was determined with *MULTAN* (Germain, Main & Woolfson, 1971). Least-squares refinement of atomic coordinates, thermal parameters, **TLS**, and a scale factor gave $R = 0{\cdot}062$ and $R_w = 0{\cdot}060$ for 92 parameters and 439 significant reflexions* $[I > 2\sigma(I)]$. Refinements in which the molecule was constrained to be symmetric (*KONSLS*; Pawley, 1971) gave significantly worse *R* values, Table 1. As there were so few significant reflexions, no refinement with individual anisotropic temperature factors was attempted. The weighting scheme was $w = \sigma(F)^{-2}$ where $\sigma(F) = [\sigma_c(F^2) + (1 + A)F^2]^{1/2} - |F|$, $\sigma_c(F^2)$ is the standard deviation of F^2 from the counting statistics and A $(=0{\cdot}03)$ a parameter chosen to make $\langle w\Delta F^2 \rangle$ independent of $|F|$. The scattering factors were those of Cromer & Mann (1968) for C and of Stewart, Davidson & Simpson (1965) for H.

Atomic coordinates are given in Table 2, thermal parameters in Table 3. Bond lengths were corrected for

Table 1. *Results of constrained refinements*

N_o is the number of reflexions, N_p the number of parameters refined. $m\|$ is the mirror plane in the plane of the naphthalene, $m\perp$ the mirror plane perpendicular to it.

Symmetry	R	R_w	N_o	N_p
*mm*2	0·068	0·065	439	49
2	0·067	0·065	439	59
$m\|$	0·066	0·066	439	66
$m\perp$	0·065	0·063	439	62
None	0·062	0·060	439	92

Table 2. *Atomic coordinates, in* Å, *relative to molecular axes*

The molecule's origin is at $X_0 = 2{\cdot}232\,(8)$, $Y_0 = 3{\cdot}389$, $Z_0 = 0{\cdot}000$ Å; the orientation is given by the Euler angles (Goldstein, 1959) $\psi = 0{\cdot}327\,(9)$, $\theta = 2{\cdot}162\,(8)$, $\varphi = 1{\cdot}310\,(6)$ rad.

	X	*Y*	*Z*
C(1)	0·00	0·00	0·00
C(2)	0·00	−1·41 (1)	0·00
C(3)	1·25 (2)	−2·02 (2)	−0·02 (2)
C(4)	2·39 (2)	−1·35 (3)	−0·01 (2)
C(5)	2·40 (1)	0·06 (2)	0·00
C(6)	1·21 (1)	0·76 (2)	−0·00 (1)
C(7)	1·06 (3)	2·20 (2)	−0·00 (2)
C(8)	−0·09 (3)	2·82 (1)	0·77 (3)
C(9)	−1·24 (2)	−2·09 (2)	0·02 (2)
C(10)	−2·38 (2)	−1·40 (3)	0·07 (2)
C(11)	−2·40 (2)	−0·00 (3)	0·06 (2)
C(12)	−1·24 (1)	0·69 (2)	0·02 (2)
C(13)	−1·19 (3)	2·17 (2)	0·03 (3)
C(14)	−0·08 (3)	2·84 (2)	−0·70 (3)
H(3)	1·20 (10)	−2·97 (11)	−0·17 (11)
H(4)	3·22 (10)	−2·00 (13)	−0·10 (10)
H(5)	3·27 (8)	0·57 (12)	0·04 (10)
H(7)	2·01 (10)	2·77 (10)	0·01 (10)
H(8)	0·12 (11)	3·69 (10)	1·38 (11)
H(9)	−1·23 (11)	−3·18 (10)	−0·11 (11)
H(10)	−3·28 (10)	−1·87 (12)	0·12 (9)
H(11)	−3·24 (8)	0·48 (10)	0·16 (9)
H(13)	−2·03 (10)	2·76 (11)	0·07 (12)
H(14)	−0·06 (12)	3·51 (11)	−1·26 (11)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32074 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

thermal vibration ($\Delta l \simeq 0{\cdot}01$ Å) and are shown together with angles in Fig. 1.

Discussion. The geometry of the bicyclobutane group is similar to that of the free molecule (Cox, Harmony, Nelson & Wiberg, 1969). C(7)–C(13) is 2·275 Å (2·277 Å in bicyclobutane), which is shorter than C(6)–C(12) in naphthalene, 2·487 Å (Pawley & Yeats, 1969), resulting in angles α, *i.e.* C(7)–C(6)–C(1) and C(13)–C(12)–C(1), smaller [117(2)°] than 120°. The naphthalene fragment is slightly strained, β [C(3)–C(2)–C(9)] being 125 (3)°. The calculated values are α = 117·4 and β = 122·5°; these were obtained by assuming bond distances to be as in naphthalene and in bicyclobutane with C(6)–C(7) = 1·48 Å, and by varying the angles to give the minimum strain energy. The deformations are smaller than those in compounds that have a five-membered ring joined to the naphthalene, *e.g.* 6b,8a-dihydrocyclobut[*a*]-acenaphthylene, α = 108·4 (2), β = 127·3 (2)°.

The packing is shown in Fig. 2. The morphology does not obey the Donnay & Harker (1937) rules. The absence of (110) can be accounted for (Hartman, 1968; Hazell, 1971) if the centre of the molecule is at $x = \pm\frac{1}{4}$ or $y = \pm\frac{1}{4}$. The centre of the molecule was found to be at $x = 0{\cdot}123, y = 0{\cdot}237$.

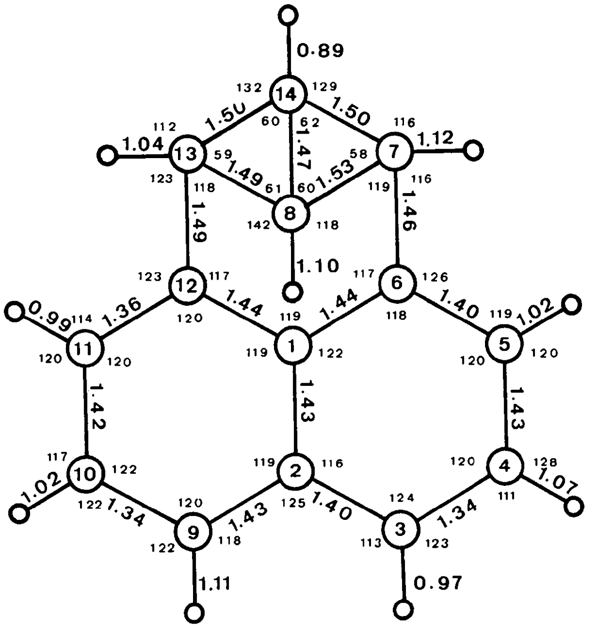

Fig. 1. Bond distances (Å) and angles (°). The average standard deviations are: σ(C–C) $\simeq$ 0·03, σ(C–H) $\simeq$ 0·1 Å, σ(C–C–C) 2 to 3° and σ(C–C–H) $\simeq$ 6°. Angles not shown: C(6)–C(7)–C(14) = 121, C(7)–C(8)–C(13) = 98, C(8)–C(7)–H(7) = 116, C(14)–C(8)–H(8) = 124, C(12)–C(13)–C(14) = 118, C(7)–C(14)–C(13) = 99, C(8)–C(13)–H(13) = 110, C(8)–C(14)–H(14) = 131°.

Table 3. *Thermal parameters* (**T** *in* Å^2 × 10^{-3}, **L** *in* deg^2, **S** *in* deg Å × 10^{-3})

L and **S** are referred to an origin $X = 2{\cdot}108$, $Y = 3{\cdot}248$, $Z = 0{\cdot}019$ Å.

$$\mathbf{T} = \begin{pmatrix} 34\,(2) & -2\,(2) & 6\,(2) \\ & 52\,(2) & 3\,(2) \\ & & 57\,(2) \end{pmatrix} \quad \mathbf{L} = \begin{pmatrix} 27{\cdot}5\,(2{\cdot}0) & 3{\cdot}5\,(1{\cdot}8) & -11{\cdot}8\,(1{\cdot}6) \\ & 32{\cdot}3\,(2{\cdot}2) & -10{\cdot}8\,(1{\cdot}8) \\ & & 32{\cdot}8\,(2{\cdot}2) \end{pmatrix}$$

$$\mathbf{S} = \begin{pmatrix} * & 7\,(53) & -142\,(37) \\ 21\,(52) & * & 58\,(46) \\ -93\,(45) & 54\,(64) & * \end{pmatrix} \qquad \begin{aligned} S_{33} - S_{22} &= -5\,(92) \\ S_{11} - S_{33} &= 184\,(72) \end{aligned}$$

* It is not possible to determine all three diagonal elements from diffraction data; the differences between the diagonal terms are given.

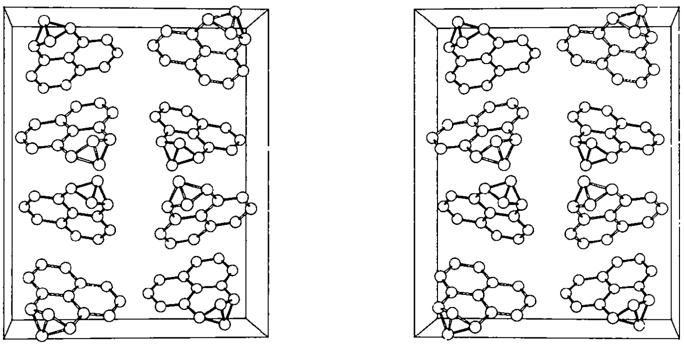

Fig. 2. A stereoscopic view of the cell contents as seen down [001]; **b** is across the page, **a** up the page. The molecules at $z = \frac{1}{2}$ are shown with filled bonds.

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Imidazo[1,2-*b*]-*as*-triazine

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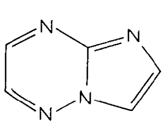
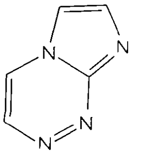
Abstract. $C_5H_4N_4$, $P2_1/n$, $Z = 4$, $a = 10{\cdot}661\ (4)$, $b = 13{\cdot}038\ (2)$, $c = 3{\cdot}816\ (2)$ Å, $\beta = 93{\cdot}29\ (2)°$, $V = 529{\cdot}6$ Å^3, $R = 6{\cdot}3\%$ for 633 observed structure factors. Stacking in columns occurs along [001] with a plane-to-plane distance of 3·36 Å.

Introduction. Acid hydrolysis of 3-amino-*as*-triazine (Rykowski & van der Plas, 1976) resulted in an imidazo-*as*-triazine which, on the available spectroscopic evidence, could be either imidazo[1,2-*b*]-*as*-triazine (I) or imidazo[2,1-*c*]-*as*-triazine (II). In order to establish which was correct a crystal structure determination was undertaken.



(I)



(II)

633 independent intensities ($I > 2{\cdot}5\sigma$) were collected on a Nonius CAD-4 automatic diffractometer with graphite-monochromated Cu $K\alpha$ radiation and the θ–2θ scan method. No absorption correction was applied (crystal dimensions $0{\cdot}25 \times 0{\cdot}3 \times 0{\cdot}3$ mm). The structure was solved from an E^2 Patterson synthesis. From the peaks surrounding the origin the orientation of the six-membered ring could be obtained. There were several acceptable Patterson peaks that could represent the distance between the centres of two six-membered rings related by a centre of symmetry, each of these providing a possible set of coordinates for the atoms of the six-membered ring. The difference synthesis based on one of these sets contained indications for the three missing non-hydrogen atoms. In the refinement of the rough structure thus obtained all atoms were at first treated as C in isotropic least-squares calculations. Discrimination between N and C was then made on the basis of the resulting thermal parameters. At a later stage a difference synthesis clearly indicated four H atoms, the positions of which confirmed the assignment of C and N. The least-squares refinement, anisotropic for C and N and isotropic for H, converged to $R = 6{\cdot}3\%$ for the 633 observed structure factors. The final parameters are listed in Table 1.*

Discussion. The molecule as found is depicted in Fig. 1. Thus the reaction product is imidazo[1,2-*b*]-*as*-triazine (I). The bond distances and angles are indicated in Fig.

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