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Structure of 4-Bromo-13α-methyl-13aαH-tetrahydropseudocoptisin

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Abstract. 4-Bromo-5,6,14,14a-tetrahydro-14α-methyl-8H-bis[1,3]benzodioxolo[5,6-a:5′,6′-g]quinolizine, $C_{20}H_{18}BrNO_4$, monoclinic, $I2/a$, $M_r = 416.271$, $a = 25.259$ (2), $b = 4.876$ (2), $c = 28.326$ (2) Å, $\beta = 96.215$ (2)°, $V = 3468.2$ Å^3, $Z = 8$, $D_m = 1.59$ (by flotation), $D_x = 1.5944$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 34.630$ cm^{-1}, $F(000) = 1696$, $R = 0.038$ for 2260 unique reflections. The molecule could be envisaged as composed by two nearly perpendicular planes with dihedral angle between rings A and D of 69.98 (9)° and torsion angles of 173.7 (2)° [C(8)—N(7)—C(13a)—C(14)] and 65.0 (2)° [C(6)—N(7)—C(13a)—C(13)]. The B/C ring fusion is *cis* and the H atoms at C(13) and C(13a) are *trans*. The C—N bonds are arranged tetrahedrally round N(7) and the lone pair on N(7) is *cis* to the H atom at C(13a).

Experimental. A yellowish parallelepiped crystal [0.35 × 0.175 × 0.075 mm] provided by Professor Pai was used for data collection on a Siemens off-line automatic four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation, and a Na(Tl)I scintillation counter. Cell parameters were determined from three high-angle axial $K\alpha_1$ and $K\alpha_2$ reflections measured on the diffractometer with Cu $K\alpha$ radiation and θ–φ scan. Space group $I2/a$ was determined from systematic absences (hkl, $h + k + l = 2n$; $h0l$, $h = 2n$) and intensity statistics (Rogers, 1965). 2589 independent reflections were measured ($0 < h < 28$, $0 < k < 5$, $-31 < l < 31$, $\sin\theta/\lambda < 0.562$ Å^{-1}) by θ–2θ scan technique using the 'five-value' (Allen, Rogers & Troughton, 1971) measuring procedure, from which 329 had $I < 2.59\sigma(I)$. Reference reflection (8,0,20) was monitored every 50 reflections with no significant deviation. The data were brought to a uniform arbitrary scale by the use of this reflection (Allen, Rogers & Troughton, 1971) and corrected for Lorentz and polarization factors but no absorption correction was applied. The structure was solved by the heavy-atom method. H atoms were located from difference Fourier syntheses and allowed to refine isotropically. Anisotropic displacement parameters were used for all non-H atoms. The structure was refined by full-matrix least squares (*XRAY*70; Stewart, Kundell & Baldwin, 1970) based on F. Unit weights were used throughout the calculations. Nine strong low-angle reflections which had $|F_o| \ll |F_c|$ were suspected of being affected by extinction and therefore removed. The refinement converged at $R = 0.038$, $S = 1.66$, $(\Delta/\sigma)_{\max} = 0.119$, $\Delta\rho_{\max} = 0.3$, $\Delta\rho_{\min} = -0.2$ e Å^{-3}. 304 parameters were varied. Final fractional coordinates with equivalent isotropic thermal parameters for all non-H atoms are listed in Table 1.† Bond lengths and valence angles are within

Table 1. *Fractional atomic coordinates* (× 10^5) *and equivalent isotropic temperature factors* (Å^2) *for non-*H *atoms, with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (ac\cos\beta)\beta_{13}].$$

	x	y	z	B_{eq}
Br	3826 (2)	5247 (12)	10618 (2)	5.44
C(1)	18689 (12)	−40846 (73)	5982 (11)	2.58
C(2)	13796 (12)	−42481 (79)	3541 (11)	2.86
C(3)	9509 (13)	−28711 (87)	4914 (12)	3.30
C(4)	9984 (13)	−12559 (83)	8920 (12)	3.25
C(4a)	14977 (13)	−10243 (74)	11596 (11)	2.70
C(5)	15517 (14)	6077 (82)	16167 (12)	3.28
C(6)	21187 (13)	8621 (74)	18465 (11)	2.79
N(7)	24160 (10)	−16606 (57)	17888 (5)	2.39
C(8)	29366 (13)	−16946 (73)	20646 (10)	2.72
C(8a)	33396 (12)	2389 (72)	18893 (11)	2.54
C(9)	37617 (13)	12106 (82)	22057 (11)	3.11
C(10)	41180 (13)	29379 (84)	20364 (12)	3.26
C(11)	40727 (13)	37036 (82)	15623 (12)	3.21
C(12)	36682 (13)	28010 (81)	12471 (11)	3.06
C(12a)	32874 (12)	10070 (71)	14112 (10)	2.42
C(13)	28203 (12)	762 (69)	10694 (11)	2.48
C(13a)	24776 (12)	−21384 (68)	12830 (10)	2.28
C(14)	19301 (12)	−24191 (68)	10074 (11)	2.33
C(15)	29938 (16)	−8671 (98)	5917 (12)	4.42
O(3)	45519 (10)	42138 (72)	22766 (10)	5.20
O(4)	44758 (10)	54918 (69)	14852 (10)	4.86
C(17)	48048 (20)	57012 (147)	19232 (16)	5.50
O(1)	12238 (8)	−57471 (62)	−536 (8)	3.99
C(16)	6708 (16)	−53266 (150)	−1543 (18)	5.41
O(2)	5044 (9)	−33530 (71)	1806 (9)	4.71

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† Lists of structure factors, anisotropic and isotropic displacement parameters, H-atom coordinates, bond lengths and valence angles including those involving H atoms, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54715 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0225]

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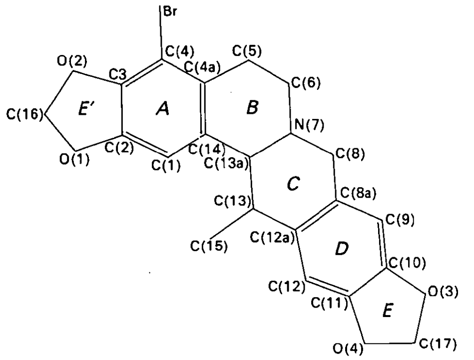

Fig. 1. Numbering of the atoms in the title compound.

the accepted values. Atomic scattering factors were taken from Doyle & Turner (1968) except those for H which were taken from Stewart, Davidson & Simpson (1965); anomalous-dispersion data for Br were from Cromer (1965). Fig. 1 shows the numbering scheme and Fig. 2 is an *ORTEP* (Johnson, 1965) representation of the packing of the molecules in the unit cell.

Related literature. The structures of the title compound and 4-bromo-13β-methyl-13aα*H*-tetrahydropseudocoptisin have been compared by Rogers, Atkinson Williams, Waight, Pai, Nagarajan, Natarajan, Suguna, Rajeswari, Chandrasekaran, Rajaraman & Manikumar (1982). Related structures are capaurimine mono-*p*-bromobenzoate (Kametani, Ihara, Honda, Shimanouchi & Sasada, 1971), capaurine hydrobromide (Shimanouchi, Sasada, Ihara & Kametani, 1969), and *cis*-5,6,13,13a-tetrahydro-3,9-dihydroxy-1,2,10-trimethoxy-8*H*-dibenzo-[*a*,*g*]quinolizine hydrobromide monohydrate (Shimanouchi, Sasada, Wakisaka, Kametani & Ihara, 1970). Work on protoberberines and tetrahydroprotoberberines is described in a review by Pai, Nagarajan, Suguna & Natarajan (1977).

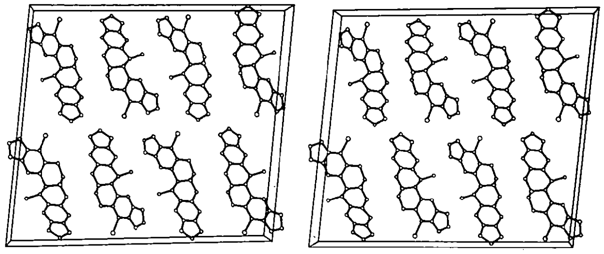

Fig. 2. *ORTEP* (Johnson, 1965) stereoscopic projection of the unit-cell contents. **a** is vertical, **c** is horizontal and **b** is out of the plane of the paper.

References

Allen, F. H., Rogers, D. & Troughton, P. G. H. (1971). *Acta Cryst.* B**27**, 1325–1337.
Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.
Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Kametani, T., Ihara, M., Honda, T., Shimanouchi, H. & Sasada, Y. (1971). *J. Chem. Soc. C*, pp. 2541–2545.
Pai, B. R., Nagarajan, K., Suguna, H. & Natarajan, S. (1977). *Heterocycles*, **6**, 1377–1439.
Rogers, D. (1965). *Computing Methods in Crystallography*, edited by J. S. Rollett, pp. 117–132. Oxford: Pergamon Press.
Rogers, D., Atkinson, A., Williams, D. J., Waight, E. S., Pai, B. R., Nagarajan, K., Natarajan, S., Suguna, H., Rajeswari, S., Chandrasekaran, S., Rajaraman, R. & Manikumar, G. (1982). *Indian J. Chem. Sect. B*, **21**, 60–62.
Shimanouchi, H., Sasada, Y., Ihara, M. & Kametani, T. (1969). *Acta Cryst.* B**25**, 1310–1319.
Shimanouchi, H., Sasada, Y., Wakisaka, K., Kametani, T. & Ihara, M. (1970). *Acta Cryst.* B**26**, 607–616.
Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The *XRAY70* system. Tech. Rep. TR-646. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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6,6″-Dibromo-4′-phenyl-2,2′:6′,2″-terpyridine

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Abstract. $C_{21}H_{13}Br_2N_3$, $M_r = 467.16$, orthorhombic, *Pbcn*, $a = 7.366$ (3), $b = 12.006$ (4), $c = 20.601$ (5) Å, $V = 1822$ (1) Å^3, $Z = 4$ (implying that each molecule lies on a twofold special position), $D_x = 1.702$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 5.36$ mm^{-1}, $F(000) = 920$, $T = 298$ K, $R = 0.037$ for 1327 unique observed reflections with $F > 4\sigma(F)$. The molecule lies on a twofold rotation axis which runs through N and one C of the central pyridyl ring. The molecule exhibits a *trans*,*trans* arrangement of

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