Structure of 2,8-Bis(2-bromoethyl)-5,11-methano-5,6,11,12-tetrahydrodibenzo[b,f][1,5]diazocine at 163 K

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Abstract. $C_{19}H_{20}Br_2N_2$, $M_r = 436.19$, triclinic, $P\bar{1}$, $a = 8.5396$ (8), $b = 12.1782$ (17), $c = 8.2348$ (8) Å, $\alpha = 93.151$ (12), $\beta = 97.182$ (9), $\gamma = 80.346$ (12)°, $V = 837.14$ (16) Å^3, $D_m(295 \text{ K}) = 1.669$, $Z = 2$, $D_x = 1.730$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 47.944$ cm^{-1}, $F(000) = 436$, $T = 163$ K, $R = 0.0412$ for 3546 reflections ($F \geq 4\sigma_F$). Molecules have approximate C_2 symmetry except for the bromomethyl groups, which deviate because of packing. The dihedral angle between the planes of the aromatic rings is 92.73 (10)°. Bond lengths are normal: C—Br 1.952, 1.955 Å; C—N, 1.432–1.477 Å; aromatic C—C, 1.378–1.399 Å; other C—C, 1.501–1.517 Å. Shortest intermolecular contacts are Br(1)···H(15)A, 3.23 (4) Å, and Br(2)···H(7)A, 3.08 (3) Å.

Experimental. Title compound prepared in 37% yield from 4-(2-bromoethyl)aniline hydrochloride (Evans & Walker, 1947), formaldehyde and aqueous hydrochloric acid by method of Wagner (1954). Suitable crystals obtained from toluene (m.p. 401.6–403 K). Data crystal cut from thin needle perpendicular to needle axis. Summary of data collection and structural refinement given in Table 1.

Br atom from Patterson map; remaining non-hydrogens from electron density maps; refined by full-matrix least squares (*SHELX*76; Sheldrick, 1976); all atomic positional parameters refined as well as anisotropic thermal parameters for non-hydrogens and isotropic for H atoms. Electron density difference map calculated at $R = 0.052$ revealed all H atoms as peaks of 0.69–1.04 e Å^{-3}. Scattering factors and anomalous-dispersion corrections for all non-H atoms from *International Tables for X-ray Crystallography* (1974); H scattering factors from Stewart, Davidson & Simpson (1965). Atomic parameters in Table 2.* Bond

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* Tables of hydrogen parameters, anisotropic thermal parameters, bond lengths and angles involving hydrogen, torsion angles, least-squares planes and structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42545 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lengths and bond angles in Table 3; atom labeling in Fig. 1 and packing in Fig. 2. Principal computer programs are given by Gadol & Davis (1982); program for least-squares-planes' calculations from Cordes (1983).

Table 1. *Crystallographic summary for* $C_{19}H_{20}Br_2N_2$

(*a*) Data collection (163 K)*†

Mode	ω scan
Scan range	Symmetrically over 1.0° about $K\alpha_{1,2}$ maximum
Background	Offset 1.0 and −1.0° in ω from $K\alpha_{1,2}$ maximum
Scan rate (° min^{-1})	3.0–6.0
Exposure time (h)	60.5
Stability analysis†	
Check reflections	052; 2$\bar{4}$0; 1$\bar{1}$1; $\bar{2}\bar{2}$2
Computed s	0.0002 (2)
t	−0.000004 (3)
Correction range (on I)	0.999–1.006
2θ range (°)	4.0–60.0
Range in hkl, min.	0,−16,−11
max.	12,17,11
Reflections measured; total, unique	4895, 4895
Crystal volume (mm^3)	0.0197
Crystal faces, dimensions (mm)	{100}, 0.17; {01$\bar{1}$}, 0.23; (0$\bar{1}$0), +cut side, 0.45
Transmission-factor range	0.332–0.478

(*b*) Structure refinement‡

Instability factor p‡	0.04
Reflections used ($F \geq 4\sigma_F$)	3546
Number of variables	288
Goodness of fit, S	1.354
R, wR	0.0412, 0.0443
R for all data	0.0692
Max. shift/e.s.d.	0.0105
Max., min. in difference map (e Å^{-3})	0.71, −0.60

* Unit-cell parameters were obtained by least-squares refinement of the setting angles of 60 reflections with $25.1 < 2\theta < 29.7°$. Crystal density was measured by flotation in aqueous $ZnCl_2$.

† Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described by Riley & Davis (1976). Crystal and instrument stability were monitored by re-measurement of 4 check reflections after every 96 reflections. As detailed by Henslee & Davis (1975), these data were analyzed to relate intensity to exposure time by the equation $y = 1.0 + sx + tx^2$, where x is exposure time (h), y is fractional intensity relative to $x = 0$ and s and t are coefficients determined by least-squeares fit.

‡ Function minimized was $\sum w(F_o - F_c)^2$, where $w = \sigma_F^{-2}$, $\sigma_F = F\sigma_I/2I$, $\sigma_I = |N_{pk} + N_{bg1} + N_{bg2} + (pI)^2|^{1/2}$.

Table 2. *Positions in fractional coordinates and U_{eq} values for non-hydrogen atoms in* $C_{19}H_{20}Br_2N_2$

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$, where A_{ij} is the dot product of the ith and jth direct-space unit-cell vectors.

|	x	y	z	$U_{eq}(\text{Å}^2)$
N(1)	0·5150 (3)	0·0860 (2)	0·8345 (3)	0·0175 (8)
N(2)	0·2624 (3)	0·1689 (2)	0·6870 (3)	0·0189 (8)
C(1)	0·5959 (4)	0·1231 (2)	0·7107 (4)	0·0150 (8)
C(2)	0·7610 (4)	0·1191 (3)	0·7400 (4)	0·0184 (9)
C(3)	0·8438 (4)	0·1556 (3)	0·6255 (4)	0·0189 (9)
C(4)	0·7643 (4)	0·1966 (3)	0·4768 (4)	0·0175 (9)
C(5)	0·5998 (4)	0·2003 (3)	0·4488 (4)	0·0177 (9)
C(6)	0·5133 (4)	0·1651 (2)	0·5636 (4)	0·0158 (9)
C(7)	0·3330 (4)	0·1755 (3)	0·5338 (4)	0·0206 (10)
C(8)	0·2685 (4)	0·2675 (3)	0·7905 (4)	0·0166 (9)
C(9)	0·1587 (4)	0·3637 (3)	0·7510 (4)	0·0192 (10)
C(10)	0·1584 (4)	0·4590 (3)	0·8502 (4)	0·0189 (9)
C(11)	0·2659 (4)	0·4622 (2)	0·9918 (4)	0·0159 (9)
C(12)	0·3730 (4)	0·3666 (3)	1·0290 (4)	0·0155 (9)
C(13)	0·3780 (4)	0·2694 (2)	0·9311 (4)	0·0148 (8)
C(14)	0·5012 (4)	0·1672 (3)	0·9741 (4)	0·0183 (9)
C(15)	0·3516 (4)	0·0713 (3)	0·7700 (5)	0·0231 (10)
C(16)	0·8549 (5)	0·2358 (3)	0·3514 (4)	0·0227 (10)
C(18)	0·2632 (4)	0·5707 (3)	1·0913 (4)	0·0184 (9)
C(17)	0·9447 (5)	0·1385 (3)	0·2638 (5)	0·0249 (11)
C(19)	0·3637 (4)	0·5669 (3)	1·2554 (4)	0·0209 (10)
Br(1)	1·07080 (5)	0·18732 (4)	0·10769 (5)	0·03333 (13)
Br(2)	0·27623 (5)	0·48878 (3)	1·41538 (4)	0·03269 (13)
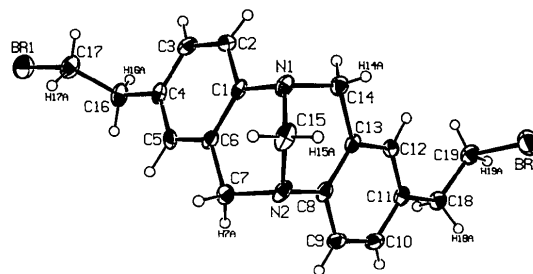
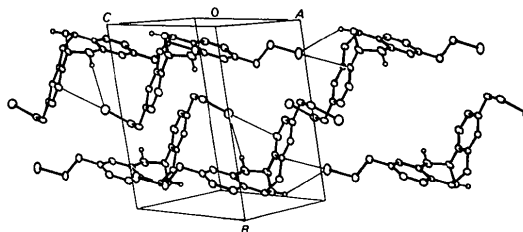Fig. 1. View of title compound illustrating atom labeling. Thermal ellipsoids scaled to 50% probability.

Fig. 2. Molecular packing diagram as viewed parallel to the ac diagonal. Closest contacts based on van der Waals radii are indicated by thin lines $|Br(1)\cdots C(13)$, 3·463 (3) Å; $Br(1)\cdots H(15)A$, 3·23 (4) Å; $Br(2)\cdots C(9)$, 3·555 (3) Å; $Br(2)\cdots H(7)A$, 3·08 (3) Å; second atom related by $1 + x, y, z - 1$ for Br(1) and $x, y, z + 1$ for Br(2)|. Thus, molecules in contact form layers parallel to the ac plane.

Table 3. *Bond lengths (Å) and bond angles (°) in* $C_{19}H_{20}Br_2N_2$

1	2	3	1—2	1—2—3
C(1)	N(1)	C(14)	1·432 (4)	111·8 (3)
C(14)	N(1)	C(15)	1·477 (4)	106·6 (3)
C(15)	N(1)	C(1)	1·465 (4)	111·2 (3)
C(7)	N(2)	C(8)	1·476 (5)	112·1 (3)
C(8)	N(2)	C(15)	1·439 (4)	110·6 (3)
C(15)	N(2)	C(7)	1·454 (4)	107·0 (3)
C(2)	C(1)	C(6)	1·393 (4)	119·5 (3)
C(2)	C(1)	N(1)		118·7 (3)
C(6)	C(1)	N(1)	1·399 (4)	121·8 (3)
C(3)	C(2)	C(1)	1·379 (5)	120·8 (3)
C(4)	C(3)	C(2)	1·399 (4)	120·8 (3)
C(5)	C(4)	C(16)	1·388 (5)	121·2 (3)
C(5)	C(4)	C(3)		118·0 (3)
C(16)	C(4)	C(3)	1·507 (5)	120·8 (3)
C(6)	C(5)	C(4)	1·397 (5)	122·2 (3)
C(7)	C(6)	C(1)	1·514 (4)	120·1 (3)
C(7)	C(6)	C(5)		121·1 (3)
C(1)	C(6)	C(5)		118·8 (3)
N(2)	C(7)	C(6)		111·8 (2)
C(9)	C(8)	C(13)	1·398 (4)	119·0 (3)
C(9)	C(8)	N(2)		118·9 (3)
C(13)	C(8)	N(2)	1·396 (4)	122·1 (3)
C(10)	C(9)	C(8)	1·382 (5)	120·4 (3)
C(11)	C(10)	C(9)	1·394 (4)	121·4 (3)
C(12)	C(11)	C(18)	1·378 (4)	123·9 (3)
C(12)	C(11)	C(10)		117·4 (3)
C(18)	C(11)	C(10)	1·514 (4)	118·6 (3)
C(13)	C(12)	C(11)	1·393 (4)	122·8 (3)
C(14)	C(13)	C(8)	1·517 (4)	120·0 (3)
C(14)	C(13)	C(12)		121·0 (3)
C(8)	C(13)	C(12)		119·0 (3)
N(1)	C(14)	C(13)		111·9 (2)
N(1)	C(15)	N(2)		112·6 (3)
C(17)	C(16)	C(4)	1·501 (5)	110·7 (3)
C(19)	C(18)	C(11)	1·506 (5)	117·0 (3)
Br(1)	C(17)	C(16)	1·952 (4)	111·4 (3)
Br(2)	C(19)	C(18)	1·955 (4)	112·2 (3)

Related literature. We have published the structure of the parent compound, 5,6,11,12-tetrahydro-2,8-dimethyl-5,11-methanodibenzo[*b,f*][1,5]diazocine or Tröger's base, with related references (Larson & Wilcox, 1986).

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