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2,8-Dibromo-6*H*,12*H*-5,11-methanodibenzo-[*b*,*f*][1,5]diazocine

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.027
wR factor = 0.069
Data-to-parameter ratio = 27.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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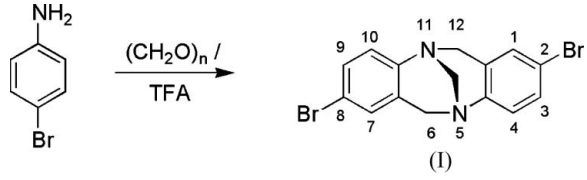
In the molecule of the title compound, $C_{15}H_{12}Br_2N_2$, the 2,8-dibromo analogue of Tröger's base, the two aryl rings are offset with respect to one another by virtue of the diazocine bridge. The dihedral angle between the two benzene rings is 94.45 (4)°.

Comment

Tröger's base is a chiral C_2-symmetric V-shaped molecule derived from the acid-catalysed condensation of *p*-toluidine and formaldehyde. Since its first reported synthesis (Tröger, 1887), numerous substituted anilines have been used to prepare a range of analogues bearing different types of substituents. 2,8-Dihalogenated systems were recently reported for the first time (Jensen & Wärnmark, 2001) and these have since been elaborated into a range of other systems *via* metal–halogen exchange reactions (Jensen, Strozyk & Wärnmark, 2002; Jensen, Tejler & Wärnmark, 2002; Kiehne & Lützen, 2004; Hof *et al.*, 2005).



(I)

We were interested in preparing a range of dihalo Tröger's base compounds as precursors for supramolecular recognition elements. The synthesis of (I) in racemic form was achieved by reacting 4-bromoaniline with paraformaldehyde in trifluoroacetic acid (TFA).

In the molecule of the title compound, (I), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987).

Rings *B* (N1/N2/C1/C6/C7/C15) and *C* (N1/N2/C8/C13–C15) are not planar, having total puckering amplitudes, Q_T, of 1.381 (3) and 0.740 (4) Å, respectively, and twist conformations $\varphi = -115.72\ (7)^\circ$ and $\theta = 109.77\ (5)^\circ$, and $\varphi = -33.87\ (6)^\circ$ and $\theta = 47.44\ (5)^\circ$ (Cremer & Pople, 1975). Rings *A* (C1–C6) and *D* (C8–C13) are, of course, planar and the dihedral angle between them is *A*/*D* = 94.45 (4)°.

The two aryl rings of Tröger's base analogues are offset with respect to one another by virtue of the diazocine bridge and they generally subtend an angle of approximately 90°. In fact, the dihedral angle has been found to vary between 82 (Solano *et al.*, 2005) and 104° (Wilcox *et al.*, 1987) for simple dibenzo Tröger's base analogues, and is dependent upon the nature of the substituents on the ring. The only other reported X-ray crystal structure of a dihalo Tröger's base is that of 3,9-

dibromo-4,10-dimethyl-6 H,12*H*-5,11-methanodibenzo[*b*,*f*]-[1,5]diazocine, which has a dihedral angle of 100.9° (Hansson *et al.*, 2003).

Experimental

The title compound was prepared according to a literature procedure (Jensen & Wärnmark, 2001) in 70% yield and recrystallized from chloroform.

Crystal data

$C_{15}H_{12}Br_2N_2$
M_r = 380.09
Triclinic, $P\overline{1}$
a = 6.364 (5) Å
b = 10.420 (5) Å
c = 10.815 (5) Å
α = 82.967 (5)°
β = 76.878 (5)°
γ = 81.744 (5)°
V = 688.2 (7) Å^3
Z = 2
D_x = 1.834 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 5.88 mm^{-1}
T = 150 (2) K
Prism, colourless
0.43 × 0.38 × 0.38 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.091, T_{max} = 0.110
10200 measured reflections
4744 independent reflections
3957 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 32.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.069
S = 1.28
4744 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.80 e Å^{-3}
$\Delta\rho_{min}$ = −0.93 e Å^{-3}

Table 1
Selected torsion angles (°).

C15—N1—C1—C6	−15.5 (2)	C1—N1—C15—N2	52.35 (18)
C15—N2—C7—C6	47.43 (17)	C14—N1—C15—N2	−70.31 (17)
C15—N2—C8—C13	−15.1 (2)	C8—N2—C15—N1	53.68 (18)
C15—N1—C14—C13	45.25 (17)	C7—N2—C15—N1	−69.79 (17)

H atoms were positioned geometrically, with C—H = 0.95 and 0.99 Å for aromatic and methylene H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 1995); cell refinement: *SAINT* (Bruker, 1995); data reduction: *SAINT* and *XPREP* (Bruker, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN for Windows* (Molecular Structure Corporation, 1998), *Xtal3.6* (Hall *et al.*, 1999) and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

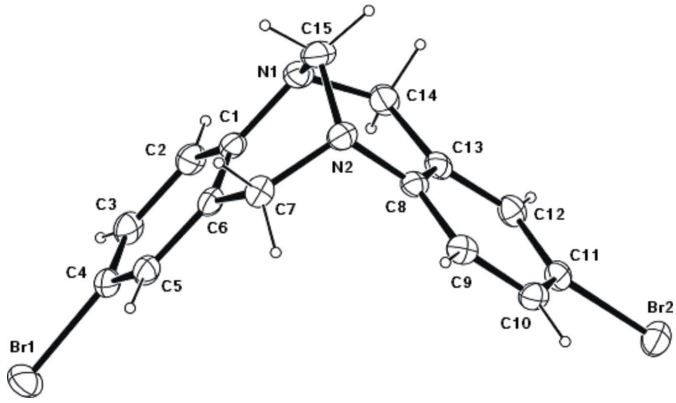


Figure 1
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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