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1,7-Dibromo-2,8-dimethyl-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 = 0.022
wR factor = 0.057
Data-to-parameter ratio = 18.7

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

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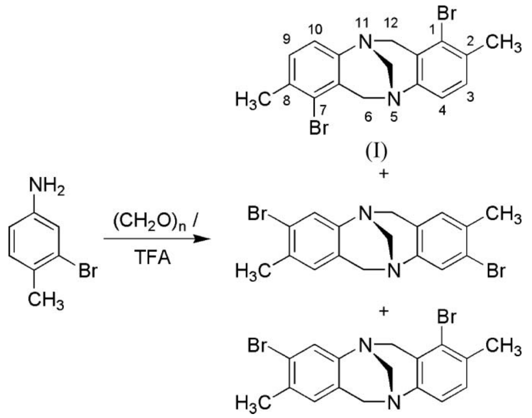
In the title compound, $C_{17}H_{16}Br_2N_2$, the 1,7-dibromo-2,8-dimethyl analogue of Tröger's base, the aryl rings are offset with respect to one another. The dihedral angle between the two benzene rings is 97.47 (5)°; the molecule is C_2-symmetric.

Comment

Tröger's base is a cleft-containing molecule that is chiral by virtue of the two tertiary N atoms in the bridge (Spielman, 1935). The presence of the methano strap between the two N atoms in the diazocine ring prevents pyramidal inversion and permits resolution of the enantiomers (Prelog & Wieland, 1944). The bridging unit also imparts a twist within the molecule such that the aryl rings are offset with respect to one another. This dihedral angle has been measured across a range of compounds to lie between 82° (Solano *et al.*, 2005) and 108° (Faroughi *et al.*, 2006) for simple dibenzo Tröger's base analogues. Compound (I) (Fig. 1) crystallizes in the space group *C*2/*c* and is one of three compounds produced in racemic form by reacting 3-bromo-4-methylaniline with paraformaldehyde in trifluoroacetic acid (TFA) (see Scheme).



The structure of a second isomer, the 3,9-dibromo-2,8-dimethyl Tröger's base analogue, is reported in the following paper (Faroughi *et al.*, 2007). The third product formed was a non-symmetric compound, the 1,9-dibromo-2,8-dimethyl Tröger's base analogue. We were interested in preparing a range of dibromo Tröger's base compounds in which the Br atoms were positioned at different sites on the framework for use as precursors in the syntheses of supramolecular recognition elements.

Compound (I) is C_2-symmetric. It packs in layers in which there are offset face-to-face (OFF) interactions between the aryl surfaces, but no significant π–π interactions. In (I), these interactions are between one *endo* and one *exo* face of the

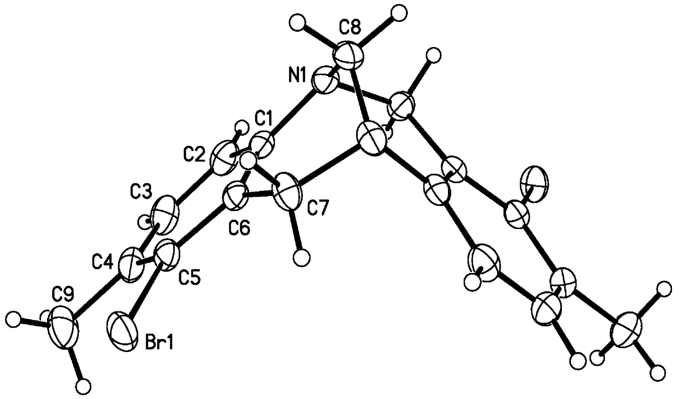


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

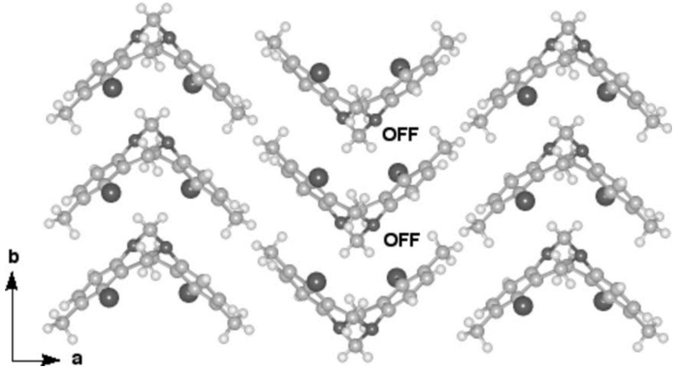


Figure 2
One layer in the packing of (I). The darkest atoms are Br and some OFF interactions are marked.

molecule (Fig. 2), which contrasts with the 3,9-dibromo-2,8-dimethyl Tröger's base where the interactions are *endo–endo* and *exo–exo* (Faroughi *et al.*, 2007).

Experimental

Compound (I) was prepared in an analogous manner to that previously described (Hansson *et al.*, 2003). 3-Bromo-4-methylaniline (861 mg, 4.63 mmol) and paraformaldehyde (222 mg, 7.41 mmol) were dissolved in trifluoroacetic acid (20 ml) and the mixture was stirred under an argon atmosphere in the dark for 20 h. The reaction mixture was then neutralized with a solution of concentrated ammonia (20 ml) in water (50 ml), rendered basic by the addition of a saturated sodium hydrogen carbonate solution (50 ml), and extracted into dichloromethane (2 × 50 ml). The combined organic layers were washed with brine (50 ml), dried over anhydrous sodium sulfate, filtered and evaporated to dryness to yield an orange solid. The material was chromatographed (silica gel, ethyl acetate–dichloromethane 1:9) to afford (I) (358 mg, 38%) as a white powder and the first major band eluted from the column [m.p. 539.8 K; literature m.p. 536–538 K (Hansson *et al.*, 2003)]. HRMS *m/z* calculated for $C_{17}H_{16}Br_2N_2$ + H^+ [M + H^+] 406.975300, observed 406.975764. Analysis calculated for $C_{17}H_{16}Br_2N_2$: C 50.03, H 3.95, N 6.86%; found: 49.90, H 3.93, N 7.07%. Single crystals of (I) were obtained by the slow evaporation of a dichloromethane solution of the compound.

Crystal data

$C_{17}H_{16}Br_2N_2$
$M_r = 408.14$
Monoclinic, $C2/c$
$a = 23.583$ (7) Å
$b = 5.096$ (2) Å
$c = 14.907$ (4) Å
$\beta = 121.921$ (4)°
$V = 1520.6$ (9) Å^3
$Z = 4$
$D_x = 1.783$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 5.33$ mm^{-1}
$T = 150$ (2) K
Prism, colourless
0.55 × 0.26 × 0.17 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: Gaussian [*GAUSSIAN* (Coppens *et al.*, 1965) and *PLATON* (Spek, 2003)]
$T_{\min} = 0.065$, $T_{\max} = 0.472$
7490 measured reflections
1813 independent reflections
1721 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.057$
$S = 1.09$
1813 reflections
97 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 1.4322P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

H atoms were included in the riding-model approximation, with C—H = 0.95–0.98 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(methyl C). The methyl group was free to rotate about the C—C bond in the refinement.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 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), *ORTEPII* (Johnson, 1976) and *WinGX* (Farrugia, 1999); software used to prepare material for publication: *WinGX*.

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o1046 Faroughi *et al.* • $C_{17}H_{16}Br_2N_2$ *Acta Cryst.* (2007). E**63**, o1045–o1047

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Acta Cryst. (2007). E**63**, o1045–o1047 Faroughi *et al.* • $C_{17}H_{16}Br_2N_2$ **o1047**