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3,9-Dibromo-2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine

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Key indicators

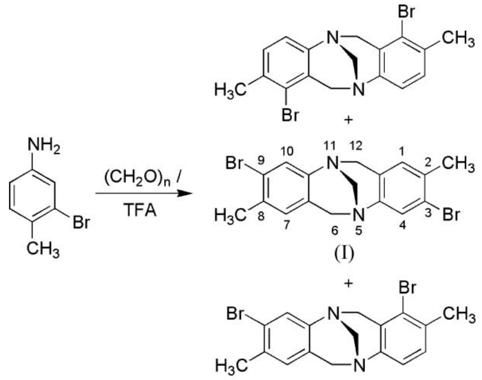
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.085
Data-to-parameter ratio = 25.2

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

In the title compound, $C_{17}H_{16}Br_2N_2$, the 3,9-dibromo-2,8-dimethyl analogue of Tröger's base, the diazocine bridge imparts a twist such that the aryl rings are offset with respect to one another. The dihedral angle between the two benzene rings is 97.10 (7)°.

Comment

Tröger's base (Tröger, 1887) is a chiral C_2-symmetric molecule that owes its chirality to the presence of the two tertiary N atoms in the bridge (Spielman, 1935). This bridging unit imparts a twist within the molecule and the resultant 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) was one of three compounds produced in racemic form by reacting 3-bromo-4-methylaniline with paraformaldehyde in trifluoroacetic acid (TFA). The structure of a second product, 1,7-dibromo-2,8-dimethyl Tröger's base, is reported in the preceding paper (Faroughi *et al.*, 2007) (see Scheme).



The halide atoms on related Tröger's base systems have been successfully converted into other functionalities (Jensen, Strozyk & Wärnmark, 2002; Jensen, Tejler & Wärnmark, 2002; Kiehne & Lützen, 2004; Hof *et al.*, 2005) and we were interested in employing analogous chemistry on different frameworks in the syntheses of new supramolecular recognition elements.

Compound (I) packs in layers in which there are offset face-to-face (OFF) interactions between the aryl surfaces (Fig. 2), but there are no significant π–π interactions. This contrasts with the isomeric compound, 1,7-dibromo-2,8-dimethyl Tröger's base, where the interactions are between one *endo* and one *exo* face of the molecule (Faroughi *et al.*, 2007). Compound (I) also exhibits interlayer Br···Br interactions,

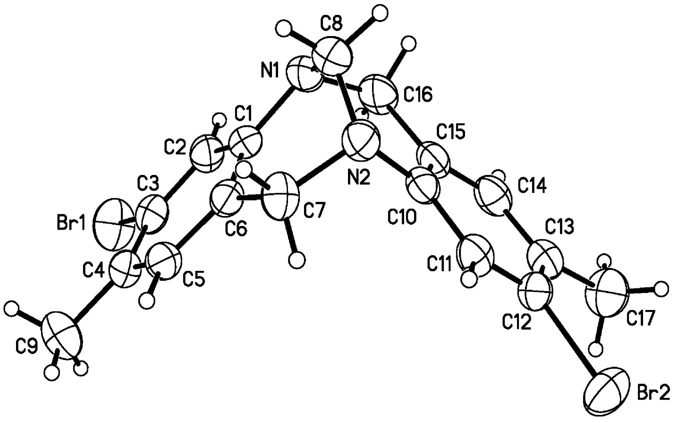


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

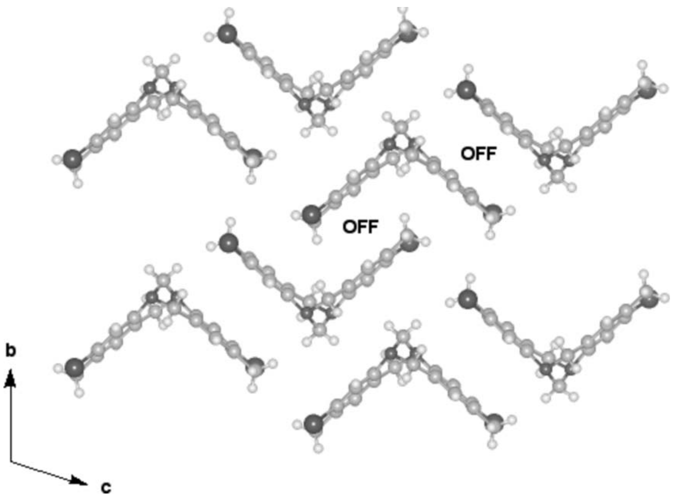


Figure 2
One layer in the packing of (I). The darkest atoms are Br and some OFF interactions are marked.

the closest of which is 3.7068 (4) Å between Br1 and Br2^{i} [symmetry code: (i) $x - 1, y, z - 1$].

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–hexane 3:7) to afford (I), (287 mg, 30%) as a white powder [m.p. 520.2 K; literature m.p. 513–515 K (Hansson *et al.*, 2003)]. HRMS *m*/*z* calculated for $C_{17}H_{16}Br_2N_2$ + H^+ [M + H^+] 406.975300, observed 406.976374. Analysis calculated for $C_{17}H_{16}Br_2N_2$: C 50.03, H 3.95, N 6.86%; found: C 50.14, H 4.06, N 6.99%. Single crystals of (I) were obtained by the slow evaporation of a dichloromethane solution.

Crystal data

$C_{17}H_{16}Br_2N_2$
$M_r = 408.14$
Triclinic, $P\bar{1}$
$a = 6.8910$ (1) Å
$b = 10.0369$ (2) Å
$c = 12.0624$ (2) Å
$\alpha = 99.826$ (1)°
$\beta = 95.971$ (1)°
$\gamma = 107.817$ (1)°
$V = 771.69$ (2) Å^3
$Z = 2$
$D_x = 1.756$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 5.25$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.37 × 0.35 × 0.24 mm

Data collection

Bruker–Nonius Kappa-APEX-II diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.226$, $T_{\max} = 0.366$ (expected range = 0.175–0.284)
30101 measured reflections
4829 independent reflections
2809 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 30.9°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.085$
$S = 1.02$
4829 reflections
192 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 0.2311P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ 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) = $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}$(methyl C). The methyl groups were free to rotate about the C—C bond in the refinement.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *modiCIFer* (Guzei, 2005).

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Bruker (2003). *SAINT* (Version 6.45) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2005). *APEX2* Version 2.0-2. Bruker AXS Inc., Madison, Wisconsin, USA.

Faroughi, M., Try, A. C. & Turner, P. (2006). *Acta Cryst.* E**62**, o3893–o3894.

Faroughi, M., Turner, P. & Try, A. C. (2007). *Acta Cryst.* E**63**, o1045–o1047.

Guzei, I. A. (2005). *ModiCIFer*. Version of December 16 2005. University of Wisconsin–Madison, Madison, Wisconsin, USA.

Hansson, A. P., Jensen, J., Wendt, O. F. & Wärnmark, K. (2003). *Eur. J. Org. Chem.* pp. 3179–3188.

Hof, F., Schar, M., Scofield, D. M., Fischer, F., Diederich, F. & Sergeyev, S. (2005). *Helv. Chim. Acta*, **88**, 2333–2344.

Jensen, J., Strozyk, M. & Wärnmark, K. (2002). *Synthesis*, pp. 2761–2765.

Acta Cryst. (2007). E**63**, o1048–o1050 Faroughi *et al.* • $C_{17}H_{16}Br_2N_2$ **o1049**

Jensen, J., Tejler, J. & Wärnmark, K. (2002). *J. Org. Chem.* **67**, 6008–6014.
Kiehne, U. & Lützen, A. (2004). *Synthesis*, pp. 1687–1695.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Solano, C., Svensson, D., Olomi, Z., Jensen, J., Wendt, O. F. & Wärnmark, K. (2005). *Eur. J. Org. Chem.* pp. 3510–3517.
Spielman, M. A. (1935). *J. Am. Chem. Soc.* **57**, 583–585.
Tröger, J. (1887). *J. Prakt. Chem.* **36**, 225–245.

o1050 Faroughi *et al.* • $C_{17}H_{16}Br_2N_2$ *Acta Cryst.* (2007). E**63**, o1048–o1050