

Acta Crystallographica Section E

**Structure Reports**

**Online**

ISSN 1600-5368

Editors: **W. Clegg** and **D. G. Watson**

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

**Masoud Faroughi, Marcia Scudder, Peter Turner, Paul Jensen and Andrew C. Try**

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site provided that this cover page is retained. Republication of this article or its storage in electronic databases or the like is not permitted without prior permission in writing from the IUCr.

Masoud Faroughi,<sup>a</sup> Marcia Scudder,<sup>b</sup> Peter Turner,<sup>c</sup> Paul Jensen<sup>c</sup> and Andrew C. Try<sup>a\*</sup>

<sup>a</sup>Department of Chemistry and Biomolecular Sciences, Building F7B, Macquarie University, NSW 2109, Australia, <sup>b</sup>School of Chemistry, The University of New South Wales, NSW 2052, Australia, and <sup>c</sup>Crystal Structure Analysis Facility, School of Chemistry, F11, The University of Sydney, NSW 2006, Australia

Correspondence e-mail: andrew.try@mq.edu.au

#### Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

$R$  factor = 0.036

$wR$  factor = 0.085

Data-to-parameter ratio = 25.2

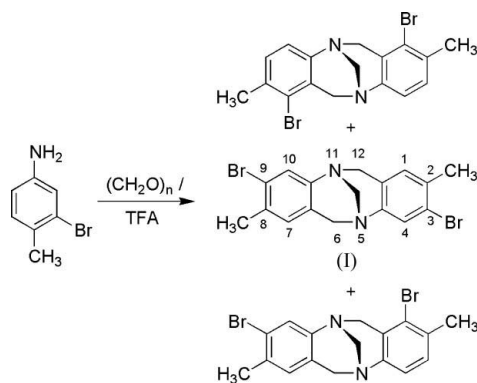
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

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

In the title compound,  $\text{C}_{17}\text{H}_{16}\text{Br}_2\text{N}_2$ , 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  $97.10(7)^\circ$ .

### 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  $82^\circ$  (Solano *et al.*, 2005) and  $108^\circ$  (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).

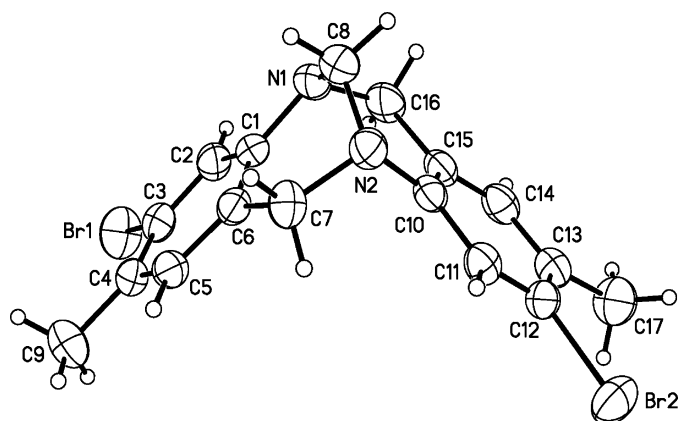


The halide atoms on related Tröger's base systems have been successfully converted into other functionalities (Jensen, Strozyk & Wärnmark, 2002; Jensen, Tejler & Wärnmark, 2002; Kiehne & Lützen, 2004; Hof *et al.*, 2005) and we were interested in employing analogous chemistry on different frameworks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

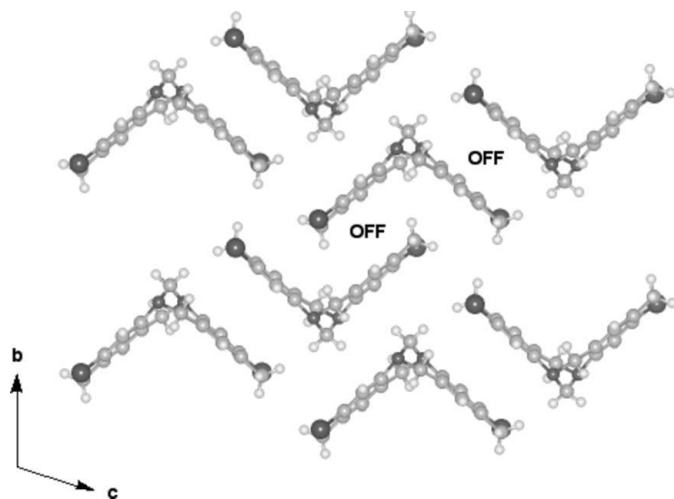
Compound (I) packs in layers in which there are offset face-to-face (OFF) interactions between the aryl surfaces (Fig. 2), but there are no significant  $\pi$ - $\pi$  interactions. This contrasts with the isomeric compound, 1,7-dibromo-2,8-dimethyl Tröger's base, where the interactions are between one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

Received 10 January 2007

Accepted 26 January 2007



**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<sup>i</sup> [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<sub>17</sub>H<sub>16</sub>Br<sub>2</sub>N<sub>2</sub> + H<sup>+</sup> [*M* + H<sup>+</sup>] 406.975300, observed 406.976374. Analysis calculated for C<sub>17</sub>H<sub>16</sub>Br<sub>2</sub>N<sub>2</sub>: 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<sub>17</sub>H<sub>16</sub>Br<sub>2</sub>N<sub>2</sub>  
*M<sub>r</sub>* = 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<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.756 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 $\mu$  = 5.25 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, colourless  
 0.37 × 0.35 × 0.24 mm

## Data collection

Bruker–Nonius Kappa-APEX-II  
 diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1996)  
*T*<sub>min</sub> = 0.226, *T*<sub>max</sub> = 0.366  
 (expected range = 0.175–0.284)

30101 measured reflections  
 4829 independent reflections  
 2809 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.041  
 $\theta$ <sub>max</sub> = 30.9°

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036  
*wR*(*F*<sup>2</sup>) = 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.50 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.50 \text{ e \AA}^{-3}$

H atoms were included in the riding-model approximation, with C–H = 0.95–0.98 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) or 1.5*U*<sub>eq</sub>(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).

The authors thank the Australian Research Council for a Discovery Project grant (No. DP0345180) to ACT and Macquarie University for the award of a Macquarie University Research Development grant to ACT.

## 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.* **E62**, o3893–o3894.  
 Faroughi, M., Turner, P. & Try, A. C. (2007). *Acta Cryst.* **E63**, 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. & Sergeev, S. (2005). *Helv. Chim. Acta*, **88**, 2333–2344.  
 Jensen, J., Strozyk, M. & Wärnmark, K. (2002). *Synthesis*, pp. 2761–2765.

## organic papers

---

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.