

2,4,8,10-Tetrabromo-6H,12H-5,11-methano-dibenzo[*b,f*][1,5]diazocineMasoud Faroughi,^a Andrew C. Try^{a*} and Peter Turner^b^aDepartment of Chemistry and Biomolecular Sciences, Building F7B, Macquarie University, NSW 2109, Australia, and ^bDepartment of Chemistry, The University of Sydney, NSW 2000, Australia

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Key indicators

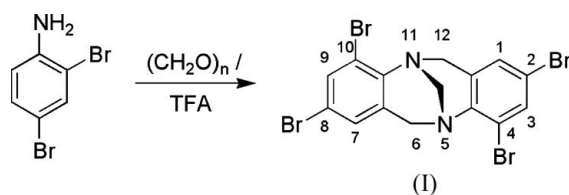
Single-crystal X-ray study
T = 150 K
Mean $\sigma(C-C)$ = 0.005 Å
R factor = 0.024
wR factor = 0.053
Data-to-parameter ratio = 19.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the molecule of the title compound, C₁₅H₁₀Br₄N₂, the 2,4,8,10-tetrabromo 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 of 108.44 (4)° between the two benzene rings is the largest yet measured for a dibenzo system.

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Comment

Tröger's base analogues derived from haloanilines were reported for the first time in 2001 (Jensen & Wärnmark, 2001) and other examples have subsequently been reported (Hansson *et al.*, 2003). The first tetrahalogenated compound (2,4,8,10-tetrafluoro Tröger's base) was recently prepared in 17% yield using the novel reaction conditions of DMSO and hydrogen chloride (Li *et al.*, 2005). The methano-strapped diazocine ring, which bridges the two aromatic rings in all Tröger's base analogues, impacts the twisted molecules such that the two 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 104° (Wilcox *et al.*, 1987) for simple dibenzo Tröger's base analogues. The only reported X-ray crystal structures of halo-aryl functionalized Tröger's bases are the 3,9-dibromo-4,10-dimethyl- and the 2,8-dibromo- analogues, which were found to have dihedral angles of 100.9° (Hansson *et al.*, 2003) and 94.4° (Faroughi *et al.*, 2006), respectively.



We were interested in converting each of the four bromo groups of the title compound, (I), into other functionalities by employing chemistry analogous to that reported on the 2,8-dibromo compound (Jensen, Strozyk & Wärnmark, 2002; Jensen, Tejler & Wärnmark, 2002; Kiehne & Lützen, 2004; Hof *et al.*, 2005).

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 0.740 (3) and 1.357 (4) Å, respectively, and twist conformations $\varphi = 143.12$ (5)°, $\theta = 131.98$ (5)° and $\varphi = 65.34$ (5)°, $\theta = 71.98$ (4)° (Cremer & Pople, 1975). Rings *A* (C1–C6) and *D* (C8–C13) are, of course, planar and the dihedral angle

between them is 108.44 (4)°, *i.e.* the largest yet measured for a dibenzo system.

Experimental

2,4-Dibromoaniline (1.0 g, 3.99 mmol) and paraformaldehyde (0.191 g, 6.38 mmol) were dissolved in trifluoroacetic acid (20 ml) and the mixture was stirred under an argon atmosphere in the dark for 21 d. The reaction mixture was then neutralized with a solution of concentrated ammonia (25 ml) in water (60 ml). The reaction mixture was rendered basic by the addition of a saturated sodium hydrogen carbonate solution (150 ml), and the crude material was extracted into dichloromethane (3 x 40 ml). The combined organic layers were washed with brine (100 ml), dried over anhydrous sodium sulfate, filtered and evaporated to dryness to yield a crude yellow glassy solid. The crude material was chromatographed (silica gel, dichloromethane) to afford the title compound, (I), as a white solid (yield 0.643 g, 60%). Single crystals of (I) were obtained by slow evaporation of a dichloromethane solution.

Crystal data

C ₁₅ H ₁₀ Br ₄ N ₂	Z = 4
M _r = 537.89	D _x = 2.323 Mg m ⁻³
Orthorhombic, <i>Pca</i> 2 ₁	Mo K α radiation
a = 8.040 (3) Å	μ = 10.46 mm ⁻¹
b = 12.475 (4) Å	T = 150 (2) K
c = 15.331 (5) Å	Plate, colorless
V = 1537.7 (9) Å ³	0.48 × 0.30 × 0.06 mm

Data collection

Bruker SMART 1000 CCD diffractometer	13979 measured reflections
ω scans	3662 independent reflections
Absorption correction: Gaussian [(Coppens <i>et al.</i> , 1965) using XPREP (Bruker, 1995)]	3419 reflections with $I > 2\sigma(I)$
T _{min} = 0.042, T _{max} = 0.519	R _{int} = 0.071
	θ_{\max} = 28.3°

Refinement

Refinement on F ²	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
R[F ² > 2 $\sigma(F^2)$] = 0.024	where $P = (F_o^2 + 2F_c^2)/3$
wR(F ²) = 0.053	(Δ/σ) _{max} = 0.002
S = 1.13	$\Delta\rho_{\max}$ = 0.60 e Å ⁻³
3662 reflections	$\Delta\rho_{\min}$ = -0.66 e Å ⁻³
191 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	1686 Friedel pairs
	Flack parameter: 0.004 (10)

H atoms were positioned geometrically, with C–H = 0.95 and 0.99 Å for aromatic and methylene H, 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; 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),

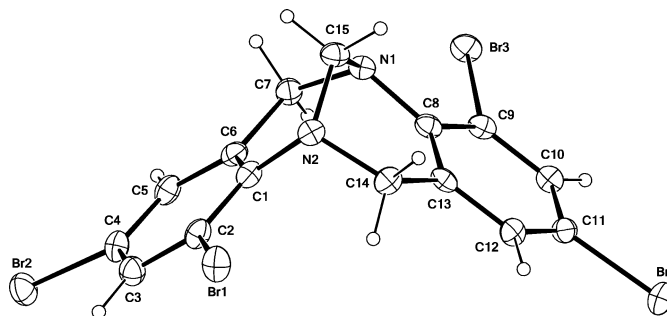


Figure 1

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Xtal3.6 (Hall *et al.*, 1999) ORTEPII (Johnson, 1976); software used to prepare material for publication: WinGX (Farrugia, 1999).

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