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

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In the molecule of the title compound, $C_{19}H_{18}N_2O_4$, the 2,8-dimethyl ester analogue of Tröger's base, the diazocine bridge imparts a twist such that the two aryl rings are offset with respect to one another. The dihedral angle between the two benzene rings is 96.51 (5)°.

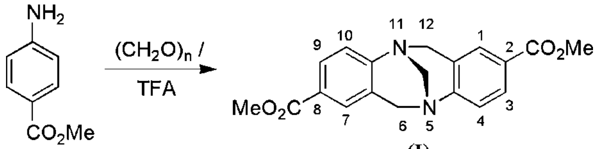
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.092
Data-to-parameter ratio = 16.8

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

Comment

Tröger's base is a chiral cleft-containing molecule (Spielman, 1935). The diazocine bridge imparts a twist within the molecule 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, and is dependent upon the nature of the substituents on the ring. Prior to 2000 it was generally regarded that Tröger's base analogues bearing electron-withdrawing groups were difficult, if not impossible, to prepare. There have only been four reports on the preparation of ester-substituted Tröger's base compounds where the carbonyl group of the ester is directly attached to the benzene ring (Becker *et al.*, 1993; Goswami *et al.*, 2000; Goswami & Ghosh, 1997; Li *et al.*, 2005). Within these four reports, three different reaction conditions were employed. We were interested in preparing a range of diester Tröger's base compounds as precursors for supramolecular recognition elements. The synthesis of (I) in racemic form was achieved by reacting methyl 4-aminobenzoate with paraformaldehyde in trifluoroacetic acid (TFA).



(I)

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

The 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 0.810 (3) and 0.667 (4) Å, respectively, and twist conformations φ = −30.46 (8)°, θ = 92.16 (6)° and φ = −52.47 (9)°, θ = 112.68 (7)° (Cremer & Pople, 1975). Rings *A* (C1–C6) and *D* (C8–C13) are, of course, planar and the dihedral angle between them is *A*/*D* = 96.51 (5)°.

Experimental

Methyl-4-aminobenzoate (4.17 g, 27.6 mmol) and paraformaldehyde (1.32 g, 44.16 mmol) were dissolved in trifluoroacetic acid (75 ml) and the mixture was stirred under an argon atmosphere in the dark for 8 d. The reaction mixture was then neutralized with a solution of concentrated ammonia (80 ml) in water (120 ml). The reaction mixture was rendered basic by the addition of a saturated sodium hydrogen carbonate solution (100 ml) and the crude material was extracted into dichloromethane (3 × 75 ml). The combined organic layers were washed with brine (100 ml), dried over anhydrous sodium sulfate, filtered and evaporated to dryness to yield an orange solid. The crude material was chromatographed (silica gel, ethyl acetate/dichloromethane, 1:4) to afford the title compound, (I), as a white solid (yield 1.08 g, 23%). Single crystals of (I) were produced by slow evaporation of a dichloromethane solution.

Crystal data

$C_{19}H_{18}N_2O_4$
$M_r = 338.35$
Monoclinic, $P2_1/c$
$a = 12.941$ (3) Å
$b = 8.1336$ (19) Å
$c = 15.260$ (4) Å
$\beta = 99.500$ (4)°
$V = 1584.2$ (7) Å^3

$Z = 4$
$D_x = 1.419$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 150$ (2) K
Prism, colourless
0.36 × 0.35 × 0.27 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: none
15205 measured reflections

3826 independent reflections
3286 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\rm max} = 28.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.092$
$S = 1.21$
3826 reflections
228 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.5P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}

Table 1
Selected torsion angles (°).

C15—N1—C1—C6	−14.38 (14)	C1—N1—C15—N2	53.33 (12)
C15—N2—C7—C6	47.55 (11)	C14—N1—C15—N2	−70.37 (11)
C15—N2—C8—C13	−13.09 (14)	C8—N2—C15—N1	51.70 (12)
C15—N1—C14—C13	47.53 (12)	C7—N2—C15—N1	−71.78 (11)

H atoms were positioned geometrically, with C—H = 0.95, 0.99 and 0.98 Å for aromatic, methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = xU_{\rm eq}({\rm C})$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H atoms.

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

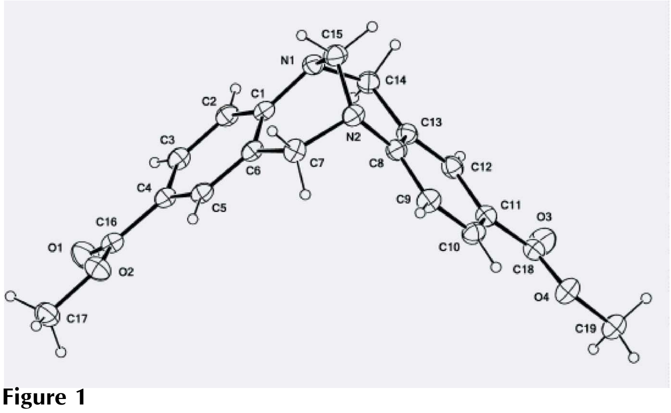


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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