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2,8-Dimethyl-1,9-dinitro-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine

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In the molecule of the title compound, $C_{17}H_{16}N_4O_4$, the 2,8-dimethyl-1,9-dinitro 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 94.75 (4)°.

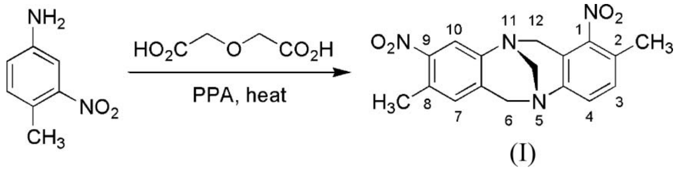
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.036
wR factor = 0.106
Data-to-parameter ratio = 15.0

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

Comment

Inspired by the first preparation of 2,8-dinitro Tröger's base (Mederski *et al.*, 2003), we have embarked on the synthesis of related dinitro Tröger's base systems in which the nitro groups are oriented in different positions on the framework of the molecule. Compound (I) is an example of a non-symmetric system that is formed in racemic form from the reaction of 3-nitro-4-methylaniline with diglycolic acid in polyphosphoric acid (PPA). This compound is one of three theoretically possible isomers, as there are two inequivalent sites *ortho* to the amino group of the aniline.



(I)

The methano-strapped diazocine ring that bridges the two aromatic rings in all Tröger's base analogues imparts a twist to the molecule such that the two aryl rings are offset with respect to one another. Rings *B* (N1/N2/C1/C7–C9) and *C* (N1/N2/C9/C10/C16/C17) have total puckering amplitudes, Q_T, of 1.3893 (6) and 0.6736 (3) Å, respectively, and twist conformations φ = −116.53 (1)° and θ = 109.03 (1)°, and φ = −52.42 (2)° and θ = 112.01 (2)° (Cremer & Pople, 1975). Rings *A* (C1–C4/C6/C7) and *D* (C10–C13/C15/C16) are planar and the dihedral angle between them is 94.75 (4)°. 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.

The bond lengths and angles for (I) are within normal ranges (Allen *et al.*, 1987), except for the length of the C—N bond between ring *A* and the disordered nitro group. That of the minor (0.1 occupied) nitro group position is short at 1.29 (2) Å compared with 1.494 (2) Å for the overlapping (0.9 occupied) nitro position and 1.473 (2) Å for the nitro group attached to ring *D*. This indicates slightly different positions for the molecule depending on the nitro group position at ring *A*. Only one position was modelled for the rest of the molecule due to the close overlap and dominance of the 0.9 component.

The two nitro groups on ring *A*, however, are rotated by 36.7 (5)° with respect to each other about the C—N bond, with the planes of the major and minor positions forming dihedral angles of 67.8 (1)° and 104.5 (4)°, respectively, with that of ring *A*. Analysis of the packing also shows that the 0.1 occupied nitro group is too close to its symmetry-equivalent. Therefore, occupation of this minor position anywhere in the crystal structure excludes occupation of the adjacent minor position.

Experimental

A mixture of diglycolic acid (1.42 g, 10.51 mmol) and polyphosphoric acid (86%, d 1.9, 10.0 g) was heated at 353 K for 2 h under a drying tube. 4-Methyl-3-nitroaniline (1.0 g, 6.57 mmol) was added to this clear solution and the reaction mixture was heated at 353 K for another 12 h. After cooling, water (100 ml) was added and the reaction mixture was neutralized with sodium hydroxide (3 *M*). The mixture was extracted with dichloromethane (3 × 100 ml) and the combined organic layers were washed with brine (100 ml), dried over anhydrous sodium sulfate and evaporated to dryness to yield a brown solid. This crude product was chromatographed (silica gel, dichloromethane) to afford (I) (91 mg, 9%) as a yellow solid. Compound (I) was the second major band eluted from the column. Single crystals of (I) were produced from the slow evaporation of a dichloromethane solution.

Crystal data

$C_{17}H_{16}N_4O_4$
$M_r = 340.34$
Triclinic, $P\overline{1}$
$a = 7.526\ (2)$ Å
$b = 8.057\ (2)$ Å
$c = 13.932\ (3)$ Å
$\alpha = 92.944\ (3)°$
$\beta = 92.930\ (3)°$
$\gamma = 115.649\ (2)°$
$V = 758.0\ (3)$ Å^3
$Z = 2$
$D_x = 1.491$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 0.11$ mm^{-1}
$T = 150\ (2)$ K
Plate, yellow
0.53 × 0.48 × 0.18 mm

Data collection

Bruker SMART CCD-1000 area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.939$, $T_{\max} = 0.981$
10018 measured reflections
3584 independent reflections
3150 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.106$
$S = 1.05$
3584 reflections
239 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.236P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

One of the nitro groups was refined over two positions with 0.9 and 0.1 occupancies. These occupancy factors were chosen to give approximately equal $U_{\rm eq}$ values for the disordered O atoms. The O atoms for the 0.1 component were refined with isotropic displacement parameters. The N atom of the 0.1 component was constrained to have the same diplacement parameters as the N atom of the 0.9 component. The N—O distances of the 0.1 component were restrained to 1.220 (5) Å.

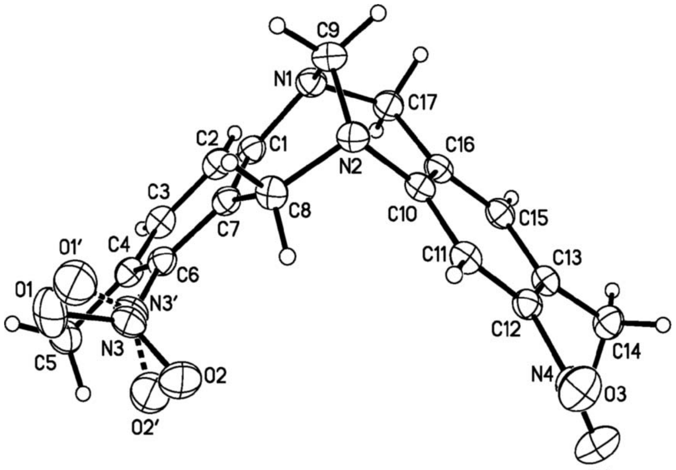


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Both disorder components are shown.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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