

meso-1,2-Bis(methylazo)-1,2-diphenylethaneCraig A. Bayse,^a Barry K. Carpenter^b and Rudy L. Luck^{a*}^aDepartment of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931, USA, and ^bDepartment of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, NY 14853, USA
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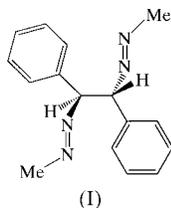
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The title compound, *meso*-1,2-bis(methyldiazenyl)-1,2-diphenylethane, C₁₆H₁₈N₄, is arranged in a disordered manner around an inversion point. The N–N atom distances in the azo group of 1.192 (8) and 1.195 (8) Å, and the C–C atom distances in the ethylene moiety at 1.512 (8) and 1.503 (8) Å in the two models [refined to 51.7 (6) and 48.3 (6)% occupancies] were not significantly different.

Comment

The syntheses of vicinal bis(azo)alkanes can be achieved through the oxidation of hydrazones by various reagents (Winter & Wiecko, 1969; Balachandran *et al.*, 1968; Bhatnagar & George, 1967). Depending upon the substituents on the azo groups, the compound can decompose by breaking the C–N bonds and eliminating nitrogen and alkyl radicals to form an alkene (Engel *et al.*, 1991). If the terminal *R* group is aryl, the central C–C bond is broken to form two α -hydrazonyl radicals (Engel *et al.*, 1993).

So far, there are only six structural reports on vicinal bis(azo) compounds (Allen *et al.*, 1983). Our interest in these compounds stems from the possibility of low-temperature production of methyl radicals through simultaneous or near-simultaneous loss of nitrogen. Here, we report the crystal structure of a vicinal bis(azo)alkane, namely *meso*-1,2-bis(methylazo)-1,2-diphenylethane, (I).



There is disorder in the arrangement of the entire molecule. As a result, the N–N distances [1.192 (8) and 1.195 (8) Å] are slightly shorter than expected (*ca* 1.22 Å), compared with other methylazo compounds (van Remoortere & Boer, 1971; Ferguson *et al.*, 1991). The two central C–C bond distances are comparable, but shorter [1.512 (8) and 1.503 (8) Å *versus*

1.532–1.555 Å] than two known bis(azo)alkanes (Kavounis & Rentzeperis, 1983, 1984). The C–N distances involving the central ethylene bridge [1.487 (8) and 1.477 (8) Å] are also not

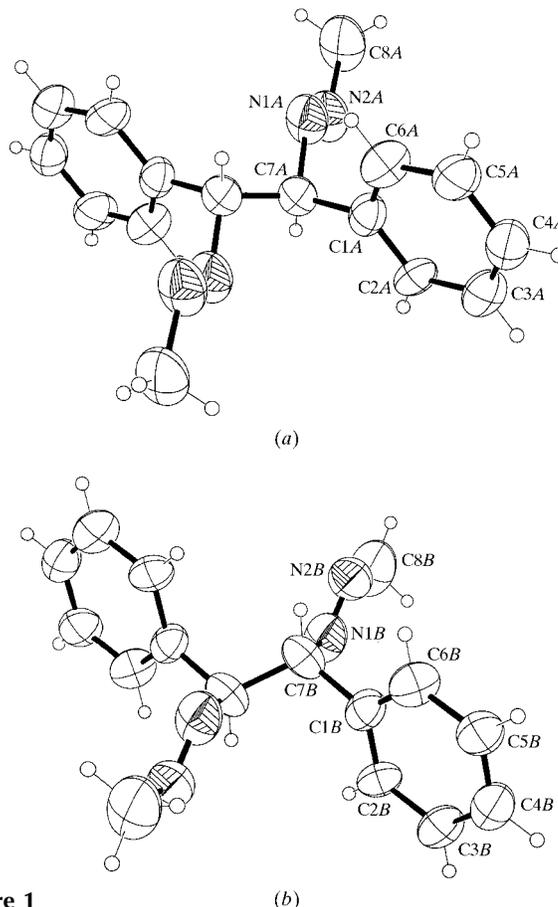


Figure 1
ORTEP-3 (Farrugia, 1997) views of (a) disorder model A and (b) disorder model B of (I), shown with 50% probability displacement ellipsoids.

significantly different and are comparable to those in the above bis(azo)alkanes (1.465–1.520 Å; Kavounis & Rentzeperis, 1983, 1984). The methylazo C–N bond distances [1.494 (6) and 1.489 (6) Å] are also comparable to previous crystal structures (van Remoortere & Boer, 1971; Ferguson *et al.*, 1991).

Experimental

The title compound was synthesized by the oxidation of benzaldehyde methylhydrazone with MnO₂, as detailed in a separate publication (Bayse *et al.*, 2001). The product was obtained as crystals from the reaction mixture. Crystals suitable for X-ray diffraction were obtained by recrystallization from chloroform.

Crystal data

C₁₆H₁₈N₄
M_r = 266.35
Monoclinic, P2₁/n
a = 5.525 (2) Å
b = 17.444 (3) Å
c = 8.194 (2) Å
β = 107.10 (2)°
V = 754.8 (4) Å³
Z = 2

D_x = 1.172 Mg m⁻³
Mo Kα radiation
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.07 mm⁻¹
T = 293 (2) K
Prism, white
0.40 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer	$R_{\text{int}} = 0.016$
Non-profiled $\omega/2\theta$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 6$
$T_{\text{min}} = 0.970$, $T_{\text{max}} = 0.992$	$k = 0 \rightarrow 20$
1465 measured reflections	$l = -9 \rightarrow 9$
1324 independent reflections	3 standard reflections
687 reflections with $I > 2\sigma(I)$	frequency: 166 min
	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.1301P]$
$R(F) = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.170$	$(\Delta/\sigma)_{\text{max}} = 0.012$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.18 \text{ e } \text{\AA}^{-3}$
1324 reflections	$\Delta\rho_{\text{min}} = -0.13 \text{ e } \text{\AA}^{-3}$
107 parameters	
H-atom parameters constrained	

In the original structure solution, the disorder in the positions of the C atoms in the ethylene moiety was apparent. This model was refined with first isotropic and then anisotropic displacement parameters to convergence. The positions and isotropic displacement parameters of the H atoms were constrained and set to 1.5 times (1.2 for aryl H atoms) the isotropic equivalent of the attached atoms. At this stage, due to some unusual bond distances and angles, a new model was constructed which required restraints (24 in total, C–C = 1.39 Å) to prevent correlation from hindering the refinement. This resulted in different orientations in the phenyl rings, for the N atoms of the azo groups and for the C atoms of the ethylene moiety. Only the C atom in the methyl group was unique, but this was refined with two sets of H atoms to fit the two independent models better.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia,

1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1209). Services for accessing these data are described at the back of the journal.

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