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Meso-1, 2-Bis (Methylazo)-1, 2-Diphenylethane

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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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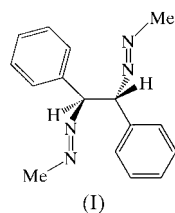
Accepted 29 September 2001

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

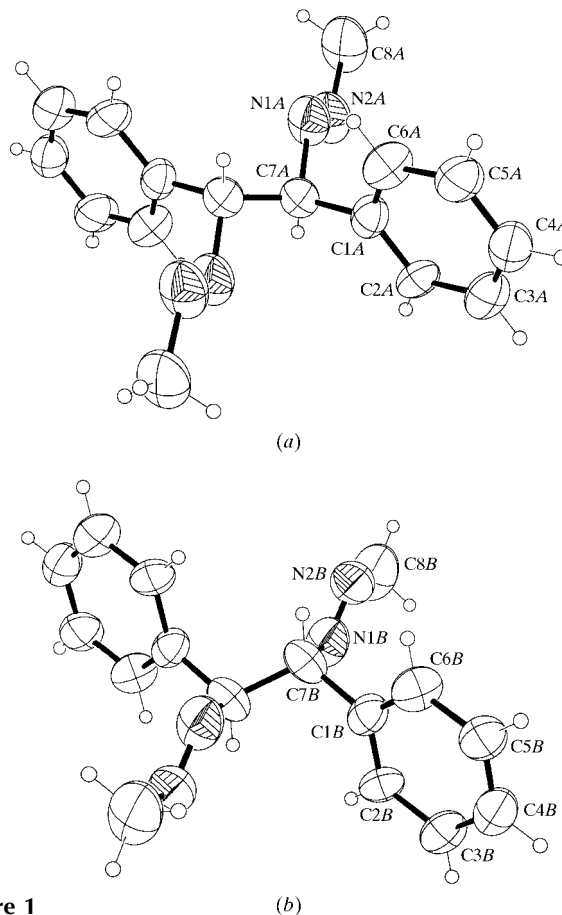


Figure 1
ORTEP-3 (Farrugia, 1997) views of (a) disorder model A and (b) disorder model B of (I), shown with 50% probability displacement ellipsoids.

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 $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.170$	$(\Delta/\sigma)_{\text{max}} = 0.012$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.18 \text{ e } \text{Å}^{-3}$
1324 reflections	$\Delta\rho_{\text{min}} = -0.13 \text{ e } \text{Å}^{-3}$
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).

This work was supported by the Eastman Kodak Company and RLL thanks Michigan Technological University for support. The suggestion by a referee regarding a more appropriate model to account for the disorder is noted.

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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supporting information

Acta Cryst. (2001). C57, 1429-1430 [doi:10.1107/S0108270101015918]

meso-1,2-Bis(methylazo)-1,2-diphenylethane

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Computing details

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).

(I)*Crystal data*

$C_{16}H_{18}N_4$

$M_r = 266.35$

Monoclinic, $P2_1/n$

$a = 5.525$ (2) Å

$b = 17.444$ (3) Å

$c = 8.194$ (2) Å

$\beta = 107.10$ (2)°

$V = 754.8$ (4) Å³

$Z = 2$

$F(000) = 256$

$D_x = 1.172$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å

Cell parameters from 25 reflections

$\theta = 10\text{--}15^\circ$

$\mu = 0.07$ mm⁻¹

$T = 293$ K

Prism, white

$0.40 \times 0.20 \times 0.10$ mm

Data collection

Enraf-Nonius Turbo-CAD4
diffractometer

non-profiled $\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.970$, $T_{\max} = 0.992$

1465 measured reflections

1324 independent reflections

687 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.3^\circ$

$h = 0 \rightarrow 6$

$k = 0 \rightarrow 20$

$l = -9 \rightarrow 9$

3 standard reflections every 166 min

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.170$

$S = 1.01$

1324 reflections

107 parameters

24 restraints

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.1301P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.012$

$\Delta\rho_{\max} = 0.18$ e Å⁻³

$\Delta\rho_{\min} = -0.13$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1A	0.7237 (17)	0.0451 (13)	0.3475 (13)	0.072 (2)	0.517 (6)
N2A	0.6975 (10)	0.0722 (3)	0.2098 (6)	0.079 (2)	0.517 (6)
C1A	1.030 (3)	0.1049 (8)	0.5936 (18)	0.0546 (18)	0.517 (6)
C2A	1.217 (3)	0.1600 (8)	0.6111 (16)	0.0590 (17)	0.517 (6)
H2A	1.3274	0.1573	0.5444	0.071*	0.517 (6)
C3A	1.240 (3)	0.2193 (7)	0.7281 (14)	0.058 (2)	0.517 (6)
H3A	1.3659	0.2562	0.7398	0.069*	0.517 (6)
C4A	1.076 (3)	0.2233 (8)	0.8277 (17)	0.060 (2)	0.517 (6)
H4A	1.0915	0.263	0.906	0.073*	0.517 (6)
C5A	0.889 (3)	0.1682 (9)	0.8102 (18)	0.064 (2)	0.517 (6)
H5A	0.7786	0.1709	0.8769	0.076*	0.517 (6)
C6A	0.866 (3)	0.1089 (9)	0.6932 (17)	0.0603 (18)	0.517 (6)
H6A	0.7401	0.072	0.6815	0.072*	0.517 (6)
C7A	0.9889 (13)	0.0394 (3)	0.4601 (9)	0.058 (2)	0.517 (6)
H7A	1.1079	0.0446	0.3926	0.069*	0.517 (6)
C8A	0.4260 (6)	0.08370 (19)	0.1109 (4)	0.1016 (12)	0.517 (6)
H8A1	0.4158	0.1045	0.0006	0.152*	0.517 (6)
H8A2	0.3487	0.1186	0.1712	0.152*	0.517 (6)
H8A3	0.339	0.0354	0.0972	0.152*	0.517 (6)
N1B	0.7669 (16)	0.0530 (14)	0.3206 (14)	0.072 (2)	0.483 (6)
N2B	0.5411 (10)	0.0517 (3)	0.2850 (6)	0.0692 (19)	0.483 (6)
C1B	0.984 (3)	0.0975 (9)	0.612 (2)	0.0546 (18)	0.483 (6)
C2B	1.165 (3)	0.1460 (9)	0.5813 (17)	0.0590 (17)	0.483 (6)
H2B	1.2396	0.134	0.4963	0.071*	0.483 (6)
C3B	1.236 (3)	0.2123 (8)	0.6774 (16)	0.058 (2)	0.483 (6)
H3B	1.357	0.2448	0.6568	0.069*	0.483 (6)
C4B	1.124 (3)	0.2303 (8)	0.8043 (19)	0.060 (2)	0.483 (6)
H4B	1.1715	0.2747	0.8686	0.073*	0.483 (6)
C5B	0.943 (3)	0.1818 (9)	0.8351 (18)	0.064 (2)	0.483 (6)
H5B	0.8686	0.1938	0.92	0.076*	0.483 (6)
C6B	0.873 (3)	0.1154 (9)	0.7390 (19)	0.0603 (18)	0.483 (6)
H6B	0.7512	0.083	0.7596	0.072*	0.483 (6)
C7B	0.8922 (13)	0.0268 (5)	0.4967 (9)	0.063 (2)	0.483 (6)
H7B	0.7673	-0.0006	0.5383	0.076*	0.483 (6)
C8B	0.4260 (6)	0.08370 (19)	0.1109 (4)	0.1016 (12)	0.483 (6)
H8B1	0.2448	0.0812	0.0829	0.152*	0.483 (6)
H8B2	0.4813	0.0544	0.0293	0.152*	0.483 (6)
H8B3	0.4776	0.1361	0.1081	0.152*	0.483 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1A	0.082 (3)	0.062 (4)	0.057 (3)	0.009 (3)	-0.003 (3)	0.010 (3)
N2A	0.094 (4)	0.071 (3)	0.060 (4)	0.014 (3)	0.006 (3)	0.009 (3)
C1A	0.060 (5)	0.043 (3)	0.056 (3)	-0.001 (2)	0.010 (2)	0.004 (3)
C2A	0.052 (6)	0.062 (5)	0.055 (4)	-0.011 (3)	0.002 (4)	-0.015 (3)
C3A	0.071 (2)	0.062 (3)	0.035 (7)	-0.009 (2)	0.008 (4)	-0.009 (3)
C4A	0.066 (6)	0.051 (3)	0.061 (4)	-0.002 (2)	0.014 (3)	-0.002 (3)
C5A	0.055 (6)	0.066 (5)	0.064 (4)	-0.009 (3)	0.009 (5)	-0.018 (3)
C6A	0.0676 (19)	0.067 (3)	0.043 (7)	-0.0130 (19)	0.012 (4)	-0.008 (3)
C7A	0.055 (4)	0.053 (4)	0.066 (4)	0.003 (3)	0.022 (3)	-0.002 (3)
C8A	0.107 (3)	0.082 (2)	0.079 (2)	0.0164 (19)	-0.0293 (19)	0.0047 (18)
N1B	0.082 (3)	0.062 (4)	0.057 (3)	0.009 (3)	-0.003 (3)	0.010 (3)
N2B	0.060 (4)	0.070 (3)	0.068 (4)	0.004 (3)	0.004 (3)	0.005 (3)
C1B	0.060 (5)	0.043 (3)	0.056 (3)	-0.001 (2)	0.010 (2)	0.004 (3)
C2B	0.052 (6)	0.062 (5)	0.055 (4)	-0.011 (3)	0.002 (4)	-0.015 (3)
C3B	0.071 (2)	0.062 (3)	0.035 (7)	-0.009 (2)	0.008 (4)	-0.009 (3)
C4B	0.066 (6)	0.051 (3)	0.061 (4)	-0.002 (2)	0.014 (3)	-0.002 (3)
C5B	0.055 (6)	0.066 (5)	0.064 (4)	-0.009 (3)	0.009 (5)	-0.018 (3)
C6B	0.0676 (19)	0.067 (3)	0.043 (7)	-0.0130 (19)	0.012 (4)	-0.008 (3)
C7B	0.049 (4)	0.076 (5)	0.061 (5)	0.016 (4)	0.010 (4)	0.006 (3)
C8B	0.107 (3)	0.082 (2)	0.079 (2)	0.0164 (19)	-0.0293 (19)	0.0047 (18)

Geometric parameters (\AA , $^\circ$)

N1A—N2A	1.192 (8)	N1B—N2B	1.195 (8)
N1A—C7A	1.487 (8)	N1B—C7B	1.477 (8)
N2A—C8A	1.494 (6)	N2B—C8B	1.489 (6)
C1A—C2A	1.39	C1B—C2B	1.39
C1A—C6A	1.39	C1B—C6B	1.39
C1A—C7A	1.551 (5)	C1B—C7B	1.545 (6)
C2A—C3A	1.39	C2B—C3B	1.39
C3A—C4A	1.39	C3B—C4B	1.39
C4A—C5A	1.39	C4B—C5B	1.39
C5A—C6A	1.39	C5B—C6B	1.39
C7A—C7A ⁱ	1.512 (8)	C7B—C7B ⁱ	1.503 (8)
N2A—N1A—C7A	115.9 (9)	N2B—N1B—C7B	112.9 (9)
N1A—N2A—C8A	113.0 (7)	N1B—N2B—C8B	110.4 (7)
C2A—C1A—C6A	120	C2B—C1B—C6B	120
C2A—C1A—C7A	122.2 (5)	C2B—C1B—C7B	119.9 (6)
C6A—C1A—C7A	117.8 (5)	C6B—C1B—C7B	120.0 (6)
C1A—C2A—C3A	120	C1B—C2B—C3B	120
C2A—C3A—C4A	120	C2B—C3B—C4B	120
C5A—C4A—C3A	120	C5B—C4B—C3B	120
C4A—C5A—C6A	120	C6B—C5B—C4B	120
C5A—C6A—C1A	120	C5B—C6B—C1B	120

N1A—C7A—C7A ⁱ	105.6 (9)	N1B—C7B—C7B ⁱ	111.5 (10)
N1A—C7A—C1A	107.5 (7)	N1B—C7B—C1B	109.0 (8)
C7A ⁱ —C7A—C1A	112.8 (11)	C7B ⁱ —C7B—C1B	111.2 (12)

Symmetry code: (i) $-x+2, -y, -z+1$.