

4,5-Dimethyl-9,10-diazaphenanthrene *N,N'*-Dioxide

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Abstract. $C_{14}H_{12}N_2O_2$, $M_r = 240.26$, monoclinic, $P2_1/c$, $a = 8.420$ (2), $b = 15.632$ (4), $c = 9.213$ (4) Å, $\beta = 112.05$ (3)°, $Z = 4$, $D_x = 1.44$, $D_m = 1.42$ Mg m^{-3} . $R = 0.032$ for 1571 observed reflexions. The molecule exists as 4,5-dimethyl-9,10-diazaphenanthrene *N,N'*-dioxide (not as 2,2'-dimethyl-6,6'-dinitrosobiphenyl) with an N–N bond length of 1.339 (2) Å. There is distortion in the central portion of the molecule to relieve the steric repulsion between the 4,5-dimethyl groups.

Introduction. This paper forms part of a projected study of the nitroso dimerization pathway. The title compound was prepared from the corresponding dinitrobiphenyl by reduction with Zn dust followed by *in situ* oxidation of the resulting dihydroxylamine with ferric chloride (Hall & Dolan, 1978). Crystals (m.p. 412–413 K) were obtained by slow evaporation of a solution in chloroform.

Intensities from a crystal, approximately 0.3 mm in edge, were collected on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator [Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 0.110$ mm^{-1} ; 2456 reflexions, 1571 with $I > 3\sigma(I)$]. The structure (Fig. 1) was solved by direct methods and refined by full-matrix least-squares analysis, using *SHELX* (Sheldrick, 1976) and *XRAY 72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). H atoms were located at an intermediate stage and refined with isotropic temperature factors. Non-hydrogen atoms were refined with anisotropic temperature factors; final cycles with modified weights (Dunitz & Seiler, 1973;

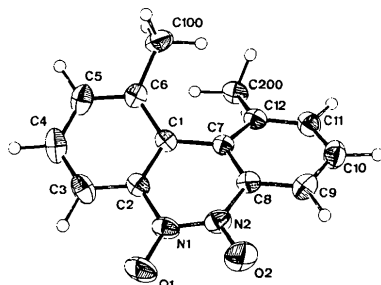


Fig. 1. View of the molecule showing atomic numbering and vibrational ellipsoids (50% probability level).

$r = 4.0$ Å²) and including an extinction correction; final $R = 0.032$, $R_w = 0.036$. Positional and equivalent isotropic vibrational parameters ($\frac{1}{3}TrU$) are given in Table 1, bond lengths, bond angles and torsion angles in Table 2;* C–H distances and H–C–H angles lie in the ranges 0.92–1.03 Å and 105.3–109.6° respectively.

* Lists of structure factors and anisotropic vibrational parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36727 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic parameters ($\times 10^4$) with *e.s.d.*'s in parentheses

For the heavy atoms U is $\frac{1}{3}TrU$ after transformation of U_{ij} components to Cartesian axes.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
C(1)	2686 (2)	1576 (1)	1167 (2)	292 (4)
C(2)	3902 (2)	1042 (1)	2199 (2)	336 (5)
C(3)	5083 (2)	1312 (1)	3695 (2)	450 (6)
C(4)	5133 (2)	2158 (1)	4132 (2)	464 (6)
C(5)	4086 (2)	2727 (1)	3032 (2)	401 (5)
C(6)	2881 (2)	2467 (1)	1549 (2)	323 (5)
C(7)	1413 (2)	1169 (1)	–234 (2)	301 (4)
C(8)	1755 (2)	384 (1)	–846 (2)	346 (5)
C(9)	717 (2)	–23 (1)	–2295 (2)	474 (6)
C(10)	–745 (2)	319 (1)	–3083 (2)	537 (6)
C(11)	–1195 (2)	1020 (1)	–2373 (2)	485 (6)
C(12)	–161 (2)	1447 (1)	–949 (2)	365 (5)
C(100)	1971 (2)	3160 (1)	343 (2)	416 (5)
C(200)	–853 (2)	2103 (1)	–123 (3)	487 (6)
N(1)	4020 (2)	185 (1)	1691 (2)	394 (4)
N(2)	3154 (2)	–60 (1)	91 (2)	385 (4)
O(1)	5064 (2)	–311 (1)	2615 (2)	592 (5)
O(2)	3483 (2)	–770 (1)	–414 (2)	569 (5)
H(3)	5831 (22)	923 (11)	4323 (23)	567 (53)
H(4)	5961 (21)	2347 (12)	5202 (23)	655 (57)
H(5)	4228 (19)	3343 (10)	3251 (21)	457 (47)
H(9)	1139 (22)	–560 (11)	–2613 (25)	604 (55)
H(10)	–1499 (21)	47 (11)	–4017 (25)	588 (55)
H(11)	–2296 (20)	1216 (10)	–2834 (23)	505 (49)
H(1001)	1372 (18)	2949 (10)	–859 (21)	392 (44)
H(1002)	–112 (23)	2241 (12)	1085 (24)	622 (56)
H(1003)	1215 (21)	3471 (11)	735 (23)	566 (53)
H(2001)	2716 (22)	3579 (10)	328 (24)	554 (52)
H(2002)	–1867 (24)	1850 (13)	–69 (27)	806 (66)
H(2003)	–1135 (24)	2641 (14)	–813 (28)	820 (66)

Table 2. Selected bond distances (Å), bond angles (°), and torsion angles (°)

E.s.d.'s lie in the ranges 0.002–0.003 Å and 0.1–0.2°.

C(1)–C(7)	1.461		
C(1)–C(2)	1.405	C(7)–C(8)	1.411
C(2)–C(3)	1.386	C(8)–C(9)	1.391
C(3)–C(4)	1.369	C(9)–C(10)	1.369
C(4)–C(5)	1.382	C(10)–C(11)	1.385
C(5)–C(6)	1.385	C(11)–C(12)	1.390
C(6)–C(1)	1.426	C(7)–C(12)	1.415
C(6)–C(100)	1.507	C(12)–C(200)	1.509
C(2)–N(1)	1.422	C(8)–N(2)	1.417
N(1)–O(1)	1.254	N(2)–O(2)	1.265
N(1)–N(2)	1.339		
C(7)–C(1)–C(6)	127.1	C(1)–C(7)–C(12)	126.4
C(1)–C(6)–C(100)	124.0	C(7)–C(12)–C(200)	123.8
C(1)–C(6)–C(5)	118.8	C(7)–C(12)–C(11)	118.8
C(5)–C(6)–C(100)	116.8	C(11)–C(12)–C(200)	116.9
C(6)–C(5)–C(4)	122.5	C(12)–C(11)–C(10)	122.2
C(5)–C(4)–C(3)	119.8	C(11)–C(10)–C(9)	120.1
C(4)–C(3)–C(2)	118.3	C(10)–C(9)–C(8)	118.2
C(3)–C(2)–C(1)	123.6	C(9)–C(8)–C(7)	123.0
C(2)–C(1)–C(6)	115.9	C(8)–C(7)–C(12)	116.5
C(1)–C(2)–N(1)	120.4	C(7)–C(8)–N(2)	120.3
C(2)–N(1)–C(2)	119.3	C(8)–N(2)–N(1)	119.6
N(2)–N(1)–O(1)	118.3	N(1)–N(2)–O(2)	117.6
C(2)–N(1)–O(1)	121.7	C(8)–N(2)–O(2)	121.7
C(2)–C(1)–C(7)	116.9	C(8)–C(7)–C(1)	116.9
C(100)–C(6)–C(1)–C(7)	–13.4	C(1)–C(7)–C(12)–C(200)	–13.7
C(6)–C(1)–C(7)–C(12)	–32.7		
C(2)–C(1)–C(7)–C(8)	–23.3		
C(2)–N(1)–N(2)–C(8)	–23.9		
O(1)–N(1)–N(2)–O(2)	–2.7		
C(7)–C(1)–C(2)–N(1)	11.5	C(1)–C(7)–C(8)–N(2)	12.6
C(1)–C(2)–N(1)–N(2)	12.3	C(7)–C(8)–N(2)–N(1)	11.2

Discussion. The molecule has an approximate, non-crystallographic twofold rotation axis. It is distorted

from planarity to relieve the steric repulsion between the methyl groups [C(100)···C(200), 3.03 Å]. The major distortions are in the torsion angles involving C–CH₃ bonds and in those involving the C atoms of the diazine ring, the atoms C(100)–C(6)–C(1)–C(7)–C(12)–C(200) forming a pronounced spiral. The diazine ring has a nearly perfect twist conformation. In spite of these distortions, the bond lengths and angles in the dinitroso moiety do not differ much from those observed in unstrained dinitroso groupings (Prout, Stothard & Watkin, 1978). The N–N bond distance of 1.339 (2) Å is slightly longer than usual (1.29–1.32 Å). There are no unusually short intermolecular contacts.

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4,5-Dichloro-9,10-diazaphenanthrene *N,N'*-Dioxide

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Abstract. C₁₂H₆Cl₂N₂O₂, *M_r* = 281.10, triclinic, *P*1̄, *a* = 7.419 (2), *b* = 9.652 (2), *c* = 16.662 (4) Å, α = 90.34 (2), β = 96.50 (2), γ = 106.04 (2)°, *Z* = 4, *D_m* = 1.62, *D_x* = 1.64 Mg m^{–3}. *R* = 0.032 for 3123 observed reflexions. The molecule exists as 4,5-dichloro-9,10-diazaphenanthrene *N,N'*-dioxide (not as 2,2'-dichloro-6,6'-dinitrosobiphenyl). The two independent molecules in the asymmetric unit have nearly identical structural parameters, which are similar to those of

4,5-dimethyl-9,10-diazaphenanthrene *N,N'*-dioxide [Whittleton & Dunitz (1982). *Acta Cryst.* **B38**, 2054–2055].

Introduction. This work forms part of a projected study of the nitroso dimerization pathway. The title compound (Fig. 1) was prepared by the method described in Whittleton & Dunitz (1982) (WD). Intensity collection [4009 reflexions, 3123 with *I* > 3σ(*I*)],