

and the average C—N(1)—C angle, 117.3 (2)°, is larger than the average C—N(2)—C angle, 112.6 (2)°. Although participation of the N(1) lone pair in the aromatic  $\pi$  system would stabilize the N atom, the long S—C bonds force the ring to exist in a boat conformation. This phenomenon has been observed in many neuroleptic drug molecules (Martin, Svensson, Bates & Ortega, 1985).

The angle between the benzo ring planes is 139.1° which compares favorably to the fold angle in other structurally similar compounds [e.g. promethazine, 141° (Marsau & Busetta, 1973); thiazinamium methyl sulfate, 136° (Marsau & Cam, 1973); diethazine, 138° (Marsau, 1971); and isothiazine, 138° (Marsau & Calas, 1971)] although wider fold angles are not uncommon [*N*-phenylphenothiazine, 162.6° and 150.7° (Klein *et al.*, 1985); 1-ethylphenothiazine, 154.8° (Chu, Napoleone, Ternay & Chang, 1982); methoxypromazine, 157.7° (Marsau & Gauthier, 1973); *etc.*].

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## Structure of *N,N*-Dimethyl-2,4-dinitro-3-toluidine\*

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**Abstract.** C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub>, *M<sub>r</sub>* = 225.20, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.645 (2), *b* = 10.147 (3), *c* = 14.416 (5) Å,  $\beta$  = 112.15 (2)°, *V* = 1035.70 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.434 (5), *D<sub>x</sub>* = 1.444 (10) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.7107 Å,  $\mu$  = 1.25 cm<sup>-1</sup>, *F*(000) = 472, *T* = 297 ± 1 K, final *R* = 0.0408 for 1365 observed intensities. Twist angles for NO<sub>2</sub> groups are 18.6 (3) and 66.0 (3)°. Non-additivity of angles was studied using the models of Domenicano & Murray-Rust [*Tetrahedron Lett.* (1979), **24**, 2283–2286] and Norrestam & Schepper [*Acta Chem. Scand. Ser. A* (1981), **35**, 91–103] models. Bond-length

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variation was analyzed using the HOSE model [Krygowski, Anulewicz & Kruszewski (1983). *Acta Cryst.* **B39**, 732–739].

**Experimental.** Compound obtained by methylation of *m*-toluidine with dimethylsulfate and further nitration with dilute nitric acid. Purified by column chromatography and recrystallization. Crystals were grown from benzene solution. *D<sub>m</sub>* measured at 293 K by flotation in an aqueous solution of KI. Monoclinic symmetry from oscillation and Weissenberg photographs. Systematic absences *h*0*l*, *l* odd, 0*k*0, *k* odd; space group *P*2<sub>1</sub>/*c*. Crystal, *ca* 0.5 × 0.4 × 0.4 mm, mounted on Syntex *P*2<sub>1</sub> single-crystal diffractometer. Cell constants determined by least-squares

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treatment of 15 reflections,  $20 < 2\theta < 25^\circ$ . Intensities collected at  $297 \pm 1$  K using Mo  $K\alpha$  radiation monochromated by graphite up to  $50.0^\circ$  ( $-8 \leq h \leq 8$ ,  $0 \leq k \leq 12$ ,  $0 \leq l \leq 17$ ). Profile analysis according to Lehmann & Larsen (1974), no significant variation for two standard reflections. 1717 unique reflections collected, 47 of them systematically absent. 1365 classified as observed [ $|F| \geq 3\sigma(F)$ ]. Correction for Lorentz-polarization effects, but not for extinction or absorption. Structure solved by routine application of *SHELX76* (Sheldrick, 1976). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *E* map gave positions of nine non-hydrogen atoms. Other seven atoms located from  $\Delta\rho$  map. Structure factors calculated for nine atoms taken from *E* maps gave  $R$  of 0.44. After refinement of the partial structure and location of all non-hydrogen atoms  $R$  decreased to 0.23, reduced by isotropic least-squares refinement to 0.14, and by anisotropic to 0.0896. H atoms located from  $\Delta\rho$  map. Final refinement of all the atomic parameters including positional parameters and isotropic thermal parameters for H atoms was carried out by full-matrix least squares and led to  $R = 0.0485$  with unit weights. The use of weights based on  $\sigma(F)$  gave  $R = 0.0408$  and  $wR = 0.0440$  where  $w_i = 1.72/[\sigma^2(F_i) + 0.00088F_i^2]$ . Number of observations per refined parameters:  $1365/189 = 7.22$  ( $\Delta/\sigma$ )<sub>max</sub> in final cycle of refinement = 0.030, average = 0.007. peaks in final difference Fourier map  $-0.17$  to  $0.16$  e  $\text{\AA}^{-3}$ .

**Discussion.** As a continuation of our studies on derivatives of *p*-nitroaniline (Maurin & Krygowski, 1986) the title compound has been chosen to investigate the role of overcrowding of substituents on the geometry of the benzene ring. The final atomic parameters are given in Table 1,\* and Table 2 contains bond lengths and angles. Fig. 1 indicates the atomic numbering. The deviations of the ring geometry from *6/mmm* are highly significant and involve bond lengths and angles. In order to study the substituent effect on valence angles in the ring the angular parameters of Domenicano & Murray-Rust (1979) and Norrestam & Schepper (1981) have been used. If Domenicano & Murray-Rust or Norrestam & Schepper parameters are applied the non-additivity of the observed geometry is very large: the sum of  $|\varphi_{\text{cal}} - \varphi_{\text{obs}}|_i = \sum_i |\Delta|$  over all angles within the ring is  $9.2$  and  $6.6^\circ$  respectively. In the molecule of the title compound the nitro groups are not coplanar with the ring; they are twisted by  $66.0$  (3) and  $18.6$  (3) $^\circ$ . This may explain the higher non-additivity predicted by the Domenicano & Murray-Rust model in

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43158 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^4$ ),  $U_{\text{eq}}$  ( $\times 10^4$ ) for non-hydrogen atoms

$$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}.$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
C(1)	7705 (1)	8078 (2)	927 (1)	364 (10)
C(2)	7471 (2)	9031 (2)	1581 (1)	373 (10)
C(3)	7296 (2)	10385 (2)	1409 (1)	384 (10)
C(4)	7353 (2)	10792 (2)	495 (1)	384 (11)
C(5)	7639 (3)	9900 (2)	-162 (2)	453 (12)
C(6)	7815 (3)	8594 (2)	42 (2)	457 (12)
N(1)	7812 (2)	6756 (2)	1094 (1)	432 (9)
N(2)	7092 (2)	12162 (2)	179 (1)	478 (10)
O(1)	7585 (3)	12492 (2)	-500 (1)	764 (12)
O(2)	6343 (2)	12924 (2)	577 (1)	644 (11)
C(7)	8324 (4)	5894 (2)	428 (2)	564 (15)
C(8)	6954 (5)	6076 (3)	1702 (2)	622 (16)
C(9)	7193 (4)	11317 (3)	2198 (2)	557 (15)
N(3)	7549 (3)	8610 (2)	2570 (1)	479 (11)
O(3)	9033 (2)	8158 (2)	3153 (1)	630 (11)
O(4)	6136 (3)	8731 (2)	2766 (1)	800 (12)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) involving heavy atoms; bond lengths corrected for libration are given in brackets

The second angle value for endocyclic angles is calculated using Domenicano & Murray-Rust (1979) parameters with angle values for the twisted nitro group taken from Norrestam & Schepper (1981).

C(1)–C(2)	1.409 (3)	[1.415]	C(6)–C(1)–C(2)	114.6 (2)	115.33
C(2)–C(3)	1.394 (3)	[1.398]	C(6)–C(1)–N(1)	120.5 (2)	
C(3)–C(4)	1.397 (3)	[1.404]	C(2)–C(1)–N(1)	124.9 (2)	
C(4)–C(5)	1.386 (3)	[1.392]	C(1)–C(2)–C(3)	125.9 (2)	126.49
C(5)–C(6)	1.353 (3)	[1.358]	C(1)–C(2)–N(3)	118.8 (2)	
C(6)–C(1)	1.411 (3)	[1.418]	C(3)–C(2)–N(3)	115.2 (2)	
C(3)–C(9)	1.503 (3)	[1.511]	C(2)–C(3)–C(4)	115.1 (2)	114.53
C(1)–N(1)	1.360 (2)	[1.364]	C(2)–C(3)–C(9)	121.0 (2)	
C(2)–N(3)	1.467 (2)	[1.475]	C(4)–C(3)–C(9)	123.8 (2)	
C(4)–N(2)	1.453 (3)	[1.458]	C(3)–C(4)–C(5)	121.4 (2)	122.18
N(1)–C(7)	1.458 (3)	[1.464]	C(3)–C(4)–N(2)	121.9 (2)	
N(1)–C(8)	1.452 (3)	[1.459]	C(5)–C(4)–N(2)	116.7 (2)	
N(2)–O(1)	1.221 (2)	[1.227]	C(4)–C(5)–C(6)	121.3 (2)	121.50
N(2)–O(2)	1.225 (2)	[1.232]	C(5)–C(6)–C(1)	121.7 (2)	119.18
N(3)–O(3)	1.218 (2)	[1.225]	C(1)–N(1)–C(7)	119.2 (2)	
N(3)–O(4)	1.222 (2)	[1.228]	C(1)–N(1)–C(8)	124.4 (2)	
			C(7)–N(1)–C(8)	114.0 (2)	
			C(2)–N(3)–O(3)	117.8 (2)	
			C(2)–N(3)–O(4)	118.7 (2)	
			O(3)–N(3)–O(4)	123.5 (2)	
			C(4)–N(2)–O(1)	117.8 (2)	
			C(4)–N(2)–O(2)	119.4 (2)	
			O(1)–N(2)–O(2)	122.8 (2)	

C–H bond lengths within the range 0.900 to 1.024  $\text{\AA}$

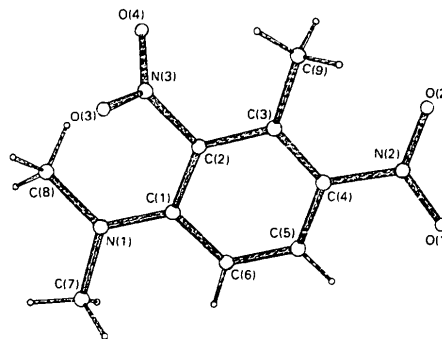
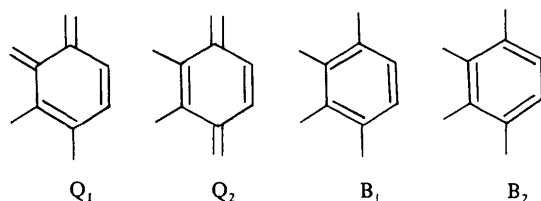


Fig. 1. View of the title compound, showing the atomic numbering.

which there is no parameter for an NO<sub>2</sub> group twisted by more than 30°. This is, however, included in the Norrestam & Schepper set of data, and it was used for our analysis together with other angular parameters taken from Domenicano & Murray-Rust (1979). For this case  $\sum |\Delta|_i = 5.4^\circ$ . To our surprise the greatest deviation is for an angle at C(6),  $\Delta_6 = 2.5^\circ$ . This may be due to the short intermolecular contact C(6)···O(2'), equal to 3.3 Å. Similar non-additivities of substituent effect on endocyclic valence angles have been found for *p*-nitroaniline (Colapietro, Domenicano; Marciante & Portalone, 1982) and *p,N,N*-dimethylaminobenzoic acid (Anulewicz, Häfeling, Krygowski, Regelmann & Ritter, 1986) as a result of strong through resonance and for 2,4-dinitrobenzoic acid (Więckowski & Krygowski, 1985) and 2,5-dinitrobenzoic acid (Grabowski & Krygowski, 1985) as a result of overcrowding.

Bond-length deformations are analyzed by use of the HOSE model (Krygowski, Anulewicz & Kruszewski, 1983) in which four resonance structures have been taken into account.



Applying bond lengths corrected for libration the following contributions have been determined:  $Q_1 = 19.9$ ,  $Q_2 = 21.6$ ,  $B_1 = 32.7$ , and  $B_2 = 25.8\%$ . The

greater contribution of  $Q_2$  compared with  $Q_1$  is explained by the much lower twist angle of NO<sub>2</sub> at C(4) than at C(2), and hence the possibility of stronger through resonance between NMe<sub>2</sub> and NO<sub>2</sub> at C(4). Lower-than-expected values of  $B_2$  and  $Q_2$  may be explained by overcrowding in the C(2)–C(3) region leading to lengthening of the C(2)–C(3) bond. In the case when no through resonance is expected for 2,4-dinitrobenzoic acid (Więckowski & Krygowski, 1985)  $B_1 = 33.9$ ,  $B_2 = 39.7$ ,  $Q_1 = 13.1$  and  $Q_2 = 13.3\%$ . The difference between these two systems is apparent, particularly in the comparison of  $\sum_i Q_i$  values: 41.5 and 26.4%, respectively.

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### Structure of an Oxidation Product of Echinocystic Acid\*

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**Abstract.** Methyl 3 $\beta$ ,16 $\alpha$ -dihydroxy-12-oxo-13 $\alpha$ -oleanan-28-oate, C<sub>31</sub>H<sub>50</sub>O<sub>5</sub>·2H<sub>2</sub>O,  $M_r = 538.7$ , monoclinic,  $P2_1$ ,  $a = 12.795$  (2),  $b = 6.904$  (1),  $c = 16.427$  (2) Å,  $\beta = 99.52$  (1)°,  $V = 1431.1$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m$ (flotation in KI solution) = 1.23,  $D_x =$

1.25 Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.093$  mm<sup>-1</sup>,  $F(000) = 592$ ,  $T = 293$  K,  $R = 0.078$  for 1999 observed reflections. All the rings have a 'chair' conformation with the hydroxyl group at C(16) in the  $\alpha$  configuration. The molecules are held together by a network of hydrogen bonds involving O(1), O(3) and the two solvent water molecules. O(1)···WO(2) = 2.80 (1); O(3)···WO(1) = 2.85 (1), WO(1)···WO(2)

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