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anti-4-Nitro-*N*-methylbenzaldoxime

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Abstract. $C_8H_8N_2O_3$, orthorhombic, $Pbc2_1$, $a=11·74$ (1), $b=10·99$ (1), $c=12·61$ (8) Å, $D_m=1·46$ (1) g cm^{-3}, $Z=8$, $D_c=1·470$ g cm^{-3}. The compound was prepared by the method of Brady, Dunn & Goldstein [*J. Chem. Soc.* (1925), pp. 2386–2403]. Elongated yellow crystals were grown from $CHCl_3$ solution: m.p. 208–209 °C.

Introduction. Cell parameters were determined from a least-squares refinement of the setting angles of 11 reflexions which had been centred on a Philips automatic diffractometer with Mo *Kα* radiation monochromatized by a flat graphite crystal. Space group $Pbc2_1$ or *Pbcm* from systematic absences, $0kl$ with k odd and $k0l$ with l odd; shown to be $Pbc2_1$ from structure analysis, with two molecules in the asymmetric unit. The intensities were obtained from a crystal (0·5 × 0·5 × 0·6 mm) mounted on the diffractometer (Mo *Kα* monochromatized, θ–2θ scan). 1767 independent reflexions were measured up to θ(Mo *Kα*) = 28°: 1667 reflexions with $F_o^2 > \sigma(F_o^2)$ were used for the analysis. Absorption [μ(Mo *Kα*) = 1·23 cm^{-1}] and extinction corrections were not applied. The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971), in the non-centrosymmetric space group. 16 atoms were identified on the first Fourier map, while the rest were located by successive difference syntheses. The least-squares refinement converged at $R=0·172$ and 0·075 with isotropic and anisotropic temperature factors respectively. At this stage H atoms were positioned geometrically and included in the structure-factor calculations, being readjusted after each cycle. The final R is 0·046 ($R_w=0·047$). The refinement was carried out with a two-block approximation of the normal-equations matrix, with one block for the positional coordinates and one block for the temperature factors and scale factor. The function minimized was $\sum w(|F_o|-|F_c|)^2$ with weights $w=4F_o^2/\sigma(F_o^2)$. Atomic form factors, given by Cromer & Mann (1968) for O, N, and C, and by Hanson, Herman, Lea & Skillman (1964) for H, were used. Table 1 gives the final positional and thermal param-

Table 1. *Final positional* (× 10^4) *and thermal parameters with their estimated standard deviations*

The form of the anisotropic temperature factor is: $\exp[-10^{-4}(h^2b_{11}+k^2b_{22}+l^2b_{33}+hkb_{12}+hlb_{13}+klb_{23})]$.

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
C(1)	1732 (3)	297 (3)	2500	49 (2)	−2 (4)	3 (7)	50 (3)	14 (6)	48 (2)
C(2)	2307 (3)	1419 (3)	2561 (7)	57 (2)	2 (4)	−3 (7)	45 (2)	−6 (6)	54 (2)
C(3)	3488 (3)	1448 (3)	2567 (6)	56 (2)	−4 (4)	12 (7)	47 (2)	−10 (6)	55 (3)
C(4)	4078 (3)	361 (3)	2507 (6)	45 (2)	4 (4)	−6 (7)	53 (3)	−3 (6)	54 (2)
C(5)	3542 (3)	−748 (3)	2418 (6)	56 (3)	14 (4)	1 (7)	41 (2)	−7 (6)	83 (4)
C(6)	2376 (3)	−783 (3)	2419 (6)	62 (3)	−4 (4)	−13 (7)	42 (3)	−7 (6)	84 (4)
C(7)	510 (3)	138 (3)	2507 (7)	50 (2)	−8 (4)	−3 (7)	52 (3)	−5 (7)	63 (3)
C(8)	−1485 (3)	670 (4)	2559 (7)	42 (2)	7 (5)	−16 (8)	94 (4)	4 (9)	83 (3)
O(1)	−51 (2)	2147 (2)	2546 (6)	65 (2)	16 (3)	−9 (7)	51 (2)	9 (6)	107 (3)
O(2)	5801 (2)	1367 (3)	2717 (6)	57 (2)	−27 (4)	−11 (6)	77 (3)	−28 (6)	130 (4)
O(3)	5858 (2)	−562 (3)	2382 (6)	60 (2)	34 (4)	16 (6)	78 (3)	−29 (6)	126 (4)
N(1)	−261 (2)	987 (3)	2548 (6)	50 (2)	2 (4)	−9 (6)	61 (2)	11 (6)	59 (2)
N(2)	5332 (2)	394 (3)	2527 (7)	49 (2)	−2 (4)	5 (7)	69 (3)	7 (6)	71 (2)
C(1′)	3201 (2)	2523 (4)	67 (5)	52 (2)	5 (6)	−3 (7)	55 (2)	−2 (4)	46 (2)
C(2′)	2640 (3)	1406 (3)	−115 (6)	54 (3)	11 (6)	6 (6)	56 (3)	−2 (5)	51 (3)
C(3′)	1461 (3)	1370 (3)	−127 (5)	58 (3)	−4 (5)	−7 (6)	45 (3)	5 (5)	57 (3)
C(4′)	856 (2)	2429 (4)	37 (6)	47 (2)	−18 (6)	−2 (7)	52 (2)	4 (5)	51 (2)
C(5′)	1373 (3)	3540 (4)	214 (6)	61 (3)	12 (6)	−6 (6)	51 (3)	−19 (6)	65 (4)
C(6′)	2543 (4)	3572 (4)	221 (6)	69 (3)	−8 (6)	−1 (7)	46 (3)	−5 (6)	69 (4)
C(7′)	4420 (3)	2694 (3)	85 (7)	54 (2)	−8 (5)	−2 (7)	62 (3)	−2 (7)	63 (3)
C(8′)	6419 (3)	2188 (4)	72 (6)	45 (2)	4 (6)	5 (8)	118 (6)	−3 (11)	96 (4)
O(1′)	4999 (3)	690 (3)	−18 (6)	71 (2)	28 (4)	7 (6)	72 (2)	8 (6)	119 (3)
O(2′)	−857 (3)	1387 (3)	−60 (6)	61 (2)	−24 (4)	−9 (7)	69 (3)	22 (6)	144 (5)
O(3′)	−931 (2)	3337 (3)	102 (6)	58 (2)	28 (4)	6 (6)	67 (3)	1 (6)	115 (4)
N(1′)	5193 (3)	1841 (3)	47 (6)	54 (2)	4 (5)	5 (5)	82 (3)	−5 (6)	65 (3)
N(2′)	−397 (2)	2396 (3)	14 (6)	52 (2)	6 (5)	2 (7)	70 (3)	5 (5)	67 (2)

Table 2. *Idealized coordinates* ($\times 10^4$) *and isotropic temperature factors for the hydrogen atoms*

	x	*y*	*z*	*B* (Å^2)
H(1)C(2)	1864	2195	2599	3·0
H(2)C(3)	3905	2240	2614	3·0
H(3)C(5)	3996	−1515	2352	3·0
H(4)C(6)	1976	−1584	2363	3·0
H(5)C(7)	4701	3552	130	3·0
H(6)C(8)	−1572	−235	2560	3·0
H(7)C(8)	−1849	1016	3209	3·0
H(8)C(8)	−1862	1016	1914	3·0
H(1′)C(2′)	3091	646	−234	3·0
H(2′)C(3′)	1053	585	−253	3·0
H(3′)C(5′)	913	4294	334	3·0
H(4′)C(6′)	2936	4368	339	3·0
H(5′)C(7′)	226	−719	2477	3·0
H(6′)C(8′)	6487	3093	122	3·0
H(7′)C(8′)	6800	1899	−591	3·0
H(8′)C(8′)	6793	1805	701	3·0

eters for the non-hydrogen atoms; the idealized positions of the H atoms are given in Table 2.*

Discussion. The analysis of *anti*-4-nitro-*N*-methylbenzaldoxime was undertaken as part of a project on the structure of *p*-substituted benzaldoximes and their derivatives (Bachechi & Zambonelli, 1972). The two independent molecules *A* and *B* in the cell are approximately planar and lie in planes parallel to the *ab* plane, about $\frac{1}{4}c$ apart. The two molecules are so oriented as to generate a pseudo centre of symmetry, as shown in Fig. 1. The relevant least-squares planes are given in Table 3.

Bond lengths and angles are given in Table 4. The corresponding bond parameters of the two independent molecules are not significantly different.

The geometry of the benzene ring is not regular, showing features similar to those observed in *syn-p*-nitrobenzaldoxime (Bachechi & Zambonelli, 1973). The presence of the strong electron-withdrawing $-NO_2$ group induces deformations in the carbon skeleton of the benzene ring (Domenicano, Vaciago & Coulson, 1975).

Valence angles and bond of the $-NO_2$ group in the present compound compare well with the values reported in the literature (Bachechi & Zambonelli, 1973; and references therein).

The geometry and dimensions of the *N*-methyloxime group, reproduced in Fig. 2 with the values of the bond

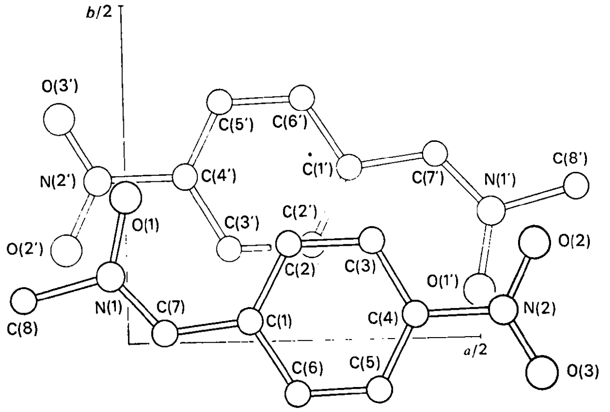

Fig. 1. The two independent molecules, referred to as *A* and *B* in the text, are shown in the projection of the asymmetric unit on the *ab* plane. Primes are used for molecule *B*.

Table 3. *Equations of least-squares planes and displacements of atoms from planes* (Å)

Planes are defined in terms of crystallographic axes. Planes labelled with a prime involve molecule *B*; atom names used in the table refer to atoms of molecule *A* for unprimed planes and to atoms of molecule *B* for primed planes.

		Dihedral angles	
φ(1)	$-0{\cdot}075x-0{\cdot}974y+12{\cdot}562z=-3{\cdot}093$	φ(2)φ(3)	7·1°
φ(2)	$-0{\cdot}008x-0{\cdot}825y+12{\cdot}576z=-3{\cdot}117$	φ(2)φ(4)	3·7
φ(3)	$-0{\cdot}246x-2{\cdot}153y+12{\cdot}365z=-2{\cdot}917$	φ(3)φ(4)	10·8
φ(4)	$0{\cdot}227x-0{\cdot}150y+12{\cdot}608z=-3{\cdot}182$		
φ(1′)	$-0{\cdot}178x-1{\cdot}406y+12{\cdot}507z=0{\cdot}308$	φ(2′)φ(3′)	4·7
φ(2′)	$-0{\cdot}065x-1{\cdot}938y+12{\cdot}414z=0{\cdot}434$	φ(2′)φ(4′)	6·7
φ(3′)	$-0{\cdot}081x-1{\cdot}046y+12{\cdot}554z=0{\cdot}218$	φ(3′)φ(4′)	2·0
φ(4′)	$-0{\cdot}088x-0{\cdot}669y+12{\cdot}588z=0{\cdot}112$		

	φ(1)	φ(1′)	φ(2)	φ(2′)	φ(3)	φ(3′)	φ(4)	φ(4′)
C(1)	−0·006	0·019	−0·002	−0·008			−0·005	0·000
C(2)	0·032	0·080	0·015	0·000				
C(3)	0·035	0·069	0·010	−0·005				
C(4)	0·009	0·002	−0·003	−0·004	−0·003	−0·003		
C(5)	0·010	−0·054	0·017	−0·001				
C(6)	−0·005	−0·037	0·011	−0·002				
C(7)	−0·039	0·043	−0·025	0·011			0·011	0·001
N(1)	−0·014	−0·015					−0·010	−0·002
O(1)	0·103	−0·100					0·005	0·001
C(8)	−0·067	0·024					−0·001	0·001
N(2)	−0·003	−0·005	−0·024	0·010	0·011	0·012		
O(2)	−0·144	−0·053			−0·004	−0·004		
O(3)	0·089	0·017			−0·004	−0·004		

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* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30939 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Bond lengths* (Å) *and angles* (°) *in the two independent molecules A and B*

Standard deviations are given in parentheses.

	A	*B*
C(1)–C(2)	1·408 (4)	1·412 (6)
C(2)–C(3)	1·387 (5)	1·385 (5)
C(3)–C(4)	1·383 (5)	1·378 (6)
C(4)–C(5)	1·375 (5)	1·382 (6)
C(5)–C(6)	1·370 (5)	1·374 (6)
C(6)–C(1)	1·410 (5)	1·401 (6)
C(1)–C(7)	1·445 (4)	1·444 (4)
C(7)–N(1)	1·301 (4)	1·306 (5)
N(1)–O(1)	1·299 (4)	1·288 (4)
N(1)–C(8)	1·479 (4)	1·489 (5)
C(4)–N(2)	1·474 (4)	1·471 (4)
N(2)–O(2)	1·226 (5)	1·238 (5)
N(2)–O(3)	1·231 (4)	1·214 (5)

	A	*B*
C(1)–C(2)–C(3)	120·0 (3)	119·5 (3)
C(2)–C(3)–C(4)	118·7 (3)	119·3 (3)
C(3)–C(4)–C(5)	122·7 (3)	122·9 (3)
C(4)–C(5)–C(6)	118·8 (3)	117·6 (4)
C(5)–C(6)–C(1)	120·8 (3)	122·0 (4)
C(6)–C(1)–C(2)	118·9 (3)	118·7 (3)
C(2)–C(1)–C(7)	125·6 (3)	125·3 (4)
C(6)–C(1)–C(7)	115·5 (3)	116·0 (4)
C(1)–C(7)–N(1)	127·2 (3)	126·5 (4)
C(7)–N(1)–O(1)	124·8 (3)	125·8 (3)
C(7)–N(1)–C(8)	120·6 (3)	119·1 (3)
O(1)–N(1)–C(8)	114·6 (3)	115·1 (3)
C(3)–C(4)–N(2)	118·6 (3)	119·5 (4)
C(5)–C(4)–N(2)	118·7 (3)	117·6 (4)
C(4)–N(2)–O(2)	118·3 (3)	117·4 (3)
C(4)–N(2)–O(3)	118·5 (3)	119·6 (3)
O(2)–N(2)–O(3)	123·2 (3)	123·0 (3)

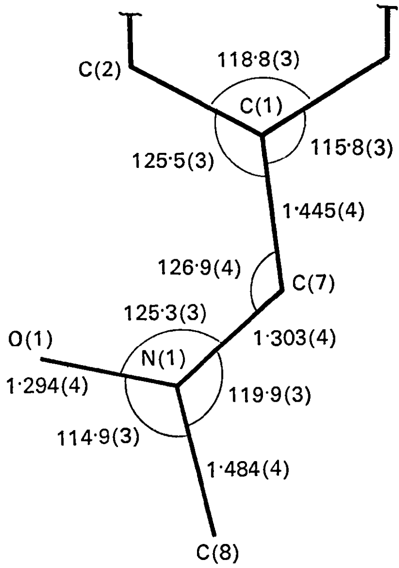

Fig. 2. Schematic drawing of the *N*-methyloxime group. The values of the bond lengths (Å) and angles (°) are averaged over the two independent molecules.

distances and angles averaged over the two independent molecules, agree well with those observed in *anti*-4-chloro-*N*-methylbenzaldoxime (Folting, Lipscomb & Jerslev, 1964) and in *anti*-2,6-dimethyl-4-chloro-*N*-methylbenzaldoxime (Jensen & Jerslev, 1969). The angles C(2)–C(1)–C(7), C(1)–C(7)–N(1) and C(7)–N(1)–O(1) are significantly larger than normal. This enlargement arises, in part, to compensate the strain caused by interaction between the side chain of the *N*-methyloxime group and the H atom in the *ortho* position C(2) [O(1)···C(2) = 2·882 (3) Å], but the high value of the angle C(7)–N(1)–O(1) is certainly due to additional reasons. In fact in *anti*-4-pyrimidinecarboxaldehyde oxime (Martinez-Ripoll & Lorenz, 1974) the value of the angle at the N of the oxime group [114·0 (5)°] does not differ much from that observed in *syn*-oximes which are not *N*-methylated (Bachechi & Zambonelli, 1972, 1973; Folting *et al.*, 1964; Martinez-Ripoll & Lorenz, 1973), where the steric hindrance is less pronounced. Therefore the reason for the high value of the C–N–O angle in the oximes which are *N*-methylated, compared with that observed in the oximes which are not, must lie in the substitution of the lone pair with a methyl group at the N atom.

The technical part of this work was performed by P. Mura.

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