

## SHORT STRUCTURAL PAPERS

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 **$\alpha$ -*p*-Nitrobenzaloxime**

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**Abstract.**  $C_7H_6N_2O_3$ , monoclinic,  $P2_1/c$ ,  $a=6.268$  (1),  $b=4.883$  (1),  $c=24.789$  (5) Å,  $\beta=94.44$  (1)°,  $D_m=1.45$  (1) g cm<sup>-3</sup>,  $Z=4$ ,  $D_c=1.458$  g cm<sup>-3</sup>. The compound was prepared by the method of Brady, Cosson & Roper [*J. Chem. Soc.* (1925), pp. 2427–2432]. Elongated pale-yellow crystals were grown from benzene solution; m.p. 129–130°C.

**Introduction.** Cell constants and their estimated standard deviations were determined by a least-squares refinement of 44  $2\theta$  values measured on  $h0l$  and  $hk0$  Weissenberg photographs, calibrated with superimposed ZnO powder lines, taken with Cu  $K\alpha$  radiation at ~23°C. Systematic absences were  $h0l$  with  $l$  odd and  $0k0$  with  $k$  odd. The intensities were obtained from

a crystal of approximate dimensions 0.60 × 0.30 × 0.10 mm mounted on a Siemens AED diffractometer (Mo  $K\alpha$ , Zr-filtered,  $\omega$ -scan, scintillation counter with pulse-height discrimination).

The unique  $b$  axis of the crystal (its longest dimension) was coincident with the  $\phi$  axis of the goniostat. 1654 independent reflexions were measured up to  $2\theta(\text{Mo } K\alpha)=56^\circ$ : 1256 reflexions with  $F_o^2 > 3\sigma(F_o^2)$  were used for the analysis. Absorption [ $\mu(\text{Mo } K\alpha)=1.20$  cm<sup>-1</sup>] and extinction corrections were not applied.

The structure was solved by Patterson and Fourier methods. The relative coordinates of the atoms of the benzene ring and of the two atoms directly bound to it were obtained from well defined peaks near the origin of the Patterson map. These eight atoms were then shifted by a displacement vector which was determined from the composite vector peaks originating from the set of vectors between centrosymmetrically related molecules. From a Fourier synthesis, phased on the contribution of these eight atoms, all the non-hydrogen atoms were located.

The full-matrix least-squares refinement converged at  $R=0.110$  with isotropic temperature factors and at  $R=0.070$  with anisotropic factors. A difference synthesis calculated at this stage revealed the positions of all the hydrogen atoms. The refinement was continued anisotropically for the non-hydrogen and isotropically

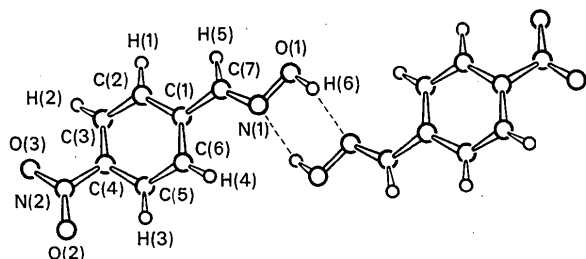


Fig. 1. Two centrosymmetrically related molecules linked by hydrogen bonds.

Table 1. Final positional ( $\times 10^4$ ) 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)	199 (4)	4665 (5)	1118 (1)	239 (7)	38 (15)	5 (3)	338 (11)	-7 (3)	13 (0)
C(2)	-457 (4)	3430 (6)	1586 (1)	217 (6)	116 (16)	26 (3)	417 (12)	6 (4)	15 (0)
C(3)	804 (4)	1499 (5)	1863 (1)	234 (7)	41 (16)	30 (3)	378 (11)	10 (4)	13 (0)
C(4)	2737 (4)	826 (5)	1668 (1)	212 (6)	22 (13)	1 (2)	273 (10)	-7 (3)	13 (0)
C(5)	3449 (4)	1991 (5)	1208 (1)	219 (6)	59 (15)	26 (3)	412 (13)	-4 (4)	15 (1)
C(6)	2171 (4)	3939 (6)	933 (1)	257 (7)	40 (16)	28 (3)	411 (13)	16 (4)	13 (0)
C(7)	-1232 (4)	6668 (6)	840 (1)	267 (8)	144 (17)	17 (3)	448 (13)	8 (4)	13 (0)
N(1)	-676 (4)	8098 (5)	452 (1)	307 (7)	-192 (15)	-2 (3)	410 (11)	-16 (3)	15 (0)
N(2)	4058 (3)	-1280 (4)	1958 (1)	243 (6)	53 (13)	6 (2)	332 (9)	-12 (3)	14 (0)
O(1)	-2334 (4)	9865 (5)	256 (1)	382 (7)	-423 (17)	11 (3)	619 (13)	-68 (4)	20 (0)
O(2)	5828 (3)	-1767 (4)	1799 (1)	285 (6)	-292 (14)	32 (2)	547 (11)	-13 (3)	20 (0)
O(3)	3351 (3)	-2416 (4)	2346 (1)	317 (6)	-116 (13)	23 (2)	478 (10)	-64 (3)	20 (0)

Table 1 (cont.)

	x	y	z	B (Å <sup>2</sup> )
H(1)	8160 (40)	4047 (56)	1729 (10)	2.0 (6)
H(2)	326 (38)	629 (55)	2157 (10)	1.8 (6)
H(3)	4847 (41)	1475 (58)	1065 (10)	2.4 (6)
H(4)	2625 (39)	4751 (57)	621 (10)	2.0 (6)
H(5)	2653 (40)	1810 (58)	4037 (10)	2.1 (6)
H(6)	-1710 (52)	717 (78)	17 (14)	4.5 (10)

for the hydrogen atoms. The final  $R$  is 0.048 ( $R_w = 0.044$ ). 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 oxygen, nitrogen and carbon, and by Hanson, Herman, Lea & Skillman (1964) for hydrogen, were used. Table 1 gives the final positional and thermal parameters. Bond lengths and angles are given in Table 2.\*

Table 2. Intramolecular bond lengths and angles with their estimated standard deviations

C(1)–C(2)	1.397 (3) Å	C(1)–C(2)–C(3)	121.0 (2)°
C(2)–C(3)	1.378 (4)	C(2)–C(3)–C(4)	118.3 (2)
C(3)–C(4)	1.378 (3)	C(3)–C(4)–C(5)	122.7 (2)
C(4)–C(5)	1.380 (3)	C(4)–C(5)–C(6)	118.5 (2)
C(5)–C(6)	1.387 (4)	C(5)–C(6)–C(1)	120.2 (2)
C(6)–C(1)	1.398 (4)	C(6)–C(1)–C(2)	119.2 (2)
C(1)–C(7)	1.463 (4)	C(1)–C(7)–N(1)	122.3 (2)
C(7)–N(1)	1.261 (4)	C(7)–N(1)–O(1)	111.2 (2)
N(1)–O(1)	1.408 (3)	C(3)–C(4)–N(2)	118.2 (2)
C(4)–N(2)	1.472 (3)	C(5)–C(4)–N(2)	119.2 (2)
N(2)–O(2)	1.229 (3)	C(4)–N(2)–O(2)	117.8 (2)
N(2)–O(3)	1.224 (3)	C(4)–N(2)–O(3)	118.4 (2)
C(2)–H(1)	1.01 (3)	O(2)–N(2)–O(3)	123.8 (2)
C(3)–H(2)	0.92 (3)	C(1)–C(2)–H(1)	118.6 (15)
C(5)–H(3)	1.00 (3)	C(3)–C(2)–H(1)	120.3 (15)
C(6)–H(4)	0.93 (5)	C(2)–C(3)–H(2)	120.3 (16)
C(7)–H(5)	0.97 (3)	C(4)–C(3)–H(2)	121.3 (16)
O(1)–H(6)	0.85 (4)	C(4)–C(5)–H(3)	122.3 (15)
		C(6)–C(5)–H(3)	119.1 (15)
		C(5)–C(6)–H(4)	119.8 (16)
		C(1)–C(6)–H(4)	119.9 (16)
		C(1)–C(7)–H(5)	116.5 (16)
		N(1)–C(7)–H(5)	121.1 (16)
		N(1)–O(1)–H(6)	100.0 (23)

**Discussion.** The analysis of this compound was undertaken as part of a project on the structures of *para*-substituted benzaldoximes (Bachechi & Zambonelli, 1972). While our work was in progress, it came to our knowledge that an independent study had been published (Brehm, 1969; Brehm & Watson, 1972). Since our results seem to be more accurate, we discuss them briefly here.

In the solid state  $\alpha$ -*p*-nitrobenzaldoxime forms a centrosymmetrical dimer through two O–H...N hydrogen bonds [O...N, 2.853 (3); H...N, 2.05 (1) Å;

\* A table of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30169 (7 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

Planes are defined in terms of the crystallographic axes.				Dihedral angles
$\varphi(1)$	$2.459x + 3.486y + 13.580z = 3.212$	$\varphi(2)\varphi(3) = 8.1^\circ$		
$\varphi(2)$	$2.550x + 3.536y + 12.981z = 3.154$	$\varphi(2)\varphi(4) = 4.1^\circ$		
$\varphi(3)$	$1.858x + 3.446y + 15.331z = 3.358$	$\varphi(3)\varphi(4) = 4.3^\circ$		
$\varphi(4)$	$2.278x + 3.437y + 14.383z = 3.305$			
	$\varphi(1)$	$\varphi(2)$	$\varphi(3)$	$\varphi(4)$
C(1)	0.019	0.002	-0.001	
C(2)	-0.025	-0.001		
C(3)	-0.038	0.001		
C(4)	-0.014	-0.002		-0.001
C(5)	0.030	0.003		
C(6)	0.039	-0.003		
C(7)	0.050		0.001	
N(1)	-0.058		0.000	
N(2)	0.002			0.005
O(1)	0.000		-0.001	
O(2)	-0.048			-0.002
O(3)	0.044			-0.002

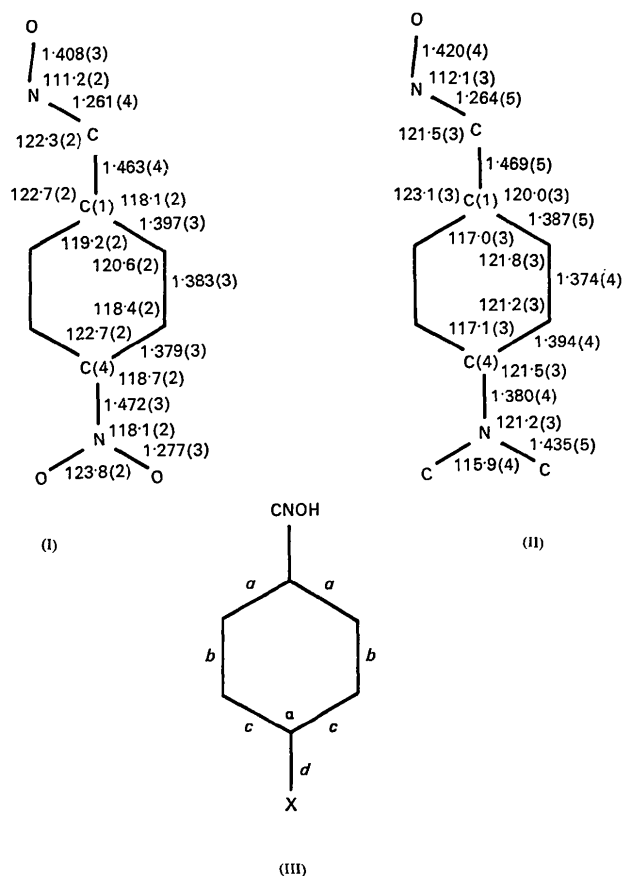


Fig. 2. (I) and (II) are the molecules of  $\alpha$ -*p*-nitrobenzaldoxime and  $\alpha$ -*p*-dimethylaminobenzaldoxime represented with averaged values reported for the 'symmetry'-related bond distances and angles. (III) is a schematic representation of the *para*-substituted benzaldoximes, in which the bond distances and angles, to be discussed, are indicated by symbols (see text).

O—H...N, 159 (3)°] as shown in Fig. 1. The monomeric molecule is approximately planar and the relevant least-squares planes are given in Table 3.

The structure of  $\alpha$ -*p*-nitrobenzaldoxime may be compared with that of  $\alpha$ -*p*-dimethylaminobenzaldoxime (Bachechi & Zambonelli, 1972). Neglecting the oxime groups we may regard the two molecules as symmetrical with a binary axis passing through C(1) and C(4). This assumption can be made since the values of the 'symmetry'-related bond distances and angles are not significantly different. In Fig. 2 the two molecules with averaged values for the 'symmetry'-related bond distances and angles are shown together with a schematic representation of the *para*-substituted benzaldoximes, in which the bonds and angles, to be used in the following discussion, are indicated by symbols.

In both molecules the aromatic carbon atom C(4) bearing the substituent X [—NO<sub>2</sub> or —N(CH<sub>3</sub>)<sub>2</sub>] does not show perfect trigonal symmetry, the deviations depending on the nature of the substituents.

It is well-known (Bent, 1961) that carbon  $\sigma$  orbitals directed towards a strong electron-withdrawing substituent (like —NO<sub>2</sub>) have more than average *p* character while those directed towards a strong electron-donating substituent [like —N(CH<sub>3</sub>)<sub>2</sub>] have less than average *p* character. In  $\alpha$ -*p*-nitrobenzaldoxime the valence angle  $\alpha$  at the carbon atom C(4) is larger than 120°, revealing a more than average *s* character of the  $\sigma$  orbitals in the directions of the *c* bonds, consistent with the enhanced *p* character of the  $\sigma$  orbital directed towards the —NO<sub>2</sub> group. Accordingly, *c* bonds are shorter than *a* bonds and than *c* bonds in  $\alpha$ -*p*-dimethylaminobenzaldoxime, and the *d* bond is considerably lengthened to approximately that of a C(*sp*<sup>3</sup>)—N(*sp*<sup>3</sup>) bond. Antithetical geometric features are observed in  $\alpha$ -*p*-dimethylaminobenzaldoxime, in conformity with a less than average *s* character of the C(4)  $\sigma$  orbitals directed along the *c* bonds. Therefore,  $\alpha$  is less than

120°, *c* bonds are longer than *a* bonds and than *c* bonds of the nitro derivative, and *d* is even shorter than a C(*sp*<sup>2</sup>)—N(*sp*<sup>2</sup>) single bond.

A possible contribution of a quinoid canonical form to the ground state of the two molecules, which would affect the  $\pi$ -components of the bonds, is masked in the nitro compound, while it appears to be enhanced in the other. From a comparison of the *b* bonds, a contribution of a quinoid form seems more pronounced in the dimethylamino derivative.

Apart from the N—O bond, significantly shorter in the nitro derivative, the oxime groups have geometry and dimensions which compare well in the two compounds. The exocyclic C(oxime)—C—C angles are significantly different in both molecules, C(7)—C(1)—C(6) being the largest, as expected from steric considerations. Valence angles and bonds of the —NO<sub>2</sub> group of the present compound compare well with the values given by Barve & Pant (1971) and Tavale & Pant (1971).

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

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## The Crystal Structure of Bis(propane-2-nitronato)copper(II)

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**Abstract.** Single crystals of bis(propane-2-nitronato)-copper(II), Cu[(CH<sub>3</sub>)<sub>2</sub>CNO<sub>2</sub>]<sub>2</sub>, are monoclinic, space group *P*2<sub>1</sub>/*a*, with unit-cell dimensions *a* = 6.792 (6), *b* = 10.343 (8), *c* = 13.366 (9) Å,  $\beta$  = 90.76 (5)°. The observed density is 1.70 g cm<sup>-3</sup> and, with four molecules per unit cell, the calculated density is 1.70 g cm<sup>-3</sup>. Each copper atom in these crystals is surrounded in a grossly

distorted octahedral manner by six oxygen atoms from four different propane-2-nitronate ions. The nitronate groups themselves are all planar.

**Experimental.** The substance was prepared by mixing, at 0°C, aqueous solutions of CuSO<sub>4</sub> · 5H<sub>2</sub>O (2 ml, 1.0M) and K[(CH<sub>3</sub>)<sub>2</sub>CNO<sub>2</sub>] (3 ml, 1.0M). Suitable single crys-