

## The Crystal and Molecular Structure of 2-Nitro-4-chlorophenol

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The crystal structure of 2-nitro-4-chlorophenol has been determined from visually estimated Cu  $K\alpha$  X-ray data. The crystals are monoclinic, space group  $P2_1/a$ , with  $a = 14.73$  (2),  $b = 5.57$  (2),  $c = 8.49$  (1) Å,  $\beta = 98.8$  (2)° and  $Z = 4$ . The structure was solved by the Patterson method and refined by block-diagonal least-squares calculations to  $R = 0.059$  for 792 non-zero reflexions. The hydroxylic group is hydrogen-bonded to one of the oxygen atoms of the nitro group [O(1)···O(2) 2.587 (6) Å, O(1)–H(0)···O(2) 140 (6)°, H(0)···O(2) 1.84 (7) Å]. An inequality of the nitrogen–oxygen bond lengths in the nitro group is remarkable [N–O(2) 1.240 (7), N–O(3) 1.199 (6) Å]. The approximately planar molecules are stacked in a column along the  $c$  axis by a succession of inversion at inter-ring spacings of 3.54 and 3.45 Å. The columns are staircase-like and packed side by side in the same way as in the paraffins.

### Introduction

A photochemical reaction of *p*-nitrophenol in the solid state found by Fritzsche (1859) has been shown to be a topochemically controlled redox reaction (Coppens & Schmidt, 1965). In addition, it is of interest that many phenols, of which 2,4-dinitrophenol is the prototype, serve as 'uncouplers' of oxidative phosphorylation (White, Handler & Smith, 1973). Although the intramolecular hydrogen bond of *o*-nitrophenol has been postulated for a long time (Pauling, 1960), the direct evidence for the bond has recently been published by Hanson (1975) and Andersen & Andersen (1975).

We have undertaken to determine the structures of a series of *o*-nitrophenols in order to obtain comparative information as to the above problems and throw light upon the molecular overlapping and stacking mode of the benzene derivatives in view of the  $\pi$ -electron interactions. The study of this series starts with 2-nitro-4-chlorophenol, reported in this paper.\*

### Experimental

The crystals were grown from an aqueous ethanol solution by slow evaporation as thin yellow plates developed on (100).

#### Crystal data

2-Nitro-4-chlorophenol,  $C_6H_4NO_3Cl$ ; M.W. 173.56; m.p. 86–87°C; monoclinic, space group  $P2_1/a$ ;  $a = 14.73$  (2),  $b = 5.57$  (2),  $c = 8.49$  (1) Å;  $\beta = 98.8$  (2)°.  $V = 688.4$  Å<sup>3</sup>;  $D_m = 1.66$  g cm<sup>-3</sup> (by flotation in KI aqueous solution),  $D_x = 1.675$  g cm<sup>-3</sup> for  $Z = 4$ ;  $\mu = 45.8$  cm<sup>-1</sup> for Cu  $K\alpha$  ( $\lambda = 1.5418$  Å);  $F(000) = 352$ .

By using specimens with dimensions 0.1 × 0.4 × 0.2 and 0.1 × 0.2 × 0.3 mm in glass capillaries, intensity data were collected on Weissenberg photographs for

the layers  $h0l$  to  $h4l$  and  $hk0$  to  $hk2$ , respectively. A total of 792 reflexions were estimated visually. Intensities were corrected for Lorentz and polarization factors and for spot shape ( $B = 5.1$  Å<sup>2</sup>).

### Structure determination and refinement

The structure was solved from the Patterson maps projected along the  $b$  and  $c$  axes. The block-diagonal least-squares calculations with three-dimensional data reduced  $R$  to 0.077. The difference Fourier synthesis at this stage revealed all the hydrogen atoms. Further least-squares refinement including the hydrogen atoms gave a final  $R$  of 0.059 for 792 non-zero reflexions.\*

The weights adopted were:  $w = 1.0$  for  $0 < |F_o| \leq 9.0$ , and  $w = (9.0/|F_o|)^2$  for  $|F_o| > 9.0$ .

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computations were performed on a NEAC 2200–500 computer at the Okayama University Computer

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31591 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

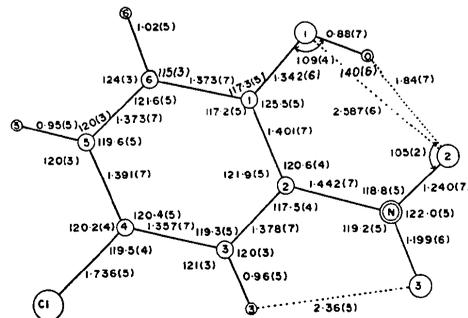


Fig. 1. Bond lengths (Å) and bond angles (°), with their e.s.d.'s in parentheses.

\* The structure of 2-nitro-4-chlorophenol, based on independent data, has recently been reported by Maeda (1976).

Table 1. *Final atomic parameters*

 Positional and thermal parameters for the non-hydrogen atoms ( $\times 10^4$ ) with their e.s.d.'s in parentheses.

 The  $\beta_{ij}$ 's are defined by:  $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - hk\beta_{12} - hl\beta_{13} - kl\beta_{23})$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cl	-1461 (1)	-3154 (3)	192 (2)	58 (1)	517 (6)	223 (2)	-43 (3)	-19 (2)	-103 (6)
O(1)	929 (2)	3213 (7)	4482 (5)	53 (2)	507 (16)	279 (7)	-32 (8)	-6 (5)	-195 (18)
O(2)	2231 (2)	278 (8)	4057 (5)	53 (2)	725 (21)	318 (8)	39 (10)	-37 (6)	-263 (22)
O(3)	1959 (2)	-2814 (7)	2577 (5)	59 (2)	623 (19)	310 (8)	103 (10)	25 (6)	-193 (20)
N	1699 (2)	-1041 (8)	3173 (5)	48 (2)	550 (21)	206 (7)	32 (10)	8 (6)	-23 (18)
C(1)	416 (3)	1672 (9)	3508 (5)	49 (2)	398 (20)	188 (7)	-17 (11)	14 (6)	49 (20)
C(2)	740 (3)	-400 (9)	2840 (5)	42 (2)	401 (20)	174 (7)	23 (10)	17 (6)	31 (19)
C(3)	167 (3)	-1876 (9)	1834 (5)	49 (2)	435 (20)	171 (7)	11 (11)	26 (6)	1 (21)
C(4)	-740 (3)	-1331 (9)	1489 (5)	49 (2)	415 (20)	168 (7)	-40 (10)	14 (6)	2 (19)
C(5)	-1087 (3)	699 (9)	2145 (6)	43 (2)	452 (22)	226 (8)	21 (11)	16 (7)	42 (22)
C(6)	-506 (3)	2159 (9)	3140 (6)	50 (2)	405 (21)	231 (9)	25 (11)	34 (7)	-17 (22)

Table 1 (cont.)

 Positional ( $\times 10^3$ ) and isotropic thermal parameters for the hydrogen atoms.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
H(0)	149 (4)	264 (12)	471 (8)	7.2 (1.7)
H(3)	41 (3)	-328 (8)	139 (5)	3.0 (1.0)
H(5)	-172 (3)	109 (8)	189 (5)	2.3 (0.9)
H(6)	-71 (3)	372 (9)	361 (6)	4.1 (1.2)

 Table 2. *The least-squares planes of the benzene ring and the displacement of the atoms from the plane*

$$X = ax + cz \cos \beta, Y = by, Z = cz \sin \beta$$

$$0.3021X + 0.5384Y - 0.7867Z + 1.7718 = 0$$

Atoms with an asterisk are used for the calculation of the plane.

Shift (Å)	Shift (Å)	Shift (Å)
C(1)* 0.005	C(6)* -0.002	N -0.003
C(2)* -0.005	Cl 0.042	H(0) -0.064
C(3)* 0.001	O(1) 0.014	H(3) -0.001
C(4)* 0.002	O(2) 0.011	H(5) 0.016
C(5)* -0.002	O(3) -0.003	H(6) 0.048

 Center. The programs used were *HBL5-5* and *DAPH* (Ashida, 1973).

## Results and discussion

The final atomic parameters are listed in Table 1. Bond lengths and angles are shown in Fig. 1. The least-squares plane of the benzene ring and the displacement of the atoms from the plane are listed in Table 2. Projection of the crystal structure viewed along the *c* axis is reproduced in Fig. 2. The molecular overlapping and stacking mode are illustrated in Fig. 3.

The molecule is planar within experimental error except for the chlorine atom. The angles of the exocyclic bonds C(1)-O(1), C(2)-N and C(4)-Cl with respect to the benzene ring plane are 0.4, 0.05 and 1.3°, respectively. The dihedral angle of the nitro group with the ring is only 0.4°. The inner angles of the ring carbon atoms attached to the chlorine atom and nitro group are close to the values expected from their electronegativities (Domenicano, Mazzeo & Vaciago, 1975).

By assuming equality of N-O bonds of a nitro group attached to a benzene ring (Williams, 1967), the *s*-character of the N atom in the orbitals pointing toward the carbon atom may be expressed in terms of the O-N-O angle  $\alpha$  as  $(1 + \cos \alpha)/(1 - \cos \alpha)$ . From recent experimental data for 130 nitro groups, the C-N bond

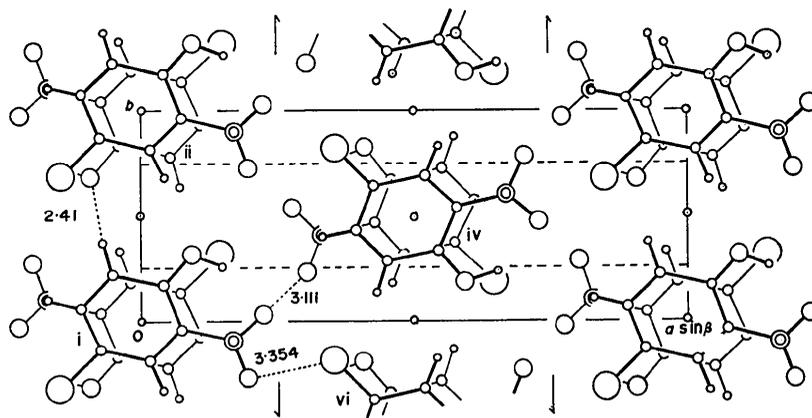


Fig. 2. Projection of the crystal structure viewed along the *c* axis. Dotted lines show intermolecular contacts. Symmetry code: (i)  $x, y, z$ ; (ii)  $-x, 1-y, 1-z$ ; (iii)  $-x, -y, 1-z$ ; (iv)  $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$ ; (v)  $-x, -y, -z$ ; (vi)  $\frac{1}{2}+x, -\frac{1}{2}-y, z$ .

length ( $L$ ) of the nitro groups attached to benzene ring can be related to the  $s$ -character ( $S$ ) of the nitrogen atoms by the equation:  $L = -(0.707 \pm 0.035)S + (1.669 \pm 0.010)$ . Thus, the C(2)–N bond length for the present compound is estimated to be 1.45 Å, which is near to the observed value.

The plot of the dihedral angles of 68 nitro groups in nitrobenzenes against the C–N bond lengths is shown in Fig. 4. No remarkable increase in the dihedral angle is evident at a bond length smaller than 1.467 Å which is close to the C( $sp^2$ )–N( $sp^2$ ) bond length of 0% double bond character assumed by Ammon (1974). The C(2)–N bond in the present compound may therefore have some double bond character resulting in the coplanarity of the nitro group with the ring.

The hydroxylic group donates a hydrogen bond to the O(2) atom of the nitro group, resulting in the six-membered ring making a dihedral angle of only 0.5° with the benzene ring. The geometry of the intramolecular hydrogen bond is very close to that of the other *o*-nitrophenols as shown in Table 3. The nitrogen–oxygen bond lengths in the nitro group differ: the N–O(3) bond length, where the O(3) atom is free from the hydrogen bond, is shorter. Such a difference is also found in 1,3-dinitrobenzene (Trotter & Williston, 1966) and 1,3,5-trinitrobenzene (Choi & Abel, 1972).

Table 3. Geometry of the intramolecular hydrogen bond, in comparison with that in the other *o*-nitrophenols

$\delta$  denotes the dihedral angle between the six-membered ring, including the hydrogen bond and the benzene ring.

	(a)	(b)	(c)	Average value
O(1)···O(2)	2.587 (Å)	2.558 (Å)	2.596 (Å)	2.580 (Å)
C(1)–O(1)	1.342	1.333	1.348	1.341
O(1)–H(0)	0.88	1.07	0.91	0.95
H(0)···O(2)	1.84	1.66	1.79	1.76
O(2)–N	1.240	1.235	1.230	1.235
O(3)–N	1.199	1.197	1.214	1.203
C(2)–N	1.442	1.464	1.450	1.452
C(2)–C(1)	1.401	1.407	1.401	1.403
C(1)–O(1)–H(0)	109°	107°	105°	107°
O(1)–H(0)···O(2)	140	138	147	142
H(0)···O(2)–N	105	109	104	106
O(2)–N–C(2)	118.8	117.7	119.0	118.5
N–C(2)–C(1)	120.6	120.1	120.6	120.4
C(2)–C(1)–O(1)	125.5	124.8	125.1	125.1
$\delta$	0.5	2.7	2.0	1.7

(a) 2-Nitro-4-chlorophenol (this work). (b) 2-Chloro-4,6-dinitrophenol (Andersen & Andersen, 1975). (c) Methyl 4-hydroxy-3-nitro-*trans*-cinnamate (Hanson, 1975).

The C(4)–Cl bond length is close to the average value of Rudman (1971). The C(1)–O(1) bond length corresponds to the value expected for  $pK_a=4$  (Andersen & Andersen, 1975).

The molecules are stacked by a succession of inversion along the  $c$  axis to form a staircase-like column. There are edge-to-edge overlaps of the benzene ring of the molecule (i) with those of the molecules (iii) and (v), inter-ring spacings  $d=3.45$  and 3.54 Å, respectively. In

the former the atom C(1<sup>i</sup>) is situated just above the middle of the atoms C(1<sup>iii</sup>) and C(6<sup>iii</sup>), while in the latter the bond C(3<sup>i</sup>)–C(4<sup>i</sup>) overlaps on the bond C(4<sup>v</sup>)–C(3<sup>v</sup>). A similar overlap is observed in 3,3'-methylenebis-(6-bromo-4-hydroxycoumarin),  $d=3.52$  Å (Alcock & Hough, 1972, illustrated in Shimizu, Kashino & Haisa, 1975), bis(2-hydroxyethyl)terephthalate (Kashino & Haisa, 1975), and diethyl terephthalate,  $d=3.50$  Å (Bailey, 1949). The closest contact is found between the atoms Cl<sup>i</sup> and C(2<sup>v</sup>), the distance being comparable with the sum of their van der Waals radii. The molecular plane makes an angle of 55.4° with the  $c$  axis.

The columns are packed side by side into a somewhat elongated hexagonal array as observed in the monoclinic form of *n*-hexatriacontane (Shearer & Vand, 1956). The shortest intercolumn contact is found between the atoms O(1<sup>i</sup>) and H(6<sup>ii</sup>), whose distance is near to the sum of the van der Waals radii.

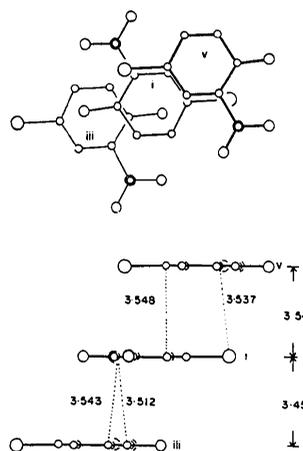


Fig. 3. The molecular overlapping and stacking, together with inter-ring spacings (Å) and intermolecular distances (Å). Symmetry code is given in the legend of Fig. 2.

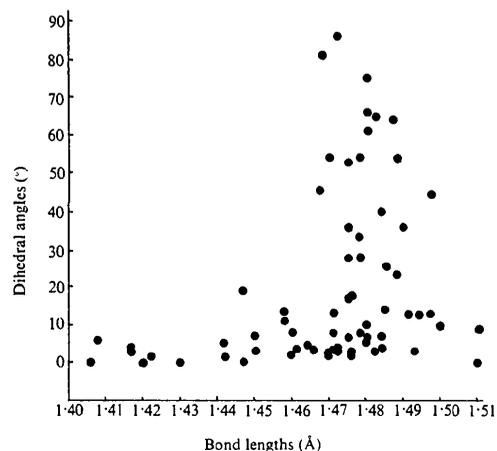


Fig. 4. The dihedral angles of nitro groups with the benzene rings in nitrobenzenes vs the C–N bond lengths.

The oxygen atoms of the nitro groups of adjacent columns fit in with each other to give a contact in the same manner as the hydrogen atoms in n-hexatriacontane.

The rather low melting point of the present compound may be attributable to the lack of an intermolecular hydrogen bond.

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## Molecular and Crystal Structure of the Alkaloid Vindolinine

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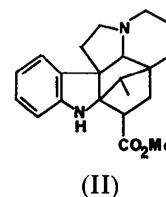
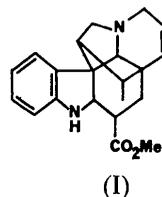
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The dihydroindole alkaloid vindolinine forms a hemihydrochloride hemiperchlorate  $C_{21}H_{25}N_2O_2 \cdot (ClO_4)_{0.5} \cdot Cl_{0.5}$  which crystallizes in the monoclinic space group *C2* with:  $a=18.181$  (5),  $b=8.959$  (4),  $c=14.765$  (3) Å,  $\beta=124.7$  (2)°,  $Z=4$  and  $V=1976$  Å<sup>3</sup>. Intensities for 2138 independent reflexions (1975 above the background) were measured on Weissenberg photographs. The structure was solved by direct methods and full-matrix least-squares refinement led to a final *R* value of 0.072. Two anions of different type appear on two separate twofold axes. One of these is the expected  $ClO_4^-$  ion, the second being an unexpected  $Cl^-$  ion. The latter is trapped between two molecules of vindolinine by strong hydrogen bonds:  $N(4)-H \cdots Cl^-$  (3.07 Å). The perchlorate ion participates in two symmetrical hydrogen bonds  $N(1)-H \cdots O$  of 3.05 Å. The X-ray results confirm the revised structure of vindolinine and establish the stereochemistry.

### Introduction

Vindolinine is an alkaloid extracted from a variety of *Catharanthus* species (Janot, Le Men & Fan, 1959; Gorman, Neuss, Svoboda & Barnes, 1959) to which structure (I) had been assigned some time ago, mostly on the basis of mass-spectra analyses (Djerassi *et al.*, 1962; Djerassi, Cereghetti, Budzikiewicz, Janot, Plat & Le Men, 1964). Recently a <sup>13</sup>C NMR analysis of vindolinine led to the allocation of the revised planar formula (II) to this alkaloid (Ahond *et al.*, 1974). The present X-ray determination was undertaken to confirm this formula and to establish the stereochemistry of vindolinine.\*



The absolute configuration was deduced from a chemical correlation with (–)-vincadifformine (Rasoanaivo, Langlois & Potier, 1974) and confirmed by the more recent X-ray analysis of (–)-pseudocopsinine (14,15-dihydrovindolinine) (Nasyrov, Andrianov & Struchkov, 1974).

### Experimental

Weissenberg films indicated space group *C2*. *Catharanthus* alkaloids are optically active and hence the

\* Presented in part at the 9th IUPAC Congress on Chemistry of Natural Products, Ottawa, 1974.