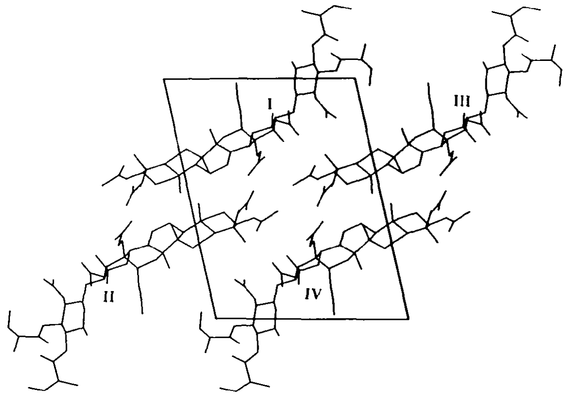

Fig. 3. Projection of the acetylated napoleogenin structure along the b axis. The positions of the molecules are; (I) at x, y, z; (II) at $\bar{x}+1, \frac{1}{2}+y, z$; (III) at $x, y, z+1$; (IV) at $x+1, \frac{1}{2}+y, \bar{z}+1$ with x, y and z coordinates given in Table 1.

about 180° about the C(7′)–C(8′) bond [the corresponding torsional angles are reported in Table 5(iii)].

One should also notice that in both angelyl and acetyl groups, the accuracy of bond lengths and valency angles is highly restricted by a large thermal motion of the end-chain atoms.

A packing diagram of the crystal structure viewed along the b axis is shown in Fig. 3. The intermolecular distances less than 3·7 Å are reported in Table 7. There is no abnormal feature in the packing, which appears to be dictated mainly by close van der Waals contacts between the molecules.

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The Structure of 2-Amino-5-nitrophenol: a Comparison with 2-Aminophenol

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Abstract

The crystal structure of 2-amino-5-nitrophenol has been determined from visually estimated Cu $K\alpha$ data, and refined to an R value of 0·072 for 1138 non-zero reflexions. The crystals are monoclinic, $P2_1/c$, with $a = 8{\cdot}49\ (1)$, $b = 10{\cdot}34\ (1)$, $c = 8{\cdot}05\ (1)$ Å, $\beta = 113{\cdot}1\ (1)°$ and $Z = 4$. The molecules, related by a glide plane, are held together by O–H$\cdots$NH$_2$ hydrogen bonds [O$\cdots$N 2·801 (3), H$\cdots$N 1·89 (4) Å, O–H$\cdots$N 174 (3)°] to form a ribbon along **c**. The ribbons are held together by dipole–dipole interactions between the molecules related by $\bar{1}$, as found commonly in mononitrophenols. The morphotropism in mononitrophenols and aminophenols is discussed.

Introduction

As part of a programme of studies on the crystal and molecular structures of phenols (Kagawa, Kawai, Kashino & Haisa, 1976) and the systemization of organic crystals (Haisa, 1978), the structure of 2-amino-5-nitrophenol has been determined in order to

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elucidate the effects of nitro-group substitution on the crystal structures of aminophenols. The result will be discussed with particular reference to the structure of 2-aminophenol (Ashfaquzzaman & Pant, 1979). An independent study by us (Haisa, Kashino & Matsumoto, unpublished) has confirmed the positions of the H atoms of the hydroxyl and amino groups as assumed by them.

Experimental

Crystals grown from an ethanol solution were red-brown prisms elongated along [001] and bounded by {100} and {110}. Crystal data: 2-amino-5-nitrophenol, $C_6H_6N_2O_3$, $M_r = 154{\cdot}1$, m.p. 480–482 K (decomposition), monoclinic, $P2_1/c$, $a = 8{\cdot}49\,(1)$, $b = 10{\cdot}34\,(1)$, $c = 8{\cdot}05\,(1)$ Å, $\beta = 113{\cdot}1\,(1)°$, $V = 650\,(1)$ Å^3, $D_m = 1{\cdot}54$ by flotation in aqueous KI solution, $D_x = 1{\cdot}575$ Mg m^{-3} for $Z = 4$; $\mu = 1{\cdot}12$ mm^{-1} for Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å), $F(000) = 320$.

Specimens with dimensions 0·25 × 0·15 × 0·35 and 0·40 × 0·50 × 0·30 mm were used for *b* and *c* axis photographs respectively. Using Cu $K\alpha$ radiation, multiple-film equi-inclination Weissenberg photographs were taken for the layers from *h*0*l* to *h*7*l* and from *hk*0 to *hk*6. In total, 1138 independent reflexions (78% of those accessible in the Cu sphere) were observed as non-zero. The intensities were estimated visually and corrected for Lorentz–polarization factors and for spot shape. Wilson's plot gave $B = 3{\cdot}5$ Å^2.

Crystal data of 2-aminophenol are: orthorhombic, *Pbca*, $a = 7{\cdot}86\,(1)$, $b = 19{\cdot}77\,(1)$, $c = 7{\cdot}28\,(1)$ Å, $V = 1131\,(2)$ Å^3, $Z = 8$ (Haisa *et al.*, unpublished). The relationships with the data of Ashfaquzzaman & Pant (**a**′,**b**′,**c**′) are: **a** = **b**′, **b** = **c**′ and **c** = **a**′.

Structure determination and refinement

The structure was solved by the Patterson method. All the H atoms were located from a difference Fourier map when *R* was 0·10. The refinements were made by block-diagonal least-squares calculations. The weighting scheme during the later stages was: $w = 1{\cdot}0$ for $0 < |F_o| \le 6{\cdot}0$, $w = (6{\cdot}0/|F_o|)^2$ for $|F_o| > 6{\cdot}0$. An extinction correction was applied for the five strongest reflexions ($\bar{2}22$, $\bar{2}12$, $\bar{2}02$, $\bar{1}21$ and 202) when $R = 0{\cdot}083$. The final *R* value was 0·072 for the non-zero reflexions. The final atomic parameters are listed in Table 1.*

Table 1. *The final atomic parameters of the non-hydrogen* ($\times 10^4$, *except* B_{eq}) *and hydrogen atoms* ($\times 10^3$, *except* B_{iso}) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq} or B_{iso} (Å^2)
O(1)	4881 (3)	−2892 (2)	586 (3)	3·04 (8)
O(2)	−1466 (3)	−166 (2)	−4113 (3)	3·69 (8)
O(3)	−637 (3)	−1993 (2)	−4754 (3)	3·68 (9)
N(1)	5365 (3)	−821 (2)	2762 (3)	2·71 (8)
N(2)	−429 (3)	−1056 (2)	−3767 (3)	2·66 (8)
C(1)	3699 (3)	−1930 (2)	−31 (3)	2·27 (8)
C(2)	3967 (3)	−837 (2)	1089 (3)	2·21 (8)
C(3)	2797 (3)	171 (3)	551 (3)	2·65 (9)
C(4)	1368 (3)	107 (3)	−1056 (4)	2·72 (10)
C(5)	1114 (3)	−980 (2)	−2107 (3)	2·20 (8)
C(6)	2253 (3)	−2001 (2)	−1633 (3)	2·35 (9)
H(1)	498 (4)	−335 (4)	−33 (4)	1·6 (7)
H(2)	615 (5)	−134 (4)	276 (5)	2·3 (7)
H(3)	591 (6)	−3 (4)	335 (6)	4·0 (10)
H(4)	301 (4)	94 (4)	128 (5)	1·9 (7)
H(5)	50 (4)	77 (3)	−143 (5)	1·4 (6)
H(6)	206 (4)	−271 (3)	−240 (4)	0·8 (6)

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computations were carried out at the Okayama University Computer Center. The programs used were *SIGM*, *HBLS*-5 and *DAPH* (Ashida, 1973).

Results and discussion

Molecular structure

Bond lengths and angles are shown in Fig. 1. The least-squares plane of the benzene ring and the displacements of atoms from the plane are listed in Table 2.

The benzene ring is planar within experimental error. The phenolic O atom lies in the ring plane, while the amino N atom deviates significantly from the plane, as

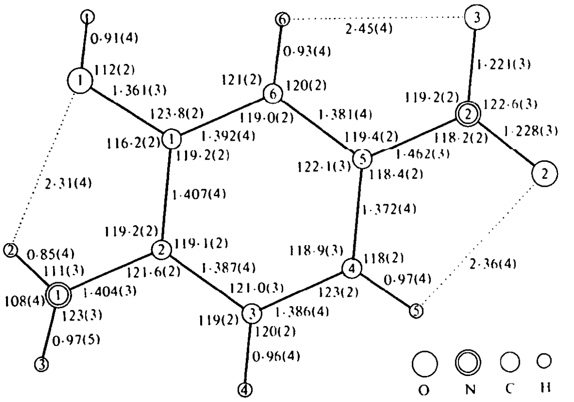

Fig. 1. Bond lengths (Å) and bond angles (°) with their e.s.d.'s in parentheses. Dotted lines show intramolecular O···H contacts.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35170 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *The least-squares plane of the benzene ring and displacements* (Å) *of atoms from the plane*

$X = ax + cz\cos\beta$, $Y = by$, $Z = cz\sin\beta$. Atoms marked with an asterisk were used for the calculation of the plane.

$$-0{\cdot}764X - 0{\cdot}426Y + 0{\cdot}484Z + 1{\cdot}560 = 0$$

C(1)*	−0·009 (3)	O(1)	0·018 (2)	H(2)	−0·19 (4)
C(2)*	0·008 (3)	N(1)	0·095 (2)	H(3)	−0·26 (4)
C(3)*	0·000 (3)	N(2)	0·046 (2)	H(4)	−0·04 (4)
C(4)*	−0·007 (3)	O(2)	0·120 (3)	H(5)	0·04 (4)
C(5)*	0·007 (3)	O(3)	0·002 (3)	H(6)	−0·02 (4)
C(6)*	0·002 (3)	H(1)	−0·39 (4)		

in 2-aminophenol (Ashfaquzzaman & Pant, 1979). The C(2)—N(1) length and the sum of the angles about N(1), 342°, correspond to values at the pyramidal N atom in anilines (Stålhandske, 1976), in contrast to 2,4,6-trinitro- and 2,3,4,6-tetranitroanilines (Holden, Dickinson & Bock, 1972; Dickinson, Stewart & Holden, 1966) in which the C—N lengths are shortened and the sums of the angles are close to 360°. C(1)—O(1) is longer than the corresponding distances in *o*-nitrophenols (Kagawa *et al.*, 1976; Iwasaki & Kawano, 1978).

The inner angle at C(5), which is attached to the nitro group, is enlarged, and the related bonds are shortened (Domenicano, Mazzeo & Vaciago, 1975). The C(5)—N(2) length agrees with the 1·457 Å estimated from the O—N—O angle (Kawai, Kashino & Haisa, 1976). The difference in the two N—O bond lengths is not significant, in contrast to *o*-nitrophenols involving an intramolecular hydrogen bond (Kawai *et al.*, 1976). The dihedral angle between the benzene ring and nitro group is 3·5°, which is comparable with those in *o*-nitrophenols.

Crystal structure

A projection of the crystal structure is shown in Fig. 2. The molecules, related by a *c* glide plane, are held together by O—H···NH$_2$ hydrogen bonds [O(1^{iii})···N(1^{i}) 2·801 (3), H(1^{iii})···N(1^{i}) 1·89 (4) Å, O(1^{iii})—H(1^{iii})···N(1^{i}) 174 (3)°, torsion angle C(6)—C(1)—O(1)—H(1) 30·9°] to form a ribbon along **c**. The long molecular axes are nearly parallel to the glide plane. The ribbons are held together by dipole–dipole interactions between molecules related by $\bar{1}$; the distances between the centres of their benzene rings are 4·37 Å for (i) and (v), and 5·07 Å for (i) and (ii), the shortest contacts being 3·40 Å for C(2^{i})···C(2^{v}) and 3·38 Å for C(4^{i})···C(4^{ii}). A short O···H contact of 2·37 Å is observed between H(3^{i}) and O(2^{iv}), but the angle N(1^{i})—H(3^{i})···O(2^{iv}) is 119°, as was found for the O(nitro) and H(phenolic) atoms in 2,4-dinitrophenol (Kagawa *et al.*, 1976).

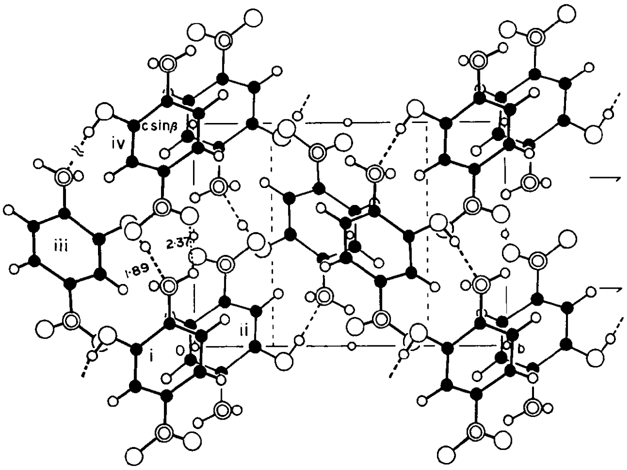

Fig. 2. Projection of the crystal structure along **a**. Broken lines show hydrogen bonds, and dotted lines intermolecular contacts. Distances are in Å. Symmetry code: (i) x,y,z; (ii) $-x,-y,-z$; (iii) $x,-\frac{1}{2}-y,\frac{1}{2}+z$; (iv) $1+x,y,1+z$; (v) $1-x,-y,-z$.

Morphotropism in amino- and nitrophenols

The crystal structures of amino- and nitrophenols are compared in Table 3, where 2-aminophenol (*Pbca*) is considered to be a prototype of these structures since the others belong to its subgroups (Haisa, 1978). The geometry of the hydrogen bonds in 2-aminophenol is as follows: O···N 2·783 (3), H···N 1·89 (5) Å, O—H···N 175 (5)°; N···O 3·122 (3), H···O 2·31 (4) Å, N—H···O 157 (4)° (Haisa *et al.*, unpublished). It should be noted that the structure of 2-aminophenol is very similar to that of benzene (Cox, Cruickshank & Smith, 1958), in spite of the existence of the intermolecular hydrogen bonds. The benzene rings in 2-aminophenol, related by a glide plane, are arranged with a dihedral angle δ of 87·7°, as in benzene ($\delta = 85{\cdot}0°$), and the cell dimensions *a*, *b* and *c* correspond to *a*, 2*b* and *c* in benzene, respectively. The doubling of *b* results from the loss of the $\bar{1}$ molecular symmetry.

In crystals of the other aminophenols the benzene rings are related by a glide plane and arranged as in 2-aminophenol [(*a*) in Table 3]. The similarity of the crystal structures is reflected in the axial length and the dihedral angle between the rings [(*b*) and (*c*) in Table 3]. The dihedral angles decrease upon descent to the non-centrosymmetric subgroups, whereas they do not change when descending to the centrosymmetric subgroup. Such an arrangement of the rings seems to be governed mainly by quadrupole–quadrupole interactions (Kihara, 1966). Crystals of 4- and 3-aminophenols choose the route of descent in symmetry which leads to the non-centrosymmetric subgroups, where no centrosymmetric pairing of the molecules by hydrogen bonds occurs [(*d*) and (*e*) in Table 3].

Table 3. *Comparison of the crystal structures of amino- and nitrophenols*

Substituent	Space group	Z	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
(1) 2-NH_2	*Pbca*	8	a-glide	a = 7·86	87·7	O–H···NH_2	2_1 along **c**
			2_1 along a	a = 7·86	82·2	HNH···OH	$\bar{1}$
(2) 4-NH_2	$Pna2_1$	4	a-glide	a = 8·19	69·8	O–H···NH_2	n-glide
(3) 3-NH_2	$Pca2_1$	4	c-glide	c = 8·287	43·7	O–H···NH_2	a-glide
(4) $2NH_2$, 4-Cl	$P2_1/c$	4	glide	c = 8·01	84·3	O–H···NH_2	2_1
						HNH···OH	$\bar{1}$
(5) 2-NH_2, 5-NO_2	$P2_1/c$	4	glide, $\bar{1}$	c = 8·05	50·4	O–H···NH_2	glide
(6) 4-NO_2 (α)	$P2_1/c$	4	$\bar{1}$, 2_1	b = 8·78	74·0	O–H···ONO	glide
(7) 4-NO_2 (β)	$P2_1/c$	4	$\bar{1}$, 2_1	b = 11·117	28·0	O–H···ONO	glide
(8) 3-NO_2	$P2_1/c$	4	$\bar{1}$, 2_1	b = 6·891	66·7	O–H···ONO	translation
(9) 2-NO_2	$P2_1/c$	4	$\bar{1}$, glide	c = 6·876	1·2	O–H···ONO	Intramolecular

(*a*) Operation relating neighbouring benzene rings. (*b*) Corresponding axes and their dimensions (Å). (*c*) Dihedral angle (°) between the benzene rings related by the glide or 2_1. (*d*) Type of hydrogen bond. (*e*) Operation relating the molecules linked by the hydrogen bond.

References: (1) Haisa *et al.*, unpublished. (2) Brown (1951). (3) de Rango, Brunie, Tsoucaris, Declercq & Germain (1974). (4) Ashfaquzzaman & Pant (1979). (5) This work. (6) Coppens & Schmidt (1965*a*). (7) Coppens & Schmidt (1965*b*). (8) Pandarese, Ungaretti & Coda (1975). (9) Iwasaki & Kawano (1978).

In the mononitrophenols, an antiparallel arrangement of the molecules related by $\bar{1}$ is observed, regardless of the type of hydrogen bonds and the operation relating the molecules linked by them, and these belong to a centrosymmetric maximal subgroup of *Pbca*. Thus, it may be said that the difference between the crystal structures of aminophenols and nitrophenols is mainly due to the remarkable dipole–dipole interactions of the nitro groups. The molecular arrangement in 2-amino-5-nitrophenol shows characteristics of both the amino- and nitrophenols; direct contacts between the benzene rings occur involving the rings related by the glide plane as well as those related by $\bar{1}$.

It is of note that the glide contact in 2-nitrophenol is determined by the nearly parallel overlapping of the aromatic rings as in weak π–π molecular complexes (Iwasaki & Kawano, 1978), and is thus different from that in the aminophenols. In the β form of 4-nitrophenol the dihedral angle takes a remarkably low value because of the side-by-side pairing of the molecules related by $\bar{1}$.

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