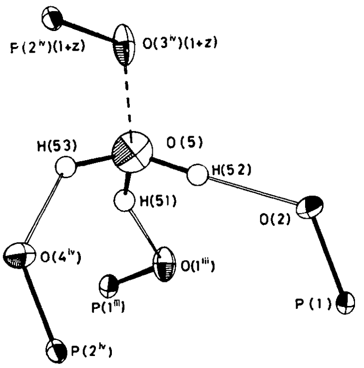

Fig. 2. The oxonium ion with four O atoms nearer than 3·0 Å to O(5); three of these are hydrogen bonded. The symmetry code is explained in Table 2.

positions. The larger difference for the transformation O(1) → O(3) can be explained by the strong hydrogen bond between these two atoms belonging to different molecules; the hydrogen-bonding pattern does not conform to $\bar{4}$ symmetry. All hydrogen bonds are listed in Table 2.

The one independent oxonium ion is shown in Fig. 2, with its four O atom neighbours having distances less than 3·0 Å from the central O atom. Only three of these O atoms are hydrogen bonded to the oxonium ion, at rather long distances; O(3) with a distance of 2·930 Å to O(5) has no H atom of the oxonium ion nearer than 2·85 Å, and its own H(3) does not bond to O(5). But O(3) as well as one more O(4) with a contact of 3·107 Å to O(5) would certainly belong to the coordination sphere of the cations in the acid alkali salts of this acid, $M_2^IH_2(NHPO_2)_4$, which are isomorphous with the dihydrate (Corbridge, 1953). There are no more contacts up to 3·34 Å.

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p-Cyanophenol

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Abstract. C_7H_5NO, orthorhombic, *Pbcn*, $a = 9{\cdot}190\,(4)$, $b = 10{\cdot}750\,(3)$, $c = 25{\cdot}460\,(4)$ Å, $Z = 16$, $D_x = 1{\cdot}259$ g cm^{-3}, μ(Cu $K\alpha$) = 7·16 cm^{-1}. The final R was 0·081 for 1825 reflexions measured photographically. The two independent molecules have similar dimensions, indicating a probable contribution from the quinonoid resonance structure, and are joined alternately head-to-tail by O–H···N hydrogen bonds to form infinite helical chains around 2_1 axes parallel to **c**.

Introduction. Colourless, plate-like crystals were grown from benzene solution. The systematic absences: $hk0$, $h + k = 2n + 1$; $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$, indicate the space group *Pbcn*. As $Z = 16$, there are two independent molecules in the asymmetric unit.

Intensity data were visually estimated from equi-inclination Weissenberg photographs taken around a and b axes with Ni-filtered Cu $K\alpha$ radiation, and reduced to a unique set of 1825 F values by application of the usual corrections. No absorption correction was applied.

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). The R value was reduced to 0·16 by block-diagonal least squares with isotropic thermal parameters. Anisotropic refinement, including isotropic H atoms located from a difference synthesis, converged to $R = 0{\cdot}11$.

Table 1. *Final atomic parameters* (× 10^4) *of the non-hydrogen atoms*

Anisotropic temperature factors are in the form: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1*A*)	2866 (3)	1386 (3)	5336 (1)	175 (4)	128 (3)	19 (1)	17 (3)	−15 (1)	−16 (1)
C(2*A*)	2119 (4)	953 (3)	4914 (1)	123 (4)	92 (3)	12 (1)	−8 (3)	−1 (1)	−2 (1)
C(3*A*)	2669 (4)	−77 (4)	4655 (1)	128 (5)	115 (4)	17 (1)	29 (4)	−7 (1)	−8 (1)
C(4*A*)	1949 (4)	−560 (4)	4226 (1)	138 (5)	123 (4)	15 (1)	26 (4)	−1 (1)	−9 (1)
C(5*A*)	673 (4)	−2 (3)	4052 (1)	118 (4)	93 (3)	12 (1)	−7 (3)	−1 (1)	0 (1)
C(6*A*)	130 (4)	1032 (3)	4316 (1)	121 (4)	90 (3)	18 (1)	5 (3)	−4 (1)	−3 (1)
C(7*A*)	842 (4)	1497 (3)	4749 (1)	130 (5)	72 (3)	19 (1)	5 (3)	−1 (1)	0 (1)
C(8*A*)	−72 (5)	−452 (4)	3599 (1)	158 (5)	110 (4)	16 (1)	−9 (4)	−6 (1)	0 (1)
N(9*A*)	−670 (4)	−795 (4)	3232 (1)	210 (6)	157 (5)	19 (1)	1 (4)	−20 (2)	−9 (1)
O(1*B*)	2544 (3)	−1943 (2)	2510 (1)	172 (4)	95 (2)	18 (1)	−32 (3)	−17 (1)	7 (1)
C(2*B*)	3323 (4)	−1175 (3)	2817 (1)	128 (4)	82 (3)	12 (1)	−7 (3)	−3 (1)	5 (1)
C(3*B*)	4335 (4)	−1725 (3)	3155 (1)	162 (5)	78 (3)	16 (1)	11 (3)	−9 (1)	5 (1)
C(4*B*)	5170 (4)	−1003 (4)	3481 (1)	150 (5)	102 (4)	15 (1)	22 (4)	−11 (1)	5 (1)
C(5*B*)	5000 (4)	286 (3)	3479 (1)	127 (4)	90 (3)	14 (1)	7 (3)	−4 (1)	−1 (1)
C(6*B*)	3989 (4)	834 (3)	3142 (1)	141 (5)	83 (3)	16 (1)	6 (3)	−7 (1)	2 (1)
C(7*B*)	3154 (4)	112 (3)	2817 (1)	123 (4)	87 (3)	15 (1)	10 (3)	−6 (1)	8 (1)
C(8*B*)	5826 (4)	1066 (4)	3823 (1)	144 (5)	114 (4)	17 (1)	17 (4)	−10 (2)	4 (1)
N(9*B*)	6452 (4)	1711 (4)	4098 (1)	203 (6)	129 (4)	24 (1)	16 (4)	−24 (2)	14 (1)

Table 2. *Positional parameters* (× 10^3) *of the hydrogen atoms and distances to the atoms to which they are bonded* (Å)

Temperature factors are assumed to be 3·67 Å^2.

	x	y	z	Distance
H(1*A*)	239 (5)	206 (4)	547 (2)	0·92 (4)
H(3*A*)	359 (4)	−39 (4)	480 (2)	0·99 (4)
H(4*A*)	229 (4)	−137 (4)	402 (2)	1·07 (5)
H(6*A*)	−76 (4)	140 (4)	418 (2)	0·97 (4)
H(7*A*)	52 (4)	222 (4)	475 (2)	0·83 (4)
H(1*B*)	191 (4)	−167 (4)	228 (2)	0·88 (4)
H(3*B*)	447 (4)	−268 (4)	315 (2)	1·03 (4)
H(4*B*)	587 (4)	−130 (4)	373 (2)	0·96 (4)
H(6*B*)	392 (4)	174 (4)	315 (2)	0·97 (4)
H(7*B*)	240 (5)	45 (4)	259 (2)	0·98 (4)

Introduction of an extinction correction for all reflexions following Zachariasen's (1963) equation reduced R to 0·081 after further refinements.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All the computations were carried out on the FACOM 230-75 computer at the Data Processing Center, Kyoto University. The programs used, except those mentioned specifically, are of the *KPAX* system including *UNICS* programs. The final atomic parameters are listed in Tables 1 and 2.*

Discussion. Bond lengths and angles are shown in Fig. 2. The corresponding values for the two independent molecules are in good agreement within the limit of experimental errors. Other structural features are also similar so that the molecular structure can be discussed with averaged dimensions.

The benzene ring is planar within experimental errors (Fig. 1). The O atom lies on the benzene plane, while the CN group deviates from it significantly. The average C—C bond length of the benzene ring (1·384 Å) is close to that in benzene, but the average value of the bonds parallel to the long molecular axis is 1·374 Å and is slightly short. Also the bonds connecting the two *para* substituents to the benzene ring, 1·353 Å for the mean C—O bond and 1·428 Å for the mean C—CN bond, are somewhat shorter than the generally accepted values, 1·36 and 1·44 Å respectively (*Molecular Structures and Dimensions*, 1972). This may be due to a contribution from the quinonoid resonance structure caused by the *para* substitution of the π-electron withdrawing and donating groups, as found in the case of *p*-nitrophenol (Coppens & Schmidt, 1965). The inequality of the two C—C—O angles, 122·4 and 117·4°, has been discussed by Hirshfeld (1964).

The two non-equivalent molecules are linked alternately head-to-tail by hydrogen bonds and form infinite helical chains around the 2_1 axes parallel to **c**. These chains are held together by van der Waals interactions. Fig. 3 shows the crystal structure.

There are two O—H···N hydrogen bonds with O···N distances of 2·82 and 2·84 Å having similar geometrical environments, both of which seem quite favourable for hydrogen bonding. In both cases the OH group lies nearly on the line of the C≡N bond and approaches the lone-pair electrons of the N atom, and the C—O···N angle, 115 or 117°, is close to the valence angle of the O atom, while the accepting N atom is

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32198 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

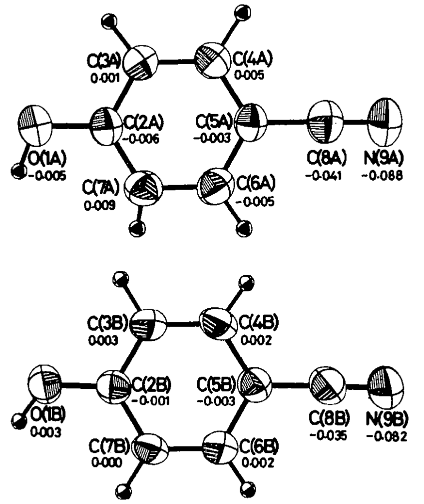

Fig. 1. *ORTEP* drawings (Johnson, 1965) of the molecules projected on each molecular plane, and deviations (Å) from the least-squares plane of benzene.

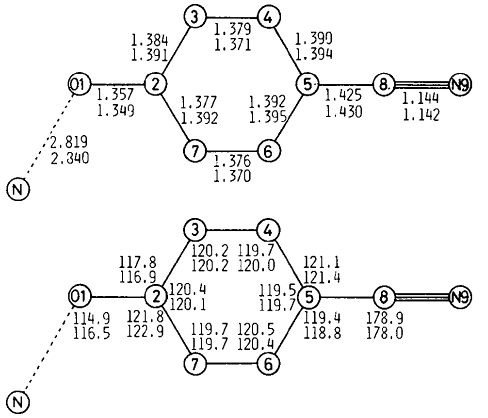

Fig. 2. Bond lengths (Å) and angles (°). E.s.d.'s are 0·04–0·06 Å for lengths, 0·3–0·5° for angles. Upper figures are values in molecule *A* and lower figures those in molecule *B*. Dashed lines represent hydrogen bonds.

located nearly on the plane of the proton-donating molecule.

The plane of each molecule is in face-to-face contact with that of its equivalent partner: molecules *A* are related by a centre of symmetry and molecules *B* by a twofold axis, with mean plane-to-plane distances of 3·55 and 3·49 Å respectively.

The intermolecular distances shorter than 3·6 Å are shown in Table 3. The shortest distance is the 3·21 Å C···O contact between two *B* molecules related by the *b*-glide operation. The others are longer than the sum of the van der Waals radii, but it may be worth noting that C···O or C···N pairs are dominant in the short contacts, suggesting Coulombic interactions between the residual charges on these atoms.

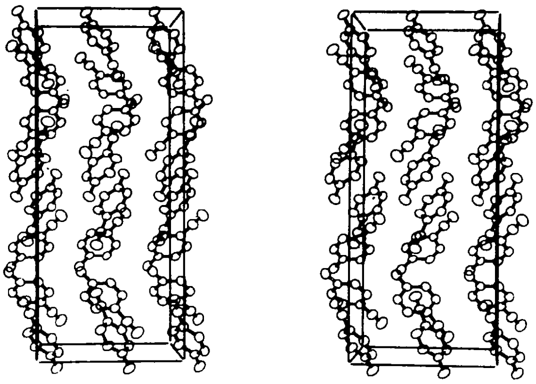

Fig. 3. Stereoscopic view of the crystal structure.

Table 3. *Intermolecular distances* (Å)

C(3*B*)···O(1*B*^{i})	3·34	C(6*B*)···O(1*B*^{iv})	3·21
C(3*B*)···C(2*B*^{i})	3·34	C(7*B*)···O(1*B*^{iv})	3·32
C(3*B*)···C(3*B*^{i})	3·55	C(7*B*)···O(1*A*^{iii})	3·54
C(4*B*)···O(1*B*^{i})	3·44	O(1*A*)···C(7*A*^{v})	3·57
C(2*B*)···C(2*B*^{i})	3·49	O(1*A*)···C(6*A*^{v})	3·58
C(2*B*)···C(4*B*^{i})	3·60	N(9*B*)···C(8*A*^{iv})	3·54
C(2*A*)···C(6*A*^{ii})	3·56	N(9*B*)···N(9*A*^{iv})	3·54
		N(9*B*)···C(7*A*^{v})	3·56

Symmetry code

(i)	$1-x,$	$y,$	$\frac{1}{2}-z$	(iv)	$\frac{1}{2}-x,$	$\frac{1}{2}+y,$	z
(ii)	$-x,$	$-y,$	$1-z$	(v)	$\frac{1}{2}+x,$	$\frac{1}{2}-y,$	$1-z$
(iii)	$1-x,$	$-y,$	$1-z$				

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