The Crystal and Molecular Structure of 2,6-Dinitrophenol

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Crystals of 2,6-dinitrophenol, $C_6H_4N_2O_5$, are orthorhombic, space group $P2_1nb$ with cell dimensions: $a = 11.943$ (9), $b = 12.430$ (9), $c = 4.829$ (6) Å and $Z = 4$. The structure was solved by the direct method and refined by the full-matrix least-squares method to the final R value of 0.041 for 657 diffractometer-collected reflexions. The hydroxyl group is linked to the oxygen atom of one nitro group forming a rather strong intramolecular hydrogen bond (O···O, 2.557 Å). This nitro group is almost coplanar with the benzene ring, the dihedral angle being 2.7°, whereas the other nitro group is twisted from the ring plane by 13.1°. The corresponding bond lengths in the two nitro groups are significantly different.

Introduction

It has been found that most of the phenols containing substituents such as nitro or carboxyl groups, both in *ortho* positions, give appreciable dielectric absorption, whereas in the corresponding mono-substituted compounds, absorption is absent. The absorption is due to the transition of the hydroxyl group from one hydrogen-bonded position to the other and the hydroxyl groups in the transition state are considerably influenced by neighbouring molecules (Meakins, 1955). The crystal structure analysis of 2,6-dinitrophenol was undertaken in order to examine the relationship between the dielectric absorption and the hydrogen-bonding scheme in the crystal.

Experimental

The crystals were grown from a cyclohexane solution of commercially available 2,6-dinitrophenol. They are yellow needles elongated along the c axis. Since the crystal sublimed slowly (m.p. 64°C), all X-ray data were obtained with the specimen enclosed in a thin glass capillary. Cell dimensions were calibrated with copper powder lines ($a = 3.6147$ Å) superposed on Weissenberg photographs (Cu K, $\bar{\alpha} = 1.5418$, $\alpha_1 = 1.5405$, $\alpha_2 = 1.5433$ Å).

Crystal data

$C_6H_4N_2O_5$, M.W. 184.1; orthorhombic, $a = 11.943$ (9), $b = 12.430$ (9), $c = 4.829$ (6) Å, $V = 716.9$ Å³; $Z = 4$, $D_x = 1.706$, $D_m = 1.70$ g cm⁻³; space group $P2_1nb$ (or $Pmnb$).

Intensity data were collected on a Rigaku automatic four-circle diffractometer using LiF-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). A specimen with approximate dimensions $0.3 \times 0.3 \times 0.2$ mm was mounted with its c axis slightly inclined to the φ axis of the diffractometer. The reflexions within the range $2\theta < 60°$ were measured by the ω–2θ scan technique at a scan rate of 1° min⁻¹. 657 independent reflexions were obtained which had intensities greater than $3\sigma(I)$.

Structure determination

Systematic absences found on the Weissenberg photographs were consistent with the space group $P2_1nb$ or

Table 1. *Statistics of the intensity data and phase assignments*

(*a*) Statistical average of the intensity data

| | | Theoretical | |
	Observed	Centric	Acentric
$\langle|E|\rangle$	1.000	1.000	1.000
$\langle|E|^2\rangle$	0.891	0.798	0.886
$\langle|E^2 - 1|\rangle$	0.733	0.968	0.736

(*b*) Phase assignments for specifying the origin and symbols

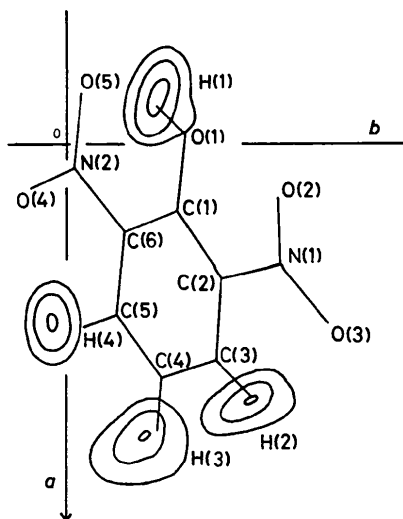| h	k	l	$|E|$	φ
0	3	1	3.92	0
3	6	0	2.80	0
1	2	1	2.45	π
11	0	1	3.30	a
7	6	2	2.29	b
4	5	3	2.20	c

Fig. 1. Sections of the difference Fourier synthesis. The contours are at intervals of 0.1eÅ⁻³, starting at 0.1eÅ⁻³.

Pmnb. The statistical average of the intensity data [Table 1(*a*)] indicated that the crystal was non-centrosymmetric and the space group *P*2₁*nb* was chosen.

The structure was solved by the symbolic addition method (Karle & Karle, 1966). Table 1(*b*) shows the reflexions used to fix the origin and the assignment of unknown symbols. From the $\sum_2$ relationships, it became apparent that *c*=*a*, *b*=*a*−*π* and *a*=*π*/3, *π* or 5*π*/3. For the set of *a*=*π*, all phases became 0 or *π*. Then *a* was chosen to be 5*π*/3 which specified the enantiomorph. The phases were extended by the tangent formula using the program *DP*-5 written by S. R. Hall.
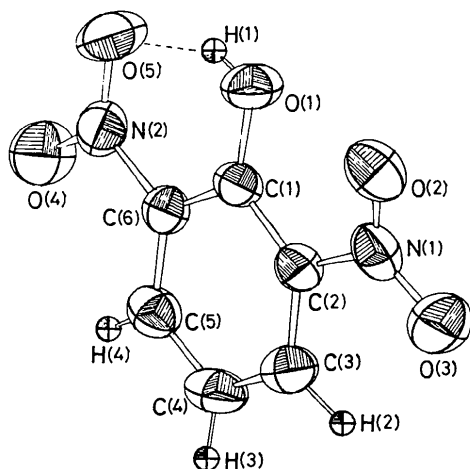

Fig. 2. Perspective drawing of the molecule showing the thermal ellipsoid with a probability of 50% [program *ORTEP* by Johnson (1965)]. Hydrogen atoms are represented by 0·1 Å radius spheres.

An *E* map using the phases for 256 reflexions with |*E*| ≥ 1·0 was calculated and this map clearly revealed the location of all the 13 non-hydrogen atoms. Three cycles of block-diagonal least-squares refinement with isotropic temperature factors gave an *R* value of 0·21. Anisotropic temperature factors were introduced and the refinement was continued to an *R* value of 0·078. The positions of four hydrogen atoms were determined on a difference Fourier map as shown in Fig. 1. Further refinement including hydrogen atoms with isotropic temperature factors was carried out by two cycles of full-matrix least-squares calculations with the program *ORFLS* (Busing, Martin & Levy, 1962). The final *R* value was 0·041 (weighted *R*=0·035). The quantity minimized was $\sum w(|F_o|-k^{-1}|F_c|)^2$ where $w=1/\sigma^2(F_o)$, as derived from counting statistics. Atomic scattering factors for carbon, nitrogen and oxygen were obtained from *International Tables for X-ray Crystallography* (1962). The hydrogen scattering factors were those of Stewart, Davidson & Simpson (1965). Final atomic parameters are listed in Table 2.*

Results and discussion

Thermal motion

The thermal ellipsoids of atoms and the numbering scheme are shown in Fig. 2. The molecular motion has been analysed in terms of the rigid-body vibrations of translation (T) and libration (ω), using the approach

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31163 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic parameters with their estimated standard deviations*

(*a*) Atomic coordinates (× 10⁴) and thermal parameters (× 10³) of non-hydrogen atoms.

The anisotropic temperature factors are of the form:

$$\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\}.$$

The B_{eq} values are the equivalent isotropic temperature factors.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
C(1)	887 (4)	1508 (4)	5214 (10)	34 (2)	42 (2)	47 (3)	5 (2)	5 (2)	8 (2)	3·2
C(2)	1767 (5)	2130 (4)	6264 (11)	39 (2)	41 (2)	44 (3)	4 (2)	−4 (2)	4 (2)	3·3
C(3)	2845 (5)	2043 (5)	5249 (12)	39 (2)	56 (3)	56 (3)	−4 (2)	1 (2)	1 (3)	4·0
C(4)	3083 (5)	1313 (5)	3152 (11)	34 (2)	68 (3)	59 (3)	7 (2)	9 (2)	4 (3)	4·2
C(5)	2257 (5)	680 (4)	2116 (11)	46 (3)	50 (3)	47 (3)	7 (2)	6 (2)	1 (2)	3·8
C(6)	1168 (5)	783 (3)	3109 (10)	40 (2)	38 (2)	43 (3)	1 (2)	4 (2)	9 (2)	3·2
N(1)	1590 (5)	2919 (3)	8498 (9)	57 (3)	44 (2)	52 (3)	14 (2)	−10 (2)	0 (2)	4·1
N(2)	314 (5)	121 (3)	1791 (9)	53 (2)	42 (2)	57 (3)	−4 (2)	−7 (2)	1 (2)	4·0
O(1)	−153 (5)	1638 (3)	6185 (8)	35 (2)	67 (2)	66 (2)	−3 (2)	8 (2)	−16 (2)	4·4
O(2)	721 (5)	2900 (3)	9805 (8)	65 (2)	65 (2)	52 (2)	13 (2)	5 (2)	−9 (2)	4·8
O(3)	2342 (5)	3562 (3)	8938 (10)	62 (2)	72 (3)	108 (3)	−7 (2)	−14 (3)	−32 (3)	6·4
O(4)	581 (5)	−477 (3)	−86 (9)	71 (3)	76 (3)	73 (3)	−3 (2)	−3 (2)	−30 (2)	5·8
O(5)	−669 (5)	206 (3)	2603 (10)	43 (2)	86 (3)	90 (3)	−16 (2)	5 (2)	−20 (3)	5·8

(*b*) Atomic coordinates (× 10³) and thermal parameters (Å²) of hydrogen atoms.

	x	y	z	B (Å²)
H(1)	−51 (4)	127 (3)	525 (9)	2·7 (11)
H(2)	341 (4)	258 (3)	573 (9)	3·2 (10)
H(3)	380 (4)	124 (4)	263 (12)	4·6 (12)
H(4)	243 (4)	24 (4)	63 (10)	4·0 (11)

Table 3. *Rigid-body thermal parameters*

Principal axes of the molecule relative to the crystal axes.

Moment of inertia (atomic weight Å²)	Direction cosines (× 10³)		
279	293	699	647
841	−895	70	361
1115	−199	712	−672

Molecular vibration tensors

Translation $\mathbf{T}$ (× 10²) (Å²)

$$\begin{pmatrix} 4\cdot8\ (2) & 0\cdot1\ (2) & -0\cdot2\ (2) \\ & 3\cdot4\ (3) & 0\cdot0\ (3) \\ & & 2\cdot6\ (4) \end{pmatrix}$$

Libration ω (deg²)

$$\begin{pmatrix} 28\ (4) & 8\ (2) & -2\ (2) \\ & 20\ (2) & 3\ (1) \\ & & 11\ (1) \end{pmatrix}$$

Principal axes of the T and ω tensors relative to the molecular axes.

R.m.s. amplitude	Direction cosines (× 10³)		
0·16 Å	82	−8	997
0·18	81	−997	−15
0·22	993	82	−81
3·0°	288	−471	834
4·2	455	−699	−552
5·8	843	538	13

described by Cruickshank (1956). Some rigid-body thermal parameters of the molecule are given in Table 3.

Molecular dimensions

The bond lengths and bond angles with their estimated standard deviations are given in Fig. 3. The hydroxyl group is linked to the oxygen atom, O(5), of one of the two nitro groups forming a rather strong intramolecular hydrogen bond (O$\cdots$O, 2·557 (8) Å). The non-bonded intramolecular distance of O(1)$\cdots$ O(2) is 2·570 (8) Å. Although the geometry is favourable for hydrogen bonding, no hydrogen atom seems to exist between these oxygen atoms: the maximum electron density at the position for a hydrogen atom between O(1) and O(2) was 0·16 e Å^{-3} in the final difference map. This is comparable with the residual electron density maxima corresponding to the bonding electrons (0·14~0·18 e Å^{-3}), whereas an average background peak was 0·10 e Å^{-3} in this difference map. The full-matrix least-squares refinement was carried out for a model in which the hydrogen atoms are disordered between two positions: H(1) and H(1'). The multiplicity for H(1'), located between O(1) and O(2), became less than 0·1 ($R=0·040$ and weighted $R=0·035$), with O(1)–H(1') and H(1')$\cdots$O(2) distances, 1·07 (42)

and 1·88 (42) Å, and C(1)O(1)H(1') and O(1)H(1')O(2) angles, 126 (30)° and 119 (22)°, respectively. A very small amount of a hydrogen atom might reverse its direction, hydrogen-bonding to the other nitro group.

The average C–C bond length in the benzene ring (1·387 Å) is close to the value found in benzene, 1·392 Å (Cox, Cruickshank & Smith, 1958), but C(1)–C(2) (1·400 Å) and C(1)–C(6) (1·399 Å) lengths are somewhat longer and C(4)–C(5) (1·358 Å) length is significantly shorter than the rest. Bond angles of C(1)C(2)–C(3) and C(1)C(6)C(5) are 121·9 and 122·3°, respectively, which are in reasonable agreement with the corresponding values for the nitrobenzenes (Iwasaki & Saito, 1970). The C(2)C(1)C(6) angle is 116·0° which is slightly smaller than the corresponding values for the other phenols (Perrin & Michel, 1973; Neuman & Gillier-Pandraud, 1973; Antona, Longchambon, Vandenborre & Becker, 1973). The bond length of C(1)– O(1), 1·337 Å, is shorter than those of isovanillin (Iwasaki, 1973), o-vanillin (Iwasaki, Tanaka & Aihara, 1975), p-hydroxybenzaldehyde (Iwasaki, Sato & Aihara, 1973), and cresols (Bois, 1970; 1972; 1973). The length of C(6)–N(2), 1·457 Å, is shorter than that of C(2)–N(1), 1·473 Å. The latter is normal for the C–N bond of nitrobenzenes. The average value of the N–O distances, except N(2)–O(5) (1·242 Å), is 1·217 Å which is the normal value for nitro compounds. The short C(1)–O(1) and N(2)–C(6) and the long N(2)–O(5) bonds are ascribed to the strong intramolecular hydrogen bond. These dimensions and significant departures from a hexagonal symmetry in the benzene ring of the molecule are quite compatible with the difference in π-bond orders calculated by the CNDO/2 method as shown in Fig. 3.

Least-squares planes through various groups of atoms in the structure are presented in Table 4. The benzene ring is planar, deviations being within 0·009 Å. The dihedral angle between planes I (benzene ring) and II (nitro group) is 13·1° and the nitro group is twisted around the C(2)–N(1) axis. The dihedral angle between planes I and III (nitro group bound by the hydrogen bond) is only 2·7°.

Molecular packing

The arrangement of the molecules in the crystal is shown in Fig. 4. Intermolecular contacts less than 3·60 Å

Table 4. *Least-squares planes*

Equations of planes are expressed in the form: $AX + BY + CZ = D$, where X, Y and Z are the coordinates in Å referred to the axes a, b and c, respectively.

		A	B	C	D
(I)	Benzene ring C(1) ~ C(6)	0·1951	−0·7005	0·6864	0·6260
(II)	Nitro group C(2), N(1), O(2), O(3)	0·4111	−0·6339	0·6555	1·1699
(III)	Nitro group C(6), N(2), O(4), O(5)	0·1642	−0·7283	0·6651	0·5209
(IV)	Hydroxyl group C(1), O(1), H(1)	0·1424	−0·7563	0·6385	0·3410
(V)	Chelate ring C(1), O(1), O(5), N(2), C(6)	0·1596	−0·7157	0·6800	0·5431

Table 4 (cont.)

Deviations (Å × 10³) of atoms from the least-squares planes

(I)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	O(1)*
	4	−7	2	6	−9	5	38
	N(1)*	O(2)*	O(3)*	N(2)*	O(4)*	O(5)*	
	−20	−27	22	64	103	99	
(II)	C(2)	N(1)	O(2)	O(3)			
	0	1	−1	1			
(III)	C(6)	N(2)	O(4)	O(5)	C(1)*	O(1)*	H(1)*
	2	−7	3	3	37	47	81
(IV)	C(1)	O(1)	H(1)	O(5)*			
	0	0	0	−154			
(V)	C(1)	O(1)	O(5)	N(2)	C(6)	H(1)*	
	3	−1	−1	2	−4	44	

* Atoms not used to define the least-squares plane.

Dihedral angles between planes

Planes		Dihedral angle
(I)	(II)	13·10°
(I)	(III)	2·67
(I)	(IV)	5·19
(I)	(V)	2·24
(III)	(IV)	2·55

Table 5. Intermolecular contacts less than 3·6 Å

Symmetry code

Super-script				Super-script			
None	x	y	z	(iv)	x	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(i)	x	y	$1+z$	(v)	x	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
(ii)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	(vi)	$-\frac{1}{2}+x$	$-y$	$-z$
(iii)	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	(vii)	$\frac{1}{2}+x$	$-y$	$1-z$

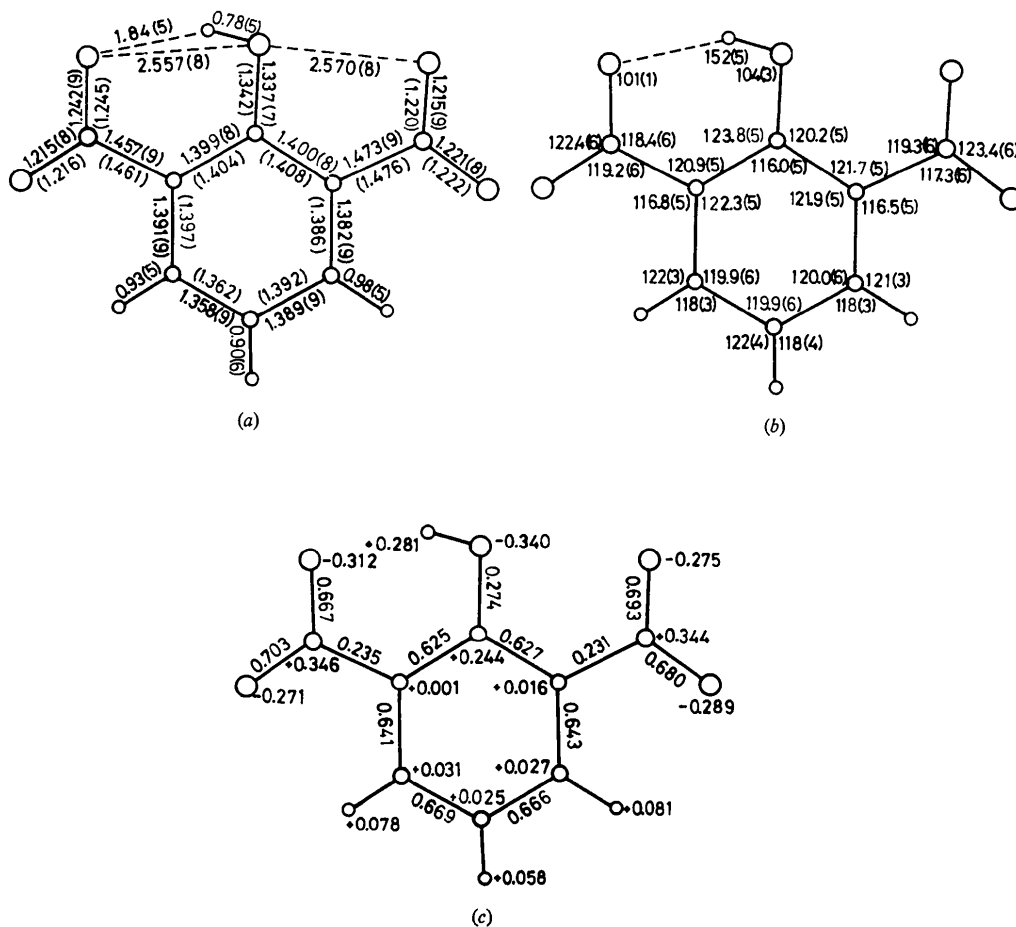|				
C(1)···O(4ⁱ)	3·372 (7)		O(2)···C(4ⁱⁱⁱ)	3·394 (8)
C(2)···C(5ⁱ)	3·403 (8)		C(2)···O(4ⁱᵛ)	3·342 (8)
N(1)···C(4ⁱ)	3·495 (8)		N(1)···O(4ⁱᵛ)	2·853 (8)
O(1)···O(4ⁱ)	3·305 (8)		O(2)···O(4ⁱᵛ)	3·048 (8)
O(2)···C(1ⁱ)	3·140 (8)		O(3)···O(4ⁱᵛ)	3·051 (8)
O(2)···C(2ⁱ)	3·494 (8)		C(5)···O(3ᵛ)	3·251 (8)
O(2)···C(5ⁱ)	3·497 (8)		C(6)···O(3ᵛ)	3·409 (8)
O(2)···C(6ⁱ)	3·123 (8)		N(2)···O(2ᵛ)	3·249 (9)
O(3)···C(4ⁱ)	3·569 (8)		O(4)···O(2ᵛ)	3·256 (8)
O(3)···O(1ⁱⁱ)	3·193 (8)		O(4)···C(4ᵛⁱ)	3·489 (8)
O(3)···O(5ⁱⁱ)	2·900 (8)		O(5)···C(5ᵛⁱ)	3·542 (9)
O(1)···C(3ⁱⁱⁱ)	3·500 (8)		C(3)···O(5ᵛⁱⁱ)	3·471 (9)
O(1)···C(4ⁱⁱⁱ)	3·439 (8)		C(4)···O(5ᵛⁱⁱ)	3·161 (9)
O(2)···C(3ⁱⁱⁱ)	3·441 (9)			

(a)

(b)

(c)

Fig. 3. (a) Bond lengths (Å) and their estimated standard deviations in parentheses. Bond lengths in parentheses are values corrected for the thermal motion. (b) Bond angles (°) and their estimated standard deviations in parentheses. (c) The π-bond orders and net charges calculated by the CNDO/2 method.

are listed in Table 5. It should be noted that all the shorter contacts involve oxygen atoms in the nitro groups, *e.g.*O(3)$\cdots$O(5)(2·900Å), O(3)$\cdots$O(4) (3·051 Å), O(2)$\cdots$O(4) (3·048 Å), C(6)$\cdots$O(2) (3·123 Å) and N(1)$\cdots$O(4) (2·853 Å). On the other hand, O(1) of the hydroxyl group has rather loose contacts with the neighbouring molecules [O(1)$\cdots$O(3), 3·193 and O(1)$\cdots$C(4), 3·439 Å], which are longer than the sum of the van der Waals radii.

Two nitro groups are not equivalent with respect to the hydrogen bonding, in spite of the molecular geometry in which both O(2) and O(5) might form an intramolecular hydrogen bond with the hydroxyl group. There must be an energy difference between the two positions of equilibrium of the hydroxyl group due to the molecule being unsymmetrically placed with regard to neighbouring molecules in the crystal lattice. The hydroxyl group might perform transitions between the two hydrogen-bonded positions over an energy barrier by an electric field which is partly determined by the energy required to break the hydrogen bond.

The molecular structure determined in the present work explains the dielectric absorption due to the rotating hydroxyl group between the two *ortho* substituents.

All crystallographic computations were performed on a HITAC 8800 computer at the Computer Centre of the University of Tokyo using the program system UNICS (Crystallographic Society of Japan, 1967; Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967). The calculation of the CNDO/2 method was performed with the program written by Dr T. Kobayashi.
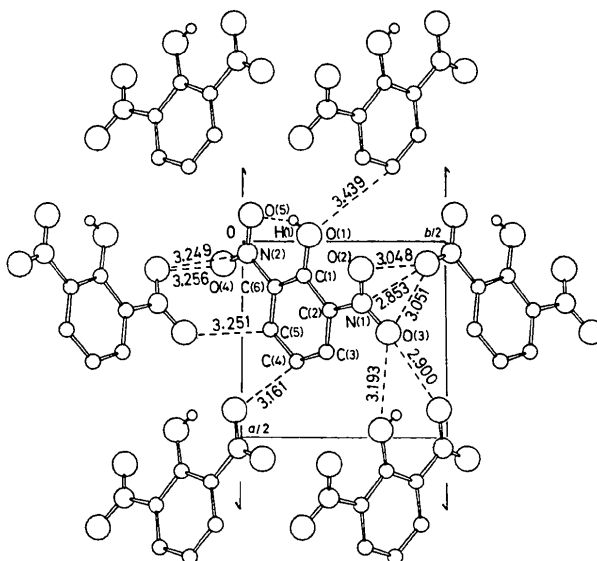
Fig. 4. Projection of the structure along the *c* axis.

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