The Crystal and Molecular Structure of 2,4-Dinitrophenol

By Fujiko Iwasaki and Yasuomi Kawano

Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo 182, Japan

Crystals of 2,4-dinitrophenol, $C_6H_4N_2O_5$, are orthorhombic, space group $P2_12_12_1$ with cell dimensions: $a =$ 6·102 (3), $b = 23·202$ (8), $c = 5·178$ (4) Å and $Z = 4$. The structure was solved by an inspection of a Patterson map and R maps and refined by the full-matrix least-squares method to the final R value of 0·048 for 885 diffractometer-collected reflexions. The hydroxyl group is linked to one of the O atoms of the *ortho*-nitro group forming an intramolecular hydrogen bond ($O \cdots O$, 2·615 Å). There is a rather short intermolecular contact between the hydroxyl O and that of the *ortho*-nitro group ($O \cdots O$, 2·894, $H \cdots O$, 2·31 Å and $O-H \cdots O$, 124°). The H atom of the hydroxyl group is involved in a bifurcated hydrogen-bonding system.

Introduction

Recently, the crystal structure of 2,6-dinitrophenol (2,6-DNP, di-*ortho* substituted phenol) has been reported, in which the intramolecular hydrogen bond is formed between the hydroxyl group and the O atom of one of the *o*-nitro groups (Iwasaki, Sato & Aihara, 1976). IR studies on dinitrophenols showed a remarkable difference between 2,6-DNP and other dinitrophenols (Aihara & Hirai, 1976). The crystal structure analysis of 2,4-dinitrophenol (2,4-DNP) was undertaken in order to examine the hydrogen-bonding scheme for mono-*ortho* substituted phenols.

Experimental

The crystals were grown from a cyclohexane–benzene solution of commercially available 2,4-dinitrophenol. They are pale-yellow pillars elongated along **c**. Cell dimensions were obtained from Weissenberg photographs calibrated against Cu powder lines ($a = 3·6147$ Å, Cu K, $\alpha_1 = 1·5405$, $\bar{\alpha} = 1·5418$ Å).

Crystal data

$C_6H_4N_2O_5$, $M_r = 184·11$; orthorhombic, $a = 6·102$ (3), $b = 23·202$ (8), $c = 5·178$ (4) Å, $U = 733·1$ Å³; $Z = 4$, $D_x = 1·668$, $D_m = 1·67$ g cm⁻³; space group $P2_12_12_1$; m.p. 114°C.

Intensity data were collected on a Rigaku automatic four-circle diffractometer, with Mo $K\alpha$ radiation monochromatized by a graphite monochromator. An ω–2θ scan technique was used to obtain intensities with a scan width $\Delta\omega = 1·0° + 0·5° \tan\theta$ and a scan speed of 2° min⁻¹ in 2θ. At both ends of the scan range for each reflexion, background was counted for 10 s. 1295 reflexions in the range $2\theta \leq 60°$ were measured, of these 885 had $|F_0| \geq 3\sigma(F)$ and were considered as observed.

Structure determination

The orientation of the benzene ring was deduced from a Patterson map. R maps were calculated with the 75 $hk0$ reflexions. The lowest R value was 0·45. z parameters were obtained from R maps of the 244 hkl reflexions ($\sin\theta \leq 0·3$). Block-diagonal least-squares refinement with isotropic temperature factors reduced the R value to 0·15 for all the reflexions. After additional cycles of least-squares refinement with anisotropic temperature factors R was reduced to 0·072. H atoms were located from a difference Fourier synthesis and were included in the full-matrix least-squares refinement with isotropic

Table 1. *Atomic parameters with their estimated standard deviations*

(a) Atomic coordinates ($\times 10^4$) of non-hydrogen atoms. The B_{eq} values are the equivalent isotropic temperature factors (Å²).

	x	y	z	B_{eq}
C(1)	109 (6)	1126 (1)	2177 (8)	3·0
C(2)	1278 (6)	913 (1)	4315 (7)	2·8
C(3)	3232 (6)	1164 (1)	5088 (7)	2·8
C(4)	3963 (5)	1630 (1)	3724 (7)	2·7
C(5)	2864 (6)	1855 (1)	1614 (7)	3·0
C(6)	944 (6)	1604 (2)	855 (8)	3·1
N(2)	501 (6)	421 (1)	5775 (7)	3·6
N(4)	6023 (5)	1914 (1)	4560 (7)	3·5
O(1)	−1792 (5)	914 (1)	1278 (6)	4·1
O(21)	−1201 (5)	182 (1)	5040 (6)	5·5
O(22)	1532 (5)	265 (1)	7671 (6)	4·7
O(41)	6892 (5)	1738 (1)	6526 (6)	5·5
O(42)	6735 (4)	2306 (1)	3237 (6)	4·3

(b) Atomic coordinates ($\times 10^3$) and thermal parameters (Å²) of hydrogen atoms

	x	y	z	B
H(1)	−205 (7)	58 (1)	203 (8)	6·3 (13)
H(3)	401 (5)	99 (1)	663 (7)	4·2 (9)
H(5)	334 (6)	220 (1)	82 (7)	4·7 (10)
H(6)	19 (5)	173 (1)	−76 (7)	2·4 (7)

temperature factors. The final R value was 0·048 for all observed reflexions. The quantity minimized was $\Sigma\ w(|F_o| - k^{-1}|F_c|)^2$ where $w = 1/\sigma^2(F_o)$, as derived from counting statistics. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are listed in Table 1.*

Results and discussion

Thermal motion

The thermal ellipsoids of the atoms and the numbering scheme are shown in Fig. 1. The molecular motion

* Lists of structure factors and the anisotropic temperature factors of the non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32493 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
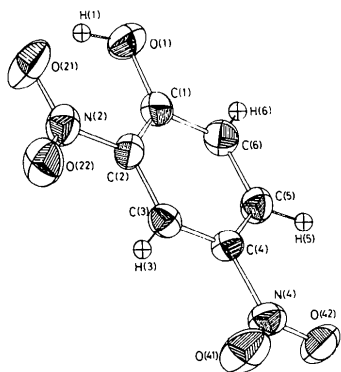

Fig. 1. Perspective drawing of the molecule showing the thermal ellipsoids with a probability of 50% [program *ORTEP* by Johnson (1965)]. Hydrogen atoms are represented by 0·1 Å radius spheres.

Table 2. *Rigid-body thermal parameters*

Molecular vibration tensors

Translation T × 10^3 (Å²)

$$\begin{pmatrix} 34\,(2) & 0\,(2) & -2\,(2) \\ & 33\,3) & 2\,(3) \\ & & 25\,(4) \end{pmatrix}$$

Libration L (deg²)

$$\begin{pmatrix} 21\,(3) & -6\,(1) & 1\,(2) \\ & 17\,(2) & 1\,(1) \\ & & 9\,(1) \end{pmatrix}$$

Principal axes of the T and L tensors relative to the crystal axes.

R.m.s. amplitude	Direction cosines (× 10^3)		
0·155 Å	−454	795	404
0·182	−269	310	−912
0·185	850	522	073
3·00°	−718	566	405
3·63	−577	−159	−801
5·02	389	809	−441

R.m.s. $\Delta(U_{ij})$ 0·0058 Å²

has been analysed in terms of the rigid-body vibrations of translation (T) and libration (L), taking into account the correlation tensors (Schomaker & Trueblood, 1968). Some rigid-body thermal parameters of the molecules are given in Table 2.

Molecular structure

The bond lengths and bond angles with their estimated standard deviations are given in Table 3. Least-squares planes through various groups of atoms in the structure are presented in Table 4. The hydroxyl group is linked to the O atom, O(21), of the *o*-nitro group forming an intramolecular hydrogen bond. The O(1)···O(21) distance is 2·615 (5) Å, which is longer than the corresponding hydrogen-bond distances found in 2,6-DNP (Iwasaki, Sato & Aihara, 1976), 2-chloro-4,6-dinitrophenol (2-Cl-4,6-DNP, Andersen & Andersen, 1975) and 2-bromo-4,6-dinitrophenol (2-Br-4,6-DNP, Neustadt & Cagle, 1975).

The benzene ring is planar, deviations being within 0·004 Å. The H(1) atom in the hydroxyl group deviates significantly from the plane of the benzene ring. The dihedral angles between the benzene ring and the planes of the substituents are 10·8° (hydroxyl group), 2·6° (*o*-nitro group) and 4·8° (*p*-nitro group).

Table 3. *Bond distances (Å) and angles (°)*

Bond lengths in parentheses are values corrected for the thermal motion.

C(1)—C(2)	1·407 (6)	(1·411)	O(1)—H(1)	0·89 (4)	
C(1)—C(6)	1·398 (6)	(1·402)	C(3)—H(3)	1·01 (4)	
C(2)—C(3)	1·385 (5)	(1·391)	C(5)—H(5)	0·95 (4)	
C(3)—C(4)	1·366 (5)	(1·371)	C(6)—H(6)	1·00 (4)	
C(4)—C(5)	1·385 (5)	(1·390)	O(21)···H(1)	1·88 (4)	
C(5)—C(6)	1·366 (6)	(1·370)			
C(1)—O(1)	1·343 (5)	(1·344)			
C(2)—N(2)	1·449 (5)	(1·452)			
C(4)—N(4)	1·484 (5)	(1·486)			
N(2)—O(21)	1·237 (5)	(1·240)			
N(2)—O(22)	1·221 (5)	(1·225)			
N(4)—O(41)	1·218 (5)	(1·220)			
N(4)—O(42)	1·219 (5)	(1·221)			
O(1)···O(21)	2·610 (5)	(2·615)			

C(2)C(1)C(6)	118·6 (4)	C(3)C(4)N(4)	118·5 (3)	
C(1)C(2)C(3)	121·1 (4)	C(5)C(4)N(4)	118·2 (3)	
C(2)C(3)C(4)	117·6 (4)	C(4)N(4)O(41)	117·6 (3)	
C(3)C(4)C(5)	123·3 (4)	C(4)N(4)O(42)	118·0 (3)	
C(4)C(5)C(6)	118·8 (4)	O(41)N(4)O(42)	124·4 (4)	
C(1)C(6)C(5)	120·6 (4)	C(1)O(1)H(1)	109 (3)	
C(2)C(1)O(1)	125·6 (4)	C(2)C(3)H(3)	118 (2)	
C(6)C(1)O(1)	115·8 (4)	C(4)C(3)H(3)	125 (2)	
C(1)C(2)N(2)	121·4 (4)	C(4)C(5)H(5)	121 (2)	
C(3)C(2)N(2)	117·5 (3)	C(6)C(5)H(5)	120 (2)	
C(2)N(2)O(21)	117·9 (3)	C(1)C(6)H(6)	118 (2)	
C(2)N(2)O(22)	119·0 (3)	C(5)C(6)H(6)	121 (2)	
O(21)N(2)O(22)	123·1 (4)	N(2)O(21)···H(1)	105 (1)	
		O(1)H(1)···O(21)	138 (4)	

Table 4. *Least-squares planes*

Deviations (Å) of atoms from the least-squares planes expressed in the form: $AX + BY + CZ + D = 0$, where X, Y and Z are the coordinates in Å referred to the axes a, b and c respectively.

(I) Benzene ring
$$0.5081X - 0.6116Y - 0.6065Z + 2.2511 = 0$$

C(1)	0.003	N(2)*	−0.005
C(2)	−0.004	N(4)*	−0.029
C(3)	0.004	O(21)*	0.038
C(4)	−0.002	O(22)*	−0.059
C(5)	0.000	O(41)*	−0.127
C(6)	−0.001	O(42)*	0.051
O(1)*	−0.003	H(1)*	0.153

(II) Nitro group
$$0.5422X - 0.6105Y - 0.5773Z + 2.1604 = 0$$

C(2)	−0.001	O(21)	−0.001
N(2)	0.003	O(22)	−0.001

(III) Nitro group
$$0.5288X - 0.6565Y - 0.5380Z + 2.2409 = 0$$

C(4)	0.000	O(41)	0.000
N(4)	−0.001	O(42)	0.000

(IV) Hydroxyl group
$$0.4937X - 0.4706Y - 0.7313Z + 2.0218 = 0$$

C(1)	0.000	H(1)	0.000
O(1)	0.000	O(21)*	−0.447

(V) Chelate ring
$$0.5176X - 0.6017Y - 0.6083Z + 2.2340 = 0$$

C(1)	0.010	O(1)	−0.011
C(2)	0.003	H(1)*	0.136
N(2)	−0.015	O(22)*	−0.068
O(21)	0.013		

Dihedral angles between planes.

Planes		Dihedral angle
(I)	(II)	2.58°
(I)	(III)	4.84
(I)	(IV)	10.83
(I)	(V)	0.79
(II)	(IV)	12.26

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

Table 5. *Comparison of some bond lengths (Å) and angles (°) in nitrophenols*

|	a^*	b^*	c	d	e	Average value	f
1	1.411	1.404	1.407	1.397	1.401	1.404	1.396
2	1.391	1.397	1.370	1.385	1.378	1.384	1.382
3	1.371	1.362	1.376	1.371	1.357	1.367	1.393
4	1.390	1.392	1.382	1.396	1.391	1.390	1.394
5	1.370	1.386	1.370	1.374	1.373	1.375	1.378
6	1.402	1.408	1.402	1.397	1.373	1.396	1.399
7	1.344	1.342	1.333	1.333	1.342	1.339	1.361
8	1.452	1.461	1.464	1.451	1.442	1.454	
9	1.240	1.245	1.235	1.230	1.240	1.238	
10	1.225	1.216	1.197	1.218	1.199	1.211	
11	1.486	1.476	1.472	1.478		1.478	1.450
12	2.615	2.562	2.558	2.559	2.587	2.584	2.84
E.s.d.	0.006	0.008	0.007	0.008	0.007		0.005
1	118.6	116.0	116.7	117.2	117.2	117.1	120.5
2	115.8	120.0	118.5	117.6	117.3	117.8	116.5
3	125.6	123.8	124.8	125.2	125.5	125.0	123.0
4	121.1	122.3	122.7	122.5	121.9	122.1	
5	121.4	120.9	120.1	120.7	120.6	120.7	
6	117.9	116.8	117.1	116.8	117.5	117.2	
7	123.1	122.4	123.4	122.3	122.0	122.6	
8	117.9	118.4	117.7	118.8	118.8	118.3	
9	119.0	119.2	118.9	118.9	119.2	119.0	
10	123.3	122.3	123.0	123.1	120.4	122.4	122.0
E.s.d.	0.4	0.5	0.4	0.5	0.5		0.4
11	109	104	107	108	109	107	113

References: (*a*) 2.4-Dinitrophenol (present work). (*b*) 2,6-Dinitrophenol (Iwasaki, Sato & Aihara, 1976). (*c*) 2-Chloro-4,6-dinitrophenol (Andersen & Andersen, 1975). (*d*) 2-Bromo-4,6-dinitrophenol (Neustadt & Cagle, 1975). (*e*) 2-Nitro-4-chlorophenol (Kawai, Kashino & Haisa, 1976). (*f*) β-*p*-Nitrophenol (Coppens & Schmidt, 1965).

* Values corrected for thermal vibration.

The average C—C bond distance in the benzene ring is 1.389 Å. The C(1)—C(2) (1.411 Å) length is somewhat longer and the bonds C(3)—C(4) (1.371 Å) and C(5)—C(6) (1.370 Å) are significantly shorter than the rest. Bond angles C(1)C(2)C(3) and C(3)C(4)C(5), at the apices of which are attached nitro groups, are 121.1 and 123.3°, respectively. These dimensions are in reasonable agreement with the corresponding values for 2,6-DNP. The C(2)C(1)C(6) angle is 118.6°, which is larger than the value for 2,6-DNP but is close to those for the other phenols.

The length of the C(1)—O(1) bond, 1.344 Å, is slightly longer than those of 2-Cl-4,6-DNP (1.333 Å)

and 2-Br-4,6-DNP (1.333 Å); but these values are shorter than the C—O bonds in vanillins (Iwasaki, 1973; Iwasaki, Tanaka & Aihara, 1976). The bond C(2)—N(2), 1.452 Å, is significantly shorter than C(4)—N(4), 1.486 Å. The length of N(2)—O(21) (1.240 Å), which is involved in the hydrogen bond, is comparable with the corresponding values for other *o*-nitrophenols. the average value of the other N—O distances is 1.222 Å, which is the normal value for nitrobenzenes.

Some bond lengths and angles in nitrophenols are compared in Table 5. The geometry of the benzene ring and the intramolecular hydrogen bond is very close to

those of the other o-nitrophenols. There are obviously quite significant departures from hexagonal symmetry in the benzene rings and short C—O, C—N bonds and long N—O bonds. Molecular dimensions in these compounds indicate the presence of a resonance hybrid involving the following structure:
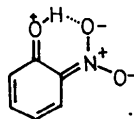
The dimensions of the benzene ring in these dinitrophenols are very different from those found in p-nitrophenol (Coppens & Schmidt, 1965). In the case of p-nitrophenol the shortening of the two C—C bonds parallel to the long axis of the molecule can be attributed to the contributions of the quinonoid resonance structure. However, no such contributions are found in 2,4-dinitrophenols in spite of the existence of a nitro group in the *para* position. The presence of other *ortho*-substituents (—NO$_2$, —Cl, —Br) having no connexion with the formation of the intramolecular hydrogen bonding has no effect on the molecular dimensions, within experimental error.

Molecular packing

The arrangement of the molecules in the crystal is shown in Figs. 2 and 3. Intermolecular contacts less than 3·60 Å are listed in Table 6.
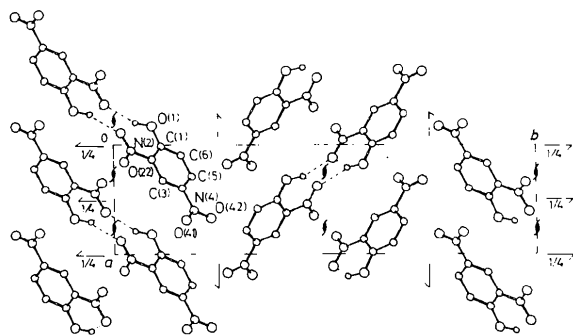

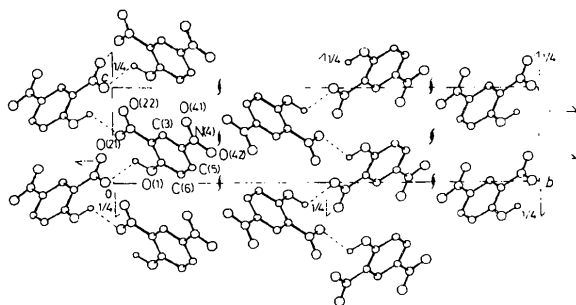Fig. 2. Projection of the structure along **c**.

Fig. 3. Projection of the structure along **a**.

Table 6. *Intramolecular contacts less than* 3·60 Å

Symmetry code

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

C(3)···C(6^i)	3·451 (6) Å	O(41)···O(1^{iii})	3·217 (4) Å
N(2)···O(1^i)	3·374 (5)	O(42)···C(5^{iv})	3·252 (5)
O(22)···C(1^i)	3·193 (5)	O(42)···C(6^{iv})	3·335 (5)
O(22)···C(6^i)	3·535 (5)	O(41)···C(5^v)	3·456 (5)
O(22)···O(1^i)	3·142 (4)	O(42)···C(4^v)	3·229 (5)
C(4)···O(1^{ii})	3·327 (5)	O(42)···C(5^v)	3·373 (5)
N(4)···C(1^{ii})	3·328 (5)	O(42)···N(4^v)	3·381 (5)
N(4)···O(1^{ii})	3·169 (5)	O(22)···C(2^{vi})	3·160 (5)
O(41)···C(1^{ii})	3·307 (5)	O(22)···C(3^{vi})	3·546 (5)
O(41)···C(2^{ii})	3·483 (5)	O(22)···N(2^{vi})	2·898 (5)
O(41)···O(1^{ii})	3·418 (4)	O(22)···O(21^{vi})	3·270 (5)
O(42)···C(1^{ii})	3·468 (5)	O(22)···O(22^{vi})	3·100 (4)
O(42)···C(6^{ii})	3·282 (5)	O(21)···O(21^{vii})	3·151 (4)
O(42)···O(1^{ii})	3·502 (4)	O(1)···O(21^{vii})	2·894 (5)
O(41)···C(6^{iii})	3·352 (5)	H(1)···O(21^{vii})	2·31 (4)

There is a rather short contact between the O atom, O(1), of the hydroxyl group and that of the nitro group, O(21^{vii}), with an O···O distance of 2·894 Å. The H(1)···O(21^{vii}) intermolecular distance is 2·31 Å and the angle O(1)–H(1)···O(21^{vii}) is 124°. Although the O–H···O angle is relatively acute for hydrogen bonding, it seems that H(1) is involved in a bifurcated hydrogen-bonding system, both intra- and intermolecular. The intermolecular hydrogen bonds are formed around the twofold screw axis parallel to **c**. Evidence for the intermolecular interaction is provided by the easy growth of crystals parallel to **c** and by the higher melting point than that of 2,6-DNP (m.p. 64 °C).

References

AIHARA, A. & HIRAI, K. (1976). Private communication.
ANDERSEN, E. K. & ANDERSEN, I. G. K. (1975). *Acta Cryst.* B31, 387–390.
COPPENS, P. & SCHMIDT, G. M. J. (1965). *Acta Cryst.* 18, 654–663.

CRYSTALLOGRAPHIC SOCIETY OF JAPAN (1967). *UNICS, The Universal Crystallographic Computation Program System.*

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 73, 102. Birmingham: Kynoch Press.

IWASAKI, F. (1973). *Chem. Lett.* pp. 227–228.

IWASAKI, F., SATO, M. & AIHARA, A. (1976). *Acta Cryst.* B32, 102–106.

IWASAKI, F., TANAKA, I. & AIHARA, A. (1976). *Acta Cryst.* B32, 1264–1266.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KAWAI, R., KASHINO, S. & HAISA, M. (1976). *Acta Cryst.* B32, 1972–1975.

NEUSTADT, R. J. & CAGLE, F. W. JR (1975). *Acta Cryst.* B31, 2727–2729.

SAKURAI, T., ITO, T., IWASAKI, H., WATANABE, Y. & FUKUHARA, M. (1967). *Rep. Inst. Phys. Chem. Res.* 43, 62–69.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–76.

Nucleic-Acid Constituents.
VI. The Crystal and Molecular Structure of 3',5'-Di-O-acetyluridine at −170°C

BY R. A. G. DE GRAAFF, G. ADMIRAAL, E. H. KOEN AND C. ROMERS

Gorlaeus Laboratoria, X-ray and Electron Diffraction Section, University of Leiden, Leiden, The Netherlands

3',5'-Di-O-acetyluridine, $C_{13}H_{16}O_8N_2$, crystallizes with two molecules in a monoclinic unit cell with space group $P2_1$: $a = 10.456$ (3), $b = 8.645$ (3), $c = 8.644$ (3) Å, $\beta = 109.2$ (3)° at −170°C. Diffractometer data (Mo $K\alpha$ radiation) were collected at −170°C. The structure was obtained by direct methods and refined by least squares ($R_w = 3.95\%$), taking into account a disorder of the acetyl group bonded to O(3'). The orientation of the nucleobase with respect to the sugar is *anti* ($\chi_{CN} = 60.4°$). The uracil ring is planar within 0.02 Å. Base–base stacking is absent. The ribose ring has a C(2')-*endo* conformation and the orientation of the acetyl group bonded to C(5') is *gauche–gauche* (g^+) with respect to O(1') and C(3').

Introduction

Nucleic-acid constituents are currently investigated in this laboratory by means of NMR studies (part I: Altona, van Boom, de Jager, Koeners & van Binst, 1974; part II: Altona, Koeners, de Jager & van Boom, 1974; part V: Altona, van Boom & Haasnoot, 1976), synthesis (part III: van Boom, Burgers, den Hartog & van der Marel, 1976) and crystal structure determinations (part IV: de Kok, Romers, de Leeuw, Altona & van Boom, 1977). The present paper (part VI) reports the structure determination of 3',5'-di-O-acetyluridine (abbreviated DAU). Knowledge of its conformation and geometry is pertinent to the interpretation of physical data on nucleosides and their correlation with nucleic-acid structures. The numbering of atoms is indicated in Fig. 1.

Experimental

DAU was obtained by means of the method of Fromageot, Griffin, Reese & Sulton (1967).

Evaporation at 44°C of a solution of DAU in *n*-butanol resulted after a few days in the appearance of clusters of lath-shaped crystals. The colourless monoclinic crystals are elongated along [010] and cleave easily perpendicular to the needle axis. The lattice
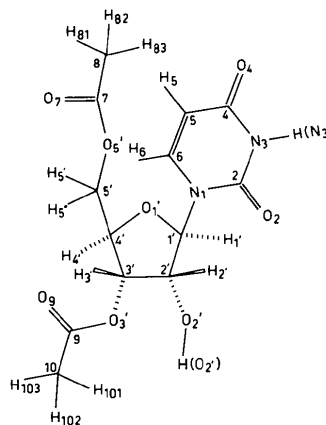

Fig. 1. The numbering of atoms in 3',5'-di-O-acetyluridine.