

## A Reinvestigation of the Structure of Tetrahydrofuran by High-Resolution Neutron Powder Diffraction

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**Abstract.**  $C_4H_8O$ ,  $M_r = 70.06$ , monoclinic,  $C2/c$ ,  $Z = 4$ ,  $D_x = 0.985 \text{ g cm}^{-3}$ . At  $T = 5 \text{ K}$ :  $a = 6.1464 (3)$ ,  $b = 8.8767 (1)$ ,  $c = 7.7154 (2) \text{ \AA}$ ,  $\beta = 107.549 (1)^\circ$ ,  $V = 401.37 \text{ \AA}^3$ ,  $R = 9.8\%$ . At  $T = 120 \text{ K}$ :  $a = 6.1905 (2)$ ,  $b = 8.9308 (1)$ ,  $c = 7.8152 (2) \text{ \AA}$ ,  $\beta = 107.0223 (1)^\circ$ ,  $V = 413.14 \text{ \AA}^3$ ,  $R = 8.3\%$ . High-resolution neutron powder diffraction data were obtained on the HRPD instrument at the spallation pulsed neutron source ISIS, England. The structure as determined by Luger & Buschmann [*Angew. Chem. Int. Ed. Engl.* (1983), **22**, 410–411] ( $T = 103$  and  $140 \text{ K}$ ) is shown to remain down to  $5 \text{ K}$ . Much improved structural parameters particularly for proton positions have been obtained and anisotropic temperature factors determined.

**Introduction.** Tetrahydrofuran is an important organic molecule that has been extensively studied by theoretical *ab initio* methods because of its role as a basic structural unit of carbohydrates. A full structural determination at  $5 \text{ K}$  (where libration is essentially absent) and improved accuracy of the existing structural information is therefore timely. The work presented here is part of a research programme into molecular crystal structures using high-resolution neutron powder diffraction. The results from this study demonstrate the power of high-resolution neutron powder diffraction ( $\Delta d/d < 1 \times 10^{-3}$ ) as a technique permitting the elucidation and refinement of moderately complex structures to a high degree of both accuracy and precision. For low-melting-point substances it can offer a complementary technique to single-crystal diffraction, in cases where single-crystal growth is prohibitive or technically difficult. Additionally, neutron powder diffraction data can be routinely collected at  $5 \text{ K}$  thus permitting accurate comparisons with *ab initio* calculations.

**Experimental.** Deuterated tetrahydrofuran melts at  $167 \text{ K}$ . A 99.5% deuterated sample supplied by Sigma Chemical Ltd was hand ground at liquid nitrogen temperatures. Approximately  $10 \text{ g}$  of the fine powder obtained were then sealed in a  $15 \text{ mm}$  diameter vanadium sample can. Diffraction data were collected on the High Resolution Powder Diffractometer (HRPD) (David, Akporiaye, Ibberson &

Wilson, 1988) at the pulsed neutron source ISIS. HRPD utilizes the time-of-flight method whereby the sample is illuminated by a polychromatic neutron beam and the scattered beam detected at some fixed angle of  $2\theta$ . Data were recorded in backscattering

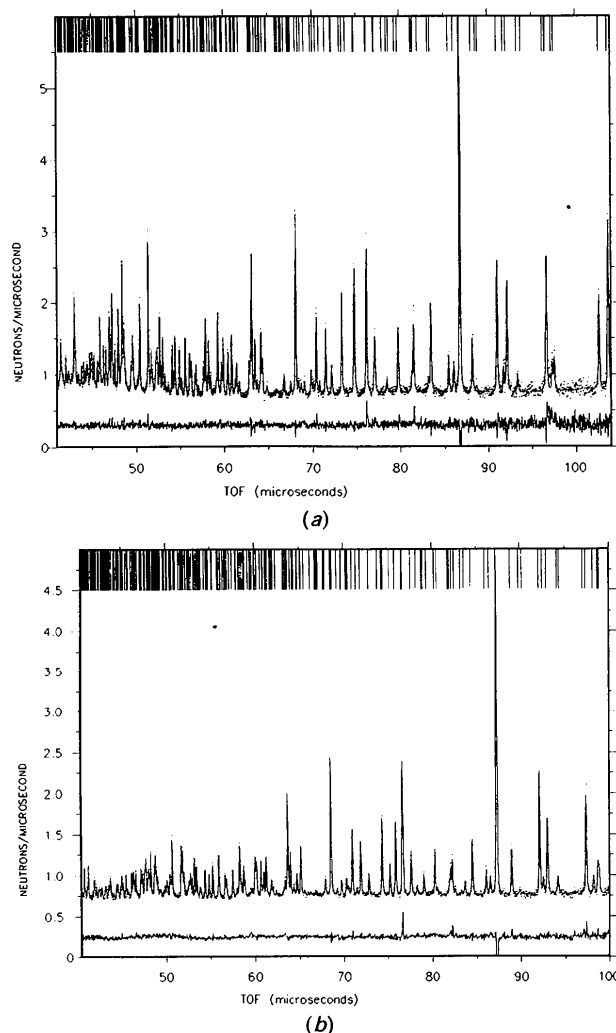


Fig. 1. Results from the full profile refinement of data at both temperatures. Observed (dots), calculated (line) and difference plot. Vertical tick marks represent calculated peak positions. (a)  $T = 5 \text{ K}$ , (b)  $T = 120 \text{ K}$ .

Table 1. Atomic coordinates and equivalent anisotropic thermal parameters ( $\text{\AA}^2 \times 10^2$ )

	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
5 K									
O1	0.0000	-0.9145 (3)	0.2500	0.44 (15)	0.88 (21)	0.64 (16)	0.00	0.49 (13)	0.00
C2	-0.1070 (4)	-0.8214 (2)	0.3533 (3)	0.78 (14)	0.21 (12)	0.68 (12)	-0.06 (7)	0.34 (8)	0.08 (9)
C3	-0.0233 (4)	-0.6623 (2)	0.3415 (3)	0.92 (14)	0.66 (13)	0.47 (12)	-0.04 (9)	0.42 (10)	-0.05 (9)
D21	-0.2931 (4)	-0.8289 (3)	0.2908 (3)	1.23 (15)	1.96 (14)	2.75 (15)	-0.13 (1)	0.06 (10)	0.00 (1)
D22	-0.0673 (5)	-0.8677 (2)	0.4908 (3)	3.41 (15)	1.14 (14)	1.91 (15)	0.28 (11)	0.15 (10)	0.17 (10)
D31	-0.1484 (4)	-0.5776 (3)	0.3521 (3)	2.32 (14)	0.91 (12)	2.72 (14)	0.49 (10)	1.39 (11)	-0.27 (10)
D32	0.1344 (5)	-0.6402 (2)	0.4511 (3)	2.10 (15)	1.47 (14)	1.70 (12)	-0.03 (1)	0.06 (11)	-0.01 (1)
120 K									
O1	0.0000	-0.9128 (3)	0.2500	4.05 (24)	2.45 (22)	3.56 (22)	0.00	3.20 (19)	0.00
C2	-0.1071 (4)	-0.8218 (2)	0.3505 (3)	3.30 (18)	1.57 (14)	2.04 (15)	0.20 (9)	1.40 (11)	0.04 (10)
C3	-0.0254 (5)	-0.6629 (3)	0.3406 (4)	2.90 (16)	1.33 (15)	2.37 (15)	-0.24 (9)	1.09 (12)	-0.38 (9)
D21	-0.2902 (5)	-0.8304 (3)	0.2902 (4)	2.76 (18)	4.81 (18)	6.64 (22)	0.43 (14)	1.65 (14)	-0.29 (15)
D22	-0.0692 (6)	-0.8660 (3)	0.4848 (4)	5.06 (24)	3.61 (16)	4.69 (20)	0.90 (15)	3.78 (16)	0.41 (14)
D31	-0.1491 (5)	-0.5801 (3)	0.3511 (4)	5.47 (18)	2.24 (13)	5.27 (18)	1.51 (13)	2.89 (14)	-0.48 (11)
D32	0.1275 (6)	-0.6391 (3)	0.4473 (4)	4.57 (19)	3.64 (16)	3.30 (15)	-0.87 (13)	0.45 (12)	-0.60 (12)

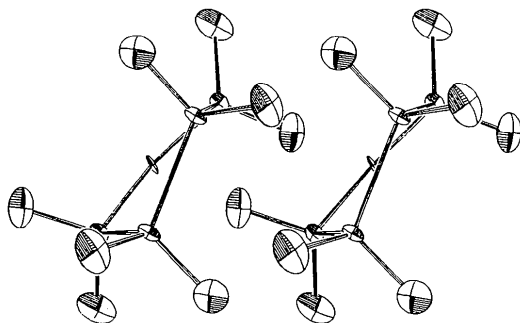


Fig. 2. ORTEP molecular diagram of tetrahydrofuran at 5 K.

Table 2. Bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ )

	5 K	120 K
C2—O1	1.438 (3)	1.422 (3)
C2—C3	1.516 (3)	1.516 (4)
C2—D21	1.101 (4)	1.095 (4)
C2—D22	1.094 (4)	1.081 (4)
C3—D31	1.096 (4)	1.083 (4)
C3—D32	1.094 (4)	1.084 (4)
C2—O1—C2'	109.9 (3)	110.2 (3)
O1—C2—C3	106.4 (2)	106.9 (3)
C2—C3—C3'	102.6 (2)	102.0 (2)
O1—C2—D21	108.1 (2)	108.5 (3)
O1—C2—D22	108.4 (3)	108.9 (3)
C2—C3—D31	112.1 (3)	112.3 (3)
C2—C3—D32	111.0 (3)	111.9 (3)
C2'—O1—C2—C3	-11.3 (2)	-11.3 (2)
O1—C2—C3—C3'	28.8 (2)	28.4 (2)
C2—C3—C3'—C2'	-34.5 (2)	-33.7 (2)

Symmetry operator: (i)  $-x, y, \frac{1}{2} - z$ .

( $2\theta_{\text{ave}} = 168^\circ$ ,  $\Delta d/d = 8 \times 10^{-4}$ ) at 120 and 5 K over the time-of-flight range 20–120 ms which corresponds to a  $d$ -spacing range of 0.4–2.4  $\text{\AA}$ . Data collection times were of the order of 6 h corresponding to approximately 120  $\mu\text{A h}$  proton beam current. The excellent quality of the data obtained is shown in Fig. 1.\* The data were normalized to an incident beam monitor spectrum and a linear attenuation correction applied taking into account beam attenuation due to the vanadium-tailed cryostat used for the experiment. A full profile refinement was performed on both data sets using program *TF12LS* (David *et al.*, 1988) taking the structure after Luger & Buschmann (1983) as a starting model. The peak shape was well modelled using a Voigt function convoluted with a double-exponential decay; only two peak-width parameters were varied. The refinements proceeded routinely without the use of structural constraints and since anisotropic temperature factors were refined some 81 independent

\* A list of observed profile intensities as a function of scattering angle has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54727 (99 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parameters were simultaneously fitted to the data. In both cases the structure refinement rapidly converged giving excellent agreement factors,  $\chi^2 = 1.37$  (5 K) and  $\chi^2 = 1.89$  (120 K). Final refined values for atomic coordinates and anisotropic temperature factors are given in Table 1. The final values of the anisotropic temperature factors for the 5 K structure are illustrated by an ORTEP model in Fig. 2.

**Discussion.** High-resolution neutron powder diffraction has enabled an accurate structural refinement of the title compound to be performed. The extent to which the present structural knowledge has been improved is well illustrated by the accurate location of proton positions and anisotropic temperature factors. The average C—D bond length is 1.097 (4)  $\text{\AA}$ . The bond length and bond angles obtained (see Table 2) are in good agreement with both the previous single-crystal X-ray diffraction study and theoretical calculations. Values obtained at 5 K fall within two standard deviations of those obtained by *ab initio* molecular orbital theory (4-31G basis)

(Cremer & Pople, 1975*b*). Luger & Buschmann (1983) had previously reported slight anomalies in the COC and OCC bond lengths for 103 and 148 K data when compared with theoretical calculations. The experimental data collected at 5 K reported above no longer show this discrepancy. Puckering parameters (Cremer & Pople, 1975*a*) are  $q_2 = 34.3$  (2) pm (5 K) and 34.0 (2) pm (120 K) and  $\psi_2 = 90$  (–)°.

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## Structure of Triethylammonium Phenylcarbamoyl Phosphate

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**Abstract.**  $C_6H_{16}N^+ \cdot C_7H_7NO_5P^-$ ,  $M_r = 318.31$ , orthorhombic, *Pbca*,  $a = 9.290$  (3),  $b = 11.160$  (4),  $c = 31.529$  (9) Å,  $V = 3269$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.31$ ,  $D_x = 1.293$  Mg m<sup>-3</sup>, Mo *K*α,  $\lambda = 0.71069$  Å,  $\mu = 1.83$  cm<sup>-1</sup>,  $F(000) = 1360$ ,  $T = 299$  (1) K, final  $R = 0.041$  for 2425 non-zero reflections. The phosphate ester bond, P—O 1.637 (2) Å, is the longest RO—P(OH)O<sub>2</sub><sup>-</sup> distance so far observed. The phenyl ring makes a dihedral angle of 7.3 (8)° with the plane through the carbamoyl group.

**Introduction.** Naturally occurring phosphate esters of carboxylic acids are effective phosphoryl donors and are a source of energy for many enzymic reactions. In particular, carbamoyl phosphate (CAP) is known to play an important role in the urea cycle and is a precursor of the pyrimidine ring in pyrimidine nucleotide synthesis (Southerland, 1990). This easily hydrolysed compound (Bergmeyer, 1970) has not been investigated in the crystalline state. The structural study reported here is the first of a compound with a carbamoyl phosphate system and is also probably the first of a compound containing a carboxyl group linked to a monoesterified phosphate group. This work is a continuation of our studies on the crystal structures of biologically important esters (Weichsel & Lis, 1990).

**Experimental.** The title compound was prepared by the reaction of phenyl isocyanate, triethylamine and crystalline orthophosphoric acid in acetonitrile solution (Cramer & Winter, 1959). Plate-shaped crystals were obtained from ethanol solution by slow evaporation.  $D_m$  by flotation in a CHCl<sub>3</sub>/C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> mixture. Specimen of dimensions 0.7 × 0.7 ×

0.25 mm was cut from a larger crystal; preliminary examination by rotation and Weissenberg photographs. Syntex *P2*<sub>1</sub> diffractometer with graphite monochromator and Mo *K*α radiation were used for lattice parameters (15 reflections in the range  $20 < 2\theta < 26^\circ$ ) and intensity measurements;  $\omega$ - $2\theta$  scans. 5198 reflections below  $2\theta = 60^\circ$  ( $-13 \leq h \leq 13$ ,  $-15 \leq k \leq 0$ ,  $0 \leq l \leq 44$ ), of which 3225 had  $I > 3\sigma(I)$ . After each group of 50 reflections, two standards were measured; variation  $\pm 3\%$ . The data were corrected for Lorentz and polarization effects. An absorption correction was made using *DIFABS* (Walker & Stuart, 1983); minimum and maximum absorption corrections 0.868 and 1.061. Symmetry-related reflections were averaged after *DIFABS* to give 2425 independent data with  $|F| > 0$ ;  $R_{\text{merge}} = 0.0172$ . Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986) and refined by *SHELXL76* (Sheldrick, 1976), based on  $F$  values with  $w = 1/\sigma^2(F_o)$ ; P, N, O and C anisotropic, H isotropic. The positional parameters of the H atoms were refined with the constraints  $d(C-H) = 1.08$ ,  $d(O-H) = 0.96$  and  $d(N-H) = 1.00$  Å. Final  $R = 0.0410$  and  $wR = 0.0394$ . Maximum  $\Delta/\sigma$  was 0.07. Residual electron density within  $-0.27$  and  $0.19$  e Å<sup>-3</sup>. The final atomic parameters are given in Table 1.\*

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54466 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0248]