Neutron Diffraction Refinement of *trans*-2,5-Dichloro-1,4-dioxane at 97 K

By G. A. Jeffrey, J. R. Ruble and P. Matias*

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, *USA*

R. K. McMullan

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, *USA*

and P. Luger and J. Buschmann

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, 1000 *Berlin* 33, *Germany*

Abstract. $C_4H_6Cl_2O_2$, $M_r = 157.00$, triclinic, $P\bar{1}$, $a = 4.504$ (2), $b = 5.423$ (2), $c = 6.592$ (3) Å, $\alpha = 85.53$ (2), $\beta = 103.75$ (2), $\gamma = 106.51$ (1)°, $V = 149.9$ (2) Å^3, $Z = 1$, $D_n = 1.739$ Mg m^{-3}, λ_n(Be, 002) $= 1.0504$ Å, $\mu = 0.1924$ mm^{-1}, $F(000) = 34.911$ fm, $T = 97$ K, $R(F^2) = 0.021$, $wR(F^2) = 0.036$ for 1183 unique reflections. The bond lengths not involving H atoms are in agreement with an earlier X-ray anlaysis to within 0.004 Å. C—Cl bonds are axial and longer than normal; C—O bonds are shorter than normal. The equatorial C—H bond lengths are significantly longer than the axial C—H bonds.

Introduction. The X-ray structure analysis of *trans*-2,5-dichloro-1,4-dioxane by Altona, Knobler & Romers (1963) is of particular interest because it was one of the first examples of the influence of the *anomeric effect* on bond lengths. Not only is the molecular conformation of the molecules such that the C—Cl bonds are axial, rather than equatorial, but the C—Cl bond lengths are longer and the C—O bond lengths shorter than the normal values (Sutton, 1958). The purpose of this neutron refinement is to provide nuclear parameters that could be used in a subsequent charge-density analysis.

Experimental. *trans*-2,5-Dichloro-1,4-dioxane was synthesized from 1,4-dioxane at 273–283 K in carbon tetrachloride as described by Bryan, Smedley & Summerbell (1950) using a falling film photoreactor (Bosse & Meijere, 1974). Large single crystals were obtained from carbon tetrachloride at 265 K. That used for neutron diffraction was 2.0 × 2.0 × 1.0 mm. The data were collected at the Brookhaven High Flux Beam Reactor using a neutron beam mono-

chromated by reflection from Be(002) planes and calibrated against KBr ($a_o = 6.6000$ Å) at 295 K. The temperature was maintained within ±0.5 of 97 K inside a double-stage helium cryostat.† The lattice parameters were determined by least-squares fit to $\sin^2\theta$ values for 30 reflections within the range $48 < 2\theta < 57°$. 1360 reflections ($-h, \pm k, \pm l$; $|h| \le 7$, $|k| \le 8$, $|l| \le 10$; $\sin\theta/\lambda \le 0.78$ Å^{-1}) were measured by the $\theta/2\theta$ step-scan method using scan widths $\Delta 2\theta = 3°$ for $\sin\theta/\lambda \le 0.45$ Å^{-1} and $\Delta 2\theta = (1.62 + 2.89\tan\theta)°$ for $\sin\theta/\lambda > 0.45$ Å^{-1}. The intensities of two reflections, monitored at regular intervals, showed no systematic variations. Integrated intensities I_o and variances $\sigma^2(I_o)$ were derived from the scan profiles as described previously (McMullan, Epstein, Ruble & Craven, 1979). Absorption corrections (de Meulener & Tompa, 1965; Templeton & Templeton, 1973) were applied using the μ/ρ value of 2475 m^2 ng^{-1} for H at $\lambda = 1.0504$ Å (Koetzle & McMullan, 1980). Averaging F_o^2 values of symmetry-related ($0 \pm k \pm l$) reflections yielded 1183 unique observations and $R_{int} \simeq 2\%$.

The initial atomic parameters were taken from the 148 K X-ray analysis of Altona, Knobler & Romers (1963); coherent neutron-scattering lengths (fm) for H -3.7409, C 6.6484, O 5.803, Cl 9.579 were from the tabulation of Koester (1977). Refinement by full-matrix least squares was carried out with a modified version of the program *ORFLS* (Busing, Martin & Levy, 1962). The quantity $\sum w|F_o^2 - F_c^2|^2$ was minimized with weights $w = [\sigma_c^2(F_o^2) + (0.02F_o^2)^2]^{-1}$, summing over the 1183 independent observations. The variable parameters were the coordinates and anisotropic thermal factors for seven non-related atoms, one scale factor, and the anisotropic secondary-extinction parameters for type I crystal with Lorentzian distribution in mosaic spread

---

* Present address: MORADO, Centro de Tecnologia Quimica e Biologica (CTQB), Rua da Quinta Grande 6, Apartado 127, 2780 Oeiras, Portugal.

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters for* trans-2,5-*dichloro*-1,4-*dioxane at* 97 K

E.s.d.'s given in parentheses refer to the least significant digit. The temperature factors ($\times 10^2$ Å^2) are of the form: T(aniso) = $\exp[-2\pi^2(U_{11}ha^{*2} + U_{22}kb^{*2} + U_{33}lc^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Extinction parameters ($\times 10^{-4}$ rad^{-1}): $g_{11} = 16.0$, $g_{22} = 11.3$, $g_{33} = 17.5$, $g_{12} = -5.9$, $g_{13} = 1.6$, $g_{23} = -2.1$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	0.22993 (6)	0.24837 (4)	0.15402 (4)	1.37 (1)	1.41 (1)	1.22 (1)	0.340 (8)	0.028 (8)	-0.358 (7)
O(1)	0.66488 (9)	0.31301 (7)	0.51237 (5)	1.13 (2)	1.15 (1)	1.20 (2)	0.53 (1)	0.21 (1)	-0.01 (1)
C(1)	0.59361 (8)	0.44263 (6)	0.32576 (5)	1.03 (1)	1.15 (1)	1.09 (1)	0.36 (1)	0.29 (1)	-0.081 (2)
C(2)	0.44809 (8)	0.29624 (6)	0.64317 (5)	1.27 (1)	1.01 (1)	1.20 (1)	0.30 (1)	0.34 (1)	0.074 (9)
H(1)	0.7815 (2)	0.4581 (2)	0.2430 (1)	2.18 (3)	3.12 (4)	2.43 (3)	0.86 (3)	1.07 (3)	-0.03 (3)
H(21)	0.5433 (2)	0.2114 (2)	0.7913 (1)	3.68 (4)	2.87 (4)	2.06 (3)	1.49 (3)	0.68 (3)	0.74 (3)
H(22)	0.2135 (2)	0.1707 (2)	0.5712 (1)	2.19 (3)	2.36 (3)	3.25 (4)	-0.24 (3)	0.70 (3)	-0.53 (3)

Table 2. *Rigid-body thermal motion analysis of* trans-2,5-*dichloro*-1,4-*dioxane at* 97 K

Origin at Ī; $I_1 \approx$ Cl···Cl'; $I_2 \approx$ O—C(2'); I_3 normal to C(2), C(2), O'. First column: C$_4$O$_2$Cl, r.m.s. ΔU_{ij} 0.0002 Å^2. Second column: C$_4$H$_6$O$_2$Cl, r.m.s. ΔU_{ij} 0.0003 Å^2.

	I_1		I_2		I_3	
	C$_4$O$_2$Cl	C$_4$H$_6$O$_2$Cl	C$_4$O$_2$Cl	C$_4$H$_6$O$_2$Cl	C$_4$O$_2$Cl	C$_4$H$_6$O$_2$Cl
T (translational) (Å$^2 \times 10^{-5}$)	991 (9)	995 (4)				
	46 (7)	54 (9)	-416 (13)	-926 (5)		
	-52 (8)	9 (9)	-66 (9)	-47 (10)	846 (15)	831 (16)
ω (translational) (rad$^2 \times 10^{-5}$)	238 (10)	239 (8)				
	8 (8)	21 (6)	113 (3)	115 (3)		
	-42 (6)	-53 (6)	10 (2)	15 (2)	89 (3)	87 (4)

Internal H-atom motion (Å)

	Radial	Scissors	Cross
H(1)	0.0734	0.1159	0.1128
H(21), H(22)	0.0734	0.1398	0.1206

Table 3. *Bond lengths* (Å) *and selected torsion angles* (°) *for trans* 2,5-*dichloro*-1,4-*dioxane at* 97 K

	Observed	Harmonic correction	Anharmonic correction	Corrected value	X-ray data* (148 K)
C(1)—Cl	1.8434 (4)	+0.003		1.846	1.845 (6)
C(1)—O	1.3843 (5)	+0.002		1.386	1.388 (7)
C(2)—O	1.4292 (6)	+0.002		1.431	1.428 (7)
C(1)—C(2)	1.5157 (5)	+0.002		1.518	1.513 (8)
C(1)—H(1)	1.092 (1)	+0.012	-0.016	1.090	
C(2)—H(21)	1.092 (1)	+0.015	-0.016	1.093	
C(2)—H(22)	1.099 (1)	+0.016	-0.016	1.101	

Cl—C(1)—O—C(2)	-70.48 (4)		H(21)—C(2)—C(1)—H(1)	68.10 (8)
Cl—C(1)—C(2)—O	71.93 (3)		H(22)—C(2)—C(1)—H(1)	-51.97 (8)
O—C(1)—C(2)—O	-50.98 (4)		H(21)—C(2)—O—C(1)	-173.49 (6)
H(1)—C(1)—O—C(2)	175.69 (6)		H(22)—C(2)—O—C(1)	67.96 (6)

* Altona, Knobler & Romers (1963).

(Thornley & Nelmes, 1974; Becker & Coppens, 1974); a total of 70 parameters. Extinction effects were significant and pervasive; the reflections most severely affected were 301 with 0.720 × F_c^2 and 201 with 0.732 × F_c^2. The refinement converged ($\Delta p_i/\sigma(p_i) < 0.001$) with fit indices $R(F^2) = 0.021$; $wR(F^2) = 0.036$; $S = 1.052$. In the final ΔF map, the largest $|\Delta\rho|$ errors were < 1% of the peak maximum for carbon in the ρ_o map.

Discussion. The atomic parameters are given in Table 1. The atomic notation and thermal ellipsoids are shown in Fig. 1. The rigid-body thermal motion

tensors given in Table 2 were calculated using *ORSBA* (Johnson, 1970). The bond lengths, uncorrected and corrected for thermal motion, are shown in Table 3.* For the bond lengths not involving H atoms, the agreement with the earlier X-ray analysis was within 0.004 Å. The equatorial C—H bond lengths C(1)—H(1) and C(2)—H(21) are significantly longer than the axial bond C(2)—H(22).
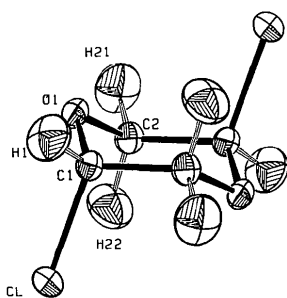
Fig. 1. *trans*-2,5-Dichloro-1,4-dioxane at 97 K. Thermal ellipsoids at 75% probability (Johnson, 1976).

It is interesting to note that the rigid-body analyses with and without the H atoms included gave very similar results with almost as good a fit. For the C—H bonds, the harmonic riding motion and anharmonic stretch corrections almost cancel at 97 K, as has been observed in other low-temperature neutron diffraction analyses (Jeffrey, 1992).

References

ALTONA, C., KNOBLER, C. & ROMERS, C. (1963). *Acta Cryst.* **16**, 1217–1225.

BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* A30, 129–147.

BOSSE, J. & MEIJERE, A. (1974). *Angew. Chem. Int. Ed. Engl.* **13**, 663–665.

BRYAN, L. A., SMEDLEY, W. M. & SUMMERBELL, R. K. (1950). *J. Am. Chem. Soc.* **73**, 2206–2010.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

JEFFREY, G. A. (1992). Accurate Crystal Structure Analysis by Neutron Diffraction. In *Accurate Molecular Structures*, edited by A. DOMENICANO, ch. 11. Oxford Univ. Press. In the press.

JOHNSON, C. K. (1970). Thermal Neutron Diffraction, edited by B. T. M. WILLIS, ch. 9, pp. 132–159. Oxford Univ. Press.

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KOESTER, L. (1977). *Springer Tracts in Modern Physics, Neutron Physics*, edited by G. HÖHLER, p. 36. Berlin: Springer.

KOETZLE, T. F. & McMULLAN, R. K. (1980). Research Memo C-4. Brookhaven National Laboratory, Upton, NY, USA.

McMULLAN, R. K., EPSTEIN, J., RUBLE, J. R. & CRAVEN, B. M. (1979). *Acta Cryst.* B35, 688–691.

MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.

SUTTON, L. E. (1958). Editor. *Tables for Interatomic Distances and Configuration in Molecules and Ions*, Special Publication No. 11. London: Chemical Society.

TEMPLETON, L. K. & TEMPLETON, D. H. (1973). Am. Crystallogr. Assoc. Meet., Storrs, Connecticut. Abstracts, p. 143.

THORNLEY, F. R. & NELMES, R. J. (1974). *Acta Cryst.* A30, 748–757.

Structure of *N*-Acetyl-L-leucyl-L-prolinamide Monohydrate

BY RAFFAELLA PULITI

Istituto per la Chimica di Molecole di Interesse Biologico CNR, Via Toiano 6, 80072 Arco Felice, Napoli, Italy

CARLO ANDREA MATTIA

Dipartimento di Chimica dell'Università 'Federico II' di Napoli, Via Mezzocannone 4, 80134 Napoli, Italy

AND TERENCE H. LILLEY

Chemistry Department and The Krebs Institute for Biomolecular Research, The University, Sheffield S3 7HF, England

Abstract. $C_{13}H_{23}N_3O_3.H_2O$, $M_r = 287.36$, orthorhombic, $P2_12_12_1$, $a = 6.3863$ (8), $b = 14.346$ (2), $c = 17.247$ (2) Å, $V = 1580.1$ (6) Å³, $Z = 4$, $D_x = 1.208$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 7.04$ cm⁻¹, $F(000) = 624$, room temperature, final $R = 0.037$ for 1693 reflections with $I \geq 2.5\sigma(I)$ and 257