

others: $\Delta l = 0.027 \text{ \AA}$, $t = 6.4$.) The bonds to each substituted atom of the benzene nucleus deviate from coplanarity; the substituted atom in each case lies 0.08 to 0.10 Å from the plane of the bonded neighbouring atoms. The bond angles adjacent to the double bonds are markedly unequal. A corresponding inequality is also observed in the similar bridging systems of [2.2]metaparacyclophane-1,9-diene (Hanson, 1971), and [2.2](2,6)pyridinoparacyclophane-1,9-diene (Weaver & Matthews, 1974). In contrast to the angles, all bond lengths are close to their typical values, and show no evidence of strain. Intermolecular distances in the structure are consistent with van der Waals interactions.

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A Neutron Diffraction Refinement of *N*-(2-Chloroethyl)-D-gluconamide

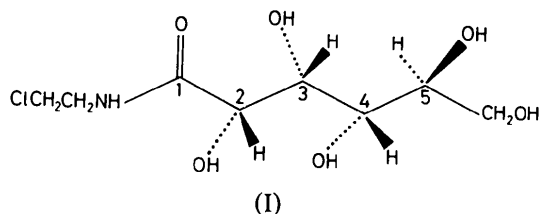
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Abstract. C₈H₁₆ClNO₆, triclinic, space group *P*1, $a = 4.807$, $b = 5.093$, $c = 11.888 \text{ \AA}$, $\alpha = 91.25$, $\beta = 84.48$, $\gamma = 94.48^\circ$, $Z = 1$. The linear molecule contains one intramolecular hydrogen bond, N—H···O; the N atom also acts as a donor to the carbonyl O atom of the adjacent molecule, related by the translation along *b*, to form a bifurcated hydrogen bond.

Introduction. The structure of *N*-(2-chloroethyl)-D-gluconamide (I) determined by X-ray diffraction (Satzke & Mackay, 1975) has established the conformation of alkyl glyconamides. The molecule was found to be linear with the extended structure maintained in the crystal by intermolecular hydrogen bonding. Although H atoms bonded to C were located on difference maps, those bonded to N and O could not be



found. This neutron analysis was undertaken to determine accurate atomic coordinates for these six H atoms, and to provide a precise description of the hydrogen bonds.

The crystal was grown from methanol solution by slow evaporation in a desiccator over sulphuric acid, and was an irregular plate of volume 4.6 mm³. It was mounted with [001] along the ϕ axis of a four-circle automatic diffractometer installed at the HIFAR reactor of the Australian Atomic Energy Commission at Lucas Heights, NSW. A set of non-equivalent intensities to a maximum 2θ of 95° were recorded with a neutron beam of wavelength $\lambda = 1.2486 \text{ \AA}$, and a step-scanning technique in the ω - 2θ mode (Elcombe, Cox, Pryor & Moore, 1971). Of the 1000 terms measured, 961 had values significantly greater than background and were considered observed. A reference reflexion, 104, was monitored every 25 reflexions and no significant variation in its intensity was noted. The intensities were corrected for Lorentz and absorption effects. The linear absorption coefficient, $\mu = 2.63 \text{ cm}^{-1}$, was calculated with an incoherent scattering cross-section for H of 40 barns, and values of σ (total scattering plus true absorption) for C, Cl, N, O

tabulated by Bacon (1962). No corrections for extinction were made. The coherent neutron scattering lengths were those given by Bacon (1972).

The cell dimensions were taken from the X-ray

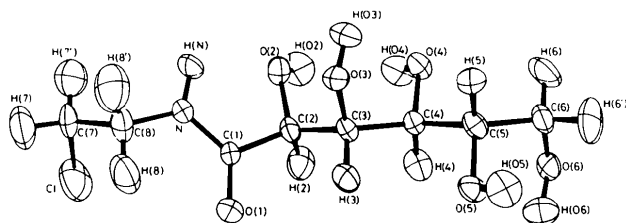


Fig. 1. A perspective view of the molecule with thermal ellipsoids scaled to 50% probability.

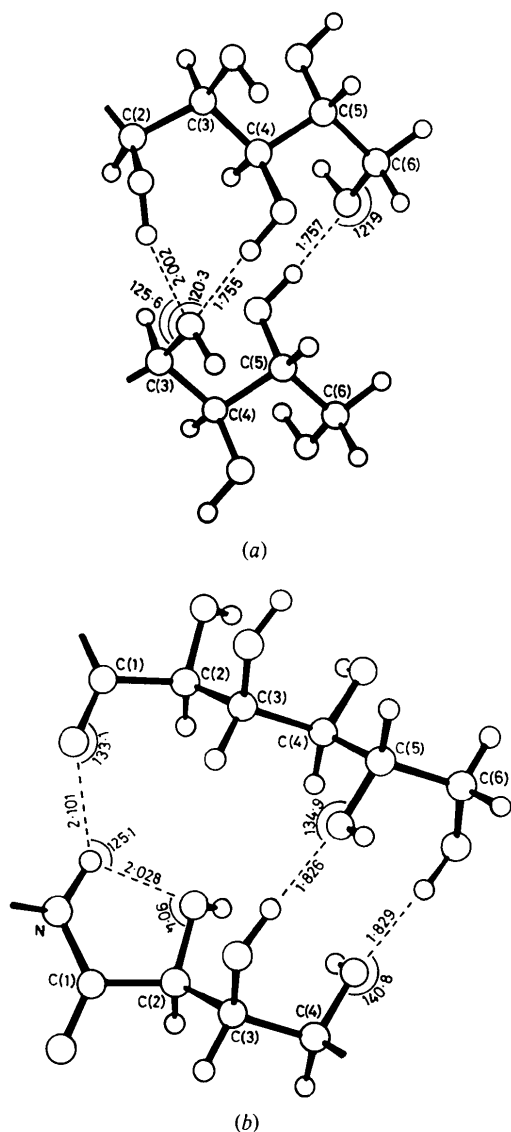


Fig. 2. Views of parts of the structure to illustrate the hydrogen bonding between molecules related by (a) the *a* translation and (b) the *b* translation.

refinement (Satzke & Mackay, 1975) as were the starting parameters. The six H atoms bonded to N and O were located from difference syntheses. Isotropic refinement of all the atoms yielded an *R* of 0.103 ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$). Subsequent full-matrix least-squares refinement with anisotropic thermal parameters for all atoms yielded a final *R* of 0.050 for the 961 observed terms.* The refinement was carried out with *ORFLS* (Busing, Martin & Levy, 1962); the function minimized was $w(|F_o| - |F_c|)^2$ with $w = 1.0$. The Fourier summations were calculated with *MUFR3* (White, 1966). Figs. 1 and 2 were prepared with *ORTEP* (Johnson, 1965).

Discussion. The final atomic coordinates are given in Table 1. The structure is similar to that resulting from the X-ray refinement (Satzke & Mackay, 1975), but this present work has provided additional details of the hydrogen bonding. A view of the molecule illustrating the conformation and atomic notation is shown in Fig.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32611 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final atomic coordinates ($\times 10^4$) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Cl	0	0	0
C(1)	-243 (20)	1275 (18)	-3037 (6)
C(2)	1987 (19)	1271 (18)	-4049 (6)
C(3)	582 (19)	2012 (17)	-5089 (6)
C(4)	2570 (19)	2794 (18)	-6122 (6)
C(5)	1003 (19)	3604 (18)	-7106 (6)
C(6)	2966 (20)	4382 (18)	-8141 (6)
C(7)	-2376 (22)	-2384 (20)	-626 (7)
C(8)	-3340 (22)	-1379 (20)	-1691 (7)
O(1)	-1276 (26)	3366 (20)	-2751 (8)
O(2)	3044 (22)	-1227 (19)	-4183 (7)
O(3)	-1417 (19)	-38 (18)	-5343 (7)
O(4)	4188 (22)	713 (19)	-6532 (7)
O(5)	-633 (21)	5703 (19)	-6711 (7)
O(6)	4998 (20)	6435 (20)	-7930 (7)
N	-1070 (18)	-1034 (16)	-2580 (6)
H(2)	3644 (31)	2799 (28)	-3881 (10)
H(3)	-605 (30)	3749 (27)	-4828 (10)
H(4)	3920 (28)	4538 (27)	-5859 (10)
H(5)	-368 (29)	1886 (23)	-7342 (10)
H(6)	4079 (32)	2743 (30)	-8471 (10)
H(6')	1707 (33)	4950 (32)	-8827 (10)
H(7)	-4089 (43)	-2773 (39)	14 (13)
H(7')	-1230 (52)	-4088 (40)	-809 (14)
H(8)	-4291 (36)	494 (34)	-1546 (12)
H(8')	-4896 (40)	-2812 (40)	-1952 (14)
H(N)	-193 (30)	-2658 (26)	-2934 (10)
H(O2)	4983 (31)	-1034 (29)	-4406 (12)
H(O3)	-494 (26)	-1511 (25)	-5720 (10)
H(O4)	5764 (32)	613 (30)	-6102 (12)
H(O5)	-2094 (28)	5913 (27)	-7197 (11)
H(O6)	4105 (29)	7930 (28)	-7530 (12)

Table 2. Bond lengths with e.s.d.'s (Å) and bond angles involving H atoms (°) (e.s.d.'s range from 0.8 to 1.3°)

C(1)–C(2)	1.533 (11)	C(2)–H(2)	1.099 (17)
C(2)–C(3)	1.532 (11)	C(3)–H(3)	1.112 (16)
C(3)–C(4)	1.522 (11)	C(4)–H(4)	1.116 (16)
C(4)–C(5)	1.531 (11)	C(5)–H(5)	1.102 (15)
C(5)–C(6)	1.517 (11)	C(6)–H(6)	1.073 (17)
C(7)–C(8)	1.503 (13)	C(6)–H(6')	1.117 (16)
C(1)–O(1)	1.237 (14)	C(7)–H(7)	1.076 (21)
C(2)–O(2)	1.407 (13)	C(7)–H(7')	1.071 (24)
C(3)–O(3)	1.411 (13)	C(8)–H(8)	1.093 (20)
C(4)–O(4)	1.414 (13)	C(8)–H(8')	1.067 (22)
C(5)–O(5)	1.421 (13)	O(2)–H(O2)	0.942 (18)
C(6)–O(6)	1.409 (14)	O(3)–H(O3)	0.980 (15)
C(1)–N	1.323 (12)	O(4)–H(O4)	0.959 (18)
C(8)–N	1.447 (12)	O(5)–H(O5)	0.965 (16)
C(7)–Cl	1.800 (10)	O(6)–H(O6)	0.993 (17)
		N–H(N)	1.115 (16)
C(1)–C(2)–H(2)	107.1	Cl–C(7)–H(7)	105.3
O(2)–C(2)–H(2)	111.4	C(8)–C(7)–H(7)	112.0
C(3)–C(2)–H(2)	109.5	Cl–C(7)–H(7')	105.8
C(2)–C(3)–H(3)	105.9	C(8)–C(7)–H(7')	110.2
O(3)–C(3)–H(3)	106.6	H(7)–C(7)–H(7')	111.6
C(4)–C(3)–H(3)	107.4	C(7)–C(8)–H(8)	111.7
C(3)–C(4)–H(4)	106.3	C(7)–C(8)–H(8')	106.6
O(4)–C(4)–H(4)	111.6	N–C(8)–H(8')	109.5
C(5)–C(4)–H(4)	108.2	H(8)–C(8)–H(8')	108.4
C(4)–C(5)–H(5)	107.5	N–C(8)–H(8)	108.5
O(5)–C(5)–H(5)	110.2	C(8)–N–H(N)	123.9
C(6)–C(5)–H(5)	107.7	C(1)–N–H(N)	113.1
C(5)–C(6)–H(6')	109.2	C(2)–O(2)–H(O2)	109.6
O(6)–C(6)–H(6')	110.1	C(3)–O(3)–H(O3)	110.6
C(5)–C(6)–H(6)	111.0	C(4)–O(4)–H(O4)	110.5
O(6)–C(6)–H(6)	106.9	C(5)–O(5)–H(O5)	110.7
H(6)–C(6)–H(6')	105.9	C(6)–O(6)–H(O6)	110.6

1. The bond lengths are given in Table 2 and also the bond angles involving H atoms; no corrections have been made for thermal effects.

The C–O bonds have a mean value of 1.412 Å (mean deviation 0.013 Å), which is 0.015 Å shorter on average than the X-ray values. Systematic shortening of neutron diffraction C–O lengths compared with X-ray values has been noted by other workers (Poppleton, Jeffrey & Williams, 1975). The C–H bonds have a mean of 1.093 Å and the O–H bonds range in length from 0.942 to 0.993 Å (mean 0.968 Å). The C–O–H angles are close to tetrahedral and have a mean value of 110.4°. These dimensions are in accord with those found in the neutron structures of sucrose (Brown & Levy, 1973) and methyl α -D-altropyranoside (Poppleton, Jeffrey & Williams, 1975).

The hydrogen bonding is illustrated in Fig. 2 and the dimensions are given in Table 3 and Fig. 2. There is only one intramolecular hydrogen bond, N–H(N)···O(2); the N atom also acts as a donor to the carbonyl O(1)^{II} of an adjacent molecule related by the translation along *b*, to form a bifurcated bond. H(N) lies within 0.010 Å of the plane of the amide group; the N–H(N) bond of 1.115 Å is significantly longer than the N–H bond of 1.010 Å in the neutron

Table 3. Hydrogen-bond dimensions

Estimated standard deviations for the distances $X\cdots O$ and $H\cdots O$ are 0.013 and 0.017 Å respectively and for the angles $X-H\cdots O$ they are 1.3°.

$X-H\cdots O$	$X\cdots O$ (Å)	$H\cdots O$ (Å)	$\angle X-H\cdots O$ (°)
O(2)–H(O2)···O(3) ^I	2.904	2.002	159.7
O(3)–H(O3)···O(5) ^{II}	2.711	1.826	148.7
O(4)–H(O4)···O(3) ^I	2.708	1.755	172.2
O(5)–H(O5)···O(6) ^{III}	2.717	1.757	172.8
O(6)–H(O6)···O(4) ^{IV}	2.741	1.829	151.1
N–H(N)···O(1) ^{II}	2.850	2.101	121.7
N–H(N)···O(2)	2.617	2.028	109.3

Symmetry code

(I)	$x + 1$	y	z	(III)	$x - 1$	y	z
(II)	x	$y - 1$	z	(IV)	x	$y + 1$	z

structure of *N*-acetylglycine (Mackay, 1975) and 1.037 Å (mean of three values) in the neutron structure of L-cysteine (Kerr, Ashmore & Koetzle, 1975). The N···O(2) and N···O(1)^{II} distances are 2.617 and 2.850 Å respectively, whereas the H(N)···O distances of 2.028 and 2.101 Å are more nearly equal as has been noted for bifurcated bonds in other structures, e.g. methyl α -D-altropyranoside. In the bifurcated bond, the angle at H(N) is 125.1° corresponding to a separation of 3.664 Å between the two acceptor O atoms. The angles N–H(N)···O are 109.3 and 121.7°, while the acceptor angles, C–O···H(N), have the very different values of 90.4 and 133.1°. In the five intermolecular bonds, the O···O distances range from 2.708 to 2.904 Å, the H···O distances from 1.755 to 2.002 Å and the O–H···O angles from 148.7 to 172.8°. These dimensions are normal and agree with values tabulated by Brown (1976). The acceptor angles, C–O···H, are smaller than the angles subtended at the H atoms, and range from 120.3 to 140.8° (see Fig. 2).

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4,8-Dimethoxy-1,5-naphthyridine

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Abstract. $C_{10}H_{10}N_2O_2$, $M_r = 190.20$, hexagonal, $R\bar{3}$ (No. 148), $Z = 9$. At -35°C , $a = 24.314$ (8), $c = 4.005$ (1) Å, $V = 2050$ Å³, $D_x = 1.386$ g cm⁻³. Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 0.77$ cm⁻¹. Full-matrix least-squares refinement using 793 reflections [$I > 2\sigma(I)$] collected with ω scans on a Syntex $P2_1$ diffractometer converged at a final R of 0.041. The center of the molecule is coincident with a crystallographic center; the methoxy substituent is in the same plane as the naphthyridine ring with the methyl group directed away from the lone pair of the ring N atom.

Introduction. Crystals were grown by vacuum sublimation and found to be hygroscopic when exposed to the atmosphere at room temperature. The colorless prisms clearly showed the presence of a threefold rotation axis. The possible space groups, $R3$ and $R\bar{3}$, were determined from oscillation and Weissenberg photographs. The crystal selected for data collection had approximate dimensions of 0.32 mm perpendicular to (001) and 0.29 mm perpendicular to the {100} form.

Mounted on a Syntex $P2_1$ diffractometer equipped with a low-temperature apparatus, the crystal was cooled to -35°C . Mo $K\alpha$ radiation, monochromated with a graphite crystal, was used throughout this study. The unit-cell dimensions were refined from the Bragg angles (as determined by the Syntex centering routine) of 15 reflections.

Intensity data for 1041 unique reflections ($4^\circ < 2\theta < 55^\circ$) were collected using the ω -scan technique. Scans of 1.0° were employed with scan rates which ranged from 1.0 to $5.0^\circ \text{ min}^{-1}$ depending on the number of counts measured in a rapid preliminary scan. Background measurements were taken at both ends of the scan with ω displaced 1.0° from the $K\alpha$ peak; the time

for each measurement was one-half of the scan time. The intensities of four standard reflections were monitored after every 96 reflections; only statistical variations were noted. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods (*MULTAN*); the E statistics suggested, and the structure was successfully solved in, the centrosymmetric space group, $R\bar{3}$. The molecular center coincides with a crystallographic center of symmetry. Refinement of the structure by the full-matrix least-squares method was carried out using only those 793 reflections for which $I > 2\sigma(I)$. The non-hydrogen

Table 1. *Final positional parameters with estimated standard deviations*

(a) Atomic coordinates for the non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	0.57417 (6)	0.52658 (6)	0.7416 (3)
C(2)	0.58478 (8)	0.58394 (8)	0.8126 (5)
C(3)	0.54744 (8)	0.60975 (8)	0.7149 (4)
C(4)	0.49422 (7)	0.57316 (7)	0.5267 (4)
C(5)	0.47908 (7)	0.51022 (7)	0.4426 (4)
O(6)	0.45379 (5)	0.59170 (5)	0.4141 (3)
C(7)	0.46871 (11)	0.65510 (10)	0.4958 (7)

(b) Atomic coordinates for the H atoms

	<i>x</i>	<i>y</i>	<i>z</i>
H(2)	0.6221 (9)	0.6107 (8)	0.947 (5)
H(3)	0.5603 (7)	0.6516 (8)	0.778 (4)
H(7A)	0.4328 (10)	0.6603 (9)	0.405 (5)
H(7B)	0.4691 (9)	0.6612 (10)	0.772 (6)
H(7C)	0.5087 (10)	0.6869 (9)	0.407 (5)