

Fig. 2. Perspective view of the crystal structure along the b axis showing the molecular conformation [the torsion angles $C(8)-N(1)-C(10)-C(11)$ and $N(1)-C(10)-C(11)-O(13)$ are -78.1 and -4.2° respectively]. The dotted line indicates the hydrogen bond.

The molecular arrangement of the benzotriazolyl group is identical within the experimental error with that found in the crystal structures of benzotriazole (Escande, Galigné & Lapasset, 1974), *cis*-1-(6-acetoxymethyltetrahydro-2-pyranyl)-5,6-dichlorobenzotriazole (*cis*-ATD) (Fayos & García-Blanco, 1972) and 2-(4-*O*-acetyl-2,3-dideoxy- β -*L*-glycero-pent-2-enopyranosyl)-5,6-dichlorobenzotriazole (*trans*-CLBA) (Lopez de Lerma, Martínez-Carrera & García-Blanco, 1973).

Bond distances indicate that substantial delocalization occurs in the heterocyclic nine-membered system. This is also strictly planar, atomic displacements from the least-squares plane being no larger than 0.01 \AA .

The crystal packing is shown in Fig. 2. The molecules are linked in infinite chains parallel to the c axis by a strong $O-H \cdots N$ hydrogen bond, which is nearly linear. It involves the carboxylic $O(12)-H$ and the $N(3^i)$ atom of the molecule related by the glide

plane [$O \cdots N$ 2.69 , $H \cdots N$ 1.69 \AA , $O-H \cdots N$ angle 169°].

This result confirms the ability of the $N(3)$ atom to behave as an excellent hydrogen-bond acceptor, as previously recognized in the crystal structures of benzotriazole and *cis*-ATD.

All the other intermolecular distances appear to be in the normal range but there are two contacts shorter than the sum of the van der Waals radii: those formed by $O(13)$ with $H(C4^i)$ at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, 2.47 \AA , on the one side, and with $H(C7^{ii})$ at $(x, y - 1, z)$, 2.42 \AA , on the other side. Moreover, the arrangement of $C(11)$, $H(C4^i)$ and $H(C7^{ii})$ around the O atom is approximately planar trigonal. This situation may be indicative of some donor character in hydrogen bonding from the C atoms in positions 4 and 7, as suggested by Fayos & García-Blanco (1972).

We thank Professor F. Sparatore for providing us with the crystalline sample.

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2-*exo*-Hydroxy-7-methylbicyclo[2.2.1]heptane-7-*syn*-carboxylic Acid*†

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Abstract. $C_9H_{14}O_3$, monoclinic, $P2_1/c$, $a = 11.58(2)$, $b = 6.874(10)$, $c = 12.02(2) \text{ \AA}$, $\beta = 115.21(5)^\circ$, $Z = 4$, $D_x = 1.306(7)$, $D_m = 1.32(1) \text{ g cm}^{-3}$, at 22°C . For 798 reflections with $I > \sigma$, $R = 0.056$ and $R_w = 0.032$. The norbornane skeleton shows little distortion by the

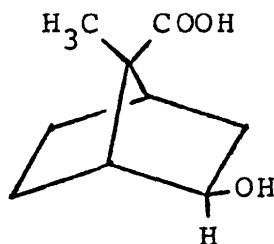
substituent groups, and the $O(\text{hydroxyl})-C(\text{carboxyl})$ distance (2.87 \AA) is less crowded than in a salt of a related 2,6,2-methylhydroxy acid which lactonizes more rapidly.

Introduction. This compound was studied as part of a program to establish the dimensions and their variation for a variety of substituted norbornane molecules (Chapuis, Zalkin & Templeton, 1973, 1977). There has

* Structures of Bicyclo[2.2.1] Systems. III.

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been contradiction in the literature concerning the identity of this isomer, and our work directly confirms the assignment made by Moriarty & Adams (1973).



This hydroxy acid was prepared from the lactone which melts at 125–126°C (Storm & Koshland, 1972*b*), and was crystallized from ethyl acetate by Hackney (1975). Photographic and diffractometer X-ray experiments were made with a crystal 0.16 × 0.14 × 0.03 mm. Absent reflections $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ indicate space group $P2_1/c$. Setting angles of 12 reflections within the range $23^\circ < 2\theta < 28^\circ$ were used for least-squares adjustment of the cell dimensions ($\lambda = 0.70926 \text{ \AA}$ for Mo $K\alpha_1$). Intensities were measured by the θ - 2θ scan technique for 2063 reflections with $2\theta < 45^\circ$ (plus 230 forbidden by the space group) in the half-sphere with k non-negative. The 2θ scan rate was 1° min^{-1} and background was counted for 10 s near each end of the scan. Averaging of equivalent pairs yielded 1146 independent reflections; for 798 of these, $I > \sigma$. With $\mu(\text{Mo}) = 1.0 \text{ cm}^{-1}$ an absorption

Table 1. Positional parameters for heavy atoms ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	2123 (3)	1437 (6)	5756 (3)
C(2)	1376 (3)	2964 (6)	4823 (3)
C(3)	2113 (4)	3148 (7)	4011 (4)
C(4)	3218 (3)	1704 (5)	4621 (3)
C(5)	4152 (4)	2563 (8)	5847 (4)
C(6)	3374 (4)	2426 (8)	6633 (4)
C(7)	2582 (3)	56 (5)	5018 (3)
C(8)	3480 (5)	-1569 (7)	5779 (5)
C(9)	1522 (3)	-1019 (6)	3985 (3)
O(1)	737 (2)	-2023 (4)	4135 (2)
O(2)	1595 (3)	-897 (4)	2917 (2)
O(3)	87 (2)	2341 (4)	4050 (2)

correction was deemed unnecessary. An empirical extinction correction added 13% to the structure factor of the strongest reflection. The structure was solved by the *MULTAN* program (Germain, Main & Woolfson, 1971). H atoms were found in difference maps or by calculation from coordinates of C atoms. The structure was refined with our full-matrix least-squares program,

Table 2. Positional ($\times 10^3$) and thermal parameters for the hydrogen atoms

The form of the temperature factor is $\exp(-B\lambda^{-2} \sin^2 \theta)$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
H(1)	156 (3)	82 (4)	615 (3)	1.7 (8)
H(2)	131 (3)	441 (5)	521 (3)	2.6 (8)
H(3)	144 (3)	275 (5)	303 (3)	2.5 (7)
H(4)	246 (3)	455 (6)	400 (3)	2.6 (9)
H(5)	365 (3)	121 (4)	405 (2)	1.4 (7)
H(6)	500 (3)	168 (5)	626 (3)	3.3 (9)
H(7)	438 (4)	407 (7)	577 (4)	5.4 (12)
H(8)	391 (3)	152 (5)	739 (3)	2.4 (9)
H(9)	321 (3)	384 (6)	688 (3)	4.0 (10)
H(10)	293 (4)	-261 (7)	611 (4)	6.2 (12)
H(11)	389 (4)	-236 (6)	525 (3)	5.2 (11)
H(12)	428 (4)	-102 (6)	647 (3)	4.0 (10)
H(13)	83 (5)	-169 (8)	228 (5)	9.9 (18)
H(14)	-38 (5)	217 (8)	459 (4)	9.2 (17)

Table 3. Bond distances (\AA)

C(1)–C(2)	1.511 (6)	C(1)–H(1)	1.04 (3)
C(1)–C(6)	1.540 (6)	C(2)–H(2)	1.11 (3)
C(1)–C(7)	1.540 (6)	C(3)–H(3)	1.13 (3)
C(2)–C(3)	1.552 (6)	C(3)–H(4)	1.05 (4)
C(3)–C(4)	1.537 (6)	C(4)–H(5)	1.06 (3)
C(4)–C(5)	1.527 (6)	C(5)–H(6)	1.08 (3)
C(4)–C(7)	1.534 (6)	C(5)–H(7)	1.08 (4)
C(5)–C(6)	1.561 (7)	C(6)–H(8)	1.06 (3)
C(7)–C(8)	1.536 (6)	C(6)–H(9)	1.06 (4)
C(7)–C(9)	1.515 (6)	C(8)–H(10)	1.14 (5)
C(2)–O(3)	1.447 (5)	C(8)–H(11)	1.09 (4)
C(9)–O(1)	1.215 (5)	C(8)–H(12)	1.02 (4)
C(9)–O(2)	1.323 (5)	O(2)–H(13)	1.04 (5)
O(2)···O(3 ⁱⁱ)	2.633 (6)	O(3)–H(14)	1.01 (5)
O(3)···O(1 ⁱ)	2.737 (6)	H(13)···O(3 ⁱⁱ)	1.64 (5)
		H(14)···O(1 ⁱ)	1.76 (5)

Symmetry code

(i) $-x, -y, 1-z$ (ii) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$

Table 4. Bond angles ($^\circ$)

C(2)–C(1)–C(6)	106.0 (4)	C(4)–C(5)–C(6)	102.0 (3)	O(1)–C(9)–O(2)	122.8 (3)
C(2)–C(1)–C(7)	103.2 (3)	C(1)–C(6)–C(5)	103.3 (3)	C(9)–O(2)–H(13)	107 (2)
C(6)–C(1)–C(7)	102.2 (3)	C(1)–C(7)–C(4)	93.1 (3)	C(2)–O(3)–H(14)	108 (3)
C(1)–C(2)–C(3)	103.3 (3)	C(1)–C(7)–C(8)	114.6 (3)	O(2)–H(13)···O(3 ⁱⁱ)	158 (4)
C(1)–C(2)–O(3)	112.3 (3)	C(1)–C(7)–C(9)	114.5 (3)	O(3)–H(14)···O(1 ⁱ)	163 (4)
C(3)–C(2)–O(3)	108.3 (3)	C(4)–C(7)–C(8)	115.4 (3)	C(2)–O(3)···C(9)	78.7 (2)
C(2)–C(3)–C(4)	102.5 (3)	C(4)–C(7)–C(9)	115.7 (3)	C(7)–C(9)···O(3)	82.0 (2)
C(3)–C(4)–C(5)	108.3 (4)	C(8)–C(7)–C(9)	103.9 (4)	O(1)–C(9)···O(3)	88.5 (2)
C(3)–C(4)–C(7)	102.2 (3)	C(7)–C(9)–O(1)	123.4 (3)	O(2)–C(9)···O(3)	104.6 (2)
C(5)–C(4)–C(7)	102.8 (3)	C(7)–C(9)–O(2)	113.6 (3)		

as modified by Olson (1975) to use polar form factors for H (Stewart, Davidson & Simpson, 1965). For other atoms we used the form factors of Doyle & Turner (1968) with dispersion corrections from Cromer & Liberman (1970). Zero weight was assigned to reflections with $I < \sigma$; otherwise, $w = [\sigma(F)]^{-2}$; $\sigma(F)$ was derived from $\sigma^2(I) = s^2 + (0.02I)^2$, where s^2 is the variance due to counting statistics. In the last cycle, no parameter shifted more than 0.15 σ . The final R ($= \Sigma |AF| / \Sigma |F_o|$) was 0.056 for 798 reflections and 0.096 including reflections of zero weight; R_w ($= [\Sigma w(AF)^2 / \Sigma wF_o^2]^{1/2}$) was 0.032. Final parameters, distances and angles are listed in Tables 1–4.*

Discussion. Fig. 1 shows the molecular shape and numbering scheme. The C(2)–C(3) and C(5)–C(6) bonds (ave 1.556 Å) are longer than the other skeletal C–C bonds (ave 1.532 Å), as was observed by Fratini, Britts & Karle (1967) in 3-*exo*-(*N*-benzyl-*N*-methylamino-methyl)-2-*endo*-hydroxybicyclo[2.2.1]heptane, and as was calculated with a valence force-field model for nor-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32373 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

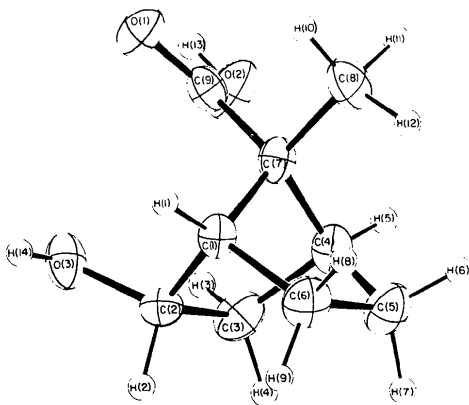


Fig. 1. A perspective view of a molecule with 50% probability thermal ellipsoids, drawn with ORTEP (Johnson, 1965). The size of the H atoms is arbitrary.

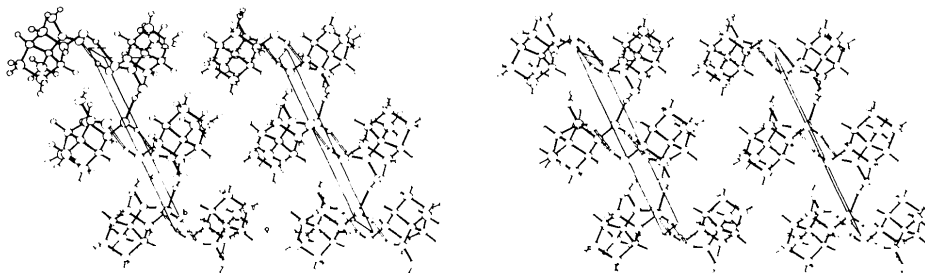


Fig. 2. A stereoscopic view of the crystal structure along b , showing hydrogen bonds between molecules.

bornane by Altona & Sundaralingam (1972). The same trend is found for the average bond lengths in the structures of several other substituted norbornanes (e.g. Flippen, 1972; Chapuis *et al.*, 1973, 1977; Albinati, Zocchi, Germain & Declercq, 1973), although in each of these cases only one of the 2–3-type bonds is longer than all the 1–2- and 1–7-type bonds. For norbornane itself, electron diffraction studies are ambiguous on this point (Morino, Kuchitsu & Yokozeki, 1967; Dallinga & Toneman, 1968; Chiang, Wilcox & Bauer, 1968).

The bond angle C(2)–C(1)–C(6) is 2.3° less than C(3)–C(4)–C(5), a distortion which increases the distance between the hydroxy and carboxyl groups. Otherwise, the skeletal bond angles conform closely to $mm2$ symmetry and give little evidence of distortion of the framework. This result is in contrast to the considerably greater distortion observed in the Na salt of 2-*exo*-methyl-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid (Chapuis *et al.*, 1977). We note that the distance between O(3) and C(9) is 2.866 (8) Å, only modestly greater than the 2.783 (3) Å observed for the salt of the 2,6,2-methylhydroxy acid. Estimates from Dreiding models (Storm & Koshland, 1972a; Moriarty & Adams, 1973) correspond to about 2.9 and 2.2 Å, respectively, for these two distances; these values also indicate that there is considerable strain in the latter compound. The 2,6,2-substituted compound undergoes acid-catalyzed lactonization with a rate about 7×10^4 times greater than the 2,7,7-substituted compound (Hackney, 1975). For reference, in discussions of these rates in the context of the work reviewed by Bürgi (1975), some angles involving the O(3)–C(9) vector are included in Table 4. It would be interesting to estimate the contribution the strain energy of the framework makes to the energy of the transition state for the lactone formation, according to a model like that of Altona & Sundaralingam (1970), for each of these cases to see how much this might explain some of the difference in rates.

Each molecule is attached to three others by a total of four hydrogen bonds (Fig. 2), forming sheets parallel to (100). Each hydroxyl group forms a hydrogen bond to O(1) of one neighboring molecule while it accepts a hydrogen bond from O(2) of another neighbor.

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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. VI. A Neutron Diffraction Study of Dicesium Tetracyanoplatinate(II) Monohydrate*

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Abstract. Cs₂[Pt(CN)₄]·H₂O, hexagonal, *P*6₁ or *P*6₅, (*C*₆² or *C*₆⁵), *a* = 9·709 (4), *c* = 19·343 (8) Å, *Z* = 6, *D*_m = 3·66, *D*_c = 3·68 g cm⁻³. The structure was determined with direct methods. The 1656 reflections collected by neutron diffraction were refined to an agreement index of *R*(*F*_o²) = 0·101 for all observed data and *R*(*F*_o) = 0·074 for 1348 data with *F*_o² > σ(*F*_o²). The Pt–Pt separation is 3·545 (1) Å and the average C–Pt–Pt–C torsional angle is –32·79 (31)°. The Pt(CN)₄²⁻ groups comprise an unusual helical Pt chain along *c*.

Introduction. Preliminary X-ray photographs showed Laue symmetry 6/*m*, and the following systematic ab-

sences were observed: 00*l* when *l* = 6*n*. These conditions establish the space group *P*6₁, or its enantiomorph *P*6₅. Cell constants were established by centering 16 reflections and carrying out a least-squares analysis of the determined angles 2θ, χ, and φ.

Preliminary crystal data on this compound have been published by Otto, Holzapfel, Yersin & Gliemann (1976). There is good agreement of *c* with their value of 19·336 (6) Å. However, their *a* [9·687 (2) Å] is 5·5 e.s.d. (this work) shorter.

A crystal weighing 85·1 mg was mounted in a lead-glass capillary for the neutron diffraction studies. The neutron source was the Argonne National Laboratory CP-5 reactor. The diffractometer was a fully automated (Sigma 5 computer control) four-circle instrument which has been described by Petersen, Dahl & Williams (1974).

Data were collected with a θ–2θ step-scan and an interval of 0·1° in 2θ. The scan widths were varied for

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