

Fig. 1. A stereoview of the unit cell of  $\text{Na}_2[\text{Pt}(\text{CN})_4\text{Br}_2] \cdot 2\text{H}_2\text{O}$  with the ellipsoids shown at 50% probability. Hydrogen-bonding interactions are weak and are indicated with thin lines.

partially oxidized compounds. A study of potassium tetracyanoplatinate(IV) dibromide may reveal why  $\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_{0.3}] \cdot 3\text{H}_2\text{O}$  is preferentially formed.

#### References

- ABYS, J. A., ENRIGHT, N. P., GERDES, H. M., HALL, T. L. & WILLIAMS, J. M. (1976). *Inorg. Synth.* **19**. In the press.
- COMÈS, R., LAMBERT, M., LAUNOIS, H. & ZELLER, H. R. (1973). *Phys. Rev. (B)*, **8**, 571–575.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- KOCH, T. R., ABYS, J. A. & WILLIAMS, J. M. (1976). *Inorg. Synth.* **19**. In the press.
- PETERSON, S. W., DAHL, L. F. & WILLIAMS, J. M. (1974). *J. Amer. Chem. Soc.* **96**, 6610–6620.
- WASHECHECK, D. M., PETERSEN, J. L., REIS, A. H. JR & WILLIAMS, J. M. (1976). *Inorg. Chem.* **15**, 74–78.
- WILLIAMS, J. M., KEEFER, K. D., WASHECHECK, D. M. & ENRIGHT, N. P. (1976). *Inorg. Chem.* **15**, 2446–2455.

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### Sodium 2-Methyl-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylate trihydrate\*†

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**Abstract.**  $\text{C}_9\text{H}_{13}\text{O}_3\text{Na} \cdot 3\text{H}_2\text{O}$ , monoclinic,  $P2_1/c$ ;  $a = 15.887$  (8),  $b = 6.459$  (4),  $c = 11.829$  (6) Å,  $\beta = 106.60$  (5)°,  $Z = 4$ ,  $D_x = 1.406$  (2),  $D_m = 1.399$  (7)  $\text{g cm}^{-3}$ , at 23 °C. For 1357 reflections with  $I > 3\sigma$ ,  $R = 0.036$  and  $R_w = 0.032$ . Each Na ion is coordinated by five water molecules and an alcohol O atom. Hydrogen bonds between water and the carboxyl groups tie the molecules together in a layer structure. The carboxyl C and hydroxyl O atoms are 2.783 (3) Å from each

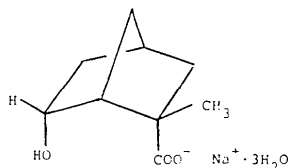
other, and bond angles indicate that the molecule has been deformed to avoid a closer contact.

**Introduction.** The title compound is one of several derivatives of norbornane which we have studied to obtain accurate molecular dimensions for the framework and for the attached groups. These data were desired for the interpretation of geometrical effects on rates of intramolecular reactions, such as lactonization, which have been studied with several such derivatives (Storm & Koshland, 1972; Hackney, 1975). The structure of one of the related lactones was reported earlier (Chapuis, Zalkin & Templeton, 1973).

\* Structures of Bicyclo[2.2.1] Systems. II.

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The crystals were prepared by Hackney (1975), with the method of Beckmann & Geiger (1961) to produce the lactone (m.p. 68–69°), which was then hydrolyzed with aqueous NaOH and crystallized to give transparent plates of the hydrated salt:



A crystal 0.045 × 0.135 × 0.27 mm in size was studied by photographic and diffractometer techniques. Absent reflections  $h0l$   $l \neq 2n$  and  $0k0$   $k \neq 2n$  indicate space group  $P2_1/c$ . Setting angles for 12 reflections with  $40^\circ < 2\theta < 45^\circ$  (Mo  $K\alpha_1$ ,  $\lambda = 0.70926$  Å) were used for least-squares adjustment of the cell dimensions. The density was measured by flotation in a solution of CCl<sub>4</sub> and petroleum spirit. Intensities were measured with graphite-monochromatized Mo  $K\alpha$  radiation and the  $\theta$ - $2\theta$  scan technique for 5376 reflections in the half sphere with  $k$  non-negative and  $2\theta < 55^\circ$ . After equivalent reflections were averaged there were 2689 unique ones of which 1357 had  $I > 3\sigma$ . The absorption coefficient is estimated to be 1.4 cm<sup>-1</sup>, and measurements of intensities at various azimuthal angles varied less than 3%. Accordingly, no correction was made for absorption.

The crystal structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). In addition to the organic anion and Na atom, three water molecules showed up in the Fourier synthesis in accordance with the observed density. All the H atoms appeared in a later difference synthesis. The structure was refined with our full-matrix least-squares program,

as modified by Olson (1975) to use polar scattering 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  $I < 3\sigma$ ; otherwise,  $w = [\sigma(F)]^{-2}$ ,  $\sigma(F)$  being derived from  $\sigma^2(F^2) = s^2 + (pF^2)^2$  where  $s^2$  is the variance due to counting statistics and  $p = 0.02$ . In the last cycle no parameter shifted more than  $0.05\sigma$ . The final residual  $R = \Sigma |\Delta F| / \Sigma |F_o|$  was 0.036 for 1357 reflections and 0.094 for 2689 reflections including those of zero weight. The weighted residual minimized

Table 2. *Parameters of the hydrogen atoms*

The form of the temperature factor is  $\exp(-B\lambda^{-2}\sin^2\theta)$ . The thermal parameters are constrained to be the same for the two H atoms of each water molecule.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	0.319 (2)	0.736 (4)	0.652 (2)	1.5 (5)
H(2)	0.313 (2)	0.266 (4)	0.416 (2)	2.5 (6)
H(3)	0.418 (2)	0.385 (4)	0.443 (2)	2.8 (6)
H(4)	0.437 (2)	0.160 (4)	0.617 (2)	1.9 (5)
H(5)	0.262 (2)	0.142 (5)	0.564 (3)	3.3 (7)
H(6)	0.319 (2)	0.125 (5)	0.716 (3)	3.6 (7)
H(7)	0.267 (1)	0.443 (3)	0.745 (2)	0.9 (4)
H(8)	0.427 (2)	0.447 (4)	0.773 (2)	2.3 (6)
H(9)	0.473 (2)	0.554 (4)	0.664 (2)	1.8 (5)
H(10)	0.382 (2)	0.741 (4)	0.367 (2)	2.8 (6)
H(11)	0.442 (2)	0.752 (4)	0.512 (2)	3.4 (7)
H(12)	0.351 (2)	0.902 (5)	0.467 (2)	3.2 (7)
H(13)	0.155 (3)	0.544 (6)	0.595 (3)	5.5 (13)
H(14)	0.140 (2)	0.621 (5)	0.048 (2)	3.3 (5)
H(15)	0.133 (2)	0.580 (5)	0.162 (3)	3.3 (5)
H(16)	0.023 (2)	0.396 (5)	0.694 (3)	3.6 (6)
H(17)	-0.066 (2)	0.358 (5)	0.623 (3)	3.6 (6)
H(18)	0.146 (2)	0.237 (5)	0.332 (3)	3.9 (6)
H(19)	0.141 (2)	0.028 (5)	0.355 (3)	3.9 (6)

Table 1. *Parameters for heavy atoms*

The form of the temperature factor is  $\exp[-0.25(h^2a^{*2}B_{11} + \dots + 2hka^*b^*B_{12} + \dots)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
C(1)	0.3260 (2)	0.5854 (4)	0.6219 (2)	2.0 (1)	1.9 (1)	1.7 (1)	-0.0 (1)	0.39 (9)	0.3 (1)
C(2)	0.3206 (1)	0.5802 (4)	0.4886 (2)	1.6 (1)	1.8 (1)	1.63 (9)	-0.05 (9)	0.64 (8)	0.08 (9)
C(3)	0.3610 (2)	0.3653 (5)	0.4770 (2)	2.1 (1)	2.3 (1)	2.0 (1)	0.7 (1)	0.70 (9)	0.1 (1)
C(4)	0.3880 (2)	0.2802 (4)	0.6036 (2)	1.9 (1)	2.4 (1)	2.1 (1)	0.8 (1)	0.26 (9)	0.4 (1)
C(5)	0.3040 (2)	0.2172 (5)	0.6339 (3)	3.0 (1)	2.5 (1)	2.1 (1)	-0.0 (1)	0.7 (1)	0.3 (1)
C(6)	0.2645 (2)	0.4279 (4)	0.6534 (2)	2.1 (1)	2.8 (1)	1.4 (1)	0.0 (1)	0.46 (9)	0.1 (1)
C(7)	0.4140 (2)	0.4766 (5)	0.6774 (2)	2.2 (1)	3.1 (1)	1.9 (1)	0.0 (1)	-0.1 (1)	0.1 (1)
C(8)	0.2280 (2)		0.4056 (2)	1.8 (1)	2.1 (1)	1.8 (1)	0.0 (1)	0.77 (8)	0.7 (1)
C(9)	0.3761 (2)	0.7552 (6)	0.4578 (3)	2.3 (1)	3.0 (2)	3.4 (1)	-0.3 (1)	0.9 (1)	0.7 (1)
O(1)	0.1984 (1)	0.4993 (3)	0.3196 (1)	2.62 (8)	3.17 (9)	1.86 (7)	-0.08 (8)	-0.16 (6)	-0.08 (7)
O(2)	0.1880 (1)	0.7770 (3)	0.4259 (2)	2.57 (8)	2.9 (1)	3.04 (9)	1.31 (8)	0.91 (7)	0.52 (8)
O(3)	0.1738 (1)	0.4362 (4)	0.5862 (2)	1.86 (8)	2.9 (1)	3.09 (9)	-0.05 (8)	0.62 (7)	0.17 (8)
O(4)	0.1003 (1)	0.5961 (4)	0.0919 (2)	2.40 (9)	4.5 (1)	2.22 (9)	0.67 (9)	0.48 (7)	0.7 (1)
O(5)	-0.0147 (1)	0.4163 (3)	0.6209 (2)	1.87 (8)	3.6 (1)	2.25 (8)	0.01 (8)	0.43 (7)	0.16 (8)
O(6)	0.1083 (1)	0.1346 (3)	0.3367 (2)	2.74 (9)	2.4 (1)	2.47 (9)	0.39 (7)	0.56 (7)	0.27 (8)
Na	0.04322 (6)	0.2499 (2)	0.48103 (9)	2.20 (4)	2.53 (5)	2.64 (5)	0.08 (4)	0.76 (3)	-0.31 (4)

by the refinement was  $R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2} = 0.032$ . Final parameters are listed in Tables 1 and 2.\*

**Discussion.** This structure determination agrees with the conclusions of Moriarty & Adams (1973) concerning the assignment of isomers, about which there has been some confusion in the literature. Fig. 1 shows the molecular shape and the atomic numbering scheme. Bond distances and angles are listed in Tables 3 and 4. The C—C distances are all between 1.528 and 1.554 Å. The angle of the bridging bonds C(1)—C(7)—C(4) is 94.1°, a value characteristic of the norbornane frame (Chapuis *et al.*, 1973, and references therein). It is noteworthy that the angle C(2)—C(1)—C(6), 112.2°, which involves the substituted C atoms, is larger than C(3)—C(4)—C(5), 107.6°, at the other side of the molecule, and that angles C(1)—C(2)—C(8), 114.2°, and C(1)—C(6)—O(3), 116.8°, are both greater than

Table 3. Bond distances (Å)

C(1)—C(2)	1.554 (3)	C(1)—H(1)	1.05 (3)
C(1)—C(6)	1.529 (4)	C(3)—H(2)	1.09 (3)
C(1)—C(7)	1.535 (3)	C(3)—H(3)	1.10 (3)
C(2)—C(3)	1.551 (4)	C(4)—H(4)	1.08 (2)
C(2)—C(8)	1.538 (4)	C(5)—H(5)	1.02 (3)
C(2)—C(9)	1.540 (4)	C(5)—H(6)	1.10 (3)
C(3)—C(4)	1.538 (4)	C(6)—H(7)	1.08 (2)
C(4)—C(5)	1.533 (4)	C(7)—H(8)	1.10 (3)
C(4)—C(7)	1.528 (4)	C(7)—H(9)	1.12 (3)
C(5)—C(6)	1.543 (4)	C(9)—H(10)	1.10 (3)
C(6)—O(3)	1.434 (3)	C(9)—H(11)	1.06 (3)
C(8)—O(1)	1.254 (3)	C(9)—H(12)	1.04 (3)
C(8)—O(2)	1.264 (3)	O(3)—H(13)	0.77 (4)
Na—O(3)	2.413 (2)	O(4)—H(14)	0.95 (3)
Na—O(4 <sup>i</sup> )	2.409 (2)	O(4)—H(15)	0.85 (3)
Na—O(4 <sup>ii</sup> )	2.619 (3)	O(5)—H(16)	0.91 (3)
Na—O(5)	2.368 (2)	O(5)—H(17)	0.90 (3)
Na—O(5 <sup>iii</sup> )	2.448 (3)	O(6)—H(18)	0.91 (3)
Na—O(6)	2.355 (2)	O(6)—H(19)	0.85 (3)
O(1)···O(4)	2.771 (3)	O(2 <sup>v</sup> )···O(6)	2.699 (3)
O(1)···O(6)	2.794 (3)	O(2 <sup>iii</sup> )···O(5)	2.927 (3)
O(2 <sup>iv</sup> )···O(4)	2.835 (3)	O(6 <sup>ii</sup> )···O(5)	2.757 (3)

## Symmetry code

- (i)  $-x, -\frac{1}{2} + y, \frac{1}{2} - z$  (iv)  $x, \frac{3}{2} - y, -\frac{1}{2} + z$   
 (ii)  $x, \frac{1}{2} - y, \frac{1}{2} + z$  (v)  $x, -1 + y, z$   
 (iii)  $-x, 1 - y, 1 - z$

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32159 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

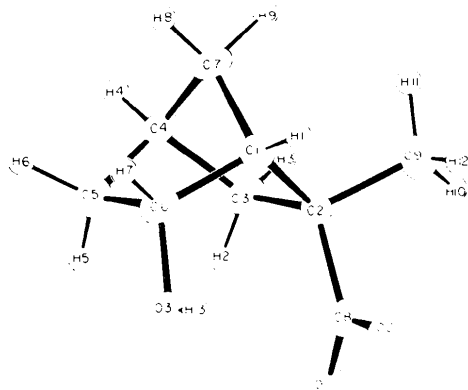


Fig. 1. Perspective view of the anion.

Table 4. Bond angles (°)

See Table 3 for symmetry code.

C(2)—C(1)—C(6)	112.2 (2)	C(1)—C(6)—O(3)	116.8 (2)
C(2)—C(1)—C(7)	101.8 (2)	C(5)—C(6)—O(3)	109.7 (2)
C(6)—C(1)—C(7)	99.1 (2)	C(1)—C(7)—C(4)	94.1 (2)
C(1)—C(2)—C(3)	101.8 (2)	C(2)—C(8)—O(1)	119.2 (2)
C(1)—C(2)—C(8)	114.2 (2)	C(2)—C(8)—O(2)	116.7 (2)
C(1)—C(2)—C(9)	110.7 (2)	O(1)—C(8)—O(2)	124.0 (2)
C(3)—C(2)—C(8)	115.5 (2)	H(14)—O(4)—H(15)	104 (4)
C(3)—C(2)—C(9)	110.8 (2)	H(16)—O(5)—H(17)	105 (4)
C(8)—C(2)—C(9)	103.9 (2)	H(18)—O(6)—H(19)	103 (4)
C(2)—C(3)—C(4)	103.9 (2)	O(1)···O(4)—H(15)	6 (2)
C(3)—C(4)—C(5)	107.6 (2)	O(2 <sup>iv</sup> )···O(4)—H(4)	13 (2)
C(3)—C(4)—C(7)	102.4 (2)	O(2 <sup>iii</sup> )···O(5)—H(17)	12 (2)
C(5)—C(4)—C(7)	101.4 (2)	O(6 <sup>ii</sup> )···O(5)—H(16)	4 (2)
C(4)—C(5)—C(6)	102.7 (2)	O(1)···O(6)—H(18)	10 (2)
C(1)—C(6)—C(5)	103.6 (2)	O(2 <sup>v</sup> )···O(6)—H(19)	13 (2)

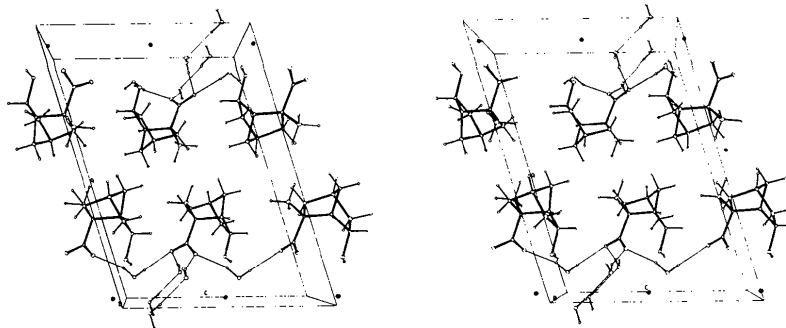


Fig. 2. Stereoscopic view of the structure. Black dots represent Na atoms and the thin lines represent hydrogen bonds.

regular tetrahedral. C(8)···O(3) is 2.783 (3) Å, and would be shorter but for the molecular deformation indicated by the above angles. The structures of the lactones of two similar compounds (Flippen, 1972; Chapuis *et al.*, 1973) exhibit about the same amount of deformation, but in the opposite direction, when the lactone bond exists between atoms corresponding to C(8) and O(3). For reference in discussions of the rate of lactonization we report also the angles O(3)–C(8)–C(2), 83.8 (1)°, and C(6)–O(3)–C(8), 87.6 (2)°.

Each Na ion has as neighbors five water molecules and an alcohol O atom, arranged in octahedral configuration. All of the water H atoms participate in hydrogen bonds, one of them to another water molecule and five to O atoms of the carboxylate group. This coordination geometry and hydrogen bonding connects the molecules into double layers parallel to (100) (Fig. 2). There are no bonds across the plane  $x = \frac{1}{2}$ , a feature which explains the easy cleavage of the crystal along (100).

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#### References

- BECKMANN, S. & GEIGER, H. (1961). *Chem. Ber.* **94**, 48–58.  
 CHAPUIS, G., ZALKIN, A. & TEMPLETON, D. H. (1973). *Acta Cryst.* **B29**, 2642–2644.  
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.  
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.  
 FLIPPEN, J. L. (1972). *Acta Cryst.* **B28**, 2046–2048.  
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.  
 HACKNEY, D. D. (1975). *Models for Chymotrypsin and the Interaction of Lysozyme with Urea*. Thesis, Univ. of California, Berkeley.  
 MORIARTY, R. M. & ADAMS, T. (1973). *J. Amer. Chem. Soc.* **95**, 4070–4071.  
 OLSON, A. J. (1975). *Polar Hydrogen Scattering Factors in X-ray Diffraction Analysis*. Thesis, Univ. of California, Berkeley.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 STORM, D. R. & KOSHLAND, D. E. (1972). *J. Amer. Chem. Soc.* **94**, 5805–5814, 5815–5825.

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## Acide Dioxo-3,17 Nor-19 (Androstène-4)-7 $\alpha$ -butyrique

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**Abstract.** C<sub>22</sub>H<sub>30</sub>O<sub>4</sub>, orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>,  $a = 9.808$  (5),  $b = 19.147$  (9),  $c = 10.618$  (5) Å,  $Z = 4$ ,  $D_x = 1.19$  g cm<sup>-3</sup>. The structure was solved by direct methods. A least-squares refinement with anisotropic thermal coefficients led to a conventional  $R$  value of 0.049 for 1450 observed reflexions. The butyric acid group in the 7 $\alpha$  position is planar.

**Introduction.** Ce composé a été synthétisé pour confectionner une colonne d'affinité utilisée pour la purification du récepteur cytosolique utérin de l'oestradiol (Bucourt *et al.*, 1977). Lors de la synthèse de cette substance il fut isolé un produit secondaire en quantité assez importante qui logiquement devait être l'isomère 7 $\beta$  (Bucourt & Torelli, 1977). Cependant, son spectre de dichroïsme circulaire, très dissemblable du produit principal 7 $\alpha$ , jetait un doute sur les structures attribuées aux deux composés 7 $\alpha$  et 7 $\beta$ . On pouvait invoquer soit une description erronée de la molécule au niveau de la

chaîne et des noyaux  $A$  et  $B$ , soit une mise en défaut des bases d'interprétation du dichroïsme circulaire pour le composé 7 $\beta$ . Afin de lever cette indétermination il fallait pouvoir obtenir une preuve irréfutable des structures et connaître les conformations des deux composés. Dans cet esprit, le présent article a pour but de donner la géométrie moléculaire du composé 7 $\alpha$  déterminée par diffraction des rayons X. L'article suivant présente la détermination de la structure du composé 7 $\beta$ .

Les dimensions de la maille ont été obtenues par affinement des positions de 14 réflexions mesurées au diffractomètre. La structure a été déterminée par méthodes directes en utilisant le programme *MULTAN* (Germain, Main & Woolfson, 1971), avec les 155 réflexions ayant une valeur de  $E > 1,55$ . La meilleure solution a permis de placer les atomes lourds sur la carte de sensibilité électronique. Les atomes d'hydrogène ont été repérés sur des cartes de fonction différence