

O7—C16	1.416 (6)	C21—C23	1.488 (8)	Cremer, D. & Pople, J. A. (1975). <i>J. Am. Chem. Soc.</i> 97 , 1354–1361.
C8—C9	1.536 (6)	O24—C25	1.367 (6)	Faulkner, D. J. (1991). <i>J. Nat. Prod. Rep.</i> 8 , 97–147, and references therein.
C8—C14	1.521 (6)	C25—O26	1.181 (6)	Ireland, C. & Faulkner, J. (1981). <i>Tetrahedron</i> , 37 , W233–W240.
C9—C10	1.560 (6)	C25—C27	1.488 (7)	Kazlauskas, R., Murphy, P. T., Wells, R. J., Noack, K., Oberhansli, W. E. & Schonholzer, P. (1979). <i>Aust. J. Chem.</i> 32 , 867–880.
C9—C11	1.550 (7)			Killean, R. C. G. & Lawrence, J. L. (1969). <i>Acta Cryst.</i> B25 , 1750–1752.
C2—C3—C4	114.0 (4)	C5—C10—C9	114.9 (4)	Mayol, L., Piccialli, V. & Sica, D. (1985). <i>Tetrahedron Lett.</i> 26 , 1357–1360.
C5—C4—C18	112.4 (4)	C5—C10—C19	107.1 (4)	Mayol, L., Piccialli, V. & Sica, D. (1986). <i>Tetrahedron</i> , 42 , 5369–5376.
C4—C5—C10	118.7 (4)	C12—C13—C14	114.5 (4)	Molinski, T. F. & Faulkner, D. J. (1987). <i>J. Org. Chem.</i> 52 , 296–298.
C15—O7—C16	109.5 (4)	C12—C13—C16	115.7 (4)	Puliti, R., De Rosa, S., Mattia, C. A. & Mazzarella, L. (1990). <i>Acta Cryst.</i> C46 , 1533–1536.
O6—C8—C9	124.9 (4)	C14—C13—C16	101.6 (4)	Puliti, R., Gavagnin, M., Cimino, G., Mattia, C. A. & Mazzarella, L. (1992). <i>Acta Cryst.</i> C48 , 2145–2147.
O6—C8—C14	122.6 (4)	C8—C14—C13	112.0 (4)	Stout, G. H. & Jensen, L. H. (1968). In <i>X-ray Structure Determination</i> . New York: Macmillan.
C8—C9—C10	117.3 (4)	C8—C14—C15	111.0 (4)	
C8—C9—C11	103.2 (4)	C13—C14—C15	101.8 (4)	
C10—C9—C11	114.2 (4)	O7—C15—C14	104.1 (4)	
C1—C10—C5	106.9 (4)	O7—C16—C13	108.0 (4)	
C1—C10—C9	107.8 (4)			
C4—C5—C10—C9	−71.0 (6)	C12—C13—C14—C15	−159.5 (4)	
C4—C5—C10—C10	165.5 (4)	C16—C13—C14—C8	84.6 (4)	
O6—C8—C9—C10	−15.4 (7)	C14—C13—C16—O24	135.9 (4)	
O6—C8—C14—C15	−9.5 (6)	C13—C14—C15—O20	−76.6 (4)	
C8—C9—C10—C5	−45.1 (6)	C15—O20—C21—O22	3.6 (9)	
C11—C9—C10—C1	74.9 (5)	C16—O24—C25—O26	−7.6 (7)	

The structure was solved using *SIR88* (Burla *et al.*, 1989) and all calculations were made using Enraf–Nonius *SDP* (B. A. Frenz & Associates Inc., 1985) software on a MicroVAX 3100 computer.

Compound (2), 9,11-dihydrogracilin A, was obtained, after purification by chromatography on silica gel, as a colourless oil from the diethyl ether soluble fraction of the acetone extract of sponge *Dendrilla membranosa*, which was collected in the Ross Sea, Antarctica, at depths of 50 m or more, during January 1990.

The derivative (1), used in the X-ray analysis, was obtained by ozonolysis of the natural compound, which has an olefinic bond at C8. The reaction was carried out using the procedure described by Ireland & Faulkner (1981). The major reaction product was purified over silica gel and recrystallized from *n*-hexane.

Characterization of (1): $[\alpha]_D^{20} = +20^\circ$ ($c = 8 \text{ g dm}^{-3}$, diethyl ether). $^1\text{H NMR}(\text{CDCl}_3)$: 0.83 (3H, *s*), 0.94 (3H, *s*), 1.05 (3H, *s*), 1.12 (2H, *m*), 1.28 (4H, *bd*), 1.45 (1H, *m*), 1.53 (1H, *d*), 1.63 (1H, *m*), 1.79 (1H, *m*), 1.96 (1H, *m*), 2.06 (3H, *s*), 2.09 (3H, *s*), 2.22 (1H, *dd*), 3.02 (1H, *d*), 3.07 (1H, *m*), 6.06 (1H, *d*), 6.72 (1H, *s*).

The $^1\text{H NMR}$ measurements were recorded on a Bruker WM 500 spectrometer.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71046 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1024]

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Structure of the Benzo-15-crown-5-3,5-Dinitrobenzoic Acid–Water (1/1/1) Complex

A. SCHOUTEN* AND J. A. KANTERS

Department of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

N. S. POONIA

Department of Chemistry, DA University, Indore 452 001, India

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Abstract

In the title complex, benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene-3,5-dinitrobenzoic acid–water (1/1/1), the structure of which was determined by X-ray diffraction methods at 100 K, the water molecule is involved as a donor in hydrogen bonding to three O atoms of the most flexible part of the crown and as an acceptor in a hydrogen bond with the carboxyl group of 3,5-dinitrobenzoic acid.

Comment

Nature discriminates markedly between the chemically similar pairs of cations Na^+ and K^+ , and Mg^{2+} and Ca^{2+}

and so a study of relevant chemical properties was undertaken (Poonia & Bajaj, 1979; Poonia, Bagdi & Sidhu, 1986). It is also useful to compare the behaviour of H^+ with that of alkali and alkaline-earth cations. X-ray structure analysis has shown that $M(\text{pic})(\text{B15C5})\cdot 2\text{H}_2\text{O}$ (where pic is picrate and B15C5 is benzo-15-crown-5) with $M = H^+$ or Li^+ are isomorphous (Baghwat, Manohar & Poonia, 1980b). The structure of the title complex, $M(\text{dnb})(\text{B15C5})\cdot \text{H}_2\text{O}$, where dnb is the more nucleophilic 3,5-dinitrobenzoate, is as expected for a strong proton donor (organic acid) with a proton-accepting macrocycle such as B15C5 (Poonia, 1974). The crown is hydrated in the crystal lattice as in $M(\text{pic})(\text{B15C5})\cdot 2\text{H}_2\text{O}$ ($M = H^+$, Li^+) (Baghwat, Manohar & Poonia, 1980b), $\text{Ca}(\text{pic})_2(\text{B15C5})\cdot 3\text{H}_2\text{O}$ (Baghwat, Manohar & Poonia, 1980a) and $\text{Ca}(\text{dnb})_2(\text{B15C5})\cdot 3\text{H}_2\text{O}$ (Cradwick & Poonia, 1977). With the water molecule hydrogen bonded to three O atoms of the flexible crown ring, the bonds $\text{O}(22)-\text{H}\cdots\text{O}(9)$ and $\text{O}(22)-\text{H}\cdots\text{O}(10)$, with $\text{O}\cdots\text{O}$ distances of 2.992 (2) and 2.934 (4) Å, respectively, must share an H atom, while the other H atom is involved in $\text{O}(22)-\text{H}\cdots\text{O}(8)$ 2.906 (4) Å. A strong hydrogen bond links the carboxyl group of Hdnb to the water molecule, $\text{O}(4)-\text{H}\cdots\text{O}(22)$ 2.526 (2) Å (Fig. 1). The benzene ring of Hdnb is nearly parallel to the crown phenyl ring (interplanar angle 3.8° , ring-ring distance 3.28 Å) but is not directly over it. The water molecule is sandwiched between B15C5 and Hdnb.

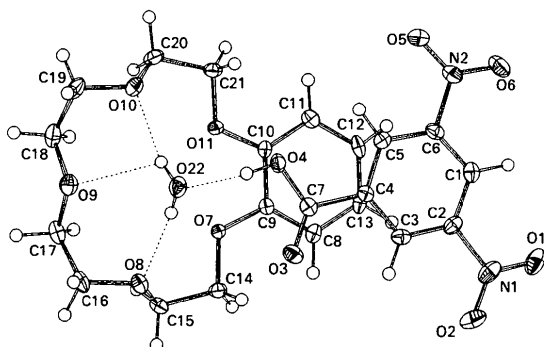


Fig. 1. ORTEP view (Johnson, 1976) of the title compound showing the labelling of the non-H atoms. Thermal ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radius.

Experimental

Crystal data

$\text{C}_7\text{H}_4\text{N}_2\text{O}_6\cdot\text{C}_{14}\text{H}_{20}\text{O}_5\cdot\text{H}_2\text{O}$
 $M_r = 498.44$
 Monoclinic
 $P2_1$
 $a = 7.0711$ (4) Å
 $b = 15.0900$ (10) Å
 $c = 11.1925$ (6) Å
 $\beta = 106.916$ (4)°

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 10.62-17.51^\circ$
 $\mu = 0.113$ mm^{-1}
 $T = 100$ K
 Rod

$V = 1142.60$ (12) Å³
 $Z = 2$
 $D_x = 1.449$ Mg m^{-3}

$0.78 \times 0.22 \times 0.17$ mm
 Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 6772 measured reflections
 3413 independent reflections
 2992 observed reflections
 $[I > 2.5\sigma(I)]$

$R_{\text{int}} = 0.041$
 $\theta_{\text{max}} = 30.26^\circ$
 $h = -10 \rightarrow 0$
 $k = -20 \rightarrow 20$
 $l = -15 \rightarrow 15$
 3 standard reflections
 frequency: 60 min
 intensity variation: 2.3%

Refinement

Refinement on F
 Final $R = 0.0332$
 $\omega R = 0.0297$
 $S = 1.49$
 2992 reflections
 420 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F)]$
 $(\Delta/\sigma)_{\text{max}} = 0.037$
 $\Delta\rho_{\text{max}} = 0.27$ e Å^{-3}

$\Delta\rho_{\text{min}} = -0.26$ e Å^{-3}
 Extinction correction: SHELX76
 Extinction coefficient: 0.0016
 Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV, Table 2.2B)

Data collection: CAD-4 software (Enraf-Nonius, 1985). Cell refinement: SET4 (de Boer & Duisenberg, 1984). Data reduction: HELENA (Spek, 1990a). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELX76 (Sheldrick, 1976). Molecular graphics: ORTEP (Johnson, 1976). Software used to prepare material for publication: PLATON (Spek, 1990b).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O7	0.7759 (2)	0.1483 (2)	0.8595 (1)	0.0165 (4)
O8	0.9036 (2)	0.0920 (2)	1.1066 (1)	0.0201 (4)
O9	0.7704 (2)	0.2561 (2)	1.2036 (1)	0.0222 (5)
O10	0.8236 (2)	0.4062 (2)	1.0574 (1)	0.0203 (4)
O11	0.7285 (2)	0.3141 (2)	0.8312 (1)	0.0167 (4)
C8	0.8208 (3)	0.1279 (2)	0.6531 (2)	0.0173 (6)
C9	0.7891 (3)	0.1795 (2)	0.7476 (2)	0.0148 (5)
C10	0.7624 (3)	0.2714 (2)	0.7320 (2)	0.0145 (5)
C11	0.7659 (3)	0.3108 (2)	0.6204 (2)	0.0191 (6)
C12	0.7939 (3)	0.2578 (2)	0.5236 (2)	0.0200 (6)
C13	0.8213 (3)	0.1683 (2)	0.5400 (2)	0.0204 (6)
C14	0.8237 (3)	0.0574 (2)	0.8892 (2)	0.0189 (6)
C15	0.7750 (3)	0.0410 (2)	1.0091 (2)	0.0200 (6)
C16	0.8293 (4)	0.1011 (2)	1.2125 (2)	0.0230 (6)
C17	0.6742 (3)	0.1724 (2)	1.1962 (2)	0.0223 (6)
C18	0.6354 (3)	0.3284 (2)	1.1757 (2)	0.0247 (6)
C19	0.7501 (4)	0.4103 (2)	1.1639 (2)	0.0237 (6)
C20	0.6815 (4)	0.4375 (2)	0.9465 (2)	0.0219 (6)
C21	0.7379 (3)	0.4089 (2)	0.8334 (2)	0.0197 (6)
O1	1.3613 (3)	0.0807 (2)	0.3648 (2)	0.0354 (6)
O2	1.3940 (3)	0.0041 (2)	0.5335 (2)	0.0355 (5)
O3	1.2881 (2)	0.1395 (2)	0.9041 (1)	0.0237 (4)
O4	1.2216 (2)	0.2852 (2)	0.8989 (1)	0.0209 (4)
O5	1.1720 (3)	0.4538 (2)	0.5268 (2)	0.0466 (8)
O6	1.2328 (3)	0.3946 (2)	0.3659 (1)	0.0312 (5)
N1	1.3635 (3)	0.0736 (2)	0.4745 (2)	0.0264 (6)

N2	1.2203 (3)	0.3911 (2)	0.4725 (2)	0.0251 (6)
C1	1.2955 (3)	0.23311	0.4740 (2)	0.0189 (6)
C2	1.3267 (3)	0.1542 (2)	0.5389 (2)	0.0195 (6)
C3	1.3228 (3)	0.1465 (2)	0.6614 (2)	0.0181 (6)
C4	1.2849 (3)	0.2215 (2)	0.7227 (2)	0.0156 (5)
C5	1.2533 (3)	0.3026 (2)	0.6615 (2)	0.0167 (6)
C6	1.2602 (3)	0.3060 (2)	0.5391 (2)	0.0189 (6)
C7	1.2673 (3)	0.2111 (2)	0.8522 (2)	0.0174 (6)
O22	1.1016 (2)	0.2578 (2)	1.0873 (2)	0.0238 (5)

Table 2. Geometric parameters (Å, °)

O7—C9	1.366 (3)	C18—C19	1.505 (4)
O7—C14	1.429 (4)	C20—C21	1.497 (3)
O8—C15	1.426 (3)	O1—N1	1.228 (3)
O8—C16	1.436 (3)	O2—N1	1.225 (4)
O9—C17	1.426 (4)	O3—C7	1.215 (4)
O9—C18	1.423 (4)	O4—C7	1.314 (4)
O10—C19	1.434 (3)	O5—N2	1.226 (4)
O10—C20	1.431 (3)	O6—N2	1.223 (3)
O11—C10	1.364 (3)	N1—C2	1.475 (4)
O11—C21	1.432 (4)	N2—C6	1.470 (4)
C8—C9	1.383 (3)	C1—C2	1.379 (3)
C8—C13	1.406 (3)	C1—C6	1.382 (3)
C9—C10	1.404 (4)	C2—C3	1.384 (3)
C10—C11	1.390 (3)	C3—C4	1.389 (4)
C11—C12	1.406 (3)	C4—C5	1.388 (4)
C12—C13	1.369 (4)	C4—C7	1.499 (3)
C14—C15	1.500 (3)	C5—C6	1.386 (3)
C16—C17	1.509 (4)		
C9—O7—C14	118.0 (2)	O11—C21—C20	106.3 (2)
C15—O8—C16	112.2 (2)	O1—N1—O2	124.3 (3)
C17—O9—C18	112.8 (2)	O1—N1—C2	117.6 (3)
C19—O10—C20	112.0 (2)	O2—N1—C2	118.1 (2)
C10—O11—C21	117.9 (2)	O5—N2—O6	124.1 (3)
C9—C8—C13	119.2 (3)	O5—N2—C6	117.6 (2)
O7—C9—C8	125.2 (3)	O6—N2—C6	118.3 (3)
O7—C9—C10	114.3 (2)	C2—C1—C6	115.8 (2)
C8—C9—C10	120.5 (2)	N1—C2—C1	118.6 (2)
O11—C10—C9	114.5 (2)	N1—C2—C3	118.2 (3)
O11—C10—C11	125.6 (3)	C1—C2—C3	123.2 (2)
C9—C10—C11	119.8 (2)	C2—C3—C4	118.9 (3)
C10—C11—C12	119.5 (3)	C3—C4—C5	120.1 (2)
C11—C12—C13	120.3 (2)	C3—C4—C7	118.3 (2)
C8—C13—C12	120.7 (2)	C5—C4—C7	121.5 (2)
O7—C14—C15	105.4 (2)	C4—C5—C6	118.3 (3)
O8—C15—C14	109.5 (2)	N2—C6—C1	117.7 (2)
O8—C16—C17	113.3 (2)	N2—C6—C5	118.5 (2)
O9—C17—C16	107.9 (2)	C1—C6—C5	123.7 (3)
O9—C18—C19	107.7 (2)	O3—C7—O4	125.2 (2)
O10—C19—C18	111.9 (2)	O3—C7—C4	121.5 (2)
O10—C20—C21	110.2 (2)	O4—C7—C4	113.3 (2)

Crystals of the title compound [m.p. 373.0 (5) K] were prepared by slow evaporation of a mixture of 3,5-dinitrobenzoic acid and benzo-15-crown-5 (0.0002 M) (1:1) in ethanol (5 ml) at 298 K.

All non-H atoms in the structure were found by direct methods and refined anisotropically. The H-atom positions were located from $\Delta\rho$ syntheses and all parameters were refined individually. The absolute structure is arbitrarily chosen. Inversion of the structure yields insignificant differences in the *R* value.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71034 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1021]

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Structure of (S)-(+)-Ibuprofen

ANDREW A. FREER*

Department of Chemistry, University of Glasgow, Glasgow G12 1RQQ, Scotland

JILLIAN M. BUNYAN, NORMAN SHANKLAND AND DAVID B. SHEEN

Department of Pharmacy, University of Strathclyde, Glasgow G1 1XW, Scotland

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Abstract

(S)-(+)-Ibuprofen, α -methyl-4-(2-methylpropyl)-benzeneacetic acid, crystallizes with two molecules in the asymmetric unit to form a cyclic hydrogen-bonded dimer. Within the dimer each molecule shows subtle conformational differences *via* rotations about the acetic C(1)—C(2) and C(10)—C(11) bonds. Bond distances and angles for (S)-(+)-ibuprofen are in close agreement with those found for the structure of the racemic compound [McConnell (1974). *Cryst. Struct. Commun.* **3**, 73–75].

Comment

The properties of enantiomers and their mixtures are relevant to the study of molecular recognition in biological systems, and to acute drug toxicity. At the molecular level, asymmetry often underlies the specificity of only one member of an enantiomeric pair for