Crystal and Molecular Structure of Potassium Hydrogen Norborn-5-ene-2-*endo*,3-*endo*-dicarboxylate Sesquihydrate, $C_9H_9KO_4,1.5H_2O$

By **Ferenc Cser**, Research Institute for Plastics Industry, Budapest
Kálmán Sasvári,* Central Research Institute for Chemistry of the Hungarian Academy of Sciences, 1525 Budapest POB 17, Hungary

The crystal and molecular structure of the title compound has been determined by *X*-ray diffraction from 830 visually estimated intensities. The structure was refined by block-diagonal least squares to *R* 0.117. The nucleus of the molecule consists of norbornene with a basket-shaped skeleton. The carboxy-groups are joined to the single-bond carbon atoms at the bottom of the basket-shaped carbocyclic ring. The structure is built up of two-dimensional layers parallel to the (100) plane. Each layer consists of a two-dimensional network of corner-sharing K^+ polyhedra covered on both sides by the norbornene molecules which are joined to the polyhedra by the carboxy-oxygens and to each other, through the layer, by hydrogen bonds. The tightly bonded layers are held together by van der Waals forces. Crystals are orthorhombic, space group *Ccc*2, with $Z = 8$ in a unit cell of dimensions: $a = 25.24(9)$, $b = 10.18(5)$, and $c = 8.27(4)$ Å.

SEVERAL derivatives of norbornene are capable of solid-state polymerization under the effects of high-energy irradiation.[1,2] In order to study the topochemistry of such reactions, we wished to determine the conformation of the molecule in a stable derivative.

EXPERIMENTAL

Preparation.—The product obtained by addition of cyclopentadiene to maleic anhydride[3] was recrystallized (×3) from its solution in benzene–light petroleum (1 : 1) and allowed to react with potassium hydroxide (2 equiv.) in ethanol–water (9 : 1). The salt thus obtained was then recrystallized (×2) from ethanol–water (equimolar). The crystals finally obtained had analysis corresponding to the title molecule (I). At 140° C the compound sublimes and decomposes.

TABLE 1

Final fractional co-ordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$)* for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
K	2 300(1)	204(4)	5 008(8)	10(0)	96(3)	98(4)	2(2)	−6(3)	7(12)
O(1)	1 576(3)	526(11)	2 615(19)	7(1)	89(10)	134(10)	15(6)	3(11)	−17(34)
O(2)	883(4)	−567(11)	1 724(19)	10(1)	64(10)	186(23)	8(7)	−31(11)	−115(34)
O(3)	1 801(4)	3 522(11)	3 677(18)	10(1)	74(10)	137(18)	−13(7)	−28(10)	−57(32)
O(4)	1 545(4)	2 170(12)	5 650(16)	12(2)	87(11)	104(17)	−12(8)	−9(10)	21(30)
O(5)	2 144(6)	3 911(19)	7 635(23)	23(2)	246(23)	152(21)	−78(12)	8(17)	−231(46)
O(6)	2 500(0)	2 500(0)	1 269(25)	19(3)	109(21)	97(26)	−10(14)	0	0
C(1)	447(5)	2 016(16)	1 271(22)	8(2)	77(15)	115(22)	7(9)	−46(11)	−97(38)
C(2)	715(5)	1 507(16)	2 758(19)	8(2)	79(16)	72(20)	2(9)	−25(12)	−7(37)
C(3)	906(6)	2 752(15)	3 709(18)	14(2)	55(14)	42(16)	−3(10)	23(12)	−15(35)
C(4)	750(6)	3 828(16)	2 337(24)	14(2)	62(13)	133(26)	31(9)	−47(13)	−87(43)
C(5)	1 087(8)	3 661(20)	882(21)	23(3)	98(20)	92(23)	3(14)	−47(16)	136(42)
C(6)	890(7)	2 560(22)	245(20)	21(3)	119(20)	71(20)	15(14)	−63(13)	−44(47)
C(7)	237(6)	3 341(16)	1 856(22)	13(2)	76(14)	150(21)	26(10)	−90(10)	−71(46)
C(8)	1 103(5)	445(11)	2 368(22)	10(2)	19(9)	94(20)	−8(7)	−16(12)	−21(32)
C(9)	1 453(5)	2 821(14)	4 333(21)	8(2)	46(10)	115(22)	−3(8)	25(11)	−109(34)

* The b_{ij} values are defined by: $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Crystal Data.—$C_9H_9O_4K,1\frac{1}{2}H_2O$, $M = 247.30$. Orthorhombic $a = 25.24(9)$, $b = 10.18(5)$, $c = 8.27(4)$ Å, $U = 2\,124.92$ Å^3, $D_m = 1.541$ g cm^{-3} (by pycnometer in light petroleum), $Z = 8$, $D_c = 1.544$. Space group *Ccc*2 (C_{2v}^{13}, No. 37) from systematic absences: hkl if $h + k$ odd, $0kl$ and $h0l$ if l odd. Cu-K_α radiation, $\lambda = 1.5418$ Å, $\mu(\text{Cu-}K_\alpha) = 44.6$ cm^{-1}. Crystal size $0.1 \times 0.16 \times 0.3$ mm.

Cell dimensions were obtained from oscillation photographs taken about the crystallographic axes. The intensities of the reflections, recorded with an integrating Weissenberg camera by the multiple-film technique, were measured by microdensitometer. For reflections with zero intensity the value of $I_o = \frac{1}{4}I_{\text{min.}}$ was taken. Altogether 1 150 reflections were collected, of which 320 were considered unobserved. Although $\mu . R \approx 0.5$, no absorption correction was made. Intensities were brought to a common scale by multiple-film scaling, and by interlayer scaling after applying Lorentz-polarization factors. The absolute scale and approximate isotropic temperature factor were determined by a Wilson plot from the three-dimensional data.

Determination of the Structure.—A three-dimensional Patterson synthesis gave the position of the K atom with an optional z co-ordinate. The origin of the unit cell was defined by taking $z = \frac{1}{2}$ for the K atom. From the K • • • O and O • • • O vector peaks four oxygen atoms could be positioned after fixing the positive direction of the c axis by the z co-ordinate of the O(1) atom. From three successive Fourier syntheses, using phases derived with the known atoms, all non-hydrogen atoms were located. Atom O(6) was found in a special position ($\frac{1}{4}$,$\frac{1}{4}$,z). After three cycles of isotropic full-matrix and a further three cycles of anisotropic block-diagonal least-squares refinement of non-hydrogen atoms, R fell from 0.36 to 0.125 for observed reflections.

---

[1] Gy. Hardy and K. Nyitrai, *Acta Chim. Acad. Sci. Hung.*, 1967, **52**, 105.

[2] Gy. Hardy, K. Nyitrai, and Cs. Sarló, *Periodica Polytech.*, 1968, **12**, 13.

[3] F. Cser, Presented at the VIIth Internat. Congress of I.U. Crystallography, Moscow, 1966.

During refinement the function minimized was $\Phi = \sum_{h} w(F_o - \frac{1}{G}|F_c|)^2$, where G is the overall scaling factor and w the weighting factor of Cruickshank[4] [$w = 1/(3 + F + 0.006F^2)$]. The positions of all but two of the hydrogen atoms were derived from a difference–Fourier synthesis. The two hydrogens of atom O(5) were located from geometric considerations. The hydrogen atom positional co-ordinates were not refined, and each hydrogen atom was accorded the isotropic thermal parameter of the atom to which it was attached. In the final three cycles of anisotropic refinement, hydrogen atoms were included with constant parameters. Final atomic parameters (Tables 1 and 2) resulted in R 0.117 and 0.151 for observed and all reflections, respectively. Structure factors, calculated with the final atomic parameters, are listed in Supplementary Publication No. SUP 21536 (2 pp.).* All atomic scattering factors were taken from ref. 5.

TABLE 2

Approximate co-ordinates for hydrogen atoms as located in a difference map. The B (Å^2) values are those obtained at the last isotropic refinement for the atoms to which hydrogen atoms are attached

Atom	x	y	z	B
H(1)	0.030	0.130	0.070	3.0
H(2)	0.051	0.101	0.345	2.6
H(3)	0.077	0.288	0.472	2.3
H(4)	0.092	0.471	0.285	2.8
H(5)	0.138	0.408	0.054	3.8
H(6)	0.110	0.216	−0.061	3.7
H(7)	0.008	0.391	0.123	3.1
H(7′)	−0.002	0.277	0.278	3.1
H[O(2)]	0.095	−0.160	0.130	3.5
H[O(5)]	0.245	0.300	0.770	3.5
H[O(5′)	0.192	0.327	0.690	3.5
H[O(6)]	0.224	0.285	0.212	3.6

TABLE 3

Equations of best least-squares planes in the organic portion of the molecule, with maximum deviations (Å) from the planes for constituent atoms. The plane constants ($Ax + By + Cz = D$) are referred to crystal axes with co-ordinates in Å

Plane	A	B	C	D	Max. devn.
(1): C(1)—(4)	−0.8777	0.1079	0.4669	−0.3109	0.042
(2): C(1), C(4), C(5), C(6)	0.6591	−0.5311	0.5324	0.2109	0.007
(3): C(2), C(3), C(5), C(6)	−0.9231	0.3843	−0.0145	−1.0936	0.019
(4): C(2), C(3), C(8), C(9)	−0.2662	−0.4610	0.8465	0.7197	0.023
(5): C(2), C(8), O(1), O(2)	−0.1324	−0.3951	0.9091	1.2295	0.004
(6): C(3), C(9), O(3), O(4)	−0.2655	0.7864	0.5577	3.3015	0.019
(7): C(1), C(2), C(6)	−0.1109	0.8927	0,4369	2.1659	
(8): C(3)—(5)	0.6689	0.6372	0.3828	4.4893	
(9): C(1), C(4), C(7)	−0.1353	−0.3812	0.9146	0.0260	

Dihedral angles (°) between planes

(1)–(2) 112.8, (1)–(9) 120.3, (2)–(9) 126.9, (3)–(7) 116.0, (3)–(8) 112.2, (3)–(9) 88.0, (1)–(3) 147.7, (1)–(4) 125.4, (2)–(3) 145.1, (4)–(5) 170.7, (4)–(6) 100.4, (5)–(6) 103.4.

DISCUSSION

The Molecular Structure.—The atom numbering system used is shown in Figure 1. The nucleus of the molecule consists of norbornene with the known basket-shaped skeleton and a boat conformation carbocyclic ring, C(1)—(6), on which the top head carbon atoms, C(1) and C(4) are linked through a bridgehead carbon atom C(7). In the bottom frame of the basket, C(5)–C(6) is a double and C(2)–C(3) a single bond. The two carboxy-groups are joined to C(2) and C(3), respectively. One of these groups is ionized.

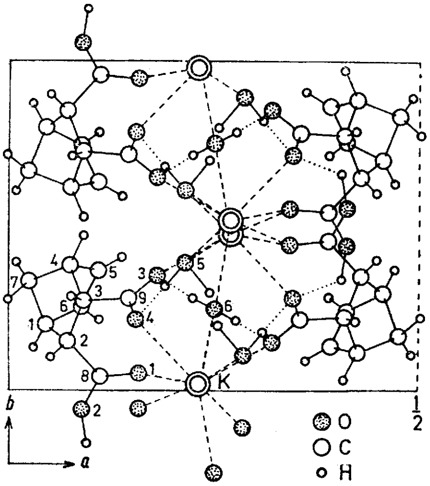

FIGURE 1 Orthogonal projection of the half unit-cell contents on the (001) plane, showing the numbering system used for the atoms. The co-ordination polyhedra of the K$^+$ ion are shown by broken lines and hydrogen bonds by dotted lines

The aforementioned organic moiety of the molecule can be characterized by nine planes. These, with plane constants, are given in Table 3, together with some relevant dihedral angles between planes.

The C(5)–C(6) bond (1.335 Å) corresponds to a normal C(sp^2)–C(sp^2) double bond. All other bond lengths in the basket skeleton are significantly scattered around the C(sp^3)–C(sp^3) single-bond value (Table 4). There are especially large differences in bond length around C(4), but this can be attributed partly to the limited accuracy of the intensity determination.

Bond angles in the basket skeleton, with the exception of two, are significantly smaller than the tetrahedral value (Table 5). The bridgehead angle [C(1)–C(7)–C(4)

---

* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

[4] D. W. J. Cruickshank, 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961.

[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

94.6°] is almost the same as that reported for norborn-5-ene-2-*endo*,3-*endo*-dicarboxylic anhydride (II) [6] (93.4°) and norbornen-7-*anti*-yl *p*-bromobenzoate (III) [7] (95.6°). All these point to the fact that the norbornene nucleus is similarly strained in the title molecule (I) as it is known to be in (II) and (III). Otherwise the norbornene nucleus of (I) is somewhat more distorted and does not show the mirror symmetry found for (II) and (III).

TABLE 4

Bond lengths (Å), with estimated standard deviations in parentheses

C(1)–C(2)	1.495(22)	C(4)–C(5)	1.483(26)
C(1)–C(6)	1.507(25)	C(4)–C(7)	1.440(24)
C(1)–C(7)	1.528(28)	C(5)–C(6)	1.335(27)
C(2)–C(3)	1.568(21)	C(8)–O(1)	1.214(19)
C(2)–C(8)	1.492(20)	C(8)–O(2)	1.285(18)
C(3)–C(4)	1.626(23)	C(9)–O(3)	1.255(19)
C(3)–C(9)	1.475(21)	C(9)–O(4)	1.295(19)

Non-bonding distance

C(1) · · · C(4)	2.182

TABLE 5

Bond angles (°), with estimated standard deviations in parentheses

C(2)–C(1)–C(6)	104.9(1.3)	C(5)–C(4)–C(7)	104.5(1.5)
C(2)–C(1)–C(7)	101.6(1.2)	C(4)–C(5)–C(6)	101.7(1.6)
C(6)–C(1)–C(7)	96.4(1.3)	C(1)–C(6)–C(5)	111.2(1.6)
C(1)–C(2)–C(3)	105.8(1.2)	C(1)–C(7)–C(4)	94.6(1.3)
C(1)–C(2)–C(8)	111.6(1.2)	C(2)–C(8)–O(1)	123.9(1.3)
C(3)–C(2)–C(8)	119.5(1.2)	C(2)–C(8)–O(2)	112.9(1.3)
C(2)–C(3)–C(4)	96.9(1.1)	O(1)–C(8)–O(2)	123.2(1.4)
C(2)–C(3)–C(9)	120.1(1.3)	C(3)–C(9)–O(3)	122.1(1.4)
C(4)–C(3)–C(9)	116.0(1.3)	C(3)–C(9)–O(4)	115.8(1.3)
C(3)–C(4)–C(5)	110.5(1.4)	O(3)–C(9)–O(4)	122.0(1.4)
C(3)–C(4)–C(7)	100.3(1.3)		

Packing of the Molecules.—The packing of the molecules in the unit cell can be seen in Figure 1 in an orthogonal projection. The organic parts of the crystal lattice are in the vicinity of a K^+ ion, and one and a half water molecules per organic moiety in such a way that the K^+ ion is enclosed in a polyhedron formed by seven oxygen atoms belonging partly to the water and partly to the carboxylic acid groups. The K · · · O contacts are designated by broken lines, and their lengths range from 2.715 to 2.987 Å.

The K^+ polyhedra are corner-sharing at atoms O(1) and O(5), thus forming infinite chains parallel to the *c* direction. The chains are also joined by corner-sharing at the O(6) atom. Thus in the crystal lattice there are two-dimensional networks of K^+ polyhedra positioned parallel to the (100) plane. These networks are covered on both sides by the norbornene molecules joined to the polyhedra by the carboxylic oxygens O(1), O(3), and O(4). Contact between the norbornene molecules and the central polyhedra network is further strengthened by the hydrogen bonds O(5)–H · · · O(4) · · · H–O(2). The norbornene molecules on the two sides of the two-dimensional network are also linked to each other through the polyhedra network by O(3) · · · H–O(6)–H · · · O(3) hydrogen bonds. Both types of hydrogen bonds are demonstrated in Figure 1. The O(3) atoms of the two ends in the second type of hydrogen bonding are in two different symmetry-related positions.

The hydrogen-bond distances involving water molecules are 2.85 and 2.86 Å for O(5)–H[O(5′)] · · · O(4) and O(6)–H[O(6)] · · · O(3), respectively and satisfy the nondition that, when represented by A–H · · · B, the H · · ·B distances are less than the sum of the van der Waals radii.[8] The intermolecular O(2)–H[O(2)] · · · O(4) hydrogen bond linking two carboxy-groups is very short (2.50 Å); in this bond the hydrogen atom is considerably shifted out of the direction of O(2) · · · O(4), resulting in an O–H–O angle of 123.6°.

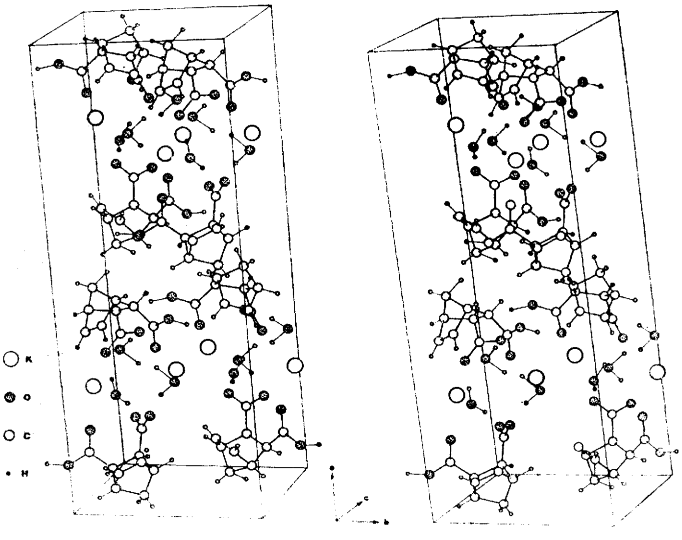

FIGURE 2 Stereoscopic projection of the unit-cell contents as viewed down the direction deviating from *c* crystal axis by twisting the unit cell about the *b* and *a* axes by angles 20 and −23°, respectively

The two-dimensional layers parallel to (100) form a three-dimensional crystal lattice. While the layers are very tightly packed, there is a very loose contact between the layers, in accordance with the statement of Kitaigorodskii,[9] that in space-group *Ccc*2 there are no co-ordination close-packed layers. The layers are held together by van der Waals forces. The molecular packing is illustrated by a stereoscopic projection of the unit cell in Figure 2.[10]

[5/326 *Received*, 17*th February*, 1975]

---

[6] R. Destro, G. Filippini, C. Maria Gramaccioli, and M. Simonetta, *Acta Cryst.*, 1969, **B25**, 2465.

[7] A. C. Macdonald and J. Trotter, *Acta Cryst.*, 1965, **19**, 456.

[8] W. C. Hamilton and J. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968.

[9] A. I. Kitaigorodskii, 'Organic Chemical Crystallography,' (English translation), Consultants Bureau, New York, 1955.

[10] C. K. Johnson, Program ORTEP, Oak Ridge National Laboratory Report ORNL 3794, Oak Ridge, Tennessee, U.S.A., 1965.