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The Crystal Structure of 2-Ethoxy-6-acetylnaphthalene, $C_{14}H_{14}O_2$

By M. P. Gupta and B. Yadav

Department of Physics, University of Ranchi, Ranchi 834-008, *India*

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The crystal structure of 2-ethoxy-6-acetylnaphthalene has been determined by X-ray diffraction and refined by least-squares methods to an R of 0·085. The crystals are monoclinic with $a=12·998$, $b=5·829$, $c=15·101$ Å, $\beta=100°$, space group $P2_1/c$, $Z=4$. The molecules are stacked in layers and are held together by van der Waals forces, the shortest contact being 3·38 Å.

Introduction

The title compound was studied in this laboratory because of an interest in the stereochemistry of the molecule. Kenyon & Sharan (1966), while studying the scheme of alkyl–oxygen fission in carboxylic esters apparently obtained two 'different' compounds, one having a melting point 73–74·5 °C and the other 82–83 °C. One was believed to be 2-ethoxy-6-acetylnaphthalene while the other was labelled as 2-ethoxy-*x*-acetylnaphthalene (Sharan, private communication). The present work was undertaken to establish the structure of the latter. X-ray diffraction soon established that the two compounds were identical, and the different melting points must be ascribed to the presence of impurities. In what follows, the crystal structure described is, therefore, of 2-ethoxy-6-acetylnaphthalene.

Experimental

Single crystals were grown from toluene. The crystals are platy with face (001), the long edge corresponding to [010]. The cell dimensions were derived from high sin θ reflexions on Weissenberg films with Ag lines superimposed as internal standards.

Crystal data

Monoclinic, $a=12·99_8$, $b=5·82_9$, $c=15·10_1$ Å
$\beta=100°$
$d_o=1·24$, $d_c=1·26$ g cm^{-3}, $Z=4$
Space group $P2_1/c$
μ(Cu $K\alpha$) = 7·9 cm^{-1}.

715 independent reflexions were collected by Weissenberg photography, estimated visually, and brought to approximate absolute scale by statistical methods.

Determination and refinement of the structure

The structure was solved by a sharpened Patterson projection down [010] which gave the orientation of the molecule. Packing considerations and Fourier refinement gave a set of parameters for full-matrix least-squares refinement (Busing, Martin & Levy, 1962). The weighting scheme ($\overline{\Delta F}=a+b\overline{F_0}$, a and b being constants for the group) was applied in the last stage of refinement, with anisotropic thermal factors for the carbon and oxygen atoms. R fell to 10·2%. The hydrogen atoms were located from a difference synthesis, and their inclusion reduced R to 0·085. The numbering of the atoms is given in Fig. 1. The positional and thermal parameters are given in Table 1. Observed and calculated structure factors are in Table 2.* Bond

Table 1. *Atomic and thermal parameters*

(*a*) Final atomic coordinates and their e.s.d.'s (×10^4, for hydrogen atoms ×10^3)

	x/a	*y/b*	*z/c*
C(1)	1320 (11)	4715 (32)	2154 (10)
C(2)	848 (11)	3233 (28)	1488 (09)
C(3)	1334 (11)	1301 (26)	1270 (09)
C(4)	2312 (11)	621 (30)	1728 (08)
C(5)	3828 (13)	1442 (30)	2874 (10)
C(6)	4256 (13)	2835 (34)	3583 (11)
C(7)	3803 (12)	4783 (32)	3810 (10)
C(8)	2855 (11)	5492 (31)	3359 (09)
C(9)	2332 (12)	4028 (30)	2630 (09)
C(10)	2840 (13)	2110 (30)	2399 (10)
C(11)	5769 (11)	415 (31)	3919 (10)
C(12)	6728 (12)	296 (31)	4618 (09)
C(13)	−231 (12)	3893 (37)	1004 (11)
C(14)	−769 (13)	6037 (32)	1185 (11)
O(1)	5201 (07)	2442 (20)	4107 (06)
O(2)	−666 (09)	2500 (23)	438 (08)
H(1)	98	609	252
H(2)	245	692	356
H(3)	403	569	444
H(4)	387	−23	254
H(5)	292	−17	140
H(6)	120	−8	78
H(7)	541	−104	388
H(8)	592	67	325
H(9)	714	169	451
H(10)	724	−84	445
H(11)	676	−31	531
H(12)	−146	523	124
H(13)	−69	735	71
H(14)	−55	615	194

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* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30371 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (*cont.*)

(*b*) Thermal parameters and their e.s.d.'s ($\times 10^4$ Å^2)

$$T=\exp\,[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	51 (11)	304 (78)	37 (8)	−24 (27)	11 (8)	−16 (22)
C(2)	46 (10)	278 (71)	27 (7)	−6 (24)	−2 (8)	−6 (19)
C(3)	69 (12)	245 (64)	34 (7)	−16 (25)	19 (8)	−9 (18)
C(4)	65 (12)	420 (73)	18 (6)	−1 (27)	4 (7)	4 (18)
C(5)	72 (14)	191 (70)	42 (9)	−13 (27)	−3 (9)	−23 (21)
C(6)	59 (13)	312 (82)	49 (9)	21 (31)	−7 (9)	2 (23)
C(7)	59 (12)	291 (73)	44 (9)	24 (28)	−13 (10)	−25 (23)
C(8)	57 (11)	249 (73)	37 (8)	−15 (27)	−2 (8)	−39 (21)
C(9)	56 (12)	205 (64)	34 (8)	6 (27)	5 (9)	−8 (19)
C(10)	68 (14)	201 (67)	35 (8)	−27 (29)	7 (9)	1 (21)
C(11)	58 (11)	401 (74)	48 (8)	32 (28)	−12 (8)	−8 (22)
C(12)	73 (11)	398 (75)	34 (7)	15 (28)	−17 (8)	4 (20)
C(13)	43 (11)	531 (96)	54 (9)	−50 (32)	−6 (9)	−6 (27)
C(14)	76 (13)	340 (71)	64 (11)	63 (29)	4 (10)	−6 (24)
O(1)	46 (7)	373 (48)	42 (5)	33 (18)	−17 (5)	−40 (14)
O(2)	70 (9)	509 (57)	65 (6)	−33 (22)	−8 (6)	−74 (19)

lengths, bond angles and intermolecular contacts are in Table 3. The symmetry-related atoms are represented by:

(I) $x, \frac{1}{2}-y, \frac{1}{2}+z$
(II) $\bar{x}, \bar{y}, \bar{z}$
(III) $x, \frac{1}{2}+y, \frac{1}{2}-z.$

Atoms related by unit translation in the **a** direction are designated ^{a}O(1, III) and so on.

Equations for least-squares planes through the various parts of the molecule are:

through all the atoms of the naphthalene group

$$X+0\cdot9216Y-1\cdot2356Z+0\cdot3239=0; \qquad (A)$$

through O(2), C(13), C(14)

$$X+0\cdot8899Y-1\cdot3548Z+0\cdot5661=0; \qquad (B)$$

through O(1), C(11), C(12)

$$X+0\cdot8936Y-0\cdot9574Z-1\cdot0159=0. \qquad (C)$$

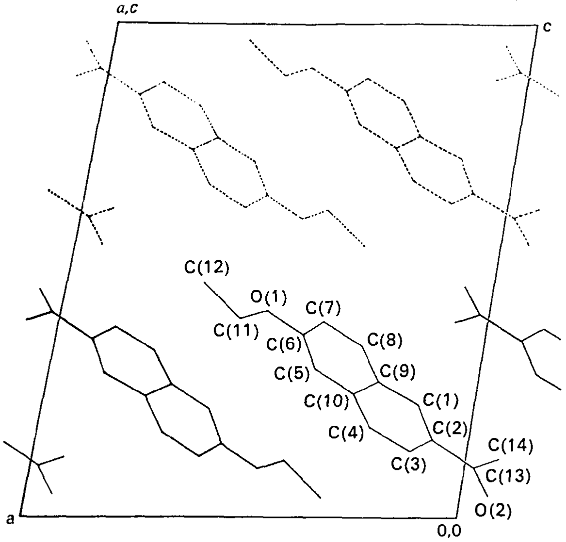

Fig. 1. Structure looking down the [010] axis.

Table 3. *Bond lengths, bond angles and interatomic distances*

(*a*) Bond lengths and their e.s.d.'s

C(1)—C(2)	1·39 (2) Å	C(1)—H(1)	1·11 Å
C(2)—C(3)	1·36 (2)	C(8)—H(2)	1·05
C(3)—C(4)	1·40 (2)	C(7)—H(3)	1·08
C(4)—C(10)	1·42 (2)	C(5)—H(4)	1·10
C(10)–C(5)	1·41 (2)	C(4)—H(5)	1·10
C(5)—C(6)	1·38 (2)	C(3)—H(6)	1·08
C(6)—C(7)	1·35 (2)	C(11)–H(7)	0·97
C(7)—C(8)	1·37 (2)	C(11)–H(8)	1·07
C(8)—C(9)	1·46 (2)	C(12)–H(9)	1·09
C(9)–C(10)	1·37 (2)	C(12) H(10)	1·00
C(9)—C(1)	1·44 (2)	C(12)–H(11)	1·09
C(6)—O(1)	1·36 (2)	C(14)–H(12)	1·03
O(1)—C(11)	1·45 (2)	C(14)–H(13)	1·06
C(11)–C(12)	1·49 (2)	C(14)–H(14)	1·13
C(2)—C(13)	1·51 (2)		
C(13)–O(2)	1·24 (2)		
C(13)–C(14)	1·48 (2)		

(*b*) Bond angles and their e.s.d.'s

C(1)–C(2)—C(3)	121·8 (1·3)°
C(3)–C(2)—C(13)	121·6 (1·3)
C(1)–C(2)—C(13)	116·6 (1·5)
C(2)–C(1)—C(9)	116·0 (1·5)
C(1)–C(9)—C(10)	122·4 (1·4)
C(8)–C(9)—C(10)	119·0 (1·3)
C(1)–C(9)—C(8)	118·5 (1·5)
C(7)–C(8)—C(9)	117·3 (1·5)
C(6)–C(7)—C(8)	121·6 (1·5)
C(5)–C(6)—C(7)	123·8 (1·5)
O(1)–C(6)—C(7)	112·5 (1·4)
O(1)–C(6)—C(5)	123·6 (1·6)
C(6)–C(5)—C(10)	116·1 (1·5)
C(5)–C(10)–C(9)	121·9 (1·4)
C(4)–C(10)–C(9)	119·1 (1·4)
C(4)–C(10)–C(5)	118·6 (1·5)
C(3)–C(4)—C(10)	117·8 (1·5)
C(2)–C(3)—C(4)	122·4 (1·3)
O(1)–C(11)–C(12)	106·9 (1·2)
O(2)–C(13)–C(14)	120·3 (1·4)
O(2)–C(13)–C(2)	116·0 (1·6)
C(2)–C(13)–C(14)	123·6 (1·4)
H(1)–C(1)—C(2)	130·6
H(1)–C(1)—C(9)	110·0
H(2)–C(8)—C(9)	119·3
H(2)–C(8)—C(7)	123·1
C(6)–O(1)—C(11)	117·5 (1·2)

Table 3 (*cont.*)

H(3)—C(7)—C(8)	112·4
H(3)—C(7)—C(6)	118·5
H(4)—C(5)—C(6)	145·9
H(4)—C(5)—C(10)	97·3
H(5)—C(4)—C(10)	105·3
H(5)—C(4)—C(3)	123·9
H(6)—C(3)—C(4)	98·5
H(6)—C(3)—C(2)	138·9
H(7)—C(11)–O(1)	117·9
H(7)—C(11)–C(12)	109·7
H(8)—C(11)–O(1)	104·8
H(8)—C(11)–C(12)	113·8
H(8)—C(11)–H(7)	103·7
H(9)—C(12)–C(11)	104·5
H(9)—C(12)–H(10)	96·0
H(10)–C(12)–C(11)	111·4
H(10)–C(12)–H(11)	96·4
H(11)–C(12)–C(11)	125·1
H(11)–C(12)–H(9)	119·1
H(12)–C(14)–C(13)	94·6
H(12)–C(14)–H(13)	124·7
H(13)–C(14)–C(13)	112·6
H(13)–C(14)–H(14)	126·9
H(14)–C(14)–H(13)	101·4
H(14)–C(14)–H(12)	90·3

(*c*) Interatomic distances

C(1)—$^{-a,-b}$C(14, III)	3·47 Å
C(2)—$^{-a,-b}$C(14, III)	3·76
C(4)—C(12, III)	3·74
C(5)—C(11, III)	3·67
C(9)—C(11, III)	3·77
C(9)—$^{-a,-b}$C(14, III)	3·41
C(10)–C(11, III)	3·49
C(10)–C(12, III)	3·69
C(10)–$^{-a,-b}$C(14, III)	3·77
C(14)–$^{-a}$C(9, III)	3·41
C(14)–$^{-a}$C(1, III)	3·47
C(14)–$^{-a}$C(2, III)	3·76
C(14)–$^{-a}$C(10, III)	3·77
C(3)—$^{-a,-b,-c}$O(2, II)	3·40
C(6)—$^{-b}$C(12, II)	3·68
C(7)—O(1, II)	3·57
C(12)–$^{-b}$O(1, II)	3·77
C(13)–$^{-a,-c}$O(2, II)	3·38
C(13)–$^{-a,-c}$C(13, II)	3·44
C(13)–$^{-a,-c}$C(14, II)	3·76
O(2)—$^{-a,-c}$O(2, II)	3·75
O(2)—$^{-a,-b,-c}$C(3, II)	3·40
C(12)–$^{-b}$C(6, II)	3·68
C(14)–$^{-a,-c}$C(13, II)	3·76
O(1)—C(7, II)	3·57
O(1)—$^{-b}$C(12, II)	3·77
O(2)—$^{-a,-c}$C(13, II)	3·38
O(2)—$^{-a,-c}$C(14, II)	3·44
O(2)—$^{-a}$O(2, III)	3·75
C(11)–$^{-b}$C(10, III)	3·49
C(11)–$^{-b}$C(5, III)	3·67
C(11)–$^{-b}$C(9, III)	3·77
C(12)–$^{-b}$C(10, III)	3·69
C(12)–$^{-b}$C(4, III)	3·74
C(12)–^{a}O(2, I)	3·63
C(12)–^{a}C(14, I)	3·76
C(14)–$^{-a,-c}$O(2, I)	3·44
C(14)–$^{-a,-c}$C(12, I)	3·76
O(2)—$^{-a,-c}$C(12, I)	3·63
C(1)—^{b}C(4)	3·77
C(4)—$^{-b}$C(1)	3·77

The deviations from plane (*A*) are given in Table 4. The angles between the various planes and their direction cosines referred to orthogonal axes *a*,*b*,*c*′ (*c*′ being normal to *a* and *b*) are in Table 5. In marked contrast to the molecule of 2-ethoxy-1-acetylnaphthalene (Gupta & Sahu, 1972), where the acetyl and ethoxy groups make angles of 63·7 and 10·3° respectively with a similar plane (*A*), the corresponding angles in the present case are only 3·4 and 6·9°. This is a consequence of greater steric hindrance in 2-ethoxy-1-acetylnaphthalene.

Table 4. *Deviations of atoms from plane* (*A*) *and their e.s.d.'s*

C(1)	0·028 (6) Å	C(9)	−0·001 (7) Å
C(2)	0·021 (5)	C(10)	0·061 (7)
C(3)	0·050 (6)	O(1)	−0·122 (4)
C(4)	0·020 (8)	C(11)	−0·098 (6)
C(5)	0·022 (6)	C(12)	−0·253 (7)
C(6)	−0·077 (7)	O(2)	−0·064 (4)
C(7)	−0·088 (6)	C(13)	0·004 (6)
C(8)	−0·036 (6)	C(14)	0·043 (5)

Table 5. *Planes in the molecule*

(*a*) Direction cosines *l*,*m*,*n* of the normal to thc planes

	l	*m*	*n*
Plane (*A*)	0·5441	0·5014	−0·6723
Plane (*B*)	0·5251	0·4673	−0·7114
Plane (*C*)	0·6069	0·5423	−0·5811

(*b*) Angles between planes

Plane (*A*) and (*B*)	3·4°
Plane (*A*) and (*C*)	6·9

The crystal and molecular structure

The packing coefficient, $K=ZV_o/V$, where V_o = molecular volume, V = unit-cell volume, is 0·75, within the range 0·6–0·8 (Kitaigorodskii, 1961). If effective intermolecular contacts are taken to be limited to a distance of 3·8 Å, the coordination number is 12, a characteristic of close packing of molecules (Kitaigorodskii, 1961).

In the crystal the molecules are stacked in layers (Fig. 1), adjacent layers being stacked with opposite slants. The layer structure is evidenced by typical diffuse reflexions $20\bar{4}$, $21\bar{3}$ and $11\bar{2}$. Since the only intermolecular linkages in the structure are of the van der Waals type, there is large thermal motion of the atoms. Calculation of the root-mean-square amplitudes of vibration of the atoms shows that the largest amplitudes of the atoms O(1), O(2), C(7), C(8), C(11) and C(14) are nearly in the same direction as the normal to the mean plane (*A*).

The bond lengths and angles in the molecule are similar to those reported for molecules of similar configuration by a number of workers (Gaultier & Hauw, 1969; Grainger & McConnell, 1969; Ammon, Sundaralingam & Stewart, 1969; Gupta & Sahu, 1972; Akimoto & Iitaka, 1969; Hulme & Szymanski, 1969).

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The Crystal Structures of the *A* and *B* Forms of Potassium D-Gluconate Monohydrate by Neutron Diffraction

BY N. C. PANAGIOTOPOULOS AND G. A. JEFFREY

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, *U.S.A.*

AND S. J. LA PLACA AND W. C. HAMILTON*

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, *U.S.A.*

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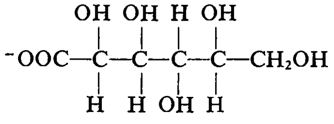
Neutron diffraction data have been used to refine the crystal structure of the *A* form of potassium D-gluconate monohydrate, $KC_6H_{11}O_7.H_2O$, $P2_12_12_1$, $a=8\cdot220$ (4), $b=17\cdot840$ (8), $c=6\cdot717$ (3) Å, $Z=4$, and to determine by direct methods and refine the structure of the *B* form, $P2_1$, $a=9\cdot353$ (7), $b=7\cdot357$ (5), $c=7\cdot229$ (5) Å, $\beta=109\cdot39$ (2)°, $Z=2$. These structures are an example of conformational dimorphism, in that the gluconate ion is a straight-chain conformer in *A* and a bent-chain conformer in *B*. The new atomic coordinates for form *A* differ from the previous X-ray results by a mean of $1\cdot5\sigma$, except for the hydrogen atoms. The more accurate hydrogen positions confirm the existence of an intramolecular hydrogen bond, which is associated with a *syn*-axial orientation of alternate hydroxyls in the straight-chain conformation. In the *B* form, there is no intramolecular hydrogen bond. The gluconate ion has one of the two most probable bent-chain conformations predicted for the DDLD configuration of the $-(CHOH)_4-$ sequence in a polyhydroxyl alkyl chain. In both structures, there is extensive intermolecular hydrogen bonding involving all the hydroxy and water hydrogens.

Introduction

The primary objective of this work was to study the conformation of the D-gluconate ion (I).



$$^{-}OOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{H}{\overset{OH}{C}}{-}CH_2OH$$

(I)

Earlier crystal-structure studies of D-glucitol (Park, Jeffrey & Hamilton, 1971) and other hexitols and pentitols (Jeffrey & Kim, 1970) and of related alditol derivatives by n.m.r. measurements (El Khadem, Horton & Page, 1968; Horton & Wander, 1969, 1970) led to the expectation that, because of its DDLD configuration, the D-gluconate ion should be the bent, or 'sickle-shaped' conformer, both in the crystalline state and predominantly in solution. This conformational preference has its origin in the repulsion of *syn*-axially related hydroxyl groups in the straight-chain conformer. An early crystal structure analysis by Littleton (1953) contradicted this prediction by showing that the gluconate ion is the straight-chain conformer in the crystal structure of anhydrous potassium D-gluconate. Jeffrey & Fasiska (1972) determined the structure of the orthorhombic *A* form of potassium D-gluconate monohydrate by X-rays and also found a straight-chain conformation for the ion. This conformation appeared to be stabilized by an intramolecular hydrogen bond between the two *syn*-axially related hydroxyls, a feature which is not generally observed either in crys-

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* Deceased.