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The low-temperature study of D- and DL-camphoric anhydride

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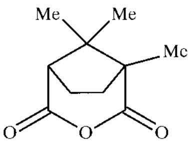
The low-temperature crystal stuctures of D- and DL-camphoric anhydride, $C_{10}H_{14}O_3$, have been determined by X-ray diffraction methods. Although the two enantiomers crystallize in different space groups, the cell volumes and densities are essentially the same. The six-membered rings deviate significantly from planarity, both exhibiting half-boat conformations. The dihedral angle between the six- and five-membered rings is 80.3 (1)° in both cases. The main difference in the molecular stuctures can be described by two torsion angles associated with the H atoms of the methyl substituents. The packing of the racemic and chiral structures are essentially the same.

Comment

The physical properties of several camphor derivatives have been studied extensively, especially in relation to their chiroptical features which are affected by the nature of the substituent attached to the bicyclic ring in the bridgehead position (Yager & Morgan, 1935; Williams & Smyth, 1962; Mjojo & Welsh, 1992; Mora & Fitch, 1997). We report hete the low-temperature structural data for D-camphoric anhydride, (I), and DL-camphoric anhydride, (II). The former was reinvestigated for comparison.



(I) the D form
(II) the DL form

The corresponding internuclear distances and angles of the two molecules are statistically equal and all geometrical parameters of the low-temperature structure of (I) compare well with those obtained earlier based on room-temperature data (Wichmann *et al.*, 1987). The conformation of the six-membered rings were determined in terms of their ring-puckering parameters (Cremer & Pople, 1975); (I): Q = 0.637 (1) Å, θ = 45.6 (1)° and φ = −3.1 (1)°; (II): Q = 0.628 (1) Å, θ = 45.1° and φ = −5.1 (1)°. These values indicate that the rings adopt half-boat conformations. The groups of atoms C7/C3/C2/C1 and C1/C6/C5/C4 lie in the least-squares planes of their respective six- and five-membered rings. In both structures, the planes form an angle of 80.3 (1)°.

Weak C—H···O-type hydrogen bonds connect molecules of the same chirality, forming linear chains. These columns of D–L, (I), and D–D, (II), isomers are held together by even weaker contacts giving rise to a remarkable similarity in the packing. This observation does not support the conclusion by Brock *et al.* (1991) that the racemic crystal tends to be denser than its chiral counterpart.

Experimental

Commercially available (I) and (II) were purchased and crystallized from benzene and toluene, respectively, by slow evaporation at room temperature.

Compound (I)

Crystal data

$C_{10}H_{14}O_3$
$M_r = 182.21$
Orthorhombic, $P2_12_12_1$
$a = 6.4262\ (3)$ Å
$b = 11.0841\ (4)$ Å
$c = 12.9142\ (5)$ Å
$V = 919.86\ (6)$ Å^3
$Z = 4$
$D_x = 1.316$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.42$–29.9°
$\mu = 0.096$ mm^{-1}
$T = 110\ (2)$ K
Rectangular block, colourless
0.45 × 0.40 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
11 128 measured reflections
1103 independent reflections
1090 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\rm max} = 26.36°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 16$
Intensity decay: negligible

Refinement

Refinement on F^2
$R(F) = 0.029$
$wR(F^2) = 0.072$
$S = 1.109$
1103 reflections
174 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.088P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C2	1.3980 (17)	C1—C7	1.5620 (17)
O1—C3	1.3989 (16)	C3—C4	1.4975 (19)
O2—C2	1.1950 (17)	C4—C7	1.5478 (17)
O3—C3	1.1954 (17)	C4—C5	1.5541 (18)
C1—C2	1.5201 (19)	C5—C6	1.544 (2)
C1—C10	1.5236 (18)	C7—C8	1.5293 (19)
C1—C6	1.5578 (18)	C7—C9	1.5327 (18)
C2—O1—C3	122.57 (10)	O2—C2—O1	115.95 (13)
C2—C1—C10	109.75 (12)	O2—C2—C1	127.18 (13)
C2—C1—C6	106.34 (10)	O1—C2—C1	116.81 (11)
C10—C1—C6	113.12 (11)	O3—C3—O1	116.31 (13)
C2—C1—C7	107.25 (10)	O3—C3—C4	127.52 (13)
C10—C1—C7	115.84 (11)	O1—C3—C4	116.10 (11)
C6—C1—C7	103.91 (10)	C3—C4—C7	110.07 (11)

C3—C4—C5	107.13 (10)	C8—C7—C4	113.34 (11)
C7—C4—C5	104.49 (10)	C9—C7—C4	109.70 (11)
C6—C5—C4	104.47 (10)	C8—C7—C1	114.11 (11)
C5—C6—C1	106.17 (10)	C9—C7—C1	111.59 (11)
C8—C7—C9	108.70 (11)	C4—C7—C1	99.15 (10)
C3—O1—C2—C1	13.84 (16)	O1—C3—C4—C7	42.21 (14)
C7—C1—C2—O1	−44.88 (14)	C3—C4—C7—C1	−69.48 (12)
C2—O1—C3—C4	−11.85 (16)	C2—C1—C7—C4	69.52 (12)

Compound (II)

Crystal data

$C_{10}H_{14}O_3$
$M_r = 182.21$
Monoclinic, $P2_1/n$
$a = 6.4152$ (4) Å
$b = 11.4413$ (8) Å
$c = 12.5623$ (8) Å
$\beta = 91.9680$ (8)°
$V = 921.51$ (10) Å^3
$Z = 4$

$D_x = 1.313$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.22$–30.1°
$\mu = 0.096$ mm^{-1}
$T = 110$ (2) K
Rectangular block, colourless
0.5 × 0.45 × 0.3 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
11 276 measured reflections
1875 independent reflections
1825 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.012$
$\theta_{\rm max} = 26.37°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 15$
Intensity decay: negligible

Refinement

Refinement on F^2
$R(F) = 0.032$
$wR(F^2) = 0.081$
$S = 1.063$
1875 reflections
174 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.3112P]$
where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

O1—C2	1.3976 (12)	C1—C6	1.5628 (13)
O1—C3	1.4008 (12)	C3—C4	1.4986 (13)
O2—C2	1.1956 (13)	C4—C7	1.5457 (13)
O3—C3	1.1952 (12)	C4—C5	1.5522 (14)
C1—C2	1.5139 (13)	C5—C6	1.5456 (15)
C1—C10	1.5224 (13)	C7—C8	1.5317 (13)
C1—C7	1.5591 (13)	C7—C9	1.5337 (13)
C2—O1—C3	122.36 (8)	C10—C1—C6	113.05 (8)
C2—C1—C10	109.51 (8)	C7—C1—C6	103.46 (8)
C2—C1—C7	107.40 (7)	O2—C2—O1	115.83 (9)
C10—C1—C7	115.88 (8)	O2—C2—C1	127.34 (9)
C2—C1—C6	106.98 (8)	O1—C2—C1	116.80 (8)
O3—C3—O1	116.20 (9)	C5—C6—C1	106.05 (8)
O3—C3—C4	127.55 (9)	C8—C7—C9	108.79 (8)
O1—C3—C4	116.17 (8)	C8—C7—C4	113.18 (8)
C3—C4—C7	110.69 (8)	C9—C7—C4	109.84 (8)
C3—C4—C5	106.82 (8)	C8—C7—C1	114.25 (8)
C7—C4—C5	104.07 (8)	C9—C7—C1	111.17 (8)
C6—C5—C4	104.46 (8)	C4—C7—C1	99.35 (7)
C3—O1—C2—C1	15.18 (13)	O1—C3—C4—C7	40.97 (11)
C7—C1—C2—O1	−46.21 (11)	C3—C4—C7—C1	−68.16 (9)
C2—O1—C3—C4	−11.84 (13)	C2—C1—C7—C4	69.49 (9)

H atoms were located from difference Fourier maps and refined isotropically. The C—H distances range from 0.91 (2) to 1.02 (2) Å. Due to the absence of suitable anomolous scatteres within (I), the determination of the absolute configuration was not possible from our X-ray data. Friedel opposites were therefore merged before the refinement.

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT-Plus* (Bruker, 1997); data reduction: *SAINT-Plus* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Shelsrick, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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