

Four novel spirooxazacamphorsultam derivatives

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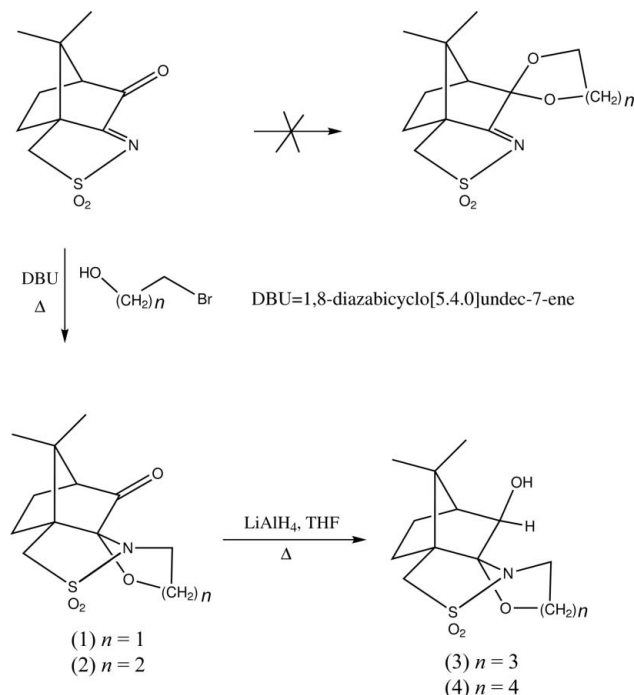
The chiral compounds (6*aS*,9*S*,10*aR*)-11,11-dimethyl-5,5-dioxo-2,3,8,9-tetrahydro-6*H*-6*a*,9-methanooxazolo[2,3-*i*][2,1]benzisothiazol-10(7*H*)-one, C₁₂H₁₇NO₄S, (1), (7*aS*,10*S*,11*aR*)-12,12-dimethyl-6,6-dioxo-3,4,9,10-tetrahydro-7*H*-7*a*,10-methano-2*H*-1,3-oxazino[2,3-*i*][2,1]benzisothiazol-11(8*H*)-one, C₁₃H₁₉NO₄S, (2), (6*aS*,9*S*,10*R*,10*aR*)-11,11-dimethyl-5,5-dioxo-2,3,7,8,9,10-hexahydro-6*H*-6*a*,9-methanooxazolo[2,3-*i*][2,1]benzisothiazol-10-ol, C₁₂H₁₉NO₄S, (3), and (7*aS*,10*S*,11*R*,11*aR*)-12,12-dimethyl-6,6-dioxo-3,4,8,9,10,11-hexahydro-7*H*-7*a*-methano-2*H*-[1,3]oxazino[2,3-*i*][2,1]benzisothiazol-11-ol, C₁₃H₂₁NO₄S, (4), consist of a camphor core with a five-membered spirooxazolidine or six-membered spirooxazine, as both their keto and hydroxy derivatives. In each structure, the molecules are linked *via* hydrogen bonding to the sulfonyl O atoms, forming chains in the unit-cell *b*-axis direction. The chains interconnect *via* weak C—H···O interactions. The keto compounds have very similar packing but represent the highest melting [507–508 K for (1)] and lowest melting [457–458 K for (2)] solids.

Comment

During the course of our studies toward the synthesis of camphor-based acetals (Wilke *et al.*, 2010), an unexpected crystalline product was discovered. X-ray diffraction confirmed that the anticipated acetalization reaction (Magnus *et al.*, 1992) of the ketone (Chen *et al.*, 1996) instead resulted in reaction of the imine to produce spirooxazolidines, (1) and (2), that were further reduced to the *exo* alcohols, (3) and (4), shown in the Scheme. The alcohol functionality may provide a logical attachment point for the use of these compounds as chiral auxiliaries.

The structures of the four compounds are shown in Fig. 1 and Table 1 gives the geometries of the functional groups in the four molecules. The only significant deviations in these geometries can be ascribed to chemical differences (C=O

versus C—OH and the five- *versus* six-membered oxaza ring). The six-membered oxaza ring (the only ring with conformational possibilities) adopts a chair conformation in (2) and (4). Perhaps the most surprising feature revealed in comparing structures is the ordering in the variation of melting points [457–458, 459–461, 474–478 and 507–508 K for (2), (4), (3) and (1), respectively]. As these are quite similar molecules, one might expect the hydroxy compounds [(3) and (4)] to have higher melting points relative to the keto compounds [(1) and (2)] based on the expected formation of O—H···O=S hydrogen bonds. However, the 5-keto structure, (1), has the highest melting point of the four compounds (by approximately 30 K) and the 6-keto structure, (2), the lowest. As the packing coefficients for the structures are about the same, with the index slightly higher for the hydroxy compounds [0.708, 0.708, 0.732 and 0.720 for (1), (2), (3) and (4), respectively, as calculated with *PLATON* (Spek, 2009)], we decided to analyze the intermolecular interactions (including C—H···O contacts) for clues to explain the melting-point anomalies. Using the method of Etter *et al.* (1990), a graph-set analysis was done for the four structures. The analysis (first level only) included traditional hydrogen-bond networks as well as those generated by all possible C—H···O motifs (any with the H···O or C···O distance less than the sum of the van der Waals radii of 2.72 and 3.22 Å, respectively). There are no intermolecular C—H···N motifs that meet the close contact criteria. Table 2 summarizes the analysis.



In each structure there is at least one contact involving each O atom. The strongest interactions (based on the shortest H···O distance) in all structures involve the sulfonyl O atoms with the donor of highest priority (see footnote of Table 2): a traditional hydrogen bond (priority 1) in the hydroxy structures and two S—C—H···O=S hydrogen bonds (priority 2) in the keto structures. The two S—C—H···O=S interactions

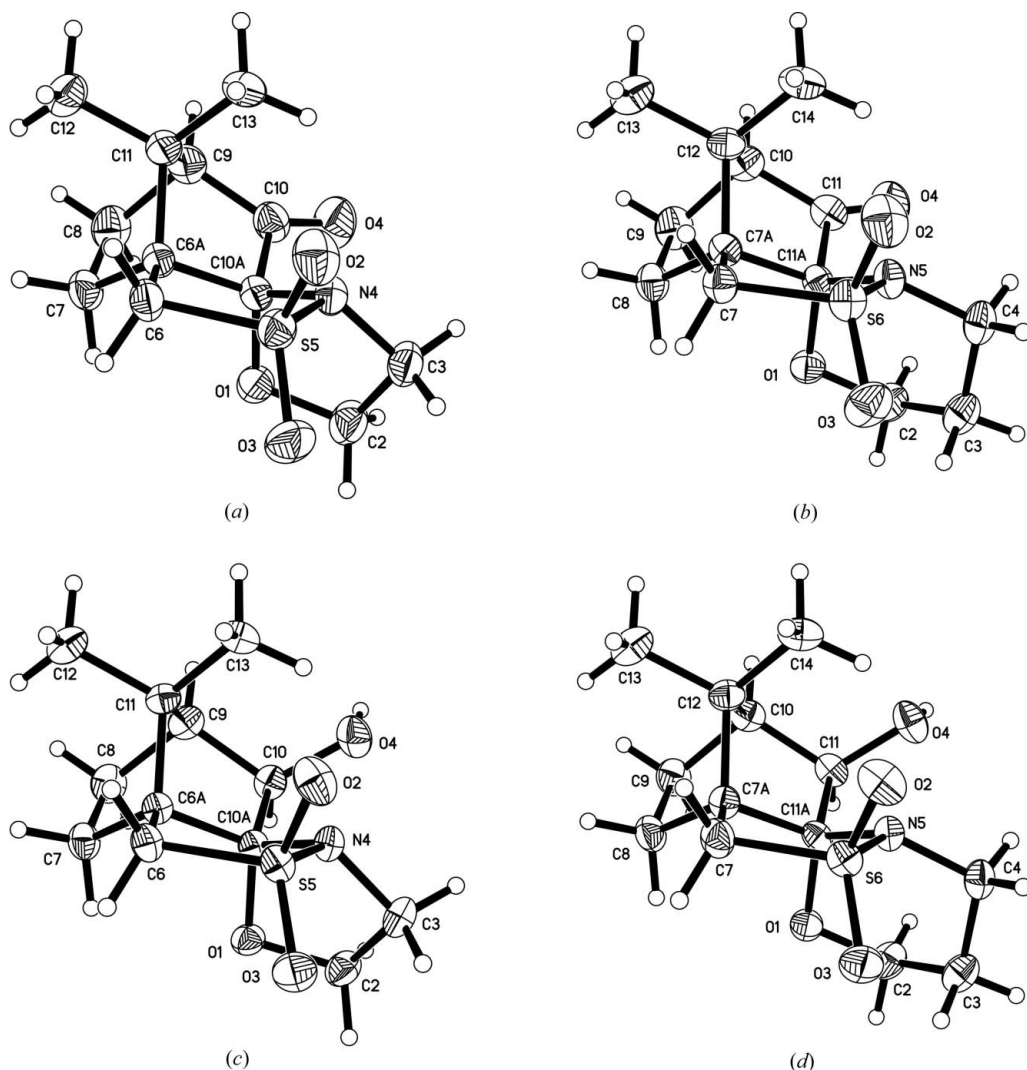
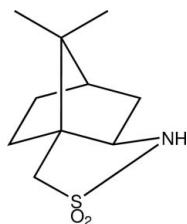


Figure 1

Views showing the structures and atom-labeling schemes of the four title camphor derivatives, *viz.* (a) (1), (b) (2), (c) (3) and (d) (4). Displacement ellipsoids are drawn at the 50% probability level in each case.

(in the keto structures) form a ring motif subset [$R_2^2(8)$] analogous to what would be considered co-operative hydrogen bonding (for traditional hydrogen bonds). In all of the following discussions, all $H \cdots O$ interactions are intermolecular and the symmetry codes of the acceptor O atoms can be found in Table 2. These strongest interactions form the columns of molecules in the *b*-axis direction. A search for $C-H \cdots O=S$ interactions in the Cambridge Structural Database



(CSD, Version 5.31, November 2009; Allen, 2002) finds 207 camphor sultams (see Scheme) with 173 having $C-H \cdots O=S$ intermolecular interactions less than the sum of van der Waals radii (2.72 Å), indicating this is a common feature of camphor

sultams. Of these, 65 have an intermolecular interaction between the methylene α (priority 2 donor) to the sulfonyl group and a sulfonyl O atom. Seven of these have two interactions forming $R_2^2(8)$ rings as found in (1) and (2).

For (1), the molecules are situated with the $>SO_2$ group near the 2_1 axis at $(0, y, 0)$ allowing formation of the two (co-operative) $S-C-H \cdots O=S$ hydrogen bonds. This orientation also allows the $C-H \cdots O$ interaction between H13A and O1 to occur. These interactions form doubled molecular columns parallel to the *b* axis. The proximity of the doubled molecular columns at $x = 0$ and $x = 1$ yields the $H3B \cdots O3$ interaction and the $H2A \cdots O2$ and $H3A \cdots O2$ close contacts connecting adjacent columns in the *a*-axis direction. The 2_1 axis at $(\frac{1}{2}, y, \frac{1}{2})$ produces the $H8B \cdots O4$ interactions that connect adjacent columns in the *c*-axis direction giving connectivity of the molecular columns in three dimensions. The geometry of the $H2A \cdots O2$ and $H3A \cdots O2$ contacts suggests they may be repulsive interactions although $C-H \cdots O$ interactions with similar geometries have been reported as attractive interactions (Steiner, 2003).

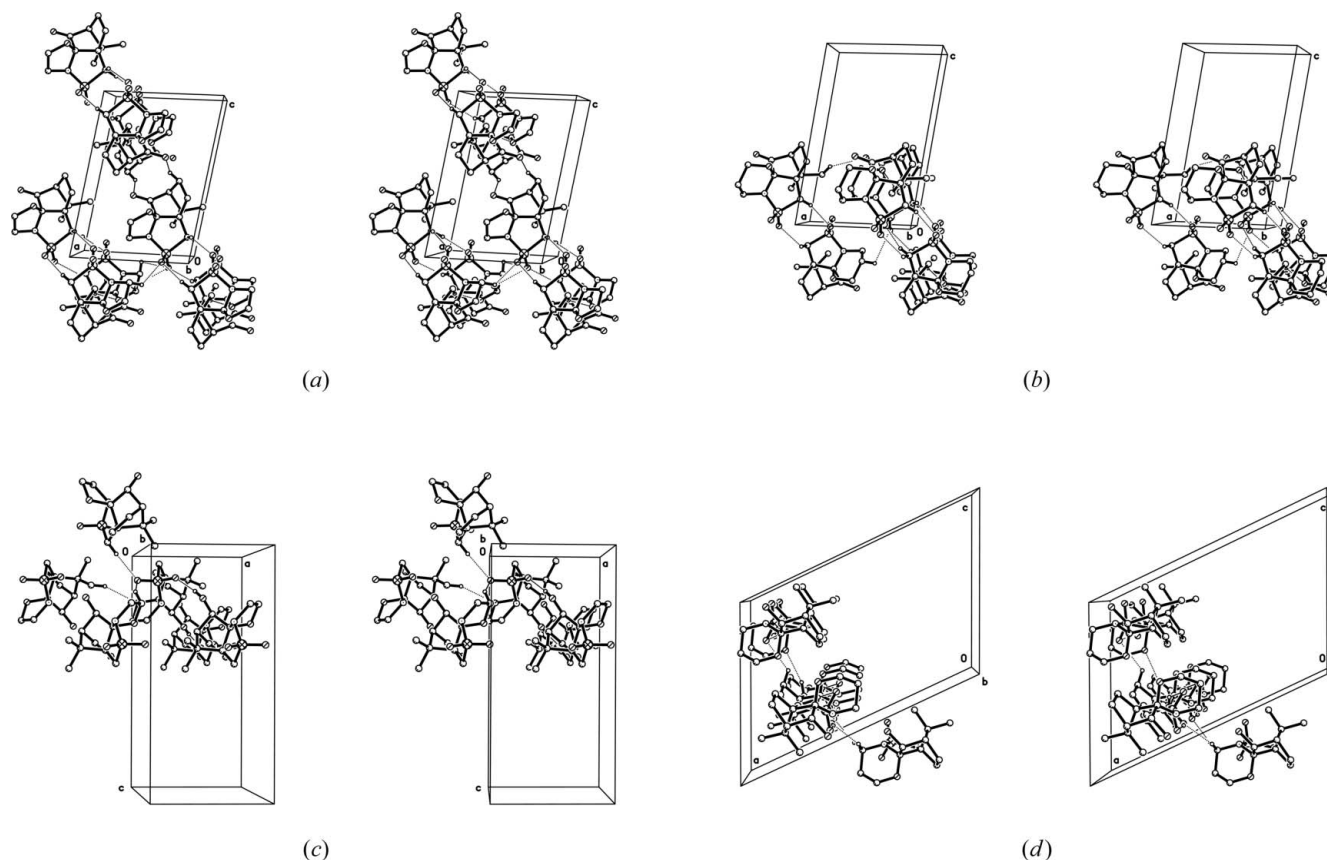


Figure 2

Molecular packing and intermolecular interactions of the four title camphor derivatives, *viz.* (a) (1), (b) (2), (c) (3) and (d) (4). Stereoviews are down the hydrogen-bond-connected molecular columns (parallel to the *b* axis) to show the interactions that interconnect the columns. The small circles represent the H atoms involved in intermolecular contacts listed in Table 2. All other H atoms have been omitted for clarity. The intermolecular contacts are shown by the small-diameter dotted lines.

As in (1), in (2) a doubled molecular column parallel to the *b* axis is generated by a 2_1 axis at $(0, y, 0)$ which allows the two (co-operative) $S-C-H \cdots O=S$ hydrogen bonds and the $H14A \cdots O1$ contact. The columns are linked in the *a*-axis direction *via* the $H3B \cdots O2$ and $H13C \cdots O4$ interactions to form molecular sheets. There are no close contacts (less than van der Waals radii sums) between the molecular sheets. The lack of three-dimensional interconnectedness correlates with (2) having the lowest melting point.

The $O-H \cdots O$ hydrogen bond in (3) forms molecular columns in the *b*-axis direction. The $H6B \cdots O3$ interaction interconnects the columns in the *c*-axis direction and the $H2A \cdots O3$ and $H13A \cdots O1$ interactions interconnect the columns in the *a*-axis direction to give the three-dimensional network.

In (4), the $O-H \cdots O$ hydrogen bond forms molecular columns also in the *b*-axis direction with an assist from the $H11 \cdots O3$ interaction. The $H4A \cdots O2$ and $H4B \cdots O4$ interactions interconnect molecular columns forming the doubled molecular columns. The $H7A \cdots O1$ and $H8B \cdots O3$ interactions connect the doubled columns into sheets. There are no close contacts (less than van der Waals radii sums) between the molecular sheets.

Although there is a correlation between the number and direction of intermolecular contacts and the melting-point

order (more contacts forming three-dimensional connectivity occur with higher melting solids, while fewer contacts and two-dimensional connectivity occur with lower melting solids), attributing the differences in melting to differences in very weak intermolecular interactions suggests there are other more important factors in play.

The packing of the keto structures [(1) and (2)] is quite similar, as also confirmed by their very similar unit-cell parameters, but their melting points differ by 50 K. There are two differences in intermolecular interactions between the two structures: (a) the presence of the $C2-H2A \cdots O2$ and $C3-H3A \cdots O2$ interactions in (1), but only the $C3-H3B \cdots O2$ interaction in (2); (b) the weak interaction with O4 in (1) ($H8B \cdots O4$) is involved in connecting adjacent columns in the *c*-axis direction and in (2) the weak interaction with O4 ($H13C \cdots O4$) is involved in connecting adjacent columns in the *a*-axis direction. Changing from a five-membered envelope conformation oxaza ring [in (1)] to the six-membered chair conformation oxaza ring of (2) precludes the doubled close contact of this ring with the O2 sulfonyl O atom, resulting in a slight twist (about the column axis, *i.e.* parallel to the *b*-cell axis) of each half of the doubled molecular columns (in opposite directions) in (2) *versus* (1). This twist also changes the closest contact of O4 from a H atom in an adjacent column in the *a*-axis direction to one in the *c*-cell direction. These

slight differences in molecular packing seem unlikely to explain the large difference in melting points on the basis of weak C—H \cdots O interactions. Considering that the sulfonyl group is highly polar, it seems more likely that the smaller five-membered oxaza ring of (1) allows for a more favorable arrangement of polar groups, resulting in a greater degree of electrostatic interaction and a higher melting point. The C2—H2A \cdots O2 and C3—H3A \cdots O2 close contacts in (1) may in fact be repulsive contacts that are ‘tolerated’ to allow the more favorable arrangement of polar groups. A recent paper by Gavezzotti (2010) presents a quantitative analysis of relative stabilities in organic crystal structures by calculating interaction energies between pairs of molecules for 1108 non-ionic and 98 ionic molecules using the PIXEL method (Gavezzotti, 2008). He concludes that repulsive destabilizing contacts regularly appear in crystals of very strongly polar compounds. We are contemplating calculating the interaction energies for this series of compounds to provide further insight to explain the differences in melting points of this series of compounds.

Experimental

Details of the preparation of the compounds can be found elsewhere (Wilke *et al.*, 2010).

Compound (1)

Crystal data

$C_{12}H_{17}NO_4S$	$V = 613.94$ (12) \AA^3
$M_r = 271.33$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 7.7873$ (9) \AA	$\mu = 0.27$ mm $^{-1}$
$b = 7.1895$ (8) \AA	$T = 210$ K
$c = 11.1111$ (12) \AA	$0.32 \times 0.29 \times 0.03$ mm
$\beta = 99.274$ (5) $^\circ$	

Data collection

Nonius KappaCCD diffractometer	15611 measured reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	2845 independent reflections
$T_{\min} = 0.918$, $T_{\max} = 0.992$	2565 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	All H-atom parameters refined
$wR(F^2) = 0.072$	$\Delta\rho_{\text{max}} = 0.18$ e \AA^{-3}
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.26$ e \AA^{-3}
2845 reflections	Absolute structure: Flack (1983)
232 parameters	Flack parameter: -0.01 (6)
1 restraint	

Compound (2)

Crystal data

$C_{13}H_{19}NO_4S$	$V = 654.81$ (13) \AA^3
$M_r = 285.35$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 7.6970$ (9) \AA	$\mu = 0.26$ mm $^{-1}$
$b = 6.9954$ (8) \AA	$T = 210$ K
$c = 12.2852$ (13) \AA	$0.22 \times 0.14 \times 0.07$ mm
$\beta = 98.145$ (5) $^\circ$	

Table 1

Bond distances (\AA) and angles ($^\circ$) of the functional groups in the four title camphor-core structures.

	(1)	(2)	(3)	(4)
S(5/6)—O2	1.4357 (14)	1.4369 (14)	1.4399 (13)	1.4396 (13)
S(5/6)—O3	1.4384 (15)	1.4405 (15)	1.4371 (12)	1.4334 (12)
S(5/6)—N(4/5)	1.6890 (15)	1.6659 (14)	1.6807 (14)	1.6534 (14)
S(5/6)—C(6/7)	1.7934 (16)	1.7898 (16)	1.7937 (17)	1.7867 (19)
O1—C2	1.439 (2)	1.449 (2)	1.441 (2)	1.440 (2)
O1—C(10A/11A)	1.421 (2)	1.417 (2)	1.427 (2)	1.429 (2)
N(4/5)—C(3/4)	1.476 (2)	1.484 (2)	1.485 (2)	1.484 (2)
N(4/5)—C(10A/11A)	1.459 (2)	1.443 (2)	1.467 (2)	1.461 (2)
C(10/11)—O4	1.213 (2)	1.209 (2)	1.423 (2)	1.421 (2)
O2—S(5/6)—O3	116.28 (9)	115.52 (9)	115.62 (8)	115.11 (8)
O2—S(5/6)—N(4/5)	108.29 (8)	108.87 (8)	108.33 (7)	108.88 (7)
O2—S(5/6)—C(6/7)	111.46 (10)	111.66 (9)	110.97 (8)	111.38 (9)
O3—S(5/6)—N(4/5)	110.66 (8)	111.26 (8)	111.10 (8)	112.51 (7)
O3—S(5/6)—C(6/7)	111.01 (10)	111.40 (9)	111.37 (8)	110.63 (9)
N(4/5)—S(5/6)—C(6/7)	97.50 (7)	96.51 (7)	98.01 (7)	96.87 (7)
C2—O1—C(10A/11A)	107.86 (14)	113.64 (13)	104.44 (13)	112.55 (14)
S(5/6)—N(4/5)—C(3/4)	115.38 (13)	116.96 (12)	115.77 (11)	115.47 (11)
S(5/6)—N(4/5)—C(10A/11A)	108.64 (11)	112.34 (11)	109.17 (10)	111.77 (10)
C(3/4)—N(4/5)—C(10A/11A)	105.50 (15)	116.79 (14)	105.36 (13)	116.80 (14)

Note: numbers in parentheses complete the atom label, with the first used being for compounds (1) and (2) and the second used being for compounds (3) and (4).

Data collection

Nonius KappaCCD diffractometer	15564 measured reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	3084 independent reflections
$T_{\min} = 0.946$, $T_{\max} = 0.982$	2783 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	All H-atom parameters refined
$wR(F^2) = 0.076$	$\Delta\rho_{\text{max}} = 0.19$ e \AA^{-3}
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.26$ e \AA^{-3}
3084 reflections	Absolute structure: Flack (1983)
249 parameters	Flack parameter: -0.01 (6)
1 restraint	

Compound (3)

Crystal data

$C_{12}H_{19}NO_4S$	$V = 1212.2$ (2) \AA^3
$M_r = 273.34$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.3091$ (8) \AA	$\mu = 0.27$ mm $^{-1}$
$b = 10.9033$ (12) \AA	$T = 190$ K
$c = 15.2110$ (16) \AA	$0.26 \times 0.24 \times 0.11$ mm

Data collection

Nonius KappaCCD diffractometer	30886 measured reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	2898 independent reflections
$T_{\min} = 0.932$, $T_{\max} = 0.970$	2662 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	All H-atom parameters refined
$wR(F^2) = 0.077$	$\Delta\rho_{\text{max}} = 0.20$ e \AA^{-3}
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.32$ e \AA^{-3}
2898 reflections	Absolute structure: Flack (1983)
240 parameters	Flack parameter: -0.01 (6)

Table 2

Motifs, motif priority, graph-set classifications and motif direction of O—H...O hydrogen bonds and C—H...O interactions in the four title camphor-core structures.

Motif	D—H (Å)	H...A (Å)	D...A (Å)	D—H...A (°)	Site symmetry of A	Priority	Graph set	Direction
Compound (1)								
C6—H6B...O3	0.99 (2)	2.41 (2)	3.390 (3)	174 (2)	$-x, y - \frac{1}{2}, -z$	2	C(4) [$R_2^2(8)$]	b axis
C6—H6A...O2	0.90 (3)	2.57 (3)	3.368 (2)	148 (2)	$-x, y + \frac{1}{2}, -z$	2	C(4) [$R_2^2(8)$]	b axis
C13—H13A...O1	1.05 (3)	2.60 (3)	3.499 (3)	143 (2)	$x, y - 1, z$	6	C(6)	b axis
C3—H3B...O3	0.94 (3)	2.70 (3)	3.409 (3)	133 (2)	$-x + 1, y - \frac{1}{2}, -z$	4	C(5)	b axis
C8—H8B...O4	0.96 (2)	2.72 (2)	3.487 (3)	137 (2)	$-x + 1, y + \frac{1}{2}, -z + 1$	5	C(5)	b axis
C3—H3A...O2	0.94 (2)	2.73 (2)	3.137 (2)	107 (2)	$-x + 1, y + \frac{1}{2}, -z$	4	C(5)	a axis
C2—H2A...O2	1.06 (3)	2.75 (3)	3.111 (3)	100 (2)	$-x + 1, y + \frac{1}{2}, -z$	3	C(5)	a axis
Compound (2)								
C7—H7B...O3	0.97 (2)	2.43 (2)	3.380 (2)	166 (2)	$-x, y - \frac{1}{2}, -z$	2	C(4) [$R_2^2(8)$]	b axis
C7—H7A...O2	0.92 (3)	2.60 (2)	3.346 (2)	139 (2)	$-x, y + \frac{1}{2}, -z$	2	C(4) [$R_2^2(8)$]	b axis
C14—H14A...O1	1.09 (3)	2.46 (3)	3.425 (2)	147 (2)	$x, y - 1, z$	6	C(6)	b axis
C3—H3B...O2	0.95 (2)	2.67 (2)	3.134 (2)	111 (1)	$-x + 1, y + \frac{1}{2}, -z$	4	C(6)	b axis
C13—H13C...O4	1.00 (3)	2.69 (3)	3.572 (3)	147 (2)	$x - 1, y, z$	6	C(6)	a axis
Compound (3)								
O4—H4...O2	0.85 (3)	2.01 (3)	2.860 (2)	174 (3)	$-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$	1	C(7)	b axis
C6—H6B...O3	0.98 (2)	2.41 (2)	3.384 (2)	175 (2)	$x + \frac{1}{2}, -y + \frac{1}{2}, -z$	2	C(4)	a axis
C2—H2A...O3	0.98 (2)	2.59 (2)	3.358 (2)	136 (2)	$-x, y - \frac{1}{2}, -z + \frac{1}{2}$	3	C(6)	b axis
C13—H13A...O1	0.97 (3)	2.65 (3)	3.581 (2)	160 (2)	$x + 1, y, z$	6	C(6)	a axis
Compound (4)								
O4—H4...O2	0.87 (3)	2.04 (3)	2.901 (2)	169 (2)	$x, y + 1, z$	1	C(7)	b axis
C8—H8B...O3	0.99 (2)	2.53 (2)	3.203 (2)	125 (1)	$-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$	5	C(6)	
C11—H11...O3	1.01 (2)	2.63 (2)	3.496 (2)	144 (1)	$x, y + 1, z$	3	C(6)	b axis
C4—H4B...O4	0.97 (2)	2.63 (2)	3.530 (2)	153 (2)	$-x + 1, y, -z$	4	$R_2^2(12)$	
C4—H4A...O2	1.02 (2)	2.64 (2)	3.646 (2)	170 (2)	$-x + 1, y, -z$	4	$R_2^2(10)$	
C7—H7A...O1	0.96 (2)	2.67 (2)	3.584 (2)	162 (2)	$-x + \frac{3}{2}, y - \frac{1}{2}, -z + 1$	2	C(5)	a axis

Note: graph-set designations of Etter *et al.* (1990) used; motif priorities based on the priority of the H-donor atom: (1) O—H...; (2) S—C—H...; (3) O—C—H...; (4) N—C—H...; (5) methylene C—H...; (6) methyl C—H...

Compound (4)

Crystal data

C₁₃H₂₁NO₄S
M_r = 287.37
 Monoclinic, C2
a = 16.5474 (18) Å
b = 7.5668 (9) Å
c = 11.5945 (13) Å
 β = 115.376 (5)°
V = 1311.7 (3) Å³
Z = 4
 Mo *K*α radiation
 μ = 0.26 mm⁻¹
T = 210 K
 0.24 × 0.07 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)
T_{min} = 0.941, *T_{max}* = 0.982
 13727 measured reflections
 3118 independent reflections
 2852 reflections with *I* > 2σ(*I*)
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.073$
S = 1.05
 3118 reflections
 257 parameters
 1 restraint
 All H-atom parameters refined
 $\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983)
 Flack parameter: -0.07 (5)

In each refinement, several low-angle reflections were excluded from the final cycles of refinement because of beam-stop shadowing effects. H atoms were fully refined with isotropic displacement parameters in all structures. The bond-distance ranges for C—H were: (1) 0.86 (2)–1.06 (2) Å, (2) 0.92 (3)–1.09 (3) Å, (3) 0.93 (2)–1.06 (2) Å and (4) 0.91 (2)–1.03 (3) Å. There are two O—H bonds, viz. one in (3) [0.85 (3) Å] and one in (4) [0.87 (3) Å]. The number of

Friedel pairs measured for (1), (2), (3) and (4) was 1265, 1394, 1281 and 1440, respectively.

For all compounds, data collection: COLLECT (Nonius, 2000); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve and refine structure: SHELXTL (Sheldrick, 2008); molecular graphics: SHELXTL; software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3184). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Chen, B. C., Murphy, C. K., Kumar, A., Reddy, R. T., Clark, C., Zhou, P., Lewis, B. M., Gala, D., Mergelberg, I., Scherer, D., Buckley, J., DiBenedetto, D. & Davis, F. A. (1996). *Org. Synth.* **73**, 159–173.
 Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Gavezzotti, A. (2008). *CrystEngComm*, **10**, 289–308.

- Gavezzotti, A. (2010). *Acta Cryst.* **B66**, 396–406.
- Magnus, P., Giles, M., Bonnert, R., Kim, C. S., McQuire, L., Merritt, A. & Vicker, N. (1992). *J. Am. Chem. Soc.* **114**, 4403–4405.
- Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Steiner, T. (2003). *Crystallogr. Rev.* **9**, 177–228.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Wilke, B. I., Goodenough, A. K., Bausch, C. C., Cline, E. N., Abrams, M. L., Fayer, E. L. & Cermak, D. M. (2010). *Tetrahedron Lett.* Submitted. doi:10.1016/j.tetlet.2010.10.105