

Pyridinium D(+)-10-camphorsulfonate hemihydrate

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Key indicators

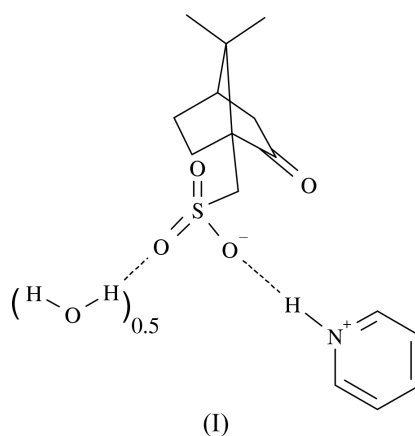
Single-crystal X-ray study
 $T = 295\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
 R factor = 0.051
 wR factor = 0.149
 Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

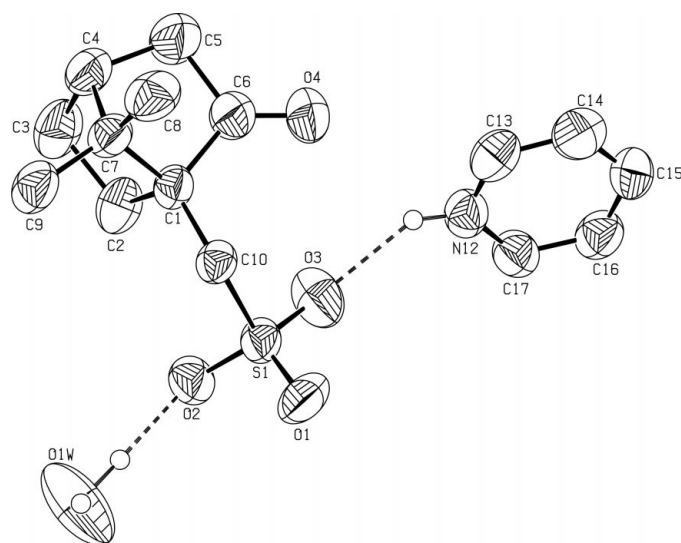
In the crystal structure of pyridinium D(+)-10-camphorsulfonate hemihydrate, $\text{C}_5\text{H}_6\text{N}^+\cdot\text{C}_{10}\text{H}_{15}\text{O}_4\text{S}^-\cdot 0.5\text{H}_2\text{O}$, a water molecule lying on a twofold axis serves as a donor of two hydrogen bonds, thus linking two camphorsulfonate anions. Each anion in its turn acts as a hydrogen-bond acceptor for the NH group of a pyridinium cation.

Comment

A number of ammonium sulfonates co-crystallize with water, resulting in a balancing of the number of hydrogen-bond donor and acceptor sites in the structure (Banerjee *et al.*, 1984; Andrews *et al.*, 1986; Laks *et al.*, 1986; Marchand *et al.*, 1990; Balasubramanian & Muthiah, 1996; Merritt & Duffin, 1970). We obtained pyridinium D(+)-10-camphorsulfonate hemihydrate, (I) (Fig. 1), as a by-product in the synthesis of allyl D(+)-10-camphorsulfonate. Crystals of (I) precipitated at 278 K from a solution in tetrahydrofuran (thf). The product was characterized by elemental analysis and its ^1H and ^{13}C NMR spectra. Adding an excess of pyridine to a solution of (I) in CDCl_3 led to merged ^1H NMR signals of pyridine and pyridinium, showing a rapid transfer of the H atom between the two, and thus implying dissociation of the pyridinium camphorsulfonate in chloroform solution.



A water molecule involved in two $\text{O}-\text{H}\cdots\text{O}$ bonds symmetrically bridges two camphor-10-sulfonate anions, and one pyridinium ion is linked to each camphorsulfonate moiety *via* an $\text{N}-\text{H}\cdots\text{O}(=\text{S})$ bridge. The $\text{S}-\text{O}$ bond lengths are within the expected range (Russell *et al.*, 1994), and do not differ significantly from each other, showing that hydrogen bonds from the water molecule and the pyridinium ion to O2 and O3, respectively, are not very strong. Nevertheless, the rather high melting point of (I) (468–469 K) indicates substantial interaction between the ions.


Figure 1

ORTEP (Johnson, 1976) view of the cation, anion and water molecule in the structure of (I). Displacement ellipsoids are shown at the 50% probability level. All H atoms bound to C atoms have been omitted for clarity. The remaining H atoms are drawn as circles of arbitrary radius.

Experimental

D(+)-10-Camphorsulfonyl chloride (10.01 g, 39.92 mmol), allyl alcohol (3.00 g, 51.65 mmol) and pyridine (3.16 g, 39.94 mmol) were dissolved in 200 ml thf and the mixture was heated to reflux for 6 h. The precipitate formed was extracted with toluene and the title compound obtained by cooling the extract to 228 K. It was recrystallized from thf at 278 K.

Crystal data

$C_5H_6N^+ \cdot C_{10}H_{15}O_4S^- \cdot 0.5H_2O$
 $M_r = 320.40$
 Monoclinic, $C2$
 $a = 24.244$ (8) Å
 $b = 6.8638$ (3) Å
 $c = 10.415$ (3) Å
 $\beta = 110.54$ (1)°
 $V = 1622.9$ (7) Å³
 $Z = 4$

$D_x = 1.311$ Mg m⁻³
 Cu $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 26$ – 40°
 $\mu = 1.94$ mm⁻¹
 $T = 295$ (2) K
 Needle, colourless
 $0.45 \times 0.10 \times 0.06$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan (CORINC; Dräger & Gattow, 1971)
 $T_{\min} = 0.90$, $T_{\max} = 0.99$
 3574 measured reflections
 3092 independent reflections

2748 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 73.9^\circ$
 $h = -30 \rightarrow 30$
 $k = -8 \rightarrow 8$
 $l = -12 \rightarrow 12$
 3 standard reflections
 frequency: 60 min
 intensity decay: 3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.149$
 $S = 1.03$
 3092 reflections
 208 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0968P)^2 + 0.7053P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³
 Absolute structure: Flack (1983);
 1293 Friedel pairs
 Flack parameter = -0.03 (3)

Table 1

Selected geometric parameters (Å, °).

S1—O1	1.446 (3)	C6—O4	1.192 (5)
S1—O2	1.458 (3)	N12—C13	1.318 (6)
S1—O3	1.448 (3)	N12—C17	1.326 (5)
S1—C10	1.782 (3)		
O1—S1—O3	113.2 (2)	O3—S1—O2	110.98 (18)
O1—S1—O2	112.47 (18)	C13—N12—C17	122.3 (4)
O1—S1—C10—C1	174.7 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N12—H12 \cdots O3	0.86	2.00	2.718 (5)	141
O1W—H1W \cdots O2	1.01	1.86	2.864 (4)	172

H atoms attached to C atoms were placed in calculated positions; H atoms bound to N and O atoms were located from a difference Fourier synthesis. Positional parameters of all H atoms were refined using a riding motion model. The displacement parameter for the H atom of the water molecule was fixed at 1.5 times the equivalent isotropic displacement parameter of the O atom. The isotropic displacement parameters for other H atoms were refined with all H atoms bonded to the same C atom constrained to have the same displacement parameter.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997).

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