

## The Structure of *trans*-4'-Hydroxy-*N*-methyl-4-stilbazolium (+)-Camphor-10-sulfonate\*

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**Abstract.**  $C_{14}H_{14}NO^+ \cdot C_{10}H_{15}O_4S^-$ , (I), monoclinic,  $P2_1$ ,  $a = 8.475$  (1),  $b = 28.192$  (3),  $c = 9.605$  (1) Å,  $\beta = 98.28$  (1)°,  $V = 2271$  Å<sup>3</sup>,  $Z = 4$ ;  $d_c = 1.297$ ,  $d_m = 1.29$  Mg m<sup>-3</sup> (flotation in CCl<sub>4</sub>/cyclohexane mixture). Final  $R(F) = 0.044$ ,  $R_w = 0.055$  for 3096 independent observed reflections. Two crystallographically independent

hydrogen-bonded cation–anion pairs interleave to form dimers in layers normal to [010]. In the dimer the cations are related by a pseudo inversion center and have a non-coplanar, antiparallel arrangement.

\* Alternative name: (*E*)-4-[2-(4-hydroxyphenyl)vinyl]-1-methylpyridinium (+)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-methanesulfonate.

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**Introduction.** The title compound (I) was prepared by dropwise addition of an absolute ethanol solution of (+)-camphor-10-sulfonic acid to 4'-hydroxy-*N*-methyl-4-stilbazolium betaine suspended in absolute ethanol. Crystals suitable for X-ray analysis were obtained from

Table 1. Positional and thermal parameters with their *e.s.d.*'s

				$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$										
	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )		<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )		<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )
S(1)	0.3772 (1)	0.107720 (4)	0.4240 (1)	4.84 (2)	C(17)	-0.0979 (5)	0.0863 (2)	-0.2221 (5)	4.6 (1)					
S(2)	0.1129 (2)	-0.10270 (5)	0.0704 (1)	5.35 (3)	C(18)	-0.0203 (5)	0.0421 (2)	-0.2311 (5)	4.0 (1)					
					C(19)	0.1068 (5)	0.0327 (2)	-0.1276 (5)	4.0 (1)					
O(1)	0.3645 (4)	-0.1352 (1)	0.4092 (4)	5.8 (1)	C(20)	0.1555 (5)	0.0635 (2)	-0.0199 (5)	4.0 (1)					
O(2)	0.1130 (4)	0.1380 (1)	0.0926 (3)	5.4 (1)	C(21)	-0.0690 (5)	0.0078 (2)	-0.3412 (5)	4.5 (1)					
O(3)	0.3595 (4)	0.1107 (2)	0.2703 (3)	6.9 (1)	C(22)	-0.2015 (5)	0.0094 (2)	-0.4344 (5)	4.4 (1)					
O(4)	0.5390 (4)	0.0973 (1)	0.4827 (4)	6.4 (1)	C(23)	-0.2483 (5)	-0.0241 (2)	-0.5479 (5)	4.0 (1)					
O(5)	0.2600 (5)	0.0777 (1)	0.4719 (4)	7.0 (1)	C(24)	-0.3934 (5)	-0.0193 (2)	-0.6362 (5)	4.2 (1)					
O(6)	0.0575 (4)	0.1922 (2)	0.5985 (4)	5.9 (1)	C(25)	-0.4408 (5)	-0.0500 (2)	-0.7414 (5)	4.3 (1)					
O(7)	0.1350 (5)	-0.1035 (2)	0.2245 (4)	8.3 (1)	C(26)	-0.2103 (6)	-0.0931 (2)	-0.6856 (5)	4.8 (1)					
O(8)	0.2355 (5)	-0.0755 (1)	0.0181 (5)	8.0 (1)	C(27)	-0.1566 (5)	-0.0635 (2)	-0.5750 (5)	4.5 (1)					
O(9)	-0.0477 (4)	-0.0898 (1)	0.0157 (4)	6.8 (1)	C(28)	-0.4000 (6)	-0.1197 (2)	-0.8827 (6)	5.7 (1)					
O(10)	-0.1872 (5)	-0.1946 (2)	-0.0443 (5)	7.8 (1)	C(29)	0.3365 (5)	0.1659 (2)	0.4757 (5)	4.4 (1)					
					C(30)	0.3439 (5)	0.1779 (2)	0.6316 (4)	3.7 (1)					
N(1)	0.8344 (4)	0.0879 (1)	1.2710 (4)	4.0 (1)	C(31)	0.3926 (6)	0.1387 (2)	0.7436 (5)	5.1 (1)					
N(2)	-0.3491 (4)	-0.0865 (1)	-0.7662 (4)	4.3 (1)	C(32)	0.4449 (6)	0.1670 (2)	0.8812 (5)	5.5 (1)					
					C(33)	0.4073 (6)	0.2176 (2)	0.8377 (5)	5.2 (1)					
C(1)	0.4025 (5)	-0.1033 (2)	0.5160 (5)	4.5 (1)	C(34)	0.4546 (6)	0.2198 (2)	0.6874 (5)	4.5 (1)					
C(2)	0.5306 (6)	-0.1144 (2)	0.6181 (5)	4.9 (1)	C(35)	0.4111 (8)	0.2658 (2)	0.6088 (6)	6.5 (1)					
C(3)	0.5775 (5)	-0.0833 (2)	0.7274 (5)	4.5 (1)	C(36)	0.6315 (6)	0.2098 (2)	0.6822 (6)	6.5 (1)					
C(4)	0.5000 (5)	-0.0404 (2)	0.7374 (5)	3.8 (1)	C(37)	0.1877 (5)	0.1962 (2)	0.6681 (5)	4.4 (1)					
C(5)	0.3721 (5)	-0.0300 (2)	0.6351 (5)	4.2 (1)	C(38)	0.2250 (7)	0.2212 (2)	0.8088 (6)	5.7 (1)					
C(6)	0.3220 (5)	-0.0611 (2)	0.5249 (5)	4.4 (1)	C(39)	0.1403 (6)	-0.1636 (6)	0.0265 (5)	5.2 (1)					
C(7)	0.5522 (5)	-0.0061 (2)	0.8487 (5)	4.2 (1)	C(40)	0.0721 (5)	-0.1794 (2)	-0.1212 (5)	3.8 (1)					
C(8)	0.6834 (5)	-0.0082 (2)	0.9427 (5)	4.1 (1)	C(41)	0.0585 (7)	-0.1439 (2)	-0.2444 (6)	6.0 (1)					
C(9)	0.7335 (5)	0.0257 (2)	1.0526 (4)	3.8 (1)	C(42)	0.0376 (9)	-0.1751 (3)	-0.3771 (6)	8.4 (2)					
C(10)	0.8771 (5)	0.0192 (2)	1.1398 (5)	4.0 (1)	C(43)	0.0352 (8)	-0.2247 (2)	-0.3149 (6)	6.7 (2)					
C(11)	0.9268 (5)	0.0503 (2)	1.2469 (5)	4.0 (1)	C(44)	0.1552 (6)	-0.2219 (2)	-0.1806 (5)	5.1 (1)					
C(12)	0.6926 (5)	0.0952 (2)	1.1872 (5)	4.6 (1)	C(45)	0.1596 (7)	-0.2670 (2)	-0.0904 (6)	6.3 (1)					
C(13)	0.6415 (5)	0.0654 (2)	1.0812 (5)	4.5 (1)	C(46)	0.3249 (8)	-0.2113 (3)	-0.2088 (8)	9.0 (2)					
C(14)	0.8893 (6)	0.1217 (2)	1.3844 (5)	5.1 (1)	C(47)	-0.0957 (6)	-0.2000 (2)	-0.1284 (6)	5.3 (1)					
C(15)	0.0758 (5)	0.1065 (2)	-0.0133 (4)	3.8 (1)	C(48)	-0.1219 (8)	-0.2298 (2)	-0.2586 (7)	7.4 (2)					
C(16)	-0.0503 (5)	0.1177 (2)	-0.1157 (5)	4.4 (1)										

a 10:1 volume mixture of acetone and ethanol. Unit-cell parameters were obtained from a least-squares analysis of 25 reflections. The observed systematic extinctions were  $0k0$ ,  $k \neq 2n$ . Since the compound is optically active, space group  $P2_1$  was chosen and was subsequently confirmed by refinement. Intensity data were collected at  $298 \pm 1$  K on an Enraf-Nonius CAD-4 automatic diffractometer using graphite-monochromatized Cu  $K\alpha$  radiation. The orange crystal used measured  $0.25 \times 0.25 \times 0.25$  mm and was mounted in a glass capillary. The total number of reflections collected was 6299; 4077 were independent. Intensities and standard deviations of intensities were calculated as  $I = S(C - RB)$  and  $\sigma(I)^2 = S^2(C + R^2B) + (pI)^2$  where  $S$  = scan rate,  $C$  = total integrated peak count,  $R$  = scan time/background counting time,  $B$  = total background count and  $p = 0.05$ . Lorentz and polarization corrections were applied to the data. A correction for extinction was applied (Zachariasen, 1963), and refined to a value of  $3.50 \times 10^{-6}$ . No absorption correction [ $\mu(\text{Cu } K\alpha) = 1.53 \text{ mm}^{-1}$ ] was made.

The structure was solved by direct methods and was refined by the full-matrix least-squares method using 3096 reflections having  $F_o^2 > 3\sigma(F_o^2)$ . The function  $\sum w(|F_o| - |F_c|)^2$  was minimized where  $w$  is  $4F_o^2/\sigma^2(F_o^2)$ . The hydroxyl H atoms were refined isotropically. All other H atoms were included in their calculated (idealized) positions with  $B = 6.0 \text{ \AA}^2$ . The rotational conformations of the methyl groups were calculated so that they agreed with the locations found in a prior difference Fourier map. Calculations were performed on a PDP 11/45 using the Enraf-Nonius structure determination package (Frenz, 1978). Atomic scattering factors for all atoms were those of Cromer & Waber (1974) and were corrected for both the real and imaginary parts of anomalous dispersion (Cromer & Liberman, 1970). The final agreement factors are  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.044$  and  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.055$ . The anion has the expected 1(S) configuration of (+)-camphor (Allen & Rogers, 1971). (Refinement of the other enantiomer yielded  $R_1 = 0.045$  and  $R_2 = 0.056$ .) The final positional parameters of the non-H atoms are given in Table 1.\*

**Discussion.** The structure of (I) was determined as part of a larger effort to study the structure-property relationships that govern the optical non-linearities of organic crystals.

The structure consists of two crystallographically independent hydrogen-bonded cation-anion pairs

\* Lists of structure factors, anisotropic thermal parameters, H-atom positional parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36298 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Figs. 1 and 2) interleaved to form dimers in layers normal to [010]. The molecular packing is shown in Fig. 3. All interatomic distances and angles in the ions appear normal. The cations have a twisted conformation with the dihedral angle between the benzene and pyridine rings being  $11(1)$  and  $13(1)^\circ$  for the N(1) and N(2) cations respectively.

Hydrogen bonding occurs through the hydroxyl groups of the cations and the sulfonated O atoms. The O(1)-O(7) and O(2)-O(3) distances are  $2.595(6)$  and  $2.616(6) \text{ \AA}$ , while the O(1)-H(1)-O(7) and

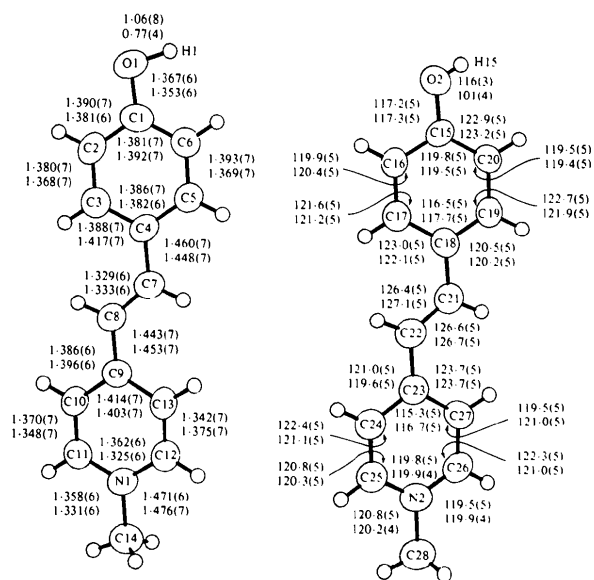


Fig. 1. Perspective views, atom labelling scheme, distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the two crystallographically independent 4'-hydroxy-*N*-methyl-4-stilbazolium cations. The upper numbers refer to the labelled cation while the lower numbers refer to the corresponding values in the other cation.

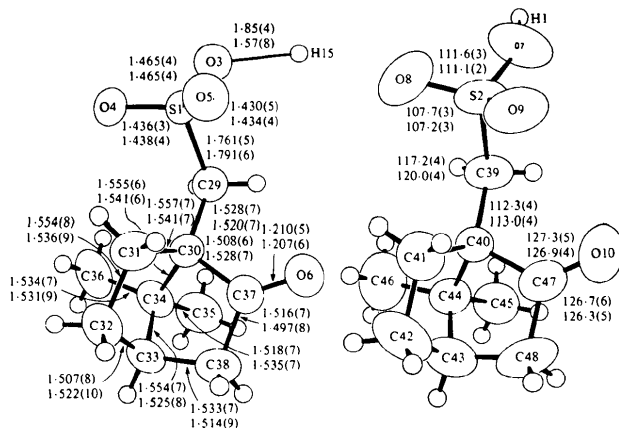


Fig. 2. Perspective views, atom labelling scheme, distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the two crystallographically independent (+)-camphor-10-sulfonate anions. The upper numbers refer to the labelled anion while the lower numbers refer to the corresponding values in the other anion.

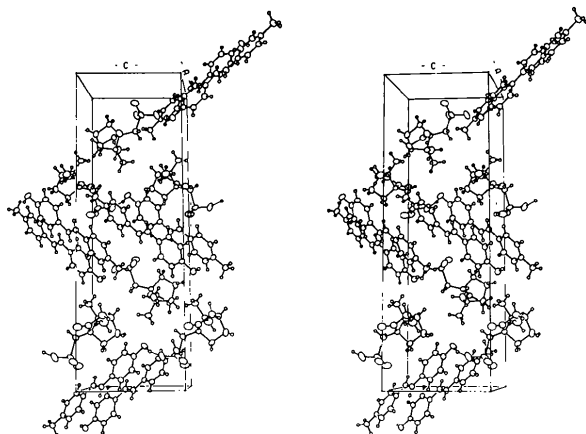


Fig. 3. Stereoscopic packing view of (I).

O(2)—H(15)—O(3) angles are 161 (7) and 171 (4) $^\circ$  respectively; H(1)—O(1)—C(1)—C(2) is 179 (1) $^\circ$  and H(15)—O(2)—C(15)—C(16) is  $-173$  (1) $^\circ$ . Exclusive of these O—O contacts, the shortest interionic contact is C(10)—C(20) ( $1 + x, y, 1 + z$ ) in the dimer at 3.243 (7) Å.

In the dimer the cations are related by a pseudo inversion center and have an antiparallel arrangement. The angle between the N(1)—C(1) and N(2)—C(15) vectors is 179.5 (5) $^\circ$ . This arrangement of the cations precludes any significant contribution of the species to

the second-order non-linear electric-dipole susceptibility which we have determined for (I) for optical second-harmonic generation to be  $< 10^{-8}$  e.s.u.

The independent anions have slightly different conformations, as seen in the torsion angles C(31)—C(30)—C(29)—S(1): 1.8 $^\circ$ , C(41)—C(40)—C(39)—S(2): 29.6 $^\circ$ , C(30)—C(29)—S(1)—O(3):  $-179.5^\circ$  and C(40)—C(39)—S(2)—O(7): 159.7 $^\circ$  (e.s.d.'s  $< 1.0^\circ$ ). Rotations take place about the C(29,39)—C(30,40) and C(29,39)—S(1,2) bonds so as to minimize SO $_3^-$  oxygen contacts with the carbonyl and bridgehead methyl groups and to stagger the non-hydrogen-bonded O—S—O moieties over the C(37,47) positions.

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