Fig. 2. The unit-cell contents (excluding H) projected down the z axis.

involving the solvent; the shortest are (to H) H(33a)···H(5a) 2·52 Å, (to O) H(32a)···O(31'') 2·93 Å and (to C) H(31b)···C(11) 3·07 Å (second atoms at $x, y, 1 + z$; x, y, z; $1 - x, 1 - y, 1 - z$ respectively). It thus appears that the oxime is capable of extracting n-hexane preferentially from petroleum simply by virtue of the good fit of the hexane into what would otherwise be 'holes' in the crystal lattice (Fig. 2). The hexane adopts a fully extended conformation (unique torsion angles $-179, 180°$).

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Bond length and Reactivity: The Beckmann Rearrangement. 2.* Structure of a Protonated Lactam: 5-*tert*-Butylhexahydro-2*H*-azepin-2-onium *p*-Toluenesulfonate Monohydrate

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Abstract. $C_{10}H_{20}NO^+.C_7H_7O_3S^-.H_2O$, $M_r = 359\cdot47$, monoclinic, $P2_1/n$, $a = 10\cdot153$ (2), $b = 6\cdot444$ (1), $c = 30\cdot523$ (5) Å, $\beta = 96\cdot65$ (1)°, $V = 1983\cdot5$ (6) Å^3, $Z = 4$, $D_x = 1\cdot203$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot5418$ Å, $\mu = 1\cdot55$ mm^{-1}, $F(000) = 776$, $T = 291$ K, $R = 0\cdot053$ for 2030 observed reflections. The substituted ε-caprolactam, as its conjugate acid, is hydrogen-bonded *via* a molecule of water to the p-toluenesulfonate anion. One of the sulfonate O atoms is also involved in an intermolecular hydrogen bond to the lactam N—H.

Introduction. As part of our broad investigation of correlations between bond length and reactivity (Jones & Kirby, 1984), we are examining crystal structures of several series of oxime derivatives known to undergo the Beckmann rearrangement (Jones *et al.*, 1986*a*). Most interesting are those derivatives, particularly phosphate and sulfonate esters, which are most reac-

tive, and we have prepared p-toluenesulfonates of three different oximes. Of these, one (from cyclopentanone) could be crystallized, but shows localized disorder; a second, from 4-phenylcyclohexanone (actually the 2-naphthalenesulfonate, Jones *et al.*, 1986*b*), has been solved at 233 K, and an accurate structure is available, which shows a very long N—O bond. We report our results with a third such compound, the p-toluenesulfonate ester of 4-*tert*-butylcyclohexanone oxime (1).

The ester (1) was prepared and characterized (m.p. 329 K) in the usual way (the ketone is commercially available), and a suitable crystal grown overnight by diffusion of n-hexane into an ether solution at 273 K. However, the structure solution showed clearly that our crystal is in fact that of the Beckmann rearrangement product, the substituted ε-caprolactam, as its conjugate acid (2), hydrogen-bonded *via* a molecule of water to the p-toluenesulfonate anion. The compound has acquired a molecule of water, evidently from the ether solvent. Further experiments confirmed the identity of

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* Part 1: Jones, Edwards & Kirby (1986*a*).

$C_{10}H_{20}NO^{+}.C_7H_7O_3S^{-}.H_2O$

(1), and showed that no crystals were obtained if sodium-dried ether was used in the crystallization procedure, though the formation of crystals of (2) (m.p. 347 K) is reproducible, and faster if ether deliberately saturated with water is used.

We have not been able to grow single crystals of (1), but report here our results with (2).

(1)   (2)
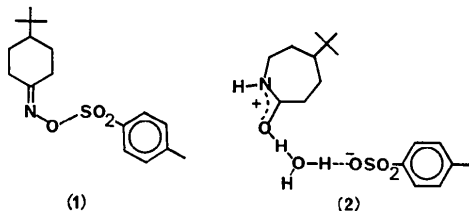
Experimental. Crystal of size 0·42 × 0·40 × 0·34 mm, Syntex $P2_1$ diffractometer, unit-cell parameters from angular values of 15 centred reflections in range $45 < 2\theta < 55°$, 3601 reflections with $2\theta \leq 120·0°$ and $h\,0\rightarrow11$, $k\,0\rightarrow6$, $l\,-33\rightarrow33$ (quadrant of data, some repeated), profile-fitted, no significant intensity variation for two standard reflections, no absorption correction, 2897 unique reflections, 2030 with $F >$ $4\sigma(F)$, $R_{int} = 0·01$; all non-H atoms from random-start multisolution direct methods, blocked full-matrix refinement on F, anisotropic thermal parameters for all non-H atoms except the disordered sulfonate O atoms; sulfonate O atoms positionally disordered over two sites and the two sets of positions refined with occupancies of k and $(1 - k)$ [k refined to 0·876 (9)], the O atoms making up the smaller component of the disorder assigned a common isotropic temperature factor; C- and N-bonded H atoms fixed with C—H 1·08 and N—H 1·00 Å, respectively, and allowed to ride on relevant heavy atom, O—H distances for H(50A) and H(50B) fixed at 0·98 Å, H(10) refining freely; each type of H assigned a common isotropic temperature factor; scattering factors from *International Tables for X-ray Crystallography* (1974), 258 parameters, $R =$ 0·053, $wR = 0·061$, $w = 2·4104/[\sigma^2(F) + 0·001F^2]$, mean $\Delta/\sigma = 0·08$, max. $= 2·2$ (oscillation of H-atom temperature factors), largest peak in final difference map $= 0·26$ e Å^{-3}, largest hole $= 0·023$ e Å^{-3}; programs: *SHELX*76 (Sheldrick, 1976), *SHELX*86 (Sheldrick, 1986).

Discussion. Final atomic coordinates are presented in Table 1 and the derived bond lengths and angles in Table 2.* Fig. 1 shows a thermal-ellipsoid plot of the

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* Tables of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42974 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times10^4$) *and equivalent isotropic or isotropic temperature factors* ($\times10^3$) *for* (2)

	x	y	z	$U_{eq}/U_{iso}(\text{Å}^2)$
C(1)	4208 (3)	4215 (6)	2931 (1)	69 (3)*
O(1)	4246 (2)	2299 (4)	2803 (1)	84 (2)*
C(2)	5445 (3)	5487 (6)	3019 (1)	73 (2)*
C(3)	5769 (3)	6091 (6)	3505 (1)	78 (2)*
C(4)	4979 (3)	7956 (6)	3657 (1)	71 (3)*
C(5)	3485 (3)	7536 (6)	3612 (1)	82 (3)*
C(6)	2850 (3)	7084 (6)	3144 (1)	85 (3)*
N(7)	3063 (3)	4969 (5)	2998 (1)	77 (2)*
C(8)	5528 (4)	8722 (8)	4121 (1)	97 (3)*
C(9)	5494 (6)	7013 (10)	4464 (1)	146 (5)*
C(10)	4716 (5)	10574 (8)	4261 (2)	122 (4)*
C(11)	6960 (5)	9495 (12)	4111 (2)	189 (7)*
S(1)	5205 (1)	7178 (1)	1796 (1)	72 (1)*
O(2)	5258 (6)	4992 (5)	1699 (1)	121 (4)*
O(3)	6472 (3)	7986 (7)	1990 (1)	81 (2)*
O(4)	4206 (3)	7655 (9)	2087 (1)	109 (3)*
O(2')	6122 (27)	−1006 (44)	1971 (8)	78 (6)
O(3')	−1188 (24)	779 (40)	3330 (7)	78 (6)
O(4')	961 (25)	1626 (38)	3101 (9)	78 (6)
C(12)	4750 (3)	8519 (9)	1300 (1)	67 (2)*
C(13)	5138 (3)	10567 (6)	1245 (1)	84 (3)*
C(14)	4707 (4)	11618 (6)	868 (2)	91 (3)*
C(15)	3913 (4)	10690 (7)	521 (1)	87 (3)*
C(16)	3525 (4)	8678 (8)	580 (1)	95 (3)*
C(17)	3931 (4)	7594 (6)	959 (1)	84 (3)*
C(18)	3447 (5)	11896 (9)	99 (1)	125 (4)*
O(5)	6402 (3)	10642 (5)	2714 (1)	111 (2)*

The atoms denoted with a prime represent the minor component of the disordered SO$_3$ fragment.

* $U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

Table 2. *Bond lengths* (Å) *and interbond angles* (°) *for* (2)

O(1)—C(1)	1·297 (5)	C(3)—C(2)	1·533 (5)
N(7)—C(1)	1·297 (5)	C(4)—C(3)	1·546 (5)
C(2)—C(1)	1·498 (5)	C(5)—C(4)	1·531 (5)
H(10)—O(1)	1·38 (6)	C(8)—C(4)	1·542 (5)
C(9)—C(8)	1·524 (7)	C(6)—C(5)	1·524 (5)
C(10)—C(8)	1·539 (7)	N(7)—C(6)	1·458 (5)
C(11)—C(8)	1·540 (7)	H(7)—N(7)	1·01 (3)
O(2)—S(1)	1·442 (4)	C(12)—S(1)	1·757 (3)
O(3)—S(1)	1·450 (3)	C(13)—C(12)	1·393 (5)
O(4)—S(1)	1·457 (4)	C(17)—C(12)	1·389 (5)
O(2')—S(1)	1·55 (3)	C(14)—C(13)	1·363 (6)
O(3')—S(1)	1·43 (3)	C(15)—C(14)	1·389 (6)
O(4')—S(1)	1·31 (4)	C(16)—C(15)	1·373 (7)
H(10)—O(5)	1·10 (6)	C(18)—C(15)	1·533 (6)
H(50A)—O(5)	0·98 (4)	C(17)—C(16)	1·373 (5)
H(50B)—O(5)	1·00 (5)		
O(1)—C(1)—N(7)	117·5 (3)	C(1)—C(2)—C(3)	113·1 (3)
O(1)—C(1)—C(2)	121·4 (3)	C(4)—C(3)—C(2)	115·4 (3)
N(7)—C(1)—C(2)	121·0 (3)	C(3)—C(4)—C(8)	112·3 (3)
C(1)—O(1)—H(10)	120 (3)	C(5)—C(4)—C(8)	112·9 (3)
O(1)—H(10)—O(5)	175 (6)	C(5)—C(4)—C(3)	112·2 (3)
C(4)—C(8)—C(9)	111·4 (4)	C(6)—C(5)—C(4)	115·2 (3)
C(4)—C(8)—C(10)	110·8 (3)	N(7)—C(6)—C(5)	113·9 (3)
C(4)—C(8)—C(11)	109·0 (4)	C(1)—N(7)—C(6)	124·5 (3)
C(9)—C(8)—C(10)	108·3 (4)	C(1)—N(7)—H(7)	117 (2)
C(9)—C(8)—C(11)	110·2 (4)	C(6)—N(7)—H(7)	118 (2)
C(10)—C(8)—C(11)	107·0 (4)	S(1)—C(12)—C(13)	121·3 (3)
O(2)—S(1)—O(3)	112·4 (3)	S(1)—C(12)—C(17)	120·9 (3)
O(2)—S(1)—O(4)	112·4 (3)	C(13)—C(12)—C(17)	117·8 (3)
O(2)—S(1)—C(12)	108·3 (2)	C(12)—C(13)—C(14)	120·3 (3)
O(3)—S(1)—O(4)	108·8 (2)	C(13)—C(14)—C(15)	122·2 (4)
O(3)—S(1)—C(12)	108·0 (2)	C(14)—C(15)—C(16)	116·9 (4)
O(4)—S(1)—C(12)	106·7 (2)	C(14)—C(15)—C(18)	121·7 (4)
H(10)—O(5)—H(50A)	116 (5)	C(16)—C(15)—C(18)	121·3 (4)
H(10)—O(5)—H(50B)	120 (5)	C(15)—C(16)—C(17)	121·7 (4)
H(50A)—O(5)—H(50B)	104 (5)	C(12)—C(17)—C(16)	121·0 (4)

hydrogen-bonded ion pair. A strong, linear hydrogen bond [O(5)—H(10)—O(1) 2·479 (5) Å] links the O-protonated lactam with the bridging water molecule, which has further weaker hydrogen bonds to O atoms of two sulfonate anions. One sulfonate O is also involved in an intermolecular hydrogen bond to the lactam N—H. A list of important hydrogen bonds is presented in Table 3 and Fig. 2 shows the inter-molecular hydrogen bonding within the unit cell.

The successful refinement locates the H in the strong O(1)—H—O(5) hydrogen bond closer to O(5), as expected for a neutral amide–hydroxonium ion pair, but the bond lengths in the amide group are very different from those expected for a neutral amide. In a series of papers Dunitz & Winkler (1975) defined structural parameters for the O-protonated amide group in several

Table 3. O—O *and* N—O *contacts which indicate the existence of hydrogen bonding in the crystal structure of* (2)

Atom (1)	Atom (2)	Distance (Å)	Symmetry operation relating coordinates of atom (1) to those of atom (2)
O(5)	O(1)	2·479 (5)	x, y, z
O(4A)	N(7)	2·732 (5)	$0·5 - x, 0·5 + y, 0·5 - z$
O(5A)	O(3)	2·703 (5)	$0·5 + z, 0·5 + y, 0·5 - z$
O(5)	O(3)	2·801 (5)	x, y, z
O(5)	O(2')	2·490 (29)	x, y, z
O(5)	O(3')	2·911 (30)	x, y, z

lactam hydrochlorides [the seven-membered-ring compound was disordered (Winkler & Dunitz, 1975b)]. The secondary amide group is generally hydrogen-bonded in the crystal, and thus in effect 'partially deprotonated', just as the O—H of a protonated amide is always hydrogen-bonded to the counterion, and so 'partially deprotonated' also. But the equal C—O and C—N bond lengths [1·297 (5) Å] in (2) both fall at the 'fully protonated' end of the range, and are closely similar to those (1·307, 1·293 Å) found for the eight-membered protonated lactam ring (Winkler & Dunitz, 1975c). For comparison, the C=O and C—N bond lengths in neutral caprolactam are 1·242 and 1·327 Å, respectively (Winkler & Dunitz, 1975a), while in the half-protonated hemihydrochloride of acetamide (Speakman, Lehmann, Allibon & Semmingsen, 1981) the difference between the two bond lengths is almost exactly halved.
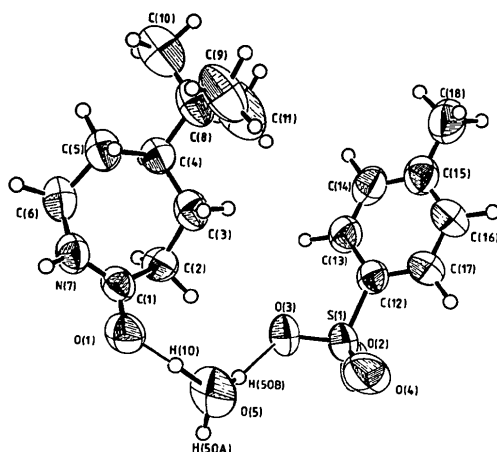

Fig. 1. Molecular geometry of the hydrogen-bonded ion pair. Thermal motion is depicted as 50% probability ellipsoids. For clarity only the major component of the disordered sulfonate O atoms is shown.
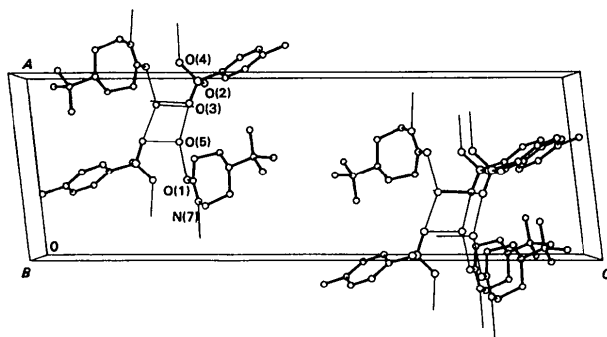

Fig. 2. The unit-cell contents showing the hydrogen-bonding pattern.

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