in agreement with the conclusion of Osawa & Musso (1982) that the double bond in crowded ethylenes is highly resistant to elongation; the longest recorded lengths are 1·358 ± 0·004 Å. The C(1)—O(1) bond length of 1·416 (5) Å is also similar to those in other enols and enol ethers (Biali & Rappoport, 1984; Kaftory, Biali & Rappoport, 1985).

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Bond Length and Reactivity: The Beckmann Rearrangement. 1. Structure of Cyclopentanone *O*-(3,5-Dinitrobenzoyl)oxime *n*-Hexane Solvate (4:1)

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Abstract. $C_{12}H_{11}N_3O_6.\frac{1}{4}C_6H_{14}$, $M_r = 314{\cdot}79$, triclinic, $P\bar{1}$, $a = 10{\cdot}712$ (3), $b = 11{\cdot}297$ (3), $c = 13{\cdot}050$ (3) Å, $\alpha = 74{\cdot}63$ (2), $\beta = 76{\cdot}78$ (2), $\gamma = 87{\cdot}52$ (2)°, $V = 1482{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1$ cm^{-1}, $F(000) = 658$, $T = 291$ K, $R = 0{\cdot}063$ for 4173 unique observed reflections. The two independent molecules differ only in the cyclopentane ring conformations. The N—O bond is lengthened with respect to free oximes by *ca* 0·055 Å. The hexane of solvation is well ordered and adopts a fully extended conformation. There are no unusually short contacts involving the solvent.

Introduction. Arising from our extensive investigations into the relationship between the length of a bond in the crystal and the rate at which it is broken in solution (Jones & Kirby, 1984), we have become increasingly interested in the geometrical consequences of the bond-lengthening effects we observe. Increasing electron withdrawal in the group *X* in a series of structures *R*—O*X* is associated with increasing *R*—O bond lengths, and the evidence is strong that this results from an increasingly important contribution to the ground-state structure from the valence tautomeric form R^+ $^-$O*X* (Allen & Kirby, 1984). If positive charge is indeed generated on the group *R*, it should in principle be possible to identify secondary changes induced by the need to accommodate that charge. Further, since it is precisely these changes which lead to classical ionic reactions in solution, the technique of the 'variable oxygen probe' (Jones & Kirby, 1984) offers the intriguing prospect of observing what happens in the early stages of suitable reactions. This paper reports the first of a series of crystal-structure determinations designed to apply this technique to a geometrically simple rearrangement reaction, the Beckmann rearrangement (review, Donaruma & Heldt, 1960).

The reaction involves the migration of the *E* substituent of a ketoxime derivative (1); no intermediate before the *N*-alkylnitrilium cation (2) has been detected, so the migration of the alkyl group is probably concerted with the departure of *X*O$^-$. The question of immediate interest is whether the extensive geometrical changes involved have proceeded to a measurable extent in suitable oxime derivatives, where *X*O$^-$ is the best leaving group consistent with a stable crystalline compound.

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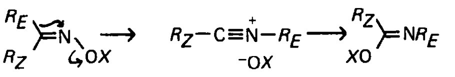
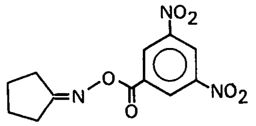


(1) (2)

We have prepared the oxime of cyclopentanone, and several derivatives. The oxime itself (m.p. 330 K) crystallizes as a cyclic, hydrogen-bonded trimer, but because of high thermal motion, and perhaps decomposition on irradiation, the structure could not be refined to $R < 0{\cdot}095$. The oxime tosylate could be crystallized with care, and the five-membered ring and *p*-toluenesulfonyl group located, but disorder in the region of the oxime group has so far prevented a satisfactory solution. Low-temperature structures are planned in both cases. The *O*-diphenylphosphoryl oxime rapidly decomposed, but the oxime 3,5-dinitrobenzoate [(3), m.p. 381–382 K] is stable. Pale-yellow single crystals of (3) in the form of thick plates were obtained by diffusion of light petroleum (b.p. 333–353 K) into a dichloromethane solution. Elemental analysis and NMR data suggested the presence of some residual petroleum component in the crystals, which were, however, air-stable.



(3)

Experimental. 9036 profile-fitted intensities (Clegg, 1981) measured on a Stoe–Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{\max}$ 55°, index ranges $|h| \leq 13$, $|k| \leq 14$, $|l| \leq 16$ for $-h \pm k \pm l$ and some $+h$ equivalents). No systematic variation in intensities of three check reflections. Crystal size 0·5 × 0·45 × 0·3 mm; no absorption correction. After Lp corrections, merging equivalents gave 6793 unique reflections ($R_{\rm int}$ 0·015), of which 4173 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*, Sheldrick, 1978). Cell constants refined from $\pm 2\theta$ values of 32 reflections in range 20–23°.

Random-start multisolution direct methods yielded an E map containing two almost complete molecules of (3), as expected; this model could not be refined, however. A tangent expansion was then performed in $P1$; four complete molecules emerged, allowing the identification of the centre of symmetry connecting two pairs. The original solution was thus shown to have been shifted by *ca* (0, –0·03, 0·10), and subtraction of this vector from all coordinates led to a refinable model in $P\bar{1}$. Isotropic refinement (on F) revealed the presence of a molecule of *n*-hexane lying across a centre of symmetry, and of alternative sites for the O atoms of the nitro group centred on N(3′). The latter were refined with half occupancy subject to the restraints that all N—O distances and both O···O distances be equal to within 0·001 and 0·005 Å respectively. After anisotropic refinement, a difference synthesis revealed all H atoms, including those of hexane. These were included in the refinement using a riding model [C—H 0·96 Å, H—C—H 109·5°, U(H) = $1{\cdot}2U_{\rm eq}$(C)]. Final R 0·063, wR 0·061; 429 parameters, max. Δ/σ 0·2 for the O···O separation, otherwise <0·1, max. and min. features of a final $\Delta\rho$ synthesis +0·25, –0·3 e Å^{-3}; weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}00025F^2$. Atomic scattering factors as incorporated in *SHELXTL*.

Discussion. Final atomic coordinates and derived parameters are given in Tables 1–4;* of the two oxime molecules in the asymmetric unit (I and II), atoms of the second are distinguished by a prime. Fig. 1 shows a thermal-ellipsoid plot of molecule (I). The independent oxime molecules differ significantly only in the cyclopentane ring conformations; the mean absolute torsion angles are 20 and 14° respectively. Apart from the centres C(3) and C(4) the molecule is planar.

The N—O bond [1·464 (3), 1·470 (4) Å] is clearly lengthened in the ester (*cf.* the mean value of 1·411 (22) Å for 20 oximes recorded in the Cambridge Structural Database, 1985), but this is not accompanied by significant shortening of C=N [1·272 (5), 1·263 (4) Å compared with 1·274 (8) Å]. Bond angles at the oxime centre generally differ significantly from 120°, primarily because of the absent second substituent on N: mean values for the 20 oximes are R_E—C—N 116·0, R_Z—C—N 125·3, C=N—OH 112·4° [sample standard deviation around 2°; see (1), X = H]. Thus each substituent is displaced from the trigonal position, in the direction expected for conversion to (2). In the oxime ester (3) both C—C—N angles are increased by 4–5° [119·3 (3), 119·8 (4) and 130·5 (3), 130·6 (3)°], reflecting the constraint of the five-membered ring, and the C—N—O angle [106·7 (3), 107·3 (3)°] is 5–6° smaller. Only with a set of accurate structures for a series of oxime derivatives will it be possible to attribute particular significance to these differences.

The *n*-hexane molecule is surprisingly well ordered; as far as we are aware, all other *n*-hexanes of solvation have exhibited either disorder or high thermal motion, or both. There are no unusually short contacts

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a figure showing the least-squares fit of the two independent molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42973 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2 HU, England.

Table 1. *Atom coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å² ×10³)

Equivalent isotropic *U* calculated from anisotropic *U*.

	x	*y*	*z*	U_{eq}
C(1)	3566 (2)	2124 (2)	1806 (2)	50 (1)
C(2)	2161 (2)	2024 (2)	2297 (2)	57 (1)
C(3)	1537 (3)	2223 (3)	1326 (2)	76 (1)
C(4)	2553 (3)	1965 (4)	425 (2)	94 (2)
C(5)	3804 (3)	2348 (3)	592 (2)	77 (1)
N(1)	4517 (2)	2021 (2)	2253 (1)	59 (1)
O(1)	3990 (1)	1793 (1)	3428 (1)	52 (1)
C(10)	4887 (3)	1707 (2)	4006 (2)	43 (1)
O(10)	6025 (2)	1805 (2)	3655 (1)	60 (1)
C(11)	4255 (2)	1454 (2)	5194 (2)	37 (1)
C(12)	5049 (2)	1253 (2)	5929 (2)	40 (1)
C(13)	4503 (2)	1014 (2)	7024 (2)	41 (1)
C(14)	3197 (2)	940 (2)	7433 (2)	42 (1)
C(15)	2436 (2)	1144 (2)	6689 (2)	38 (1)
C(16)	2928 (2)	1412 (2)	5571 (2)	39 (1)
N(3)	5354 (2)	852 (2)	7792 (2)	56 (1)
O(31)	6502 (2)	936 (2)	7418 (1)	76 (1)
O(32)	4857 (2)	642 (2)	8760 (1)	84 (1)
N(5)	1034 (2)	1103 (2)	7096 (2)	46 (1)
O(51)	381 (2)	1629 (2)	6471 (1)	63 (1)
O(52)	612 (2)	546 (2)	8047 (1)	63 (1)
C(1′)	2131 (3)	6399 (2)	1197 (2)	54 (1)
C(2′)	2343 (4)	6201 (3)	70 (2)	92 (2)
C(3′)	2035 (4)	7384 (3)	−613 (2)	98 (2)
C(4′)	2138 (4)	8333 (3)	−73 (2)	107 (2)
C(5′)	2027 (3)	7724 (2)	1122 (2)	65 (1)
N(1′)	2048 (2)	5487 (2)	2018 (1)	68 (1)
O(1′)	1860 (2)	5967 (1)	2984 (1)	53 (1)
C(10′)	1745 (2)	5071 (2)	3911 (2)	44 (1)
O(10′)	1756 (2)	3995 (1)	3989 (1)	64 (1)
C(11′)	1572 (2)	5604 (2)	4869 (2)	37 (1)
C(12′)	1434 (2)	4778 (2)	5888 (2)	41 (1)
C(13′)	1259 (2)	5221 (2)	6797 (2)	42 (1)
C(14′)	1197 (2)	6451 (2)	6742 (2)	43 (1)
C(15′)	1349 (2)	7248 (2)	5716 (2)	39 (1)
C(16′)	1545 (2)	6856 (2)	4780 (2)	38 (1)
N(3′)	1139 (2)	4338 (2)	7878 (2)	53 (1)
O(31′)	1149 (15)	3241 (7)	7927 (14)	73 (4)
O(32′)	819 (15)	4776 (24)	8656 (14)	73 (4)
O(31″)	1385 (14)	3270 (7)	7902 (11)	60 (3)
O(32″)	1040 (17)	4720 (25)	8682 (16)	83 (5)
N(5′)	1296 (2)	8576 (2)	5639 (1)	49 (1)
O(51′)	935 (2)	8881 (1)	6481 (1)	72 (1)
O(52′)	1640 (2)	9287 (1)	4739 (1)	68 (1)
C(31)	4929 (3)	5239 (3)	5488 (2)	73 (1)
C(32)	4777 (3)	4346 (3)	6559 (3)	89 (2)
C(33)	4615 (4)	4829 (4)	7545 (3)	108 (2)

Table 2. *Bond lengths* (Å)

C(1)–C(2)	1·491 (5)	C(1′)–C(2′)	1·511 (5)
C(1)–N(1)	1·272 (5)	C(1′)–N(1′)	1·263 (4)
C(3)–C(4)	1·490 (5)	C(3′)–C(4′)	1·450 (7)
N(1)–O(1)	1·464 (3)	N(1′)–O(1′)	1·470 (4)
C(10)–O(10)	1·199 (4)	C(10′)–O(10′)	1·192 (4)
C(11)–C(12)	1·392 (5)	C(11′)–C(12′)	1·388 (4)
C(12)–C(13)	1·373 (4)	C(12′)–C(13′)	1·377 (4)
C(13)–N(3)	1·475 (5)	C(13′)–N(3′)	1·477 (4)
C(15)–C(16)	1·388 (4)	C(15′)–C(16′)	1·376 (4)
C(1)–C(5)	1·499 (4)	C(1′)–C(5′)	1·475 (5)
C(2)–C(3)	1·526 (5)	C(2′)–C(3′)	1·467 (6)
C(4)–C(5)	1·505 (6)	C(4′)–C(5′)	1·508 (5)
C(10)–O(1)	1·337 (4)	C(10′)–O(1′)	1·340 (3)
C(10)–C(11)	1·498 (4)	C(10′)–C(11′)	1·498 (4)
C(11)–C(16)	1·392 (4)	C(11′)–C(16′)	1·387 (4)
C(13)–C(14)	1·376 (4)	C(13′)–C(14′)	1·372 (4)
C(14)–C(15)	1·374 (5)	C(14′)–C(15′)	1·379 (4)
C(15)–N(5)	1·472 (4)	C(15′)–N(5′)	1·476 (4)
N(3)–O(31)	1·212 (4)	N(3′)–O(31′)	1·224 (11)
		N(3′)–O(31″)	1·218 (10)
N(3)–O(32)	1·217 (4)	N(3′)–O(32′)	1·219 (24)
		N(3′)–O(32″)	1·218 (26)
N(5)–O(51)	1·214 (4)	N(5′)–O(51′)	1·212 (4)
N(5)–O(52)	1·222 (3)	N(5′)–O(52′)	1·219 (3)
C(31)–C(31*a*)	1·486 (8)		
C(31)–C(32)	1·470 (5)		
C(32)–C(33)	1·498 (7)		

Table 3. *Bond angles* (°)

C(2)–C(1)–C(5)	110·2 (3)	C(2′)–C(1′)–C(5′)	109·6 (3)
C(5)–C(1)–N(1)	119·3 (3)	C(5′)–C(1′)–N(1′)	130·6 (3)
C(2)–C(3)–C(4)	105·5 (4)	C(2′)–C(3′)–C(4′)	108·6 (4)
C(1)–C(5)–C(4)	103·2 (3)	C(1′)–C(5′)–C(4′)	104·9 (3)
N(1)–O(1)–C(10)	113·4 (3)	N(1′)–O(1′)–C(10′)	112·4 (3)
O(1)–C(10)–C(11)	109·4 (3)	O(1′)–C(10′)–C(11′)	110·4 (3)
C(10)–C(11)–C(12)	117·4 (3)	C(10′)–C(11′)–C(12′)	116·7 (3)
C(12)–C(11)–C(16)	120·1 (3)	C(12′)–C(11′)–C(16′)	119·8 (3)
C(12)–C(13)–C(14)	122·9 (3)	C(12′)–C(13′)–C(14′)	122·7 (3)
C(14)–C(13)–N(3)	118·7 (3)	C(14′)–C(13′)–N(3′)	118·4 (3)
C(14)–C(15)–C(16)	123·0 (3)	C(14′)–C(15′)–C(16′)	122·9 (3)
C(16)–C(15)–N(5)	118·5 (3)	C(16′)–C(15′)–N(5′)	119·6 (3)
C(2)–C(1)–N(1)	130·5 (3)	C(2′)–C(1′)–N(1′)	119·8 (4)
C(1)–C(2)–C(3)	104·5 (3)	C(1′)–C(2′)–C(3′)	104·3 (4)
C(3)–C(4)–C(5)	106·1 (4)	C(3′)–C(4′)–C(5′)	108·0 (4)
C(1)–N(1)–O(1)	106·7 (3)	C(1′)–N(1′)–O(1′)	107·3 (3)
O(1)–C(10)–O(10)	126·7 (3)	O(1′)–C(10′)–O(10′)	126·1 (3)
O(10)–C(10)–C(11)	124·0 (4)	O(10′)–C(10′)–C(11′)	123·5 (3)
C(10)–C(11)–C(16)	122·5 (3)	C(10′)–C(11′)–C(16′)	123·5 (3)
C(11)–C(12)–C(13)	119·0 (3)	C(11′)–C(12′)–C(13′)	119·0 (3)
C(12)–C(13)–N(3)	118·4 (3)	C(12′)–C(13′)–N(3′)	118·8 (3)
C(13)–C(14)–C(15)	116·9 (3)	C(13′)–C(14′)–C(15′)	116·8 (3)
C(14)–C(15)–N(5)	118·4 (3)	C(14′)–C(15′)–N(5′)	117·6 (3)
C(11)–C(16)–C(15)	118·1 (3)	C(11′)–C(16′)–C(15′)	118·8 (3)
C(15)–N(5)–O(51)	118·0 (3)	C(15′)–N(5′)–O(51′)	117·4 (3)
O(51)–N(5)–O(52)	124·7 (3)	O(51′)–N(5′)–O(52′)	124·6 (3)
C(15)–N(5)–O(52)	117·3 (3)	C(15′)–N(5′)–O(52′)	117·9 (3)
C(13)–N(3)–O(31)	117·9 (3)		
O(31)–N(3)–O(32)	124·3 (4)		
C(13)–N(3)–O(32)	117·8 (3)		
C(31)–C(32)–C(33)	118·0 (4)		
C(32)–C(31)–C(31*a*)	118·0 (4)		

Table 4. *Selected torsion angles* (°)

C(5)–C(1)–C(2)–C(3)	−1·2 (4)	C(5′)–C(1′)–C(2′)–C(3′)	−13·9 (5)
C(2)–C(1)–C(5)–C(4)	−18·0 (4)	C(2′)–C(1′)–C(5′)–C(4′)	1·8 (5)
C(2)–C(1)–N(1)–O(1)	−1·2 (5)	C(2′)–C(1′)–N(1′)–O(1′)	179·4 (4)
C(1)–C(2)–C(3)–C(4)	20·3 (4)	C(1′)–C(2′)–C(3′)–C(4′)	21·2 (5)
C(3)–C(4)–C(5)–C(1)	30·7 (4)	C(3′)–C(4′)–C(5′)–C(1′)	11·4 (5)
N(1)–O(1)–C(10)–O(10)	0·5 (4)	N(1′)–O(1′)–C(10′)–O(10′)	−1·7 (5)
O(1)–C(10)–C(11)–C(12)	175·8 (3)	O(1′)–C(10′)–C(11′)–C(12′)	179·7 (3)
O(10)–C(10)–C(11)–C(12)	−3·8 (4)	O(10′)–C(10′)–C(11′)–C(12′)	0·7 (5)
N(1)–C(1)–C(2)–C(3)	−179·3 (4)	N(1′)–C(1′)–C(2′)–C(3′)	164·9 (4)
N(1)–C(1)–C(5)–C(4)	160·3 (4)	N(1′)–C(1′)–C(5′)–C(4′)	−176·9 (4)
C(5)–C(1)–N(1)–O(1)	−179·2 (3)	C(5′)–C(1′)–N(1′)–O(1′)	−2·1 (5)
C(2)–C(3)–C(4)–C(5)	−32·2 (4)	C(2′)–C(3′)–C(4′)–C(5′)	−20·9 (5)
C(1)–N(1)–O(1)–C(10)	−177·8 (3)	C(1′)–N(1′)–O(1′)–C(10′)	179·4 (3)
N(1)–O(1)–C(10)–C(11)	−179·1 (3)	N(1′)–O(1′)–C(10′)–C(11′)	179·3 (3)
O(1)–C(10)–C(11)–C(16)	−4·0 (4)	O(1′)–C(10′)–C(11′)–C(16′)	−0·3 (4)
O(10)–C(10)–C(11)–C(16)	176·4 (3)	O(10′)–C(10′)–C(11′)–C(16′)	−179·3 (3)
C(31*a*)–C(31)–C(32)–C(33)	−179·1 (5)		

Sign convention as defined by Klyne & Prelog (1960).

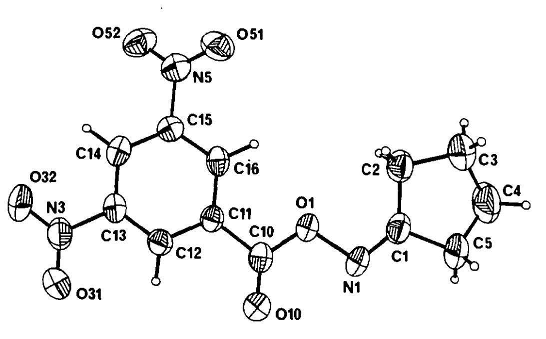

Fig. 1. Thermal-ellipsoid plot (50% probability level) of molecule (I), showing the atom-numbering scheme.

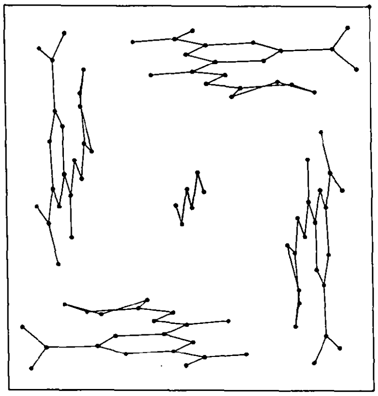

Fig. 2. The unit-cell contents (excluding H) projected down the z axis.

involving the solvent; the shortest are (to H) H(33*a*)···H(5*a*) 2·52 Å, (to O) H(32*a*)···O(31′′) 2·93 Å and (to C) H(31*b*)···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. $C_{10}H_{20}NO^+.C_7H_7O_3S^-.H_2O$, $M_r = 359{\cdot}47$, monoclinic, $P2_1/n$, $a = 10{\cdot}153\,(2)$, $b = 6{\cdot}444\,(1)$, $c = 30{\cdot}523\,(5)$ Å, $\beta = 96{\cdot}65\,(1)°$, $V = 1983{\cdot}5\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}203$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}55$ mm^{-1}, $F(000) = 776$, $T = 291$ K, $R = 0{\cdot}053$ 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 reactive, 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*).