Acta Cryst. (1986). C**42**, 1228–1230

Bond Length and Reactivity: The Beckmann Rearrangement. 3.* Structure of 4-Phenylcyclohexanone *O*-(2-Naphthalenesulfonyl)oxime at 233 K

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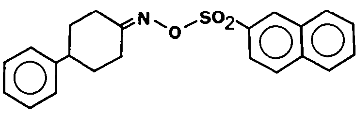
(*Received* 14 *November* 1985; *accepted* 15 *March* 1986)

Abstract. $C_{22}H_{21}NO_3S$, $M_r = 379{\cdot}48$, orthorhombic, $Pca2_1$, $a = 19{\cdot}297\,(5)$, $b = 6{\cdot}205\,(2)$, $c = 15{\cdot}666\,(5)$ Å, $V = 1876$ Å^3, $Z = 4$, $D_x = 1{\cdot}34$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2$ cm^{-1}, $F(000) = 800$, $T = 233$ K, $R = 0{\cdot}047$ for 3380 unique observed reflections. The molecule adopts a folded conformation, which brings the 4-phenylcyclohexyl and naphthalene systems together. The N—O bond is very long [1·502 (4) Å]. The difference between the two C—C—N angles is 16·3 (5)°, consistent with motion in the direction of the Beckmann rearrangement as the N—O bond stretches.

Introduction. In an attempt to establish bond length–reactivity correlations (Jones & Kirby, 1984) for oxime derivatives undergoing the Beckmann rearrangement, we have prepared compounds derived from several ketoximes. The N—O bond shows the expected lengthening in the 3,5-dinitrobenzoate ester of cyclopentanone oxime (Jones, Edwards & Kirby, 1986), but the structures of both the parent oxime and its *p*-toluenesulfonate ester were disordered, preventing detailed comparisons within the series. The most interesting derivatives are the most reactive, and thus the least stable, and we are looking at arenesulfonate esters as likely limiting members of each series. The *p*-toluenesulfonate of the oxime from 4-*tert*-butylcyclohexanone could be made, but underwent the Beckmann rearrangement when we attempted to grow single crystals at 273 K (Edwards *et al.*, 1986). We have now prepared, and grown, crystals of the *β*-naphthalenesulfonate ester (1) of the oxime derived from 4-phenylcyclohexanone, and report its crystal and molecular structure at 233 K.



(1)

Experimental. The oxime, prepared in the usual way from the commercially available ketone, was esterified using 2-naphthalenesulfonyl chloride in cold water–acetone–KOH. The crude powder produced was dried over P_2O_5; single crystals in the form of colourless prisms were grown by the diffusion of dry petroleum ether into a solution in dichloromethane. The crude powder and the crystals had identical IR and NMR spectra, and decomposed on heating above 365 K.

5551 profile-fitted intensities (Clegg, 1981) measured on a Stoe–Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{max}$ 55°, index ranges $|h| < 25$, $|k| < 8$, $|l| < 20$ for $+h+k+l$, $-h-k-l$ and some $-h+k+l$ equivalents). Three check reflections; no systematic intensity variation. Crystal size 0·7 × 0·5 ×

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

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

	x	*y*	*z*	U_{eq}
S	4875 (1)	8587 (1)	5000	47 (1)
O(1)	5200 (1)	7364 (3)	5807 (1)	52 (1)
O(2)	5247 (1)	7667 (4)	4316 (1)	68 (1)
O(3)	4879 (1)	10849 (3)	5132 (1)	58 (1)
C(1)	3509 (1)	8899 (4)	5352 (1)	38 (1)
C(2)	4015 (1)	7652 (4)	5002 (2)	36 (1)
C(3)	3869 (1)	5586 (4)	4666 (2)	44 (1)
C(4)	3205 (1)	4856 (4)	4680 (1)	43 (1)
C(4a)	2663 (1)	6096 (3)	5041 (2)	35 (1)
C(5)	1964 (1)	5373 (4)	5060 (2)	45 (1)
C(6)	1457 (1)	6622 (5)	5387 (2)	52 (1)
C(7)	1612 (1)	8650 (5)	5740 (2)	53 (1)
C(8)	2279 (1)	9416 (4)	5740 (2)	46 (1)
C(8a)	2819 (1)	8157 (4)	5381 (1)	34 (1)
N	4894 (1)	8233 (4)	6619 (1)	51 (1)
C(11)	4705 (1)	6670 (4)	7084 (2)	46 (1)
C(12)	4700 (1)	4290 (4)	6909 (2)	54 (1)
C(13)	3951 (1)	3463 (4)	6950 (2)	43 (1)
C(14)	3581 (1)	4105 (4)	7776 (1)	37 (1)
C(15)	3622 (1)	6532 (4)	7906 (2)	43 (1)
C(16)	4371 (1)	7339 (4)	7913 (2)	50 (1)
C(21)	2852 (1)	3213 (4)	7794 (1)	36 (1)
C(22)	2301 (1)	4224 (4)	7377 (1)	45 (1)
C(23)	1645 (1)	3331 (5)	7378 (2)	53 (1)
C(24)	1520 (1)	1389 (5)	7780 (2)	51 (1)
C(25)	2055 (1)	352 (4)	8181 (2)	49 (1)
C(26)	2712 (1)	1273 (4)	8199 (1)	41 (1)

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* Part 2: Edwards, Holden, Kirby & Raithby (1986).

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0·25 mm; no absorption correction. After Lp corrections, merging equivalents gave 4281 unique reflections (R_{int} 0·0212), of which 3380 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*, Sheldrick, 1978). Cell constants refined from $\pm 2\theta$ values of 80 reflections in range 20–23°.

Routine multisolution direct methods yielded a recognizable fragment of 21 atoms; remaining six non-H atoms located in a subsequent difference synthesis. Refinement on *F* proceeded to *R* 0·047, *wR* 0·044 [H atoms included using riding model with C—H 0·96 Å, H—C—H 109·5°, $U(\text{H}) = 1·2\,U_{\text{eq}}(\text{C})$; weighting scheme $w^{-1} = \sigma^2(F) + 0·00025F^2$; 243 parameters; $S = 1·4$; max. Δ/σ 0·4, max. and min. features in final $\Delta\rho$ synthesis +0·5 (near S), −0·4 e Å^{-3}]. Atomic scattering factors from *SHELXTL*. The absolute structure (Jones, 1984, 1986) was established with an η refinement (Rogers, 1981); η −0·93 (16), whereupon structure inverted for the final cycles. Final atomic coordinates are given in Table 1, and derived parameters in Table 2.*

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

O(1)—S	1·603 (3)	O(2)—S	1·411 (3)
O(3)—S	1·419 (3)	C(1)—C(2)	1·361 (4)
C(1)—C(8a)	1·411 (4)	C(2)—S	1·758 (3)
C(2)—C(3)	1·414 (4)	C(3)—C(4)	1·358 (5)
C(4)—C(4a)	1·418 (4)	C(4a)—C(5)	1·422 (4)
C(4a)—C(8a)	1·417 (4)	C(5)—C(6)	1·349 (5)
C(6)—C(7)	1·407 (5)	C(7)—C(8)	1·372 (4)
C(8)—C(8a)	1·418 (4)	N—O(1)	1·502 (4)
C(11)—N	1·268 (5)	C(11)—C(12)	1·502 (5)
C(11)—C(16)	1·509 (5)	C(12)—C(13)	1·534 (4)
C(13)—C(14)	1·531 (4)	C(14)—C(15)	1·522 (4)
C(14)—C(21)	1·511 (4)	C(15)—C(16)	1·529 (5)
C(21)—C(22)	1·397 (4)	C(21)—C(26)	1·387 (4)
C(22)—C(23)	1·383 (5)	C(23)—C(24)	1·381 (5)
C(24)—C(25)	1·370 (5)	C(25)—C(26)	1·391 (5)

O(1)—S—O(2)	102·0 (2)	O(1)—S—O(3)	110·6 (2)
O(2)—S—O(3)	120·5 (2)	O(1)—S—C(2)	102·2 (2)
O(2)—S—C(2)	110·4 (2)	O(3)—S—C(2)	109·4 (2)
S—O(1)—N	110·1 (2)	C(2)—C(1)—C(8a)	120·3 (3)
S—C(2)—C(1)	119·3 (3)	S—C(2)—C(3)	119·1 (3)
C(1)—C(2)—C(3)	121·5 (3)	C(2)—C(3)—C(4)	118·9 (3)
C(3)—C(4)—C(4a)	121·4 (3)	C(4)—C(4a)—C(5)	122·5 (3)
C(4)—C(4a)—C(8a)	118·9 (3)	C(5)—C(4a)—C(8a)	118·6 (3)
C(4a)—C(5)—C(6)	120·9 (3)	C(5)—C(6)—C(7)	120·6 (3)
C(6)—C(7)—C(8)	120·6 (3)	C(7)—C(8)—C(8a)	119·9 (3)
C(1)—C(8a)—C(4a)	118·9 (3)	C(1)—C(8a)—C(8)	121·8 (3)
C(4a)—C(8a)—C(8)	119·3 (3)	O(1)—N—C(11)	109·0 (3)
N—C(11)—C(12)	130·4 (4)	N—C(11)—C(16)	114·1 (3)
C(12)—C(11)—C(16)	115·2 (3)	C(11)—C(12)—C(13)	109·1 (3)
C(12)—C(13)—C(14)	112·9 (3)	C(13)—C(14)—C(15)	110·3 (3)
C(13)—C(14)—C(21)	110·8 (3)	C(15)—C(14)—C(21)	114·1 (3)
C(14)—C(15)—C(16)	112·0 (3)	C(11)—C(16)—C(15)	107·9 (3)
C(14)—C(21)—C(22)	122·3 (3)	C(14)—C(21)—C(26)	120·5 (3)
C(22)—C(21)—C(26)	117·1 (3)	C(21)—C(22)—C(23)	121·1 (3)
C(22)—C(23)—C(24)	120·7 (4)	C(23)—C(24)—C(25)	119·1 (4)
C(24)—C(25)—C(26)	120·2 (3)	C(21)—C(26)—C(25)	121·7 (3)

O(2)—S—O(1)—N	176·6 (3)	O(3)—S—O(1)—N	47·2 (3)
C(2)—S—O(1)—N	−69·2 (3)	O(1)—S—C(2)—C(1)	98·7 (3)
O(1)—S—C(2)—C(3)	−79·2 (3)	O(2)—S—C(2)—C(1)	−153·4 (3)
O(2)—S—C(2)—C(3)	28·8 (3)	O(3)—S—C(2)—C(1)	−18·6 (3)
O(3)—S—C(2)—C(3)	163·6 (3)	S—O(1)—N—C(11)	131·8 (3)
C(8a)—C(1)—C(2)—S	−178·3 (3)	S—C(2)—C(3)—C(4)	179·0 (3)
O(1)—N—C(11)—C(12)	−5·0 (4)	O(1)—N—C(11)—C(16)	−178·5 (3)
N—C(11)—C(12)—C(13)	−118·1 (4)	C(16)—C(11)—C(12)—C(13)	55·4 (4)
N—C(11)—C(16)—C(15)	116·9 (3)	C(12)—C(11)—C(16)—C(15)	−57·7 (4)
C(11)—C(12)—C(13)—C(14)	−52·1 (4)	C(12)—C(13)—C(14)—C(15)	53·9 (4)
C(12)—C(13)—C(14)—C(21)	−178·7 (3)	C(13)—C(14)—C(15)—C(16)	−56·5 (4)
C(21)—C(14)—C(15)—C(16)	178·0 (3)	C(13)—C(14)—C(21)—C(22)	−81·8 (4)
C(13)—C(14)—C(21)—C(26)	95·1 (4)	C(15)—C(14)—C(21)—C(22)	43·4 (4)
C(15)—C(14)—C(21)—C(26)	−139·7 (3)	C(14)—C(15)—C(16)—C(11)	57·0 (4)
C(14)—C(21)—C(22)—C(23)	177·7 (3)	C(14)—C(21)—C(26)—C(25)	−176·1 (3)

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

Discussion. A thermal-ellipsoid plot of (1) is shown in Fig. 1. The oxime ester crystallized in a folded conformation, which brings the 4-phenylcyclohexyl and naphthalene systems together, though the aromatic rings are not parallel. This is possible because the torsion angle S—O(1)—N—C(11) is 131·8 (3)°, though in all other oxime derivatives we have found in the literature this system is planar (180 ± 3°). Evidently the electronic preference for planarity is overridden by packing factors, and no doubt also reduced by electron withdrawal from the sulfonate group. The angle at O [S—O(1)—N 110·1 (2)°] is far from the trigonal angle, but this is normal for oximes and their derivatives (Gieren & Dederer, 1977).

The second notable feature of the structure is the very long N—O bond, 1·502 (4) Å, compared with a mean value of 1·400 (16) Å for the 23 most accurate structures ($R < 0·049$) found in the Cambridge Structural Database (1985) for oxime derivatives (see also Jones *et al.*, 1986). The C=N bond is also relatively short at 1·268 (5) Å compared with 1·282 (14) Å, but the difference may not be significant. As far as changes in the direction expected for the Beckmann rearrangement are concerned, there is no significant difference in the lengths of the C—C bonds *syn* and *anti* to the sulfonate group [C(11)—C(12) 1·502 (5), C(11)—C(16) 1·509 (5) Å], but the NCC angles at C(11) are interesting. The angle N—C(11)—C(16) to the *anti* group, which will migrate, is low [114·1 (3)°] and the angle N—C(11)—C(12) to the *syn* group, which will increase to 180°, is 130·4 (5)°. The *difference* between these two angles, of 16·3 (5)°, is larger than in any aliphatic ketoxime derivative so far measured, though a few compounds with more or less severe 1,3-in-plane non-bonded interactions between the N—O bond and a substituent at the *syn*-α-C have similar, or slightly longer, differences (though none with $R < 0·07$).

These parameters may be significant for the reaction pathway in the present system, but only careful comparison of a series of related structures will allow us

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42975 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

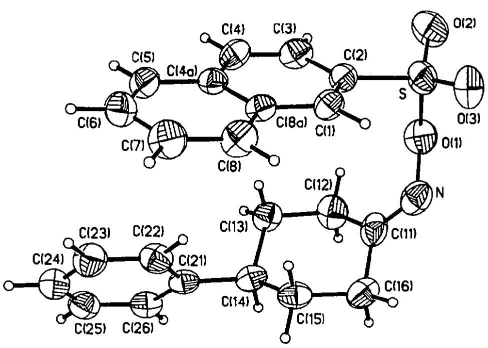

Fig. 1. Thermal-ellipsoid plot (50% level) of (1), showing the atom-numbering scheme.

to make a considered judgement. We hope to report structures of further derivatives of 4-phenylcyclohexanone oxime shortly.

The shortest intramolecular contact between non-H atoms is C(26)···C(15)(*x*, −1+*y*, *z*) 3·46 (1) Å.

PGJ thanks the Cambridge Philosophical Society and the Verband der Chemischen Industrie for financial support.

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Acta Cryst. (1986). C**42**, 1230–1232

Bond Length and Reactivity: The Beckmann Rearrangement. 4.* Structure of 4-Phenylcyclohexanone Oxime *O*-Triphenylmethyl Ether at 233 K

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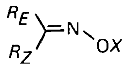
(*Received* 14 *November* 1985; *accepted* 13 *March* 1986)

Abstract. $C_{31}H_{29}NO$, $M_r = 431{\cdot}58$, monoclinic, $P2_1/n$, $a = 9{\cdot}654\ (3)$, $b = 23{\cdot}949\ (8)$, $c = 10{\cdot}930\ (3)$ Å, $\beta = 109{\cdot}94\ (3)°$, $V = 2375{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}21$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}7$ cm^{-1}, $F(000) = 920$, $T = 233$ K, $R = 0{\cdot}056$ for 3615 unique observed reflections. The phenyl group is equatorial to the cyclohexylidene chair and the oxime group is close to planar [the torsion angle about the N—O bond is −176·3 (2)°]. The N—O bond length [1·429 (3) Å] is used as the 'anchor point' in discussing this series of compounds.

Introduction. In our attempt to establish bond length–reactivity correlations (Jones & Kirby, 1984) for oxime derivatives undergoing the Beckmann rearrangement (Jones *et al.*, 1986*a*,*b*), we have prepared derivatives of a number of ketoximes (1). The questions of interest involve possible changes in the oxime group, particularly differences in behaviour between the potential migrating group (R_E) and the *syn* group (R_Z) which remains at the migration origin, as the effective electronegativity of the 'leaving group', O*X*, is varied. We have therefore used only symmetrical ketoximes (R_E=R_Z), and need the widest possible range of leaving group O*X*.



(1)

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[*] Part 3: Jones, Edwards & Kirby (1986*b*).

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