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Bond Length and Reactivity: The Beckmann Rearrangement. 5. Structure of 4-Phenylcyclohexanone Oxime *O*-4-Nitrobenzoate Ester at 290 K

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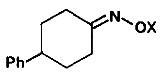
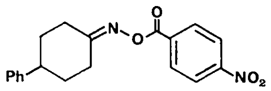
Abstract. $C_{19}H_{18}N_2O_4$, $M_r = 338{\cdot}35$, orthorhombic, $Pbc2_1$ (non-standard $Pca2_1$, No. 29), $a = 5{\cdot}652$ (2), $b = 12{\cdot}584$ (4), $c = 47{\cdot}625$ (18) Å, $V = 3387$ (2) Å^3, $Z = 8$, $D_x = 1{\cdot}327$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}69$ mm^{-1}, $F(000) = 1424$, $T = 290$ K, $R = 0{\cdot}042$ for 3438 reflections. The asymmetric unit contains two independent but structurally similar molecules. The 4-phenyl ring is equatorial on the cyclohexylidene system, and the oxime group is approximately planar, although both carboxylic ester and nitro groups are rotated out of the plane of the benzoate ring.

Introduction. We are looking for correlations between bond length and reactivity (Jones & Kirby, 1984) in ketoxime derivatives known to undergo the Beckmann rearrangement. Data in the literature refer to a random collection of structures, and are too few and too disparate to be a useful source of the kind of trends in which we are interested. So we have set out to apply our 'variable oxygen probe' technique (Jones & Kirby, 1984), measuring structures of a homogeneous series of compounds with varying effective electronegativities of the 'leaving group' oxygen.

After failing to produce suitable crystals in several series, particularly of the most reactive – and therefore the most interesting – oxime arenesulfonate esters, we recently reported structures for two derivatives (1) of 4-phenylcyclohexanone oxime, the 2-naphthalenesulfonate ester (1, X = 2-naphthalenesulfonyl; Jones, Edwards & Kirby, 1986*a*), and the trityl ether (1, X = triphenylmethyl; Jones, Edwards & Kirby, 1986*b*), which have very good ($XO^- = ArSO_3^-$) and very poor (triphenylmethoxide) leaving groups, respectively. The oxime groups of the two compounds show significant differences in geometry. In particular, the N—O bond is very long [1·502 (4) Å] in the sulfonate ester compared with the ether [1·429 (3) Å] – or indeed with any other oxime or derivative for which accurate data are available. We report here the crystal structure of a third derivative in this series, the 4-nitrobenzoate ester (2) of the oxime, which has a leaving group (XO^- = *p*-nitrobenzoate) of intermediate basicity.



(1)



(2)

Experimental. The oxime was acylated using 4-nitrobenzoyl chloride in methylene chloride with pyridine as base. Crystals were grown by diffusing pentane into a solution in methylene chloride. After initial difficulties, a suitable, block-shaped, transparent single crystal was obtained, and was mounted in a 0·5 mm Lindemann capillary in the presence of mother liquor.

Crystal 0·43 × 0·35 × 0·28 mm, Syntex $P2_1$ diffractometer with 200 Å diffracted beam chamber attachment; unit-cell parameters refined from diffractometer angles of 15 centred reflections ($40 < 2\theta < 50°$); 4566

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reflections with $3 < 2\theta < 100°$ (*hkl* range: *h* 0–5, *k* 0–11, *l* −42–42); profile analysis; no significant variations for two standard reflections; no absorption correction applied. 3511 unique reflections ($R_{\text{int}} = 0{\cdot}007$), 3438 with $F > 4\sigma(F)$. Structure solved by random-start multisolution direct methods, blocked full-matrix refinement on *F*, anisotropic thermal parameters for all non-H atoms; H atoms fixed to C with C—H 1·08 Å, and allowed to ride on the relevant C atom; each type of H within each molecule assigned a common isotropic temperature factor; scattering factors from *International Tables for X-ray Crystallography* (1974); 455 parameters, $R = 0{\cdot}042$, $wR = 0{\cdot}048$, $w = 0{\cdot}698/[\sigma^2(F_o) + 0{\cdot}0005F_o^2]$, mean $\Delta/\sigma = 0{\cdot}05$, max. = 0·17, largest peak in final difference map = 0·02, largest hole = −0·27 e Å^{-3}; programs *SHELX76* (Sheldrick, 1976), *SHELX86* (Sheldrick, 1986).

Because of the high reactivity of oxime arenesulfonate esters (Edwards, Holden, Kirby & Raithby, 1986) data on the two previous compounds in the series were collected at 233 K. However, the long *c*-axis length in the title compound necessitated the use of a diffractometer with a 200 Å diffracted beam chamber and no low-temperature apparatus was available on this instrument.

Discussion. Final atom coordinates and equivalent isotropic temperature factors are listed in Table 1, and derived parameters in Table 2.* Thermal ellipsoid plots of the two independent molecules of (2), showing the atom-numbering scheme, are shown in Fig. 1. The asymmetric unit contains the two independent

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3) *for* (2)

	x	*y*	*z*	*U**
O(1)	−7215 (5)	7487 (2)	2072	116 (20)
O(2)	−7511 (4)	8991 (2)	1857 (1)	94 (16)
N(1)	−6606 (5)	8112 (2)	1894 (1)	77 (18)
C(1)	−4618 (5)	7788 (2)	1712 (1)	60 (16)
C(2)	−3891 (6)	6741 (2)	1709 (1)	72 (16)
C(3)	−2064 (6)	6449 (2)	1533 (1)	69 (18)
C(4)	−944 (4)	7220 (2)	1366 (1)	52 (15)
C(5)	−1717 (5)	8276 (2)	1382 (1)	58 (17)
C(6)	−3555 (5)	8562 (2)	1551 (1)	61 (17)
C(7)	988 (5)	6878 (2)	1179 (1)	59 (17)
O(3)	1591 (5)	5989 (2)	1135 (1)	93 (17)
O(4)	1961 (3)	7740 (1)	1057 (1)	61 (11)
N(2)	3945 (4)	7527 (2)	867 (1)	65 (13)
C(8)	4744 (5)	8409 (2)	782 (1)	56 (16)
C(9)	3844 (5)	9502 (2)	847 (1)	62 (17)
C(10)	3751 (5)	10188 (2)	580 (1)	62 (16)
C(11)	6144 (5)	10211 (2)	432 (1)	60 (15)
C(12)	6793 (5)	9085 (2)	345 (1)	73 (19)
C(13)	6900 (5)	8341 (2)	597 (1)	74 (18)
C(14)	6253 (5)	10970 (2)	183 (1)	59 (16)
C(15)	4526 (6)	11024 (2)	−18 (1)	76 (19)
C(16)	4708 (7)	11718 (2)	−245 (1)	84 (21)
C(17)	6619 (7)	12373 (2)	−268 (1)	80 (22)
C(18)	8347 (6)	12343 (3)	−67 (1)	85 (22)
C(19)	8149 (5)	11657 (2)	160 (1)	74 (20)
O(5)	12173 (5)	5171 (2)	2061 (1)	119 (22)
O(6)	12525 (4)	3677 (2)	2281 (1)	97 (18)
N(3)	11635 (5)	4539 (3)	2244 (1)	77 (19)
C(20)	9607 (5)	4846 (2)	2429 (1)	61 (18)
C(21)	8840 (6)	5889 (2)	2429 (1)	72 (20)
C(22)	7015 (5)	6162 (2)	2608 (1)	66 (18)
C(23)	5958 (5)	5388 (2)	2773 (1)	53 (15)
C(24)	6748 (5)	4348 (2)	2760 (1)	61 (18)
C(25)	8596 (5)	4064 (2)	2589 (1)	61 (16)
C(26)	3993 (5)	5715 (2)	2966 (1)	57 (17)
O(7)	3393 (4)	6607 (2)	3009 (1)	90 (16)
O(8)	3040 (3)	4846 (1)	3081 (1)	65 (11)
N(4)	1086 (4)	5037 (2)	3271 (1)	63 (13)
C(27)	286 (5)	4135 (2)	3351 (1)	55 (15)
C(28)	−1849 (5)	4159 (2)	3539 (1)	71 (18)
C(29)	−1542 (5)	3436 (2)	3796 (1)	63 (16)
C(30)	−762 (5)	2323 (2)	3713 (1)	58 (15)
C(31)	1493 (5)	2383 (2)	3542 (1)	67 (17)
C(32)	1196 (6)	3056 (2)	3278 (1)	66 (17)
C(33)	−596 (5)	1588 (2)	3964 (1)	58 (15)
C(34)	−2409 (5)	854 (2)	4017 (1)	68 (18)
C(35)	−2302 (6)	176 (3)	4246 (1)	78 (21)
C(36)	−392 (7)	212 (2)	4420 (1)	81 (22)
C(37)	1395 (7)	934 (3)	4380 (1)	82 (23)
C(38)	1272 (6)	1617 (2)	4150 (1)	76 (21)

* Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} matrix.

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

C(7)—C(4)	1·473 (4)	C(26)—C(23)	1·500 (4)
O(3)—C(7)	1·189 (3)	O(7)—C(26)	1·191 (3)
O(4)—C(7)	1·348 (3)	O(8)—C(26)	1·337 (3)
N(2)—O(4)	1·464 (3)	N(4)—O(8)	1·447 (3)
C(8)—N(2)	1·265 (3)	C(27)—N(4)	1·278 (3)
C(8)—C(13)	1·505 (4)	C(28)—C(27)	1·506 (4)
C(10)—C(9)	1·536 (4)	C(32)—C(27)	1·493 (4)
C(11)—C(10)	1·525 (4)	C(29)—C(28)	1·535 (4)
C(12)—C(11)	1·522 (4)	C(29)—C(30)	1·520 (3)
C(14)—C(11)	1·523 (4)	C(33)—C(30)	1·517 (4)
C(13)—C(12)	1·523 (4)	C(30)—C(31)	1·513 (4)
C(9)—C(8)	1·498 (3)	C(32)—C(31)	1·526 (4)
O(3)—C(7)—C(4)	126·5 (3)	O(7)—C(26)—C(23)	125·2 (3)
O(4)—C(7)—C(4)	109·1 (2)	O(8)—C(26)—C(23)	109·0 (2)
O(4)—C(7)—O(3)	124·3 (3)	O(8)—C(26)—O(7)	125·8 (3)
N(2)—O(4)—C(7)	115·5 (2)	N(4)—O(8)—C(26)	115·4 (2)
C(8)—N(2)—O(4)	108·2 (4)	C(27)—N(4)—O(8)	107·9 (2)
C(9)—C(8)—N(2)	128·1 (2)	C(28)—C(27)—N(4)	116·3 (2)
C(13)—C(8)—N(2)	115·3 (2)	C(32)—C(27)—N(4)	128·1 (2)
C(13)—C(8)—C(9)	116·6 (2)	C(32)—C(27)—C(28)	115·6 (2)
C(10)—C(9)—C(8)	110·9 (2)	C(29)—C(28)—C(27)	111·9 (2)
C(11)—C(10)—C(9)	112·2 (2)	C(30)—C(29)—C(28)	111·7 (2)
C(12)—C(11)—C(10)	108·8 (2)	C(31)—C(30)—C(29)	109·8 (2)
C(14)—C(11)—C(10)	114·1 (2)	C(33)—C(30)—C(29)	111·9 (2)
C(14)—C(11)—C(12)	111·2 (2)	C(33)—C(30)—C(31)	113·7 (2)
C(13)—C(12)—C(11)	111·5 (2)	C(32)—C(31)—C(30)	112·1 (2)
C(12)—C(13)—C(8)	113·2 (2)	C(31)—C(32)—C(27)	110·7 (2)
C(7)—O(4)—N(2)—C(8)	−176·6 (3)	C(26)—O(8)—N(4)—C(27)	176·3 (3)
O(4)—N(2)—C(8)—C(9)	−2·1 (2)	O(8)—N(4)—C(27)—C(28)	−177·1 (2)
O(4)—N(2)—C(8)—C(13)	176·4 (3)	O(8)—N(4)—C(27)—C(32)	2·5 (2)
N(2)—C(8)—C(9)—C(10)	−135·8 (3)	N(4)—C(27)—C(28)—C(29)	−132·0 (3)
C(13)—C(8)—C(9)—C(10)	45·7 (3)	C(32)—C(27)—C(28)—C(29)	48·3 (3)
N(2)—C(8)—C(13)—C(12)	137·2 (2)	N(4)—C(27)—C(32)—C(31)	130·7 (3)
C(9)—C(8)—C(13)—C(12)	−44·1 (2)	C(28)—C(27)—C(32)—C(31)	−49·7 (3)
C(8)—C(9)—C(10)—C(11)	−54·3 (3)	C(27)—C(28)—C(29)—C(30)	−50·7 (3)
C(9)—C(10)—C(11)—C(12)	61·3 (3)	C(28)—C(29)—C(30)—C(31)	56·1 (3)
C(9)—C(10)—C(11)—C(14)	−173·9 (2)	C(28)—C(29)—C(30)—C(33)	−176·6 (3)
C(10)—C(11)—C(12)—C(13)	−58·6 (3)	C(29)—C(30)—C(31)—C(32)	−58·6 (2)
C(14)—C(11)—C(12)—C(13)	175·0 (3)	C(33)—C(30)—C(31)—C(32)	175·2 (3)
C(10)—C(11)—C(14)—C(15)	−46·1 (3)	C(29)—C(30)—C(33)—C(34)	101·7 (3)
C(10)—C(11)—C(14)—C(19)	132·5 (3)	C(29)—C(30)—C(33)—C(38)	−77·3 (3)
C(12)—C(11)—C(14)—C(15)	77·4 (2)	C(31)—C(30)—C(33)—C(34)	−133·2 (3)
C(12)—C(11)—C(14)—C(19)	−104·1 (3)	C(31)—C(30)—C(33)—C(38)	47·9 (2)
C(11)—C(12)—C(13)—C(8)	49·8 (2)	C(30)—C(31)—C(32)—C(27)	54·6 (3)

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

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* Lists of H-atom coordinates and U_{iso} values, geometry parameters for the phenyl and nitrophenyl groups, structure factors, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43377 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecules in similar extended conformations, approximately as depicted in (2). The 4-phenyl ring is equatorial on the cyclohexylidene system, as expected, and the oxime group is close to planar in both molecules. The carboxylic ester and nitro groups are rotated out of the plane of the benzoate ring, by 6–7 and 13–15°, respectively.

The biggest difference between the two molecules is the length of the N—O bond, which is 1·464 (3) Å in molecule 1, 1·447 (3) Å in molecule 2, a difference of more than five standard deviations. It is possible that this discrepancy is not significant; in view of the very long *c* axis [47·625 (18) Å] somewhat larger e.s.d.'s (0·005 Å) in these lengths might be more realistic. But the longer N—O bond is associated with a shorter C=N distance [1·265 (3) compared with 1·278 (3) Å in molecule 2]; and other bond lengths (and angles) do not differ significantly. Torsion angles also are similar in detail, apart from a small increase in the puckering of the cyclohexylidene ring at the oxime C atom (C—C—C=N torsion angles 130·7, −132·0° in molecule 2 compared with −135·8, 137·2° in molecule 1). It is not obvious how this could cause the bond-length differences in the oxime group. The torsion angle itself is presumably a manifestation of packing forces: in the 2-naphthalenesulfonate ester of (1), where the ester group is folded back over the cyclohexylidene ring, these dihedral angles are below 120° (−118·1, 116·9°, Jones *et al.*, 1986*a*).

As expected, the N—O bond length in both molecules lies between the values (1·429, 1·502 Å) previously determined for the less reactive ether and more reactive sulfonate ester derivatives of (1) (Jones *et al.*, 1986*a*,*b*). But the bond-length–reactivity correlation obviously cannot be linear for both values, and it is in fact linear for neither (the better correlation, using data for molecule 1, has a correlation coefficient *r* of 0·953). This is because neither N—O bond is as long as predicted on the basis of a two-point plot for N—O bond lengths previously available *vs* the pK_a of XOH. This most probably reflects the unique conformation of (1, X = 2-naphthalenesulfonyl), where the O—S bond is twisted out of the plane of the oxime group by almost 50°, whereas the oxime—O—C bonds of (1, X = CPh_3) and of (2), like those of all other oxime derivatives for which structures are available, are in the C=N—O plane.

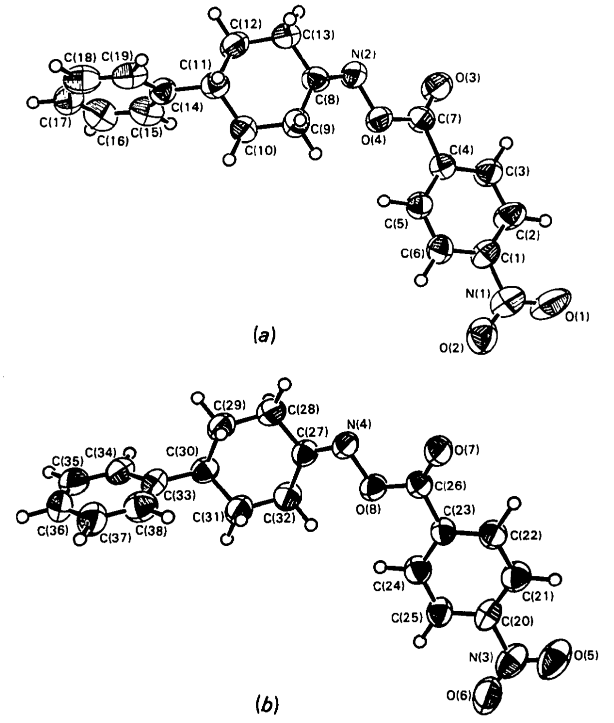


Fig. 1. The molecular geometries of the two independent molecules of (2): (*a*) molecule 1, (*b*) molecule 2. Thermal motion is depicted as 50% probability ellipsoids.

Table 3. *Geometry of the oxime group*

		(1a)[a]	(2)[b] Molecule 1	(2)[b] Molecule 2	(1b)[c]
Bond lengths (Å)					
(*anti*)	C–CN	1·507	1·505	1·506	1·509
(*syn*)	C–CN	1·497	1·498	1·493	1·507
	C=N	1·276	1·265	1·278	1·268
	N–O	1·429	1·464	1·447	1·502
Bond angles (°)					
(*anti*)	C–C–N	116·4	115·3	116·3	114·1
(*syn*)	C–C–N	127·4	128·1	128·1	130·4
	C–N–O	110·3	108·2	107·9	109·0

Notes: (*a*) $X = CPh_3$ (Jones *et al.*, 1986*b*), (*b*) this paper, (*c*) X = 2-naphthalenesulfonyl (Jones *et al.*, 1986*a*).

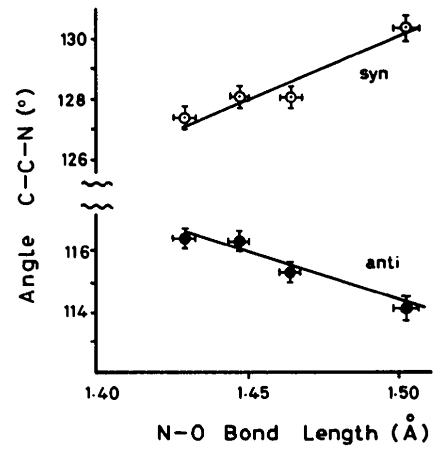
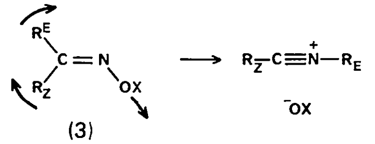


Fig. 2. Bond-angle changes at the migration origin in the molecules listed in Table 3, as a function of the N—O bond length.

In these circumstances it is more useful to use the structure-correlation approach pioneered by Bürgi & Dunitz (1983). We use the N—O bond length as the reference parameter, and look for trends in the geometrical changes in the oxime group associated with the lengthening of the N—O bond. The data, summarized in Table 3, show that there are no significant trends in bond lengths C—C or C=N, or in bond angles C—N—O. But small changes are apparent in the bond angles at the oxime C centre, where very large changes of angle must take place during reaction. These changes are summarized in formula (3), and plotted in Fig. 2, which shows that as the N—O*X* bond lengthens, as a result of increasing electron-withdrawal in the group *X*, the *syn* substituted (R_Z) moves closer to linearity. The *anti* substituent moves in the same (clockwise) sense, also without change in the C—C bond length, with the result that the C atom of the group which will migrate in the Beckmann rearrangement (R_E) is brought closer to the migration terminus. [The N—C_E distance falls, as N—O lengthens, from 2·368 Å in the oxime ether to 2·334 Å in the 2-naphthalenesulfonate (1). In molecules 1 and 2 of (2) it is 2·344 (5) and 2·368 (5) Å.] The angle C—N—O is not expected to change significantly as the leaving group (XO$^-$) departs, as it is already close [mean value 108·9 (1·1)° for the four molecules] to the Bürgi–Dunitz angle for addition of a nucleophile to a π system.



(3)

Thus as the O atom is made more electronegative in ketoximine derivatives (1→3), the N—O bond lengthens substantially, but further changes, primarily in the bond angles at the potential migration origin, are relatively minor. The trends can be interpreted in terms of progress along the reaction coordinate for the Beckmann rearrangement, but the effects on bond lengths in particular suggest that the positive charge induced by increasing polarization of the N—O*X* bond in the sense N$^+$ $^-$O*X*, is largely localized on nitrogen. More substantial progress in the direction of reaction, which might reveal more details of the intriguing and extensive geometrical changes which must occur on rearrangement, is probably not to be expected from the study of ground-state structures, at least in this system.

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Structure of (8*S*)-8-Hydroxymethyl-6,9-diazaspiro[4.5]decane-7,10-dione, a Spirocyclic Dipeptide

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Abstract. $C_9H_{14}N_2O_3$, $M_r = 198{\cdot}22$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}437\ (6)$, $b = 20{\cdot}187\ (15)$, $c = 6{\cdot}241\ (4)$ Å, $V = 937\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}40\ (1)$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 8{\cdot}44$ cm^{-1}, $F(000) = 424$, $T = 295$ K. Final $R = 0{\cdot}0831$ for 570 reflections. The 2,5-piperazinedione ring adopts a flat boat conformation with the axially substituted hydroxymethyl group twisted over the ring to which the

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