

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.

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

BY PETER G. JONES

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

AND MARTIN R. EDWARDS AND ANTHONY J. KIRBY

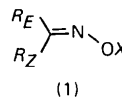
University Chemical Laboratory, Cambridge CB2 1EW, England

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Abstract. C₃₁H₂₉NO, *M_r* = 431.58, monoclinic, *P*2₁/*n*, *a* = 9.654 (3), *b* = 23.949 (8), *c* = 10.930 (3) Å, β = 109.94 (3)°, *V* = 2375.6 Å³, *Z* = 4, *D_x* = 1.21 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.7 cm⁻¹, *F*(000) = 920, *T* = 233 K, *R* = 0.056 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’, OX, is varied. We have therefore used only symmetrical ketoximes (*R_E* = *R_Z*), and need the widest possible range of leaving group OX.



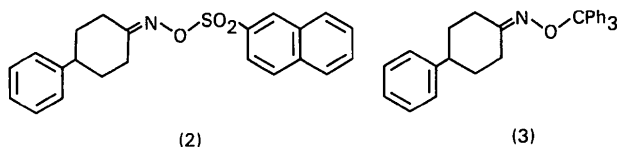
(1)

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

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After many failures we have obtained good structural data for a ketoxime arenesulfonate, the 2-naphthalene-sulfonate (2) of 4-phenylcyclohexanone (Jones *et al.*, 1986b), measured at 233 K because such compounds rearrange very readily. For comparison we need a series of derivatives of the same oxime with less electron withdrawal on oxygen. Crystals of the parent oxime and of its methyl ether proved unsuitable, so we prepared the triphenylmethyl ether (3) and report its crystal and molecular structure, determined at 233 K.



Experimental. The oxime was alkylated using triphenylmethyl chloride in dichloromethane, in the presence of triethylamine and catalytic quantities of 4-dimethylaminopyridine. Pale-yellow irregular crystals, m.p. 431–432 K (dec.) were grown by diffusing petrol into a dichloromethane solution.

7331 profile-fitted reflections (Clegg, 1981) measured on a Stoe-Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{\max}$ 55° , index ranges $|h| < 12$, $k < 31$, $|l| < 14$ for $-h+k+l$ and some $+h$ equivalents). Three check reflections; no systematic intensity variation. Crystal size $0.7 \times 0.5 \times 0.3$ mm; no absorption correction. After Lp corrections, merging equivalents gave 5445 unique reflections (R_{int} 0.0213), of which 3615 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*, Sheldrick, 1978). Cell constants refined from $\pm 2\theta$ values of 64 reflections in range 20 – 23° .

Structure solution by routine direct methods; refinement on F to R 0.056, wR 0.051 [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 $w^{-1} = \sigma^2(F) + 0.0002F^2$; 298 parameters; $S = 1.7$; max. Δ/σ 0.04; max. and min. features in final $\Delta\rho$ synthesis $\pm 0.25 \text{ e \AA}^{-3}$]. Atomic scattering factors as incorporated in *SHELXTL*. Final atomic coordinates are given in Table 1, with derived parameters in Table 2.*

Discussion. A plot is shown in Fig. 1. The compound crystallizes in an unexceptional conformation, with the 4-phenyl group equatorial on the cyclohexylidene chair,

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	Equivalent isotropic U calculated from anisotropic U .			
	x	y	z	U_{eq}
C(11)	4951 (2)	4938 (1)	7465 (2)	38 (1)
C(12)	4971 (2)	5416 (1)	6574 (2)	49 (1)
C(13)	6543 (2)	5572 (1)	6675 (2)	42 (1)
C(14)	7512 (2)	5683 (1)	8083 (2)	42 (1)
C(15)	7521 (2)	5171 (1)	8918 (2)	47 (1)
C(16)	5984 (2)	4984 (1)	8839 (2)	51 (1)
C(21)	9060 (2)	5861 (1)	8215 (2)	40 (1)
C(22)	10000 (2)	5507 (1)	7876 (2)	53 (1)
C(23)	11426 (2)	5666 (1)	8026 (2)	66 (1)
C(24)	11916 (2)	6184 (1)	8506 (2)	80 (1)
C(25)	11009 (3)	6539 (1)	8850 (2)	81 (1)
C(26)	9576 (2)	6382 (1)	8698 (2)	58 (1)
N	4042 (1)	4544 (1)	6969 (1)	42 (1)
O	4123 (1)	4127 (1)	7927 (1)	41 (1)
C(1)	3162 (2)	3658 (1)	7355 (1)	33 (1)
C(31)	3562 (2)	3411 (1)	6232 (2)	36 (1)
C(32)	5042 (2)	3381 (1)	6356 (2)	52 (1)
C(33)	5480 (3)	3114 (1)	5439 (2)	68 (1)
C(34)	4461 (3)	2866 (1)	4371 (2)	68 (1)
C(35)	2982 (3)	2890 (1)	4225 (2)	59 (1)
C(36)	2544 (2)	3161 (1)	5155 (2)	43 (1)
C(41)	3564 (2)	3228 (1)	8467 (1)	32 (1)
C(42)	4210 (2)	3385 (1)	9753 (2)	43 (1)
C(43)	4494 (2)	2998 (1)	10747 (2)	51 (1)
C(44)	4133 (2)	2445 (1)	10469 (2)	49 (1)
C(45)	3492 (2)	2283 (1)	9194 (2)	50 (1)
C(46)	3206 (2)	2670 (1)	8201 (2)	42 (1)
C(51)	1547 (2)	3838 (1)	7006 (1)	32 (1)
C(52)	821 (2)	4129 (1)	5857 (2)	43 (1)
C(53)	–648 (2)	4274 (1)	5540 (1)	51 (1)
C(54)	–1420 (2)	4138 (1)	6347 (2)	49 (1)
C(55)	–709 (2)	3868 (1)	7507 (2)	45 (1)
C(56)	758 (2)	3723 (1)	7825 (2)	37 (1)

and the oxime group close to planar. This includes the bond to the alkyl group [the torsion angle about the N–O bond is -176.3 (2) $^\circ$], which, uniquely, was twisted out of plane in the sulfonate ester (2).

Since this structure is intended to act as an 'anchor point' in indentifying trends in oxime geometry as the group attached to O is varied, it is important to establish that the geometry is normal for an oxime or oxime alkyl ether. [The small differences in orbital interactions with O–H compared with O–C σ bonds are reduced still further in the crystals because the oxime group is generally intermolecularly hydrogen-bonded (Bertolasi, Gilli & Veronese, 1982).] In Table 3, bond lengths and angles in the oxime group of (3) are compared with mean values for 20 different oxime structures ($R < 0.10$) taken from the Cambridge Structural Database (1985). Differences are insignificant. [The N–O bond in (3) appears long compared with that in three out of four oxime *O*-methyl ethers in the literature where it is below 1.400 Å (Laurent, Parmentier, Evrard & Durant, 1981; Laurent, Durant & Evrard, 1981; Jones, Kennard & Sheldrick, 1978), but all three have the oxime C=N bond cross-conjugated with C=O, which is expected to reduce the polarization of, and hence shorten, the N–O bond (see Allen & Kirby, 1984). In the fourth (Guilhelm, 1977) the N–O bond has the same length as in (3).]

* 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 42976 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(11)—C(12)	1.507 (4)	C(11)—C(16)	1.497 (3)
C(11)—N	1.276 (3)	C(12)—C(13)	1.529 (4)
C(13)—C(14)	1.527 (3)	C(14)—C(15)	1.527 (4)
C(14)—C(21)	1.513 (4)	C(15)—C(16)	1.523 (4)
C(21)—C(22)	1.381 (4)	C(21)—C(26)	1.381 (4)
C(22)—C(23)	1.383 (4)	C(23)—C(24)	1.367 (4)
C(24)—C(25)	1.361 (5)	C(25)—C(26)	1.388 (4)
N—O	1.429 (3)	C(1)—O	1.456 (3)
C(1)—C(31)	1.527 (4)	C(1)—C(41)	1.538 (3)
C(1)—C(51)	1.535 (3)	C(31)—C(32)	1.390 (4)
C(31)—C(36)	1.385 (3)	C(32)—C(33)	1.371 (5)
C(33)—C(34)	1.378 (4)	C(34)—C(35)	1.383 (5)
C(35)—C(36)	1.389 (4)	C(41)—C(42)	1.381 (3)
C(41)—C(46)	1.386 (3)	C(42)—C(43)	1.383 (4)
C(43)—C(44)	1.377 (4)	C(44)—C(45)	1.373 (4)
C(45)—C(46)	1.382 (4)	C(51)—C(52)	1.399 (3)
C(51)—C(56)	1.386 (4)	C(52)—C(53)	1.385 (4)
C(53)—C(54)	1.373 (4)	C(54)—C(55)	1.380 (3)
C(55)—C(56)	1.383 (3)		

C(12)—C(11)—C(16)	116.2 (2)	C(12)—C(11)—N	116.4 (2)
C(16)—C(11)—N	127.4 (3)	C(11)—C(12)—C(13)	111.7 (2)
C(12)—C(13)—C(14)	111.6 (3)	C(13)—C(14)—C(15)	109.8 (2)
C(13)—C(14)—C(21)	113.0 (3)	C(15)—C(14)—C(21)	111.4 (2)
C(14)—C(15)—C(16)	113.3 (2)	C(11)—C(16)—C(15)	112.4 (2)
C(14)—C(15)—C(26)	121.4 (3)	C(14)—C(15)—C(26)	120.4 (3)
C(22)—C(21)—C(26)	118.2 (3)	C(21)—C(22)—C(23)	121.2 (3)
C(22)—C(23)—C(24)	119.7 (3)	C(23)—C(24)—C(25)	120.1 (3)
C(24)—C(25)—C(26)	120.4 (3)	C(21)—C(26)—C(25)	120.4 (3)
C(11)—N—O	110.3 (2)	N—O—C(1)	110.9 (2)
O—C(1)—C(31)	110.2 (2)	O—C(1)—C(41)	103.0 (2)
C(31)—C(1)—C(41)	108.1 (2)	O—C(1)—C(51)	109.6 (2)
C(31)—C(1)—C(51)	115.1 (2)	C(41)—C(1)—C(51)	110.2 (2)
C(1)—C(31)—C(32)	118.4 (2)	C(1)—C(31)—C(36)	123.3 (3)
C(32)—C(31)—C(36)	118.0 (3)	C(31)—C(32)—C(33)	121.0 (3)
C(32)—C(33)—C(34)	120.7 (3)	C(33)—C(34)—C(35)	119.4 (3)
C(34)—C(35)—C(36)	119.6 (3)	C(31)—C(36)—C(35)	121.2 (3)
C(1)—C(41)—C(42)	121.8 (2)	C(1)—C(41)—C(46)	120.1 (2)
C(42)—C(41)—C(46)	118.0 (3)	C(41)—C(42)—C(43)	121.1 (3)
C(42)—C(43)—C(44)	120.3 (3)	C(43)—C(44)—C(45)	119.3 (3)
C(44)—C(45)—C(46)	120.5 (3)	C(41)—C(46)—C(45)	120.9 (3)
C(1)—C(51)—C(52)	121.2 (3)	C(1)—C(51)—C(56)	121.3 (2)
C(52)—C(51)—C(56)	117.5 (3)	C(51)—C(52)—C(53)	120.4 (3)
C(52)—C(53)—C(54)	121.0 (3)	C(53)—C(54)—C(55)	119.5 (3)
C(54)—C(55)—C(56)	119.7 (3)	C(51)—C(56)—C(55)	121.9 (3)

C(16)—C(11)—C(12)—C(13)	47.9 (3)	N—C(11)—C(12)—C(13)	-133.1 (3)
C(12)—C(11)—C(16)—C(15)	-45.5 (3)	N—C(11)—C(16)—C(15)	135.6 (3)
C(12)—C(11)—N—O	-178.9 (2)	C(16)—C(11)—N—O	0.0 (4)
C(11)—C(12)—C(13)—C(14)	-53.4 (3)	C(12)—C(13)—C(14)—C(15)	57.2 (3)
C(12)—C(13)—C(14)—C(21)	-177.8 (2)	C(13)—C(14)—C(15)—C(16)	-55.2 (3)
C(21)—C(14)—C(15)—C(16)	178.8 (2)	C(13)—C(14)—C(21)—C(22)	-63.7 (3)
C(13)—C(14)—C(21)—C(26)	117.2 (3)	C(15)—C(14)—C(21)—C(22)	60.5 (3)
C(15)—C(14)—C(21)—C(26)	-118.6 (3)	C(14)—C(15)—C(16)—C(11)	48.9 (3)
C(11)—N—O—C(1)	-176.3 (2)	N—O—C(1)—C(31)	57.1 (2)
N—O—C(1)—C(41)	172.3 (2)	N—O—C(1)—C(51)	-70.4 (3)
O—C(1)—C(31)—C(32)	38.0 (3)	O—C(1)—C(31)—C(36)	-148.9 (2)
C(41)—C(1)—C(31)—C(32)	-73.8 (3)	C(41)—C(1)—C(31)—C(36)	99.2 (3)
C(51)—C(1)—C(31)—C(32)	162.5 (3)	C(51)—C(1)—C(31)—C(36)	-24.4 (3)
O—C(1)—C(41)—C(42)	22.3 (3)	O—C(1)—C(41)—C(46)	-161.2 (3)
C(31)—C(1)—C(41)—C(42)	139.0 (3)	C(31)—C(1)—C(41)—C(46)	-44.6 (3)
C(51)—C(1)—C(41)—C(42)	-94.5 (3)	C(51)—C(1)—C(41)—C(46)	81.9 (3)
O—C(1)—C(51)—C(52)	81.2 (3)	O—C(1)—C(51)—C(56)	-98.0 (3)
C(31)—C(1)—C(51)—C(52)	-43.6 (3)	C(31)—C(1)—C(51)—C(56)	137.2 (3)
C(41)—C(1)—C(51)—C(52)	-166.1 (2)	C(41)—C(1)—C(51)—C(56)	14.7 (3)
C(1)—C(31)—C(32)—C(33)	173.5 (3)	C(1)—C(31)—C(36)—C(35)	-173.1 (3)
C(1)—C(41)—C(42)—C(43)	176.5 (3)	C(1)—C(41)—C(46)—C(45)	-176.7 (3)
C(1)—C(51)—C(52)—C(53)	178.1 (2)	C(1)—C(51)—C(56)—C(55)	-178.2 (2)

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

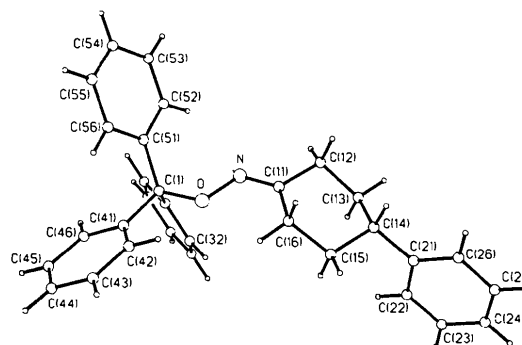


Fig. 1. The molecule of (3) in the crystal, showing the atom-numbering scheme. Radii are arbitrary.

Using the data for (3) for comparison, we can now confirm that the N—O bond of (2) shows substantial lengthening [1.502 (4) Å], as expected if the strong electron withdrawal by the sulfonyl group leads to a substantial contribution to the ground-state structure from the =N⁺—OX valence tautomer (Jones & Kirby, 1984). It is this process which leads eventually to bond cleavage and, in this case, rearrangement, and differences in the angles in the oxime group between (2) and (3) are also in the expected direction. We prefer to leave more detailed discussion of these changes until data are available for more compounds in this series.

There are no intermolecular contacts < 3.4 Å between non-H atoms in (3).

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Table 3. Mean oxime geometries compared with compound (3)

	Compound (3)	Mean values
N—O	1.429 (3) Å	1.411 (22) Å
N=C(11)	1.276 (3)	1.274 (8)
C(11)—N—O	110.3 (2)°	112.4 (1.3)°
C(12)—C(11)—N	116.4 (2)	116.0 (1.7)
C(16)—C(11)—N	127.4 (3)	125.3 (2.6)