The Structure of a Substituted Cyclohexene Oxime, 6-Acetoxyimino-2-phenyl-1-cyclohexenyl Acetate

By Mary Jane Heeg

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

Abstract. $C_{16}H_{17}NO_4$, $M_r = 287.316$, monoclinic, $P2_1/c$, $a = 7.9709$ (9), $b = 10.7235$ (11), $c = 17.9983$ (15) Å, $\beta = 100.954$ (7)°, $V = 1510.4$ (2) Å^3, $Z = 4$, $D_x = 1.263$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1.54178$ Å, $\mu = 7.14$ cm^{-1}, $F(000) = 608$, $T = 298$ (2) K, $R = 0.041$ for 1511 unique observed reflections. The endocyclic torsion angles of the cyclohexene ring indicate an envelope conformation with the out-of-plane atom C3. There is clearly thermal motion in the out-of-plane direction for this atom. The conjugated C5=C6—C1=N1 sequence is planar (root-mean-square deviation = 0.039 Å) and forms dihedral angles with the planes of the substituents of 128.3 (1)° with the phenyl ring on C5, 79.7 (2)° with the OAc group on C6, and 16.0 (5)° with the OAc group on N1. Endocyclic torsion angles for the cyclohexene ring are ω(C1, C2) = 19.6 (4), ω(C2, C3) = −48.7 (3), ω(C3, C4) = 53.5 (3), ω(C4, C5) = −28.5 (4), ω(C5, C6) = −1.4 (4), ω(C6, C1) = 6.1 (4)°.

Experimental. The title compound (2) was obtained by reaction of 2,3-epoxy-3-phenylcyclohexanone oxime, (1), with the catalyst magnesium perchlorate in methylene chloride, followed by additions of pyridine and acetyl chloride. Crystallization was from a hexane/ethyl acetate solution. The crystal structure was undertaken to determine unambiguously the relative position of the acetoxy group, *i.e.* whether the epoxy ring opening occurred in the α or β position.
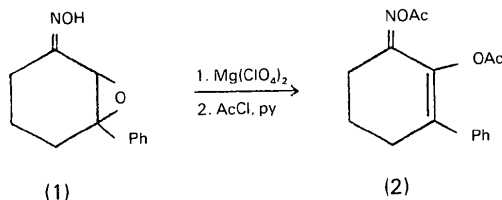
Colorless triangular plates, 0.50 × 0.50 × 0.20 mm, Nicolet *R*3 diffractometer, lattice parameters from 25 high-angle reflections ($2\theta > 40°$) constrained monoclinic, no absorption corrections or corrections for secondary extinction, $\theta/2\theta$ scans, 8 ≤ 2θ ≤ 110°, 0 ≤ h ≤ 9, 0 ≤ k ≤ 12, −20 ≤ l ≤ 20, three standard reflec-

Table 1. *Atomic parameters*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$$

	x	y	z	U_{eq}(Å^2)
C1	0.2336 (3)	0.0974 (3)	0.75462 (16)	0.0537 (12)
C2	0.1596 (5)	0.0553 (3)	0.67645 (17)	0.0637 (14)
C3	0.0557 (5)	−0.0633 (3)	0.67606 (19)	0.0692 (14)
C4	0.1511 (4)	−0.1624 (3)	0.72719 (17)	0.0621 (13)
C5	0.2135 (3)	−0.1147 (3)	0.80651 (15)	0.0533 (11)
C6	0.2487 (3)	0.0078 (3)	0.81631 (15)	0.0523 (11)
C7	0.3433 (4)	0.4011 (3)	0.72657 (21)	0.0665 (14)
C8	0.2916 (7)	0.4861 (5)	0.6606 (3)	0.0906 (20)
C9	0.2303 (4)	0.1342 (3)	0.92127 (16)	0.0644 (13)
C10	0.3442 (7)	0.2056 (5)	0.9826 (3)	0.0998 (20)
C11	0.2343 (3)	−0.2052 (3)	0.86958 (15)	0.0545 (11)
C12	0.3150 (4)	−0.3186 (3)	0.86276 (18)	0.0621 (13)
C13	0.3307 (4)	−0.4070 (3)	0.91936 (20)	0.0725 (14)
C14	0.2631 (5)	−0.3853 (3)	0.98290 (22)	0.0801 (16)
C15	0.1819 (5)	−0.2730 (4)	0.99007 (21)	0.0812 (16)
C16	0.1679 (4)	−0.1840 (3)	0.93383 (18)	0.0669 (14)
N1	0.2924 (3)	0.20670 (23)	0.77504 (12)	0.0647 (10)
O1	0.26585 (24)	0.28665 (18)	0.71006 (11)	0.0711 (9)
O2	0.4365 (3)	0.42384 (19)	0.78464 (13)	0.0869 (10)
O3	0.32579 (22)	0.05303 (16)	0.88769 (10)	0.0574 (7)
O4	0.0799 (3)	0.14423 (19)	0.90185 (11)	0.0782 (9)

tions fluctuated less than 2%, 2248 total reflections, 1888 unique, 1511 observed with $I_o \geq 2.5\sigma(I)$, direct methods (*SHELXTL*; Sheldrick, 1978), full-matrix refinement *via* *SHELX*76 (Sheldrick, 1976) on *F*'s minimizing $\sum w(F_o - |F_c|)^2$, all nonhydrogen atoms anisotropic, H atoms placed in observed positions and refined isotropically. For observed reflections $R = 0.041$, $wR = 0.034$, $S = 4.89$, $w = (\sigma_F)^{-2}$. Including weak reflections, $R = 0.052$, $wR = 0.035$. In a final cycle $(\Delta/\sigma)_{max} < 0.1$ (associated with an H atom), $(\Delta\rho)_{max} = 0.11$, $(\Delta\rho)_{min} = −0.16$ e Å^{-3}. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Table 1* gives the atomic coordinates and U_{eq} values. A view of the molecule is shown in Fig. 1.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44102 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
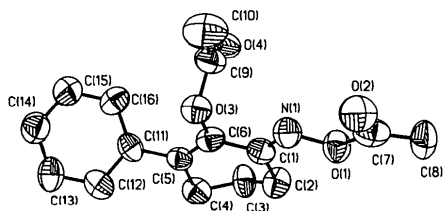
Fig. 1. A diagram of the title molecule viewed with 50% probability ellipsoids.

Related literature. The complete synthesis has been published (Tubergen, 1986). Examples of structurally similar oximes that may be used as comparisons are L-carvoxime (Kroon, van Gurp, Oonk, Baert & Fouret, 1976) and the oxime of 11-methyl-10-epieudesm-4-en-3-one (Huffman, Swain, Jacobus & McPhail, 1980).

References

HUFFMAN, J. W., SWAIN, W. E., JACOBUS, J. & McPHAIL, A. T. (1980). *J. Org. Chem.* **45**, 3088–3096.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
KROON, J., VAN GURP, P. R. E., OONK, H. A. J., BAERT, F. & FOURET, R. (1976). *Acta Cryst.* B**32**, 2561–2564.
SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.
TUBERGEN, M. W. (1986). PhD Thesis, Wayne State University, USA.

Structure of (5*SR*,6*SR*)-4-Methoxy-7,7-bis(methoxycarbonyl)-5-[bis(methoxycarbonyl)(phenylthio)methyl]-1-oxaspiro[5.2]oct-3-en-2-one

BY F. FLORENCIO, S. MARTÍNEZ-CARRERA AND S. GARCÍA-BLANCO

Departamento de Rayos X, Instituto Rocasolano, CSIC, Serrano 119, 28006-Madrid, Spain

Abstract. $C_{23}H_{24}O_{11}S$, $M_r = 508\cdot496$, triclinic, $P\bar{1}$, $a = 14\cdot758$ (1), $b = 10\cdot522$ (1), $c = 8\cdot398$ Å, $\alpha = 106\cdot40$ (1), $\beta = 75\cdot80$ (1), $\gamma = 104\cdot05$ (1)°, $V = 1191\cdot5$ (1) Å^3, $Z = 2$, $D_x = 1\cdot417$ g cm^{-3}, Cu $K\alpha$ $\lambda = 1\cdot5418$ Å, $\mu = 16\cdot957$ cm^{-1}, $F(000) = 532$, $R = 0\cdot051$, $wR = 0\cdot054$ for 3375 observed reflections of 4068 unique data. The six-membered heterocyclic ring displays a distorted C_6 envelope conformation. The methoxy group is coplanar with the six-membered ring. The ester groups are planar and C10 and C34 are *trans*.

Experimental. The title compound was obtained by P. de March, M. Moreno-Manas and I. Ripoll of the Departamento de Química, Universidad Autonoma de Barcelona, Spain, who provided the crystals. Unit-cell parameters were obtained from least-squares refinement of 45 high-angle reflections (max. angle 60°) measured on a Philips PW1100 four-circle diffractometer; graphite-monochromated Cu $K\alpha$ radiation. Intensities were measured from a crystal of dimensions $0\cdot15 \times 0\cdot20 \times 0\cdot30$ mm on the same diffractometer for $2 < \theta < 65°$. ω–2θ scan technique. Two standard reflections measured every 100 reflections with no
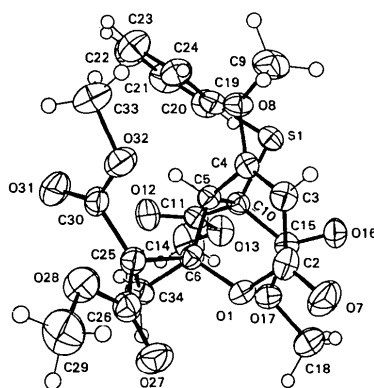

Fig. 1. A view of the molecule with the numbering scheme.

intensity variation. Of the 4008 measured independent reflections, 3375 were considered as observed with $I > 2\sigma(I)$, $0 < h < 17$, $-12 < k < 12$, $-10 < l < 10$. Lorentz, polarization and absorption (Walker & Stuart, 1983) corrections were applied. The min. and max. transmision factors are $0\cdot867$ and $1\cdot324$ respectively.

The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain,