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Acta Cryst. (1990). **C46**, 1942–1944

Structure of *endo,endo*-2,3-Diphenylbornane-2,3-ozonide

BY EDUARDO PALOMINO,* A. PAUL SCHAAAP, A. F. M. MAQSUDUR RAHMAN† AND MARY JANE HEEG‡

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

(Received 9 August 1989; accepted 26 February 1990)

Abstract. 6,9,9-Trimethyl-*endo,endo*-2,5-diphenyl-3,4,10-trioxatricyclo[4.2.1.1^{2,5}]decane, C₂₂H₂₄O₃, *M_r* = 336.43, orthorhombic, *P*2₁2₁2₁, *a* = 11.016 (4), *b* = 20.921 (8), *c* = 7.678 (2) Å, *V* = 1770 (1) Å³, *Z* = 4, *D_x* = 1.263 g cm⁻³, λ(Mo *Kα*) = 0.71073 Å, μ = 0.77 cm⁻¹, *F*(000) = 720, *T* = 298 (2) K, *R* = 0.046 and *wR* = 0.050 for 1146 observed [*I*_o ≥ 2.5σ(*I*)] reflections. The title molecule is similar to its precursor molecule, *endo,endo*-2,3-diphenyl-2,3-epoxybornane [Palomino, Schaap, Rahman & Heeg (1990). *Acta Cryst.* **C46**, 1940–1942], where a peroxy group has been inserted into the C–C (epoxide) bond forming an ozonide ring and an eight-membered peroxy ring. The eight-membered ring consists of three planar four-atom segments which intersect at angles of 111.9 (2) and 112.2 (2)°. The bicyclo bridge plane containing the apical C atom (defined by atoms C1, C4 and C7) intersects the backbone at dihedral angles of 126.8 (4) and 121.3 (3)° and cants slightly toward the ozonide end of the molecule. The plane containing the apical O atom (defined by atoms O1, C2 and C3) makes an

angle of 119.7 (3)° with the central backbone. The bond angles at the bridgehead atoms C7 and O1 are 95.7 (4) and 101.2 (3)°, respectively. Both five-membered rings are in envelope conformations. For the cyclopentane ring ΔC₅ is 0.40°. The ozonide ring is a less ideal envelope (ΔC₅ = 5.3°) with some puckering evidence from the C–O–O–C torsion angle [–4.3 (4)°]. The dihedral angle between the flap and the body of the ozonide ring envelope is 128.1 (3)°. Distances and angles in the ozonide ring are within published ranges. The central six-membered tetrahydropyran ring is distorted a few degrees from an ideal boat conformation and ΔC_{2,5,5} is 4.0°. The title molecule is spatially much larger than the contracted and strained epoxide molecule discussed in the previous paper (Palomino *et al.*, 1990). Here the interplanar angles describing the framework are larger and the rehybridization at atoms C2 and C3 spreads out the pendent phenyl groups so that the distance between their centroids is 7.068 Å compared with 5.126 Å in diphenyl-2,3-epoxybornane.

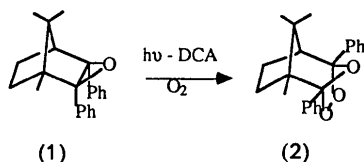
Experimental. The title molecule (2) was prepared by the photosensitized oxygenation (Schaap, Siddiqui, Prasad, Palomino & Lopez, 1984) of *endo,endo*-2,3-diphenyl-2,3-epoxybornane (1) in the presence of 9,10-dicyanoanthracene (DCA). The ozonide was

* Present address: Department of Chemistry, Michigan Cancer Foundation, 110 E. Warren, Detroit, Michigan 48201, USA.

† Present address: Department of Chemistry, University of Toledo, Toledo, Ohio 43606–3390, USA.

‡ To whom correspondence should be addressed.

purified by low-temperature column chromatography on silica gel and crystallized from *n*-pentane by slow evaporation.



Colorless irregular crystals, $0.38 \times 0.30 \times 0.30$ mm; mounted in a thin-wall capillary, Nicolet $P2_1$ diffractometer, monochromated $\text{Mo K}\alpha$; $\theta/2\theta$ scans; $4 \leq 2\theta \leq 50^\circ$; lattice parameters from 40 reflections ($2\theta > 20^\circ$); no absorption corrections applied; $0 \leq h \leq 13$, $0 \leq k \leq 24$, $0 \leq l \leq 9$; three standard reflections fluctuated 2%; 1895 total reflections, 1816 unique, 1146 observed with $I_o \geq 2.5\sigma(I)$; $I = P - rB$ where P = scan counts, r = scan time/background ratio, B = sum of background counts; $\sigma_I^2 = P + r^2B + (pI)^2$ where $p = 0.05$. Direct methods; full-matrix refinement via *SHELX76* (Sheldrick, 1976) minimizing $\sum w(|F_o| - |F_c|)^2$; all C and O atoms anisotropic; H atoms were placed in observed positions and held invariant. Number of parameters varied was 228. For observed reflections $R = 0.046$, $wR = 0.050$, $S = 1.32$, $w = (\sigma_F)^{-2}$. For all reflections $R = 0.093$, $wR = 0.066$. In a final cycle $(\Delta/\sigma)_{\max} < 0.01$, $(\Delta\rho)_{\max} = 0.19$, $(\Delta\sigma)_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$. An empirical correction for extinction was applied: $F_{\text{corr}} = F(1 - 0.001x F^2/\sin\theta)$ where x refined to 0.00105; in addition the reflection (210) was omitted due to secondary-extinction problems. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Table 1* gives the atom coordinates and Table 2 lists bond distances and angles. Fig. 1 illustrates the geometry and labeling scheme.

Related literature. The work reported herein was abstracted in part from a thesis (Palomino, 1986). Synthetic details have been published (Palomino, Schaap & Heeg, 1989). Structural details for molecules containing an ozonide ring have been retrieved from the Cambridge Structural Database (1989). Of these there are 12 structures (Cambridge Structural Database refcodes BPEBXP, BUMRIK, BUMROQ, BUVBAV, CENKIP, CETHAK, DAFXEN, DUMLIG, FELROD, FEXYEM, GAFJEC and

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares-planes data and the full references for the Cambridge Structural Database refcodes mentioned here have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52819 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (\AA^2)
O1	0.9821 (3)	0.8237 (1)	0.1667 (4)	0.039 (1)
O2	0.9616 (3)	0.9158 (2)	0.3061 (4)	0.052 (1)
O3	0.8848 (3)	0.8671 (2)	0.3881 (4)	0.055 (1)
C2	0.9905 (4)	0.8902 (2)	0.1349 (6)	0.039 (2)
C1	0.8930 (4)	0.9114 (2)	-0.0089 (6)	0.045 (2)
C6	0.7957 (5)	0.9523 (3)	0.0783 (8)	0.065 (2)
C5	0.7089 (5)	0.9045 (3)	0.1685 (8)	0.068 (2)
C4	0.7658 (4)	0.8386 (3)	0.1238 (7)	0.053 (2)
C3	0.8679 (4)	0.8197 (2)	0.2520 (6)	0.041 (2)
C7	0.8191 (4)	0.8505 (3)	-0.0601 (6)	0.052 (2)
C21	1.1204 (4)	0.9083 (2)	0.0983 (6)	0.038 (2)
C22	1.1597 (5)	0.9693 (2)	0.1398 (7)	0.054 (2)
C23	1.2795 (5)	0.9866 (3)	0.1064 (8)	0.062 (2)
C24	1.3588 (5)	0.9439 (3)	0.0306 (8)	0.065 (2)
C25	1.3193 (5)	0.8837 (3)	-0.0090 (7)	0.063 (2)
C26	1.2003 (5)	0.8667 (2)	0.0239 (7)	0.053 (2)
C11	0.9528 (5)	0.9435 (3)	-0.1665 (7)	0.065 (2)
C31	0.8538 (4)	0.7565 (2)	0.3434 (6)	0.041 (2)
C32	0.9557 (5)	0.7219 (2)	0.3893 (7)	0.054 (2)
C33	0.9446 (5)	0.6644 (2)	0.4800 (8)	0.065 (2)
C34	0.8321 (6)	0.6422 (3)	0.5290 (7)	0.064 (2)
C35	0.7313 (5)	0.6772 (3)	0.4876 (8)	0.066 (2)
C36	0.7414 (5)	0.7345 (2)	0.3933 (7)	0.054 (2)
C71	0.8885 (6)	0.7948 (3)	-0.1445 (7)	0.071 (2)
C72	0.7150 (6)	0.8680 (3)	-0.1898 (8)	0.086 (2)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

O1—C2	1.416 (5)	C7—C71	1.538 (8)
O1—C3	1.421 (5)	C7—C72	1.562 (8)
O2—O3	1.467 (5)	C21—C22	1.384 (6)
O2—C2	1.455 (6)	C21—C26	1.364 (7)
O3—C3	1.453 (5)	C22—C23	1.393 (8)
C1—C2	1.604 (7)	C23—C24	1.379 (8)
C1—C6	1.526 (7)	C24—C25	1.365 (8)
C1—C7	1.562 (7)	C25—C26	1.382 (7)
C1—C11	1.533 (7)	C31—C32	1.382 (7)
C2—C21	1.507 (7)	C31—C36	1.375 (7)
C3—C4	1.546 (7)	C32—C33	1.396 (7)
C3—C31	1.505 (6)	C33—C34	1.376 (9)
C4—C5	1.552 (7)	C34—C35	1.367 (9)
C4—C7	1.549 (7)	C35—C36	1.405 (8)
C5—C6	1.547 (8)		
O1—C2—O2	101.1 (3)	C3—C4—C7	110.2 (4)
O1—C2—C1	110.3 (3)	C3—C31—C32	119.7 (4)
O1—C2—C21	110.0 (3)	C3—C31—C36	121.1 (4)
O1—C3—O3	100.3 (3)	C4—C3—C31	116.6 (4)
O1—C3—C4	109.6 (4)	C4—C5—C6	103.0 (4)
O1—C3—C31	111.0 (4)	C4—C7—C71	116.8 (4)
O2—O3—C3	103.8 (3)	C4—C7—C72	109.9 (4)
O2—C2—C1	111.9 (4)	C5—C4—C7	102.2 (4)
O2—C2—C21	106.5 (4)	C6—C1—C7	101.6 (4)
O3—O2—C2	105.0 (3)	C6—C1—C11	113.8 (4)
O3—C3—C4	112.1 (4)	C7—C1—C11	112.5 (4)
O3—C3—C31	106.1 (4)	C21—C22—C23	119.6 (5)
C1—C2—C21	115.9 (4)	C21—C26—C25	121.6 (5)
C1—C6—C5	105.6 (4)	C22—C21—C26	118.8 (5)
C1—C7—C4	95.7 (4)	C22—C23—C24	120.6 (5)
C1—C7—C71	117.7 (4)	C23—C24—C25	119.3 (5)
C1—C7—C72	110.6 (4)	C24—C25—C26	119.9 (5)
C2—O1—C3	101.2 (3)	C31—C32—C33	120.5 (5)
C2—C1—C6	108.9 (4)	C31—C36—C35	120.0 (5)
C2—C1—C7	107.2 (3)	C32—C31—C36	119.1 (4)
C2—C1—C11	112.2 (4)	C32—C33—C34	120.4 (5)
C2—C21—C22	119.1 (4)	C33—C34—C35	119.2 (5)
C2—C21—C26	122.0 (4)	C34—C35—C36	120.8 (5)
C3—C4—C5	112.4 (4)	C71—C7—C72	105.9 (4)

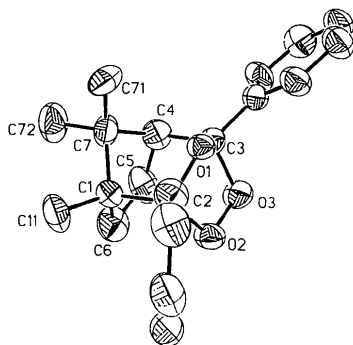


Fig. 1. ORTEP (Johnson, 1965) drawing at 50% probability of *endo,endo*-2,3-diphenylbornane-2,3-ozonide showing the adopted labeling. The labels for the phenyl carbons have been omitted for clarity and are assigned C21–C26 on C2 and C32–C36 on C3.

NBEPXP10) in which the ozonide ring is part of a more complex fused-ring system and their range of structural parameters includes those of the title structure [*cf.* average C—O(—C) = 1.420 (9), C—O(—O) = 1.448 (22) and O—O = 1.475 Å in the CSD files and 1.419, 1.454 and 1.467 Å for those parameters in the title structure; bond angles are more variable in the literature but the ranges include our values]. Far less common are those structural determinations in which the ozonide ring is 'strain-free', *i.e.* not part of

a larger fused system (Groth, 1970; Schaap, Siddiqui, Prasad, Rahman & Oliver, 1984). Hitchcock & Beheshti (1979) have discussed O—O bond lengths according to ring size. Asymmetry parameters (ΔC_1 and ΔC_2) are described by Ladd & Palmer (1985).

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Acta Cryst. (1990). **C46**, 1944–1946

8-(*N*-Methyl-*N*-*p*-tolylsulfonylamino)bicyclo[4.2.0]octan-7-one

By B. TINANT AND J.-P. DECLERCQ

Laboratoire de chimie physique et de cristallographie, Université Catholique de Louvain,
1 place Louis Pasteur, 1348 Louvain la Neuve, Belgium

AND B. GOBEAUX

Laboratoire de chimie organique de synthèse, Université Catholique de Louvain, 1 place Louis Pasteur,
1348 Louvain la Neuve, Belgium

(Received 29 January 1990; accepted 19 March 1990)

Abstract. C₁₆H₂₁NO₃S, $M_r = 307.41$, triclinic, $P\bar{1}$, $a = 6.473$ (6), $b = 16.012$ (6), $c = 15.791$ (6) Å, $\alpha = 106.22$ (3), $\beta = 92.83$ (6), $\gamma = 91.22$ (6)°, $V = 1569$ (2) Å³, $Z = 4$, $D_x = 1.30$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.17$ cm⁻¹, $F(000) = 656$, $T = 291$ K, $R = 0.053$ for 2956 observed reflections. The two independent molecules in the asymmetric unit have similar geometry. The configuration of the substituent at C8 is *exo*. The puckering of the cyclobutanone ring as indicated by the dihedral angle

about the C1—C7 diagonal is 31 (1)° in molecule *A* and 29 (1)° in molecule *B*.

Experimental. The title compound results from a (2 + 2) cycloaddition of a keteniminium salt to cyclohexene. Because stereochemical assignments in four-membered ring systems based on ¹H NMR coupling constants are ambiguous, an X-ray analysis was undertaken in order to assess the configuration at C8. Crystals obtained by evaporation from cyclo-