$$C_{24}H_{42}N_4^{4+}.4Cl^-.1.72H_2O$$

Related literature. Crystals of the title compound were obtained as an unintentional reaction product of the synthesis of related tantalum chlorine complexes (van der Zeijden, 1988; Abbenhuis, Grove, van Koten, van der Sluis & Spek, 1990).

Data were collected by A. J. M. Duisenberg. This work was supported in part (ALS) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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Structure of endo,endo-2,3-Diphenyl-2,3-epoxybornane

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

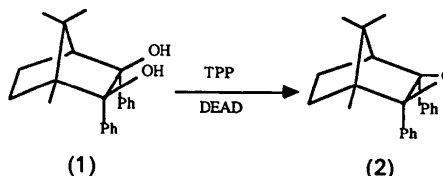Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

Abstract. $C_{22}H_{24}O$, $M_r = 304.43$, monoclinic, $C2$, $a = 18.862 (3)$, $b = 9.958 (2)$, $c = 10.262 (1)$ Å, $\beta = 117.47 (1)°$, $V = 1709.9 (4)$ Å^3, $Z = 4$, $D_x = 1.182$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.66$ cm^{-1}, $F(000) = 656$, $T = 298 (2)$ K, $R = 0.039$ and $wR = 0.039$ for 2238 observed $[I_o \geq 2.5\sigma(I)]$ reflections including Friedel pairs. The molecule is a diphenyl-substituted bornane system fused to an exo-oriented epoxide, typical of all known compounds of this type. The central six-membered ring is bent with an interplanar angle of 106.6 (1)°. The planar flap containing the apical C atom of the bornane adopts an unsymmetrical disposition relative to the two coalesced envelopes, canting toward the unsubstituted end of the bornane backbone with intersection angles of 122.8 (2) and 130.7 (2)°. The plane of the epoxide ring forms a dihedral angle of 111.3 (1)° at the epoxide–bornane interface. The torsion angles described by O—C—C—C(apical) are −27.9 (2) and 33.0 (3)°, and the distance between the centroids of the phenyl rings is 5.126 (3) Å. The three-membered

epoxide ring is characterized by (i) long C—O single-bond lengths [1.442 (2) and 1.454 (2) Å], (ii) small intra-ring bond angles [59.7 (1), 58.9 (1) and 61.4 (1)°], and (iii) a short C—C single-bond length [1.479 (3) Å]. These can be explained through an increase in p-orbital contribution in the C—O bonds with a concomitant decrease in p-character in the C—C bond. Other distances and angles are within published ranges for similar molecules.

Experimental. The title molecule (2) was prepared by dehydration of the precursor endo,endo-2,3-diphenyl-bornane-2,3-diol (1) via a syn-Mitsunobu reaction using the reagents triphenylphosphine (TPP) and diethyl azodicarboxylate (DEAD). Crystals were obtained from ethanol.

Colorless triangular crystals, 0.36 × 0.36 × 0.36 mm; mounted in a thin-wall capillary, Nicolet

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
O1	−0·23983 (8)	−0·15580	−0·4250 (2)	0·0415 (6)
C1	−0·2081 (1)	−0·1130 (3)	−0·1611 (2)	0·047 (1)
C2	−0·2656 (1)	−0·1702 (3)	−0·3135 (2)	0·040 (1)
C3	−0·2924 (1)	−0·0541 (3)	−0·4149 (2)	0·0379 (9)
C4	−0·2508 (1)	0·0657 (3)	−0·3156 (3)	0·045 (1)
C5	−0·2974 (1)	0·0797 (3)	−0·2252 (2)	0·054 (1)
C6	−0·2661 (2)	−0·0413 (3)	−0·1172 (2)	0·054 (1)
C7	−0·1699 (1)	0·0106 (3)	−0·1993 (2)	0·046 (1)
C11	−0·1514 (2)	−0·2124 (3)	−0·0500 (3)	0·064 (1)
C21	−0·3107 (1)	−0·2965 (3)	−0·3234 (2)	0·042 (1)
C22	−0·2749 (2)	−0·4188 (3)	−0·3216 (3)	0·055 (1)
C23	−0·3133 (2)	−0·5386 (3)	−0·3265 (3)	0·071 (2)
C24	−0·3868 (2)	−0·5376 (4)	−0·3306 (3)	0·077 (2)
C25	−0·4234 (2)	−0·4178 (4)	−0·3326 (3)	0·069 (1)
C26	−0·3856 (2)	−0·2970 (3)	−0·3392 (3)	0·054 (1)
C31	−0·3696 (1)	−0·0361 (3)	−0·5512 (2)	0·0404 (9)
C32	−0·4036 (1)	−0·1420 (3)	−0·6480 (3)	0·051 (1)
C33	−0·4734 (2)	−0·1257 (3)	−0·7778 (3)	0·062 (1)
C34	−0·5097 (2)	−0·0013 (4)	−0·8131 (3)	0·067 (1)
C35	−0·4770 (2)	0·1037 (3)	−0·7198 (3)	0·067 (1)
C36	−0·4070 (1)	0·0879 (3)	−0·5898 (3)	0·054 (1)
C71	−0·1067 (1)	−0·0210 (3)	−0·2503 (3)	0·060 (1)
C72	−0·1282 (2)	0·1088 (3)	−0·0690 (3)	0·064 (1)

R3 diffractometer, monochromated Mo $K\alpha$; $\theta/2\theta$ scans; $5 \le 2\theta \le 50°$; lattice parameters from 24 reflections $(2\theta > 20°)$ refined with α and γ constrained to be 90°; no absorption or extinction corrections applied; $0 \le h \le 22$, $0 \le k \le 11$, $-13 \le l \le 12$ plus Friedel pairs; three standard reflections fluctuated 10% downward and a decay correction was applied; 3405 total reflections, 3012 unique, 2238 observed with $I_o \ge 2·5\sigma(I)$. Direct methods; full-matrix refinement *via* SHELX76 (Sheldrick, 1976) minimizing $\Sigma w(|F_o| - |F_c|)^2$; all C and O atoms anisotropic; H atoms were placed in observed positions and held invariant. Number of parameters varied was 208. For observed reflections $R = 0·039$, $wR = 0·039$, $S = 1·35$, $w = (\sigma_F + 0·0003F^2)^{-2}$. For all reflections $R = 0·057$, $wR = 0·042$. In a final cycle $(\Delta/\sigma)_{max} < 0·01$, $(\Delta\rho)_{max} = 0·27$, $(\Delta\rho)_{min} = -0·29$ e Å^{-3}. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Table 1* gives the atomic coordinates and Table 2 lists bond distances and angles. Fig. 1 illustrates the geometry and labeling scheme.

Related literature. The work reported here was abstracted in part from a thesis (Palomino, 1986). The term *syn*-Mitsunobu has been coined by Palomino, Schaap & Heeg (1989) to describe the special class of intramolecular dehydration reactions

Table 2. *Bond lengths (Å) and angles (°)*

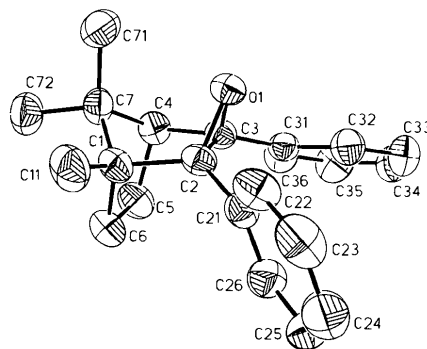|			
O1—C2	1·442 (2)	C7—C72	1·546 (3)
O1—C3	1·454 (2)	C21—C22	1·388 (4)
C1—C2	1·544 (3)	C21—C26	1·387 (3)
C1—C6	1·537 (3)	C22—C23	1·385 (4)
C1—C7	1·565 (3)	C23—C24	1·367 (5)
C1—C11	1·516 (4)	C24—C25	1·374 (5)
C2—C3	1·479 (3)	C25—C26	1·390 (5)
C2—C21	1·495 (4)	C31—C32	1·387 (4)
C3—C4	1·529 (3)	C31—C36	1·386 (4)
C3—C31	1·493 (3)	C32—C33	1·384 (3)
C4—C5	1·551 (2)	C33—C34	1·381 (5)
C4—C7	1·540 (3)	C34—C35	1·359 (4)
C5—C6	1·556 (4)	C35—C36	1·386 (3)
C7—C71	1·539 (3)		
O1—C2—C1	115·6 (2)	C3—C31—C32	120·6 (2)
O1—C2—C3	59·7 (1)	C3—C31—C36	121·5 (2)
O1—C2—C21	114·8 (2)	C4—C3—C31	120·6 (2)
O1—C3—C2	58·9 (1)	C4—C5—C6	102·8 (2)
O1—C3—C4	115·7 (2)	C4—C7—C71	117·1 (1)
O1—C3—C31	114·8 (2)	C4—C7—C72	111·8 (2)
C1—C2—C3	106·1 (2)	C5—C4—C7	101·6 (1)
C1—C2—C21	119·4 (2)	C6—C1—C7	100·4 (2)
C1—C6—C5	103·8 (1)	C6—C1—C11	115·7 (1)
C1—C7—C4	93·9 (2)	C7—C1—C11	117·1 (2)
C1—C7—C71	116·3 (2)	C21—C22—C23	120·9 (2)
C1—C7—C72	112·9 (1)	C21—C26—C25	120·3 (3)
C2—O1—C3	61·4 (1)	C22—C21—C26	118·4 (3)
C2—C1—C6	101·9 (2)	C22—C23—C24	120·1 (3)
C2—C1—C7	103·0 (1)	C23—C24—C25	120·2 (3)
C2—C1—C11	116·3 (2)	C24—C25—C26	120·1 (3)
C2—C3—C4	103·7 (1)	C31—C32—C33	121·4 (3)
C2—C3—C31	128·5 (2)	C31—C36—C35	120·6 (2)
C2—C21—C22	118·7 (2)	C32—C31—C36	117·8 (2)
C2—C21—C26	122·9 (2)	C32—C33—C34	119·6 (3)
C3—C2—C21	127·6 (2)	C33—C34—C35	119·8 (2)
C3—C4—C5	102·2 (2)	C34—C35—C36	120·8 (3)
C3—C4—C7	105·0 (2)	C71—C7—C72	105·0 (2)

Fig. 1. *ORTEP* (Johnson, 1965) drawing (at 50% probability) of *endo,endo*-2,3-diphenyl-2,3-epoxybornane showing the adopted labeling.

of *cis*-glycols to form epoxides (Kimura, Hashimoto & Mitsunobu, 1974) without inversion of configuration. As for structural comparisons, the structures of related norbornane–epoxide molecules are available (Stevenson, Essig, Shafizadeh, Jensen & Stenkamp, 1983; Bartlett, Combs, Le, Watson, Galloy & Kimura, 1982; Lehr, Hildebrand, Fritz, Knothe, Kruger & Prinzbach, 1982; Subramanyam, Bartlett, Iglesias, Watson & Galloy, 1982; DeLacy & Ken-

nard, 1972). The search and data retrieval for these molecules was obtained *via* the Cambridge Structural Database (1989). The structural characteristics of carbon–oxygen rings have been surveyed and discussed by Hitchcock & Beheshti (1979).

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

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Abstract. 6,9,9-Trimethyl-*endo,endo*-2,5-diphenyl-3,4,10-trioxatricyclo[4.2.1.1^{2,5}]decane, $C_{22}H_{24}O_3$, M_r = 336·43, orthorhombic, $P2_12_12_1$, $a = 11·016$ (4), $b = 20·921$ (8), $c = 7·678$ (2) Å, $V = 1770$ (1) Å^3, $Z = 4$, $D_x = 1·263$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·77$ cm^{-1}, $F(000) = 720$, $T = 298$ (2) K, $R = 0·046$ and $wR = 0·050$ for 1146 observed $[I_o \geq 2·5\sigma(I)]$ reflections. The title molecule is similar to its precursor molecule, *endo,endo*-2,3-diphenyl-2,3-expoxybornane [Palomino, Schaap, Rahman & Heeg (1990). *Acta Cryst.* C46, 1940–1942], where a peroxo group has been inserted into the C—C (epoxide) bond forming an ozonide ring and an eight-membered peroxo 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 ΔC_s is 0·40°. The ozonide ring is a less ideal envelope ($\Delta C_s = 5·3°$) 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 $\Delta C_{2,s,s}$ 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

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