Refinement

Refinement on F^2
$R(F) = 0.0434$
$wR(F^2) = 0.1259$
$S = 1.084$
1795 reflections
253 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0962P)^2 + 0.6339P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.136$
$\Delta\rho_{\max} = 0.191$ e Å^{-3}
$\Delta\rho_{\min} = -0.200$ e Å^{-3}
Extinction correction: see below
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.3 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
O1	−0.34829 (12)	−0.0049 (5)	0.04055 (12)	0.0639 (7)
O2	0.16313 (11)	−0.0849 (5)	0.17900 (11)	0.0532 (6)
O3	0.16988 (14)	0.2262 (6)	0.2460 (2)	0.0839 (10)
O4	0.48761 (12)	−0.0462 (6)	0.30235 (12)	0.0612 (7)
C1	−0.27720 (7)	0.0027 (4)	0.05606 (9)	0.0461 (8)
C2	−0.23853 (9)	0.1832 (4)	0.03748 (10)	0.0568 (9)
C3	−0.16643 (9)	0.1703 (4)	0.05673 (11)	0.0540 (9)
C4	−0.13300 (7)	−0.0232 (4)	0.09456 (10)	0.0406 (7)
C5	−0.17167 (9)	−0.2037 (4)	0.11314 (10)	0.0519 (9)
C6	−0.24377 (9)	−0.1907 (4)	0.09389 (10)	0.0535 (9)
C7	−0.05314 (7)	−0.0395 (4)	0.11687 (9)	0.0419 (7)
C8	−0.01358 (9)	0.1370 (4)	0.09802 (10)	0.0566 (9)
C9	0.05849 (9)	0.1251 (4)	0.11921 (12)	0.0607 (9)
C10	0.09101 (7)	−0.0635 (4)	0.15927 (12)	0.0464 (8)
C11	0.05145 (10)	−0.2400 (4)	0.17813 (12)	0.0624 (10)
C12	−0.02062 (10)	−0.2280 (4)	0.15693 (12)	0.0627 (10)
C14	0.27385 (7)	0.0263 (4)	0.24376 (8)	0.0424 (7)
C15	0.31600 (9)	0.1927 (4)	0.28519 (9)	0.0497 (8)
C16	0.38767 (9)	0.1619 (4)	0.30401 (10)	0.0509 (8)
C17	0.41719 (7)	−0.0352 (4)	0.28139 (10)	0.0478 (8)
C18	0.37505 (9)	−0.2016 (3)	0.23995 (10)	0.0472 (8)
C19	0.30338 (9)	−0.1708 (4)	0.22114 (9)	0.0461 (8)
C13	0.1984 (2)	0.0697 (7)	0.22500 (15)	0.0485 (8)
C20	0.5211 (2)	−0.2467 (9)	0.2821 (2)	0.0712 (11)
C21	−0.3894 (2)	0.1812 (7)	0.0010 (2)	0.0562 (8)
C22	−0.4633 (2)	0.1104 (8)	−0.0052 (2)	0.0570 (9)
C23	−0.5195 (2)	0.2726 (7)	−0.0469 (2)	0.0507 (8)
C24	−0.5909 (2)	0.1791 (7)	−0.0469 (2)	0.0511 (8)
C25	−0.6526 (2)	0.3181 (7)	−0.0876 (2)	0.0516 (8)
C26	−0.7206 (2)	0.2079 (7)	−0.0842 (2)	0.0564 (9)
C27	−0.7857 (2)	0.3350 (8)	−0.1231 (2)	0.0669 (10)
C28	−0.8515 (2)	0.2140 (11)	−0.1178 (3)	0.0907 (15)

In the refinement, each benzene ring was constrained to have a regular hexagon with a C—C distance of 1.39 Å. H atoms were calculated geometrically (C—H 0.96 for primary, 0.97 for secondary and 0.93 Å for aromatic) and were included in the refinement but not refined. At the final stage of refinement, five reflections ($11\bar{2}$, $20\bar{6}$, $11\bar{4}$, 002 and 111) whose large discrepancies ($F_o < F_c$) were considered to have suffered from extinction effects were omitted.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: OA1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris[2-(2-methoxyethoxy)phenyl]phosphine Oxide Monohydrate

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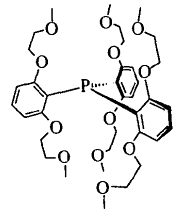
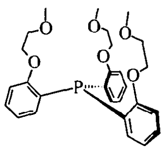
Abstract

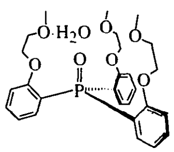
The geometry about the P atom in the title compound, $C_{27}H_{33}O_7P.H_2O$, is virtually indistinguishable from that of triphenylphosphine oxide and several analogs. Threefold symmetry is absent, surprisingly, and each 2-methoxyethoxy side chain is unique. One is involved in an internal hydrogen bond to water, another is on the same side of the plane formed by the three phosphorus-bearing C atoms as is the hydrogen-bonding side chain, and the third is on the other side of this plane.

Comment

Tris[2,6-di-(2-methoxyethoxy)phenyl]phosphine, (1), has been studied with regard to its ionophoric capabilities (Mao, 1991). As part of that study, tris[2-(2-methoxyethoxy)phenyl]phosphine, (2), was prepared to assess the contribution of 'pre-organization' to the binding characteristics of (1). Therefore, it was of interest to explore the disposition of the side chains of (2) relative to the plane formed by the three phosphorus-bearing C atoms. Whereas a suitable crystal of (2) has not yet been obtained, its oxidation product, as the monohydrate (3), has yielded a workable crystal. Fig. 1 shows an *ORTEP*II (Johnson, 1976) plot and Fig. 2 a packing diagram of (3).


(1)


(2)


(3)

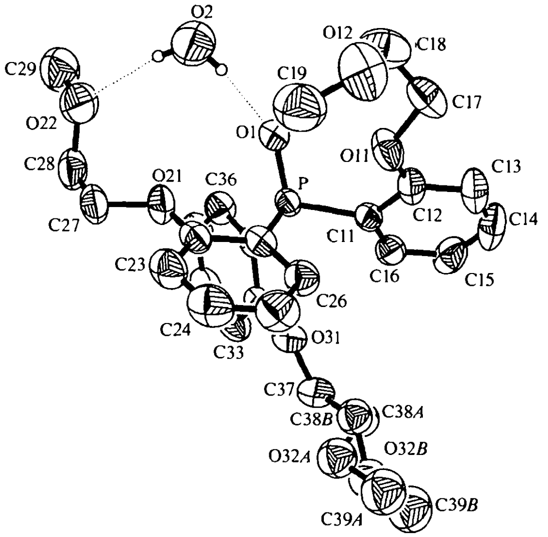


Fig. 1. *ORTEP*II (Johnson, 1976) view of (3). Displacement ellipsoids are drawn at the 50% probability level. H atoms bound to C atoms have been omitted for clarity.

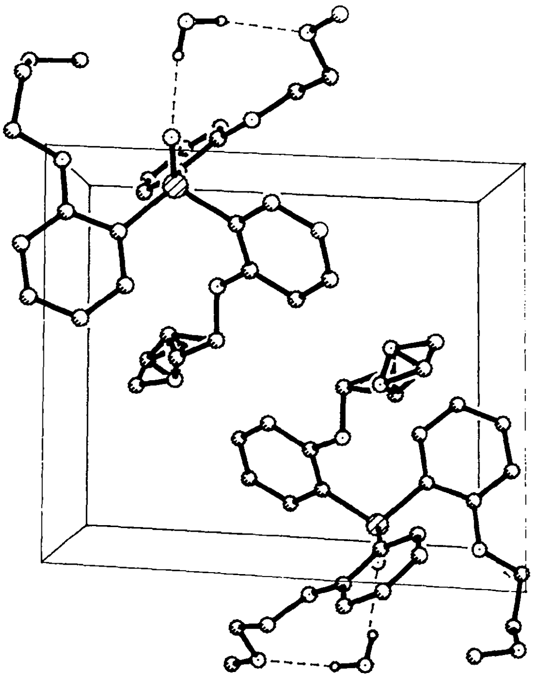


Fig. 2. View down the *c* axis.

As far as we are aware, only one other tris(2-substituted phenyl)phosphine oxide has been examined crystallographically, *i.e.* tri-*o*-tolylphosphine oxide, (4) (Cameron & Dahlèn, 1975). However, the structure of a triaryl phosphine oxide with substituents at all *ortho* positions, tris(2,6-dimethoxyphenyl)phosphine oxide hydrate, (5) (Chaloner, Harrison & Hitchcock, 1993), has been reported recently. The geometry about the P atom in (3) is virtually indistinguishable from that in (4) and (5) [average values for (3), (4), and (5), respectively: P—C 1.813 (2), 1.810 (7), 1.822 (11) Å; O—P—C 112.1 (24), 113.0 (6), 111.7 (31)°; C—P—C 106.7 (9), 105.7 (11), 107.3 (42)°]. These values are in turn barely distinguishable from those of triphenylphosphine oxide (TPPO) itself [P—C 1.799 (5)–1.803 (5) Å; O—P—C 112.0 (5)–112.5 (7)°; C—P—C 106.4 (4)–106.9 (17)°; Baures, 1991; Baures & Silverton, 1990; Brock, Schweizer & Dunitz, 1985; Spek, 1987; Thomas & Hamor, 1993]. For the purposes of the remaining discussion, we arbitrarily define 'up' or 'toward the top of the molecule' to be the direction of a vector normal to the plane defined by the three phosphorus-bearing ring-C atoms and pointing toward the phosphoryl-O atom. In (3), one methoxyethoxy side chain is up and involved in hydrogen bonding to water, another is up and not hydrogen bonded, and the third is down. The threefold symmetry which ordinary chemical intuition might impute to (3) is absent; each aryl unit is unique. By contrast, all three *ortho* methyl groups of (4) are up.

The aryl rings of triarylphosphine oxides are normally canted toward the phosphoryl-O atom. The top P—C—C angle of TPPO [average of six reports, 118.1 (10)°] is smaller than the bottom P—C—C angle [122.9 (9)°] (Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970; Baures, 1991; Baures & Silverton, 1990; Brock, Schweizer & Dunitz, 1985; Spek, 1987; Thomas & Hamor, 1993). The difference is more pronounced in the case of (5) [top P—C—C 117.5 (18)°, bottom P—C—C 126.0 (19)°]. In (4), the steric requirements of the methyls are met, apparently, by eliminating the upward cant of the aromatic rings; top [121.0 (9)°] and bottom [119.7 (7)°] P—C—C angles become nearly equal. The average top [117.7 (12)°] and bottom [123.6 (12)°] P—C—C angles in (3) are more comparable to the analogous angles in TPPO and (5) than to those in the the more sterically distressed compound (4).

In (4), the CH_3—C—C angle facing the P atom is consistently larger than the other exocyclic CH_3—C—C angle [average 123.2 (10)° *versus* 119.2 (6)°]. The analogous O—C—O angles in (3) [116.0 (2), 115.9 (2), 116.4 (2)° facing P; 123.1 (2), 124.2 (2), 123.0 (2)° away from P] are essentially reversed. This results in P···O11, P···O21, and P···O31 distances of 2.899 (2), 2.876 (2) and 3.046 (2) Å, respectively. Such P···O contacts in phosphine oxides have been discussed previously (Chaloner, Harrison, & Hitchcock, 1993). The phosphoryl-O atom to water-O atom distance [O(1)···O(2), 2.877 (3) Å] may be compared to other analogous hydrogen bonds in TPPO [2.856 (3) Å (Baures & Silverton, 1990) and 2.910 (3) Å (Baures, 1991)] and in tri-*p*-tolylphosphine oxide, [2.810 (4) Å; Churchill, See, Randall & Atwood, 1993].

Experimental

The title compound was prepared by a literature method (Mao, 1991).

Crystal data

$C_{27}H_{33}O_7P.H_2O$
$M_r = 518.5$
Triclinic
$P\overline{1}$
$a = 9.962\,(2)$ Å
$b = 11.400\,(3)$ Å
$c = 11.897\,(2)$ Å
$\alpha = 83.93\,(2)°$
$\beta = 87.19\,(2)°$
$\gamma = 86.95\,(2)°$
$V = 1340.4\,(5)$ Å^3
$Z = 2$
$D_x = 1.285$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 7.5$–$15°$
$\mu = 0.143$ mm^{-1}
$T = 294$ K
Clear block
0.64 × 0.55 × 0.50 mm
Colorless

Data collection

Siemens *R*3*m*/*V* diffractometer
θ–2θ scans
Absorption correction: empirical, ψ scan (*XEMP* in *SHELXTL-Plus*; Sheldrick, 1991)
$T_{\min} = 0.930$, $T_{\max} = 0.947$
4992 measured reflections
4697 independent reflections

3921 observed reflections [$F > 4\sigma(F)$]
$R_{\rm int} = 0.014$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
2 standard reflections monitored every 100 reflections

Refinement

Refinement on F
$R = 0.0516$
$wR = 0.0843$
$S = 1.46$
3921 reflections
321 parameters
H atoms refined with riding model, fixed isotropic U
$w = 1/[\sigma^2(F) + 0.0027F^2]$
$(\Delta/\sigma)_{\max} = 0.282$

$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 0.0027 (7)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	$U_{\rm eq}$
P	0.0671 (1)	0.2657 (1)	0.7966 (1)	0.039 (1)
O1	−0.0442 (2)	0.2611 (1)	0.8838 (1)	0.051 (1)
O2	−0.3325 (2)	0.2922 (2)	0.8793 (2)	0.097 (1)
C11	0.1898 (2)	0.1441 (2)	0.8238 (2)	0.043 (1)
C12	0.1460 (3)	0.0286 (2)	0.8368 (2)	0.052 (1)
C13	0.2334 (3)	−0.0666 (2)	0.8693 (2)	0.069 (1)
C14	0.3649 (3)	−0.0474 (3)	0.8865 (3)	0.078 (1)
C15	0.4109 (3)	0.0647 (3)	0.8751 (2)	0.066 (1)
C16	0.3235 (2)	0.1602 (2)	0.8454 (2)	0.052 (1)
O11	0.0142 (2)	0.0166 (1)	0.8155 (2)	0.065 (1)
C17	−0.0489 (3)	−0.0888 (2)	0.8589 (2)	0.066 (1)
C18	−0.1963 (4)	−0.0677 (3)	0.8548 (3)	0.085 (1)
O12	−0.2447 (3)	−0.0680 (2)	0.7469 (2)	0.095 (1)
C19	−0.2592 (4)	0.0417 (4)	0.6856 (3)	0.101 (2)
C21	0.0154 (2)	0.2645 (2)	0.6529 (2)	0.042 (1)
C22	−0.0789 (2)	0.3530 (2)	0.6112 (2)	0.046 (1)
C23	−0.1222 (3)	0.3547 (3)	0.5018 (2)	0.063 (1)
C24	−0.0711 (3)	0.2697 (3)	0.4350 (2)	0.073 (1)
C25	0.0223 (3)	0.1846 (3)	0.4731 (2)	0.070 (1)
C26	0.0661 (3)	0.1821 (2)	0.5825 (2)	0.054 (1)
O21	−0.1214 (2)	0.4324 (2)	0.6836 (1)	0.057 (1)
C27	−0.2055 (3)	0.5320 (2)	0.6437 (3)	0.063 (1)
C28	−0.2317 (3)	0.6069 (2)	0.7375 (3)	0.068 (1)
O22	−0.3281 (2)	0.5557 (2)	0.8162 (2)	0.079 (1)
C29	−0.3594 (4)	0.6236 (3)	0.9076 (3)	0.096 (1)
C31	0.1556 (2)	0.4006 (2)	0.7977 (2)	0.043 (1)
C32	0.2679 (2)	0.4302 (2)	0.7301 (2)	0.048 (1)
C33	0.3343 (3)	0.5327 (2)	0.7427 (3)	0.064 (1)
C34	0.2838 (3)	0.6048 (2)	0.8213 (3)	0.072 (1)
C35	0.1696 (3)	0.5805 (2)	0.8863 (3)	0.066 (1)
C36	0.1060 (3)	0.4777 (2)	0.8738 (2)	0.055 (1)
O31	0.3090 (2)	0.3540 (2)	0.6517 (1)	0.058 (1)
C37	0.4473 (3)	0.3524 (3)	0.6111 (3)	0.088 (1)
C38*A*	0.4972 (6)	0.2580 (4)	0.5635 (4)	0.060 (1)
C38*B*	0.4364 (7)	0.2369 (6)	0.5256 (6)	0.060 (1)
O32*A*	0.4608 (4)	0.2743 (3)	0.4503 (3)	0.078 (1)
O32*B*	0.5554 (6)	0.2493 (5)	0.4574 (4)	0.078 (1)
C39*A*	0.5075 (8)	0.1798 (7)	0.3893 (7)	0.096 (2)
C39*B*	0.5773 (10)	0.1531 (9)	0.3899 (9)	0.096 (2)

Table 2. *Selected geometric parameters* (Å, °)

P—O1	1.480 (2)	C24—C25	1.365 (4)
P—C11	1.812 (2)	C25—C26	1.390 (4)
P—C21	1.812 (2)	O21—C27	1.428 (3)
P—C31	1.815 (2)	C27—C28	1.479 (4)
C11—C12	1.400 (3)	C28—O22	1.412 (4)
C11—C16	1.394 (3)	O22—C29	1.413 (5)
C12—C13	1.389 (4)	C31—C32	1.381 (3)
C12—O11	1.365 (3)	C31—C36	1.383 (3)
C13—C14	1.368 (5)	C32—C33	1.397 (4)
C14—C15	1.372 (5)	C32—O31	1.375 (3)
C15—C16	1.384 (4)	C33—C34	1.369 (4)
O11—C17	1.423 (3)	C34—C35	1.368 (4)
C17—C18	1.478 (5)	C35—C36	1.386 (4)
C18—O12	1.393 (4)	O31—C37	1.437 (4)
O12—C19	1.384 (5)	C37—C38*A*	1.330 (6)
C21—C22	1.409 (3)	C37—C38*B*	1.758 (8)
C21—C26	1.384 (3)	C38*A*—O32*A*	1.403 (6)
C22—C23	1.389 (4)	C38*B*—O32*B*	1.409 (9)
C22—O21	1.352 (3)	O32*A*—C39*A*	1.408 (9)
C23—C24	1.379 (4)	O32*B*—C39*B*	1.429 (12)
O1—P—C11	111.4 (1)	C22—C23—C24	119.2 (2)
O1—P—C21	114.8 (1)	C23—C24—C25	121.7 (3)
O1—P—C31	110.1 (1)	C24—C25—C26	119.5 (3)
C11—P—C21	107.5 (1)	C21—C26—C25	120.5 (2)
C21—P—C31	105.7 (1)	C22—O21—C27	119.1 (2)
C11—P—C31	106.8 (1)	O21—C27—C28	108.1 (2)
P—C11—C12	118.8 (2)	C27—C28—O22	110.0 (2)
P—C11—C16	123.0 (2)	C28—O22—C29	113.0 (2)
C12—C11—C16	117.8 (2)	P—C31—C32	125.0 (2)

C11—C12—C13	120.9 (2)	P—C31—C36	116.4 (2)
C11—C12—O11	116.0 (2)	C32—C31—C36	118.6 (2)
C13—C12—O11	123.1 (2)	C31—C32—C33	120.6 (2)
C12—C13—C14	119.5 (3)	C31—C32—O31	116.4 (2)
C13—C14—C15	121.1 (3)	C33—C32—O31	123.0 (2)
C14—C15—C16	119.7 (3)	C32—C33—C34	118.7 (3)
C11—C16—C15	120.9 (2)	C33—C34—C35	122.0 (3)
C12—O11—C17	119.1 (2)	C34—C35—C36	118.5 (3)
O11—C17—C18	108.8 (2)	C31—C36—C35	121.4 (2)
C17—C18—O12	113.7 (3)	C32—O31—C37	118.4 (2)
C18—O12—C19	115.4 (3)	O31—C37—C38*A*	118.2 (4)
P—C21—C22	118.0 (2)	O31—C37—C38*B*	96.2 (3)
P—C21—C26	122.8 (2)	C37—C38*A*—O32*A*	106.4 (4)
C22—C21—C26	119.1 (2)	C37—C38*B*—O32*B*	100.9 (5)
C21—C22—C23	119.9 (2)	C38*A*—O32*A*—C39*A*	112.5 (5)
C21—C22—O21	115.9 (2)	C38*B*—O32*B*—C39*B*	110.8 (6)
C23—C22—O21	124.2 (2)	O1···O2···O22	93.8
O1—P—C11—C16	−117.8	C17—C18—O12—C19	−94.2
O1—P—C21—C26	−124.6	C23—C22—O21—C27	−6.7
O1—P—C31—C36	−1.9	O21—C27—C28—O22	−76.4
C13—C12—O11—C17	19.3	C27—C28—O22—C29	−179.3
O11—C17—C18—O12	76.9		

Table 3. *Contact distances (Å)*

O1···O2	2.877 (3)	P···O11	2.899 (2)
O2···O22	3.021 (3)	P···O21	2.876 (2)
O1···O21	3.019 (2)	P···O31	3.046 (2)
O1···O11	3.005 (2)		

During solution of the structure, it became apparent that several atoms on one side chain (C38, O32 and C39) were disordered. These atoms were refined as pairs of disordered atoms with a common isotropic temperature factor for each pair of disordered atoms and with occupancies constrained to add to 1.00. During the refinement process, it was noted that the occupancies of the 'major' site for each atom had refined to the same value. Therefore occupancies of C38*A*, O32*A* and C39*A* were held equal [refined value 0.567 (3)]. Although we did not refine C37 as disordered, we did note a peak in all difference maps within 0.5 Å of C37, which suggests that this atom too is disordered. The decision to refine C37 as non-disordered may explain the unusual distances between C37 and the two images of C38.

Data collection: *P*3 *Software* (Siemens, 1989). Cell refinement: *P*3 *Software*. Data reduction: *SHELXTL-Plus* (VMS) (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (VMS). Program(s) used to refine structure: *SHELXTL-Plus* (VMS). Molecular graphics: *Chemdraw* 2.1.2. Software used to prepare material for publication: Microsoft *Word* 5.1a.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1225). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Torturing the 7-Oxabicyclo[2.2.1]heptane Skeleton with an Oxetane Ring: 4,7-Dioxatricyclo[3.2.1.0^{3,6}]octane at 190 K

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Abstract

The low-temperature phase of 4,7-dioxatricyclo-[3.2.1.0^{3,6}]octane, $C_6H_8O_2$, has been structurally characterized by X-ray diffraction at 190 K. Only minor bond differentiation is observed here compared to oxetane and 7-oxabicylo[2.2.1]heptanes.

Comment

Annulation of a molecule with small rings leads to bond-angle deformations that are sometimes accompanied by bond-length changes. A recent example is the bond alternation of the benzene unit in tris(bicyclo-[2.2.1]hexeno)benzene (Bürgi, Baldridge, Hardcastle, Frank, Gantzel, Siegel & Ziller, 1995). During our studies of the chemistry of 7-oxabicyclo[2.2.1]heptenes (Vogel, Fatton, Gasparini & le Drian, 1990; le Drian & Vogel, 1988), we found that the oxetane unit in 4,7-dioxatricyclo[3.2.1.0^{3,6}]octane derivatives was not very reactive. For the title parent diether, (1), we observed that strong acids such as CF_3SO_3H or HSO_3F in CD_2Cl_2 quantitatively protonate the ethereal function of the oxetane moiety, giving the corresponding oxetanium ion