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2,2′-Methylenebis(5,5-dimethyl-1,3,2-dioxaphosphorinane 2-oxide)

C. Scott Browning, Timothy E. Burrow, David H. Farrar* and Alan J. Lough

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1. E-mail: dfarrar@chem.utoronto.ca

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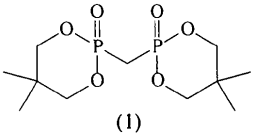
Abstract

The title compound, $C_{11}H_{22}O_6P_2$, contains two tetrahedral P^V atoms connected by a bridging methylene group. The two P═O vectors are rotated away from each other, with an O—P···P—O torsion angle of −135.1 (1)°. Each P atom is contained in a six-membered ring with two O and three C atoms. The six-membered rings are in chair conformations, with the O atom of the P═O moiety in an equatorial position.

Comment

Bisphosphonate compounds are under study by pharmaceutical companies because of their potential medical applications. Ethane-1-hydroxy-1,1-diphosphonic acid, $CH_3C(OH)(PO_3H_2)_2$ (EHDP), has been extensively studied (Francis & Centner, 1978) and the disodium salt of EHDP is currently used to treat osteoporosis (Berkow & Fletcher, 1992). While EHDP and many of its salts have been structurally studied, very few structures of the alkoxide derivatives of diphosphonic acid have been reported in the literature (Allen & Kennard, 1993). We are interested in the structural changes in bisphosphonate and related compounds upon complexation to transition metals. In order to gain more insight into the structures of uncoordinated bisphosphonate compounds, we undertook the crystal structure determination of the compound $CH_2[P(O)(OCH_2)_2C(CH_3)_2]_2$, (1).



(1)

The P^V atoms in compound (1) have slightly distorted tetrahedral geometries. In accordance with the predictions of VSEPR (valence-shell electron-pair repulsion) theory, the six angles subtended at the P atoms involving both P═O bonds are all several degrees larger than the ideal tetrahedral value and range from 111.95 (9) to 113.97 (9)° (Bader, Gillespie & MacDougall, 1988). The remaining angles are significantly less than 109.5° and vary between 105.01 (8) and 107.18 (8)°. The two P═O bonds, P1═O1 and P2═O4, are statistically equal and average 1.461 (3) Å. These values are comparable with the distances of 1.472 (6) and 1.438 (9) Å observed in the structure of $CBr_2[P(O)(OCH_3)_2]_2$ and the distance of 1.453 (3) Å reported for $CCl_2\{P(O)[OCH(CH_3)_2]_2\}_2$ (Vepsalainen, Nupponen, Pohjala, Ahlgren & Vainiotalo, 1992). The average P═O bond length in $(RO)_3P{=}O$ compounds is 1.449 (7) Å, while the average bond length in $R_3P{=}O$ compounds is 1.489 (10) Å, where *R* is a hydrocarbon group (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

The two tetrahedral P atoms are connected by a bridging methylene group (Fig. 1). The P—C11 distances are statistically equivalent and average 1.802 (5) Å. The average P—C distance in $R_3P{=}O$ compounds is 1.801 (11) Å (Allen *et al.*, 1987). The two P tetrahedra, linked by a methylene bridge, are nearly eclipsed when viewed down the P···P vector. The torsion angle O1—P1···P2—O6 is −23.0 (1)°. The two P═O groups are rotated away from each other, with an O1—P1···P2—O4 torsion angle of −135.1 (1)°.

The P1—O2 and P1—O3 distances are indistinguishable and average 1.581 (3) Å. The P2—O5 and P2—O6 distances are statistically different (5.9σ); however, both values [1.587 (1) and 1.574 (2) Å, respectively] are comparable with the average value of 1.581 (3) Å observed for P1. Each O—P—O linkage is contained within a six-membered ring and each ring is completed by three tetrahedral C atoms. The six-membered rings

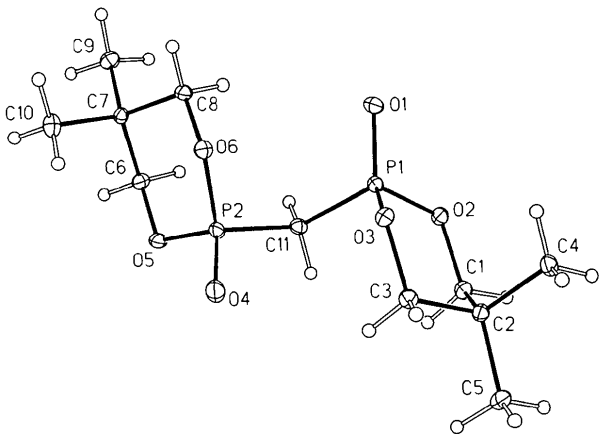


Fig. 1. View of the title molecule with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 25% probability level for non-H atoms and, for clarity, H atoms are drawn as open circles.

are in chair conformations with the O atoms of the P=O moieties in equatorial positions. The same conformation is observed in the solid-state structure of $O[P(O)(OCH_2)_2C(CH_3)_2]_2$ (Cook & White, 1976).

All remaining distances and angles in the title structure are normal (Allen *et al.*, 1987).

Experimental

Compound (1) was synthesized according to the literature method of Maier (1976) and crystals were grown from an acetone/hexanes/methanol mixture.

Crystal data

$C_{11}H_{22}O_6P_2$
M_r = 312.23
Monoclinic
$P2_1/c$
a = 6.359 (1) Å
b = 16.752 (2) Å
c = 13.653 (1) Å
β = 94.23 (1)°
V = 1450.4 (3) Å^3
Z = 4
D_x = 1.430 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 49 reflections
θ = 5.0–17.5°
μ = 0.319 mm^{-1}
T = 173 (2) K
Block
0.40 × 0.38 × 0.22 mm
Colourless

Data collection

Siemens $P4$ diffractometer
ω–2θ scans
Absorption correction: none
3651 measured reflections
3376 independent reflections
2648 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0210

θ_{max} = 27.99°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 19$
$l = -18 \rightarrow 17$
3 standard reflections monitored every 100 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R(F)$ = 0.0397
$wR(F^2)$ = 0.1027
S = 1.015
3375 reflections
193 parameters
H atoms riding, with *SHELXL*93 (Sheldrick, 1993) *AFIX*28 and *AFIX*138 constraints; C—H 0.94–0.99 Å

$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.5869P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.405 e Å^{-3}
$\Delta\rho_{min}$ = −0.282 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
P1	0.15866 (8)	0.46512 (3)	0.13954 (4)	0.01805 (13)
P2	0.28477 (8)	0.29984 (3)	0.07123 (4)	0.01967 (13)
O1	−0.0697 (2)	0.46893 (10)	0.11659 (11)	0.0274 (3)
O2	0.2638 (2)	0.55080 (8)	0.14040 (10)	0.0223 (3)
O3	0.2196 (2)	0.42970 (8)	0.24492 (10)	0.0204 (3)
O4	0.4265 (3)	0.27160 (10)	0.15269 (11)	0.0322 (4)
O5	0.3395 (2)	0.26277 (9)	−0.03080 (10)	0.0245 (3)
O6	0.0476 (2)	0.27753 (9)	0.08330 (10)	0.0210 (3)
C1	0.4729 (3)	0.56273 (12)	0.18942 (14)	0.0218 (4)
C2	0.4895 (3)	0.53009 (12)	0.29407 (14)	0.0193 (4)
C3	0.4330 (3)	0.44179 (12)	0.28914 (14)	0.0211 (4)
C4	0.3436 (3)	0.57525 (13)	0.3593 (2)	0.0267 (4)
C5	0.7188 (3)	0.53959 (14)	0.3341 (2)	0.0287 (5)
C6	0.1807 (3)	0.26538 (13)	−0.11380 (14)	0.0215 (4)
C7	−0.0298 (3)	0.23242 (12)	−0.08690 (13)	0.0183 (4)
C8	−0.1041 (3)	0.28148 (12)	−0.00226 (14)	0.0206 (4)
C9	−0.1859 (3)	0.24250 (14)	−0.1767 (2)	0.0290 (5)
C10	−0.0121 (4)	0.14450 (13)	−0.0584 (2)	0.0280 (5)
C11	0.2959 (3)	0.40665 (12)	0.05419 (14)	0.0206 (4)

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

P1—O1	1.4640 (15)	O5—C6	1.462 (2)
P1—O3	1.5780 (14)	O6—C8	1.461 (2)
P1—O2	1.5831 (15)	C1—C2	1.526 (3)
P1—C11	1.797 (2)	C2—C3	1.522 (3)
P2—O4	1.458 (2)	C2—C5	1.527 (3)
P2—O6	1.5742 (15)	C2—C4	1.532 (3)
P2—O5	1.5871 (14)	C6—C7	1.518 (3)
P2—C11	1.806 (2)	C7—C8	1.521 (3)
O2—C1	1.458 (2)	C7—C10	1.525 (3)
O3—C3	1.458 (2)	C7—C9	1.528 (3)
O1—P1—O3	112.62 (8)	C3—C2—C1	107.9 (2)
O1—P1—O2	111.95 (9)	C3—C2—C5	109.5 (2)
O3—P1—O2	105.01 (8)	C1—C2—C5	107.2 (2)
O1—P1—C11	113.97 (9)	C3—C2—C4	110.7 (2)
O3—P1—C11	106.73 (9)	C1—C2—C4	111.3 (2)
O2—P1—C11	105.90 (9)	C5—C2—C4	110.1 (2)
O4—P2—O6	112.72 (9)	O3—C3—C2	111.3 (2)
O4—P2—O5	112.30 (9)	O5—C6—C7	111.9 (2)
O6—P2—O5	105.83 (8)	C6—C7—C8	108.4 (2)
O4—P2—C11	113.07 (9)	C6—C7—C10	111.3 (2)
O6—P2—C11	107.18 (8)	C8—C7—C10	110.4 (2)
O5—P2—C11	105.15 (9)	C6—C7—C9	107.3 (2)
C1—O2—P1	119.88 (12)	C8—C7—C9	109.3 (2)
C3—O3—P1	118.94 (12)	C10—C7—C9	110.0 (2)
C6—O5—P2	119.02 (12)	O6—C8—C7	111.06 (15)
C8—O6—P2	119.14 (12)	P1—C11—P2	115.53 (11)
O2—C1—C2	112.2 (2)		

Compound (1) crystallizes in the monoclinic system and space group $P2_1/c$ was determined by the unique systematic absences ($h0l$ absent if $l = 2n + 1$, $0k0$ absent if $k = 2n + 1$).

Data collection: Siemens *P*4 software. Cell refinement: Siemens *P*4 software. Data reduction: Siemens *P*4 software. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

This research was supported by NSERC, Canada, and the University of Toronto.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1133). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Zinc–Acetic Anhydride Reduction of Pyridines

ROY L. BEDDOES, NUSRAT ARSHAD AND JOHN A. JOULE*

Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, England. E-mail: j.a.joule@man.ac.uk

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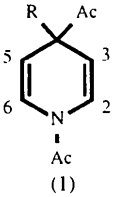
Abstract

The crystal structure determination of 1,4-diacetyl-1,4-dihydro-4-phenylpyridine, $C_{15}H_{15}NO_2$, shows the six atoms of the heterocyclic ring and the atoms of the *N*-acetyl substituent to be essentially coplanar.

Comment

There have been only two papers discussing the products of the reduction of 4-substituted pyridines with a combination of zinc and acetic anhydride (Johnson & Anthony, 1972; Atlani, Biellmann & Moron, 1973). Both reports agreed that the products, formed in moderate-to-good yields, were 1,4-dihydropyridines carrying acetyl groups at the N atom and 4 position, *i.e.* (1). Johnson & Anthony (1972) described the ^{1}H NMR signals for the protons at the 2 and 6 positions of (1) (*R* = Me) as a 'double doublet', while Atlani, Biellmann & Moron (1973) used the phrase 'two doublets'. Neither group commented on the apparent anomaly that the molecule is symmetrical about a plane through the N atom and the C atom at the 4 position yet the protons at the 2 and 6 positions are magnetically non-equivalent.



(1)

Intrigued by the possibilities for synthetic exploitation inherent within such easily accessible structures, we have repeated some of the reductions and confirmed the earlier findings, but noted that when the 4-substituent is larger than a methyl group, not only are the protons at the 2 and 6 positions non-equivalent, but that the protons at the 3 and 5 positions also resonate at different chemical shifts. In order to shed further light on this, and to confirm the 1,4-dihydropyridine structure, we have examined crystals of 1,4-diacetyl-1,4-dihydro-4-phenylpyridine, (1) (*R* = Ph).

The crystal structure of (1) (*R* = Ph) shows the six atoms of the heterocyclic ring and the atoms of the *N*-acetyl unit to be essentially coplanar. We take this

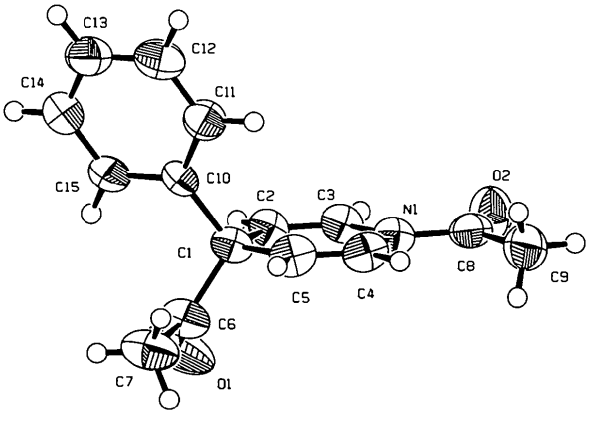


Fig. 1. *PLUTO* drawing (Motherwell & Clegg, 1978) of compound (1) (*R* = Ph), with ellipsoids plotted at the 50% probability level.