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Notes

Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

Crystal and Molecular Structure of a Novel Dioxaphosphorinane

Judith C. Gallucci and Robert R. Holmes*

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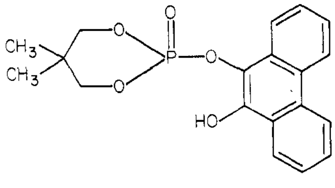
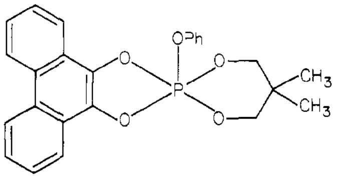
Structural studies of several 2-oxo-1,3,2-dioxaphosphorinanes have revealed the distorted chair conformation of the six-membered ring, with the equatorial positioning of the phosphoryl group.[1] An electronic effect is invoked to explain the placement of the P=O group in an equatorial site,[2] where repulsions between the π-electron density in the P—O ring bonds are reduced. We report the structural details of a new compound in this class: 2-oxo-2-(phenanthrenequinoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane (I).



I

Experimental Section

An effort to prepare the spirooxyphosphorane II according to a previous method[3] was unsuccessful. Instead, crystals corresponding to the composition of I were isolated, as subsequently established by the X-ray diffraction study. In this method, equimolar amounts of phenanthrenequinone and phenyl 2,2-dimethyl-1,3-propanediol cyclic phosphite were heated together at 115 °C for 30 min under a nitrogen atmosphere. The reaction mixture was dissolved in hot benzene. Upon cooling of the mixture, a white powdery solid formed, mp 162–164 °C (uncor) dec. The white powder slowly turned yellow upon exposure to air.



II

Crystal Data. Single crystals of $OP(O_2C_5H_{10})(O_2C_{14}H_9)$ were obtained as extremely long, thin, colorless rods by slow diffusion of pentane vapor into a toluene solution of the compound. The crystal used for data collection was a clear, rectangular plate of dimensions 0.5 × 0.2 × 0.05 mm sealed in a glass capillary.

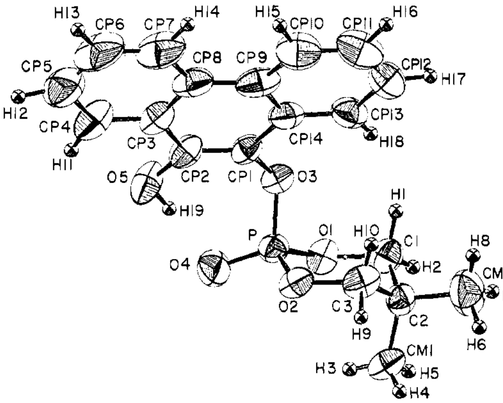


Figure 1. ORTEP plot of the $OP(O_2C_5H_{10})(O_2C_{14}H_9)$ molecule with thermal ellipsoids at the 50% probability level for nonhydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius.

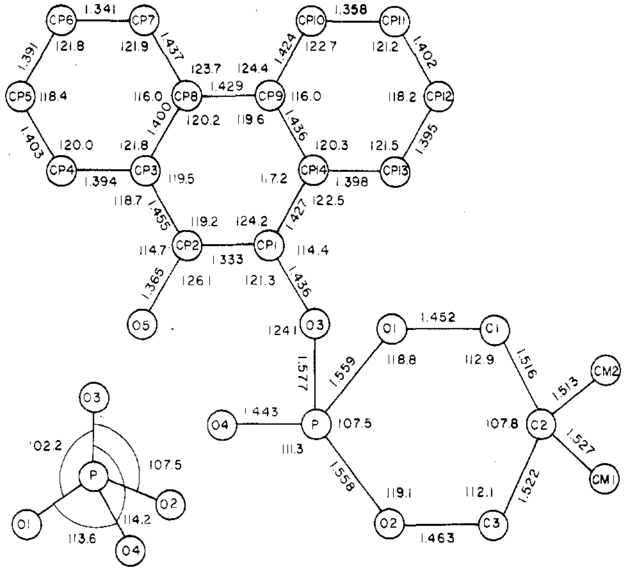


Figure 2. Schematic diagram of $OP(O_2C_5H_{10})(O_2C_{14}H_9)$ illustrating bond parameters (lengths, Å; angles, deg). Esd's either are given in Table II or are 0.006–0.013 Å and 0.5–0.9°.

Crystals of I are monoclinic, of space group $P2_1/c$ (C_{2h}^5; No. 14) with a = 21.111 (10) Å, b = 5.547 (7) Å, c = 15.551 (8) Å, β = 104.79 (4)°, Z = 4, and D_{calcd} = 1.35 g/cm^3. A total of 4034 independent reflections ($+h,+k,\pm l$) with $2° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 55°$ was measured with the use of an Enraf-Nonius CAD4 automated diffractometer, the θ–2θ scan mode, and graphite-monochromated Mo K$\bar{\alpha}$ radiation.

All 25 nonhydrogen atoms were located by direct methods (MULTAN). Anisotropic, variable-weighted, full-matrix least-squares refinement[4] of the structural parameters for all the nonhydrogen atoms and isotropic refinement of the parameters for 16 hydrogens (one methyl group was disordered and its parameters fixed) resulted in a conventional residual, R, of 0.104 and a weighted residual, R_w, of 0.076 for the 1656 reflections with $I > \sigma(I)$.

Discussion

An ORTEP plot of the molecule is shown in Figure 1. Bond lengths and angles are shown schematically in Figure 2. Atomic coordinates appear in Table I. Some selected bond

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[1] (a) Beineke, T. A. *Acta Crystallogr., Sect. B* **1969**, *B25*, 413. (b) Saenger, W.; Mikołajczyk, M. *Chem. Ber.* **1973**, *106*, 3519. (c) Geise, H. J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 362. (d) Ul-Haque, M.; Caughlan, C. N.; Moats, W. L. *J. Org. Chem.* **1970**, *35*, 1446. (e) Ul-Haque, M.; Caughlan, C. N.; Hargis, J. H.; Bentrude, W. G. *J. Chem. Soc. A* **1970**, 1786. (f) Silver, L.; Rudman, R. *Acta Crystallogr., Sect. B* **1972**, *B28*, 574. (g) Killean, R. C. G.; Lawrence, J. L.; Magennis, I. M. *Ibid.* **1971**, *B27*, 189. (h) Drew, M. G. B.; Rodgers, J. *Ibid.* **1972**, *B28*, 924.

[2] (a) Verkade, J. G. *Phosphorus Sulfur* **1976**, 251. (b) Mosbo, J. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 4659.

[3] Ramirez, F.; Nagabhushanam, M.; Smith, C. P. *Tetrahedron* **1968**, *24*, 1785.

[4] The function minimized was $\sum w(|F_o| - |F_c|)^2$. Scattering factors for all atoms were taken from "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974: Vol. IV, p 71.

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Table I. Atomic Coordinates in Crystalline $OP(O_2C_5H_{10})(O_2C_{14}H_9)$ with Standard Deviations in Parentheses

atom[a]	10^4x	10^4y	10^4z
P	3705.3 (8)	9352 (4)	6464 (1)
O_1	4282 (2)	11056 (9)	6914 (2)
O_2	3394 (2)	8405 (8)	7207 (3)
O_3	3202 (2)	11156 (8)	5869 (2)
O_4	3899 (2)	7387 (10)	5978 (3)
O_5	2876 (2)	7287 (11)	4590 (3)
C_1	4209 (3)	12610 (15)	7634 (5)
C_2	3990 (3)	11257 (12)	8355 (4)
C_3	3341 (3)	10033 (15)	7925 (5)
CM_1	4501 (4)	9383 (17)	8789 (5)
CM_2	3885 (4)	13043 (16)	9040 (5)
CP_1	2543 (3)	10523 (14)	5407 (4)
CP_2	2421 (3)	8748 (14)	4809 (4)
CP_3	1748 (3)	8290 (15)	4313 (4)
CP_4	1627 (4)	6440 (18)	3686 (5)
CP_5	984 (5)	5969 (20)	3192 (5)
CP_6	481 (5)	7420 (22)	3330 (6)
CP_7	594 (4)	9174 (20)	3944 (6)
CP_8	1243 (3)	9724 (14)	4469 (5)
CP_9	1384 (3)	11568 (15)	5133 (5)
CP_{10}	902 (4)	13045 (18)	5367 (6)
CP_{11}	1059 (4)	14858 (18)	5971 (6)
CP_{12}	1712 (4)	15340 (16)	6417 (5)
CP_{13}	2201 (3)	13927 (15)	6215 (4)
CP_{14}	2052 (3)	12028 (13)	5606 (4)

[a] Atoms are labeled to agree with Figure 1.

Table II. Selected Bond Lengths (Å) and Angles (Deg) in $OP(O_2C_5H_{10})(O_2C_{14}H_9)$ with Standard Deviations in Parentheses

	Bond Lengths		
$P-O_1$	1.559 (5)	O_1-C_1	1.452 (8)
$P-O_2$	1.558 (4)	C_1-C_2	1.516 (8)
$P-O_3$	1.577 (4)	C_2-C_3	1.522 (9)
$P-O_4$	1.443 (5)	C_3-O_2	1.463 (8)
	Bond Angles		
O_1-P-O_2	107.5 (2)	$P-O_1-C_1$	118.8 (4)
O_1-P-O_3	102.2 (3)	$O_1-C_1-C_2$	112.9 (6)
O_1-P-O_4	113.6 (3)	$C_1-C_2-C_3$	107.8 (6)
O_2-P-O_3	107.5 (2)	$C_2-C_3-O_2$	112.1 (5)
O_2-P-O_4	111.3 (3)	C_3-O_2-P	119.1 (4)
O_3-P-O_4	114.2 (3)	$P-O_3-CP_1$	124.1 (4)

lengths and angles are listed in Table II. A complete compilation of bond parameters for the nonhydrogen atoms, thermal parameters, and refined parameters for hydrogen atoms are provided as supplementary material.

In compound I the six-membered ring is in a distorted chair conformation with the P=O bond occupying an equatorial position. The chair conformation is partly flattened at the O–P–O end of the ring. The dihedral angle between planes $O_1C_1C_3O_2$ and O_1PO_2 is 32.2°. Between planes $O_1C_1C_3O_2$ and $C_1C_2C_3$ the angle is 51.6°. In the comparable cyclohexane molecule, these dihedral angles are 49.2°.[5]

This ring flattening observed in related compounds has been attributed to two factors:[1e]

1. The C–O–P ring angles are much larger than the C–C–C ring angles of cyclohexane, resulting in ring flattening at the phosphorus end. In compound I, these C–O–P angles are about 119°, as compared to the C–C–C angles of 111.5° in cyclohexane.

2. Steric interactions between the axial group bonded to phosphorus and the axial methylene hydrogens of the ring may result in a flattening of the ring at the phosphorus end. The phenanthrene quinone ring in the axial site in compound I is both large and planar. It avoids these steric interactions not only by the above ring flattening mechanism but also by a tilting of the quinone ring with respect to the $O_1C_1C_3O_2$ plane (the dihedral angle between these planes being 50°). As a result of this tilting, the shortest distance between the axial ring hydrogens and the quinone ring hydrogens is 2.5 Å, slightly larger than the sum of the van der Waals radii (2.4 Å).[6]

Perhaps the most unique feature of I is the presence of a strong intramolecular hydrogen bond between O_4 and O_5. The following distances are observed: $O_4\cdots O_5$ = 2.635 (6) Å; O_5-H_{19} = 0.82 (7) Å, $O_4\cdots H_{19}$ = 1.82 (6) Å. The $O_4-H_{19}-O_5$ angle is 176 (9)°. For O–H···O hydrogen bonds, the O···O distances fall in the range 2.5–3.5 Å while the O–H···O angles are between 140 and 180°.[7] This hydrogen bond results in the formation of a seven-membered ring, with the O_5, CP_2, CP_1 and O_3 atoms lying in a plane and the P, O_4 and H_{19} atoms lying on one side of this plane.

A short intermolecular distance of 3.26 Å is present between the O_5 atom and the C_3 atom in the symmetry-related molecule at x, $^3/_2 - y$, $z - {}^1/_2$. The $C_3-H_9\cdots O_5$ angle is 150°, with the $H_9\cdots O_5$ distance being 2.30 Å. A survey of C–H···O hydrogen bonds in crystals, where the carbon is either part of a CH, CH_2, or CH_3 group, gives the C···O distances in the range 3.00–3.24 Å, with the C–H···O angle between 102.6 and 173.3°.[8]

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Registry No. I, 74577-94-9; phenanthrene quinone, 84-11-7; phenyl 2,2-dimethyl-1,3-propanediol cyclic phosphite, 3057-08-7.

Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes, bond parameters for nonhydrogen atoms, thermal parameters, and refined hydrogen parameters for 2-oxo-2-(phenanthrenequinoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane (10 pages). Ordering information is given on any current masthead page.

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(5) Davis, M.; Hassel, O. *Acta Chem. Scand.* **1963**, *17*, 1181.

(6) Pauling, Linus. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

(7) Jeffrey, G. A.; Takagi, S. *Acc. Chem. Res.* **1978**, *11*, 264.

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Contribution from the Department of Chemistry,
National Tsing Hua University, Hsinchu, Taiwan, China

Electrosynthesis of the Metal Phthalocyanine Complexes

C. H. Yang, S. F. Lin,[1a] H. L. Chen,[1b] and C. T. Chang*

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Since their discovery in the early 1930s the metal phthalocyanine complexes (MPc) have been intensively investigated and have found industrial application as pigments and dyeing agents, owing to their intense colors, chemical inertness, and thermal stability. Because of their resemblance to the porphyrins, an understanding of the physical and chemical behavior of the MPc might provide an important clue to the biological process. The metal phthalocyanines can be prepared by various methods; however, the routes based upon phthal-

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(1) (a) Provincial Hsinchu Teachers' College, Hsinchu, Taiwan. (b) Department of Chemistry, Polytechnic Institute of New York.