The Crystal Structure of a Phosphite Ozonide, $C_2H_5C(CH_2O)_3PO_3$

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The crystal structure of $C_2H_5C(CH_2O)_3PO_3$ shows that this ozonide contains a symmetric, almost planar, four-membered PO_3 ring with two crystallographically different, but otherwise essentially equal, molecules in the asymmetric unit cell.

Generally, ozonides are salts containing the O_3^- anion[1] or the reaction products of ozone with unsaturated organic materials. In the latter case it is common to distinguish between primary ozonides having a 1,2,3-trioxacyclopentane ring and secondary ozonides with a 1,2,4-trioxacyclopentane ring. The organic ozonides are thought to be formed by a sequence of [2 + 3] addition and reversion reactions ("Criegee mechanism"), and there is abundant evidence for this mechanism.[2]

Ozone also adds across the 9,10 position of a substituted anthracene, and this "primary" ozonide is the first one that is stable enough to be characterized by a single-crystal structure determination.[3] From this it is evident, in spite of some disorder in the structure, that the O_3 molecule has simply added across the central carbon atoms of the anthracene molecule, a reaction that, at least formally, can be described as a [3 + 4] addition reaction.

There is yet another class of ozonides, the phosphite ozonides, which could be classified as inorganic covalent ozonides. They were first observed in 1961.[4] They are formed in the reaction between organic phosphites and ozone at low temperatures. There is abundant work on triphenylphosphite ozonide.[4−15] The thermal stability of some phosphite ozonides reach almost room temperature, especially if cyclic and polycyclic phosphite ozonides are considered.[16−26]

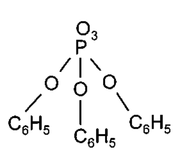
Phosphite ozonides are very convenient precursors of singlet oxygen, since they all tend to evolve singlet oxygen with simultaneous formation of the stable phosphates. These ozonides are assumed to have a four-membered, λ^5-PO_3 ring. In this context a high resolution ^{17}O NMR spectrum could be informative; however, the results are not conclusive (see below).

Of particular interest would be the detailed structure of such a phosphite ozonide. This could finally answer the questions as to whether these ozonides definitely contain a four-membered PO_3 ring, whether this ring is C_{2v} symmetric (planar and with equal bond lengths), and what is the general coordination around the five-coordinate phosphorous atom.

In the following sections we will describe the crystal structure of a well-selected phosphite ozonide to address these questions. At this point the remarkable formation of a PO_2 three-membered ring (dioxaphosphirane) from a three-valent phosphorus precursor and molecular oxygen should be noted.[27]

Results

At the beginning of this survey we had to select one of the more stable phosphite ozonides. The candidates were triphenylphosphite ozonide (**1**), 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane ozonide (**2**),[16,23] or 1-phospha-2,8,9-trioxaadamantane ozonide (**3**).[18,23] We have chosen **2** as a compromise between stability of **3** and ease of preparation of **1**. After all, the triol starting material for the preparation of **2** is commercially available and **2** is said to be stable below −15 °C. Such temperatures can easily be maintained for preparation, crystal growth, and single-crystal structure determination.



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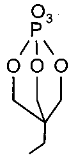
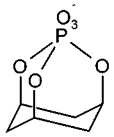


2



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The preparation of **2** followed the published procedures. Crystal growth was monitored by ^{31}P NMR spectroscopy, which readily helps to analyze the amounts of starting material phosphite, product phosphite ozonide, and phosphate as the major decomposition product. Obtaining suitable single crystals was, however, not trivial. Compound **2** of about 90% purity did not recrystallize from various solvents at all, or it formed microcrystalline powders. Single crystals were, however, obtained from CH_2Cl_2 solution.

In the first and reproducibly monoclinic crystalline modification the organic part of the molecule is at least twofold, possibly even threefold, disordered, whereas the environment around the phosphorous is reasonably well resolved. The four-membered PO_3 ring looks very much the same as in the crystallographic determination of modification 3. Therefore, and also because the criteria for a good crystal

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Table 1. Crystal and structure refinement data for **2** $[\{2C_2H_5C(CH_2O)\}_3PO_3]\cdot 3CHFCl_2$

	Modification 1	Modification 2	Modification 3
Mol. form.	$C_2H_5C(CH_2O)_3PO_3C_6H_{11}O_6P$	$C_2H_5C(CH_2O)PO_3$	$2C_2H_5C(CH_2O)_3PO_3\cdot 3CHFCl_2$
Mol. wt.	210.12	210.12	728.99
a[pm]	757.9(1)	883.2(2)	877.1(3)
b[pm]	660.7(1)	1008.3(2)	1064.5(4)
c[pm]	1706.1(2)	1009.3(2)	1543.9(6)
α[°]	90	97.189(3)	93.37(1)
β[°]	91.548(2)	104.025(4)	95.19(1)
γ[°]	90	96.797(4)	97.62(1)
Vol. [10^6 pm^3]	854.1	854.8	1419.3
Z	4	4	2
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Density, calcd. [Mg m^{-3}]			1.706
Absorption coefficient [mm^{-1}]			0.792
F(000)			740
Crystal size [mm]			0.3 × 0.3 × 0.2
Color			colorless
θmin, max [°]			1.9, 26.37
Index range			$-10 \leq h \leq 10$ $-13 \leq k \leq 13$ $-19 \leq l \leq 19$
Reflections collected/unique			13150/5772
R_{int}			0.076
Completeness to 2θ = 52.7°			99.7%
Refinement method			Full-matrix least-squares on F^2
Data/parameters			5772/343
Goodness of fit			1.025
Final *R* values [$I > 2\sigma(I)$]			$R_1 = 0.0777$, $wR_2 = 0.2114$
All data			$R_1 = 0.0925$, $wR_2 = 0.2279$
Largest difference peak, hole			0.951, $-1.007\cdot 10^{-6}$ e pm^{-3}

structure are only modestly met, we include in Table 1 only the lattice constants of this modification. In a second modification, which has been obtained only once, there was no disorder, but the crystallographic criteria are even worse than in the first modification, due to an imperfect crystal.

Acceptable results were obtained by recrystallization from $CHFCl_2$ solution. These crystals also contain solvent molecules. The crystal structure data are also summarized in Table 1 and detailed bond distances and bond lengths are collected in Table 2. The asymmetric unit of the cell contains two molecules of **2** along with three molecules of $CHFCl_2$. The two crystallographic different molecules of **2** differ significantly only in the orientation of the terminal ethyl group with respect to the PO_3 ring plane.

The coordination polyhedron around the phosphorous atoms is clearly a tetragonal pyramid (Figure 1). The O3 and O23 atoms are considered as apexes and have bond angles of 102−105° to the other four oxygen atoms bonded to phosphorous. The apical P−O bond is, as expected, the shortest of the P−O bonds. The PO_2 angles within the basal part are strongly influenced by the four-membered PO_3 ring, since the PO_2 inner-ring angle is only 78°. All other inner ring angles are slightly above 90° so that an inner-ring-angle sum of 360° is obtained, indicating near planarity of the ring. The dihedral angles of the four-membered rings are about 7°.

The distances within the four-membered ring are pairwise about equal. The O−O bond lengths of 146 pm indicate the single-bond character of these bonds, in contrast to the bond lengths of 127 pm in free ozone. The O−O bond lengths compare nicely with those in $F_3{-}O{-}O{-}O{-}CF_3$ [143.7(2) crystal, 145.2(5) gas],[28] but not so well with 9-*tert*-butyl-10-methylanthracene 9,10-ozonide [136.1(6) and 142.8(6) pm]. In the latter, however, the central oxygen atom is disordered over two symmetrically equivalent positions, and, strictly speaking, all the other atoms as well, so that the estimated standard deviations may be much larger than given. This also holds for the O−O−O bond angle of 113.3(4)°. This is found to be 106.4(1)° in $CF_3{-}O{-}O{-}O{-}CF_3$,[28] but only 92° in **2**.

The NMR spectra are inconclusive for the structure of **2**. While the ^{31}P resonance shows the expected septets due to ^{1}H-^{31}P coupling, the ^{17}O resonance of **2** made from ^{17}O enriched ozone exhibits a broad line at $\delta = 411.7$ with a shoulder at $\delta = 470.6$, which can be assigned to the phosphorous-bonded oxygen atoms of the O_3 unit and the cent-

Table 2. Selected bond lengths (pm), angles, and dihedral angles [°] of **2**

Molecule I		Molecule II	
P1−O1	160.8(2)	P2−O21	160.9(3)
P1−O2	161.8(3)	P2−O22	161.6(2)
P1−O3	157.6(3)	P2−O23	157.0(3)
P1−O4	166.7(3)	P2−O24	167.1(8)
P1−O5	167.0(3)	P2−O25	167.8(3)
O4−O6	146.2(4)	P2−O26	145.8(4)
O5−O6	146.3(4)	P2−O21	145.6(4)
O1−P1−O2	98.1(1)	O21−P2−O22	98.2(1)
O1−P1−O3	102.7(1)	O21−P2−O23	102.8(1)
O1−P1−O4	85.7(1)	O21−P2−O24	85.5(1)
O1−P1−O5	149.7(1)	O21−P2−O25	150.8(2)
O2−P1−O3	102.7(1)	O22−P2−O23	103.5(1)
O2−P1−O4	150.7(1)	O22−P2−O24	149.3(1)
O2−P1−O5	84.6(1)	O22−P2−O25	85.1(1)
O3−P1−O4	104.7(1)	O23−P2−O24	105.4(2)
O3−P1−O5	105.5(1)	O23−P2−O25	104.6(1)
O4−P1−O5	78.2(1)	O24−P2−O25	77.7(1)
P1−O4−O6	94.4(2)	P2−O24−O26	94.6(2)
P1−O5−O6	94.6(2)	P2−O25−O26	94.4(2)
O4−O6−O5	92.1(2)	O24−O26−O25	92.3(2)
O5−P1−O4−O6	6.3(2)	O25−P2−O24−O26	−7.1(2)

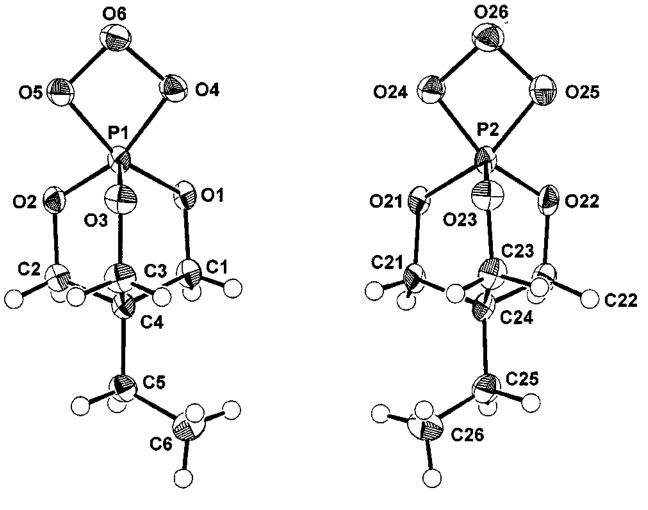

Figure 1. The crystallographically different molecules of **2**; ORTEP representation with 50% probability ellipsoids

ral oxygen atom. In $CF_3{-}O{-}O{-}O{-}CF_3$ the chemical shift values for the corresponding oxygen atoms are $\delta = 321$ and 479.[29] In ozone, extremely high shifts of $\delta = 1590$ and 1020 are observed.[30]

Experimental Section

General: All chemicals and solvents were dried prior to use and handled in a glove box and/or glass vacuum line. NMR spectra: JEOL multinuclear instrument at 400 MHz for ^1H. Spectra are recorded relative to $H_3{}^{31}PO_4$, ^{13}C-TMS, and $H_2{}^{17}O$ as external standards. Raman spectra: Bruker RPS 100 S instrument with Nd: YAG laser excitation, $\lambda = 1064$ nm. Samples were kept in glass tubes, and Raman scattering of the tubes was subtracted digitally. Crystal structures: A suitable crystal was fixed on the tip of a glass needle with the help of a special cooling device[31] and mounted on the Bruker SMART CCD 1000 TU diffractometer equipped with Mo-K_α irradiation, a graphite monochromator. The data set was measured in steps of 0.3° in ω, and 3 times 600 scans in $\psi = 0°$, 90°, and 240°, with exposure times of 10 sec/frame and a detector to crystal distance of 4.0 cm. A full shell of data up to $2\theta = 53°$ was measured. Data were reduced to intensities and corrected for background (SAINT). The structures were solved[32] and refined[33] with the SHELTL program suite.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155612. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of 4-Ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane: This compound was prepared according to the literature procedure from $CH_3CH_2C(CH_2OH)_3$ and PCl_3,[34] and recrystallized from n-pentane. M.p. 55.7 °C, ^{31}P NMR ($CDCl_3$): $\delta = 93.1$ ($^3J_{P,H}$ = 1.9 Hz). − ^1H NMR ($CDCl_3$): $\delta = 0.75$ (^3J = 7.8 Hz, CH_3), 1.11 ($CH_3{-}CH_2$), 3.92 ($^3J_{H,P}$ = 1.9 Hz, CH_2O). − ^{13}C NMR ($CDCl_3$): $\delta = 6.79$ (CH_3), 24.40 ($^4J_{C,P}$ = 5.4 Hz, $CH_3{-}CH_2$), 34.39 ($^3J_{C,P}$ = 22.1 Hz, C), 70.49 (CH_2O).

Preparation of 4-Ethyl-1-phospha-2,6,7-trioxabicyclo [2.2.2]octane Ozonide(2):[16,17] The phosphite (100 mg) was dissolved in 4 mL of CH_2Cl_2 or $CHFCl_2$ in a 10 mm-diameter glass tube. This was connected via a septum and two 1.5 mm-diameter inlet and outlet tubes of PFA (perfluoroether-tetrafluoroethylene copolymer) with an ozone generator. At −78 °C an O_3/O_2 stream was bubbled through the solution until it turned blue due to dissolved ozone at the end of the reaction. The excess of ozone and about half of the solvent were pumped out at −78 °C on the vacuum line. In the case of $CHFCl_2$ as a solvent the tube was sealed. In case of CH_2Cl_2 as a solvent, about 1 mL of $CFCl_3$ was added to the concentrated solution of the ozonide before sealing the tube. Suitable single crystals for X−ray diffraction were grown at −85 °C.

For experimental details of the crystal structures see Table 1; for numerical values of the structure see Table 2.

The purity of the samples was monitored by recording ^{31}P NMR spectra: ^{31}P NMR: $\delta = -43.1$. ($^3J_{H,P}$ = 8.9 Hz; ref.[17] −43.6). At −78 °C only the signal of the ozonide and at room temperature only those of the phosphate were present: Raman spectrum (solid), bands below 1500 cm^{-1}: $\tilde{\nu}$ = 1474(30), 1446(10), 1345(3), 1286(9), 1256(11), 1156(15), 1088(10), 1047(15), 981(4), 964(6), 905(8)*, 887(50)*, 867(25)*, 853(35), 838(4), 820(3), 792(70), 776(2), 762(8), 727(7), 671(100), 629(3), 598(3), 516(9), 488(12), 471(6), 458(25), 443(2), 409(20), 388(25), 367(4), 325(30), 307(4), 280(6), 217(4), 193(1), 160(4), 116(10) cm^{-1}. The bands marked with an asterisk are not present in the phosphite starting material or the phosphate decomposition product and are therefore assigned to the PO_3 ring vibrations.

For ^{17}O NMR measurements, the ozonide was synthesized using ozone prepared by the discharge method in a closed system[35] with oxygen enriched to 35% ^{17}O. CD_2Cl_2 (3 mL) in a 10 mm-diameter glass tube was saturated at −78 °C with the labeled ozone. An aliquot of a 0.2 M solution of the phosphite in CD_2Cl_2 was added slowly from a precooled syringe connected to a 1.5 mm-diameter inlet tube of FEP into the O_3 solution until only a pale blue color of dissolved ozone remained (typically 1−2 mL of the solution were needed). After the addition was complete, the excess ozone and part of the solvent were pumped out at −78 °C. The remaining solution was transferred into an NMR tube and the tube sealed. According to the ^{31}P NMR spectra some phosphate was always formed.

^{17}O NMR spectra were recorded at −70, −40, −20, 0 °C and at room temperature. At −70 °C two broad signals at $\delta = 470.6$ (the smaller one probably belonging to the central oxygen of the trioxaphosphetane ring of the ozonide) and at $\delta = 411.6$ (main signal, probably due to the two terminal oxygens of the trioxaphosphetane ring) were observed. Upon raising the temperature the signals broadened. At −20 °C the low-field signal was no longer observable, and the remaining signal at $\delta = 412$ had a $\Delta\nu 1/2$ value of 928 Hz.

At room temperature these signals disappeared and the signal of the labeled $P{=}^{17}O$ part of the phosphate increased: ^{17}O NMR (CD_2Cl_2): $\delta = 65.75$ (d, $^1J_{P,O} = 153$ Hz).

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