# Isolation, Characterization, and Toxicological Aspects of Volatile Organophosphorus Compounds from the Combustion of Flame-Retarded Epoxy Resins with Phosphonate Substructures

**Kathrin Kampke-Thiel, Dieter Lenoir,* Antonius Kettrup, Eberhardt Herdtweck, Dieter Gleich, and Werner R. Thiel***

**Abstract:** The thermal behavior of epoxy resins used for electronic materials as laminates and moulding compounds bearing phosphonate substructures as new fire retardants was investigated at 400, 600, and 800 °C. While the phosphorus species are converted at higher temperatures to $P_4O_{10}$, at lower temperatures a transesterification reaction occurs that results in the formation of a cyclic phosphonic ester **1** and homologues. Independent synthesis of **1** allowed the final elucidation of its molecular structure, and its spectroscopic, structural, and toxicological features.

**Keywords:** combustion · environmental chemistry · phosphorus · polymers · toxicology

## Introduction

Technical combustion processes play an important role in the industrialized world, for example in energy conversion (power plants, etc.) or in thermal waste treatment for energy recovery. In addition to these controlled processes, accidental fires give rise to the loss of human lives and economic value. Thus, combustible materials like synthetic polymers, wood, or fabrics are often treated with fire retardants for preventive fire protection. Fire retardant compounds minimize the probability of ignition and the rate of fire propagation and therefore reduce the extent of economic damage and help to save lives.[1] At present, about 650000 t of fire retardants (worth about 1200 million US$) are used worldwide,[2] mostly for protection of polymers like polyesters, polyolefins, and epoxy resins.

Electronic devices consist not only of different metallic parts but also duroplastic epoxy resins, which are either applied as laminates or as moulding compounds for the encapsulation of transistors, condensators, etc. Preventive fire protection of these materials is mostly realized by the addition of brominated aromatic compounds, such as brominated diphenyl ethers or bisphenol-A, and of $Sb_2O_3$; these exhibit a synergistic effect in the presence of halogenated fire retardants. In the event of fire, these brominated compounds liberate HBr, which quenches the reactive OH and H radicals in the radical chain reactions, but which also may destroy thermally unaffected parts owing to its corrosive nature and lead to health problems when inhaled. Additionally, these compounds are known to generate highly toxic polybrominated dibenzodioxines and furans in considerable yields when combusted.[3] Carcinogenic $Sb_2O_3$ is liberated from burning polymers as dust or aerosol, and may act as a synergist in the formation of halogenated dibenzodioxins and furans.[4] Thus, halogen-free duroplastic polymers have been developed during recent years for electronic applications. The fire retardancy of these materials is achieved with special nitrogen and phosphorus compounds, and the mechanisms responsible for their fire-retardant efficiency have been studied in detail.[5]

In contrast, few toxicological investigations of the thermal combustion products of organophosphates have been reported. $P_4O_{10}$, which is known to be produced from burning polymers containing phosphorus fire retardants,[6] is strongly hygroscopic and harms mucous membranes like other acidic compounds. Volatile tributyl and triphenyl phosphate, often used as fire retardants, inhibit the enzyme acetylcholine esterase.[7] Highly toxic combustion products of fire retardants based on organophosphates were first observed by Petajan et al., who found that 4-ethyl-1-phospha-2,6,7-trioxybicyclo[2.2.2]octan-1-oxide is formed during the combustion of a phosphorus fire-retarded polyurethane foam.[8]

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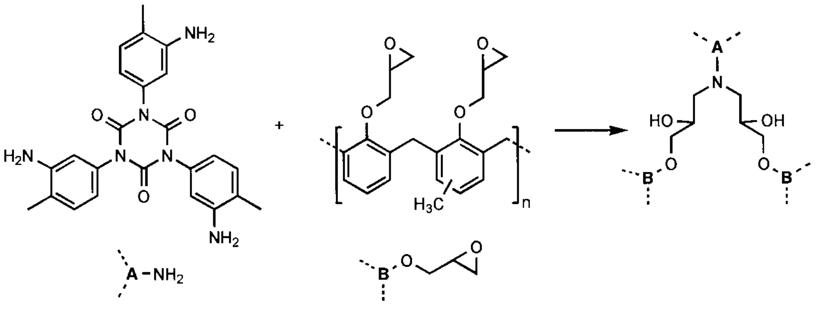
[*] Prof. Dr. D. Lenoir, K. Kampke-Thiel, Prof. Dr. A. Kettrup
Institut für Ökologische Chemie
GSF-Forschungszentrum für Umwelt und Gesundheit
Ingolstädter Landstrasse 1
D-85758 Neuherberg bei München (Germany)
Fax: (+49) 89-3187-3322
E-mail: lenoir@gsf.de

Priv.-Doz. Dr. W. R. Thiel, Dr. E. Herdtweck, D. Gleich
Anorganisch-chemisches Institut, Technische Universität München
Lichtenbergstrasse 4, D-85747 Garching bei München (Germany)
Fax: (+49) 89-2891-3473
E-mail: thiel@arthur.anorg.chemie.tu-muenchen.de

In a study on epoxy resins containing covalently fixed phosphonate substructures, we investigated the toxicological potential of these new fire retardants and of their combustion products for the first time. Herein we report the isolation, characterization and toxicological evaluation of the major volatile organophosphorus compounds formed during the combustion of these new polymeric materials.

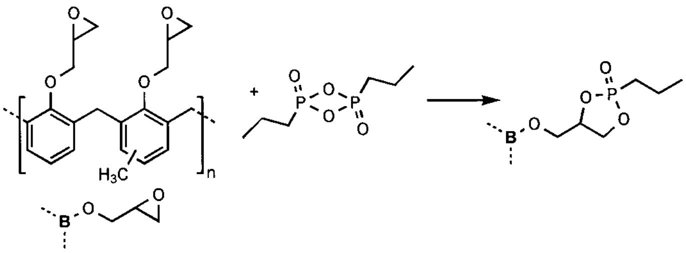
## Results and Discussion

The epoxy phenol and cresol novolak resins discussed in this work were obtained by condensation of phenol with formaldehyde, followed by partial crosslinking of the epoxide functions with trimeric (3-amino-4-methyl)phenylisocyanurate to give a three-dimensional polymer. These materials were developed by Siemens AG, Erlangen (Germany) as part of a BMBF program[9] and are now commercially available (Scheme 1).



Scheme 1. Polymer crosslinking

The efficiency of organophosphorus compounds in fire retardancy can be increased by binding them covalently to the polymer matrices. This reduces migration effects and volatility and leads to a constant fire protection for the whole lifetime of the polymer. Thus, the reactive resin component is treated with subequimolar amounts of propylphosphonic acid anhydride to give cyclic phosphonic esters. To fulfil the flammability criterium UL 94-V0, a total phosphorus mass content of about 3% is sufficient for this kind of polymeric material (Scheme 2).



Scheme 2. Introduction of the phosphonate fragment.

Three different fire situations at 400, 600, and 800 °C were simulated by using the VCI incineration apparatus (Heraeus) with synthetic air as oxygen source.[10] The volatile parts of the combustion products were adsorbed in two tubes, each loaded with 500 mg of Tenax and analyzed after elution and purification (see Experimental Section). Phosphorus mass balances were carried out with volatile components and nonvolatile residues of the combustions for a complete evaluation of the fate of phosphorus.[11]

At a combustion temperature of 800 °C, the organophosphorus compounds are completely converted into $P_4O_{10}$ and phosphoric acid. However, at a combustion temperature of 600 °C, small amounts, and at a combustion temperature of 400 °C, considerable amounts of volatile organophosphorus compounds are formed, which display $^{31}P$ NMR resonances of $\delta = 50-25$. With a combination of extraction techniques and column chromatography, non-phosphorus compounds could be separated from other combustion products, and four volatile phosphorus containing derivatives (GC/FPD) were finally enriched. GC/MS investigations gave a molecular mass of 288 for the major (> 90% by $^{31}P$ NMR spectroscopy and GC) and one of the minor compounds. The two other minor species have molecular masses of 302. The final elucidation of the molecular structure of the major compund was achieved by a combination of 1D and 2D NMR spectroscopic methods.

Surprisingly, the $^{13}C$ NMR spectrum of this compound exclusively shows resonances in the regions of $\delta = 148-122$ (aromatic carbon atoms) and $\delta = 34-15$ (aliphatic carbon atoms). There are no resonances observed that would support an aliphatic C–O fragment and would therefore be consistent with a molecular structure similar to the cyclic phosphonic acid ester of the flame-retardent component in the polymer (Scheme 2). Three of the aliphatic $^{13}C$ resonances are split into doublets ($\delta = 27.5$, $^1J_{P,C} = 143.0$ Hz; 16.1, $^2J_{P,C} = 5.8$ Hz; 15.2, $^3J_{P,C} = 17.9$ Hz); this confirms the preservation of the $PCH_2CH_2CH_3$ fragment. A fourth $^{13}C$ resonance in the aliphatic region is shifted to lower field ($\delta = 33.7$), characteristic for an aliphatic carbon atom bound to two electron-rich aromatic fragments. Corresponding resonances are observed in the $^1H$ NMR spectrum for the $PCH_2CH_2CH_3$ fragment at $\delta = 2.17$ (dt, $^2J_{P,H} = 18.2$ Hz, $^3J_{H,H} = 8.5$ Hz), 1.96 (m), and 1.16 (dt, $^3J_{H,H} = 7.3$ Hz, $^4J_{P,H} = 1.8$ Hz) and for the diastereotopic protons of a $CH_2$ group bound to two aromatic rings at $\delta = 4.33$ (dd, $^2J_{H,H} = 13.4$ Hz, $^5J_{H,H} = 2.4$ Hz) and 3.73 (d).

**Abstract in German:** *Das thermische Verhalten von Epoxidharzen mit neuartigen flammhemmenden Phosphonat-Substrukturen, die in elektronischen Bauteilen in Form von Laminaten und Gießharzen eingesetzt werden, wurde bei 400, 600 und 800 °C untersucht. Während die Phosphorverbindungen bei hohen Verbrennungstemperaturen zu $P_4O_{10}$ abgebaut werden, findet bei niedrigeren Temperaturen eine Umesterung statt, die schließlich zur Bildung des cyclischen Phosphonsäureesters **1** und einiger Homologen führt. Die unabhängige Synthese von **1** ermöglichte die Bestimmung der Molekükstruktur sowie von spektroskopischen und toxikologischen Parametern dieser neuartigen Verbindung.*

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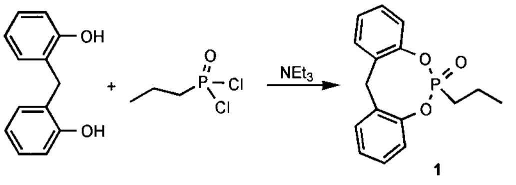
Six $^{13}C$ resonances in the region of $\delta = 148-122$ are characteristic of an asymmetrically substituted aromatic system, two of them are split into doublets due to coupling to one phosphorus atom ($\delta = 147.9$, $J_{P,C} = 10.9$ Hz; 122.4, $J_{P,C} = 3.7$ Hz). The $^1H$ NMR spectrum of the major compound, which shows resonances of four aromatic protons in the region of $\delta = 7.30-7.05$, can be assigned to an asymmetrically *ortho*-substituted aromatic system. In combination with the intensities of the $^1H$ NMR spectrum, the major compound **1** was postulated to be a cyclic ester of propylphosphonic acid and 2,2′-methylene bisphenol, probably formed by a transesterification reaction during the combustion process (Scheme 3).



Scheme 3.

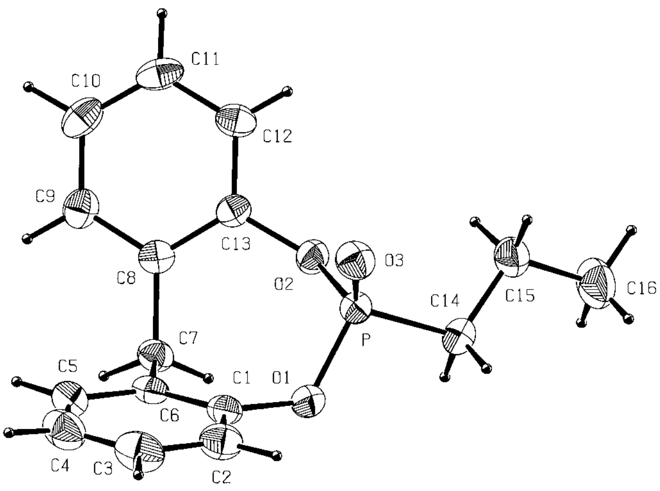


Figure 1. Solid-state structure of **1** (PLATON[12] plot). Characteristic bond lengths [Å] and angles [°]: P–O1 1.601(1), P–O2 1.587(1), P–O3 1.463(2), P–C14 1.782(2), O1–C1 1.414(2), O2–C13 1.396(2), C6–C7 1.515(3), C7–C8 1.508(3), $C_{ar}-C_{ar}$ 1.386 (av distance); O1-P-O2 106.0(1), O1-P-O3 113.8(1), O2-P-O3 114.7(1), O2-P-C14 100.1(1), O1-P-C14 101.5(1), O3-P-C14 118.9(1), P-O1-C1 120.5(1), P-O2-C13 129.9(1), C6-C7-C8 111.0(1).

The molecular structure of **1** was finally confirmed by synthesis from propylphosphonic acid dichloride and 2,2′-methylene bisphenol. The spectroscopic data and the retention times (GC) of the synthesized compound and those of the species isolated from the combustion of the polymer were found to be identical. Since we used technical grade propylphosphonic acid dichloride containing 5% of the isopropyl derivative, the corresponding isopropyl isomer of **1** was also obtained. The latter displayed the same retention times and an identical mass spectrum ($M^+ = 288$) as one of the minor combustion products. The generation of the two other minor combustion products ($M^+ = 302$) can be explained by a partial inclusion of cresol instead of phenol fragments. They bear an additional $CH_3$ group at one of the aromatic rings and show again a *n*-propyl/isopropyl ratio of 95/5.

As a result of its eight-membered ring, **1** can exist in two conformers with either the oxo or the propyl substituent occupying an axial position. Since we observed only one set of $^1H$ NMR resonances for the diastereotopic protons of the $CH_2$ unit down to −60°C, one of the conformers might be thermodynamically favored or a fast ring inversion process might take place. We therefore carried out an X-ray structure analysis of **1** and investigated its thermochemical and dynamic properties by way of molecular mechanics and semiempirical calculations.

The cyclic phosphonic acid diaryl ester **1** crystallizes from $CH_2Cl_2$/hexane 1:1 in the triclinic space group $P\bar{1}$ as large colorless bricks. The molecular structure of **1** in the solid state (Figure 1) consists of three ring systems: two aromatic six-membered rings of the 2,2′-methylene bisphenol unit and an eight-membered ring, which is formed during the condensation reaction of 2,2′-methylene bisphenol and propylphosphonic acid dichloride. A conformational analysis with PLATON[12] confirms that this ring does not adopt a crown or a twisted crown conformation, which would be typical for an eight-membered ring.[13] Due to the rigid anellated aromatic fragments (C1–C6, C8–C13), the number of possible conformers is reduced and the eight-membered ring adopts a long chair conformation.[14] This conformation, which implies local $C_s$ symmetry for the eight-membered ring, is also found in the solid-state structures of some other phosphadioxadibenzocins.[15] However, most of these compounds adopt a twisted conformation in the solid state.[16] The angle between the planes, defined by the two aromatic rings, is 108°. While the P–O3 distance of 1.46 Å is characteristic for a phosphorus–oxygen double bond, the distances between the phosphorus atom and the phenolic oxygen atoms O2 and O3 (about 1.59 Å) are typical for phosphorus–oxygen single bonds.[13, 15, 16] The formal $C_s$ symmetry of the molecule is broken in the solid state by the propyl substituent which undergoes an intramolecular contact between one proton at C15 and O2 ($d_{H-O}$ 2.60(3) Å). This interaction is responsible for slightly different distances P–O2 and P–O3 and distinct differences in the bond angles at O2 and O3. The oxo substituent at phosphorus (O1) occupies an axial (*endo*) position.

In order to compare the solid-state structure of **1** with the structure based on the NMR spectroscopic data, we calculated the energetic minima of **1** and the corresponding methyl derivative **2** in the gas phase, with the oxo substituent either in *endo* (**1a**, **2a**) or *exo* (**1b**, **2b**) position (Table 1 ).

According to the solid-state structure, the deepest minima display chair conformations and almost $C_s$-symmetrical eight-membered ring systems. In the case of **1**, different orientations of the propyl chain are responsible for a series of local minima with either total $C_s$ or $C_1$ symmetry. The global minimum **1a/1**, determined by molecular mechanics calculations, shows $C_1$ symmetry, with the oxo substituent O1 in *endo* position. The global minima of **2a, 2b** ($CH_3$ substituent at phosphorus) are completely $C_s$-symmetric. Structures obtained from molecular mechanics calculations were used as starting geometries for AM1 calculations, which resulted in slightly higher energy differences between the conformers **a** and **b**. The conformers

Table 1. Energies of formation of **1a, b** (cvff[17]) and **2a, b** (AM1[18]).

| Compound | Structure | $E$ [kcal mol$^{-1}$][a] | Symmetry ring | Symmetry global |
|---|---|---|---|---|
| **1a** | 1 | 0[b] | $C_s$ | $C_1$ |
|  | 2 | 0.1[b] | $C_s$ | $C_1$ |
|  | 3 | 0.1[b] | $C_s$ | $C_s$ |
| **1b** | 1 | 2.9[b] | $C_s$ | $C_1$ |
|  | 2 | 3.1[b] | $C_s$ | $C_s$ |
| **2a** | 1 | 0[b] | $C_s$ | $C_s$ |
|  | 1 | 0[c] | $C_s$ | $C_s$ |
| **2b** | 1 | 2.1[b] | $C_s$ | $C_s$ |
|  | 1 | 4.1[c] | $C_s$ | $C_s$ |

[a] Relative energies. [b] MM calculation. [c] AM1 calculation.

can be interconverted with barriers of about 5 kcal mol$^{-1}$. Evidently, therefore, **1** should adopt both conformations in solution.

The residues of combustions of phosphorus flame-retardant materials at 800, 600, and 400 °C and the pure incineration product **1** were investigated for their toxicolocical behavior on luminescent bacteria (microtox test[19]) and *daphnia magna STRAUS.*[20] Polymers with analogous structures, either not treated with any fire retardant or equipped with conventional halogen-based fire retardants, were used as reference materials. Both tests clearly proved that the covalently bound, phosphorus-based fire retardants do not affect any significant increase in toxicity compared to the phosphorus-free materials. However, combustion products of polymers that were treated with conventional halogen-based fire retardants give $EC_{50}$ values about 15 (at 400 °C) and 4.5 times (at 600 °C) lower than those of polymers protected with propylphosphonic acid derivatives, indicating a dramatic decrease in toxicity for the phosphorus-containing materials. At a temperature of 800 °C, the three classes of polymers (unprotected, phosphorus-protected and halogen-protected) give combustion products of almost identical toxicity.

Table 2 shows the $EC_{50}$ values (*daphnia magna*) of the propylphosphonic ester **1**, some other technically important aromatic compounds, chlorinated phenols,[9] and three esters of phosphoric acid, which are used as insecticides.[21]

Evidently, **1** shows moderate toxicity on *daphnia magna*, which is comparable to that of benzene and which is between 2 and 5 orders of magnitude lower than those of the technical phosphoric esters disulfotone, fenitrothione, and dichlorvos.

Table 2. $EC_{50}$ values of **1**, some aromatic compounds, and commercial insecticides.

| Compound | $EC_{50}$ [mg L$^{-1}$] |
|---|---|
| toluene | 470 |
| phenol | 300 |
| **1** | 18 |
| benzene | 18 |
| 2,4-dichlorophenol | 4 |
| pentachlorophenol | 0.6 |
| aniline | 0.5 |
| disulfotone | 0.055 |
| fenitrothione | 0.0002 |
| dichlorvos | 0.00006 |

## Conclusion

This work shows an important example of the concept of product-controlled protection of the environment. The thermal fate of the phosphonate substructure implied as a new flame-retardant principle in epoxy resins was investigated thoroughly, and the structural, spectroscopic, and toxicological features of the major volatile phosphorus combustion products were elucidated in detail. Our investigations clearly demonstrate that the new phosphorus-containing polymers for electronic devices discussed herein combine an excellent fire retardancy and a greatly reduced toxicity compared to conventional materials protected with bromine fire retardants.

## Experimental Section

**Combustion of the polymeric samples**: The samples were obtained as powders from Siemens AG, Erlangen. Combustions of samples of 100 mg were carried out in the VCI incineration apparatus (Heraeus), equipped with a thermocontrol unit and supplied with synthetic air as oxygen source.[10] The less volatile parts of the combustion gases partially condensated at the wall of the oven, the major share of the volatiles was adsorbed in two tubes, each loaded with 500 mg of Tenax.

**Isolation and identification of the volatile combustion products**: The compounds were eluated from the adsorbent with acetone or aqueous KOH (10 %) and the eluates were analyzed qualitatively by GC/MS (Hewlett Packard HP 5890 Series II gas chromatograph with HP 5970 Series Mass Selective Detector; HP Ultra 2 capillary column, length: 50 m, diameter 0.2 mm, film thickness 0.33 μm; carrier gas He; temperature program 60 °C, 3 min, 5 K min$^{-1}$, 280 °C, 20 min) and $^{31}$P NMR spectroscopy (Bruker DPX 400 spectrometer). Volatile phosphorus compounds were detected by GC/FPD (Carlo Erba gas chromatograph with FP detector, DB5 capillary column, length 50 m, diameter 0.2 mm, film thickness 0.33 μm, carrier gas He, temperature 60 °C, 20° min$^{-1}$, 200 °C, 2 K min$^{-1}$, 260 °C, 20 min). For a complete spectroscopic identification of the volatile organophosphorus compounds by $^{1}$H, $^{13}$C, $^{31}$P NMR spectroscopy (Bruker DPX 400 spectrometer), IR spectroscopy (Perkin-Elmer 1600 series FTIR) and mass spectrometry (Hewlett Packard HP 5970), about 100 mg of a purified fraction (see below) were used. Owing to the low concentration of these compounds in the combustion material, this was obtained by sampling the eluates of about 50 single combustions.

**Quantification of phosphorus**: For a complete quantification of phosphorus, volatile combustion products and nonvolatile residues were dissolved together with the silica wool of the oven in aqueous HF and the phosphorus content of the solution was determined by ICP/AES (recovery rate: 80 – 98 %).[22] The phosphorus content of volatile combustion products was determined by ICP/AES after eluation of the Tenax absorbents with acetone and aqueous KOH. Depending on the nature of the polymer and the combustion temperature, 10 – 80 % of the total phosphorus content was found in the volatile fraction.

**Isolation of volatile organophosphorus compounds**: Ethanolic eluates of about 50 combustions (oven temperature 400 °C) were combined, the solvent was evaporated in vacuo, the solid residue was treated with hexane (100 mL), and the resulting suspension heated to reflux for 15 min. After filtration, the organic phase was extracted with 0.1 M $K_2CO_3$ (3 × 50 mL) to remove phenolic by-products, dried over $Na_2SO_4$, and reduced to 5 mL. The organophosphorus compounds were purified by column chromatography with $SiO_2$. After eluation of colored combustion products with toluene, **1** and the other cyclic phosphonic esters were eluated with hexane/ethyl acetate (2:3). The performance of all steps was monitored by GC/FPD.

**Synthesis of 1**: The synthesis was carried out under an atmosphere of dry nitrogen with dried solvents. In a 1-L two-necked flask equipped with two dropping funnels, triethylamine (10 mL, 70 mmol) was dissolved in toluene (400 mL). 2,2′-methylene bisphenol (6.1 g, 30 mmol) and propylphosphonic acid dichloride (4.9 g, 30 mmol), both dissolved toluene/dichloromethane (1:1; 100 mL) were added simultaneously and dropwise under vigorous stirring. After 1 h of stirring at room temperature, the mixture was extracted with water (3 × 250 mL) and the organic phase was dried over $MgSO_4$. The solvent was removed in vacuo to yield a pale brown solid, which was recrystallized from dichloromethane/hexane 1:1 (6.0 g, 69 %). m.p. 89.5 °C. Elemental analysis calcd. for $C_{16}H_{17}O_3P$ (288.29): C 66.6, H 5.9, O 16.7, P 10.7, found: C 66.4, H 5.8, O 17.1, P 10.5. IR (KBr, $cm^{-1}$): $\nu =$ 3103 (s), 3077 (s), 3057 (s), 3026 (s), 2960 (s), 2948 (m), 290 w, 2871 (m), 1609 (s), 1583 (m), 1487 (vs), 1451 (s), 1410 (s), 1304 (s), 1270 (vs) ($\nu_{P=O}$), 1241 (vs), 1230 (vs), 1215 (vs) ($3 \times \nu_{C-O}$), 1178 (s), 1169 (s), 1110 (vs), 1076 (m), 1035 (m), 955 (vs), 947 (s), 924 (vs), 901 (s), 880 (m), 860 (s), 845 (s), 824 (s), 794 (m), 771 (vs), 744 (s), 732s, 715 (m), 612 (s), 600 (m), 552 (s), 539 (m), 524 (m), 489 (m), 470 (st), 442 (s), 409 (s). $^1H$ NMR (400.13 MHz, 25 °C, $CDCl_3$): $\delta = 7.30$ (dd, $^3J_{c,d} = 7.5$ Hz, $H_d$), 7.16 (t, $^3J_{a,b} = {}^3J_{b,c} = 7.5$ Hz, $H_b$), 7.08 (t, $H_c$), 7.05 (d, $H_a$), 4.33 (dd, $^2J_{g,g'} = 13.4$ Hz, $^5J_{P,g} = 2.4$ Hz, $H_g$), 3.73 (d, $H_{g'}$), 2.17 (dt, $^2J_{P,h} = 18.2$ Hz, $^3J_{h,i} = 8.5$ Hz, $H_h$), 1.96 (m, $H_i$), 1.16 (dt, $^3J_{i,k} = 7.3$ Hz, $^4J_{P,k} = 1.8$ Hz, $H_k$). $^{13}C\{^1H\}$ NMR (100.60 MHz, 25 °C, $CDCl_3$): $\delta = 147.9$ (d, $^2J_{P,f} = 10.9$ Hz, $C_f$), 132.8 (s, $C_e$), 130.2, 128.5 ($2 \times$ s, $C_b$, $C_d$), 126.0 (s, $C_c$), 122.4 (d, $^3J_{P,a} = 3.7$ Hz, $C_a$), 33.7 (s, $C_g$), 27.5 (d, $^1J_{P,h} = 143.0$ Hz, $C_h$), 16.1 (d, $^2J_{P,k} = 5.8$ Hz, $C_k$), 15.2 (d, $^3J_{P,i} = 17.9$ Hz, $C_i$). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, $CDCl_3$): $\delta = 25.1$ (s).

**Crystal structure determination of 1**: The crystal was fixed inside a Lindemann class capillary and the intensity data were obtained at 208 K with graphite-monochromated $Cu_{K\alpha}$ radiation on an Enraf Nonius CAD4 diffractometer. Preliminary positions of heavy atoms were found by direct methods (SIR92[23]), while positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with an initially isotropic least squares refinement (SHELXL93[24]) with the program system STRUX-V.[25] The hydrogen atoms were refined with individual isotropic thermal parameters. Crystal properties and experimental details of data collection and structure refinement are summarized in Table 3.[26]

Table 3. Crystal data and summary of intensity data collection and structure refinement of **1**.

| | |
|---|---|
| mol. formula | $C_{16}H_{17}O_3P$ |
| formula weight | 288.28 |
| color/shape | colorless prisms |
| crystal dimension [$mm^3$] | $0.56 \times 0.51 \times 0.51$ |
| crystal system | triclinic |
| space group | $P\bar{1}$ (no. 2) |
| $T$ [°C] | − 65 |
| $a$ [Å] | 8.1800(11) |
| $b$ [Å] | 9.2303(12) |
| $c$ [Å] | 10.4997(14) |
| $\alpha$ [°] | 109.344(7) |
| $\beta$ [°] | 103.696(8) |
| $\gamma$ [°] | 94.428(9) |
| $V$ [$Å^3$] | 716.19(17) |
| $\rho_{calcd}$ [$g\,cm^{-3}$] | 1.337 |
| $Z$ | 2 |
| $F(000)$ | 304 |
| $\mu_{calcd}$ [$cm^{-1}$] | 17.4 |
| diffractometer | Enraf-Nonius CAD4 |
| scan type | $\Theta/2\Theta$-scan |
| radiation, graphite-monochrom. | $Cu_{K\alpha}$, $\lambda = 1.54184$ Å |
| $\Theta$ range [°] | $4.7 \leq \Theta \leq 68.0$ |
| range of h, $k$, $l$ | − 9/9, − 11/10, 0/12 |
| reflections measured | 2718 |
| independent reflections | 2565 |
| refl. observed $F_0 > 2\sigma(I)$ | 2503 |
| refined parameters | 250 |
| $R$[a](all data) | 0.0402 |
| $\omega R_2$[b] (all data) | 0.1090 |
| GOF[c] | 1.133 |
| Largest features final diff. map [$e\,Å^{-3}$] | 0.48/ − 0.44 |

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $\omega R_2 = [\Sigma\omega(F_o^2 - F_c^2)^2 / \Sigma\omega F_o^4]^{1/2}$. [c] $GOF = [\Sigma\omega(F_o^2 - F_c^2)^2/(NO-NV)]^{1/2}$.

**Molecular mechanics and semiempirical calculations**: All calculations were performed on a Silicon Graphics workstation O2 R5000 with the Insight/Discover 95.0 program package. For the MD simulations (cvff force field, $T = 1000$ K, 100 ps), every 1 ps a structure was taken and minimized.

**Toxicological tests**: The tests (luminescent bacteria, *daphnia magna*) were carried out with diluted (water) ethanolic eluates of the volatile combustion products as described elsewhere.[19, 20]

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