Straightforward synthesis of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivatives containing P-N bonds

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Abstract

The *H*-phosphinate 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), a commercial compound of interest for its flame retardant properties, was successfully converted to related phosphonamidates following a recently patented one-pot method based on the oxidation of the species in the presence of a suitable aliphatic or aromatic amine under mild conditions. In this way, the compounds 6-morpholinodibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide, 6-(4-acetylpiperazino)dibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide, 6-*p*-tolylaminodibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide and 6-(methyl(phenyl)amino)dibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide, where the P-H bond is formally replaced by P-N bonds, were isolated with good yield and high purity. The characterization data were supported by the single-crystal X-ray structure determinations of 6-morpholinodibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide and 6-(methyl(phenyl)amino)dibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide.

Keywords: *H*-phosphinates, DOPO, phosphonamidates, P-N bond formation, flame retardants.

Short Communication

In 1972 Sanko Chemical Co. patented a class of cyclic organophosphorus compounds and the related process for their preparation (Saito 1972). The synthetic pathway involves a catalytic reaction between ortho-phenylphenols and PCl_3, followed by hydrolysis. The use of 2-phenylphenol as precursor allowed the isolation of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), a compound of industrial interest because of its flame retardant properties (Pack 2015). Being a *H*-phosphinate, DOPO shows two different tautomeric forms in equilibrium when it is dissolved in an opportune solvent, and due to this equilibrium the compound can act both as nucleophile or as electrophile (Stawinski and Kraszewski 2002; Montchamp 2014). The reactivity of the P-H bond gives the possibility to formally replace the hydrogen atom with several functional groups, with the production of different compounds having specific properties, but keeping the flame retardant activity both in gas and condensed phase because of the organophosphorus structure (Artner et al. 2008; Rakotomalala et al. 2010; Lee et al. 2014; Salmeia and Gaan 2015; Vasiljević et al. 2020).

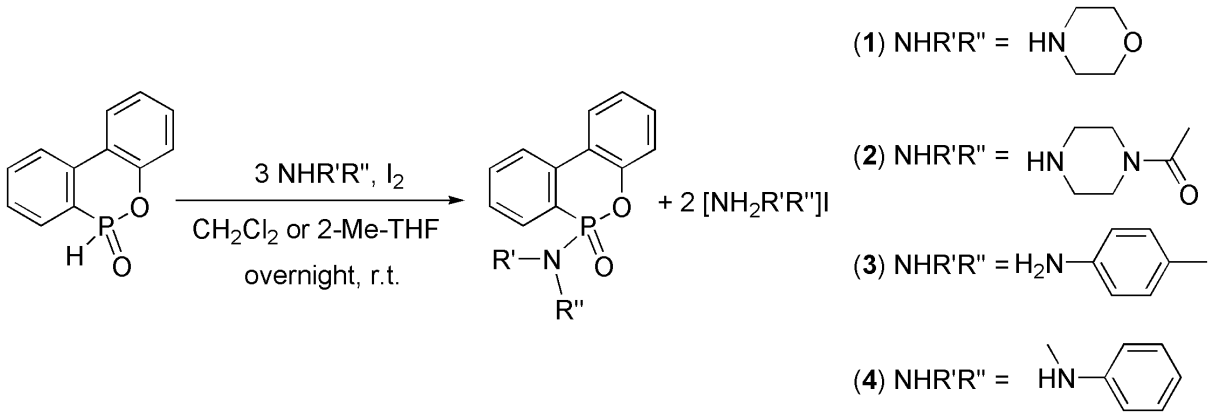
The chemical versatility and the low toxicity (Waaijers et al. 2013; Hirsch et al. 2017) make DOPO derivatives viable alternatives to halogenated flame retardants. The P-H bond can be replaced with a P-C bond through different types of reactions, based on the nucleophilic attack on electron-poor carbon atoms (White et al. 2010; Shree Meenakshi et al. 2011; Lin et al. 2014; Lin et al. 2016; Wang et al. 2019; Chen et al. 2021), on the Michael addition (Wang and Shieh 1998; Bai et al. 2013; Kishimoto and Umeki, 2013; Liu et al. 2013; Zhang et al. 2013) and on the Michaelis-Arbuzov rearrangement (Dittrich et al. 2005; Artner et al. 2007; Koenig and Kroke 2012). On the other hand, the approaches to obtain DOPO derivatives with P-N or P-O bonds are generally based on the Atherton-Todd reaction, first reported by Atherton et al. (1945), that starts with the initial deprotonation of DOPO, followed by reaction with carbon tetrachloride. The reaction found widespread application for the synthesis of DOPO derivatives (Wagner et al. 2012; Gaan et al. 2013; Buczko et al. 2014; Le Corre et al. 2014; Jian et al. 2016; Stelzig et al. 2017; Zhang et al. 2017), and the formation of the intermediate 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-chloride (DOPO-Cl) is the fundamental step allowing further substitutions with nucleophiles. The high toxicity of CCl_4 prompted to investigate alternative approaches for the preparation of DOPO-Cl, such as the use of sulfuryl chloride, trichlorocyanuric acid (Gaan et al. 2013; Neisius et al. 2014), chlorine gas (Salmeia et al. 2018a) and N-chlorosuccinimide (Salmeia et al. 2018b, 2018c).

Given our interest towards cyclic organophosphorus compounds (Bortoluzzi and Gobbo 2019; Bortoluzzi et al. 2020), recently extended to DOPO (Ferraro et al. 2023), some of us patented an alternative approach for the preparation of DOPO derivatives with P-N and P-O bonds, working under mild conditions and avoiding the use of chlorinated reactants (Agostinis et al. 2023). Herein we report the synthesis and characterization of the phosphonamidates 6-morpholinodibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide (**1**), 6-(4-acetylpiperazino)dibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide (**2**), 6-*p*-tolylaminodibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide (**3**) and 6-(methyl(phenyl)amino)dibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide (**4**). It is worth noting that alternative syntheses of **1** (Ávila-Zárraga et al. 2017) and **3** (Wu et al. 2020; Yu et al. 2022) are already present in the literature.

The reactants and solvents were Merck products, except DOPO, which was purchased from Fluorochem, and they were used all as received. The reactions are sketched in Scheme 1. In a typical preparation, DOPO (1.08 g, 5.00 mmol) was dissolved in 25 mL of dichloromethane or 2-methyltetrahydrofuran (2-Me-THF), then the proper amine (16.5 mmol) was added (morpholine, 1.44 g; 1-acetylpiperazine, 2.13 g; *p*-toluidine, 1.77 g; *N*-

methylaniline, 1.8 mL). Solid I_2 (1.26 g, 5.00 mmol) was slowly added to the stirred solution. The reaction mixture was kept under stirring overnight at room temperature. When morpholine, 1-acetylpiperazine and *p*-toluidine were used as reactants, the corresponding organic iodide salts by-products of the reaction were removed by filtration. The solvent was then evaporated under reduced pressure. To isolate compound **1**, cold ethanol (10 mL) was added, and the resulting solution was kept at -20°C until a white solid separated (about 2 hours). The product was then filtered, washed with 5 mL of cold ethanol and 5 mL of diethyl ether. The crude compound **2** was instead dissolved with boiling cyclohexane (3 x 10 mL), the hot solution was purified by filtration and the product was separated as solid after evaporation of the solvent. Compound **3** was isolated as solid by addition of diethyl ether (10 mL), collected by filtration and washed with diethyl ether (3 x 5 mL aliquots). In the case of **4**, the reaction mixture was washed with abundant water and the organic solution was dried with anhydrous Na_2SO_4. The solvent was then removed under reduced pressure and diethyl ether (10 mL) was added to separate a solid, collected by filtration. All the products were finally dried under vacuum. Elemental analysis data, obtained with an Elementar Unicube microanalyzer, and yields are summarized in Table 1.

Scheme 1 Synthesis of the phosphonamidates



The elemental analyses were in agreement with the proposed formulae. The yields resulted comprised between 93% and 62% working in dichloromethane. As observable in Table 1, the use of the greener solvent 2-methyltetrahydrofuran, while keeping intact the other experimental conditions, caused a general lowering of the yields, but the purity of the products after work-up did not change.

Table 1 Characterization data of the phosphoramidates

Compound	Formula	M_r	ω_i (calc.)/% ω_i (found)/%			Yield /% [*]
			C	H	N	
1	$C_{16}H_{16}NO_3P$	301.28	63.79	5.35	4.65	93
			63.53	5.37	4.67	(66)
2	$C_{18}H_{19}N_2O_3P$	342.33	63.15	5.59	8.18	80
			62.90	5.62	8.21	(52)
3	$C_{19}H_{16}NO_2P$	321.31	71.02	5.02	4.36	81
			70.98	5.00	4.35	(72)
4	$C_{19}H_{16}NO_2P$	321.31	71.02	5.02	4.36	62
			70.82	4.99	4.38	(40)

[*] Values in parenthesis are referred to the reactions carried out in 2-methyltetrahydrofuran.

The NMR spectra were obtained with a Bruker Avance 400 instrument operating at 400.13 MHz of ^{1}H resonance. NMR data are summarized in Table 2, while the NMR spectra are available as Supplementary data. The ^{1}H NMR spectra showed the disappearance of the DOPO P-H resonance (δ = 8.05 ppm, $^1J_{PH}$ = 592.5 Hz, $CDCl_3$, 298 K), while eight resonances related to the biphenyl fragment were always present in the aromatic region, some of them with J_{PH} couplings evidenced by the $^1H\{^{31}P\}$ NMR spectra.

The aliphatic region of the ^{1}H NMR spectrum of **1** showed two groups of resonances, the first one centred at 3.70 ppm and related to the O-bonded CH_2 fragments, while the other at lower frequency attributable to CH_2-N and characterized by a $^3J_{PH}$ coupling constant of 8.0 Hz. The spin system was resolved using simulation techniques, because it is complicated not only by the $^3J_{HH}$ and $^3J_{PH}$ couplings, but also by the lack of chemical equivalence of the N-CH_2 protons, which are diastereotopic due to the chirality on the phosphorus atom. Accordingly, a geminal coupling constant of 13.0 Hz was measured. HSQC and $^{13}C\{^1H\}$ NMR spectra helped to confirm the proposed formulae since only two resonances were detected for the morpholine fragment (δ = 67.12 and 44.04 ppm), both showing coupling with ^{31}P. The NMR characterization of **2** was similar to that of **1**, and the coupling between ^{31}P and the CH_2 fragments bonded to the {N-P} fragment was also observed for this compound. The aliphatic region of the ^{1}H NMR spectrum resulted complicated not only be the chirality of phosphorus, but also by the lack of free rotation of the N-C(O)CH_3 bond, which removes the equivalence of the two halves of the piperazine ring. Accordingly, four resonances were assigned for the piperazine carbon atoms in the 47 – 41 ppm range, all exhibiting couplings with the ^{31}P nucleus.

Table 2 NMR data of the phosphoramidates

	NMR data [**]
1	**^{1}H NMR** ($CDCl_3$, 300 K): δ 8.03 (dd, 1H, J_{HH} = 8.1 Hz, J_{PH} = 6.0 Hz, arom), 7.96 (dd, 1H, J_{HH} = 8.3 Hz, J_{HH} = 1.8 Hz, arom), 7.87 (ddd, 1H, J_{PH} = 14.4 Hz, J_{HH} = 7.7 Hz, J_{HH} = 1.4 Hz, arom), 7.71 (dddd, 1H, J_{HH} = 8.1 Hz, J_{HH} = 7.7 Hz, J_{HH} = 1.4 Hz, J_{PH} = 1.2 Hz, arom), 7.53 (tdd, 1H, J_{HH} = 7.7 Hz, J_{PH} = 3.3 Hz, J_{HH} = 1.0 Hz, arom), 7.39 (tdd, 1H, J_{HH} = 7.8 Hz, J_{HH} = 1.4 Hz, J_{PH} = 1.3 Hz, arom), 7.29 – 7.24 (m, 2H, arom), 3.70, 3.25, 3.22 (8H, A_2BCX spin system, X = ^{31}P, J_{BC} = 13.0 Hz, J_{AB} = J_{AC} = 4.4 Hz, J_{BX} = J_{CX} = 8.0 Hz, O-CH_2(A)-CH_2(B,C)-N). **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ 14.32 (s). **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K): δ 150.06 (d, J_{PC} = 7.7 Hz, arom-C_{ipso}), 137.68 (d, J_{PC} = 7.2 Hz, arom-C_{ipso}), 132.97 (d, J_{PC} = 2.5 Hz, arom-CH), 130.39 (s, arom-CH), 129.84 (d, J_{PC} = 9.0 Hz, arom-CH), 128.32 (d, J_{PC} = 14.5 Hz, arom-CH), 124.93 (d, J_{PC} = 1.0 Hz, arom-CH), 124.34 (s, arom-CH), 123.75 (d, J_{PC} = 11.6 Hz, arom-CH), 123.35 (d, J_{PC} = 167.2 Hz, arom-C_{ipso}), 121.73 (d, J_{PC} = 11.6 Hz, arom-C_{ipso}), 120.49 (d, J_{PC} = 6.3 Hz, arom-CH), 67.12 (d, J_{PC} = 5.0 Hz, O-C), 44.04 (d, J_{PC} = 1.5 Hz, N-C).
2	**^{1}H NMR** ($CDCl_3$, 300 K): δ 8.03 (dd, 1H, J_{HH} = 8.1 Hz, J_{PH} = 6.0 Hz, arom), 7.97 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.5 Hz, arom), 7.82 (ddd, 1H, J_{PH} = 14.5 Hz, J_{HH} = 7.7 Hz, J_{HH} = 1.2 Hz, arom), 7.72 (dddd, 1H, J_{HH} = 8.1 Hz, J_{HH} = 7.5 Hz, J_{HH} = 1.3 Hz, J_{PH} = 1.3 Hz, arom), 7.52 (tdd, 1H, J_{HH} = 7.5 Hz, J_{PH} = 3.2 Hz, J_{HH} = 0.9 Hz, arom), 7.39 (dddd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 8.0 Hz, J_{HH} = 1.5 Hz, J_{PH} = 1.5 Hz, arom), 7.30 – 7.22 (m, 2H, arom), 3.60 (m, 2H, N(COMe)-CH_2), 3.49 (m, 2H, N(COMe)-CH_2), 3.32 (m, 2H, N(P)-CH_2), 3.13 (m, 2H, N(P)-CH_2), 2.11 (s, 3H, C(O)CH_3). **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ 14.63 (s). **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K): δ 169.21 (s, C(O)CH_3), 149.91 (d, J_{PC} = 7.7 Hz, arom-C_{ipso}), 137.66 (d, J_{PC} = 7.3 Hz, arom-C_{ipso}), 133.16 (d, J_{PC} = 2.5 Hz, arom-CH), 130.50 (s, arom-CH), 129.76 (d, J_{PC} = 9.1 Hz, arom-CH), 128.41 (d, J_{PC} = 14.7 Hz, arom-CH), 124.98 (d, J_{PC} = 0.9 Hz, arom-CH), 124.49 (s, arom-CH), 123.85 (d, J_{PC} = 11.7 Hz, arom-CH), 123.09 (d, J_{PC} = 167.5 Hz, arom-C_{ipso}), 121.67 (d, J_{PC} = 11.7 Hz, arom-C_{ipso}), 120.45 (d, J_{PC} = 6.4 Hz, arom-CH), 46.94 (d, J_{PC} = 4.6 Hz, N(COMe)-C), 43.92 (d, J_{PC} = 18.3 Hz, N(P)-C), 43.90 (d, J_{PC} = 18.0 Hz, N(P)-C), 41.69 (d, J_{PC} = 4.6 Hz, N(COMe)-C), 21.37 (s, C(O)CH_3).
3	**^{1}H NMR** ($CDCl_3$, 300 K): δ 8.05 (dd, 1H, J_{HH} = 8.2 Hz, J_{PH} = 5.7 Hz, arom), 8.02 (dd, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.4 Hz, arom), 7.92 (dd, 1H, J_{PH} = 14.7 Hz, J_{HH} = 7.5 Hz, arom), 7.68 (t, 1H, J_{HH} = 7.7 Hz, arom), 7.47 - 7.37 (m, 2H, arom), 7.36 - 7.26 (m, 2H, arom), 6.87 (d, 2H, J_{HH} = 8.1 Hz, arom), 6.78 (s, br, 1H, NH), 6.72 (d, 2H, J_{HH} = 8.1 Hz, arom), 2.18 (s, 3H, CH_3). **^{1}H NMR** (DMSO-d_6, 300 K): δ 8.51 (d, 1H, J_{PH} = 9.1 Hz, NH), 8.26 (dd, 1H, J_{HH} = 8.2 Hz, J_{PH} = 5.9 Hz, arom), 8.24 (dd, 1H, J_{HH} = 8.1 Hz, J_{HH} = 1.5 Hz, arom), 7.81 - 7.71 (m, 2H, arom), 7.56 (td, 1H, J_{HH} = 7.6 Hz, J_{PH} = 3.3 Hz, arom), 7.47 (tdd, 1H, J_{HH} = 7.7 Hz, J_{HH} = 1.3 Hz, J_{PH} = 1.2 Hz, arom), 7.36 (t, 1H, J_{HH} = 7.7 Hz, arom), 7.31 (dd, 1H, J_{HH} = 8.1 Hz, J_{HH} = 1.2 Hz, arom), 6.93 (d, 2H, J_{HH} = 8.4 Hz, arom), 6.81 (d, 2H, J_{HH} = 8.4 Hz, arom), 2.14 (s, 3H, CH_3). **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ 9.14 (s). **^{31}P{^{1}H} NMR** (DMSO-d_6, 300 K): δ 7.92 (s). **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K): δ 149.69 (d, J_{PC} = 6.8 Hz, arom-C_{ipso}), 136.89 (d, J_{PC} = 7.0 Hz, arom-C_{ipso}), 136.47 (s, arom-C_{ipso}), 133.14 (s, arom-CH), 131.76 (s, arom-C_{ipso}), 130.44 (s, arom-CH), 130.37 (d, J_{PC} = 10.0 Hz, arom-CH), 129.66 (s, arom-CH), 128.58 (d, J_{PC} = 14.9 Hz, arom-CH), 124.99 (s, arom-CH), 124.65 (s, arom-CH), 123.78 (d, J_{PC} = 11.3 Hz, arom-CH), 123.76 (d, J_{PC} = 162.8 Hz, arom-C_{ipso}), 121.89 (d, J_{PC} = 11.6 Hz, arom-C_{ipso}), 120.81 (d, J_{PC} = 6.3 Hz, arom-CH), 118.84 (d, J_{PC} = 6.6 Hz, arom-CH), 20.55 (s, CH_3).
4	**^{1}H NMR** ($CDCl_3$, 300 K): δ 7.93 (dd, 1H, J_{HH} = 8.1 Hz, J_{PH} = 6.2 Hz, arom), 7.87 (dd, 1H, J_{HH} = 8.1 Hz, J_{HH} = 1.7 Hz, arom), 7.85 (ddd, 1H, J_{PH} = 14.5 Hz, J_{HH} = 7.6 Hz, J_{HH} = 1.4 Hz, arom), 7.61 (dddd, 1H, J_{HH} = 8.7 Hz, J_{HH} = 7.2 Hz, J_{HH} = 1.4 Hz, J_{PH} = 1.4 Hz, arom), 7.44 (tdd, 1H, J_{HH} = 7.5 Hz, J_{PH} = 3.3 Hz, J_{HH} = 1.0 Hz, arom), 7.34 (dddd, 1H, J_{HH} = 8.6 Hz, J_{HH} = 6.9 Hz, J_{HH} = 1.5 Hz, J_{PH} = 1.4 Hz, arom), 7.25 - 7.16 (m, 6H, arom), 7.05 (m, 1H, arom), 3.21 (d, 3H, J_{PH} = 9.6 Hz, CH_3). **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ 12.21 (s). **^{13}C{^{1}H} NMR** ($CDCl_3$, 300 K): δ 150.24 (d, J_{PC} = 7.7 Hz, arom-C_{ipso}), 143.41 (d, J_{PC} = 4.1 Hz, arom-C_{ipso}), 137.13 (d, J_{PC} = 6.9 Hz, arom-C_{ipso}), 132.84 (d, J_{PC} = 2.5 Hz, arom-C_{ipso}), 130.26 (s, arom-CH), 129.99 (d, J_{PC} = 9.1 Hz, arom-CH), 128.98 (s, arom-CH), 128.23 (d, J_{PC} = 14.8 Hz, arom-CH), 125.12 (s, arom-CH), 124.98 (d, J_{PC} = 3.7 Hz, arom-CH), 124.88 (s, arom-CH), 124.26 (s, arom-CH), 123.88 (d, J_{PC} = 165.0 Hz, arom-C_{ipso}), 123.59 (d, J_{PC} = 11.6 Hz, arom-CH), 121.73 (d, J_{PC} = 11.6 Hz, arom-C_{ipso}), 120.36 (d, J_{PC} = 6.6 Hz, arom-CH), 37.35 (d, J_{PC} = 5.5 Hz, CH_3).

[**] ^{1}H NMR chemical shifts referred to the partially non-deuterated fraction of the solvent, itself quoted to tetramethylsilane. ^{31}P{^{1}H} NMR resonances referred to 85% H_3PO_4 in water. ^{13}C{^{1}H} NMR resonances referred to the solvent signal, itself quoted to tetramethylsilane.

The formation of new P-N bonds was highlighted in the case of **3** by the NH resonance, falling at 8.51 ppm in DMSO-d_6 solution, with $^2J_{PH}$ coupling constant of 9.1 Hz. The assignment was confirmed by the lack of HSQC cross-peaks. Moreover, as expected for hydrogen atoms subjected to chemical exchange, the resonance resulted strongly affected by

the solvent used, and in $CDCl_3$ solution the NH signal was broad and shifted towards lower frequencies. The ^1H NMR spectra also showed signals related to the N-containing substituents in the high-frequency region, and a singlet attributable to the methyl substituent was observed, at 2.14 ppm in DMSO-d_6 and at 2.18 ppm in $CDCl_3$. The $^{13}C\{^1H\}$ NMR spectrum confirmed the formation of the desired products, being the number of CH and C_{ipso} resonances in agreement with the proposed compounds. Similar considerations were done for the NMR characterization of **4**. In this case, the most diagnostic signal is the doublet at 3.21 ppm in the ^1H NMR spectrum related to the N-bonded methyl group, showing a $^3J_{PH}$ coupling constant of 9.6 Hz and correlated to a doublet at 37.35 ppm (J_{PC} = 5.5 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. Only a single sharp signal in the range of 14.3 – 7.7 ppm was observable for all the compounds in the $^{31}P\{^1H\}$ NMR spectra.

The reactions were carried out from racemic DOPO without any chiral auxiliary, thus the phosphonamidates here described are expected to be racemic mixtures. Such a hypothesis was confirmed by the single-crystal X-ray structures of **1** and **4**, collected at 100 K (CryoStream 800) using a Bruker D8 Venture Photon II CMOS detector and Mo-Kα radiation (λ = 0.71073 Å) generated by an Incoatec Microfocus Source IμS. Crystal data and details on the structure refinement are collected in the Supplementary data. In both the crystal structures the symmetry operation -x, -y, -z is present, indicating that the crystals are centrosymmetric and thus composed by racemic mixtures. One of the enantiomers of both the compounds is shown in Fig. 1, while the other can be observed in the Supplementary Data. CCDC 2270746 and 2270747 contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

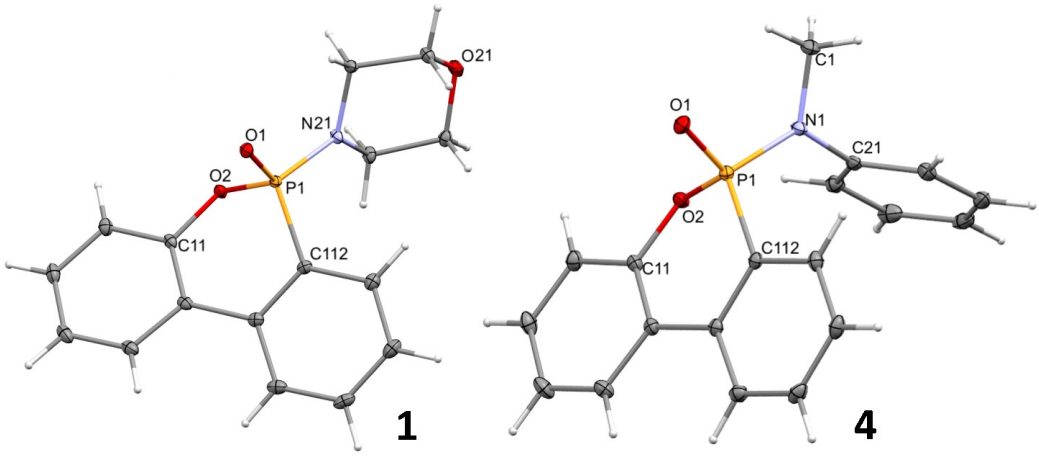


Fig. 1 ORTEP views of compounds **1** and **4** (*S* enantiomer)

Comparable data between the two compounds were obtained concerning some geometrical parameters (see the bond lengths and angles collected in Table 3), but there are important differences in the conformation of the oxaphosphaphenanthrene fragment. Both the structures contain a DOPO molecule where the phosphorus atom is bonded to a nitrogen atom from an amine group, an aspect scarcely studied in the literature from a crystallographic point of view (Keglevich et al. 2005; Ciesielski et al. 2008; Wagner et al. 2012; Weinert et al. 2018; Weinert and Döring 2021). The amine group of **1** belongs to a morpholine ring exhibiting chair conformation, while in **4** it is composed of a phenylmethyl amine fragment. Some geometrical parameters in the oxaphosphaphenanthrene oxide moiety are strictly similar to those in the free DOPO molecule (Schäfer et al. 2007). For instance, the P(1)-O(1) formal double bonds have a length of around 1.47 Å, and the formal single P(1)-C(112) bonds are around 1.78 Å. The endocyclic P(1)-O(2) bonds are around 1.61 Å long for both compounds. In both cases, they are shorter than the P(1)-C(112) bonds because of a partial delocalization of the oxygen valence electrons in the ring, although they are slightly longer than in free DOPO, 1.549(4) Å. The endocyclic C(11)-O(2)-P(1) angle goes from 117.37(7)° in **1** to 122.50(7)° in **4**. The same angle is 125.1(3)° in the free DOPO molecule, but it is 120.9(6)° in the more related diethylamino derivative (Keglevich et al. 2005). The angles around the phosphorus atom are consistent with a tetrahedral environment, being the τ_4 parameter 0.93 (Yang et al. 2007). However, the endocyclic O(2)-P(1)-C(112) angle is the most deviated from the theoretical 109.5°, with values of 100.28(5) for **1** and 101.72(5)° for **4**, even more distorted than in the free DOPO molecule, where it is 105.3(2)°. It is evident that this angle also belongs to a six-membered ring (expected 120° if planar), so the conclusion is that the ring is also highly wrapped. In fact, in **4** the heterocyclic POC_4 ring has a quasi half-chair conformation, with puckering parameters Q = 0.3485(9) Å, θ = 118.74(18)° and φ = 207.4(2)° (Cremer and Pople 1975). On the other hand, the heterocyclic POC_4 ring in **1** is highly distorted, between a half-chair or an envelope on the P atom (Pérez et al. 2012), with puckering parameters Q = 0.5186(10) Å, θ = 113.54(13)° and φ = 198.46(15)°. As a consequence, the dihedral angle between the two benzene rings of the oxaphosphaphenanthrene fragment is 20.80(6)° for **1**, but only 8.49(6)° for **4**. The related diethylamino derivative and the methyl-P-substituted DOPO (10-methyl-10*H*-9-oxa-10-phosphaphenanthrene) showed values in the middle, respectively 13.3(11)° and 13.0° (Keglevich et al. 2005; Artner et al. 2007). The sum of the angles around the nitrogen atoms is 358.3° for **1** and 359.9° for **4**, but the C-N-P angles are slightly bigger than 120°, and consequently the C-N-C angle is lower than 120°, up to 113.87(9)° for the morpholine

endocyclic angle in **1**. The supramolecular network also implies the oxaphosphaphenanthrene moiety, since the two phenyl rings are involved in a face-to-face π,π' stacking interaction, with distances between centroids of 3.8012(7) Å and a ring slippage of 1.397 Å in the case of **4**. The same distance is longer for **1**, 4.0833(8) Å, probably because of the more distorted condensed three-rings system. A picture of the intermolecular interactions is provided in the Supplementary Data.

Table 3 Selected bond lengths [Å] and angles [°] for **1** and **4**

1		**4**	
P(1)-O(1)	1.4758(8)	P(1)-O(1)	1.4727(9)
P(1)-O(2)	1.6155(8)	P(1)-O(2)	1.6063(9)
P(1)-N(21)	1.6255(9)	P(1)-N(1)	1.6368(10)
P(1)-C(112)	1.7779(11)	P(1)-C(112)	1.7768(12)
O(2)-C(11)	1.3965(12)	O(2)-C(11)	1.3955(13)
N(21)-C(21)	1.4692(13)	N(1)-C(1)	1.4726(15)
N(21)-C(24)	1.4657(13)	N(1)-C(21)	1.4396(15)
O(1)-P(1)-O(2)	113.46(5)	O(1)-P(1)-O(2)	113.24(5)
O(1)-P(1)-N(21)	112.98(5)	O(1)-P(1)-N(1)	111.52(5)
O(2)-P(1)-N(21)	104.75(5)	O(2)-P(1)-N(1)	104.07(5)
O(1)-P(1)-C(112)	115.34(5)	O(1)-P(1)-C(112)	115.58(5)
O(2)-P(1)-C(112)	100.28(5)	O(2)-P(1)-C(112)	101.72(5)
N(21)-P(1)-C(112)	108.83(6)	N(1)-P(1)-C(112)	109.73(5)
C(11)-O(2)-P(1)	117.37(7)	C(11)-O(2)-P(1)	122.50(7)
C(24)-N(21)-C(21)	113.85(7)	C(21)-N(1)-C(1)	115.69(9)
C(24)-N(21)-P(1)	121.85(7)	C(21)-N(1)-P(1)	123.16(8)
C(21)-N(21)-P(1)	122.57(7)	C(1)-N(1)-P(1)	121.10(8)

To conclude, in this communication we reported the straightforward synthesis of four phosphonamidates starting from DOPO, operating under mild conditions and avoiding the use of chlorinated reactants. The products are also isolated using a green solvent such as 2-methyltetrahydrofuran. Considering the synergistic effects in the flame retardant behaviour that can occur on mixing or reacting phosphorus- and nitrogen-based compounds (Leu and Wang 2004; Li et al. 2005; Gaan et al. 2008; Nguyen and Kim 2008; Neisius et al. 2013; Bauer et al. 2017; Sykam et al. 2019), the one-pot conversion of DOPO to related phosphonamidates appears of interest for the development of flame retardants with improved features.

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Supplementary data

Electronic Supplementary Material associated with this article can be found in the online version of this paper (DOI: xxxxxxxxxx).

Conflict of interest statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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