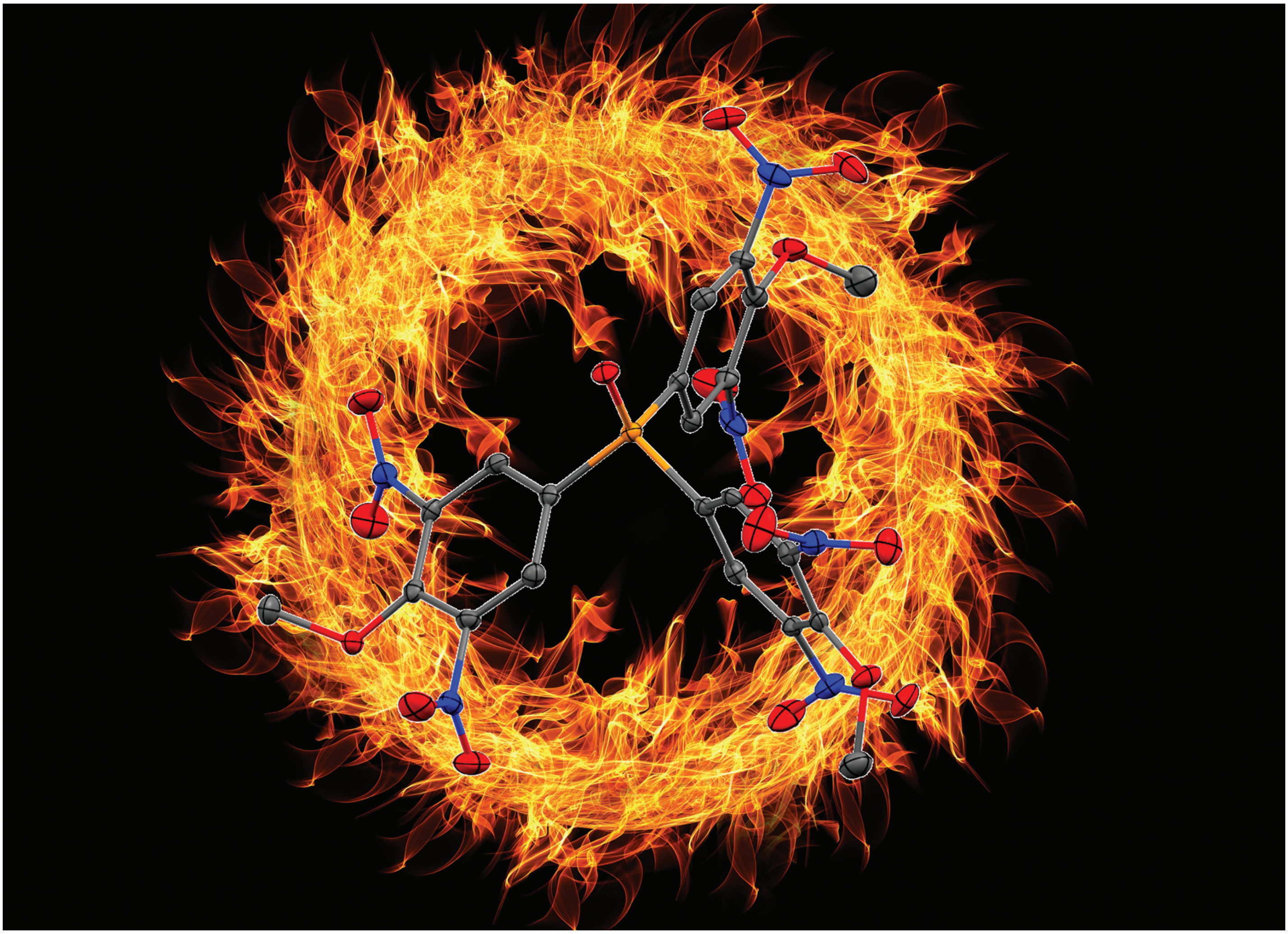

Showcasing research from Professor Guillaume Bélanger-Chabot's laboratory, Department of Chemistry, Laval University, Québec, Canada.

Nitrated triarylphosphine oxides: accessible triarylphosphoryl molecules with up to six nitro groups

This work displays that a range of tris(nitroaryl)phosphine oxides can be synthesized in a straightforward manner. The compounds are thermally quite stable, with decomposition temperatures above 240 °C. Two tris(methoxydinitrophenyl)phosphine oxide isomers, in particular, possess an unusually large nitro content for main-group compounds and could be relevant as a novel analogue of DNAN, an insensitive explosive.

Acknowledgement: Ring by geralt *via* Pixabay.

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Nitrated triarylphosphine oxides: accessible triarylphosphoryl molecules with up to six nitro groups†

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Few nitroaryl-substituted phosphoryl compounds have ever been reported. They are appealing as precursors towards "electron-poor" phosphorus(III) and (V) compounds. In this contribution, we show that these compounds can be prepared using standard nitrating procedures on commercially available substrates. Indeed, we report several examples of fully characterized, unprecedented tris(dinitro)arylphosphine oxides.

Nitro groups typically bring about noteworthy properties in compounds that bear them. The nitro group is among the most electron-withdrawing of common aryl substituents, with a Hammett constant of *ca* +0.7.[1] This makes polynitro compounds unusually acidic (picric acid and trinitromethane, for example, are strong water-soluble acids).[2,3] The oxidizing character of the nitro group also makes it a very common explosophore. Indeed, one finds nitro groups in a large proportion of organic energetic materials. While they are very common substituents in organic substances, they are much less common in heavier main-group element molecules. This is in part because classical nitration methods require harsh acidic conditions that may destroy bonds in the substrates of interest. Still, the interesting properties displayed by organic nitro compounds can reasonably be expected to extend to main-group species. Because of that, our group is interested in extending the introduction of the nitro functionality to main-group substrates, notably those of phosphorus.

An obvious starting point for such an endeavour is the family of triarylphosphoryl compounds, as one can envisage simple nitration reactions on triarylphosphine or triarylphosphoryl compounds. As we shall see, direct nitration of arylphosphorus substrates has seen limited exploration. Representative work in the field is summarized in Fig. 1. Several reports invoke nitroaryl-phosphorus[4] compounds, many in the form of arylphosphonic acids (Fig. 1a).[5,6] The most extensive work has been done by Schiemenz *et al.* in the 60s through the 80s. It covered several synthetic methods towards nitroaryl-phosphorus compounds, which were characterized by vibrational and NMR spectroscopy.[7–11] Their synthesis most related to the following discussion is that of tris(*m*-nitro-aryl)phosphine oxide, which is, to our knowledge, the most nitro-substituted homoleptic triarylphosphine oxide to be fully characterized(Fig. 1b [11,12]). A few reports claim the synthesis of several nitrated triarylphosphoryl species, including tris(dinitroaryl)phosphoryl derivatives, but with limited spectroscopic and no structural data to support their existence.[13–17] Others indicate interesting reactivities[18–24] involving nucleophilic aromatic substitutions by phosphorus(III) substrates,

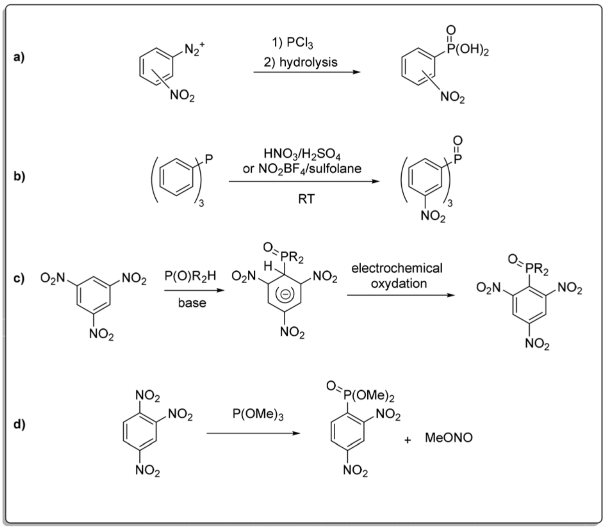

Fig. 1 Selected representative examples of previous work on (nitroaryl) phosphoryl compounds.

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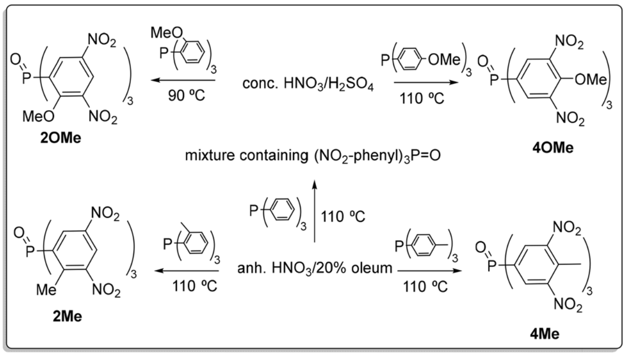
yielding phosphoryl compounds bearing one polynitroaryl substituent (Fig. 1c [21] and Fig. 1d [23,24]).

Still, a broad survey indicates that relatively few nitroaryl-phosphoryl compounds are known, and no tris(polynitroaryl) phosphorus compound has ever been conclusively identified. To our knowledge, only three structurally-characterized (nitroaryl)-substituted phosphorus compounds of the type Ar$_3$P═O can be found on the CCDC database,[12,25,26] and only one of them bears three nitroaryl groups. We wondered whether this scarcity was indicative of the sensitivity, the explosiveness or of the high reactivity of this family of compounds. Moreover, we wondered if tris(*poly*nitroaryl)phosphoryl compounds could be accessed without resorting to extremely harsh conditions (anhydrous H$_2$O$_2$, for example) or multi-step protocols.[27] These compounds would be important starting points for developing novel main-group energetic materials and study new families of optoelectronic and electrochemically active phosphorus-based compounds.[28–31] Herein, we report on the successful synthesis of six tris(nitroaryl)phosphine oxides, including four unprecedented tris(dinitroaryl) phosphine oxides *via* classical nitration conditions.

Tris(*m*-nitrophenyl)phosphine oxide has been made at ambient temperature by treatment of triphenylphosphine with nitrating acids.[12] We wondered whether more vigorous nitration at elevated temperature (*ca.* 90–140 °C) would result in polynitrations, as suggested by Stachlewska-Wroblowa and Okon from a few claimed tris(dinitroaryl)phosphoryl compounds.[13–17] Unfortunately, only a mixture of species was obtained, with only HRMS evidence for tris(mononitroaryl) phosphoryl isomers as major species, even when anhydrous HNO$_3$/oleum was used as the nitrating mixture (Scheme 1). Although we obtained some HRMS evidence for trace amounts of polynitrated rings, it was not possible to isolate these species, nor favour their formation to a meaningful extent.

We therefore turned to more activating ring substituents. To our delight, the nitration of *o*-tolyl-, *o*-methoxy-, *p*-tolyl- and *p*-methoxy-substituted triarylphosphines yielded species with the expected HRMS signals for tris(dinitroaryl)phosphine oxides (Scheme 1). ^{31}P NMR spectra were consistent with all the compounds bearing the expected phosphoryl (P═O) moiety, with chemical shifts of 16.5 to 33 ppm. ^{1}H NMR supported the isomer assignment depicted in Scheme 1, which is also in line with the expected directing group patterns (see ESI†), where the nitro groups are in *meta* to the phosphoryl group. For compounds soluble enough to yield a strong enough signal, ^{14}N NMR spectra displayed a resonance at *ca* −15 ppm, in the expected region for nitro compounds. IR and Raman spectroscopy indicated the appearance of characteristic new bands at *ca.* 1530 and 1345 cm^{-1}, in the expected range for the asymmetric and symmetric nitro O–N–O stretching modes, respectively. Finally, crystals suitable for X-ray diffraction analysis confirmed our assignment for **2Me** and **4OMe** (Fig. 2 and 3) and, by extension, our assignments for all other compounds. Proof of connectivity was also obtained for **2OMe** and **4Me** *via* X-ray diffraction structural data (see ESI†).

Compounds **4OMe** and **2OMe** could be obtained in *ca.* 40% yield after purification. The nitration reaction is selective, and ^{31}P NMR analyses of the crude mixtures indicate that the isolated compounds are the ones almost exclusively formed. Nitration reactions to form **4Me** and **2Me** were less selective, and at least two major species were formed. Meaningful conversions required harsher anhydrous nitric acid/oleum nitrating conditions. **2Me** could still be isolated in 20% yield, while clean **4Me** could only be observed in solution and in the solid state (see ESI†). When treated under conditions similar to those in Scheme 1, tris(*m*-methoxyphenyl)phosphine led to at least three species, which included tris(dinitroaryl)phosphoryl species, as suggested by HRMS. Similar attempts on tris(*m*-tolyl)phosphine led to the formation of many species as observed by ^{31}P NMR. This lack of selectivity is unsurprising, since all directing groups are favoring electrophilic attacks at



Scheme 1 Successful syntheses of tris(dinitroaryl)phosphoryl compounds.

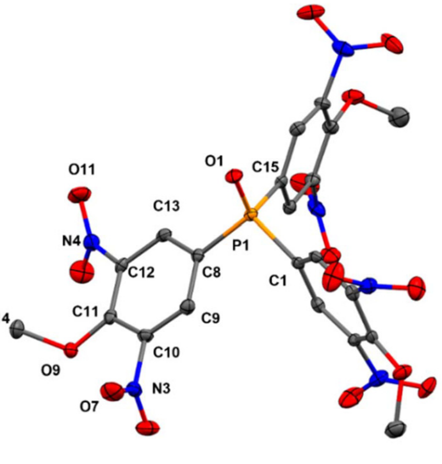


Fig. 2 Solid-state structure of **4OMe**. The asymmetric unit is composed of two molecules, only one of which is displayed for clarity. The other molecule displays a two-part disorder in which one nitro group is found in two orientations (see ESI†). Hydrogen atoms were omitted for clarity. Selected parameters: bond distances (Å) O1–P1 1.479(1), P1–C8 1.813(2), P1–C1 1.811(3), C15–P1 1.813(2); bond angles (°) C8–P1–C1 103.6(1), C1–P1–C15 108.2(1), C15–P1–C8 105.3(1); torsion angles (°) O7–N3–C10–C9 76.0(3), C14–O9–C11–C10 138.8(2), O11–N4–C12–C13 44.2(3).

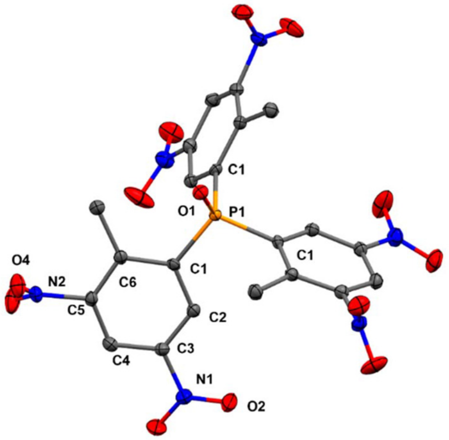
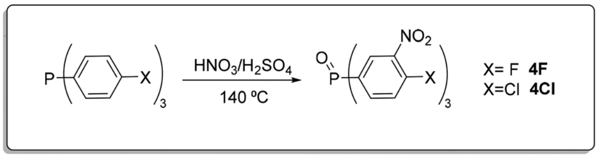


Fig. 3 Solid-state structure of **2Me**. The asymmetric unit is composed of 1/3 of the molecule. The compound crystallizes with one (disordered) dichloromethane molecule per $Ar_3P{=}O$ molecule (not shown, see ESI†). Hydrogen atoms were omitted for clarity. Selected parameters: bond distances (Å) P1–C1 1.820(3), P1–O1 1.488(4); bond angles (°) C1–P1–C1 105.4(1); torsion angles (°) O2–N1–C3–C2 11.3(5), O4–N2–C5–C6 −61.1(5).

different positions. So far, we have been unable to isolate nitration products for these last two substrates.

To verify whether halogens would have a significant deactivating effect, we attempted the nitration of *p*-fluoro- and *p*-chlorophenyl-substituted triarylphosphines. Even with anhydrous HNO_3/oleum as the nitrating agent, no evidence for polynitration could be obtained. Still, the tris(4-halo-3-nitrophenyl)phosphine oxides **4F** and **4Cl** were formed as major compounds and could be isolated in 54 and 33% yields, respectively (Scheme 2). Proof-of-connectivity structural data could be obtained for **4Cl**, thus indirectly confirming that of **4F** (see ESI†).

All compounds can be stored indefinitely at room temperature and show no sign of sensitivity to air or moisture. The two nitro groups per ring in **2Me**, **2OMe**, **4Me** and **4OMe** evoke, rightfully so, a potentially explosive behaviour. Indeed, compounds **2OMe** and **4OMe** are related to DNAN (2,4-dinitroanisole), which finds applications as a low-sensitivity explosive. None of the compounds exhibited signs of shock and friction sensitivity and no incident occurred through the course of this study (see safety disclaimer in ESI nonetheless†). Differential thermal analyses, however, showed decomposition exotherms between 250 and 330 °C for all the compounds in this study. In contrast, $Ph_3P{=}O$ melts at *ca.* 150 °C but shows no decomposition exotherm under the same conditions. Only **4OMe** displayed a sharp and intense exotherm resembling that of an explosive decomposition, with an onset at *ca.* 250 °C. The decomposition onset for compounds **4F**, **2Me**, **4Me** and **2OMe** overlaps with or follows a (melting) endotherm. The rather high thermal stability of the compounds will warrant future work towards potential applications as energetic materials.



Scheme 2 Synthesis of tris(nitro-haloaryl)phosphoryl compounds.

Compounds **4OMe** and **2Me** are the first instance of structurally characterized (polynitroaryl)phosphine oxides. Compound **4OMe** (Fig. 2) crystallizes in space group $P\bar{1}$ with $Z = 4$. The asymmetric unit is composed of two independent molecules differing mostly by the orientation of the OMe and NO_2 functional groups with respect to their respective aryl planes. In the unit cell, the molecules form alternating “layers” (approximately parallel to the bc plane) of Ar_3PO with the P═O groups all pointing up or down (roughly along or opposite to the *a*-axis), with no clear π-stacking between the aryl rings (see ESI†).

The structure of the rings in **4OMe** is comparable to that in tris(*p*-methoxyphenyl)phosphine oxide ($(anis)_3P{=}O$)[32,33] and 2,6-dinitroanisole.[34] Carbon–carbon bond distances range between 1.374(3) and 1.412(3) Å (1.344(9) to 1.42(1) Å in 2,6-dinitroanisole, 1.380(2) to 1.408(2) Å in $(anis)_3P{=}O$). C–N bond distances range between 1.468(3) and 1.480(3) Å (1.454(9) and 1.50(1) Å in 2,6-dinitroanisole). P–C bond lengths range between 1.809(2) and 1.813(2) Å (1.796(1) to 1.805(1) Å for $(anis)_3P{=}O$). C–P–C bond angles range between 103.6(1) and 108.2(1)° (105.14(6) 107.72(6)° in $(anis)_3P{=}O$). P–O bond lengths range between 1.479(1) and 1.481(1) Å and are slightly shorter than those in $(anis)_3P{=}O$ (1.492(1) and 1.494(1) Å). The conformation of the OMe and nitro groups are also comparable to that in 2,6-dinitroanisole. The methoxy group is often almost perpendicular to the plane of the aryl ring, while nitro group ONO planes make an angle of *ca.* 35 to 78° with their respective aryl plane. This is in expectedly stark contrast with the conformation of the methoxy groups in $(anis)_3P{=}O$, in which the methoxy groups are all virtually in-plane with the aryl rings.

Compound **2Me** (Fig. 3) crystallizes in space group *P*31*c* with $Z = 2$. The P═O axis of the molecule lies on a three-fold rotation axis. The compound co-crystallized with one dichloromethane molecule. In the unit cell, all the P═O bonds point in the same direction along the *c*-axis, with no clear π-stacking between the aryl rings of the neighbouring $Ar_3P{=}O$ molecules (see ESI†). The compound is again comparable to both tris(*p*-tolyl)phosphine oxide ($tol_3P{=}O$)[35] and 2,4-dinitrotoluene.[36,37] C–P–C bond angles are 105.4(3)° (105.1(1) to 107.0(1) for $tol_3P{=}O$). The P–O bond length is 1.488(4) Å (1.477(2) Å in $tol_3P{=}O$). The P–C bond lengths are 1.820(3) Å (1.811(2) to 1.820(3) Å in $tol_3P{=}O$). The nitro group in *para* to the methyl group is nearly in-plane with the aryl ring (*ca.* 13°) and the nitro group in *ortho* to the methyl group is out-of-plane with the aryl ring (*ca.* 60°), qualitatively similar to what is found in 2,4-dinitrotoluene.

In conclusion, we have shown that traditional nitrating conditions could successfully yield several tris(nitroaryl)phosphine oxides and, most interestingly, several tris(dinitroaryl) phosphine oxides. They are all quite thermally stable, opening the way for further studies. Because nitro groups are an uncommon tuning handle for arylphosphoryl-based ligands, this paves the way for coordination studies, where the unusual combination of somewhat sterically crowding, yet highly electron-withdrawing character of the nitro substituent are expected to provide some of the "exotic" properties sought through this study. Moreover, the large amount of electron accepting nitro groups (which can theoretically accept up to seven electrons per molecule in tris(dinitroaryl)phosphoryl compounds) make the synthons appealing for electrochemical studies, as both phosphoryl[28] and dinitroarenes have been shown to be promising electron acceptors in electrochemical storage systems.[29] We are currently exploring those avenues and the use of the reported compounds as precursors to other exciting (polynitroaryl)phosphorus species.

Conflicts of interest

There are no conflicts to declare.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its ESI.† Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 2451556–2451560.†

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