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Substituent effects on the ³¹P NMR chemical shifts of arylphosphorothionates

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Abstract—Six tris(aryloxy)phosphorothionates substituted in the *para* position of the aromatic rings were synthesized and studied by ³¹P NMR, X-ray diffraction techniques and ab initio calculations at a RHF/6-31G** level of theory, in order to find the main structural factors associated with the δ^{31} P in these compounds. As the electron-withdrawing (EW) ability of the substituents was increased, an 'abnormal' shielding effect on δ^{31} P of the arylphosphorothionates was observed. The analyses of the geometrical properties obtained through both experimental and theoretical methods showed that a propeller-type conformation is preferred for the arylphosphorothionates, except in the case of the tris(*O*-4-methylphenyl)phosphorothionate, since one of the aromatic rings is not rotated in the same direction as the other two in the solid state. The main features associated with the δ^{31} P NMR of compounds **1–6** were a decrease of the averaged O–P–O angle and mainly the shortening of the P=S bond length, which is consistent with an increase of the thiophosphoryl bond order as δ^{31} P values go upfield. On the other hand, comparison of the experimental and calculated bond lengths and bond angles involving α bonded atoms to phosphorus of the six compounds suggested that stereoelectronic interactions of the type n_{π} O- σ^*_{P-OAr} and n_{π} S- σ^*_{P-OAr} could be present in the arylphosphorothionates **1–6**.

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1. Introduction

During the last three decades, numerous groups have been interested in understanding the factors that contribute to the δ^{31} P chemical shift of organophosphorus compounds.¹ In this context, many correlations between chemical shifts and molecular structure have been performed.² Among them one of the most known is the relationship found by Gorenstein between the ³¹P NMR chemical shift of cyclic and acyclic phosphate esters and OPO bond angles.^{2a} In the case of organic phosphorus compounds with aromatic rings,

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the effect that an electron withdrawing (EW) or electron releasing (ER) group in the *para* position of the ring has on the ³¹P chemical shift, seems related to the type of phosphorylated function present in the molecule and/or to the electronegativity of the α -atoms directly linked to phosphorus.²ⁱ However, these two factors cannot always be separated so as to understand their behavior. For instance, it has been reported that an increase in the EW power of the *para* substituent causes a deshielding of the ³¹P signal in *N*-aryltriphenylphospha- λ^5 -azenes^{2m} and *O*-aryl diethylphosphinates,^{2e} whereas the opposite behavior is observed in aryldihexylphosphates.^{2j}

In spite of their commercial importance, few reports dealing with the correlation between ³¹P chemical shift and the structure of thiophosphoryl compounds have appeared.³ For instance, the phosphorothionates have been applied worldwide as insecticides⁴ but also as motor and transmission oil additive, plasticizer, antioxidant⁵ and lubricant of magnetic

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recording materials.⁶ Reported in this work is the study of the electronic effect that EW and ER groups exert on the ³¹P chemical shift of the arylphosphorothionates shown in Figure 1. The δ^{31} P of the six compounds are correlated with the Hammett constants (σ_p) within the context of LFER theory.⁷ We analyzed thoroughly the experimental and theoretical structural parameters obtained through X-ray diffraction techniques of the resulting crystalline compounds and from the ab initio calculations of the complete series in order to find the principal structural features that determine the δ^{31} P of arylphosphorothionates.



Figure 1.

2. Results

The synthesis of arylphosphorothionates has been described before by several authors.^{5,6,8} Treatment of thiophosphoryl chloride with 3 equiv of the corresponding substituted phenol is a one-step synthetic route to prepare triaryl phosphorothionates. However, phase transfer catalysts are needed due to the low reactivity of PSCl₃ with phenols, even under forcing conditions.^{8c} In this work, the synthesis of arylphosphorothionates **1–6** was accomplished as summarized in Scheme 1. The use of THF as solvent in the first step of the synthesis contributes to increase the solubility of the corresponding phosphites, making easier its extraction (by filtration) from the triethylammonium chloride, produced during the reaction. Then, the phosphites were reacted with sulfur in toluene under reflux to produce the corresponding arylphosphorothionates. The desired products were purified from the crude of the reaction by chromatographic column.

PCl₃ + 3HOAr
$$\xrightarrow{\text{THF}}_{\text{Et}_3\text{N}}$$
 P(OAr)₃ $\xrightarrow{\text{S}_8}_{\text{toluene}}$ S=P(OAr)₃

Scheme 1.

The structures of the synthesized compounds were confirmed from the ³¹P, ¹H, ¹³C NMR spectra and EI mass spectrometry. The ³¹P chemical shifts of the six arylphosphorothionates are given in Table 1. Homogeneous solutions with the same concentration (0.03 mol L⁻¹) of compounds **1–6** were prepared, and their corresponding ³¹P NMR spectra were acquired in CDCl₃ at 25 °C. The reproducibility of the ³¹P chemical shifts was evaluated through repeated measurements under similar conditions, and resulted better than ±0.01 ppm. The effect of the concentration on ³¹P chemical shift was measured for compound **5**. Only a small shielding of the signal (0.042 ppm) was observed when the concentration was increased from 0.03 to 0.14 mol L⁻¹.

Table 1. ³¹P chemical shifts of *p*-X-arylphosphorothionates 1–6

Compound	1	2	3	4	5	6
δ^{31} P (ppm)	56.56	54.92	53.71	53.81	50.47	50.09

Five of the six compounds were solids, only tris(O-4-methoxyphenyl)phosphorothionate (compound 1) resulted a colorless oil. We were able to get crystals with quality enough for an X-ray diffraction study of compounds 2, 3, 4 and 5. The ORTEP drawings of them are shown in Figures 2–5. Data collection and refinement parameters, bond lengths and bond angles are provided in Tables 2–4. Compounds 2, 4 and 5 crystallized in the monoclinic system, the space group found was $P2_1/n$, in the cases of 2 and 4 and $P2_1/c$ for compound 5. On the other hand, compound 3 crystallized in the non-centrosymetric space group $P2_12_12_1$ of the orthorhombic system.



Figure 2. ORTEP drawing of tris(O-4-methylphenyl)phosphorothionate (2).



Figure 3. ORTEP drawing of tris(O-phenyl)phosphorothionate (3).

Geometry optimization of the six compounds was carried out at a RHF 6-31G** level of theory. The vibrational frequencies were computed for each molecule to characterize them as true minima. No imaginary frequencies were found. The RHF method and the 6-31G** basis set have been used before succesfully to describe related molecules.⁹



Figure 4. ORTEP drawing of tris(O-4-chlorophenyl)phosphorothionate (4).

The numerical results from our theoretical analyses are shown in Tables 5 and 6.

3. Discussion

3.1. Substituent effect on δ^{31} P NMR

The ³¹P chemical shift for the six compounds reported here (Table 1) is distributed between 50.09 (X=NO₂) and 56.56 (X=OMe) ppm. The δ^{31} P of compounds **1–6** show an 'abnormal' shielding effect when the EW power of the substituent increases. A plot of Hammett $\sigma_{\rm p}$ constant versus δ^{31} P gives a straight line, whose slope is -5.66 with a correlation coefficient of 0.974 (Fig. 6).¹⁰

In analogy to these results, recently it was reported a similar reversible correlation between the Hammett σ_p constant and the ³¹P NMR signals of the anancomeric axial and equatorial 2-*p*-X-aryloxy-2-thio-1,3,2 λ^5 -dioxaphosphorinanes (X=EW or ER groups).^{3e} Through the structural

data obtained with X-ray diffraction techniques for some of these heterocyclic compounds, it was observed a shortening of the P–O_{endocyclic} bonds of the 1,3,2-dioxaphosphorinane ring as the EW power of the substituent increases, in agreement with the presence of the known $n_{\pi}O$ - σ^*_{P-OAr} and $n_{\pi}O$ - $\sigma^*_{P=S}$ hyperconjugative interactions acting on the axial and equatorial thiophosphates, respectively, but also with the possible transfer of charge density by endocyclic oxygen atoms to phosphorus (Fig. 7).

In spite of the structural differences between the cyclic thiophosphates and the arylphosphorothionates 1-6, it is interesting to note that the presence of an EW group in the aromatic ring causes the same shielding effect on the ³¹P chemical shift in both kind of systems, which reveals that in addition to the transfer of charge density from the endocyclic oxygen atoms toward phosphorus nucleus proposed for the anancomeric dioxaphosphorinanes there are other structural and electronic factors that could contribute to observe the same behavior in the cyclic and acyclic thiophosphates.



Figure 5. ORTEP drawing of tris(O-4-cyanophenyl)phosphorothionate (5).

Table 2.	X-ray	crystal	data fo	r arylph	osphoro	thionates	2, 3, 4	and 5 ^a

	2	3	4	5
Formula	C ₂₁ H ₂₁ O ₃ PS	C ₁₈ H ₁₅ O ₃ PS	C ₁₈ H ₁₂ C ₁₃ O ₃ PS	C ₂₁ H ₁₂ N ₃ O ₃ PS
FW	384.41	342.33	445.66	417.37
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P 1 21/n 1	P 2(1)2(1)2(1)	P2(1)/n	P1 21/c 1
Crystal size (mm ³)	$0.392 \times 0.28 \times 0.28$	$0.4 \times 0.4 \times 0.4$	$0.7 \times 0.5 \times 0.5$	$0.75 \times 0.45 \times 0.45$
Radiation	Μο Κα	Μο Κα	Μο Κα	Μο Κα
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	10.161(4)	7.941(2)	11.243(2)	8.8272(3)
$b(\mathbf{A})$	12.68(14)	13.183(3)	17.469(4)	18.5137(5)
c (Å)	15.753(6)	16.133(3)	11.279 (2)	12.6684(5)
α	90.00	90.00	90.00	90.00
β	97.93 (3)	90.00	118.85(3)	91.7030(10)
γ	90.00	90.00	90.00	90.00
$\dot{V}(\text{\AA}^3)$	2010.2(13)	1688.9(7)	1940.3(7)	2069.41(12)
Z	4	4	4	4
$2\theta_{\max}(^{\circ})$	54.98	55.24	54.98	55.02
$D_{\text{calcd}} (\text{Mg m}^{-3})$	1.270	1.346	1.526	1.340
Absortion coefficient (mm^{-1})	0.258	0.297	0.678	0.260
No. of reflections collected	2553	2234	9153	8793
No. of independent reflection	2433	2234	4446	4704
No. of observed reflections	2316	1374	2911	3064
$R1[F > 4\sigma(F)]$	0.0556	0.0295	0.0534	0.0499
WR2	0.1178	0.0789	0.1334	0.1180
R1 (all data)	0.0587	0.0822	0.0881	0.0881
WR2	0.1197	0.0954	0.1446	0.1374
GOF on F2	1.096	1.016	1.034	1.014
Max. shift for final cycle of least squares Δ/σ	0.000	0.001	0.003	0.000
Max. peak in final difference syntheses $(e/Å^3)$	0.234	0.201	0.534	0.248
Max. difference hole $(e/Å^3)$	-0.263	-0.224	-0.355	-0.272

^a Standard deviations are in parentheses.

Table 3. Selected bond lengths (Å) for arylphosphorothionates 2–5^a

	P=S	P-O1	Р-О2	Р-О3	01–C	O2–C	O3–C
2	1.8987(16)	1.572(3)	1.581(3)	1.575(3)	1.412(4)	1.414(4)	1.414(4)
3	1.8981(12)	1.567(2)	1.579(2)	1.578(2)	1.414(3)	1.399(4)	1.406(3)
4	1.8968(10)	1.579(2)	1.5862(19)	1.5908(18)	1.418(3)	1.401(3)	1.418(3)
5	1.8888(8)	1.5704(16)	1.5869(17)	1.5811(16)	1.402(3)	1.394(3)	1.403(3)

^a Standard deviations are in parentheses.

Table 4. Selected bond angles (θ) in degree for anylphosphorothionates 2–5^a

	O1PO2	O2PO3	O3PO1	SPO1	SPO2	SPO3
2	106.23(15)	100.98(15)	100.78(15)	111.91(12)	17.03(12)	117.98(11)
3	100.05(12)	99.14(12)	101.30(12)	117.01(10)	118.02(9)	117.98(9)
4	100.48(10)	99.85(10)	99.95(10)	118.04(8)	117.78(8)	117.36(8)
5	100.60(9)	99.06(9)	99.06(9)	117.51(7)	117.93(7)	117.64(7)

^a Standard deviations are in parentheses.

Table 5.	Selected calculated	parameters of	arylphosphorothionate	es 1–6

RHF 6-31G**						
	Bond	Lengths	(Å)	Bond	Angles	(Degrees)
	P=S	P–O ^a	O–C ^a	OPO	OPO	OPO
1	1.918	1.584	1.388	100.78	100.78	100.78
2	1.918	1.584	1.386	100.76	100.76	100.76
3	1.916	1.584	1.386	100.72	100.73	100.74
4	1.914	1.585	1.384	100.61	100.61	100.61
5	1.910	1.586	1.381	100.46	100.48	100.48
6	1.909	1.586	1.379	100.40	100.40	100.40

^a The calculated P–O1, P–O2 and P–O3 bond lengths were identical in each case, an only one value is reported. It was the same case for C–O1, C–O2 and C–O3.

Table 6. Calculated natural charges on heteroatoms of arylphosphorothionates 1-6

Compound	S	Р	O ^a
1	-0.677	2.360	-0.917
2	-0.675	2.359	-0.917
3	-0.670	2.356	-0.917
4	-0.658	2.349	-0.914
5	-0.643	2.340	-0.913
6	-0.635	2.336	-0.912

^a As the calculated molecules have a C_3 symmetry, O1, O2 and O3 are equivalent into each molecule, and as a consequence, the natural charges too.



Figure 6. Relationship between the calculated σ_p and the experimental ³¹P NMR chemical shift for arylphosphorothionates 1–6 (correlation coefficient = 0.974, slope = -5.66).



Figure 7.

3.2. Structural analysis

Three of the four arylphosphorothionates analyzed by X-ray diffraction techniques have almost a propeller-type conformation in solid state,¹¹ since the three OAr groups are rotated more or less in one direction, except in the case of the compound **2**, as can be visualized in the ORTEP drawings (Figs. 2–5). The optimized geometries of the six compounds gave also molecular propellers, but in this case all of them have C_3 symmetry, therefore the three OAr groups of each structure were equivalent among them.

The analysis of all the O–P–O bond angles found for the crystalline compounds 2–5 (Table 4), reveals that in most of them this angle is of around 100° , only O1–P–O2 in compound 2 is considerably more opened [106.23° (15)].

The averaged O–P–O bond angles found for compounds 2, 3, 4 and 5 are 102.66, 100.16, 100.09 and 99.57°, respectively. As can be observed, it is clear that this parameter reaches its greater value when the *para* substituent at the aromatic ring is an ER group and the smallest one when X is an EW group. In addition, the compounds 3 and 4 have almost the same averaged O–P–O bond angle, and it is interesting that the chemical shifts of both compounds have very close values (53.71 ppm for 3 and 53.81 ppm for 4).

A similar behavior was found from the analysis of calculated O–P–O bond angles (Table 5). Since the geometry optimization of the six compounds gave in all the cases the same conformation, important changes between the averaged O–P–O bond angles of the six arylphosphorothionates were not found. However, as the EW power of the *para* substituent decreases, the averaged O–P–O angle is opened very slightly, from 100.40 degrees in compound **6** to 100.78 in compound **1**. A plot of the averaged O–P–O angle against ³¹P chemical shift gave an acceptable correlation (the correlation coefficient was 0.947) (Fig. 8), showing that even a minimum difference in the OPO angle might also be correlated succesfully to the shielding effect observed for this kind of compound.



Figure 8. Relationship between the calculated O–P–O bond angle and the experimental ³¹P NMR chemical shift for arylphosphorothionates 1-6 (correlation coefficient=0.946, slope=14.80).

On the other hand, although significant variations of the P=S bond length were not observed among the X-ray diffraction data of compounds **2**, **3** and **4** [the difference between the bond lengths are less than $2.7 \sigma (>99\%$ confidence level¹²)], when the *para* substituent is a strong EW group (X=CN in compound **5**) the P=S bond length become significantly shorter [1.8888(8) Å in **5** against 1.8987(16), 1.8981(12) and 1.8968(10) in **2**, **3** and **4**, respectively (see Table 3)]. This result supports the idea that a participation of sulfur in the transference of the charge density towards the phosphorus atom exists in the arylphosphorothionates when EW substituents are bonded to them. RHF calculations reinforce the experimental observation, the calculated P=S bond length (Table 5) is distributed

between 1.918 (compounds 1 and 2) and 1.909 Å, (compound 6). In addition, the linear regression of calculated P=S bond length against the experimental δ^{31} P chemical shift correlates satisfactorily, as can be visualized from Figure 9 (coefficient of correlation was 0.9634). The result suggests an increasing thiophosphoryl bond order as δ^{31} P values go upfield, which is in agreement with an effect of back-bonding from sulfur to phosphorus atom.^{3a,e}



Figure 9. Relationship between the calculated P=S bond length and the experimental ³¹P NMR chemical shift for arylphosphorothionates 1-6 (correlation coefficient=0.964, slope=621.70).

Nevertheless those significant differences among the averaged P-O bond lengths of compounds 2, 3, 4 and 5 (1.576, 1.575, 1.585 and 1.579 Å, respectively) were not observed in solid state. The fact that P-O1 bond length is shorter than P-O2 and P-O3 in compounds 3, 4 and 5 [1.567(2) against 1.579(2) and 1.578(2) Å in 3, 1.579 (2) against 1.5862 (19) and 1.5908 (18) Å in 4 and 1.5704 (16) against 1.5869 (17) and 1.5811 (16) Å in 5] is consistent with the presence of at least a n_{π} O- σ^*_{P-OAr} or n_{π} O- $\sigma^*_{P=S}$ interaction per molecule in solid state, as it has been proposed for analogous phosphorus containing compounds.13 The changes in the calculated geometrical parameters of these systems also could be related to the existence of stereoelectronic interactions^{9a,b} of the n_{π} O- $\sigma^*_{P=S}$ type, for example, since an increase of the ER power of the para substituent at the aromatic rings produces a slight shortening of the calculated averaged P–O bond lengths (from 1.584 \AA in compounds 1-3 to 1.586 Å in compound 6) accompanied by a lengthening of the P=S bond distance, as it was discussed above. However, a plot of the calculated averaged P-O bond lengths against the experimental δ^{31} P did not give a linear relationship.

The electronic effect of the *para* substituent (X) on arylphosphorothionates **1–6** can be summarized by the canonical structures **I–IV** (Scheme 2). Natural charges evaluated to the RHF 6-31G** level of theory (Table 6) are well described by these resonance structures. The charges at S are ca. -0.7 and those at P are ca. +2.4, whereas the calculated charges at O are ca. -0.9. These

data are in agreement with the theoretical data reported before by Kuivalainen in the study of a series of O,Odialkyl O-aryl phosphorothionates.^{3a} The presence of EW groups on the aromatic rings of arylphosphorothionates lead to a decrease of the positive charge on phosphorus, accompanied also by a decreasing of the net charge on sulfur and oxygen atoms and the shortening of the P==S bond length, whereas the ER groups produce a slight shortening of the P–O bond length. As can be assumed, structures I and IV must be favored over the other two when X is an EW group, whereas II and III should have important contributions when X is an ER group.



Scheme 2.

The plot of natural charges on phosphorus and sulfur atoms against experimental ³¹P chemical shift of compounds **1–6** gave good correlation coefficients (0.955 and 0.954, respectively) (Figs. 10 and 11), however an analogous plot of natural charges at oxygen atoms against δ^{31} P was not satisfactory (the correlation coefficient was 0.7), which suggests a minor participation of the aryl oxygen atoms to the 'abnormal' shielding of the ³¹P chemical shift observed experimentally.



Figure 10. Relationship between the natural charge on phosphorus atom and the experimental 31 P NMR chemical shift for arylphosphorothionates 1–6 (correlation coefficient=0.955, slope=238.16).



Figure 11. Relationship between the natural charge on sulfur atom and the experimental ³¹P NMR chemical shift for arylphosphorothionates **1–6** (correlation coefficient=0.954, slope=-137.89).

4. Conclusion

The ³¹P chemical shifts of a series of *p*-X-arylphosphorothionates 1-6 are analyzed in terms of the electronic effect of the *p*-substituent. As the electronwithdrawing (EW) power of the X substituent increases, an 'abnormal' shielding on the ³¹P NMR signal is observed, which is expressed in the reversible correlation between the Hammett constant σ_p and δ^{31} P. The detailed analyses of the experimental and theoretical structural parameters of the six arylphosphorothionates, obtained through X-ray diffraction techniques and ab initio calculations showed that the features associated with the shielding of the ³¹P NMR signal of the arylphosphorothionates are the decreasing of the O-P-O averaged angle and the shortening of the P=S bond length. An increase of the thiophosphoryl bond order as a result of the back-bonding effect from sulfur toward the phosphorus atom is observed for arylphosphorothionate substituted with EW groups. Additionally, the changes observed in the experimental and theoretical structural parameters could be related to the presence of stereoelectronic interactions of the type n_{π} O- $\sigma^*_{P=S}$, and n_{π} O- σ^*_{P-OAr} , as has been proposed before for analogous systems. Further efforts in the theoretical study of this kind of compound are currently underway, and will be reported soon.

5. Experimental

Melting points are uncorrected. The ¹H, ¹³C and ³¹P spectra were recorded on a Bruker AVANCE 400 spectrometer operating at 400 MHz at a probe temperature of 25.0 °C. Bruker MSL-200 spectrometer operating at 50.32 MHz and Varian Mercury Plus (300 MHz) spectrometers, respectively, using deuterated CDCl₃ as solvent. Phosphorus NMR spectra are reported in ppm downfield (+) from 85% H₃PO₄ used as external standard. Mass spectra were measured on Varian Saturn Star 3400 CX spectrometer using electron impact (El) at 70 eV. The reactions were performed under an atmosphere of nitrogen in oven-dried glassware. Solvents and solutions were transferred by

syringe-septum and cannula techniques. THF and toluene were of reagent grade and were dried and distilled immediately before use from sodium/benzophenone. Triethylamine was dried and distilled from LiAlH₄. Products were purified by flash column chromatography on silica gel 230-400 mesh using as eluent mixtures of AcOEt/hexanes. Yields are given for isolated products. AcOEt/hexanes or CH2Cl2/hexanes mixtures were used for recrystallization of 2-5. Crystallographic work was performed in the difractometers Enraf-Nonius CAD-4 and Kappa CCDC. Data collection: CAD-4¹⁴ and Kappa CCDC Software.¹⁵ Cell refinement: CAD-4 and Kappa CCDC Software. Data reduction WinGX.¹⁶ The structures were resolved by direct methods with SHELXS97¹⁷ and refined with SHELXL97.¹⁸ Molecular graphics: Diamond¹⁹ and dihedral angles: PARST 95.²⁰ Crystallographic Data Center and the deposition numbers are: CCDC 284418 for compound 2, CCDC 284416 for 3, CCDC 284415 for compound 4 and CCDC 284417 for 5. Ab initio calculations were performed employing the Gaussian 98 program.²¹

5.1. General procedure for the synthesis of compounds 1–6

In a three-necked 500 mL flask, fitted with dropping funnel, stir bar and rubber septa, were placed 34.2 mmol of p-X phenol, 5.28 mL of Et₃N (37.9 mmol) and 200 mL of dry THF. Then 1.57 g of PCl₃ (11.4 mmol) were added via syringe. The reaction mixture was stirred at room temperature for 24 h then, the resultant triethylammonium chloride was filtered off through a filter tipped cannula. The solid was washed two times with 15 mL of dry THF collecting the filtrate in a round-bottomed flask. The solvent was removed under reduced pressure to dryness to give the intermediate p-X-phenyl phosphite in ~80% yield as a thick oil, which was used in subsequent reaction without further purification.

In a round-bottomed 100 mL flask, fitted with a reflux condenser, stir bar and rubber septa, were placed 0.36 g (11.4 mmol) of elemental sulfur. A solution of the p-X-phenylphosphite (11.4 mmol) in dry toluene (80 mL) was added to the flask and the resulting suspension was stirred under reflux in an oil bath for 24 h. After cooling, the unreacted sulfur was filtered off and the suspension was concentrated under vaccum. The residue was washed with an aqueous solution of 10% sodium bicarbonate. The product was extracted with methylene chloride and the organic layer dried over sodium sulfate. The solvent was removed in a rotary evaporator and the oily residue was chromatographed on silica gel using hexanes/ethyl acetate as eluent.

5.1.1. Tris(*O*-4-methoxyphenyl)phosphorothionate (1).^{8f} According to the general procedure described above, 4.25 g (34.2 mmol) of *p*-MeO-phenol was treated with 1.57 g (11.4 mmol) of PCl₃ and 4.7 mL (34.2 mmol) of Et₃N. The resulting 3.64 g of phosphite (9.1 mmol) were reacted with 0.3 g (9.1 mmol) of elemental sulfur. Flash chromatography (hexanes/ethyl acetate 80:20) gave 3.1 g (80%) of a colorless oil. ¹H NMR δ 3.79 (s, 9H), 6.86 (d, ³J_{HH} = 9.0 Hz, 6H), 7.13 (dd, ³J_{HH} = 9.0 Hz, ⁴J_{HP} = 1.7 Hz, 6H), RMN ¹³C δ 55.48 (s, OCH₃), 114.57 (s, C_m), 121.76 (d,

 ${}^{3}J_{CP}$ =3.9 Hz, C_o), 144.24 (d, ${}^{2}J_{CP}$ =8.1 Hz, C_i), 157.09 (s, C_p), RMN ${}^{31}P \delta$ 56.56; MS (EI) *m*/*z* 432, 401, 309, 123. Anal. Calcd for C₂₁H₂₁O₆PS: C 58.33, H 4.89, S 7.42. Found: C 58.80, H 4.68, S 7.14.

5.1.2. Tris(*O*-4-methylphenyl)phosphorothionate (2).^{8a,8d} According to the general procedure described above, 3.53 g (34.2 mmol) of *p*-Me-phenol were treated with 1.57 g (11.4 mmol) of PCl₃ and 4.7 mL (34.2 mmol) of Et₃N. The resulting 3.53 g (10.0 mmol) of phosphite were reacted with 0.3 g (10.0 mmol) of elemental sulfur. Flash chromatography (hexanes/ethyl acetate 95:5) gave 3.27 g (85%) of a white solid. Recrystallization from a mixture hexanes-CHCl₃ (90/10) gave colorless crystals (mp 89–90 °C). ¹H NMR δ 2.26 (s, 9H), 7.03 (dd, ³J_{HH}=8.7 Hz, ⁴J_{HP}=1.2 Hz, 6H), 7.07 (d, ³J_{HH}=8.7 Hz, 6H), RMN ¹³C δ 20.75 (s, *C*H₃), 148.55 (d, ²J_{CP}=8.3 Hz, *C_i*), 135.20 (s, *C_p*), 120.44 (d, ³J_{CP}=4.4 Hz, *C_o*), 130.09 (s, *C_m*), RMN ³¹P δ 54.92. MS (EI) *m*/z 384 (100), 293, 277, 107, 91. Anal. Calcd for C₂₁H₂₁O₃PS: C 65.61, H 5.51, S 8.34. Found: C 65.15, H 5.03, S 8.41.

5.1.3. Tris(*O*-**phenyl**)**phosphorothionate** (3).^{5,8d} According to the general procedure described above, 3.2 g (34.2 mmol) of phenol were treated with 1.57 g (11.4 mmol) of PCl₃ and 4.7 mL (34.2 mmol) of Et₃N. The resulting 2.83 g (9.1 mmol) of phosphite were reacted with 0.3 g (9.1 mmol) of elemental sulfur. Flash chromatography (hexanes/ethyl acetate 98:2) gave 2.74 g (88%) of colorless needles. Recrystallization from a mixture of hexanes–ethyl acetate (80/20) gave colorless crystals (mp 53–54 °C). ¹H NMR δ 7.14 (m, 3H), 7.16 (d, ³J_{HH}=8.3 Hz, 6H), 7.29 (d, ³J_{HH}=8.3 Hz, 6H), ¹³C NMR δ 121.13 (d, ³J_{CP}=4.4 Hz, C_o), 125.68 (s, C_p), 129.67 (s, C_m), 150.69 (d, ²J_{CP}=7.7 Hz, C_i), ³¹P NMR δ 53.71. MS (EI) *m/z* 342 (100), 265, 249, 93. Anal. Calcd for C₁₈H₁₅O₃PS: C 63.15, H 4.42, S 9.37. Found: C 62.94, H 3.89, S 9.68.

5.1.4. Tris(*O*-4-chlorophenyl)phosphorothionate (4).^{8a} According to the general procedure described above, 4.39 g (34.2 mmol) of *p*-chlorophenol were treated with 1.57 g (11.4 mmol) of PCl₃ and 4.7 mL (34.2 mmol) of Et₃N. The resulting 3.6 g (8.7 mmol) of phosphite were reacted with 0.27 g (8.7 mmol) of elemental sulfur. Flash chromatography (hexanes/ethyl acetate 80:20) gave 3.87 g (76%) of colorless crystals (mp 80–82 °C). ¹H NMR δ 7.15 (dd, ³*J*_{HH}=9.1 Hz, ⁴*J*_{HP}=2.0 Hz, 6H), 7.34 (dd, ³*J*_{HH}= 9.1 Hz, ⁵*J*_{HP}=0.8 Hz, 6H), ¹³C NMR δ 122.3 (d, ²*J*_{CP}= 4.9 Hz, C_o), 129.7 (d, ²*J*_{CP}=1.7 Hz, C_m), 131.4 (s, C_p), 148.6 (d, ²*J*_{CP}=7.7 Hz, C_i), ³¹P NMR δ 53.81. MS (EI) *m/z* 445, 333, 127. Anal. Calcd for C₁₈H₁₂O₃PSCl₃: C 48.51, H 2.71, S 7.19. Found: C 48.67, H 2.30, S 7.45.

5.1.5. Tris(*O*-4-cyanophenyl)phosphorothionate (5).^{8c} According to the general procedure described above, 4.06 g (34.2 mmol) of *p*-cyanophenol were treated with 1.57 g (11.4 mmol) of PCl₃ and 4.7 mL (34.2 mmol) of Et₃N. The resulting 3.86 g (10.0 mmol) of phosphite were reacted with 0.32 g (10.0 mmol) of elemental sulfur. Flash chromatography (hexanes/ethyl acetate 80:20) gave 3.27 g (85%) of colorless needles. Recrystallization from a mixture of hexanes–ethyl acetate (80/20) gave colorless crystals (mp 155–156 °C). ¹H NMR δ 7.34 (dd, ³J_{HH}=8.6 Hz, ⁴J_{HP}=

1.4 Hz, 6H), 7.73 (d, ${}^{3}J_{HH}$ =8.6 Hz, 6H), 13 C NMR δ 110.37 (s, C_p), 117.58 (s, CN), 122.05 (d, ${}^{3}J_{CP}$ =5.2 Hz, C_o), 134.25 (s, C_m), 152.99 (d, ${}^{2}J_{CP}$ =7.4 Hz, C_i), 31 P NMR δ 50.47. MS (EI) *m*/*z* 417, 315, 299, 118, 102. Anal. Calcd for C₂₁H₁₂N₃O₃PS: N 10.07, C 60.43, H 2.90, S 7.68. Found: N 10.19, C 60.80, H 2.43, S 8.02.

5.1.6. Tris(*O*-4-nitrophenyl)phosphorothionate (6).^{8a,8e} According to the general procedure described above, 4.06 g (34.2 mmol) of *p*-nitrophenol were treated with 1.57 g (11.4 mmol) of PCl₃ and 4.7 mL (34.2 mmol) of Et₃N. The resulting 2.57 g of phosphite were reacted with 0.18 g (5.7 mmol) of elemental sulfur. Flash chromatography (hexanes/ethyl acetate 60:40) gave 0.81 g (30%) of colorless needles. Recrystallization from a mixture hexanes–ethyl acetate (80/20) gave ligth yellow crystals (mp 175.0—175.1 °C) ¹H NMR δ 7.43 (dd, ³*J*_{HH}=9.0 Hz, ⁴*J*_{HP}=1.5 Hz, 6H), 8.35 (d, ³*J*_{HH}=9.0 Hz, 6H), ¹³C NMR δ 121.83 (d, ³*J*_{CP}=4.3 Hz, C_o), 125.86 (s, C_m), δ 145.80 (s, C_p), 154.30 (d, ²*J*_{CP}=7.4 Hz, C_i), ³¹P NMR δ 50.09. MS (EI) *m*/*z* 477, 355, 339, 138, 122. Anal. Calcd for C₁₈H₁₂N₃O₉PS: N 8.80, C 45.29, H 2.53, S 6.72. Found: N 8.74, C 45.38, H 2.11, S 6.95.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC.

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