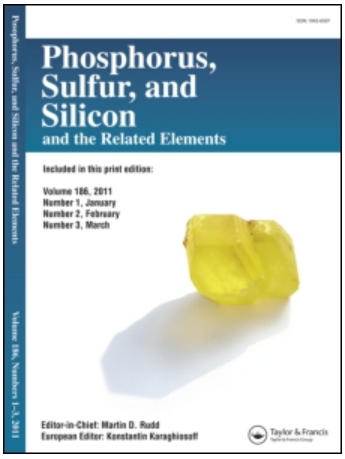

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SUBSTITUENT EFFECTS ON ^{31}P NMR CHEMICAL SHIFTS AND $^{1}J_{P-Se}$ OF TRIARYLSELENOPHOSPHATES

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The effect of electron-withdrawing (EW) and electron-releasing (ER) substituents on the ^{31}P NMR chemical shifts and the structural parameters of a series of* tris-(p-*X*-aryl)*selenophosphates is reported in this article. Similarly to O-aryl phosphates and O-aryl thiophosphates, EW groups attached to aromatic rings induce a shielding effect on the ^{31}P NMR signal. After a detailed experimental and theoretical analysis, we confirmed that the selenium atom is the main part responsible for the charge density transfer toward phosphorus through a back-bonding effect. The obtained $^{1}J_{P\text{-}Se}$ values for the complete series agree with this observation.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords DFT calculations; ^{31}P NMR; selenophosphates; solvent effect

INTRODUCTION

Phosphates, and their sulfur analogues, are systems with relevant biological and commercial importance. While the phosphate group is a fundamental part of several molecules of biological relevance, such as ATP,[1] the thiophosphoryl group is a primary component of insecticides applied worldwide.[2] In contrast, the chemistry of selenophosphates has been

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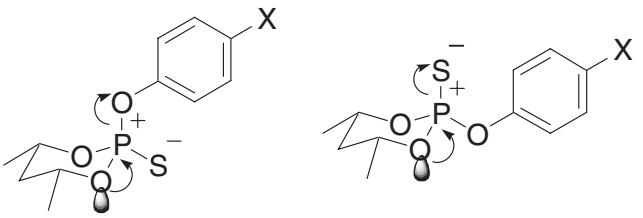

Figure 1 Hyperconjugate interactions at the anancomeric 2-*p*-X-aryloxy-2-thio-1,3,2λ^5-dioxaphosphorinanes.

less studied.[3,4] Recently the discovery of two eukaryotic enzymes, type I iodothyronine 5′-deiodinase and mammalian thioredoxin reductase, emphasized the biological importance of the selenophosphate group.[5,6]

The ^{31}P NMR chemical shift is a very sensitive parameter for monitoring structural changes of organophosphorus compounds. Several correlations between ^{31}P chemical shifts and molecular structure have been found.[7–19] For instance, the effect of the electron-withdrawing (EW) groups at the *para* position of the phenyl rings on the ^{31}P chemical shift of O-aryl phosphates[13,14] and O-aryl thiophosphates has been analyzed by several authors.[16–19] Interestingly, an "abnormal" shielding effect of the ^{31}P NMR signal was found when the electron-withdrawing (EW) power of the substituent was increased in these types of compounds.

Theoretical and experimental results have suggested that the π bond character of the O–P and S–P bonds is related to the shielding of the δ^{31}P in O-aryl chalcogenphosphates. However, other parameters could be involved. Recently, we found that, the P–O endocyclic bond lengths of the anancomeric axial and equatorial 2-*p*-X-aryloxy-2-thio-1,3,2λ^5-dioxaphosphorinanes in the solid state become shorter as the EW power of the substituent X increases.[18] This effect was explained by the presence of the $n_\pi O \rightarrow \sigma^*_{P\text{-}OAr}$ and $n_\pi O \rightarrow \sigma^*_{P\text{-}S}$ hyperconjugative interactions (Figure 1), but also an electron transfer from the endocyclic oxygen atoms to the phosphorus atom could be involved.

In a subsequent study, we found that *tris*(*p*-X-aryloxy)phosphorothionates (TAPTs) prefer a propeller-type conformation.[17] This geometrical arrangement allows interactions between the oxygen lone pairs and polar bonds that keep an antiperiplanar disposition. As shown in Figure 2, there is a lone pair at each oxygen atom with an antiperiplanar disposition to the P–S bond, whereas the other occupied orbital is antiperiplanar respect to their contiguous P–OAr bonds. The X-ray diffraction data show that one of the three P–O bonds is significantly shorter than the other two bonds (the difference is higher than 2.76 σ). At least three of the four reported crystalline structures show this trend, which suggests

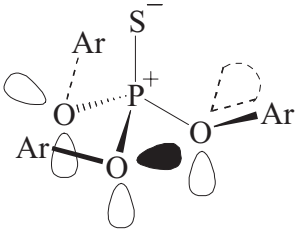

Figure 2 TAPTs adopted conformation.

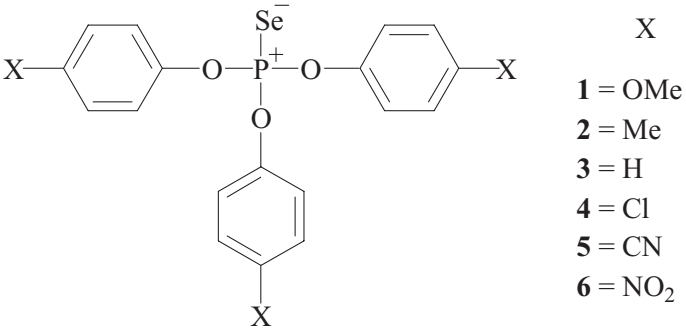

Figure 3 Studied selenophosphates in this article.

the existence of the hyperconjugative interactions, similar to those described before for analogous systems.

The electronic substituent effect on the ^{31}P chemical shift, in terms of its structure, is an attractive problem. Clearly, a complete analysis should include the bonding properties of the α-bonded atoms to phosphorus, as well as the possible stereoelectronic interactions that play an important role on structure and conformation. In this article, we report a detailed analysis of the substitution effect on ^{31}P NMR chemical shift and $^{1}J_{P\text{-}Se}$ coupling constant of *tris*-(*p*-X-aryl)selenophosphates (Figure 3). This NMR study is supported by density functional theory (DFT) calculations, which provide insight into the electronic effect of the *para*-substituent on the structure.

RESULTS AND DISCUSSION

The synthesis of arylselenophosphates **1**–**6** was achieved by adding elemental selenium to a triarylphosphite solution in refluxing toluene, using the same methodology described for the preparation of the phosphorothionate analogues.[17] The synthesis of the six compounds was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectra; EI mass spectroscopy; and elemental analysis. All compounds reported here are solids. However, we only obtained crystals of suitable quality for **2**, **3**, **4**, and **5**. The isomorphism of the previously reported four crystalline phosphorothionates[17] offers us an opportunity to compare experimental structural parameters for each pair of chalcogenphosphates in the solid state. The ORTEP drawings of compounds **2**, **3**, **4**, and **5** are shown in Figure 4. Selected bond lengths, bond angles, data collection, and refinement parameters are provided in Tables I and II. Compounds **2**, **4**, and **5** were crystallized in the monoclinic system. While the space group for **2** and **4** is $P2_1$/n, in the case of compound **5** it corresponds to $P2_1$/c. Finally, compound **3** was crystallized in the non-centrosymmetric space group $P2_12_12_1$ of the orthorhombic system.

Several authors have found that trimethyl chalcogenphosphates (O-P(OMe)$_3$, S-P(OMe)$_3$, and Se-P(OMe)$_3$) adopt at least three different conformers, usually addressed in terms of their overall symmetry as C_3, C_1, and C_s.[3,4,20–22] The triarylselenophosphates structures reported in this article seem to have a similar behavior. Three of the four compounds analyzed by X-ray diffraction adopted a conformation with an almost C_3 symmetry, whereas compound **2** preferred a conformation with a C_1 symmetry in the solid state (see Figure 4).

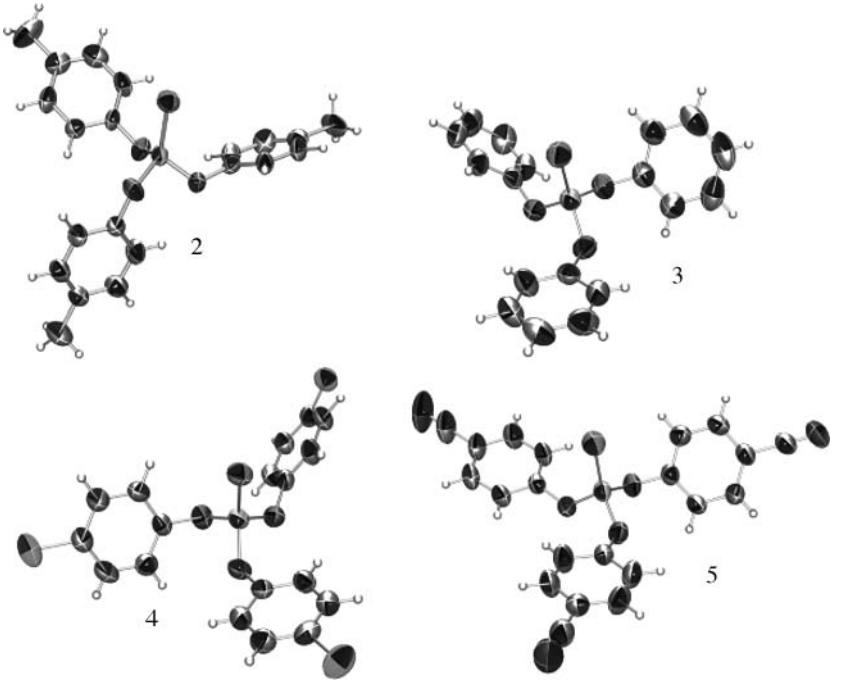

Figure 4 ORTEP drawing of *tris*(*p*-X-aryl)selenophosphates **2**–**5**.

One may speculate that triarylselenophosphates **1**–**6** present more than one conformation in solution, depending on the dielectric constant. Obviously, these facts may have an effect on the ^{31}P chemical shift and on the $^{1}J_{P\text{-}Se}$ coupling constant of compounds **1**–**6**. Taking this into account, we acquired the ^{31}P NMR spectra of the six compounds employing solvents with distinct dielectric constants: CCl_4, C_6D_6, $CDCl_3$, $CO(CD_3)_2$, CD_3OD, and $(CD_3)_2SO$.

Table I Selected bond lengths (Å) and bond angles (°) for arylselenophosphates **2**–**5**[a]

	2	**3**	**4**	**5**
P–Se	2.0520(14)	2.0522(8)	2.0451(10)	2.0397(10)
P–O1	1.577(3)	1.5746(19)	1.586(2)	1.573(2)
P–O2	1.578(3)	1.584(2)	1.586(3)	1.589(3)
P–O3	1.587(3)	1.579(2)	1.587(2)	1.586(2)
O1–C	1.425(5)	1.416(3)	1.408(4)	1.403(4)
O2–C	1.421(5)	1.415(4)	1.414(4)	1.396(4)
O3–C	1.405(5)	1.409(3)	1.414(4)	1.406(4)
O1PO2	100.65(16)	100.09(11)	100.48(10)	100.60(9)
O2PO3	100.83(18)	99.42(11)	99.85(10)	99.06(9)
O3PO1	106.11(18)	101.39(11)	99.95(10)	99.06(9)
SePO1	111.89(14)	117.18(9)	117.18(9)	117.51(7)
SePO2	118.63(13)	117.66(8)	117.66(8)	117.93(7)
SePO3	116.73(13)	117.85(8)	117.85(8)	117.64(7)

[a]Standard deviations are in parentheses.

Table II X-ray crystal data for arylselenophosphates **2**, **3**, **4**, and **5**[a]

	2	**3**	**4**	**5**
Formula	$C_{21}H_{21}O_3PSe$	$C_{18}H_{15}O_3PSe$	$C_{18}H_{12}C_{l3}O_3PSe$	$C_{21}H_{12}N_3O_3PSe$
FW	431.33	389.33	492.56	464.27
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
Crystal size (mm^3)	$0.125 \times 0.3 \times 0.6$	$0.62 \times 0.5 \times 0.5$	$0.5 \times 0.5 \times 0.25$	$0.5 \times 0.32 \times 0.25$
Radiation	MoKα	MoKα	MoKα	MoKα
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	10.185(5)	7.8399(2)	11.1932(2)	9.0132(2)
b (Å)	12.726(4)	13.5557(3)	17.5004(4)	18.2540(5)
c (Å)	15.779(5)	16.1392(4)	11.3704 (4)	12.6938(3)
α	90.00	90.00	90.00	90.00
β	97.65 (4)	90.00	118.1300(1)	91.8290(10)
γ	90.00	90.00	90.00	90.00
V ($Å^3$)	2026.9(14)	1715.20(7)	1964.21(9)	2087.41(9)
Z	4	4	4	4
2θmax(°)	53.96	55.00	55.04	54.98
Dcalc (Mg m^{-3})	1.41	1.507	1.666	1.477
Absortion coefficient (mm^{-1})	1.948	2.293	2.416	1.902
No. of reflections collected	4872	16860	13165	13805
No. of independent reflection	4411	3909	4474	4763
No. of observed reflections	1473	3021	2907	3018
$R_1[F>4\sigma(F)]$	0.0422	0.0351	0.0477	0.0510
WR2	0.015	0.0576	0.0950	0.0853
R1 (all data)	0.1908	0.0592	0.0896	0.1010
WR2	0.0401	0.0646	0.1120	0.1024
GOF on F2	1.122	1.151	1.093	1.071
Max. shift for final cycle of least squares Δ/σ	0.0062	0.000	0.001	0.001
Max. Peak in final difference syntheses (e/$Å^3$)	0.33	0.177	0.328	0.290
Max. Difference hole (e/$Å^3$)	−0.33	−0.199	−0.348	−0.289

[a]Standard deviations are in parentheses.

^{31}P NMR Analysis

The ^{31}P chemical shifts of triarylselenophosphates are given in Table III, and their corresponding phosphorus–selenium coupling constants are in parentheses. Homogeneous

Table III ^{31}P Chemical shifts of *p*-X-arylselenophosphates **1–6**

	1	**2**	**3**	**4**	**5**	**6**
CCl_4	62.36 (1017)	59.90 (1023)	58.69 (1029)	59.90 (1032)	55.93 ([a])	55.53 ([a])
C_6D_6	63.41 (1019)	60.99 (1023)	59.53 (1028)	60.16 (1034)	56.40 (1046)	55.83 (1049)
$CDCl_3$	62.37 (1007)	60.20 (1010)	58.84 (1016)	59.82 (1025)	56.22 (1042)	55.92 (1045)
$CO(CD_3)_2$	62.40 (1014)	60.07 (1018)	59.09 (1022)	60.20 (1028)	56.85 (1041)	56.47 (1044)
CD_3OD	62.64 (1012)	60.31 (1016)	59.44 (1023)	60.58 (1029)	57.19 ([a])	56.86 ([a])
DMSO	62.23 (1007)	60.08 (1012)	59.13 (1016)	60.18 (1021)	56.97 (1034)	55.49 (1036)

[a]It was not observed due to the low solubility of the compound.

solutions with the same concentration (0.05 mol·L^{-1}) of compounds **1–6** were prepared in each solvent. Because **5** and **6** have a very low solubility in CCl_4 and CD_3OD, it was not possible to distinguish $^1J_{P\text{-}Se}$ from the noise of the corresponding spectra. The ^{31}P chemical shift reproducibility was evaluated through repeated experiments under similar conditions, and resulted in better than $\pm$ 0.01 ppm.

As can be observed from Table III, the ^{31}P chemical shift of the six selenophosphates shows an "abnormal" shielding effect in the selected solvents when the electron-withdrawing power of the substituent increases. The phosphorus–selenium coupling constants found for **1–6** are between 1007–1049 Hz, which belong to typical values for phosphorus–selenium "double" bonds coupling constants,[23,24] and they turn greater when the *para*-substituents are strong EW groups (CN or NO_2). The $^1J_{P\text{-}Se}$ values in the series of compounds reported here are consistent with (1) an increase of the π character of the P-Se bond, and (2) the electron transfer from the chalcogen toward the phosphorus atom as an effect of the EW power of the substituent at the aromatic rings.

The linear fittings between Hammett constant σ_p^{25} *vs* ^{31}P chemical shifts and $^1J_{P\text{-}Se}$ of compounds **1–6** are shown in Figures 5 and 6, respectively. A simple analysis of the plots reveals that the substituent effect on $\delta^{31}P$ has almost the same trend and does not depend on the solvent employed in the measurements. Only benzene induces a slight deshielding effect on the ^{31}P NMR signal of compounds **1** (X = OMe) and **2** (X = Me), which could be explained in terms of an aromatic solvent induced shift (ASIS) on the electronically rich systems.[26]

From Figure 6, it is clear that σ_p constants have a better correlation with the phosphorus–selenium coupling constants (obtained from the six different solvents) than

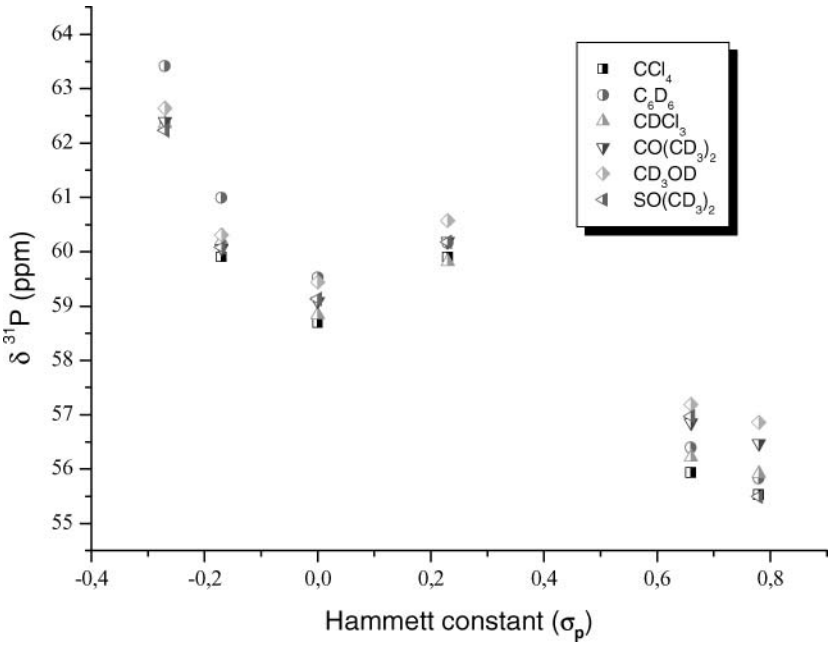

Figure 5 Relationship between the Hammett constant σ_p and the experimental ^{31}P NMR chemical shift for triarylselenophosphates **1–6**.

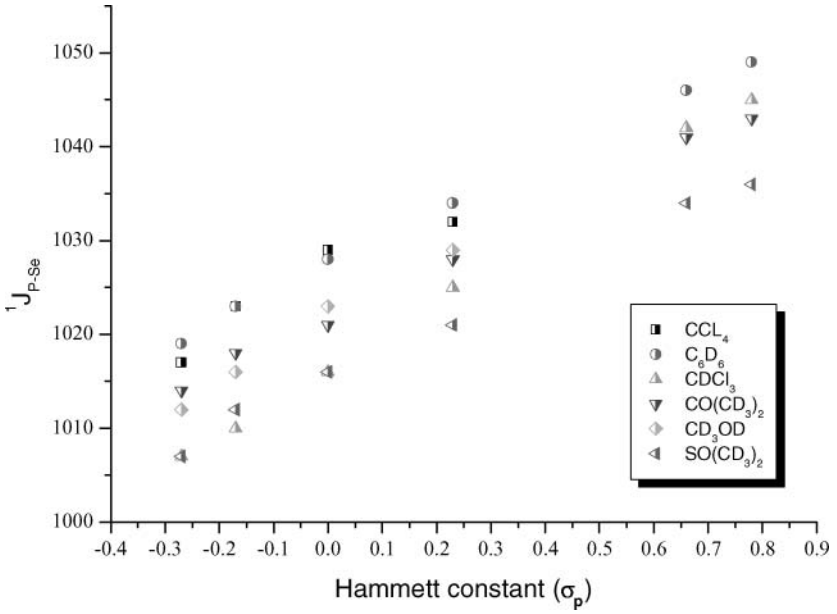

Figure 6 Relationship between the Hammett constant σ_p and the experimental $^1J_{P\text{-}Se}$ coupling constant for triarylselenophosphates **1**–**6**.

the one obtained with the ^{31}P chemical shifts. This agrees with the strong effect of the *para*-substituent on the phosphorus–selenium bond. In addition, the values of $^1J_{P\text{-}Se}$ in compounds **1**–**6** are slightly greater when the spectra were acquired in C_6D_6. In contrast, the $^1J_{P\text{-}Se}$ coupling constants observed in d_6-DMSO, for five of the six compounds of the series, reached some of the smallest values. However, a linear relationship between dielectric constants of the six employed solvents in the analysis and $^1J_{P\text{-}Se}$ was not found.

Since the substituent effect on the $\delta^{31}P$ of triarylselenophosphates remains almost the same, even if the dielectric constant is dramatically changed, we concluded that the structural features related to the abnormal shielding effect of the ^{31}P NMR signal of the series **1**–**6** are not very different between the six solvents.

Structural Analysis

As mentioned above, three of the four triarylselenophosphates analyzed by X-ray diffraction techniques (**3**, **4,** and **5**) have a similar propeller conformation. In contrast, compound **2** adopts a different conformation in the solid state with a C_1 local symmetry (Figure 4). It is interesting that the isomorphous triarylphosphorothionates reported before have exactly the same conformation in the solid state as their analogous **2**–**5**, which reveals that a change in the nature of the phosphorus–chalcogen bonding does not have a strong influence in the conformation into the crystalline cell.

There is not a significant variation between the P-Se bond lengths found for compound **2** and **3** (2.052 Å). However, when the substituent at the *para* position of the aromatic ring is an EW group, as Cl or CN, the P-Se bond length becomes slightly shorter (2.045 Å and 2.040 Å, in each case). This result agrees with the observed magnitude trend of the $^1J_{P\text{-}Se}$ coupling constant discussed before, supporting the idea that the selenium atom is involved

in the charge transfer toward phosphorous when EW groups are attached to the aromatic ring.

The analysis of the averaged P–O bond lengths of compounds **2**, **3**, **4**, and **5** (1.581, 1.579, 1.586, and 1.583 Å, respectively) reveals that there is not an appreciable variation among them. In addition, contrary to the experimental data obtained for the triarylphosphorothionates, significant variations among the three P–O bond lengths for each molecule of triarylselenophosphate were not found, except for compound **5**, where P–O1 bond length is shorter than P–O2 and P–O3 (1.573, 1.589, and 1.586 Å). The shortening of one of the three P–O bond lengths observed in most of arylphosphorothionates reported before was attributed to the presence of at least one $n_{\pi}O\text{-}\sigma^{*}_{P\text{-}OAr}$ or $n_{\pi}O\text{-}\sigma^{*}_{P\text{-}S}$ interaction per molecule in the solid state. However, from the experimental results, it is not clear that the analogous interactions exist for the reported crystalline triarylselenophosphates.

On the other hand, most of the O–P–O angles are approximately 100° for the crystalline compounds **2**–**5** (Table II). Only O1–P–O3, in compound **2**, is considerably larger (106.1°) as a consequence of its particular conformation. The averaged O–P–O bond angles found for compounds **2**, **3**, **4**, and **5** are 102.5, 100.3, 100.1, and 99.6 degrees, respectively. As it can be observed, the angle value is larger when the *para*-substituent at the aromatic ring is an electron releasing (ER) group.

DFT Calculations

The structures of triarylselenophosphates have been optimized without geometry restrictions at the B3LYP/6-31+G(d,p) level.

It is easier to find trends if other electron-withdrawing (EW) and/or electron-releasing (ER) groups are included in the analysis. Of course, this exercise is easy to do *in silico*. We have chosen to study two extra EW groups (−F and −Br) and one more ER group ($-NH_2$) for our purpose. Some general trends are identified from the results summarized in Table S1 (available online in the Supplemental Materials):

1. The P–O bond lengths are longer for those molecules containing an EW group.
2. The P–Se and C–O distances are shorter for those arylselenophosphates containing a *p*-EW substituent.
3. There is a linear correlation between the P–Se bond distance and the $\delta_{DFT}(^{31}P)$, but it is necessary to separate the EW to the ER groups (see Figure S1, Supplemental Materials).
4. The presence of an EW group induces a larger electron transfer from Se→P, and the immediate consequence is the stronger shielding on the observed ^{31}P NMR signal.

CONCLUSIONS

Analogous to the O-aryl phosphates and O-aryl thiophosphates studied in a previous contribution,[17] EW groups attached to the *para* position of the aromatic rings induce a shielding effect on the ^{31}P NMR signal of a series of *tris*-(*p*-X-aryl)selenophosphates. After a detailed analysis of experimental and calculated structural data and also of $^{1}J_{P\text{-}Se}$ values of the complete series, we confirmed that the presence of an EW group induces a larger electron transfer from Se→P and the immediate consequence is a stronger shielding on the observed ^{31}P NMR signal. The electronic effect of the substituent observed in both NMR parameters (^{31}P and $^{1}J_{P\text{-}Se}$) does not suffer appreciable changes if the dielectric constant of the media is changed.

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{31}P spectra were recorded on a Varian Mercury Plus spectrometer operating at 300 MHz at a probe temperature of 25°C. Phosphorus NMR spectra are reported in ppm downfield (+) from 85% H_3PO_4 used as external standard. Mass spectra were measured on a Hewlett Packard 5989A spectrometer and on a Varian Saturn Star 3400 CX spectrometer using electron impact (EI) 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 $LiAlH_4$. The products were purified by flash column chromatography on silica gel 230–400 mesh using mixtures of AcOEt/hexanes as eluent. Yields are given for isolated products. AcOEt/hexanes or CH_2Cl_2/hexanes mixtures were used for recrystallization of all compounds.

Crystallographic work, data collection, and cell refinement was performed in the Enraf-Nonius CAD-4 and Kappa CCDC diffractometers.[27,28] The data reduction was performed in WinGX.[29] The structures were resolved by direct methods with SHELXS97 and refined with SHELXL97.[30] Molecular graphics (diamond and dihedral angles) were created using PARST 95.[31,32] Crystallographic Data Center and the deposition numbers are CCDC 642423 for compound **2**, CCDC 642424 for **3**, CCDC 642425 for **5**, and CCDC 642426 for **4**.

General Procedure for the Synthesis of Compounds 1–6

In a three-necked 500 mL flask, fitted with a dropping funnel, stir bar, and rubber septa, *p*-X phenol (34.2 mmol), PCl_3 (1.57 g, 11.4 mmol), and dry THF (200 mL) were placed. Then Et_3N (4.7 mL, 34.2 mmol) was added via syringe. The reaction mixture was stirred at room temperature for 24 h. Then the resulting triethylammonium chloride was filtered off through a filter tipped cannula. The solid was washed with dry THF (2 × 15 mL) and 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 as 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, elemental selenium (0.9 g, 11.4 mmol) was placed. A solution of the *p*-X-phenylphosphite 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 selenium was filtered off, and the suspension was concentrated under vacuum. The residue was washed with an aqueous solution of 10% sodium bicarbonate (30 mL). The product was extracted with methylene chloride, and the organic layer was 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.

Tris(*O*-4-methoxyphenyl)phosphoroselenoate (1). According to the general procedure described above, *p*-MeO-phenol (4.25 g, 34.2 mmol) was treated with of PCl_3 (1.57 g, 11.4 mmol) and Et_3N (4.7 mL, 34.2 mmol). The resulting phosphite (3.65 g, 7.6 mmol) was reacted with elemental selenium (0.90 g, 11.4 mmol). Flash chromatography (hexanes:ethyl acetate, 98:2) gave 1.1 g (25%) of a white solid. Mp 51–52°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.79$ (s, 9H; OCH_3), 6.87 (d, $^{3}J(HH) = 9.0$ Hz, 6H; CH), 7.14 (dd, $^{3}J(HH) = 9.0$ Hz, $^{4}J(HP) = 1.8$ Hz, 6H; CH), ^{13}C NMR (75.5 MHz, $CDCl_3$,

25°C, TMS): $\delta = 55.89$ (s, O*C*H$_3$), 114.79 (d, ^4J(CP) = 1.7 Hz, C$_m$), 122.47 (d, ^3J (CP) = 4.3 Hz, C$_o$), 144.40 (d, ^2J(CP) = 8.0 Hz, C$_i$), 157.36 (d, ^5J(CP) = 2.0 Hz, C$_p$), ^{31}P NMR (121.5 MHz, CDCl$_3$, 25°C, H$_3$PO$_4$): $\delta = 62.37$ (s, ^1J(PSe^{77}) = 1007 Hz); MS (70 eV, EI): m/z (%): 480 (71) [M$^+$], 123 (100) [CH$_3$OC$_6$H$_4$O$^+$]; elemental analysis: calcd. (%) for C$_{21}$H$_{21}$O$_6$PSe: C 52.62 H 4.42; found: C 52.66 H 4.44.

Tris(*O*-4-methylphenyl)phosphoroselenoate (2). According to the general procedure described above, *p*-Me-phenol (3.53 g 34.2 mmol) was treated with PCl$_3$ (1.57 g, 11.4 mmol) and Et$_3$N (4.7 mL, 34.2 mmol). The resulting phosphite (3.19 g, 9.0 mmol) was reacted with elemental selenium (0.9 g, 11.4 mmol). Flash chromatography (hexanes:ethyl acetate, 98:2) gave 1.97 g (51%) of a white solid. Recrystallization from a solution of hexanes/ethyl acetate (9:1) gave colorless crystals. Mp 108–109°C. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 2.33$ (d, ^7J(PH) = 1.6 Hz, 9H), 7.12 (dd, ^3J(HH) = 8.9 Hz, ^4J(HP) = 1.6 Hz, 6H), 7.16 (d, ^3J(HH) = 8.9 Hz, 6H), ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C, TMS): $\delta = 20.94$ (s, *C*H$_3$), 121.00 (d, ^3J(CP) = 4.9 Hz, C$_o$), 130.04 (d, ^4J(CP) = 1.1 Hz, C$_m$), 135.32 (d, ^5J(CP) = 2.1 Hz, C$_p$), 148.42 (d, ^2J(CP) = 9.2 Hz, C$_i$), ^{31}P NMR (121.5 MHz, CDCl$_3$, 25°C, H$_3$PO$_4$): $\delta = 60.20$ (s, ^1J(PSe^{77}) = 1010 Hz). MS (70 eV, EI): m/z (%): 432 (100) [M$^+$], 342 (20) [M$^+$-C$_7$H$_7$], 107 (14) [M$^+$-C$_7$H$_7$O], 91 (61) [C$_7$H$_7^+$]; elemental analysis: calcd. (%) for C$_{21}$H$_{21}$O$_3$PSe: C 58.48, H 4.91; found: C 58.26, H 5.05.

Tris(*O*-phenyl)phosphoroselenoate (3). According to the general procedure described above, phenol (3.2 g, 34.2 mmol) was treated with PCl$_3$ (1.57 g, 11.4 mmol) and Et$_3$N (4.7 mL, 34.2 mmol). The resulting phosphite (2.8 g, 9.0 mmol) was reacted with elemental selenium (0.9 g, 11.4 mmol). Flash chromatography (hexanes:ethyl acetate, 98:2) gave 2.6 g (74%) of colorless needles. Recrystallization from a solution of hexanes:ethyl acetate (98:2) gave colorless crystals. Mp 73–74°C; ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.23$ (m, 3H), 7.25 (m, 6H), 7.38 (dd, ^3J(HH) = 8.9, ^{3}J(HH) = 6.2 Hz, 6H), ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C, TMS): $\delta = 121.31$ (d, ^{3}J(CP) = 5.1 Hz, C$_o$), 125.76 (d, ^{5}J(CP) = 2.0 Hz, C$_p$), 129.60 (d, ^{4}J(CP) = 1.7 Hz, C$_m$), 150.53 (d, ^{2}J(CP) = 7.7 Hz, C$_i$), ^{31}P NMR (121.5 MHz, CDCl$_3$, 25°C, H$_3$PO$_4$): $\delta = 58.84$ (s, ^{1}J(PSe^{77}) = 1016 Hz); MS (70 eV, EI): m/z (%): 390 (100) [M$^+$], 313 (15) [M$^+$-C$_6$H$_5$], 77 (58) [C$_6$H$_5^+$]; elemental analysis: calcd. (%) for C$_{18}$H$_{15}$O$_3$PSe: C 55.54, H 3.88; found: C 55.39, H 3.87.

Tris(*O*-4-chlorophenyl) phosphoroselenoate (4). According to the general procedure described above, *p*-chlorophenol (4.39 g, 34.2 mmol) was treated with PCl$_3$ (1.57 g, 11.4 mmol) and Et$_3$N (4.7 mL, 34.2 mmol). The resulting phosphite (3.77 g, 9.1 mmol) was reacted with elemental selenium (0.91 g, 11.4 mmol). Flash chromatography (hexanes:ethyl acetate, 80:20) gave 2.36 g (53%) of colorless crystals. Mp 87–88°C. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C, TMS): $\delta = 7.35$ (dd, ^{3}J(HH) = 9.1 Hz, ^{4}J(HP) = 1.8 Hz, 6H), 7.16 (dd, ^{3}J(HH) = 9.1 Hz, ^{4}J(HP) = 2.0 Hz, 6H), ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C, TMS): $\delta = 122.62$ (d, ^{3}J(CP) = 4.9 Hz, C$_o$), 129.78 (d, ^{4}J(CP) = 2.0 Hz, C$_m$), 131.55 (d, ^{5}J(CP) = 2.6 Hz, C$_p$), 148.68 (d, ^{2}J(CP) = 7.7 Hz, C$_i$), ^{31}P NMR (121.5 MHz, CDCl$_3$, 25°C, H$_3$PO$_4$): $\delta = 59.82$ (s, ^{1}J(PSe^{77}) = 1025 Hz). MS (70 eV, EI): m/z (%): 493 (100) [M$^+$], 365 (11) [M$^+$-ClC$_6$H$_4$O], 127 (18) [ClC$_6$H$_4$O$^+$]; elemental analysis: calcd. (%) for C$_{18}$H$_{12}$Cl$_3$O$_3$PSe: C 43.89, H 2.46. Found: C 43.55, H 2.13.

Tris(*O*-4-cyanophenyl) phosphoroselenoate (5). According to the general procedure described above, *p*-cyanophenol (4.06 g, 34.2 mmol) was treated with PCl$_3$ (1.57 g, 11.4 mmol) and Et$_3$N (4.7 mL, 34.2 mmol). The resulting phosphite 3.55 g (9.2 mmol) was reacted with elemental selenium (0.9 g, 11.4 mmol). Flash

chromatography (hexanes:ethyl acetate, 7:3) gave 1.16 g (28%) of colorless needles. Recrystallization from hexanes/ethyl acetate mixture (80/20) gave colorless crystals Mp 174–175°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 7.36 (dd, ^3J(HH) = 8.5 Hz, ^4J(HP) = 1.6 Hz, 6H), 7.74 (d, ^3J(HH) = 8.5 Hz, 6H), ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C, TMS): δ 110.64 (d, ^5J(CP) = 2.0 Hz, C_p), 117.60 (s, *C*N), 122.30 (d, ^3J(CP) = 5.1 Hz, C_o), 134.16 (d, ^4J(CP) = 1.7 Hz, C_m), 152.84 (d, ^2J(CP) = 7.4 Hz, C_i), ^{31}P NMR (121.5 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 56.22 (s, $^1J(PSe^{77})$ = 1042 Hz). MS (70 eV, EI): m/z (%): 465 (89) [M^+], 347 (30) [M^+ -OC_6H_4CN], 102 (25) [$C_6H_4CN^+$]; elemental analysis: calcd. (%) for $C_{21}H_{12}N_3O_3PSe$: C 54.33, H 2.61. Found: C 53.96, H 2.42.

Tris(*O*-4-nitrophenyl) phosphoroselenoate (6). According to the general procedure described above, *p*-nitrophenol (4.06 g, 34.2 mmol) was treated with PCl_3 (1.57 g, 11.4 mmol) and Et_3N (4.7 mL, 34.2 mmol). The resulting phosphite (1.52 g, 3.4 mmol) was reacted with elemental selenium (0.9 g, 11.4 mmol). Flash chromatography (hexanes:ethyl acetate, 7:3) gave 1.19 g (66.5%) of colorless crystals. Mp 170–171°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 7.43 (dd, ^3J(HH) = 9.0 Hz, ^4J(HP) = 1.6 Hz, 6H), 8.34 (d, ^3J(HH) = 9.0 Hz, 6H), ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C, TMS): δ = 122.07 (d, ^3J(CP) = 5.1 Hz, C_o), 125.79 (d, ^4J(CP) = 1.7 Hz, C_m), δ 145.72 (d, ^5J(CP) = 2.4 Hz, C_p), 154.14 (d, ^2JCP = 7.2 Hz, C_i), ^{31}P NMR (121.5 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 55.92 (s, $^1J(PSe^{77})$ = 1045 Hz). MS (70 eV, EI): m/z (%): 525(100) [M^+],; elemental analysis: calcd. (%) for $C_{18}H_{12}N_3O_9PSe$: C 41.24, H 2.31, N 8.02. Found: C 41.20, H 2.05, N 7.86.

COMPUTATIONAL DETAILS

The geometry optimizations and electronic structure calculations were performed using Gaussian 98.[33] Structures were optimized using Becke's exchange (B),[34] Lee, Yang, and Parr (LYP) correlation,[35] and within the hybrid functional (B3LYP) approach, as implemented in Gaussian. All calculations were done using the 6-31+G(d,p) basis set.[36] Every stationary point on the potential energy surface was characterized by a harmonic analysis using the same theoretical methodology as the one used in the optimization. The natural population analysis was employed to calculate the atomic charges.[37] NMR chemical shifts were computed using gauge including atomic orbitals (GIAO)[38] at B3LYP/6-31+G(d,p). The calculated chemical shieldings were converted to chemical shifts using the following Equation:

$$\delta_{\mathrm{DFT}}\mathrm{P(X)} = \sigma_{\mathrm{DFT}}(\mathrm{PH_3}) - \sigma_{\mathrm{DFT}}(\mathrm{X}) - 266.1$$

suggested by van Wullen,[39] where X denotes the molecule for which we calculate the ^{31}P chemical shift, and 266.1 ppm is the difference between the absolute experimental chemical shielding of PH_3 (594.5 ppm) and 85% H_3PO_4 (328.4 ppm) at 300 K.[40] The chemical shielding of PH_3 calculated at the B3LYP/6-31+G(d,p) is 591.3 ppm.

See the Supplemental Materials available online for the complete computational details.

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