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Correlation of the ^{31}P NMR Chemical Shift with the Position of Bond Critical Points in Some Phosphorothionates

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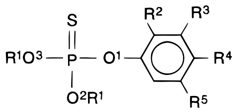
The origin of the chemical shift for the phosphorus nucleus is discussed widely in the literature.[1] Within a series of structurally related tricoordinated phosphorus compounds and tetracoordinated phosphoryl compounds, there are many studies dealing with the correlations between ^{31}P chemical shifts ($\delta(^{31}P)$) and molecular structures.[2] Gorenstein observed that the variation of $\delta(^{31}P)$ in both cyclic and acyclic phosphate esters was primarily determined by O−P−O bond angles and torsional angles.[2a,c] This empirical observation was established by using the semiempirical quantum mechanical CNDO/2 calculations.[2b,d] Only a few publications that report the correlation between $\delta(^{31}P)$ and the structure of the thiophosphoryl compounds have appeared.[3] No publications reporting the correlations within phosphorothionates have appeared earlier. *O*,*O*-Dialkyl *O*-aryl phosphorothionates are one of the most important classes of organophosphorus pesticides.[4] Their structures involve the biologically significant P−O and P−S bonds. We carried out an Atoms in Molecules (AIM)[5] study of the bonding properties of *O*,*O*-dialkyl *O*-aryl phosphorothionates. We report here how $\delta(^{31}P)$ of *O*,*O*-dialkyl *O*-aryl phosphorothionates correlates with the bond critical points (BCP) lying between phosphorus and its neighboring atoms.

Table 1. ^{31}P Chemical Shifts of *O*,*O*-Dialkyl *O*-Arylphosphorothionates



compd	R^1	R^2	R^3	R^4	R^5	$\delta(^{31}P)$ (ppm)[a]	$\Delta\delta(^{31}P)$ (ppm)[b]
1	CH_3			NO_2	−	65.56	−0.98
2	CH_3		CH_3	NO_2	−	65.63	−0.91
3	CH_3	Cl		I	Cl	65.96	−0.58
4	CH_3	Cl		Br	Cl	66.08	−0.46
5	CH_3	Cl			Cl	66.09	−0.45
6	CH_3	Cl		Cl	Cl	66.25	−0.29
7	CH_3	Cl				66.31	−0.23
8	CH_3	Cl		Cl		66.42	−0.12
9	CH_3		Cl	Cl		66.48	−0.06
10	CH_3					66.54	
11	CH_3			Cl		66.63	+0.09
12	CH_3CH_2			NO_2		62.00	−1.01
13	CH_3CH_2	Cl		Cl	Cl	62.65	−0.36
14	CH_3CH_2	Cl		Cl		62.81	−0.20
15	CH_3CH_2					63.01	
16	CH_3CH_2			Cl		63.14	+0.13

[a] Values of chemical shifts δ (ppm) from $P(OH)_4{}^+ClO_4{}^-$ as external reference. [b] $\Delta\delta(^{31}P) = \delta(^{31}P)$ substituted $-$ $\delta(^{31}P)$ unsubstituted.

The measured ^{31}P chemical shifts[6] of 16 *O*,*O*-dimethyl and *O*,*O*-diethyl *O*-aryl phosphorothionates are given in Table 1. Repeated measurements under identical conditions indicated that the reproducibility of ^{31}P chemical shifts was better than ±0.01 ppm. The variation of $\delta(^{31}P)$ with concentration was studied for compound **11**. Only a small downfield shift (+0.05 ppm) was observed when the concentration varied from 0.5 to 0.05 mol L^{-1}. Compounds **1**−**4**, **6**, **12**, and **14** are commercial insecticides; the others are of interest as potential pesticides or as substances that enhance the activity of the known pesticides. Compounds **5**, **7**, **8**, **9**, **10**, **11**, **13**, **15**, and **16** were synthesized by the methods described previously, see Supporting Information. The structures of the synthesized compounds were confirmed by recording high-resolution EI mass spectra. The ^{31}P chemical shifts distributed between 65.56 and 66.63 ppm for *O*,*O*-dimethyl *O*-aryl phosphorothionates **1**−**11** and between 62.00 and 63.14 ppm for *O*,*O*-diethyl *O*-aryl phosphorothionates **12**−**16**. Thus, the variations of $\delta(^{31}P)$ due to the substituent/substituents on the benzene ring (given as $\Delta\delta(^{31}P)$ in Table 1) are less than 1.01 ppm. The results show that electron-withdrawing substituent/substituents other than *p*-Cl cause an "abnormal" shielding effect on the phosphorus. The strongest shielding was observed for *p*-NO_2 compounds **1** and **12**. The *p*-Cl compounds **11** and **16** exhibited the "normal" although small deshielding of the phosphorus. A downfield shift of about 0.1 ppm was observed for **11** and **16** as a result of the *p*-Cl substituent. Further examination of the chemical shifts represented in Table 1 reveals that there is an upfield shift of −3.49 to −3.61 ppm as a result of replacing the methoxy groups by the ethoxy groups.

The AIM method[5] is based on the study of the topology of the electron density $\rho(r)$. In this preliminary study, phosphorothionates **1**, **10**, **11**, **12**, and **15** were selected as target compounds. AIM analyses were performed with the AIMPAC series of program[7] using the wave function at the b3lyp/6-311+g* (Gaussian 98)[8]

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(6) ^{1}H-decoupled ^{31}P NMR spectra were recorded at 40.48 MHz using a JEOL PFT-100 spectrometer. Samples were dissolved in $CDCl_3$ at a concentration of 0.5 mol L^{-1}. ^{31}P chemical shifts (in ppm) were measured relative to the external reference: 0.2 mol L^{-1} solution of $P(OH)_4{}^+ClO_4{}^-$ in D_2O.

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Table 2. Bond Length R (Å), Distance from BCP to P (Å), Charge Density $\rho(r)$ at BCP (e/a_0^3), Laplacian of the Charge Density $\nabla^2\rho(r)$ (e/a_0^5), Ellipticity ϵ, Electronic Energy Density $E_d(r)$, Kinetic Energy Density $G(r)$, and Potential Energy Density $V(r)$ (hartree/a_0^3) at b3lyp/6-311+g* for Compounds **1**, **10**, **11**, **12**, and **15**

	R	BCP−P	$\rho(r)$	$\nabla^2\rho(r)$	ϵ	$E_d(r)$	$G(r)$	$V(r)$
1								
P−S	1.9239	0.9057	0.179	- 0.310	0.022	−0.142	0.064	−0.206
P−O1	1.6276	0.6443	0.166	0.627	0.050	−0.119	0.275	−0.394
P−O2	1.6171	0.6398	0.175	0.654	0.068	−0.130	0.293	−0.423
P−O3	1.6016	0.6342	0.181	0.720	0.071	−0.134	0.314	−0.447
10								
P−S	1.9292	0.9099	0.177	−0.307	0.023	−0.139	0.063	−0.202
P−O1	1.6139	0.6396	0.172	0.681	0.060	−0.123	0.293	−0.416
P−O2	1.6207	0.6411	0.173	0.638	0.068	−0.129	0.288	−0.417
P−O3	1.6035	0.6349	0.180	0.712	0.073	−0.133	0.311	−0.444
11								
P−S	1.9244	0.9059	0.178	−0.309	0.028	−0.141	0.064	−0.205
P−O1	1.6280	0.6446	0.168	0.609	0.062	−0.123	0.275	−0.397
P−O2	1.6015	0.6342	0.180	0.723	0.072	−0.133	0.314	−0.447
P−O3	1.6210	0.6412	0.173	0.637	0.077	−0.129	0.288	−0.417
12								
P−S	1.9339	0.9061	0.176	−0.302	0.009	−0.138	0.062	−0.200
P−O1	1.6360	0.6474	0.164	0.586	0.043	−0.118	0.265	−0.383
P−O2	1.6012	0.6340	0.181	0.720	0.069	−0.134	0.314	−0.448
P−O3	1.6007	0.6341	0.181	0.723	0.056	−0.134	0.315	−0.448
15								
P−S	1.9409	0.9092	0.174	−0.298	0.004	−0.135	0.061	−0.196
P−O1	1.6244	0.6432	0.170	0.618	0.069	−0.125	0.279	−0.404
P−O2	1.6029	0.6352	0.179	0.713	0.052	−0.132	0.310	−0.442
P−O3	1.6025	0.6351	0.179	0.713	0.056	−0.132	0.311	−0.443

Table 3. Atomic Charges for the Structures **1**, **10**, **11**, and **15** at the b3lyp/6-311+g* Level

	P	S	O^1	O^2	O^3
1	2.687	−0.564	−1.287	−1.276	−1.273
10	2.698	−0.583	−1.295	−1.276	−1.271
11	2.681	−0.569	−1.292	−1.266	−1.275
15	2.709	−0.618	−1.288	−1.273	−1.270

level as input. The b3lyp/6-311+g* vibrational frequencies were computed for each optimized species to characterize them as true minima. No imaginary frequencies were found. The DFT method using b3lyp exchange correlation functional and the basis set including polarization and diffuse functions has been tested in earlier studies and found as best in describing the structures of this kind of hypervalent molecules.[9,10] The numerical results obtained from our AIM analyses are presented in Tables 2 and 3. Table 2 summarizes the properties of $\rho(r)$ at BCP for the P−S and P−O bonds. A local electronic energy density $E_d(r)$ is defined by a local kinetic energy density $G(r)$ and a local potential energy density $V(r)$: $E_d(r) = G(r) + V(r)$. For the P−S bonds, the Laplacians $\nabla^2\rho(r)$ are negative, the ϵ values are very small, and the negative $E_d(r)$ values are dominated by $V(r)$. Table 3 presents the atomic charges for P, S, and O atoms. The charges at S are ca. −0.6 and those at P are ca. +2.7. On the basis of these results, the P−S bonds can be regarded as single σ bonds, which are slightly polarized toward the S atom. This can be seen also in Figure 1, which shows the contour of the Laplacian of the charge density for compound **10** in the plane S−P−O1. The electronic charge density is concentrated on the P−S bond between both basins. For the P−O bonds, the $\nabla^2\rho(r)$ are positive and the $E_d(r)$ values are negative with large $G(r)$ contribution. Although the ϵ values are small, they are a little higher than those for the P−S bonds. This might suggest some π bond character as a result of back-bonding toward the phosphorus. The charges at the alkoxy oxygens are ca −1.27 and those at the phenoxy oxygen are ca. −1.29. These data are compatible with very polar bonds. The polar bond character can be seen also from the Laplacian distribution presentation (Figure S1); the electronic charge density is not shared equally, the charge is concentrated on the oxygen basins. Table 2 summarizes the distances of BCP to P for P−S and P−O bonds. The BCP−P distances for P−S bonds were shortened as a result of introduction of electron-withdrawing para-substituent on the benzene ring. Also the average value of BCP−P distances for P−O2 and P−O3 bonds was shortened. On the contrary, the BCP−P distances for P−O1 bonds were lengthened.

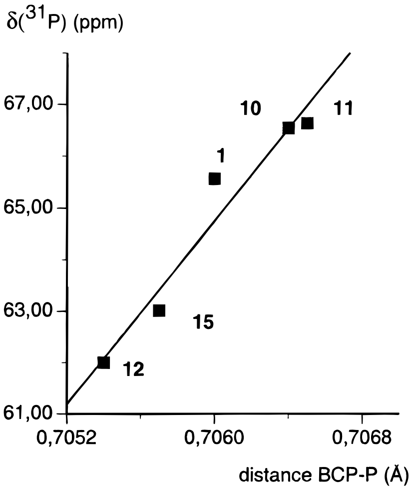

Figure 1. Plot of the experimental ^{31}P NMR chemical shifts versus the calculated average distances between the phosphorus atom and the bond critical points for the phosphorothionates **1**, **10**, **11**, **12**, and **15**.

To find the principal structural features that determine the δ(^{31}P) of *O*,*O*-dialkyl *O*-aryl phosphorothionates, we performed regression analyses for the experimental ^{31}P chemical shifts and a number of data obtained from the DFT (geometrical parameters) and AIM calculations. Each parameter was tested separately, one by one. The analyses were carried out using the linear least-squares method. The only parameter that correlates very well with the measured ^{31}P chemical shifts is the average value of the BCP−P distances for P−S and the three P−O bonds (eq 1). The coefficient of correlation is $r^2 = 0.947$. Figure 1 visualizes the situation.

$$\delta(^{31}\mathrm{P})_{\mathrm{expt}} = 4451(\mathrm{BCP{-}P\ distance}) - 3078 \qquad (1)$$

Although the changes in the δ(^{31}P) values and in the average BCP−P distances are quite small, the result is chemically reasonable. The shortening of the average BCP−P distance causes more effective electronic shielding of the phosphorus nucleus. Further studies among other phosphorus compounds are in progress. To summarize, our results indicate that in compounds studied here, the calculated positions of the bond critical points between the phosphorus and its neigboring atoms correlates with the measured ^{31}P chemical shifts.

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Supporting Information Available: References for the synthetic procedures, mass spectroscopic data for the synthesized compounds and contour map of $\nabla^2\rho(r)$ for compound **10** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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