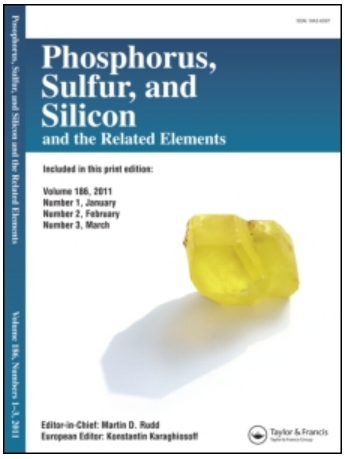

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GENERALIZED CORRELATION OF P=O AND P=S BOND STRETCHING VIBRATIONAL FREQUENCIES WITH ELECTRONIC STRUCTURE IN ORGANOPHOSPHORUS COMPOUNDS*

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A generalized relationship has been employed to correlate P=O and P=S bond stretching frequencies with molecular electronic structures for organophosphorus compounds. The calculated results are in good agreement with the available experimental data. The standard deviations are only 3.7 and 5.4 cm^{-1} for the P=O and P=S bonds, respectively.

Keywords: P=O bond stretching frequency; P=S bond stretching frequency; Maximum bond order hybrid orbital; Correlation analysis; Organophosphorus compound

INTRODUCTION

Since the 1950s much attention has been devoted to the measurement and interpretation of characteristic stretching frequencies of bonds between phosphorus and oxygen and phosphorus and sulfur in organophosphorus compounds [1–48]. The molecules of special interest are tetrahedral structure as represented by a formula $R_1R_2R_3P{=}X$ (X = O and S), where R_1, R_2 and R_3 are substituents which vary widely in electronegativity, mass and size. With the increasing number of these compounds for which spectroscopic data have been published, numerous studies, such as those summa-

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rized by Bellamy [1,2], which correlate infrared absorption bands with specific structural characters have been reported [4,16–18,22,24,34,35].

The absorption bands due to the stretching vibration of P=O bond are usually strong and appear in the region 1140–1420 cm^{-1} [3–15]. The P=O bond stretching vibrational frequencies are influenced significantly by the chemical nature of the substituents bonded to the phosphorus atom [4,16–18]. Many attempts were made to establish a means of predicting the P=O bond stretching frequencies, including correlation of $\nu_{P=O}$ with the assumed Pauling electronegativities of the substituents [17], with Taft constants (σ) [16,18] and with phosphorus inductive or Π constants [4,19]. Among those correlation relationships, the following one gives the P=O bond stretching frequencies of various organophosphorus compounds with a reasonable accuracy [4]:

$$\nu_{P=O} = 930 + 40 \sum \Pi \tag{1}$$

where Π is the phosphorus inductive constant of a given substituent group, which is an empirical value, deduced from experimental data for giving the optimum agreement with the datum line and determined only by the atom directly attached to the phosphorus atom.

The absorption bands related to the P=S stretching vibration occur at 730–550 cm^{-1} and 862–685 cm^{-1} [16,19] and are of medium-to-strong intensities. Between the two different bands, many authors [18,20,21] prefer to regard the lower-frequency bands as due to P=S, mainly because of the better agreement shown with attempts to predict $\nu_{P=S}$ from force-constant data. It is believed that [19], like the phosphonyl groups, the position of the P=S absorption band is also affected by the electronegativities of adjacent groups although the effect is not as remarkable as for the phosphonyl group since P=S bond has less ionic character. Hence it seems reasonable to employ the similar empirical relationship which has been used successfully for the P=O stretching frequencies to elucidate the P=S frequencies. However, the results obtained in this way for the P=S frequencies were not as good as for the P=O frequencies [22–24]. For example, Zingaro [24] tested a series of correlation relationships between the P=S frequencies and the steric and polar parameters of the substituents for 18 molecules, and the most useful relationship was obtained when the trimethyl and triethyl derivatives were excluded:

$$\nu_{P=S} = 599 - 2.81 \sum E_S + 14.1 \sum \sigma^* - 0.406 \sum (E_S)(\sigma^*) \; (r = 0.890) \tag{2}$$

where E_S is steric factors and $\sigma^*$the polar substituent constant whose values had been reported elsewhere[23]. Chittenden and Thomas [19] extracted all the data available on both bands and found that both bands are sensitive to the nature of the substituents, and neither of them follows the relationship like Eq.(1). It follows that the factors affecting the P=S bond stretching frequencies are much more complicated and can not be reflected by those empirical parameters such as Π, σ^* and E_S *etc.*.

In our previous work [49–51], based on a further theoretical analysis of the Fermi contact coupling interaction and the correlation of the bond stretching force-constant or frequency with the coupling constants, a relationship was introduced to calculate the bond stretching frequency:

$$\nu_{AB} = K_{AB}(s\%)_A(s\%)_B + K_{QA}Q_A(s\%)_A + K_{QB}Q_B(s\%)_B + K_A(s\%)_A + K_B(s\%)_B + C_{AB} \quad (3)$$

which has been employed to successfully elucidate the C-H bond stretching frequencies [50] as well as the P=S bond stretching frequencies [51]. These studies encourage us to do further research on the P=O stretching frequencies.

In this paper, based on the generalized semiempirical relationship [52] for calculating nuclear spin-spin coupling constants and the correlation of the bond stretching frequencies with the coupling constants, a generalized semiempirical relationship, which includes the characters of hybrid orbitals and net atomic charges, has been introduced to elucidate the P=O stretching frequencies as well as the P=S stretching frequencies.

GENERALIZED RELATIONSHIPS

Our inspiration originates in the studies of the relation between the bond stretching frequency and nuclear spin-spin coupling constant of directly bonded atoms. It has been reported [53–58] that, for C-H, single C-C, double C=C and triple C≡C bonds *etc.*, there exists a well linear relationship between their bond stretching vibrational frequencies (or force-constants) and their nuclear spin-spin coupling constants, respectively. One could assume from the above-mentioned reports that the linear relationship between the bond stretching frequencies and nuclear spin-spin coupling constants might be generalized case in the nature, at least for P=O and P=S bonds it might be so. Based on this assumption, one could have

$$\nu_{AB} = aJ_{AB} + c \quad (4)$$

where ν_{AB} is the A-B bond stretching frequency, and $J_{AB}$is the nuclear spin-spin coupling constant of directly bonded atoms A and B.

In our previous paper [52], based on a further theoretical analysis of the Ramsey theory of nuclear spin-spin coupling constants, a new generalized semiempirical relationship for calculating indirect nuclear spin-spin coupling constants between directly bonded atoms has been derived:

$$J_{AB} = \sum_{i=j}^{l^A_{max}-1} \sum_{j=0}^{l^B_{max}-1} k_{ijAB} W_{iA} W_{jB} + \sum_{l=0}^{l^A_{max}-1} k_{lQA} Q_A W_{lA} + \sum_{l=0}^{l^A_{max}-1} k_{lA} W_{lA} + \sum_{l=0}^{l^B_{max}-1} k_{lQB} Q_B W_{lB} + \sum_{l=0}^{l^B_{max}-1} k_{lB} W_{lB} + k_{EA} Q_A + k_{EB} Q_B + c_{AB} \quad (5)$$

where l^A_{max} and l^B_{max} are the maximum angular momentum numbers of the atomic orbitals in the hybrid orbitals ϕ_A and ϕ_B, respectively; W_{iA} and W_{iB} represent the characters of the atomic orbitals associated with the angular momentum quantum number l=i in the hybrid orbitals ϕ_A and ϕ_B, respectively, hence, $W_{0A} \equiv (s\%)_A$ and $W_{0B} \equiv (s\%)_B$, $W_{1A} \equiv (p\%)_A$ and $W_{1B} \equiv (p\%)_B$ *etc.*; Q_A and Q_B are the net charges of atoms A and B; k_{ijAB}, k_{lQA}, k_{lA}, k_{lQB}, k_{lB}, k_{EA}, k_{EB} and c_{AB} are independent parameters which are constants for the same kind of chemical bond. Substituting Eq.(5) into Eq.(4), one may obtain:

$$\nu_{AB} = \sum_{i=j}^{l^A_{max}-1} \sum_{j=0}^{l^B_{max}-1} K_{ijAB} W_{iA} W_{jB} + \sum_{l=0}^{l^A_{max}-1} K_{lQA} Q_A W_{lA} + \sum_{l=0}^{l^A_{max}-1} K_{lA} W_{lA} + \sum_{l=0}^{l^B_{max}-1} K_{lQB} Q_B W_{lB} + \sum_{l=0}^{l^B_{max}-1} K_{lB} W_{lB} + K_{EA} Q_A + K_{EB} Q_B + C_{AB} \quad (6)$$

Equation (6) is a generally parameterized relationship for employing the atomic hybrids and net atomic charges to calculate the bond stretching frequency. When $l^A_{max} > 1$ or $l^B_{max} > 1$, generally speaking, Eq. (6) should be used. If we do not distinguish, however, the contributions of different kinds of non-*s* orbitals, Eq.(6) may further be simplified as:

$$\nu_{AB} = K_{AB} W_{0A} W_{0B} + K_{QA} Q_A W_{0A} + K_A W_{0A} + K_{QB} Q_B W_{0B} + K_B W_{0B} + K_{EA} Q_A + K_{EB} Q_B + C_{AB} \quad (7)$$

which involves totally eight independent coefficents to be determined by fitting some reliable experimental data. Specially, when $l_{max} = 1$ for *s-p* hybrid orbitals, Eq.(7) is exactly the same as Eq.(6). For $l^{A}_{max} > 1$ or $l^{B}_{max} > 1$, Eq.(7) is an approximate form of Eq.(6).

Comparing with Eq.(3), Eq.(7) has two additional terms $K_{EA}Q_A$ and $K_{EB}Q_B$, except for using different notations to represent the *s*-characters. If the changes of these two terms are not important, or if their main changes can be canceled with each other, or if the deviations caused by ignoring these two terms can be balanced by changing values of the adjustable parameters in other terms, then Eq.(7) can be simplified approximately as Eq.(3). This is why Eq.(3) could be employed to successfully elucidate the C-H and P=S bond stretching frequencies in our previous work [50,51].

CALIBRATION

For a given kind of atom pair, the parameters in Eq.(6), which has a certain concrete form correspondingly, may be determined by seeking the best fit to enough experimental bond stretching frequencies in various molecules in which the characters of the hybrid orbitals and net atomic charges can be evaluated with a certain theoretical scheme.

For P=O bond, $l^{P}_{max} = 2$ and $l^{O}_{max} = 1$, hence Eq.(6) may be expressed as the following concrete form:

$$\begin{aligned}\nu_{P=O} = {} & K_{00PO}W_{0P}W_{0O} + K_{0QP}Q_PW_{0P} + K_{0QO}Q_OW_{0O} + K_{0P}W_{0P} \\ & + K_{0O}W_{0O} + K_{EP}Q_P + K_{EO}Q_O \\ & + K_{10PO}W_{1P}W_{0O} + K_{1QP}Q_PW_{1P} + K_{1P}W_{1P} + C_{PO} \end{aligned} \quad (8)$$

If we ignore the contribution of *p*-orbital of P atom to the P=O bond stretching frequency, Eq.(8) may be simplified as:

$$\begin{aligned}\nu_{P=O} = {} & K_{PO}W_{0P}W_{0O} + K_{QP}Q_PW_{0P} + K_{QO}Q_OW_{0O} \\ & + K_PW_{0P} + K_OW_{0O} + K_{EP}Q_P + K_{EO}Q_O + C_{PO} \end{aligned} \quad (9)$$

For P=S bond, $l^{P}_{max} = 2$ and $l^{S}_{max} = 2$, hence Eq.(6) may be expressed as the following concrete form:

$$\begin{aligned}\nu_{P=S} = {} & K_{00PS}W_{0P}W_{0S} + K_{0QP}Q_PW_{0P} + K_{0QS}Q_SW_{0S} + K_{0P}W_{0P} \\ & + K_{0S}W_{0S} + K_{EP}Q_P + K_{ES}Q_S + K_{10PS}W_{1P}W_{0S} \\ & + K_{1QP}Q_PW_{1P} + K_{1P}W_{1P} + K_{01PS}W_{0P}W_{1S} + K_{1QS}Q_SW_{1S} \\ & + K_{1S}W_{1S} + K_{11PS}W_{1P}W_{1S} + C_{PS} \end{aligned} \quad (10)$$

If we ignore the contribution of p-orbital of S atom to the P=S bond stretching frequency, Eq.(10) may be simplified as:

$$\begin{aligned}\nu_{P=S} = {} & K_{00PS}W_{0P}W_{0S} + K_{0QP}Q_PW_{0P} + K_{0QS}Q_SW_{0S} + K_{0P}W_{0P} \\ & + K_{0S}W_{0S} + K_{EP}Q_P + K_{ES}Q_S + K_{10PS}W_{1P}W_{0S} \\ & + K_{1QP}Q_PW_{1P} + K_{1P}W_{1P} + C_{PS} \end{aligned} \quad (11)$$

If we further ignore the contribution of p-orbital of P atom to the P=S bond stretching frequency, Eq.(11) may be simplified as:

$$\begin{aligned}\nu_{P=S} = {} & K_{PS}W_{0P}W_{0S} + K_{QP}Q_PW_{0P} + K_{QS}Q_SW_{0S} + K_PW_{0P} \\ & + K_SW_{0S} + K_{EP}Q_P + K_{ES}Q_S + C_{PS} \end{aligned} \quad (12)$$

In order to calibrate the coefficients in Eqs.(8)-(12), we carried out MBOHO calculations [59] on a number of organophosphorus compounds. For each organophosphorus molecule, geometry was optimized with MNDO method [60–62], followed by an EHMO [63] calculation (including the necessary d-orbitals for P and S atoms *etc.*) which gives the density matrix required for performing the MBOHO procedure as well as the net atomic charges. All parameters adopted in the MNDO calculations came from literature [60–62], and all the parameters used to perform the EHMO calculations are the default values in the EHMO program [63]. Finally, we performed the least-squares procedure of the theoretical P=O and P=S bond stretching frequencies versus the available experimental frequencies for the P=O and P=S bonds, respectively.

RESULTS AND DISCUSSION

The net atomic charges and orbital characters of the MBOHOs based on density matrix calculated with the EHMO method for the P=O and P=S bonds are listed in Table I. Comparing the calculated results for the P=O bonds with those for the P=S bonds listed in Table I, one can see that the tendencies for the change of the calculated s-characters and the net atomic charges for both P=O and P=S bonds are very similar. For instance, the s-characters of the phosphorus atoms increase with increasing electronegativities of the substituents attached to the phosphorus atoms in both $R_1R_2R_3P{=}O$ and $R_1R_2R_3P{=}S$ compounds, which is in good agreement with the conclusion obtained from Bent's rule [64]. It is expected from these results that the electronegativities of the substituents may play a similar role in determining both P=O and P=S stretching frequencies.

TABLE I The calculated *s*- and *p*-orbital characters of MBOHOs and net atomic charges for P=O and P=S bonds in $R_1R_2R_3P{=}X$ (X=O and S) compounds

R_1	R_2	R_3	$R_1R_2R_3P{=}S$						$R_1R_2R_3P{=}O$				
			$(s\%)_P$	$(s\%)_S$	$(p\%)_P$	$(p\%)_S$	Q_P	Q_S	$(s\%)_P$	$(s\%)_O$	$(p\%)_P$	Q_P	Q_O
F	F	F	38.09	46.57	56.76	52.47	1.673	–0.161	30.86	68.46	57.82	2.279	–0.862
Cl	F	F	36.18	48.79	57.84	50.41	1.304	–0.191	28.72	69.61	58.61	1.888	–0.902
Cl	Cl	F	35.42	50.90	58.22	48.70	0.940	–0.201	27.30	70.56	59.08	1.512	–0.925
Cl	Cl	Cl	34.51	52.89	58.94	46.62	0.578	–0.196	26.12	71.34	59.45	1.141	–0.940
Cl	Cl	OCH_3	35.95	51.48	58.20	48.34	0.741	–0.219	27.44	70.29	59.12	1.298	–0.931
Cl	Cl	OC_2H_5	35.69	51.30	58.18	48.57	0.743	–0.219	27.43	70.28	59.12	1.298	–0.932
Cl	Cl	OC_3H_7	35.67	50.88	58.18	48.14	0.743	–0 220	27.43	70.27	59.12	1.298	–0.932
Cl	OCH_3	OCH_3	36.74	49.53	57.23	48.92	0.898	–0.244	28.29	69.75	58.48	1.450	–0.933
Cl	OC_2H_5	OC_2H_5	36.68	49.90	57.25	49.25	0.902	–0.250	28.30	69.71	58.47	1.454	–0.934
Cl	OC_3H_7	OC_3H_7	36.74	50.17	57.23	49.67	0.903	–0.249	28.33	69.70	58.47	1.453	–0.933
Cl	OC_4H_9	OC_4H_9	36.78	49.83	57.21	49.30	0.901	–0.247	28.37	69.59	58.50	1.454	–0.933
Cl	Cl	$NHCH_3$	34.60	51.75	59.18	47.69	0.575	–0.253	26.29	70.70	59.75	1.129	–0.954
Cl	Cl	NHC_2H_5	34.35	51.87	59.09	47.59	0.581	–0.269	26.33	70.67	59.72	1.133	–0.953
Cl	Cl	NHC_3H_7-i	34.72	51.43	59.18	47.80	0.590	–0.242	26.56	70.13	60.22	1.121	–0.944
Cl	Cl	$N(CH_3)_2$	33.97	51.24	59.57	48.17	0.577	–0.291	26.27	70.45	59.92	1.143	–0.965
Cl	Cl	$N(C_2H_5)_2$	33.75	51.08	59.56	48.26	0.624	–0.321	26.27	70.23	59.99	1.166	–0.974
Cl	$N(CH_3)_2$	$N(CH_3)_2$	33.18	49.97	60.25	49.31	0.594	–0.399	26.15	69.51	60.71	1.138	–0.996
Cl	$N(C_2H_5)_2$	$N(C_2H_5)_2$	32.35	49.49	60.46	49.54	0.639	–0.431	25.77	69.42	60.74	1.183	–1.026
Cl	OCH_3	$NHCH_3$	35.41	50.39	58.31	48.90	0.734	–0.291	27.32	69.72	59.42	1.287	–0.951

R_1	R_2	R_3	$R_1R_2R_3P{=}S$						$R_1R_2R_3P{=}O$				
			$(s\%)_P$	$(s\%)_S$	$(p\%)_P$	$(p\%)_S$	Q_P	Q_S	$(s\%)_P$	$(s\%)_O$	$(p\%)_P$	Q_P	Q_O
Cl	OCH_3	NHC_2H_5	35.46	50.38	58.31	48.91	0.738	–0.289	27.36	69.71	59.38	1.291	–0.950
Cl	OCH_3	NHC_3H_7-i	35.59	50.07	58.45	49.17	0.717	–0.285	27.46	69.44	59.66	1.270	–0.945
Cl	OC_2H_5	$NHCH_3$	35.42	50.41	58.30	48.88	0.736	–0.292	27.35	69.71	59.37	1.288	–0.950
Cl	OC_2H_5	NHC_2H_5	35.42	50.42	58.29	48.86	0.740	–0.294	27.36	69.74	59.35	1.291	–0.950
Cl	OC_2H_5	NHC_3H_7-i	35.66	50.43	58.38	49.38	0.714	–0.283	27.49	69.43	59.64	1.271	–0.945
Cl	OC_3H_7-i	$NHCH_3$	35.63	49.76	58.23	48.55	0.724	–0.290	27.46	69.64	59.41	1.277	–0.947
Cl	OC_3H_7-i	NHC_2H_5	35.69	50.57	58.21	49.29	0.727	–0.288	27.51	69.62	59.42	1.279	–0.945
Cl	OC_3H_7-i	NHC_3H_7-i	35.84	50.37	58.31	49.43	0.703	–0.280	27.57	69.38	59.66	1.261	–0.941
Cl	OCH_3	$N(CH_3)2$	33.91	50.85	58.61	48.52	0.804	–0.445	27.08	69.35	58.56	1.243	–1.001
Cl	Cl	SCH_3	33.21	53.00	60.02	46.52	0.290	–0.246	24.82	71.23	60.06	0.832	–0.969
Cl	Cl	SC_2H_5	33.19	53.17	59.85	46.37	0.286	–0.252	24.87	71.19	60.35	0.830	–0.963
Cl	SCH_3	SCH_3	31.31	53.06	60.36	46.51	0.027	–0.362	23.20	71.29	59.85	0.528	–1.021
Cl	SC_2H_5	SC_2H_5	31.38	53.03	60.39	46.53	0.022	–0.360	23.29	71.21	59.95	0.525	–1.018
Cl	SC_3H_7-i	SC_3H_7-i	31.75	53.14	60.44	46.38	0.039	–0.345	23.44	71.20	60.16	0.476	–1.011
OCH_3	OCH_3	OCH_3	38.37	48.02	56.32	50.85	1.050	–0.260	30.06	68.15	58.11	1.602	–0.924
OC_2H_5	OC_2H_5	OC_2H_5	38.45	48.00	56.27	50.85	1.057	–0.264	30.14	68.08	58.09	1.608	–0.924
OCH_3	OCH_3	$NHCH_3$	36.67	48.76	57.63	50.30	0.883	–0.310	28.50	68.42	59.13	1.432	–0.949
OC_2H_5	OC_2H_5	$NHCH_3$	36.78	48.65	57.57	50.38	0.892	–0.302	28.58	68.57	59.09	1.431	–0.945
OCH_3	OCH_3	NHC_3H_7-i	36.73	48.64	57.73	50.44	0.895	–0.289	28.49	68.49	59.23	1.413	–0.945
OC_2H_5	OC_2H_5	NHC_3H_7-i	36.78	48.62	57.68	50.41	0.969	–0.276	28.63	68.38	59.22	1.417	–0.943

R_1	R_2	R_3	$R_1R_2R_3P{=}S$						$R_1R_2R_3P{=}O$				
			$(s\%)_P$	$(s\%)_S$	$(p\%)_P$	$(p\%)_S$	Q_P	Q_S	$(s\%)_P$	$(s\%)_O$	$(p\%)_P$	Q_P	Q_O
OC_2H_5	OC_2H_5	C_2H_5	35.71	48.57	59.00	50.50	0.836	–0.347	27.72	67.79	60.64	1.394	–0.954
OCH_3	OCH_3	$N(CH_3)_2$	36.39	48.31	57.89	50.69	0.881	–0.340	28.61	68.24	59.25	1.423	–0.959
CH_3	$N(CH_3)_2$	$N(CH_3)_2$	31.25	49.21	61.92	50.09	0.529	–0.521	24.66	68.42	62.16	1.040	–1.040
$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$	32.86	49.55	59.39	49.64	0.629	–0.527	25.78	69.65	59.76	1.123	–1.042
SC_2H_5	SC_2H_5	$NHCH_3$	31.31	51.88	61.05	48.00	0.138	–0.369	23.30	70.22	60.61	0.508	–1.030
SCH_3	SCH_3	SCH_3	29.50	52.43	63.11	47.06	–0.210	–0.379	21.85	70.15	62.11	0.282	–1.030
SC_2H_5	SC_2H_5	SC_2H_5	29.65	52.45	62.95	47.03	–0.215	–0.384	21.95	70.18	61.96	0.275	–1.030
SC_3H_7	SC_3H_7	SC_3H_7	29.57	52.57	62.76	46.93	–0.221	–0.388	21.94	70.25	61.79	0.267	–1.032
SCH_3	SC_3H_7-i	SC_3H_7-i	29.69	52.61	62.61	–0.235	–0.235	–0.390	21.82	70.47	61.46	0.221	–1.040
CH_3	CH_3	CH_3	29.42	48.56	64.70	50.92	0.418	–0.565	23.10	66.25	64.79	0.918	–1.058
C_2H_5	C_2H_5	C_2H_5	30.20	48.81	64.00	50.62	0.406	–0.585	23.57	66.55	64.39	0.908	–1.051
H	OC_4H_9	OC_4H_9	36.56	47.87	59.22	51.06	0.679	–0.219	28.16	66.47	61.75	1.275	–0.898
CH_3	OC_2H_5	OC_2H_5	35.49	48.78	59.07	50.34	0.831	–0.336	27.72	67.94	60.59	1.383	–0.955
H	OC_3H_7-i	OC_3H_7-i	36.85	52.41	59.00	55.50	0.649	–0.218	28.20	66.66	61.61	1.240	–0.897
CH_3	OC_3H_7	$N(CH_3)_2$	33.55	48.79	60.62	50.40	0.680	–0.417	26.24	67.89	61.63	1.216	–0.992
CH_3	OC_4H_9	$N(CH_3)_2$	33.61	48.87	60.58	50.34	0.676	–0.413	26.25	67.91	61.61	1.212	–0.992
C_2H_5	OC_2H_5	OC_2H_5	35.75	48.96	58.92	50.65	0.838	–0.336	27.67	67.96	60.52	1.385	–0.955
C_2H_5	OC_3H_7-i	OC_3H_7-i	36.09	48.97	58.77	50.66	0.808	–0.329	27.74	67.98	60.54	1.353	–0.949
Cl	Cl	CH_3	33.53	51.97	60.54	47.54	0.518	–0.286	25.61	69.90	61.28	1.074	–0.959
Cl	Cl	C_2H_5	33.76	51.96	60.34	47.54	0.521	–0.292	25.82	69.85	61.17	1.077	–0.955

R_1	R_2	R_3	$R_1R_2R_3P{=}S$						$R_1R_2R_3P{=}O$				
			$(s\%)_P$	$(s\%)_S$	$(p\%)_P$	$(p\%)_S$	Q_P	Q_S	$(s\%)_P$	$(s\%)_O$	$(p\%)_P$	Q_P	Q_O
F	OCH_3	OCH_3	38.21	47.60	56.47	51.12	1.245	–0.228	30.19	68.31	58.03	1.817	–0.908
F	OC_2H_5	OC_2H_5	38.27	47.27	56.43	50.72	1.249	–0.230	30.24	68.29	58.01	1.819	–0.907
H	OCH_3	OCH_3	36.49	47.65	59.33	51.12	0.683	–0.214	28.09	66.49	61.91	1.274	–0.899
H	OC_2H_5	OC_2H_5	36.58	47.63	59.21	51.35	0.679	–0.217	28.15	66.49	61.76	1.275	–0.898
H	OC_3H_7	OC_3H_7	36.56	47.95	59.19	51.03	0.679	–0.219	28.15	66.51	61.74	1.274	–0.899
CH_3	OC_2H_5	SC_2H_5	32.71	49.86	61.08	49.42	0.384	–0.397	24.96	68.51	61.85	0.896	–0.998
C_2H_5	OC_2H_5	SC_2H_5	32.86	49.89	60.99	49.38	0.383	–0.401	25.13	68.52	61.69	0.900	–0.997
C_2H_5	OC_2H_5	SCH_3	32.81	49.85	61.06	49.42	0.385	–0.400	25.05	68.49	61.84	0.903	–0.997
CH_3	OC_2H_5	$N(CH_3)_2$	33.59	48.87	60.59	50.33	0.677	–0.415	26.24	67.89	61.63	1.215	–0.992
Cl	C_6H_5	C_6H_5	31.02	51.20	62.55	48.32	0.402	–0.455	23.96	69.56	62.19	0.900	–1.012
Cl	OC_6H_5	OC_6H_5	37.35	49.63	56.88	48.91	0.899	–0.235	28.56	69.79	58.32	1.451	–0.929
Cl	Cl	OC_6H_5	35.96	51.15	57.97	48.09	0.745	–0.214	27.25	70.72	58.89	1.297	–0.934
Cl	OC_2H_5	$N(CH_3)_2$	35.08	50.17	58.50	49.08	0.751	–0.323	27.25	69.72	59.38	1.299	–0.965
OC_3H_7-i	OC_3H_7-i	OC_3H_7-i	38.84	48.05	56.16	50.76	0.998	–0.253	30.07	68.18	58.17	1.548	–0.915

The P=O bond stretching frequencies calculated with Eq.(8), and P=S bond stretching frequencies with Eq.(10) are listed in Table II. Results of the calibrations of Eqs.(7)-(12) are summarized in Table III. One can see from the standard deviations (SD) and correlation coefficients (r) listed in Table III that the standard deviation of Eq.(8) for the P=O bonds and that of Eq.(10) for the P=S bonds are only 3.7 and 5.4 cm^{-1}, respectively. The simplified forms of Eqs.(8) and (10), including the simplest Eq.(7), can also give reasonable results. The standard deviations of the simplest Eq.(7) for the P=O and P=S stretching frequencies are 4.6 and 6.2 cm^{-1}, respectively. The frequencies calculated with various relationships summarized in Table III are very close to each other. So, we list only one set of the calculated frequencies in Table II. For the molecules whose experimental frequency is available, the calculated frequencies are compared with the experimental data. For the molecules whose experimental frequencies are not available, the calculated frequencies are given as our theoretical prediction.

A survey of the data listed in Table II reveals that the calculated P=O and P=S stretching frequencies are all in good agreement with the available experimental data. They adequately reflect some interesting tendencies, *e.g.* experimental $\nu_{P=O}$ values in the compounds $Cl_nF_{(3-n)}P=O$ (n=0, 1, 2, 3) decrease with increasing n, which is just contrary to the case in the $Cl_nF_{(3-n)}P=S$ (n=0, 1, 2, 3) compounds; experimental $\nu_{P=O}$ values in the compounds $Me_3P=X$ (X=S and O) are larger than those in $Et_3P=X$ (X=S and O); for $Cl_2XP=S$, the experimental P=S stretching frequency becomes lower and lower in going from X=Cl to F, SMe, OMe, NHMe and NMe_2, whereas for $Cl_2XP=O$, the experimental P=O stretching frequency becomes lower and lower from X=F to OPh, Cl, NMe_2 and Me; for $Cl_{(3-n)}(NMe_2)_nP=S$ (n=0,1,2,3), the experimental P=S stretching frequency becomes lower and lower with increasing n; and in general case, the P=O and P=S frequencies in compounds containing two Cl substituents are higher than those in compounds containing only one Cl substituent with an exception of F-substituted compounds. These substituent effects are all qualitatively reproduced by Eq.(8) and Eq.(10). It follows that the generalized semiempirical relationship Eq.(6) employed in this study is quite reasonable for calculation of the P=O and P=S stretching frequencies of organophosphorus compounds.

TABLE II The calculated P=O and P=S stretching frequencies (in cm^{-1}) for $R_1R_2R_3P=X$ (X=O and S) compounds compared with the available experimental data

R_1	R_2	R_3	$\nu_{P=S}$ ($R_1R_2R_3P=S$)				$\nu_{P=O}$ ($R_1R_2R_3P=O$)		
			Expt.			*Calc.*	*Expt.*		*Calc.*
			Rept.[a]	*Ref.*	*Used*[b]	*Eq.(10)*	*Expt.*	*Ref.*	*Eq.(8)*
F	F	F	696	[36]	696	701.7	1415	[40]	1412.0
Cl	F	F	727	[36]	727	716.9	1358	[41]	1363.7
Cl	Cl	F	741	[36]	741	735.4	1331	[41]	1325.5
Cl	Cl	Cl	750	[35]	750	754.8	1290	[42]	1292.9
Cl	Cl	OCH_3	720–703	[35]	712	709.5			1291.7
Cl	Cl	OC_2H_5	725–699	[28]	712	713.2			1291.2
Cl	Cl	OC_3H_7	712–689	[37]	701	697.7			1291.1
Cl	OCH_3	OCH_3	665–655	[35]	660	664.7	1286	[44]	1292.8
Cl	OC_2H_5	OC_2H_5	671–656	[28]	664	668.2	1289	[44]	1292.2
Cl	OC_3H_7	OC_3H_7	670–661	[28]	666	670.4	1291	[44]	1292.2
Cl	OC_4H_9	OC_4H_9	670–662	[28]	666	666.6			1290.3
Cl	Cl	$NHCH_3$	721–687	[35]	704	700.9			1277.1
Cl	Cl	NHC_2H_5	725–688	[38]	707	703.0			1277.2
Cl	Cl	NHC_3H_7-i	727–690	[38]	709	697.0			1271.3
Cl	Cl	$N(CH_3)_2$	673	[36]	673	683.5	1268	[47]	1270.6
Cl	Cl	$N(C_2H_5)_2$	671	[36]	671	674.1			1266.1
Cl	$N(CH_3)_2$	$N(CH_3)_2$	613	[36]	613	619.2	1241	[47]	1241.3
Cl	$N(C_2H_5)_2$	$N(C_2H_5)_2$	611	[36]	611	613.7			1233.0

R_1	R_2	R_3	$\nu_{P=S}$ ($R_1R_2R_3P=S$)				$\nu_{P=O}$ ($R_1R_2R_3P=O$)		
			Expt.			*Calc.*	*Expt.*		*Calc.*
			Rept.[a]	*Ref.*	*Used*[b]	*Eq.(10)*	*Expt.*	*Ref.*	*Eq.(8)*
Cl	OCH_3	$NHCH_3$	660–639	[36]	650	659.8			1273.9
Cl	OCH_3	NHC_2H_5	663–639	[36]	651	659.7			1274.3
Cl	OCH_3	NHC_3H_7-i	673–643	[36]	658	650.4			1270.0
Cl	OC_2H_5	$NHCH_3$	666–643	[36]	655	659.7			1274.3
Cl	OC_2H_5	NHC_2H_5	663–643	[36]	653	659.4			1274.8
Cl	OC_2H_5	NHC_3H_7-i	673–647	[36]	660	655.3			1269.6
Cl	OC_3H_7-i	$NHCH_3$	660–639	[36]	650	647.6			1272.3
Cl	OC_3H_7-i	NHC_2H_5	663–642	[36]	653	656.5			1272.7
Cl	OC_3H_7-i	NHC_3H_7-i	665–645	[36]	655	651.3			1269.0
Cl	OCH_3	$N(CH_3)2$	633	[36]	633	628.2			1236.1
Cl	Cl	SCH_3	737–717	[35]	727	729.5			1259.8
Cl	Cl	SC_2H_5	730	[36]	730	732.5			1259.8
Cl	SCH_3	SCH_3	708–690	[35]	699	702.5			1235.1
Cl	SC_2H_5	SC_2H_5	705	[36]	705	700.3			1233.2
Cl	SC_3H_7-i	SC_3H_7-i	705	[36]	705	700.5			1227.4
OCH_3	OCH_3	OCH_3	620–598	[35]	609	618.1	1272	[45]	1271.8
OC_2H_5	OC_2H_5	OC_2H_5	635–614	[36]	625	616.0	1270	[46]	1270.4
OCH_3	OCH_3	$NHCH_3$	630–597	[36]	614	612.8			1259.0
OC_2H_5	OC_2H_5	$NHCH_3$	640–608	[36]	624	614.0			1262.9
OCH_3	OCH_3	NHC_3H_7-i	645–611	[36]	628	620.0			1260.6

R_1	R_2	R_3	$\nu_{P=S}$ ($R_1R_2R_3P=S$)				$\nu_{P=O}$ ($R_1R_2R_3P=O$)		
			Expt.			*Calc.*	*Expt.*		*Calc.*
			Rept.[a]	*Ref.*	*Used*[b]	*Eq.(10)*	*Expt.*	*Ref.*	*Eq.(8)*
OC_2H_5	OC_2H_5	NHC_3H_7-i	650–617	[36]	634	632.6			1258.9
OC_2H_5	OC_2H_5	C_2H_5	606–584	[20]	595	598.4			1255.1
OCH_3	OCH_3	$N(CH_3)_2$	588	[36]	588	593.4			1246.1
CH_3	$N(CH_3)_2$	$N(CH_3)_2$	569	[36]	569	568.3	1205	[28]	1206.6
$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$	565	[36]	565	561.1			1221.2
SC_2H_5	SC_2H_5	$NHCH_3$	693–663	[36]	678	678.8			1211.3
SCH_3	SCH_3	SCH_3	698–682	[35]	690	688.7			1207.7
SC_2H_5	SC_2H_5	SC_2H_5	685	[30]	685	684.0	1206	[28]	1206.4
SC_3H_7	SC_3H_7	SC_3H_7	685	[30]	685	687.3			1206.8
SCH_3	SC_3H_7-i	SC_3H_7-i	685	[30]	685	684.4			1206.2
CH_3	CH_3	CH_3	558	[22]	558	557.2	1174	[39]	1172.3
C_2H_5	C_2H_5	C_2H_5	535	[22]	535	535.4	1166	[22]	1171.1
H	OC_4H_9	OC_4H_9				622.9	1263	[34]	1260.2
CH_3	OC_2H_5	OC_2H_5				610.0	1250	[48]	1254.6
H	OC_3H_7-i	OC_3H_7-i				716.1	1261	[45]	1256.7
CH_3	OC_3H_7	$N(CH_3)_2$				586.5	1234	[47]	1228.5
CH_3	OC_4H_9	$N(CH_3)_2$				588.4	1234	[47]	1228.0
C_2H_5	OC_2H_5	OC_2H_5				603.4	1250	[48]	1256.1
C_2H_5	OC_3H_7-i	OC_3H_7-i				598.7	1252	[43]	1255.2
Cl	Cl	CH_3				695.9	1265	[28]	1266.6

R_1	R_2	R_3	$\nu_{P=S}$ ($R_1R_2R_3P=S$)				$\nu_{P=O}$ ($R_1R_2R_3P=O$)		
			Expt.			*Calc.*	*Expt.*		*Calc.*
			Rept.[a]	*Ref.*	*Used*[b]	*Eq.(10)*	*Expt.*	*Ref.*	*Eq.(8)*
Cl	Cl	C_2H_5				689.4	1265	[28]	1265.8
F	OCH_3	OCH_3				647.0	1318	[39]	1315.5
F	OC_2H_5	OC_2H_5				647.0	1314	[39]	1315.5
H	OCH_3	OCH_3				622.5	1260	[43]	1261.0
H	OC_2H_5	OC_2H_5				620.2	1259	[43]	1260.6
H	OC_3H_7	OC_3H_7				624.3	1256	[43]	1259.8
CH_3	OC_2H_5	SC_2H_5				609.2	1215	[43]	1214.4
C_2H_5	OC_2H_5	SC_2H_5				605.3	1215	[43]	1212.9
C_2H_5	OC_2H_5	SCH_3				606.0	1215	[43]	1214.0
CH_3	OC_2H_5	$N(CH_3)_2$				588.0	1234	[47]	1228.3
Cl	C_6H_5	C_6H_5				631.2	1235	[39]	1235.4
Cl	OC_6H_5	OC_6H_5				663.5	1297	[43]	1292.6
Cl	Cl	OC_6H_5				703.6	1305	[43]	1296.7
Cl	OC_2H_5	$N(CH_3)_2$				646.5	1269	[48]	1268.3
OC_3H_7-i	OC_3H_7-i	OC_3H_7-i				611.6	1272	[45]	1271.3

a. The experimental values with numbers in brackets refer to references. The physical states of the compounds when the frequencies were observed were described in the corresponding papers cited.

b. The experimental frequency adopted in the least-squares process is chosen as the middle value of the band reported, if the position of the peak for the band was not given in the literature. For example, because the band of eighth compound listed for P=S was reported as 665–655 cm^{-1}, the middle value, *i.e.* (665 + 655)/2 = 660 cm^{-1}, is regarded as the position of the peak adopted in this work.

TABLE III Calibrated parameter values, correlation coefficients (r) and standard deviations (SD) of Eqs.(7)-(12)

Parameters[a]	*P=S bonds*	*P=O bonds*
	Calibration of Eq. (10)	
K_{00PS}	−7.014156	
K_{0QP}	0.8833	
K_{0QS}	175.4276	
K_{0P}	605.8847	
K_{0S}	405.7538	
K_{EP}	454.43	
K_{ES}	−18122.01	
K_{10PS}	−1.538237	
K_{1QP}	−6.8437	
K_{1P}	−9.7619	
K_{01PS}	−5.579309	
K_{1QS}	199.7133	
K_{1S}	150.2041	
K_{11PS}	1.739810	
C_{PS}	−26204.05	
r	0.994	
SD (cm^{-1})	5.4	
n	50	
	Calibration of Eqs.(8) and (11)	
	Eq.(11)	Eq.(8)
K_{00PX}	−0.802425	2.761376
K_{0QP}	5.6273	11.1409
K_{0QX}	−18.8659	−104.5703
K_{0P}	20.9875	−219.5078
K_{OX}	83.3459	−168.9781
K_{EP}	321.28	−783.58
K_{EX}	1404.26	7868.27
K_{10PX}	−0.822091	0.121493
K_{1QP}	−8.5450	10.2073
K_{1P}	45.1686	−21.0474
C_{PX}	−2978.06	14925.14
r	0.993	0.997
SD (cm^{-1})	5.9	3.7
n	50	38
	Calibration of Eqs (9) and (12)	
	Eq.(12)	Eq.(9)

Parameters[a]	*P=S bonds*	*P=O bonds*
K_{PX}	−0.467214	1.763163
K_{QP}	4.2459	5.5053
K_{QX}	−7.3809	−103.6257
K_P	5.9416	−143.6326
K_X	36.2021	−133.6212
K_{EP}	−55.33	−19.39
K_{EX}	821.18	7789.88
C_{PX}	−480.27	11523.38
r	0.993	0.997
SD (cm^{-1})	6.0	3.8
n	50	38
	Calibration of Eq. (7)[b]	
K_{PX}	−1.260328	−0.915239
K_{QP}	2.7664	4.6443
K_{QX}	9.1508	10.4907
K_P	45.7729	41.5154
K_X	68.2882	46.1007
C_{PX}	−2092.43	−801.91
r l	0.992	0.995
SD (cm^{-1})	6.2	4.6
n	50	38

a. X is O or S, and n is the number of available experimental data used for P=O and P=S.
b. Calibration of Eq.(7) for P=S bonds is actually the same as that of Eq.(3) reported previously in ref.[51].

CONCLUSION

A generalized semiempirical relationship has been employed to elucidate the P=O and P=S bond stretching vibrational frequencies for a series of organophosphorus compounds. The calculated results are in good agreement with the available experimental data, which indicates that the P=O and P=S stretching frequencies are determined by the characters of the hybrid orbitals of the atoms P and X (X=O and S) and the corresponding net atomic charges.

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