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X-Ray Determination of the Effective Charges on Sulfur and Phosphorus Atoms in Chemical Compounds

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ABSTRACT

The dependencies of Kα line shifts of the P and S atoms on effective charges of the atoms, calculated by CNDO/S, CNDO/2, INDO, and MNDO methods in the minimal and extended basis sets, have been investigated for model compounds. Good linear relationships between Kα shifts and atomic charges have been obtained for all cases investigated except for CNDO/2 and INDO calculations in the extended basis set. It is found that the P=S bond ionicity is a nearly constant value, whereas the P—S bond ionicity increases linearly with an increase in the positive charge of the central P atom. It is shown that the P and S atom charge in sulfides and phosphines containing no substituents with a strong M-effect at the central atom depend only on inductive substituent effects. Also, the positive charge on the central atom increases with the growth of the π-donor properties of substituents in sulfides and phosphines containing substituents exerting a strong M-effect, as well as in phosphoryl and thiophosphoryl compounds and sulfones.

INTRODUCTION

As stated in references 1–8, the Kα line shifts of the 2nd Row element such as Al, Si, P, S and Cl are determined by the effective charges of these atoms. This follows from comparison of the Kα line energies of free atoms and their ions obtained by non-empirical calculations with the ion charges. However, all the obtained relationships between the Kα shifts and the atomic charges had two drawbacks: 1) they were untrue for the Kα line

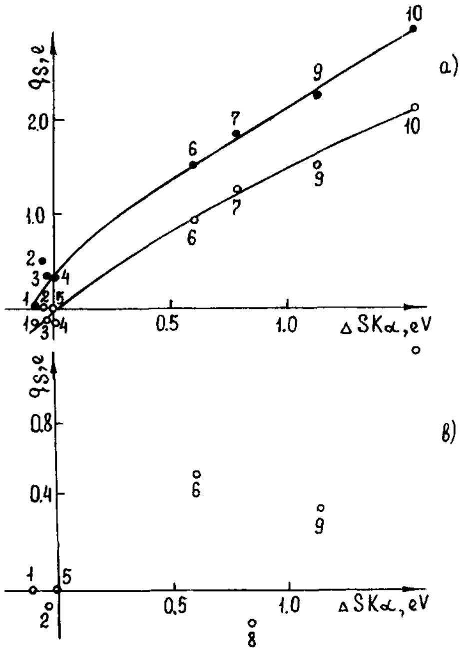

FIGURE 1 Dependencies between SKα shifts and q_S values obtained by a) *ab initio* calculations in [9] and b) CNDO/2 calculations in [10]. Points represent calculations carried out in the minimal basis set and circles represent calculations carried out in the extended basis set. 1 H_2S, 2 thiophene, 3 CS_2, 4 OCS, 5 S_8, 6 SO_2, 7 F_2SO, 8 SO_3^{2-}, 9 SO_4^{2-}, 10 SF_6.

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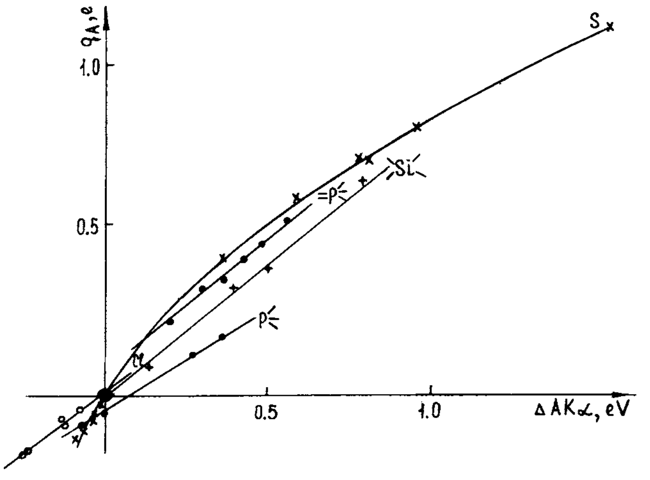

FIGURE 2 Dependencies between AKα shifts and q_A values calculated by the electronegativity equalization procedure [14]. × represent sulfur compounds: S_8, H_2S, Me_2S, thiophene, CS_2, OCS, Me_2SO, F_2SO, SO_2, SF_4, Me_2SO_2, SF_6. · represent phosphorus compounds: PH_3, PMe_3, PCl_3, PBr_3, Me_3PO, Cl_2MePO, Cl_3PO, Me_3PS, Cl_2MePS, Cl_3PS. + represent silicon compounds: $Si_{elem.}$, $SiMe_4$, SiF_4, $SiCl_4$, $SiBr_4$. ○ represent chlorine compounds: Cl_2, HCl, MeCl, PCl_3, CrO_2Cl_2, $OVCl_3$.

negative shifts (with respect to free atoms); 2) the obtained atom charge values coordinated poorly with those obtained by quantum-chemical calculations.

We believe that another way of finding relationships between the Kα shifts and the atom charges, i.e. correlation of the experimental Kα shifts of the above elements in a series of model compounds with the calculated effective charges of the corresponding atoms, looks more promising. There have been both successful and unsuccessful attempts to make such comparisons. The former are reported by Gelius, Roos, and Siegbahn [9] who found that the Kα shifts of the sulfur atom (ΔSKα) for a number of simple molecules were correlated with the effective charges on the S atom (q_s) obtained by *ab initio* calculations in which optimized Gaussian functions were used. This resulted in sufficiently smooth q_s versus ΔSKα dependence as shown in Figure 1a. In one of the unsuccessful attempts at finding such dependence [10], the experimental ΔSKα values corresponding to simple sulfur-containing compounds were correlated with q_s values obtained by CNDO/2 calculations in the extended basis set (see Figure 1b).

TABLE 1 Experimental SKα shifts and q_S values calculated by different quantum-chemical methods

Molecular	*ΔSKα, eV · 100*	*q_S, e · 100*								
		CNDO / S				*CNDO / 2*		*INDO*		*MNDO*
		PSS1[15]		*[16]*						
		sp	*spd*	*sp*	*spd*	*sp*	*spd*	*sp*	*spd*	*sp*
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
CS_2	−2.9(11)*	−12.2	−10.8	−14.2	−10.4	−11.6	−2.6	−14.7	−4.6	11.6
OCS	−0.5(12)	−22.3	−19.7	−5.9	−2.6	−19.1	−10.3	−23.9	−13.4	−3.6
MeNCS	−4.7(8)	−29.8	−28.0	−25.5	−26.7	−29.0	−24.3	−33.4	−27.0	−15.3
Me_3PS	−12.1(14)	−76.7	−44.7	−72.3	−56.4	−70.0	−4.8	−67.0	−5.0	−43.3
Cl_3PS	−10(2)	−61.8	−27.2	−62.0	−39.2	−50.7	11.3	−55.0	9.3	−10.7
S_8	0	0	0	0	0	0	0	0	0	0
H_2S	−8.6(9)	−10.4	−9.5	−10.6	−9.7	−9.3	−1.6	−12.9	−4.3	7.1
Me_2S	−6.3(6)	−5.3	−7.7	−4.9	−7.0	−4.2	−12.7	−9.5	−17.5	−1.5
F_3CSCH_2Cl	−2.9(11)	5.5	2.8	8.1	6.3	−1.2	−11.0	−8.6	−16.6	13.9
F_3CSCl	2.5(16)	13.4	11.4	17.2	15.6	7.1	−2.3	4.3	−4.6	31.2
$S(SiMe_3)_2$	−22.6(8)	−28.3	−15.7	−23.7	−21.5	−37.1	11.7	−43.3	16.8	−61.1
$P(SMe)_3$	−6.6(12)	−7.2	−5.7	−9.5	−9.6	−9.8	−1.2	−14.4	−1.4	−2.5
$H_2C=CHSMe$	−4.3(6)	−0.3	−3.4	0.9	−2.1	−0.3	−13.5	−5.5	−17.9	9.1
$Cl_2C=CHSMe$	−2.1(6)	1.0	−3.4	1.4	−2.9	1.2	−9.3	−2.8	−12.0	13.5
$ClC\equiv CSMe$	3.3(7)	6.4	1.4	8.0	3.6	6.1	−11.3	2.4	−13.6	27.0
$CH=CHSCH=CH$	−3.6(12)	5.7	3.2	6.2	3.2	9.4	−4.8	5.9	−7.1	28.8
PhSMe	−2.3(6)	−1.7	−4.6	−1.6	−5.4	−1.9	−20.1	−7.6	−24.9	5.9
SO_2	59.3(8)	86.6	57.8	108.3	95.0	81.6	23.0	90.4	30.7	123.2
Me_2SO	35.9(9)	68.6	40.0	68.3	55.8	57.5	4.9	60.5	4.1	89.7
F_2SO	78.7(11)	117.5	75.8	122.0	100.3	108.0	37.2	121.9	41.9	155.2
SF_4	97.0(8)	139.7	89.3	147.1	101.9	137.5	49.4	151.6	57.6	185.5
Me_2SO_2	80.5(6)	140.4	75.2	139.9	109.8	127.0	19.3	148.7	30.4	160.3
H_2SO_4	117(1)	175.5	94.2	184.9	147.6	160.8	32.2	191.5	48.2	197.0
SF_6	155.3(14)	227.2	143.6	239.9	151.5	224.2	74.7	255.1	101.7	244.4

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* Here and further the mean-square errors in the last significant digit taken for 95% confidence interval by Student's criterion are given in parenthesis.

Satisfactory correlations shown in Figure 2 were first obtained by us [11–13]. In these works the experimental shifts of AKα lines (A=Si, P, S, Cl) were correlated with the q_A values obtained by Jolly and Perry [14] by means of the electronegativity equalization procedure. All these dependencies except those corresponding to compounds of sulfur in the highest oxidation states, were close to linear. As a result, the possibility of estimating q_A values for different A atoms with the help of experimental AKα shifts in a single scale of effective charge values has been achieved. However, the dependencies obtained have two defects: 1) the calculations used were completely empirical; 2) there was no possibility of their practical application to such compounds as sulfonium and phosphonium salts, sulfides, and phosphines coordinated to a metal, etc.

Therefore, at present, there is a need to establish more reliable analytical correlations between AKα shifts and q_A values for various elements A.

METHODS

This can be achieved by comparison of the experimental AKα shifts for a sufficiently large number of A-containing compounds with q_A values obtained by various quantum-mechanical calculations. In the present work, this problem is solved for the S and P atoms. The following methods of calculation were used: CNDO/S in PSS1 [15] and Takata's [16] parametrizations, CNDO/2 [17], INDO [18] in minimal and extended basis sets and MNDO [19] in a minimal basis set. The present results give the following possibilities: 1) to calibrate the BKα shifts (B=S, P) on the basis q_B values belonging to various charge value scales; 2) to determine the q_B values for different B atoms in a single charge value scale that must allow for tracing quantitatively the changes in the PS bond ionicity in chemical compounds; 3) to check the validity of different quantum-chemical methods for the definition of q_B values.

Fluorescent SKα and PKα spectra were obtained by use of the X-ray spectrometer "Stearate." The spectra were excited by AgL-radiation (X-ray tube operated at 0.4 A and 6–10 kV) and analyzed by quartz crystal (plane of rhombohedron, bend radius 500 mm). Samples of solids and viscous liquids were prepared by rubbing on a checkered nickel plate. Samples of gases and volatile liquids were prepared by evaporating the investi-

TABLE 2 Experimental PKa shifts and q_P values calculated by different quantum-chemical methods

		q_P, *e · 100*								
		CNDO/S				*CNDO/2*		*INDO*		*MNDO*
		PSS1[15]		*[16]*						
Molecule	$\Delta PK\alpha$, *eV · 100*	*sp*	*spd*	*sp*	*spd*	*sp*	*spd*	*sp*	*spd*	*sp*
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
PH_3	−7(2)	5.5	4.6	7.0	7.0	10.5	19.8	10.2	20.8	25.2
PEt_3	−0.5(5)	19.1	10.3	19.1	15.8	31.9	−11.7	12.3	−17.2	5.4
$PhPMe_2$	5.1(7)	18.5	9.2	18.7	14.4	19.8	−26.4	14.0	−32.5	7.1
4-$COOEtC_6H_4PMe_2$	5.1(6)	19.5	10.0	19.0	15.4	19.3	−26.3	13.4	−32.4	5.0
PPh_3	6.6(6)	17.2	6.9	17.8	10.9	16.2	−55.9	11.0	−63.1	35.2
$P(CN)_3$	40.7(13)	34.5	22.4	39.1	34.9	28.0	0.7	23.7	−4.1	97.2
$MePCl_2$	21.1(10)	38.3	27.0	34.6	29.2	18.7	−12.8	25.4	−12.6	59.5
$PhPCl_2$	25.0(8)	37.8	25.6	34.8	29.0	39.3	−25.9	44.0	−25.4	70.6
PCl_3	37.3(7)	47.2	34.5	42.5	35.1	49.0	−16.8	58.6	−14.0	80.6
$P(OMe)_3$	48.2(9)	55.2	23.1	70.9	60.6	73.6	−1.4	82.4	−3.5	89.9
$P(SMe)_3$	15.6(6)	25.0	6.9	22.9	17.0	27.8	−32.4	33.3	−34.6	−7.0
Me_3PO	29.5(9)	92.5	50.3	75.2	60.5	91.7	3.4	102.6	7.7	68.3
$PhP(O)Me_2$	34.4(6)	93.2	47.6	75.5	59.4	86.8	0.2	97.8	4.5	71.0
Cl_3PO	55.8(6)	114.1	67.2	95.6	74.0	118.5	−16.8	142.8	−7.2	101.1
$MeP(O)Cl_2$	48.3(6)	106.8	62.0	88.9	68.6	110.2	−6.3	130.2	1.6	90.5
$(MeO)_3PO$	70.4(6)	133.8	64.0	126.8	102.6	147.2	18.1	172.4	27.6	137.2
Me_3PS	19.8(7)	76.1	44.2	62.2	47.5	78.2	−14.0	85.9	−12.2	12.7
Cl_3PS	43.0(8)	98.7	57.1	83.0	57.2	103.8	−34.0	124.5	−26.6	59.7
$Ph_3P \cdot BF_3$	7.6(6)	63.2	64.0	47.8	43.7	49.7	5.5	48.1	6.1	−3.7
$[4\text{-}Me_2NC_6H_4P\text{-}(NMe_2)_2Me]^+Cl^-$	38.1(9)	95.9	67.5	84.2	68.2	104.2	13.5	111.5	14.1	95.3
PCl_5	56.5(6)	108.2	75.7	94.2	67.4	120.4	−16.9	141.3	−5.8	89.2
NH_4PF_6	123.0(1)	181.3	92.8	165.0	98.0	211.7	48.5	236.4	69.4	197.9

TABLE 3 Parameters of correlations $q_B = a\Delta BK\alpha + b$ (q_B in e · 100, $\Delta BK\alpha$ in eV · 100)

B	*Class*	*The method of calculation*	*a*	*b*	*r*	*s*	*n*	*The number of the correlation*
S	All compounds except S =	CNDO / S, PSS1, sp	1.45(3)	6(2)	0.997	6	19	(2)
		CNDO / S, PSS1, spd	0.89(2)	2(1)	0.995	5	19	(3)
		CNDO / S, [16], sp	1.52(3)	7(1)	0.997	6	19	(4)
		CNDO / S, [16], spd	1.14(4)	5(3)	0.986	10	19	(5)
		CNDO / 2, sp	1.41(2)	3(1)	0.997	5	19	(6)
		INDO, sp	1.64(3)	0(2)	0.997	6	19	(7)
		MNDO, sp	1.64(7)	15(4)	0.985	15	19	(8)
	S =	CNDO / S, PSS1, sp	5.7(8)	−5(5)	0.961	9	6	(9)
		CNDO / S, [16], sp	6.0(2)	0(1)	0.997	3	6	(10)
		CNDO / S, [16], spd	4.4(4)	0(2)	0.985	4	6	(11)
		CNDO / 2, sp	4.5(6)	−6(4)	0.960	7	6	(12)
		INDO, sp	4.8(7)	−8(5)	0.950	9	6	(13)
P	$\mathrm{P}\!\begin{smallmatrix}\diagup\\ -\\ \diagdown\end{smallmatrix}$	CNDO / S, PSS1, sp	0.88(6)	15(1)	0.980	3	10	(14)
		CNDO / S, [16], sp	0.69(7)	15(2)	0.960	3	10	(15)
		CNDO / S, [16], spd	0.60(6)	13(1)	0.962	3	9	(16)
		CNDO / 2, sp	1.11(9)	13(2)	0.978	5	8	(17)
		INDO, sp	1.4(1)	0(2)	0.977	6	9	(18)
		MNDO, sp	2.2(2)	6(5)	0.965	10	8	(19)
	All compounds except $\mathrm{P}\!\begin{smallmatrix}\diagup\\ -\\ \diagdown\end{smallmatrix}$	CNDO / S, PSS1, sp	1.01(3)	57(2)	0.994	13	11	(20)
		CNDO / S, PSS1, spd	0.64(4)	36(2)	0.974	4	8	(21)
		CNDO / S, [16], sp	0.99(3)	42(1)	0.996	3	10	(22)
		CNDO / S, [16], spd	0.47(4)	42(2)	0.971	4	9	(23)
		CNDO / 2, sp	1.36(5)	46(3)	0.993	5	11	(24)
		INDO, sp	1.58(8)	51(4)	0.988	8	11	(25)
		MNDO, sp	1.7(1)	−3(9)	0.967	15	10	(26)

gated compounds at 10^{-5} Torr on an iridium or nickel plate maintained at 77 K. During exposure time (about 5 s. for one BKα spectrum) the samples were maintained at liquid nitrogen temperature.

ΔBKα values were obtained by the following procedure: consecutive registration of 8–10 tops of the BKα spectra of the standard (elemental sulfur or red phosphorus), then 16–20 tops of spectra of sample and again 8–10 spectra of the standard. The maximum position was obtained as the middle of the section of the spectrum at ~0.9 of its height, with subsequent statistical treatment. The possibility of radiative decomposition of the samples was controlled by the width and form of the BKα doublet and also by the presence (or absence) of systematic changes in the position of the doublet maximum. The greater precision of determination of ΔBKα values was achieved by measurement of N independent ΔBKα values ($\Delta BK\alpha_1$, $\Delta BK\alpha_2$, . . ., $\Delta BK\alpha_N$) by the method described above. The mean-square errors $\sigma(\Delta BK\alpha_i)$ for these measurements were determined for the corresponding confidence interval (by Student's criterion) $k_i = 0.95^{1/N}$ to obtain finally the N values of ΔBKα: $\Delta BK\alpha_i^{\pm}\ \sigma(\Delta BK\alpha_i)$. The common interval of overlapping of these values corresponds to the final $\Delta BK\alpha^{\pm}\ {}^{\pm}\sigma(\Delta BK\alpha)$ value, where $\sigma(\Delta BK\alpha)$ corresponds to a 95% confidence interval.

RESULTS AND DISCUSSION

The experimental BKα shifts for sufficiently large series of B-containing compounds and the q_B val-

TABLE 4 Parameters of correlation equations $\Delta BK\alpha = a\Sigma\sigma_I + b\Sigma\sigma_R^0 + c$

B		*Class of compounds*	*a*	*b*	*c*	*r*	*s*	*n*
S	XSY	X, Y = R, Cl, SCl, CN	17.4(6)	−1(1)	−5.7(5)	0.982	1.1	31
		X, Y = SiR_3, $Si(OR)_3$, COMe, CF_3, SR are present	22(1)	−16(1)	−13.6(6)	0.987	1.2	16
	$XYSO_2$	Any X, Y	19(1)	−32(1)	−69.6(7)	0.984	1.4	26
P	XYZP	X, Y, Z = R, Cl, Br, SR, CN	20(1)	1(1)	2(1)	0.976	2.3	30
		X, Y, Z = OR, NR_2 are present	33(6)	−18(9)	−6(8)	0.962	5	9
	XYZPO	Any X, Y, Z	14(2)	−30(2)	18(2)	0.980	3.4	31
	XYZPS	Any X, Y, Z	11(3)	−41(5)	1(3)	0.979	3.4	12

TABLE 5 SKα shifts and sums of σ_I and σ_R^0 constants of substituents at sulfur atom

Compound	*ΔSKα, eV · 100*	$\Sigma\sigma_I$	$\Sigma\sigma_R^0$
Me_2S	−6.3(6)	−0.02	−0.32
Et_2S	−6.1(9)	−0.02	−0.28
Pr_2S	−4.7(6)	−0.02	−0.32
$i\text{-}Pr_2S$	−6.6(6)	−0.02	−0.32
Bu_2S	−4.7(6)	−0.02	−0.32
MeSEt	−6.1(15)	−0.02	−0.30
EtSPr-i	−4.6(7)	−0.02	−0.30
EtSBu-t	−6.7(14)	−0.02	−0.34
$PhCH_2SEt$	−5.7(9)	0.02	−0.27
$(PhCH_2)_2S$	−6.1(10)	0.06	−0.26
$(VinCH_2)_2S$	−4.9(7)	0.04	−0.28
$EtSCH_2Cl$	−2.9(11)	0.16	−0.22
VinSMe	−4.3(6)	0.10	−0.31
VinSEt	−4.2(9)	0.10	−0.29
VinSPr-i	−3.0(7)	0.10	−0.31
VinSBu-t	−3.3(14)	0.10	−0.33
Vin_2S	−1.6(6)	0.22	−0.30
PhSMe	−2.3(6)	0.11	−0.27
PhSEt	−5.2(6)	0.11	−0.25
PhSBu-t	−4.6(14)	0.11	−0.29
C_6F_5SMe	1.7(8)	0.30	−0.51
Ph_2S	0.8(9)	0.24	−0.22
$(C_6F_5)_2S$	3.6(6)	0.62	−0.70
$(4\text{-}O_2NC_6H_4)_2S$	2.3(6)	0.46	0.06
MeSCN	4.3(12)	0.56	−0.08
$PhCH_2SCN$	5.4(11)	0.60	−0.05
PhSCN	5.0(8)	0.69	−0.03
C_6F_5SCN	9.4(8)	0.88	−0.27
PhSCl	4.5(6)	0.59	−0.36
SCl_2	12.5(7)	0.94	−0.25
S_2Cl_2	9.4(11)	0.87	−0.17
CH_2ClSCF_3	−2.9(11)	0.57	0.03
$PhSCF_3$	−0.5(12)	0.52	0.00
$4\text{-}O_2NC_6H_4SCF_3$	−0.5(8)	0.63	0.14
$C_6F_5SCF_3$	7(2)	0.71	−0.24
$C_6F_5SC(O)Me$	1(1)	0.61	−0.15
$S(SiEt_3)_2$	−22.6(8)	−0.22	0.24
$BuSSi(OEt)_3$	−11.7(9)	−0.01	−0.03
$T\text{-}BuSSi(OEt)_3$	−14.8(11)	−0.01	−0.05
Me_2S_2	1.0(6)	0.29	−0.47
Et_2S_2	0.8(8)	0.25	−0.44
Pr_2S_2	−0.6(7)	0.24	−0.45
$i\text{-}Pr_2S_2$	−1.5(6)	0.25	−0.43
Bu_2S_2	−2.0(9)	0.24	−0.44
$(C_5H_{11})_2S_2$	−0.6(8)	0.24	−0.44
$(PhCH_2)_2S_2$	−0.5(9)	0.29	−0.43
Ph_2S	0.9(6)	0.43	−0.35
Me_2SO_2	80.5(6)	−0.02	−0.32
Pr_2SO_2	80.2(6)	−0.02	−0.32
$PhSO_2Me$	80.6(8)	0.11	−0.27
$4\text{-}ClC_6H_4SO_2Me$	80.2(10)	0.14	−0.19
$4\text{-}ClC_6H_4SO_2Pr$	78.1(7)	0.14	−0.19
$4\text{-}ClC_6H_4SO_2Pr\text{-}i$	77.5(6)	0.14	−0.19
$PhSO_2CF_3$	80.8(9)	0.52	0.00
$4\text{-}ClC_6H_4SO_2CF_3$	77.7(11)	0.55	0.08
$4\text{-}FC_6H_4SO_2CF_3$	76.5(10)	0.53	0.04
$4\text{-}MeC_6H_4SO_2CF_3$	77.8(10)	0.50	−0.02
$4\text{-}H_2NC_6H_4SO_2CF_3$	81.8(11)	0.49	−0.02
$4\text{-}O_2NC_6H_4SO_2CF_3$	77.9(7)	0.63	0.14
$4\text{-}ClC_6H_4SO_2(CF_2)_2CF_3$	77.6(6)	0.54	0.06
Ph_2SO_2	81.4(12)	0.24	−0.22
$(4\text{-}HOC_6H_4)_2SO_2$	84.9(7)	0.18	−0.36
$PhSO_2Vin$	80.8(6)	0.23	−0.26
$4\text{-}MeC_6H_4SO_2Vin$	82.0(12)	0.21	−0.28
$4\text{-}ClC_6H_4SO_2Vin$	81.9(8)	0.26	−0.18
$4\text{-}BrC_6H_4SO_2Vin$	78.8(9)	0.26	−0.18
$4\text{-}MeOC_6H_4SO_2Vin$	83.1(6)	0.22	−0.34
$4\text{-}O_2NC_6H_4SO_2Vin$	77.9(14)	0.34	−0.12
$PhSO_2NH_2$	93.6(6)	0.29	−0.53
$4\text{-}MeC_6H_4SO_2NH_2$	93.5(6)	0.27	−0.55
$PhSO_2NEt_2$	90(2)	0.29	−0.55
$4\text{-}ClC_6H_4SO_2F$	98.2(9)	0.69	−0.47
$(MeO)_2SO_2$	109.2(7)	0.60	−0.88

continues

TABLE 5 (*continued*)

ues calculated by the quantum-chemical methods mentioned above are given in Tables 1 and 2. The relationships between the ΔBKα and q_B values were expressed by equations

$$q_B = a\Delta BK\alpha + b \qquad (1)$$

whose parameters are present in Table 3 (where *r* is the correlation coefficient, *s* is the standard error of estimation and *n* is the number of points).

It follows from Tables 1–3 that all calculation methods used except CNDO/2 and INDO in an extended basis set, lead to quite good dependencies (2)–(8) which are true for all sulfur-containing molecules except for the compounds containing the S-fragment. The latter are satisfied by their own dependencies (9)–(13). Phosphorus-containing compounds with the minimal coordination number of the P atom ($k_P = 3$), like sulfur-containing ones, are satisfied by correlations (14)–(19) different from these (20)–(26) that are true for all the rest of the phosphorus-containing compounds with $k_P = 4$, 5, 6. The q_P values determined in the spd-basis set by CNDO/2 and INDO methods, as in the case of sulfur compounds, do not correlate with PKα shifts. The satisfactory correlations for phosphines (as well as for sulfur compounds with $k_S = 1$) are absent in the case of CNDO/S calculations in PSS1 parametrization in the spd-basis set.

TABLE 6 The SKα shifts of sulfones and their derivatives

Compounds	*ΔSKα, eV*
RSO_2R'	0.77–0.86
RSO_2NH_2	0.94–0.99
RSO_2OH	1.07–1.12
$RSO_2C^-<$	0.87–0.91
$RSO_2O^-N^+(R')H_3$	1.13–1.18
$(MeO)_2SO_2$	1.08–1.10
M_2SO_4	1.14–1.19

TABLE 7 Experimental SKα and PKα shifts and q_S, q_P, i_{PS} values, calculated with the help of the correlations obtained

Compound	$\Delta SK\alpha$, $\Delta PK\alpha$, eV · 100	q_S, e · 100 q_P, e · 100 i_{PS}, %*				
		CNDO/S			CNDO/2	INDO
		PSS1	[16]			
		sp	sp	spd	sp	sp
1	2	3	4	5	6	7
Me_3PS	−12.1(14)	−74(13)	−73(9)	−49(8)	−60(10)	−66(12)
	19.8(7)	77(2)	62(1)	51(2)	73(3)	82(4)
		76(7)	67(4)	50(4)	67(5)	74(6)
Pr_3PS	−13.8(10)	−84(13)	−83(7)	−56(7)	−68(10)	−74(12)
	17.0(7)	75(2)	59(1)	50(2)	69(3)	78(4)
		80(7)	71(3)	53(4)	69(5)	76(6)
i-Pr_3PS	−15.3(7)	−92(14)	−92(5)	−62(7)	−75(10)	−81(12)
	20.2(6)	78(2)	62(1)	52(2)	73(3)	83(4)
		85(7)	77(3)	57(4)	74(5)	82(6)
$[CH_3(CH_2)_7]_3PS$	−11.8(9)	−72(12)	−71(6)	−48(8)	−59(9)	−65(11)
	17.7(6)	75(2)	60(1)	50(2)	70(3)	79(4)
		74(6)	65(3)	49(3)	65(5)	72(6)
Ph_3PS	−13.1(9)	−80(13)	−79(6)	−53(7)	−65(10)	−71(12)
	23.8(6)	82(2)	66(1)	53(2)	78(3)	89(4)
		81(7)	72(3)	53(4)	72(5)	80(6)
Cl_3PS	−10(2)	−62(15)	−60(12)	−41(9)	−51(12)	−56(13)
	43.0(8)	101(3)	85(2)	62(3)	104(4)	119(5)
		82(8)	72(6)	52(5)	78(6)	88(7)
$Cl_2(Me)PS$	−11.6(12)	−71(13)	−70(8)	−47(7)	−57(10)	−64(12)
	36.1(9)	94(2)	78(2)	59(2)	95(4)	108(5)
		83(7)	74(4)	53(4)	76(5)	86(7)
$Cl_2(EtO)PS$	−9.7(9)	−70(11)	−58(6)	−40(6)	−50(8)	−55(9)
	54.2(10)	113(3)	96(2)	68(3)	120(4)	137(6)
		87(6)	77(3)	54(3)	85(4)	96(5)
$Me_2P(S)OPh$	−13.5(20)	−82(16)	−81(12)	−55(10)	−67(13)	−65(13)
	36.2(6)	94(2)	78(2)	59(2)	95(4)	108(5)
		88(8)	79(6)	57(6)	81(7)	91(7)
PhO(Ph)P(S)Me	−11.9(17)	−73(14)	−71(10)	−49(9)	−60(11)	−65(13)
	37.4(6)	96(2)	79(2)	60(2)	97(4)	110(5)
		85(7)	75(5)	54(5)	79(6)	88(7)
$Ph_2P(S)OPh$	−13.4(10)	−81(13)	−80(7)	−55(7)	−66(10)	−72(12)
	39.5(7)	98(2)	81(2)	61(3)	100(4)	113(5)
		90(7)	81(3)	58(4)	83(5)	93(7)
$(BuO)_3PS$	−9.1(13)	−57(12)	−55(8)	−37(7)	−47(9)	−52(10)
	64.9(6)	124(3)	106(2)	72(3)	134(4)	154(7)
		91(6)	80(4)	55(4)	91(5)	103(6)
$Cl_2P(O)SEt$	−5.5(9)	−2(2)	−1(2)	−1(3)	−5(2)	−9(2)
	52.7(8)	111(3)	94(2)	67(3)	118(4)	134(6)
		57(2)	48(1)	34(2)	62(2)	72(3)
$P(SMe)_3$	−6.6(12)	−4(3)	−3(2)	−2(3)	−6(2)	−11(3)
	15.6(6)	28(1)	27(2)	22(1)	31(2)	33(3)
		16(2)	15(1)	12(2)	19(1)	22(2)
$P(SEt)_3$	−8.5(11)	−6(3)	−6(2)	−5(3)	−9(2)	−14(3)
	14.8(8)	28(1)	26(2)	22(1)	30(3)	32(3)
		17(2)	16(1)	14(2)	20(2)	23(2)
$P(SC_6F_5)_3$	−8.9(19)	−7(3)	−6(3)	−5(4)	−10(3)	−15(4)
	12.1(18)	25(2)	24(3)	20(2)	27(3)	28(3)
		16(2)	15(2)	13(2)	19(2)	22(2)

continues

TABLE 7 *(continued)*

		q_S, e · 100 q_P, e · 100 i_{PS}, %*				
		CNDO/S			CNDO/2	INDO
	ΔSKα, ΔPKα, eV · 100	PSS1	[16]			
Compound		sp	sp	spd	sp	sp
1	2	3	4	5	6	7
$(EtS)_2PEt$	−7.8(11)	−5(3)	−5(2)	−4(3)	−8(2)	−13(3)
	10.8(6)	24(1)	23(2)	19(1)	26(2)	27(2)
		15(2)	14(1)	12(2)	17(1)	20(2)
EtSP(Ph)Et	−8.6(11)	−6(3)	−6(2)	−5(3)	−9(2)	−14(3)
	7.9(7)	22(1)	21(2)	18(1)	23(2)	23(2)
		14(2)	14(1)	12(2)	16(1)	19(2)
$EtSPCl_2$	−7.9(16)	−5(3)	−5(3)	−4(3)	−8(2)	−13(3)
	27.0(8)	38(2)	34(3)	29(2)	43(3)	48(3)
		22(2)	20(2)	17(2)	26(2)	31(2)
$(PrS)_2PNEt_2$	−9.6(10)	−8(2)	−8(2)	−6(3)	−11(2)	−16(3)
	22.4(6)	34(2)	31(3)	26(2)	36(3)	42(3)
		21(1)	20(2)	16(2)	25(2)	29(2)

* i_{PS} = 100% when $P^{+1.00}S^{-1.00}$

The lack of satisfactory correlation dependencies of type (1) for the sulfur and phosphorus atoms in the case of CNDO/2 and INDO calculations in the extended basis set and the existence of such dependencies obtained by using CNDO/S calculations seem to be explained by an NDO approximation peculiarity that simulates calculations in the symmetry–orthogonalized basis set. Here, the lack of inverse transformation of the density matrix from the formally orthogonalized basis set to an initial atomic one should lead to significant exaggeration of the d_B – AOs population [20]. These orbitals contribute much to the chemical bonding in compounds where S and P atoms exist in the highest oxidation states [6, 21–23]. At the same time, the peculiarity of the CNDO/S method is that the overlap integrals S_{ij} are supposed to be equal to $0.3\delta_{ij}$ ($\delta_{ij} = 1$ when $i = j$ and $\delta_{ij} = 0$ when $i \neq j$) if one or both i and j valent AOs are d-orbitals. For s- and p-orbitals in the CNDO/S method and any other NDO calculations, the S_{ij} values are equal to δ_{ij}. This leads to a considerable diminution of the electron density exaggeration on d_B-orbitals in the CNDO/S method in contrast to that considered for the CNDO/2 and INDO ones. Actually, the data presented in Tables 1 and 2 prove that the positive q_S and q_P values were decreased more in CNDO/2 and INDO calculations than in CNDO/S in going from minimal to extended basis sets. The data obtained are in good agreement with those [10] given in Figure 1b.

From the data obtained, it follows that the results of the five quantum-chemical methods examined agree well with the BKα shifts obtained for all types of compounds investigated. These methods are CNDO/S in both PSS1 [15] and Takata's [16] parametrizations, CNDO/2 and INDO in the sp-basis set and CNDO/S in the parametrization by Takata in the spd-basis set. These methods can be successfully used for any compounds containing S and P atoms both for SKα and PKα shifts calibration and independent calculations of q_S and q_P values.

Thus, the availability of linear dependencies between ΔBKα and q_B values have been proved. It was interesting to trace the dependence of BKα shifts (in compounds where the B atom is the central one) on the inductive and resonance effects of substituents. These dependencies were evaluated according to the following equation

$$\Delta BK\alpha(\mathrm{eV} \cdot 100) = a\Sigma\sigma_I + b\Sigma\sigma_R^0 + c \qquad (27)$$

whose parameters are presented in Table 4. The SKα shifts and sums of inductive and resonance constants of substituents at the sulfur atom for the sulfur compounds investigated were taken from [24] as presented in Table 5. Previously, we obtained similar data for phosphines [25], phosphoryl [26], and thiophosphoryl [12] compounds.

From the data given in Table 4, it follows that, in sulfides and phosphines not containing substituents at the central atom having a strong M-effect (in that case $|\sigma_R^0| > 0.25$ for donors* and

---

* It is true for sulfides only as SR substituents are strong π-donors in sulfides and are not them in phosphines.

$\sigma_R^0 > 0.08$ for acceptors), the q_B values depend only on the inductive substituent effects. It testifies to the correctness of the simple two-level scheme at Bock [27] for the description of p_π–p_π interactions (in such compounds).

Nevertheless, in sulfides and phosphines containing substituents at the central atom having a strong M-effect, and in phosphoryl and thiophosphoryl compounds and sulfones the contribution by the resonance substituent effect to the q_B values is rather high and the total electron density of the heteroatoms decreases with the growth of the π-donor properties of the substituents. This effect becomes stronger in the presence of the negative charge on the atom bonded directly to the SO_2 group. Thus, the positive q_S has been found to increase in trifluoromethylsulfonyl-containing Meisenheimer complexes, phosphorus ylides (containing the $>C^-SO_2CF_3$ fragment) [28] and also in organoammonium salts of sulfonic acids (containing O^-SO_2X fragment) [29] with respect to the corresponding sulfones and sulfonic acids (see Table 6). This observation can probably explain the known fact that, in most of the inorganic sulfates (structural formula $O^-—SO_2—O^-$), the positive q_S value is larger than in organic sulfates. The influence of the resonance substituent effect can be illustrated by the considerable contribution of resonance structure (C):

$$-\text{I-effect} \quad X \leftarrow S{=}O \rightarrow X^-—S^+{=}O^+$$

$$+\text{M-effect}$$

$$\underset{(A)}{X—S{=}O} \leftrightarrow \underset{(B)}{X^+{=}S—O^-} \leftrightarrow \underset{(C)}{X—S^+—O^-}$$

In fact, the investigation of the frequencies and intensities of valence vibrations of the SO_2 group in sulfones of the type $RSO_2CH{=}CHX$ ($X{=}H$, OR', NR'_2, SR'; $R, R' = Alk, Ar$) [30], where these vibrations can be considered equally localized or delocalized, has shown the increase of π-donor properties of substituents X to be accompanied by a decrease of double-bond character and an increase of the $S{=}O$ bond polarity.

The analysis of the dependencies presented in Table 4, in combination with information obtained from $SL_{2,3}$ fluorescent spectra [6, 21–23], suggests the observed influence of the resonance substituent effects to be due to polarization of π-electron density and its donation on relatively diffusive d_B, σ^*-orbitals.

Thus, it is of interest to evaluate quantitatively the changes of the $P{=}S$ and $P—S$ bond ionicities under the effect of substituents at the phosphorus central atom, because the calculation of the inductive and resonance substituent effects leads to simbate and antibate changes in electron densities of the S and P atoms, respectively. The experimental $BK\alpha$ shifts, the q_S and q_P values obtained with the help of correlations found by the use of five recommended methods of effective charge calculations, and the PS bond ionicity values (i_{PS}) are presented in Table 7.

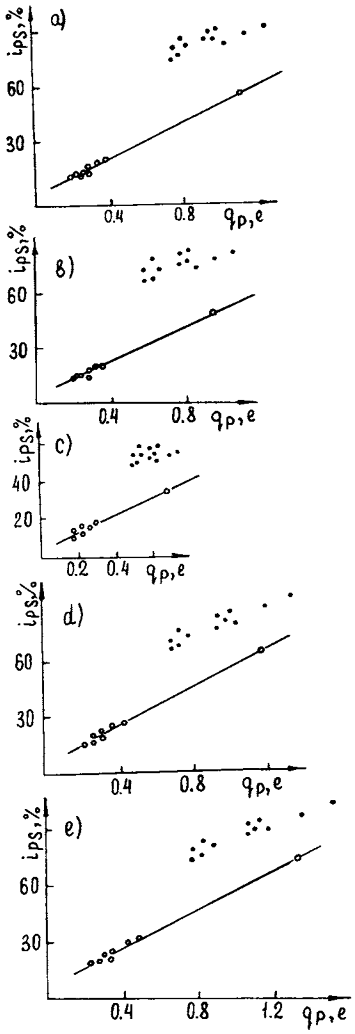

FIGURE 3 Relations between i_{PS} and q_P values derived via experimental $PK\alpha$ and $SK\alpha$ shifts and the obtained correlations. The calculation of model compounds is produced by following methods: a) CNDO / S, parametrization PSS1, sp-basis set; CNDO / S, Takata's parametrization, sp-basis set; c) CNDO / S, Takata's parametrization, spd-basis set; d) CNDO / 2, sp-basis set; e) INDO, sp-basis set. Points represent thiophosphoryl compounds and circles represent compounds containing the P—S bonds.

The dependencies between i_{PS} and q_P values for the compounds presented in Table 7 are shown in Figure 3. It is clear that the electron densities of the S and P atoms in thiophosphoryl compounds change simbately to each other, so the change in $i_{P=S}$ are small. Contrary to this in the compounds containing P—S bonds, the q_S values do not vary much, so i_{P-S} values increase linearly with the q_P growth.

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