Heteroatom Chemistry
Volume 6, Number 6, 1995

X-Ray Spectral Determination of the Effective Charges on Phosphorus, Sulfur, and Chlorine Atoms in Chemical Compounds with a Nonempirical Charge Scale

G. N. Dolenko*

Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, 664033 Irkutsk, Russia

Z. Latajka and H. Ratajczak

Institute of Chemistry, University of Wroclaw, 14 Joliot-Curie St., 50-383 Wroclaw, Poland

Received 1995

ABSTRACT

Linear dependence between the experimental K_α line shifts and Mulliken atomic charges obtained by SCF ab initio calculations with 4-31G, 4-31G, and 4-31G** basis sets for the P, S, and Cl atoms have been found. The electron density redistribution of PCl_3 and $SPCl_3$ free ligands on their complexation with $AlBr_3$ has been investigated. It has been shown that a significant transfer of the total ligand electron density to the acceptor is absent, but there is an essential growth of the ionicity of all bonds on complexation. The P=S and P–S bond ionicities are found to increase linearly with the growth of the positive charge on the central phosphorus atom.* © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

One of the most suitable methods for studying the effective atomic charge on the second row elements (A) is the measurement of AK_α line shifts (ΔAK_α) [1–5]. In our prior studies [3–5], we have reported the relationship between the experimental AK_α shifts (A = P, S, Cl) and the effective A atom charges. The calculations of atomic charges were performed by the electronegativity equalization procedure [3,6] and by semiempirical quantum-chemical CNDO/S, CNDO/2, INDO, MINDO/3, and MNDO methods in the large series of model compounds [4,5]. By using all the previously mentioned semiempirical methods in the minimal basis set and CNDO/S in the extended basis set, we have found that the dependence was split into two linear relationships for the S and P atoms. One held true for the compounds in which the heteroatom considered had the minimal coordination number (1 for S and 3 for P) and the other for all of the remaining compounds.

It is very likely that the splitting of the dependence may be explained by a shortcoming of the parametrization of the above-mentioned semiempirical methods. In the present work, we have carried out SCF ab initio calculations on a large series of model compounds in order to examine this suggestion and to achieve the possibility of obtaining effective A atoms charges (q_A) in a stricter charge scale.

METHODS

All quantum-chemical calculations were carried out using the Gaussian 92 package of programs [7] at the HF level with 4-31G$^+$, 4-31G* and 4-31G** basis sets. In the basis set denoted as 4-31G$^+$, the d polarization

---

Dedicated to the great chemist Professor Shigeru Oae on the occasion of his 75th birthday.

*To whom correspondence should be addressed.

© 1996 John Wiley & Sons, Inc.
1042-7163/96/060553-05

functions were placed only on the second row central atoms. The exponents of polarization functions were adopted from the 6-31G** basis set [8–10]. The experimental molecular structure for the gas phase had been used previously for all molecules taken into consideration [11–13]. The values of structure parameters not defined experimentally were obtained by MNDO optimization.

The experimental values of AK_α shifts (A = P, S, Cl) were taken from Ref. [14].

RESULTS AND DISCUSSION

The results of SCF ab initio calculations in the large series of model compounds are gathered in Figures 1–3 where in the calculated Mulliken A atom charges are connected with the experimental AK_α shifts. The results of this connection are presented in Table 1.

From the analysis of data gathered in Table 1 and Figures 1–3, one can see that the q_A vs. ΔAK_α dependence is close to linearity in all cases and does not split. For the S atom, a good linear relationship is observed for any basis set used and for all series of compounds considered. The attempted correlations of q_P vs. ΔPK_α are somewhat worse. This may be explained by the anomanously high acceptor effect of the Me group bonded to the P atom that occurred by consideration of calculation data. Nevertheless, these dependence obtained with 4-31G* and 4-31G** basis sets become satisfactory after removal of Me_3P and $OPMe_3$ molecules from consideration.

Essentially poorer dependences are seen for the Cl atom. We think that this may be explained by the fact that the ratio between the ΔAK_α value changing region and the experimental errors of AK_α definition is one order of magnitude smaller for A = Cl than for A = S, P. Taking into consideration the errors of the ClK_α shift measurement, one can draw a conclusion that the q_{Cl} vs. ΔClK_α dependences presented in Figures 2 and 3 are also satisfactory. Hence, the possibility of determining the effective charges on the different A atoms in single charge scales according to SCF ab initio calculations with three basis sets by using the experimental AK_α shifts only has been achieved. The best results are obtained at the 4-31G** level of theory.* From Table 1, it follows that the basis set expansion leads to the improvement of agreement between the experimental AK_α shifts and q_A values.**

It was of interest to utilize the data obtained for the investigation of the electron density redistribution on complexation between a donor molecule PCl_3 or $SPCl_3$ (where one can define the effective charges on all atoms by their K_α shifts) and an acceptor molecule $AlBr_3$ containing no interfered atoms. The data presented in Table 2 show that, in spite of positive q_P growth on complexation the total ligand electron density does not decrease (in the range of accuracy achieved) due to a strong dampening effect of the Cl atoms. This leads to a sufficient growth of the ionicity*** of all bonds of the ligands and (taking into consideration our prior data [5,15] that the positive charge on a central acceptor atom grows sufficiently

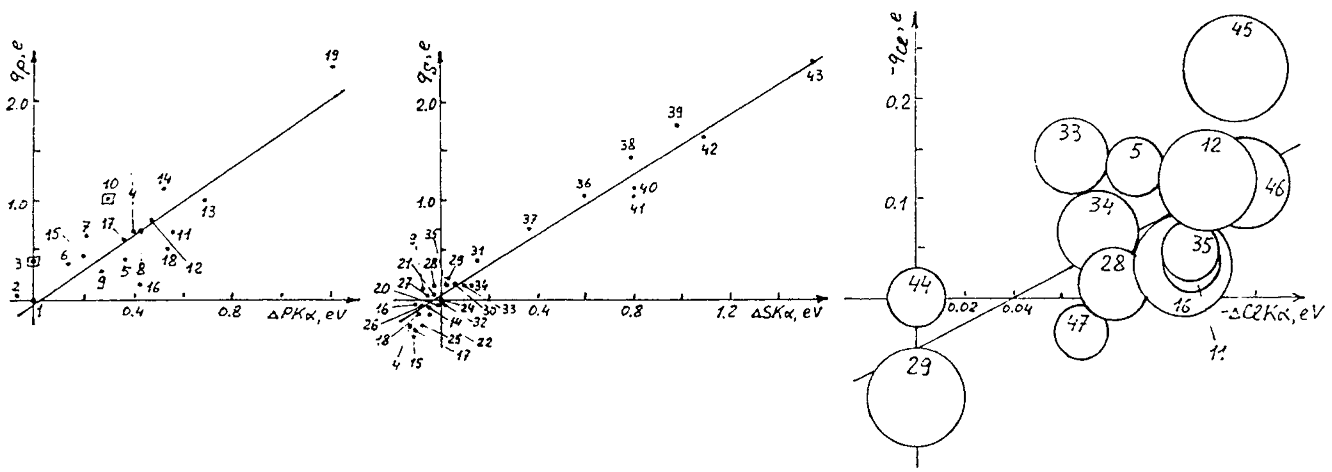

FIGURE 1 q_A vs. ΔAK_α dependences. q_A values are calculated by use of the 4-31G$^+$ basis set. Squares represent compounds not satisfying the correlation obtained. Radius of circles is equal to the error of measurements ΔAK_α. 1 P_{red}, 2 PH_3, 3 PMe_3, 4 $P(CN)_3$, *5 PCl_3*, 6 Me_2PCl, 7 $MePCl_2$, 8 $MeOPCl_2$, 9 $MeSPCl_2$, 10 Me_3PO, 11 Cl_3PO, 12 $MeP(O)Cl_2$, 13 $MeOP(O)Cl_2$, 14 $MeSP(O)Cl_2$, 15 Me_3PS, 16 Cl_3PS, 17 $MeP(S)Cl_2$, 18 $MeOP(S)Cl_2$, 19 PF_6^-, 20 OCS, 21 CS_2, 22 MeNCS, 23 $(H_2N)_2CS$, 24 S_8, 25 H_2S, 26 EtSH, 27 Me_2S, 28 F_3CSCH_2Cl, 29 ClCCSMe, 30 MeSCN, 31 $S(CN)_2$, 32 Me_2S_2, 33 Cl_2S_2, 34 Cl_2S, 35 F_3CSCl, 36 SO_2, 37 Me_2SO, 38 F_2SO, 39 SF_4, 40 Me_2SO_2, 41 $MeSO_2Cl$, 42 $(MeO)_2SO_2$, 43 SF_6, 44 Cl, 45 HCl, 46 MeCl, 47 PhCl.

---

*Below we shall use only this charge scale for atomic charge definition; i.e., in Equations 3, 6, and 9.

Although differences between q_A values obtained with 4-31G* and 4-31G basis sets are not large (see Figures 1–3 and Table 1), these are sufficient if data at the 4-31G$^+$ level of theory are taken into consideration.

***The ionicity of the AB bond (i_{AB}) is equal to $(|q_A - q_B|/2) \cdot 100\%$.

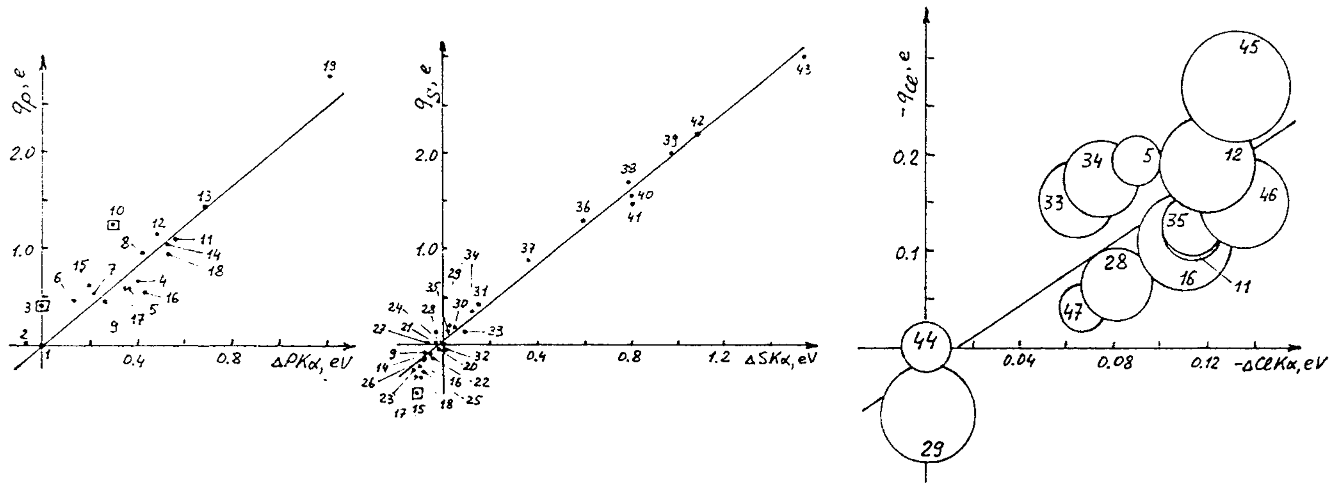

FIGURE 2 q_A vs. ΔAK_α dependences. q_A values are calculated by use of the 4-31G* basis set. The designations correspond to those in Figure 1.

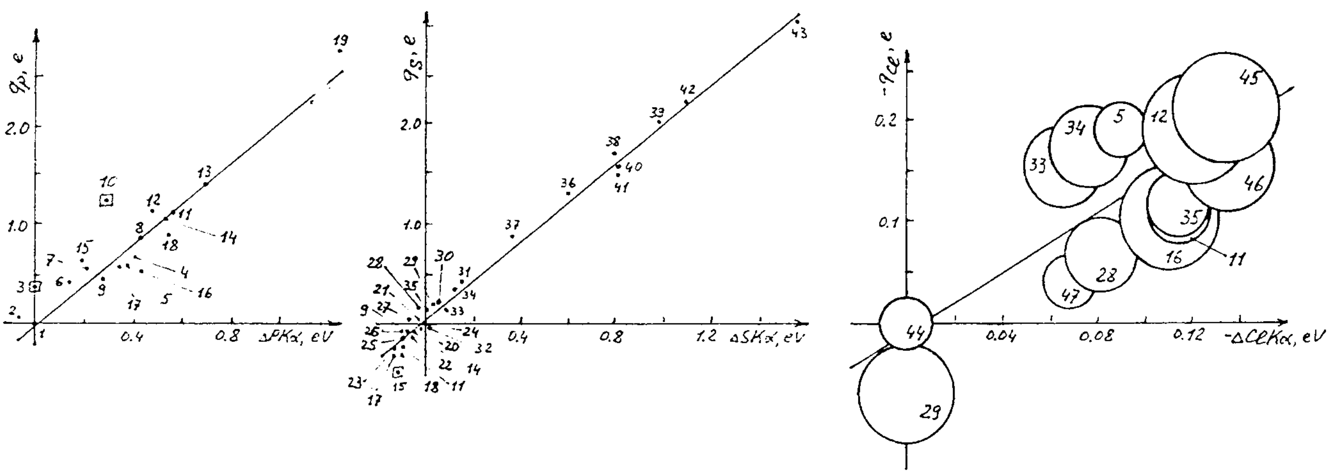

FIGURE 3 q_A vs. ΔAK_α dependences. q_A values are calculated by use of the 4-31G** basis set. The designations correspond to those in Figure 1.

TABLE 1 Parameters[a] of Correlation Equations $q_A = a\Delta AK_\alpha + b$ (q_A in e, ΔAK_α in eV)

A	*Basis Set*	*a*	*b*	*r*	*s*	*n*	*Compounds Not Satisfying the Correlation Obtained*	*Correlation Equation No.*
P	4-31G+	1.7(2)	−0.04(1)	0.912	0.22	17	3, 10	(1)
	4-31G*	2.04(15)	−0.01(1)	0.962	0.17	17	3, 10	(2)
	4-31G**	2.03(15)	−0.01(1)	0.963	0.17	17	3, 10	(3)
S	4-31G+	1.54(5)	0.04(3)	0.985	0.12	30	—	(4)
	4-31G*	1.96(4)	0.04(3)	0.994	0.09	29	5	(5)
	4-31G**	1.95(4)	0.05(2)	0.994	0.09	29	5	(6)
Cl	4-31G+	1.3(4)	0.05(1)	0.661	0.06	13	—	(7)
	4-31G*	1.6(4)	0.02(1)	0.793	0.05	13	—	(8)
	4-31G**	1.5(3)	0.01(1)	0.802	0.05	13	—	(9)

[a] *r* is the correlation coefficient, *s* is the standard deviation, *n* is the number of points for which the correlation was obtained. Here and subsequently the mean-square errors in the last significant digit, taken for the 95% confidence interval by Student's criterion, are given in parentheses.

TABLE 2 Change of Atomic Charges and Bond Ionicities of Free Ligands on Their Complexation

	ΔAK_α, eV			Ionicities of Bonds, %		Change of Effective Atomic Charge (δq_A) of Ligands on Their Complexation[a]			
Compound	A = P	A = S	A = Cl	PS	PCl	A = P	A = S	A = Cl	$\Sigma \delta q_i$
PCl_3	0.373(7)	—	−0.09(1)	—	44(5)	0.5(1)	—	−0.10(7)	0.2(2)
$AlBr_3 \cdot PCl_3$	0.599(8)	—	−0.156(15)	—	72(7)				
$SPCl_3$	0.430(8)	−0.10(2)	−0.11(2)	50(6)	51(6)	0.4(1)	0.04(6)	−0.1(1)	0.1(2)
$AlBr_3 \cdot SPCl_3$	0.616(8)	−0.080(9)	−0.171(14)	68(7)	74(8)				

[a] The positive sign of δq_A corresponds to a decrease of the *A* atom electron density on complexation.

TABLE 3 Atomic Charges and Bond Ionicities Calculated by Experimental SK_α and PK_α Shifts

Molecule	ΔPK_α, eV	ΔSK_α, eV	q_P, e	q_S, e	i_{PS}, %
Me_3PS	0.198(7)	−0.121(14)	0.39(3)	−0.19(3)	29(3)
Pr_3PS	0.170(7)	−0.138(10)	0.34(3)	−0.22(3)	28(3)
$i\text{-}Pr_3PS$	0.202(6)	−0.153(7)	0.40(3)	−0.25(2)	32(3)
$[CH_3(CH_2)_7]_3PS$	0.177(6)	−0.118(9)	0.35(3)	−0.18(3)	26(3)
Ph_3PS	0.238(6)	−0.131(9)	0.47(4)	−0.20(3)	33(3)
Cl_3PS	0.430(8)	−0.10(2)	0.86(7)	−0.14(4)	50(6)
$MeP(S)Cl_2$	0.361(9)	−0.116(12)	0.72(6)	−0.18(3)	45(5)
$MeOP(S)Cl_2$	0.542(10)	−0.097(9)	1.09(8)	−0.14(3)	62(6)
$PhOP(S)Me_2$	0.362(6)	−0.135(20)	0.72(6)	−0.21(4)	46(5)
$PhO(Ph)P(S)Me$	0.374(6)	−0.119(17)	0.75(6)	−0.18(4)	46(5)
$PhOP(S)Ph_2$	0.395(7)	−0.134(10)	0.79(6)	−0.21(3)	50(5)
$(BuO)_3PS$	0.649(6)	−0.091(13)	1.31(10)	−0.13(3)	72(7)
$AlBr_3 \cdot SPCl_3$	0.616(8)	−0.080(9)	1.24(9)	−0.11(3)	68(7)
$MeSP(O)Cl_2$	0.527(8)	−0.055(9)	1.07(8)	−0.06(3)	56(6)
$(MeS)_3P$	0.156(6)	−0.066(12)	0.31(3)	−0.08(3)	20(3)
$(EtS)_3P$	0.148(8)	−0.085(11)	0.29(3)	−0.12(3)	20(3)
$(C_6F_5S)_3P$	0.121(18)	−0.089(19)	0.24(4)	−0.12(4)	18(4)
$(EtS)_2PEt$	0.108(6)	−0.078(11)	0.21(2)	−0.10(3)	16(3)
$EtSP(Ph)Et$	0.079(7)	−0.086(11)	0.15(2)	−0.12(3)	14(3)
$MeSPCl_2$	0.270(8)	−0.079(16)	0.54(4)	−0.10(4)	32(4)
$(PrS)_2PNEt_2$	0.224(6)	−0.096(10)	0.44(4)	−0.14(3)	29(3)

on complexation while the electron density on acceptor geminal atoms does not decrease) acceptor.

The other example of data obtained may be analysis of the dependence between the ionicities of the P=S and P–S bonds and central phosphorus atom K_α line shifts. In our prior research [4], we investigated this dependence by using q_S vs. ΔSK_α relationships reported previously. There the slope coefficient for compounds containing the S= fragment exceeds remarkably that for the –S– compounds. As a result, the changes in $i_{P=S}$ values were small, although, in thiophosphoryl compounds, SK_α shifts change rather less than PK_α shifts and in the same direction. On the contrary, in compounds containing P–S bonds, the $i_{P\text{-}S}$ values increased linearly with the growth of the positive charge on the central phosphorus atom. At the q_P and q_S values calculated from Equations 3 and 6, respectively, the $i_{P\text{-}S}$ and $i_{P=S}$ values satisfy the single i_{PS} vs. ΔPK_α dependence (see Table 3). The values of the PS bond ionicities increase linearly with the growth of the positive charge on a central phosphorus atom:

$$i_{PS}, \% = 100(3)\Delta PK_\alpha + 8(2)\ (r = 0.991, s = 2, n = 21) \quad (10)$$

REFERENCES

[1] L. N. Mazalov, V. D. Yumatov, V. V. Murakhtanov, F. Kh. Gel'mukhanov, G. N. Dolenko, E. S. Gluskin, A. V. Kondratenko: *Rentgenovskie Spektry Molekul*, Nauka, Novosibirsk (1977).

[2] A. Meisel, G. Leonhardt, R. Szargan: *X-Ray Spectra and Chemical Binding*, Springer-Verlag, Berlin (1989).

[3] G. N. Dolenko: in L. I. Belen'kii (ed.): *Chemistry of Organosulfur Compounds. General Problems*, Ellis Horwood, New York, pp. 287–362 (1990).

[4] G. N. Dolenko, A. L. Litvin, V. P. Elin, *Heteroatom Chem.*, *3*, 1992, 311.

[5] G. N. Dolenko, A. L. Litvin, V. P. Elin, O. Kh. Poleshchuk, *J. Mol. Struct. (Theochem.)*, *251*, 1991, 11.
[6] W. L. Jolly, W. B. Perry, *Inorg. Chem.*, *13*, 1974, 2686.
[7] GAUSSIAN 92, M. J. Frish, G . W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. P. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gompert, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defress, J. Baker, J. J. P. Stewart, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1992.
[8] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.*, *56*, 1972, 2257.
[9] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta, 28*, 1979, 213.
[10] M. S. Gordon, *Chem. Phys. Lett.*, *76*, 1980, 163.
[11] Landolt-Börnstein: *Structure Data of Free Polyatomic Molecule*. Springer-Verlag, Berlin, vol. 7 (1976).
[12] I. Hargittai: *Strukturnaya Khimiya Soedinenii Sery*, Nauka, Moskva (1986).
[13] V. A. Naumov, L. V. Vilkov, *Molekulyarnye Struktury Phosphororganicheskikh Soedinenii*, Nauka, Moskva (1986).
[14] G. N. Dolenko, *J. Mol. Struct.*, *291*, 1993, 23.
[15] O. Kh. Poleshchuk, B. Nogaj, G. N. Dolenko, V. P. Elin, *J. Mol. Struct.*, *297*, 1993, 295.