Effect of substituents on electronegativities of Ar_3Si and Ar_3Sn groups: comparison of the results of *ab initio* quantum-chemical calculation and ^{19}F NMR data for $Ar_3MQC_6H_4F$-4 compounds

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Ab initio calculations of group electronegativities (χ) of Ar_3Si and Ar_3Sn groups containing 13 types of *meta*-, *para*- and polysubstituted phenyl groups have been performed. Calculated values of $\chi(Ar_3Si)$ and $\chi(Ar_3Sn)$ correlate better with the σ^0 Taft constants than with the σ Hammett constants, which is indicative of the inductive nature of the effect of aryl groups on electronegativities of Ar_3M groups. Good correlations have been found between ^{19}F chemical shifts and the corresponding values of $\chi(Ar_3Si)$ and $\chi(Ar_3Sn)$ for the $Ar_3SiC_6H_4F$-4, $Ar_3SnC_6H_4F$-4, $Ar_3SnCH_2C_6H_4F$-4, and $Ar_3SnSC_6H_4F$-4 compounds.

Key words: electronegativity, effect of substituents, ^{19}F NMR, quantum chemistry, silicon, tin.

Quantitative determination of such properties of L_nE groups as electronegativity, hardness, and softness is of importance for predicting electronic structures of L_nEX compounds and reactivities of E—X bonds in these compounds. Most experimental and theoretical investigations are devoted to studies of the group electronegativity on different electronegativity scales (see Refs. 1—7). In most studies, group electronegativities of organic groups L_nE (E = C, N, O, P, and S) were determined, whereas data on organometallic groups (E = M) are rather scarce. For the most part, these are experimental data based on the establishment of empirical relationships between parameters of the corresponding indicator groups and the values of group electronegativities (χ) by physical methods.[8—12] Calculations of group electronegativities of L_nE groups with the use of additive schemes are also available.[13] The Mulliken group electronegativity of the $(CO)_5Mn$ organometallic group was experimentally determined most rigorously.[6] Quantum-chemical calculations were used for determining group electronegativities of only some groups with forth-row transition metals.[2]

Not only the determination of group electronegativities of L_nE groups but also the studies of the effect of the nature of substituents in the L ligand on group electronegativities of these groups are of particular interest. However, no calculation studies of the effect of substituents in an aromatic ring on group electronegativities of Ar_3E groups have been reported. At the same time, data on ^{19}F chemical shifts for the $Ar_3SiC_6H_4F$-4 (**1**), $Ar_3SnC_6H_4F$-4 (**2**), $Ar_3SnCH_2C_6H_4F$-4 (**3**), and $Ar_3SnSC_6H_4F$-4 (**4**) compounds are available; based on these data, empirical estimations of the effect of substituents on group electronegativities of Ar_3Si and Ar_3Sn groups would be convenient to perform.[14—16]

In this context, in this work, quantum-chemical calculations of group electronegativities of Ar_3Si and Ar_3Sn groups with different *meta*- and *para*-substituents in the phenyl ring have been performed and these values were compared with ^{19}F chemical shifts in corresponding compounds **1**—**4**.

Computation Procedure

Presently, *ab initio* methods, which are the most precise of quantum-chemical methods, can be applied to virtually all compounds. However, computer time and memory capacity impose certain limits on the number of atoms in compounds. Groups discussed below are rather large; therefore, calculations of electronegativities were performed with some sacrifice of accuracy.

The electronegativity was determined as a half-difference between total energies of the Ar_3M^+ cation and Ar_3M^- anion: $\chi = 1/2(E_c - E_a)$ (the ΔSCF method).[17] This is a rather crude approximation of a differential representation $\chi = -dE/dN$ (where E is the total energy of the group, N is the number of electrons); however, in most cases, this approximation is quite adequate.[2]

A geometry of the group was calculated by the MNDO method and was taken to be equal for an anion and a cation as the ΔSCF method requires. Calculations of geometry were performed for the whole $4\text{-}FC_6H_4SiAr_3$ and $4\text{-}FC_6H_4SnAr_3$ molecules with each substituent on the phenyl ring; then the indicator $4\text{-}FC_6H_4$ group was excluded, and the total energies of a cation and an anion were calculated only for Ar_3M groups with the use of the GAMESS program (see Ref. 18). Calculations of energies were performed by the self-consistent field method in the Hartree—Fock approximation[19] with the use of the MINI basis[20] and diffuse functions[21] for a better description of an anion. Diffuse functions were included in calculations only on the key atom of the Ar_3M group (Si or

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1921—1924, October, 1995.

Table 1. Calculated values of electronegativities of the Ar_3Si and Ar_3Sn groups and ^{19}F chemical shifts in compounds **1—4**, as well as the σ Hammett constants and σ^0 Taft constants for the corresponding substituents

Substituent	χ/eV		FCS/ppm				σ	σ^0
	Ar_3Si	Ar_3Sn	**1**	**2**	**3**	**4**		
$4-Me_2NC_6H_4$	2.97	2.92	−0.8	−0.16			−0.82	−0.44
$4-MeOC_6H_4$	3.10	3.04	−1.8	−1.13	6.93		−0.27	−0.16
$4-MeC_6H_4$	3.33	3.25	−1.7	−1.13	6.91	3.41	−0.17	−0.15
$3-MeC_6H_4$	3.37	3.29	−1.8	−1.15	7.04	3.41	−0.07	−0.07
Ph	3.48	3.39	−2.3	−1.52	6.71	2.94	0.00	0.00
$4-FC_6H_4$	3.97	3.84	−3.1	−2.31	6.05	2.18	0.06	0.17
$3-FC_6H_4$	4.03	3.90	−3.7		5.74	1.90	0.34	0.35
$4-ClC_6H_4$	4.23	4.09	−3.5	−2.63	5.64	1.81	0.23	0.27
$3-ClC_6H_4$	4.23	4.18	−4.0	−3.07	5.59	1.68	0.37	0.37
$3-CF_3C_6H_4$	4.41	4.23		−3.43			0.415	0.48
$3,4-Cl_2C_6H_3$	4.81	4.63	−5.0	−3.91	4.77	0.73	0.60	0.64
$3,5-Cl_2C_6H_3$	4.88	4.69		−4.53	4.39	0.20	0.74	0.74
$3,4,5-Cl_3C_6H_2$	5.38	5.15	−6.4	−5.25		−0.35	0.97	1.01

Sn). This simplification substantially decreases the computer time, improves convergence, and affects only slightly the values of $E_c - E_a$, which was found after performing test calculations of some groups with the 6-31G basis set and with diffuse functions on all atoms. Apparently, this is attributable to the fact that the maximum change in charge in going from an anion to a cation is observed for the key atom of the group; this change is equal to ~1.2 e, whereas charges on other atoms are changed only slightly, and inclusion of diffuse functions on these atoms has very little effect on the $E_c - E_a$ difference.

Results and Discussion

Results of calculations of group electronegativities of Ar_3Si and Ar_3Sn groups as well as ^{19}F chemical shifts for the corresponding compounds **1—4** are given in Table 1. From the data obtained it follows that group electronegativities of Ar_3M groups increase with increasing electron-withdrawing properties of substituents in the aryl radical, *i.e.*, with increasing electronegativity of this radical. The difference in group electronegativity between Ar_3Si and Ar_3Sn groups, which run to 0.23 eV for the strong electron-withdrawing $3,4,5-Cl_3C_6H_2$ radical, is virtually nil (0.05 eV) for the groups with aryl radicals containing the strong donor substituent $4-Me_2N$. At the same time, the Si and Sn atoms substantially differ in atomic electronegativity determined according to Mulliken (4.77 and 4.30 eV, respectively).

Figures 1—4 show correlation processing of the obtained data. It follows from the relationship between group electronegativities of Ar_3Si groups and group electronegativities of Ar_3Sn groups with analogous substituents (see Fig. 1) that substituents have a more pronounced effect on the group electronegativity of a silicon-containing group compared to a tin-containing group. Apparently, this is due to smaller interatomic distances between the key metal atom and aryl rings.

A satisfactory correlation between calculated values of electronegativities of Ar_3M groups and the values of the σ Hammett constants[22] and σ^0 Taft constants[23] is observed (see Fig. 2); in the latter case, correlation is substantially better than in the former case. Therefore, the effect of aryl groups on group electronegativities of Ar_3Si and Ar_3Sn groups is determined by their inductive effect. This is in agreement with conclusions, which were made previously[16,17] based on analysis of ^{19}F chemical shifts in compounds **1** and **2**, that electronic effects of substituents along the Si—C(Ar) and Sn—C(Ar) bonds are transferred mainly by an inductive mechanism.

It is interesting to note that good linear relationships are observed between ^{19}F chemical shifts for compounds **1** and **2** and the corresponding values of group electronegativities of Ar_3M groups (see Fig. 3); these relationships are characterized by large correlation coefficients.

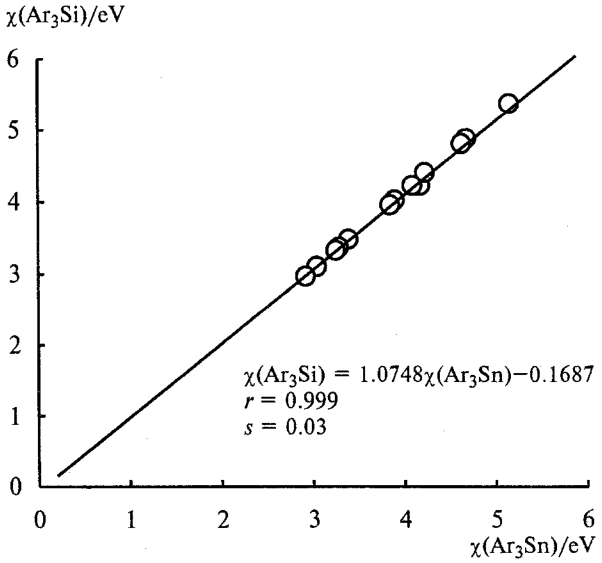

Fig. 1. Dependence of the electronegativity (χ/eV) of the Ar_3Si group on the electronegativity of the Ar_3Sn group for substituted aryl groups.

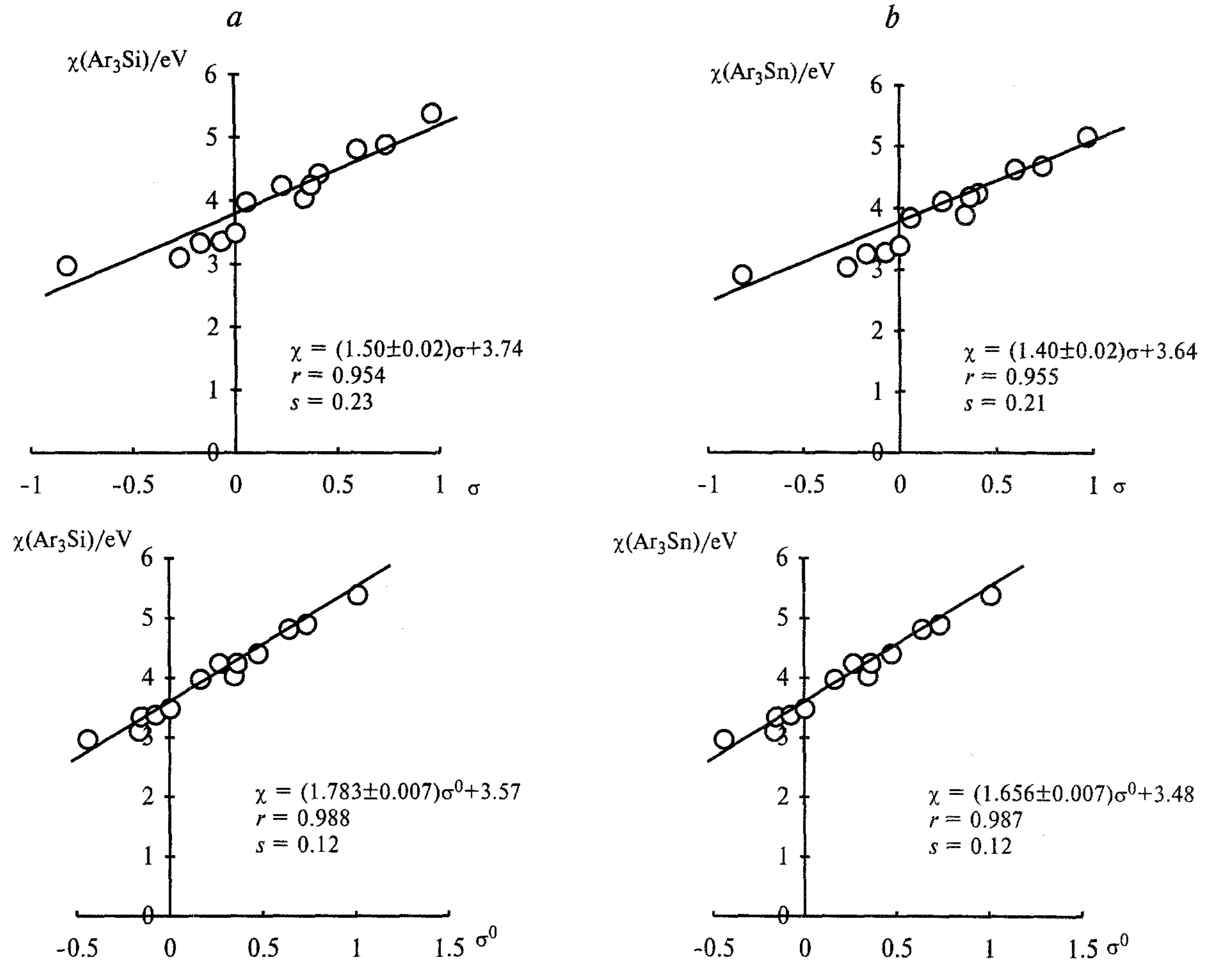

Fig. 2. Dependence of the calculated values of group electronegativities of the Ar_3Si (*a*) and Ar_3Sn (*b*) groups on the values of σ and σ^0 for some substituents in aryl rings.

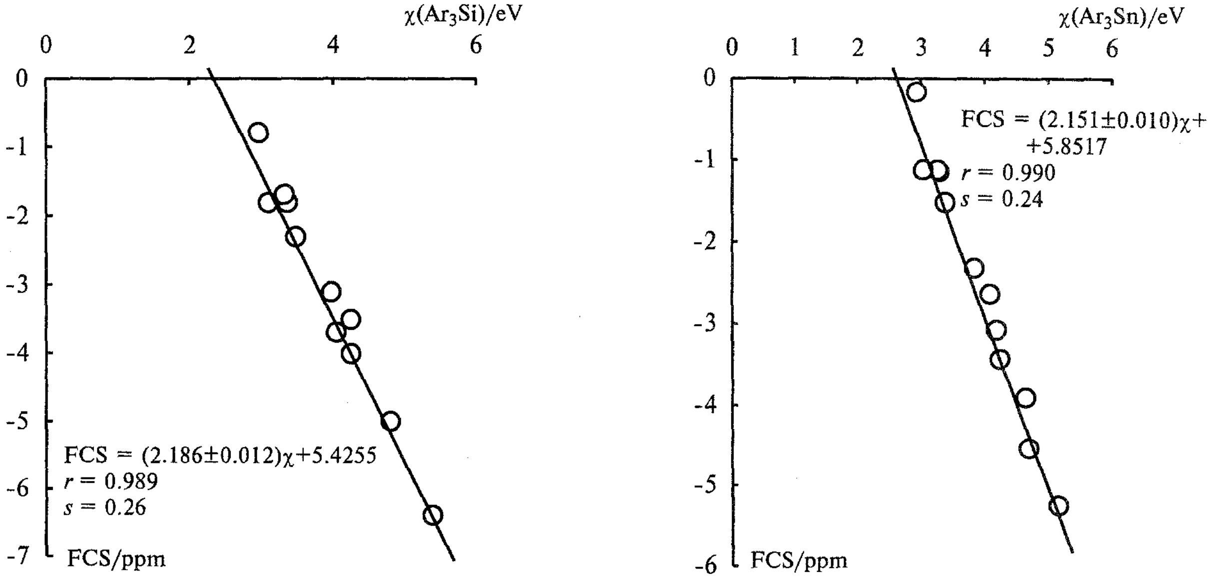

Fig. 3. Dependence of the values of ^{19}F chemical shifts in compounds **1** (*a*) and **2** (*b*) on the calculated values of electronegativities of the Ar_3Si and Ar_3Sn groups, respectively.

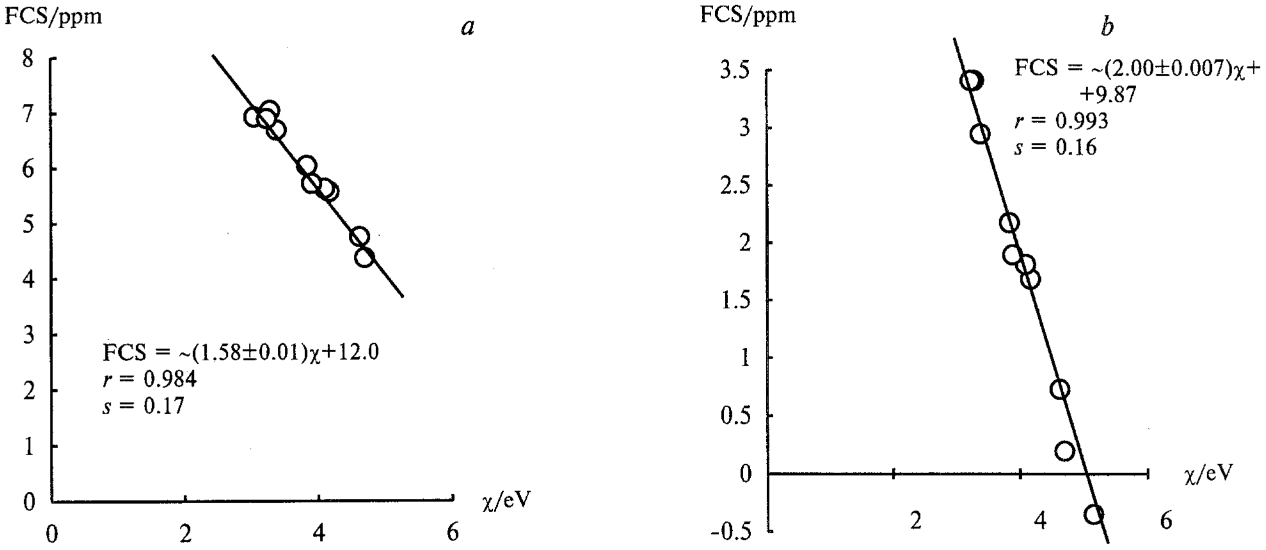

Fig. 4. Dependence of ^{19}F chemical shifts of compounds **3** (*a*) and **4** (*b*) on the calculated values of electronegativities of the Ar_3Sn group.

This fact suggests that a change in ^{19}F chemical shifts in compounds **1** and **2** under the effect of substituents quantitatively reflects, with a large degree of certainty, the corresponding change in group electronegativities of Ar_3Si and Ar_3Sn groups.

A comparison of calculated values of group electronegativities of Ar_3Sn groups with ^{19}F chemical shifts in compounds **3** and **4** also provides good linear dependences with large correlation coefficients (see Fig. 4); for compound **4**, substantially better agreement with the calculated values of group electronegativities was observed. It would be expected that in the more general case of $Ar_nEQC_6H_4F$-4 compounds a change in ^{19}F chemical shifts can serve as the quantitative measure of the change in the group electronegativity of Ar_nE groups under the effect of substituents. The comparative polarity of E—Q bonds can also be estimated with a large degree of certainty based on studies of the regularities of changes in ^{19}F chemical shifts in $Ar_nE—QC_6H_4F$-4 compounds.[24]

We thank M. V. Shmidt for providing the latest version of the GAMESS program.

The work was supported by the Russian Foundation for Basic Research (Project No. 93-03-05528).

References

1. K. D. Sen, M. C. Böhm, and P. S. Schmidt, in *Structure and Bonding*, 66, Berlin, 1987, 99.
2. J. Mullay, in *Structure and Bonding*, 66, Berlin, 1987, 1.
3. R. J. Boyd and K. J. Edgecombe, *J. Am. Chem. Soc.*, 1988, **110**, 4182.
4. R. J. Boyd and S. L. Boyd, *J. Am. Chem. Soc.*, 1992, **114**, 1652.
5. L. H. Reed and L. S. Allen, *J. Phys. Chem.*, 1992, **96**, 157.
6. R. G. Pearson, *J. Org. Chem.*, 1989, **54**, 1423.
7. F. De Proft, W. Langenaecker, and P. Geerlings, *J. Phys. Chem.*, 1993, **97**, 1826.
8. N. Imamoto and S. Masuda, *Chem. Lett.*, 1982, 1003.
9. W. Gordy, *J. Chem. Phys.*, 1946, **14**, 305.
10. A. F. Clifford, *J. Phys. Chem.*, 1959, **63**, 1227.
11. R. P. Stewart and P. M. Treichel, *J. Am. Chem. Soc.*, 1970, **92**, 2710.
12. R. V. Parish and P. J. Rowbotham., *Chem. Phys. Lett.*, 1971, **11**, 1379.
13. J. E. Huheey, *J. Phys. Chem.*, 1965, **69**, 3284.
14. S. I. Pombrik, D. N. Kravtsov, A. S. Peregudov, E. I. Fedin, and A. N. Nesmeyanov, *J. Organomet. Chem.*, 1977, **131**, 355.
15. D. N. Kravtsov, B. A. Kvasov, T. S. Khazanova, and E. I. Fedin, *J. Organomet. Chem.*, 1973, **61**, 219.
16. S. I. Pombrik, L. S. Golovchenko, E. V. Polunkin, A. S. Peregudov, and D. N. Kravtsov, *J. Organomet. Chem.*, 1985, **292**, 81.
17. P. S. Bagus, *Phys. Rev.*, 1965, 139 A, 619.
18. M. W. Schmidt, K. K. Baldridge, and J. A. Boatz, *J. Comput. Chem.*, 1993, **14**, 1347.
19. C. C. J. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.
20. S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzino-Andzelm, Y. Sakai, and H. Tatewaki, in *Gaussian Basis for Molecular Calculations,* Elsevier, Amsterdam, 1984.
21. M. J. Frisch, J. Q. Pople, and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.
22. P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1968, **6**, 204.
23. P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1968, **6**, 150.
24. D. N. Kravtsov, *Metalloorg. Khim.*, 1989, **2**, 157 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].

Received January 10, 1995