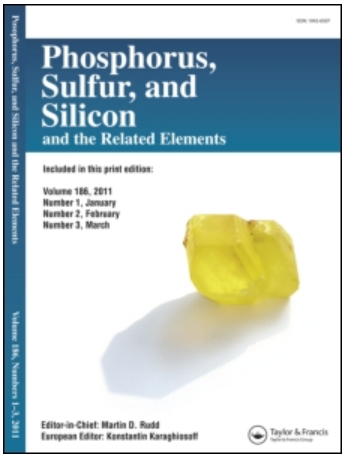

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Multinuclear NMR Spectroscopy and Quantum-Chemical Studies of Sulfur Compounds with Strong Electron-Withdrawing Groups

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MULTINUCLEAR NMR SPECTROSCOPY AND QUANTUM-CHEMICAL STUDIES OF SULFUR COMPOUNDS WITH STRONG ELECTRON-WITHDRAWING GROUPS

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The compounds CH_3XCH_3 (1), CH_3XCF_3 (2), $C_6H_5XCF_3$ (3) and $C_6H_5XC_6H_5$ (4), where X: a, S(O), b, $S(NSO_2CF_3)$, c, SO_2, d, $S(O)NSO_2CF_3$, e, $S(NSO_2CF_3)_2$, were studied by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and by MO-SCF method in MNDO-PM3 valence approximation. The peculiarity of the structure of the X group is a deficiency of electron density on the sulfur atom and a high negative charge on the neighboring O and N atoms. The S-N bond polarity is higher than that of the S-O bond. The S-N bond index is nearly unity (1b 1.06, 1d 0.98, 1e 1.02) and is lower than for the S-O bond (1a 1.24, 1c 1.19). Hence, the S-O and S-N bonds in 1-4 cannot be considered as double ones. They are strongly polarized with a prevailing contribution of the electrostatic component, the covalent contribution being low. In compounds with NSO_2CF_3 groups total electronic charge on the X group is higher than in 1a-4a and 1c-4c. As a consequence, total electronic charge on the CH_3, CF_3 and C_6H_5 groups is lower in compounds 1-4b, d, e than in corresponding compounds with X = SO, SO_2. Changes of total charge on the benzene ring in 3 and 4 are mainly related to the σ electron density change.

The ^1H and ^{19}F nuclei of the CH_3 and CF_3 groups are deshielded from 1a, 2a to 1b, 2b, in harmony with the decrease of calculated charges on these atoms; the ^{13}C nuclei shielding increases, however. The ^1H and ^{13}C nuclei of the CH_3 group are deshielded from 1c to 1d. The paramagnetic term of the ^{13}C nuclei shielding constant for the CH_3 and CF_3 groups is considerably affected by the changes in the nearest electron environment. This is the reason of an irregular character of the δC changes in 1-2. A linear relation exists between δH values of the CH_3 group and calculated charges on H atoms ($r = 0.991$). The δC^{para} and δC^{m} in 3a-d (ppm from TMS) imply the increases of electron-withdrawing properties of the XCF_3 moiety towards the benzene ring when introducing nitrogen-containing groups; δC^{m}: 130.5 (3a), 132.2 (3b); 131.3 (3c), 132.2 (3d); δC^{para}: 134.5 (3a), 137.2 (3b); 138.1 (3c), 139.8 (3d). The δC^{para} values are linearly correlated with π and total charges on C atoms ($r = 0.994$). The σ_I and σ_R constants of the XCF_3 groups were evaluated from ^{13}C NMR spectra; σ_I(X): 0.63 (a), 0.95 (c), 1.08 (b), 1.32 (d); σ_R(X): 0.17 (a), 0.22 (b), 0.29 (c), 0.33

(d). The σ_R values practically coincide with the available data from ^{19}F NMR spectra; σ_I values are in satisfactory accord with them. The X moieties with NSO_2CF_3 groups are stronger electron-withdrawing substituents than the NO_2 group ($\sigma_I = 0.57$; $\sigma_R = 0.20$). The series 4 was the only one where an extremely strong withdrawing effect of the X moiety was demonstrated for 4e. On the ground of our theoretical and experimental results we suggest that the $S(NSO_2CF_3)_2CF_3$ substituent will be a champion of electron-withdrawing properties among all known neutral substituents.

Compounds 1-4 were prepared by Dr. N. V. Kondratenko, Dr. R. Yu. Garlauskaite, and Professor L. M. Yagupolsky.