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## Phosphorus, Sulfur, and Silicon and the Related Elements

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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  $\text{CH}_3\text{XCH}_3$  (**1**),  $\text{CH}_3\text{XCF}_3$  (**2**),  $\text{C}_6\text{H}_5\text{XCF}_3$  (**3**) and  $\text{C}_6\text{H}_5\text{XC}_6\text{H}_5$  (**4**), where X: a, S(O), b, S(NSO<sub>2</sub>CF<sub>3</sub>), c, SO<sub>2</sub>, d, S(O)NSO<sub>2</sub>CF<sub>3</sub>, e, S(NSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>, were studied by <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>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<sub>2</sub>CF<sub>3</sub> 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<sub>3</sub>, CF<sub>3</sub> and C<sub>6</sub>H<sub>5</sub> groups is lower in compounds **1-4b**, **d**, **e** than in corresponding compounds with X = SO, SO<sub>2</sub>. Changes of total charge on the benzene ring in **3** and **4** are mainly related to the  $\sigma$  electron density change.

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

(d). The  $\sigma_R$  values practically coincide with the available data from  $^{19}\text{F}$  NMR spectra;  $\sigma_I$  values are in satisfactory accord with them. The X moieties with  $\text{NSO}_2\text{CF}_3$  groups are stronger electron-withdrawing substituents than the  $\text{NO}_2$  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  $\text{S}(\text{NSO}_2\text{CF}_3)_2\text{CF}_3$  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. Garlauskaitė, and Professor L. M. Yagupolsky.