Evaluation of the reactivity of new activated difluoroaromatic compounds

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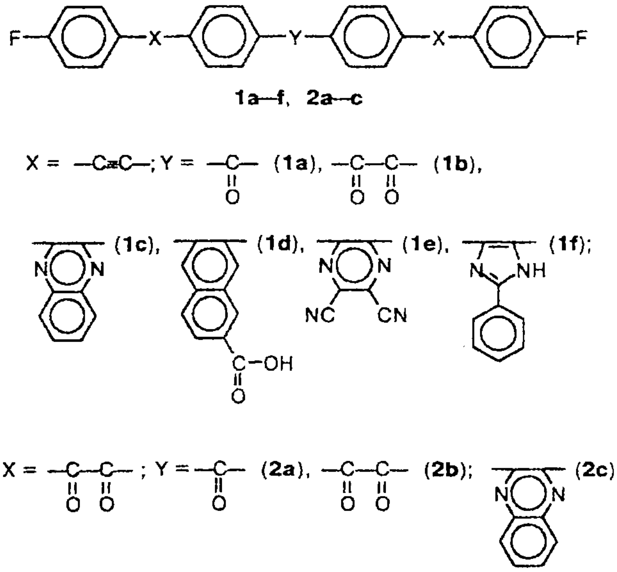
To evaluate the reactivity of new difluoroaromatic compounds in nucleophilic substitution, the positive charges on carbon atoms of C—F bonds were calculated using the quantum-chemical semiempirical PM3 method. A correlation between the charges calculated and the chemical shifts in the ^{19}F NMR spectra was established.

Key words: reactivity, difluoroaromatic compounds, ^{19}F NMR, chemical shift, charge, correlation.

Previously,[1] new activated difluoroaromatic compounds (ADFC) incorporating α-diketone and acetylenic fragments were synthesized. These compounds were used for the synthesis of aromatic polyethers[2,3] containing the units mentioned above. This is of considerable interest due to their possible transformation into heterocyclic fragments (in the case of α-diketone groups) and "cross-linking" (through the acetylenic fragments). The efficiency of the synthesis of high-molecular aromatic polyethers depends directly on the reactivity of ADFS, hence attempts to evaluate it are of considerable interest.

The reactivity of ADFS is usually assessed by quantum-chemical calculations of charges $q(C_F)$ on carbon atoms of C—F bonds[4—8] and by calculating[9—12] the chemical shifts $\delta(^{19}F)$ in ^{19}F NMR spectra. We used these approaches to study the reactivity of a series of ADFS (**1a—f**, **2a—c**). For comparison, we also studied fluorobenzene (**3**) and the simplest ADFS previously used for the synthesis of aromatic polyethers,[5,8,13] namely, 4,4′-difluorobenzophenone (**4**), 4,4′-difluorotolan (**5**), 4,4′-difluorobenzil (**6**), and 2,3-bis(4-fluorophenyl)quinoxaline (**7**).

Atomic charges $q(C_F)$ accepted as reactivity indices of ADFC are presented in Table 1 along with chemical shifts $\delta(^{19}F)$ in the ^{19}F NMR spectra of these compounds. Analysis of $q(C_F)$ and $\delta(^{19}F)$ values listed in Table 1 suggests, in agreement with the literature data,[12,14] that there is a correlation between them, as shown in Fig. 1. A comparison of the data in Table 1 also shows that all ADFC are more reactive than fluorobenzene (**3**) and that the differences between them depend considerably on the nature of groups located *para* relative to the F atoms. For example, all of the ADFC can be divided in two main groups, where the compounds belonging to group 1 contain carbonyl (α-dicarbonyl) fragments at these *para* positions (**2a—c**, **4**, **6**), while those belonging to group 2 contain acetylenic fragments (**1a—f**, **5**). The first group has much higher indices of reactivity than the second one, in agreement with results reported previously.[5]



In the series of ADFC with acetylenic fragments located *para* relative to the F atoms, 4,4′-difluorotolan (**5**) should be the most reactive. Complication of the structure of acetylene-containing ADFC by introduction of electron-withdrawing central groups results in some increase in their reactivity. The most noticeable changes are observed when the 2,3-dicyanopyrazine-5,6-diyl fragment serves as the central group (**1e**).

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Table 1. Chemical shifts ($\delta(^{19}F)$) and atomic charges ($q(C_F)$) for a series of aryl fluorides

Compound	$\delta(^{19}F)$	$q(C_F)$ (au)	Compound	$\delta(^{19}F)$	$q(C_F)$ (au)
1a	−109.722	0.071	**2b**	−101.125	0.099
1b	−109.691	0.072	**2c**	−101.434	0.101
1c	−109.640	0.069	**3**	−112.770	0.065
1d	−109.828	0.070	**4**	−106.010	0.095
1e	−109.677	0.074	**5**	−110.130	0.070
1f	−109.745	0.070	**6**	−101.443	0.103
2a	−101.272	0.101	**7**	−111.950	0.074

4,4′-Difluorobenzil (**6**) is more reactive than 4,4′-difluorobenzophenone (**4**), in agreement with the literature data.[5] The transition to more complicated monomers, which incorporate not only α-dicarbonyl *para*-substituents but also additional electron-withdrawing central groups, results in minor changes in reactivity (**2a—c**). Finally, the data related to ADFC with a quinoxal-2,3-diyl group (**7**) indicate, in agreement with a previous study,[5] that this heterocyclic fragment is a very weak activator of the F atoms.

The ADFC with $\delta(^{19}F) > -107$ are activated rather strongly, which facilitates the synthesis of high-molecular aromatic polyethers. Conversely, the monomers with $\delta(^{19}F) < -109$ are weakly activated and require longer reaction times and higher temperatures to complete polycondensation. This conclusion agrees well with the result of the synthesis of aromatic polyethers.[15,16]

Experimental

The difluoroaromatic compounds were synthesized according to the procedures suggested previously.[1]

^{19}F NMR spectra were recorded on a Bruker AC-200 spectrometer (188.3 MHz) using CCl_3F (δ 0.0) as the internal standard. DMSO-d_6 was used as the solvent.

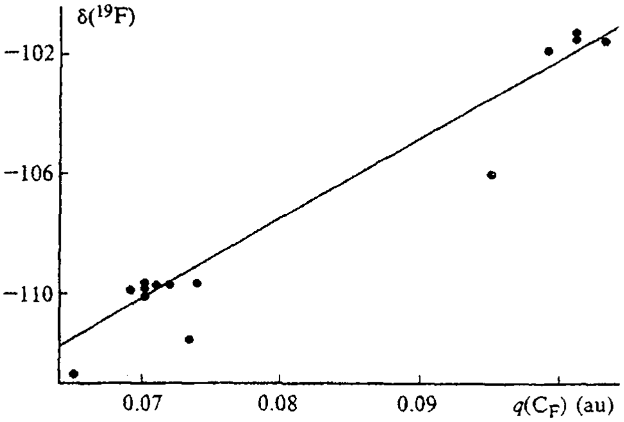

Fig. 1. Correlation between charges $q(C_F)$ and chemical shifts $\delta(^{19}F)$ in ^{19}F NMR spectra of ADFC.

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