# Organic Chemistry

## New unsymmetrical difluoroaromatic compounds and estimation of their reactivities in nucleophilic substitution

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A series of previously unknown unsymmetrical difluoroaromatic compounds, *viz.*, *p*-fluorobenzoylphenyl(*p*-fluorophenyl)-substituted imidazoles, pyrazines, and quinoxalines, were synthesized according to multistep procedures with the use of chloral as the key compound. The reactivities of the resulting difluoroaromatic compounds were estimated based on $^{19}F$ and $^{13}C$ NMR spectral data and the results of quantum-chemical calculations. The calculated charge densities on the $C_{ipso}$ atoms correlate linearly with the experimental chemical shifts in the $^{19}F$ and $^{13}C$ NMR spectra. Difluoroaromatic compounds, which are characterized by $\delta_F > -110$ and $\delta_C > 163$ and by the charge density on the $C_{ipso}$ atom higher than 0.08 e, are sufficiently activated to be used for the preparation of high-molecular-weight polyethers.

**Key words:** difluoroaromatic compounds, quinoxalines, pyrazines, imidazoles, reactivity, $^{13}C$ and $^{19}F$ NMR spectroscopy, charge density, correlation.

Difluoroaromatic compounds (DFAC) are widely used for the preparation of aromatic polyethers (APE) possessing improved thermal and mechanical properties.[1—5] The syntheses of APE are performed primarily with the use of symmetrical DFAC, whereas available unsymmetrical APE are few in number.[6—8] However, the use of unsymmetrical DFAC in the synthesis of APE offers considerable possibilities of varying the microstructure of the target polymers (head-to-head, head-to-tail, or tail-to-tail) and, correspondingly, their properties. Consequently, the

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development of procedures for the synthesis of new unsymmetrical DFAC is of great interest. The aim of the present study was to synthesize unsymmetrical DFAC based on chloral, which is widely used for the preparation of condensation monomers and polymers.[9,10]

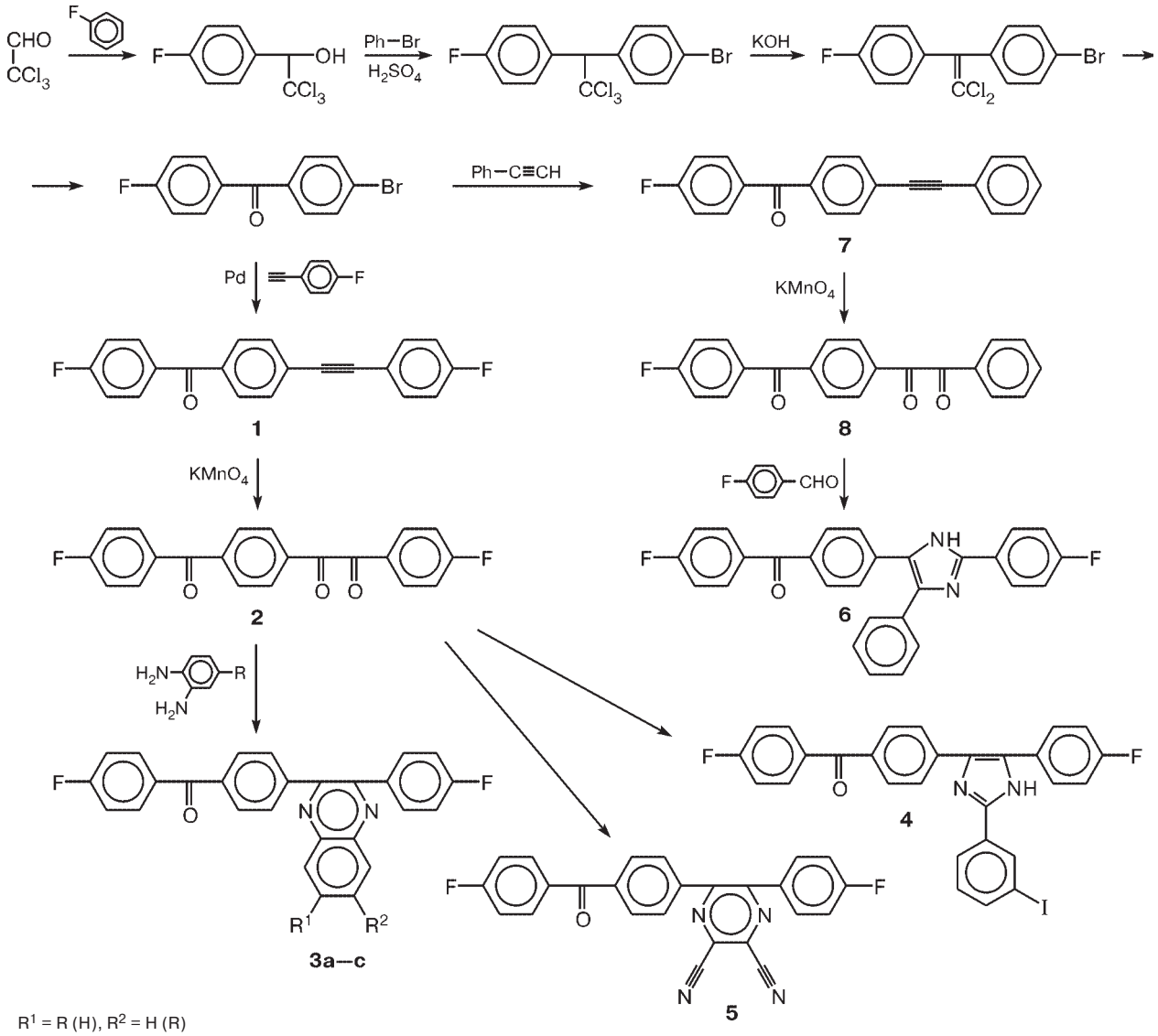
## Results and Discussion

Unsymmetrical DFAC were synthesized according to Scheme 1.

Intermediate trichloromethyl(*p*-fluorophenyl)carbinol (TFC), 2-(*p*-bromophenyl)-1,1,1-trichloro-2-(*p*-fluorophenyl)ethane (BTF), 2-(*p*-bromophenyl)-1,1-dichloro-2-(*p*-fluorophenyl)ethylene (BDF), and 4-bromo-4´-fluorobenzophenone (BFB) were prepared according to procedures published earlier.[11—13]

Unsymmetrical DFAC **1—6** (Table 1) have not been described previously. Diarylacetylene **1** and 4-fluoro-4´-(phenylethynyl)benzophenone (**7**) were synthesized by the reactions of BFB with equimolar amounts of *p*-fluorophenylacetylene and phenylacetylene, respectively, under the conditions of Pd-catalyzed cross-coupling.[14] The curves of differential scanning calorimetry (DSC) have narrow peaks of melting endotherms at 176 and 151 °C and broad exothermic transformations with maxima at 423 and 410 °C, respectively. No exothermic transformations were observed in the DSC curves upon repeated heating, which is apparently attributable to cross-linking *via* triple bonds. After thermal treatment of com-

**Scheme 1**




$R^1$ = R (H), $R^2$ = H (R)

R = H (**a**), $NO_2$ (**b**), Me (**c**)

**Table 1.** Selected physicochemical characteristics of DFAC **1—6**

| Compound | Yield (%) | M.p. /°C | Found / Calculated (%) | | | | Molecular formula |
|---|---|---|---|---|---|---|---|
| | | | C | H | F | N | |
| **1** | 89 | 176—178 | 79.01 | 3.39 | 11.81 | | $C_{21}H_{12}F_2O$ |
| | | | 79.23 | 3.79 | 11.93 | | |
| **2** | 95 | 139—141 | 71.48 | 3.34 | 10.31 | | $C_{21}H_{12}F_2O_3$ |
| | | | 71.99 | 3.45 | 10.84 | | |
| **3a** | 98 | 163—165 | 76.45 | 3.74 | 8.65 | 6.52 | $C_{27}H_{16}N_2F_2O$ |
| | | | 76.77 | 3.82 | 9.00 | 6.63 | |
| **3b** | 92 | 174—176 | 69.21 | 3.15 | 8.00 | 8.75 | $C_{27}H_{15}F_2N_3O_3$ |
| | | | 69.37 | 3.20 | 8.12 | 8.98 | |
| **3c** | 95 | 158—160 | 77.21 | 4.18 | 8.49 | 6.35 | $C_{28}H_{18}F_2N_2O$ |
| | | | 77.05 | 4.15 | 8.70 | 6.41 | |
| **4*** | 85 | 207—209 | 59.91 | 3.12 | 6.52 | 4.78 | $C_{28}H_{17}F_2IN_2O$ |
| | | | 59.80 | 3.04 | 6.75 | 4.98 | |
| **5** | 50 | 141—143 | 71.01 | 2.84 | 8.85 | 13.20 | $C_{25}H_{12}F_2N_4O$ |
| | | | 71.08 | 2.86 | 8.99 | 13.26 | |
| **6** | 83 | 255—257 | 71.10 | 4.20 | 8.61 | 6.31 | $C_{28}H_{18}F_2N_2O$ |
| | | | 77.05 | 4.15 | 8.70 | 6.41 | |

* The I content (%): found, 22.41; calculated, 22.56.

pounds **1** and **7**, the Raman spectra have no peaks at 1900—2220 $cm^{-1}$ characteristic of triple bonds and the products were insoluble in organic solvents. This is additional evidence that the reactions proceeded at the ethynyl groups. Triketones **2** and 4′-fluoro-4-(phenylglyoxalyl)benzophenone (**8**) were synthesized by oxidation of diarylacetylenes **1** and **7**, respectively, with $KMnO_4$ according to a procedure described previously.[15]

Quinoxaline derivatives **3a—c** were prepared by treatment of compound **2** with *o*-phenylenediamine, 1,2-diamino-4-nitrobenzene, and 3,4-diaminotoluene, respectively. Compounds **3b,c** were obtained as mixtures of two isomeric DFAC characterized by very close chromatographic retention indices. The ratios of the isomers of quinoxaline derivatives **3b,c** were established by $^{19}F$ and $^{13}C$ NMR spectroscopy. The $^{19}F$ NMR spectrum of an isomeric mixture of compound **3b** (Table 2) has three singlet signals at $\delta_F$ −104.87, −109.42, and −109.70 with the integral intensity ratio of 2 : 1 : 1, which is indicative of the isomer ratio of 1 : 1. The assignment of the signals in the $^{13}C$ NMR spectrum of compound **3c** was made analogously. In the absorption region of the carbon atom of the methyl group, the $^{13}C$ NMR spectrum of an isomeric mixture of compound **3c** has two signals at $\delta_C$ 21.85 and 21.82 belonging to two possible isomers in a ratio of 1 : 1.

Pyrazine **5** was synthesized in ~50% yield by the reaction of an equimolar amount of triketone **2** with dinitrile of diaminomaleic acid in a mixture of AcOBu and AcOH.

Imidazoles **4** and **6** were prepared by the reactions of compounds **2** and **8**, respectively, with equimolar amounts of the corresponding aldehydes in AcOH in the presence of an excess of $NH_4OAc$. The presence of four signals in the $^{19}F$ NMR spectrum of imidazole **4** is, apparently, associated with the hindered rotation of the *m*-iodophenyl substituent about the C—C bond. It is less probable that the observed magnetic nonequivalence of the fluorine nuclei results from the principally possible slowed-down tautomeric process because the $^{19}F$ NMR spectrum of a close analog, *viz.*, of compound **6**, has one signal for the fluorine atom at position 4′.

Since the efficiency of the synthesis of high-molecular-weight APE is associated with the reactivity of DFAC, estimations of the latter are of considerable interest. For this purpose, two methods are primarily used,[16—20] *viz.*, quantum-chemical calculations of the charge density on the $C_{ipso}$ atoms and $^{13}C$ and $^{19}F$ NMR spectroscopy. The results of the application of both methods are presented in Table 3.

The presence of electron-withdrawing groups at the *para* position with respect to the fluorine atom in DFAC leads to strong activation of these compounds by reducing the electron density on the carbon atom of $C_{ipso}$—F. The reactivity depends substantially on the nature of the substituents. Traditionally, DFAC are activated with electron-withdrawing groups (CO or $SO_2$), which increase the electrophilicity of $C_{ipso}$—F and reduce the energy of the transition state. The $^{13}C$ and $^{19}F$ NMR spectra are a valuable tool in estimating the electronegative effect of substituents in DFAC because chemical shifts are very sensitive to changes in the electron density on the aromatic ring caused by the inductive and resonance effects.

A comparison of the chemical shifts of new DFAC with those of the usual activated monomers, such as

**Table 2.** Spectral characteristics of compounds **1—6**

| Compound | NMR ($CDCl_3$), δ (*J*/Hz) | | | IR, ν/cm$^{-1}$ |
|---|---|---|---|---|
| | $^1$H | $^{13}$C | $^{19}$F | |
| **1** | 7.01—7.07 (m, 2 H); 7.11—7.17 (m, 2 H); 7.50—7.54 (m, 2 H); 7.60 (d, 2 H, *J* = 8); 7.74 (d, 2 H, *J* = 8); 7.79—7.84 (m, 2 H) | 193.95 (CO); 165.36 (CF); 162.78 (CF); 136.79, 133.68, 132.39, 131.29, 129.69, 127.39, 118.84, 118.80, 115.64, 115.38, 91.37 (C≡C); 88.26 (C≡C) | −105.33, −109.52 | 2220 (C≡C); 1645 (C=O); 1217 (C—F) |
| **2** | 7.13—7.21 (m, 4 H); 7.80—7.85 (m, 4 H); 7.99—8.04 (m, 2 H); 8.07 (d, 2 H, *J* = 8) | 193.88 (CO); 192.85 (CO); 191.75 (CO); 167.47 (CF); 164.90 (CF); 142.58, 135.01, 132.72, 132.62, 129.84, 129.70, 129.01, 128.99, 116.37, 115.64 | −100.19, −103.92 | 1662 (CO); 1652 (CO); 1210 (CF) |
| **3a** | 6.99—7.04 (m, 2 H); 7.10—7.14 (m, 2 H); 7.48—7.52 (m, 2 H); 7.63 (d, 2 H); 7.74 (d, 2 H); 7.76—7.82 (m, 4 H); 8.13—8.16 (m, 2 H) | 194.42 (CO); 166.47 (CF); 164.28 (CF); 163.94 (CF); 161.80 (CF); 151.90, 151.75, 142.67, 141.09, 140.89, 137.27, 134.42, 134.39, 133.28, 133.26, 132.47, 132.38, 131.67, 131.58, 130.39, 130.14, 129.69, 129.63, 129.01, 128.94 | −105.12, −111.23 | 1650 (CO); 1224 (CF) |
| **3b** | 9.08—9.06 (m, 1 H); 8.57—8.54 (m, 1 H); 8.33—8.30 (m, 1 H); 7.88—7.80 (m, 4 H); 7.72—7.69 (m, 2 H); 7.62—7.57 (m, 2 H); 7.20—7.67 (m, 4 H) | 194.24 (CO); 166.77 (CF); 165.04 (CF); 164.96 (CF); 164.23 (CF); 162.54 (CF); 162.45 (CF); 154.85, 154.79, 154.26, 154.19, 148.23, 148.05, 143.54, 143.29, 141.74, 141.68, 140.08, 139.81, 138.33, 138.24, 133.67, 133.60, 133.56, 133.33, 132.49, 132.03, 131.92, 131.83, 130.78, 130.71, 129.83, 129.80, 129.73 | −104.87, −109.42, −109.70 | |
| **3c** | 8.085—8.04 (m, 1 H); 7.95 (s, 1 H); 7.85—7.74 (m, 2 H); 7.75 (d, 2 H, *J* = 8.4); 7.63 (d, 3 H, *J* = 8.4); 7.52—7.49 (m, 2 H); 7.15 (t, 2 H, *J* = 8.4); 7.03 (t, 2 H, *J* = 8.4); 2.62 (s, 3 H) | 164.62 (CO); 166.64, 164.39, 164.35, 164.11, 161.91, 161.87, 151.93, 151.75, 151.17, 150.98, 143.03, 141.35, 141.22, 141.15, 140.92, 139.77, 139.58, 137.34, 137.29, 134.74, 133.49, 132.89, 132.64, 132.48, 131.74, 131.72, 131.66, 131.64, 129.78, 129.73, 128.66, 128.59, 127.94, 127.88, 21.85 (Me); 21.82 (Me) | −105.07, −111.39 | |
| **4** | 12.90 (s, 1 H); 8.50 (s, 1 H); 8.13—7.13 (m, 15 H) | 193.59, 193.52, 165.85, 165.71, 163.35, 163.20, 162.58, 160.76, 160.76, 160.15, 144.69, 144.24, 139.10, 138.15, 136.80, 136.09, 135.59, 133.53, 133.46, 132.34, 132.25, 132.16, 132.09, 131.17, 130.83, 130.70, 130.09, 129.90, 129.79, 129.50, 129.42, 129.34, 127.70, 127.32, 126.95, 126.47, 124.61, 124.46, 115.80, 115.64, 115.58, 115.53, 115.43, 115.31, 115.24, 115.02, 94.90 (Cl) | −105.63, −106.01, −112.16, −114.18 | |
| **5** | 7.85—7.79 (m, 2 H); 7.78 (d, 2 H, *J* = 8.4); 7.67 (d, 2 H, *J* = 8.4); 7.59—7.56 (m, 2 H); 7.17 (t, 2 H, *J* = 8.4); 7.09 (t, 2 H, *J* = 8.4) | 193.96 (CO); 166.84 (CF); 105.76 (CF); 114.30 (CF); 163.23 (CF); 154.30, 153.82, 139.39, 138.57, 132.85, 132.80, 132.75, 131.65, 131.60, 130.62, 130.00, 129.50, 115.99, 116.04, 116.24, 116.29, 112.78 | −104.18, −106.29 | |
| **6** | 12.81 (s, 1 H); 8.17—7.29 (m, 17 H) | 193.62 (CO); 165.75 (CF); 163.50 (CF); 163.25 (CF); 161.02 (CF); 139.02, 136.60, 132.07, 131.88, 130.26, 129.23, 129.13, 128.18, 127.36, 126.71, 125.63, 124.66, 118.49, 116.77, 116.21, 115.80 | −105.97, −112.18 | |

4,4′-difluorobenzophenone, and nonactivated fluorobenzene provides information on the reactivities of DFAC and also allows the prediction of the relative reactivities in the series of quinoxalines **3a—c** (see Table 3). Since positions 4 and 4′ in DFAC are nonequivalent, the chemical shifts of two fluorophenyl groups of DFAC are different. The chemical shifts $\delta_F$ of the fluorophenyl group at position 4 of DFAC and 4,4′-difluorobenzophenone have close values (from −103.92 to −105.63), whereas the signals of the fluorophenyl group at position 4′ are in the $\delta_F$ range from −100.19 to −112.18. The signals for the F atom at position 4′ in compound **2** (α-diketone) and in compound **5** containing the dicyanopyrazine ring are observed at $\delta_F$ −100.19 and −106.29, respectively, whereas the corresponding signals in the spectra of compounds **4** and **6** bearing the imidazole ring are observed at $\delta_F$ −112.16 and −112.18, respectively, which are comparable with that observed for fluorobenzene.

**Table 3.** Chemical shifts (δ) in the $^{13}C$ and $^{19}F$ NMR spectra and the charge densities ($q$) on the carbon atom ($C_{ipso}$—F) calculated by the quantum-chemical PM3 and AM1 methods for difluoroaromatic compounds **1—6**

| Compound | δ | | $q(C_{ipso}—F)$/e | |
|---|---|---|---|---|
| | $^{19}F$ | $^{13}C$ | PM3 | AM1 |
| Ph—F | −112.77 | 162.80 | 0.064 | 0.089 |
| **1** | −105.33 | 165.32 | 0.094 | 0.1221 |
| | −109.52 | 162.81 | 0.072 | 0.1024 |
| **2** | −103.92 | 165.62 | 0.0952 | 0.1240 |
| | −100.19 | 166.76 | 0.1030 | 0.1313 |
| **3a** | −105.12 | 165.20 | 0.0917 | 0.1173 |
| | −111.23 | 163.04 | 0.0733 | 0.0998 |
| **3b** | −104.87 | 165.71 | 0.0940 | 0.1195 |
| | −109.42 | 163.43 | 0.0784 | 0.1047 |
| **3c** | −105.07 | 165.37 | 0.092 | 0.1170 |
| | −111.39 | 163.15 | 0.074 | 0.0996 |
| **4** | −105.63 | 164.52 | 0.0884 | 0.1153 |
| | −112.16 | 162.51 | 0.0703 | 0.0951 |
| **5** | −104.18 | 165.57 | 0.0933 | 0.1201 |
| | −106.29 | 164.60 | 0.0856 | 0.1105 |
| **6** | −105.97 | 164.50 | 0.086 | 0.1154 |
| | −112.18 | 162.14 | 0.071 | 0.1013 |

It was demonstrated that the monomers characterized by $\delta_F > -110$ are strongly activated,[17] whereas DFAC characterized by $\delta_F \leq -112.80$ (fluorobenzene) are not invloved in the reactions giving rise to APE.[19] Actually, our attempts to prepare high-molecular-weight compounds based on imidazole-containing monomers failed. Interesting results were obtained[21] for compounds giving signals at $\delta_F$ from −110 to −112. The latter DFAC entered into the reactions yielding APE, though under more drastic conditions. Analogous results were obtained in the studies by $^{13}C$ NMR spectroscopy. The $C_{ipso}$—F groups in DFAC give signals at $\delta_C$ from 166.76 to 161.58, whereas nonactivated fluorobenzene gives a signal at $\delta_C$ 162.80. Hence, the α-diketone fragment is the strongest activating group ($\delta_C$ 166.76), whereas the signal for the carbonyl group is observed at $\delta_C$ 164.90. The imidazole rings are the weakest activating groups ($\delta_C$ 161.58) and exhibit electron-donating properties with respect to fluorobenzene (162.8). Our studies demonstrated that the shifts $\delta_F$ are more sensitive to the electron density redistribution in the aromatic ring because the difference between the chemical shifts of the most active α-diketone ($\delta_F$ −100.19) and inactive fluorobenzene ($\delta_F$ −112.8) is larger than 12 ppm, whereas the corresponding difference between the corresponding shifts $\delta_C$ is ~5. For DFAC, the $\delta_F$ and $\delta_C$ values correlate well with each other (Fig. 1).

The reactivities of DFAC were also estimated from the charge densities ($q$) on the carbon atom of $C_{ipso}$—F, which were calculated by the semiempirical quantum-chemical PM3 and AM1 methods. More activated DFAC

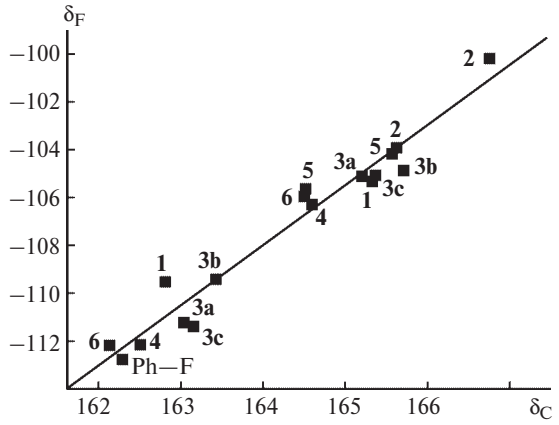



**Fig. 1.** Plot of the chemical shifts in the $^{19}F$ NMR spectra ($\delta_F$) *vs.* chemical shifts for the carbon atom of $C_{ipso}$—F of difluoroaromatic compounds **1—6** ($R$ = 0.97742) in the $^{13}C$ NMR spectra ($\delta_C$). The figures at the points correspond to the ordinal numbers of the compounds.

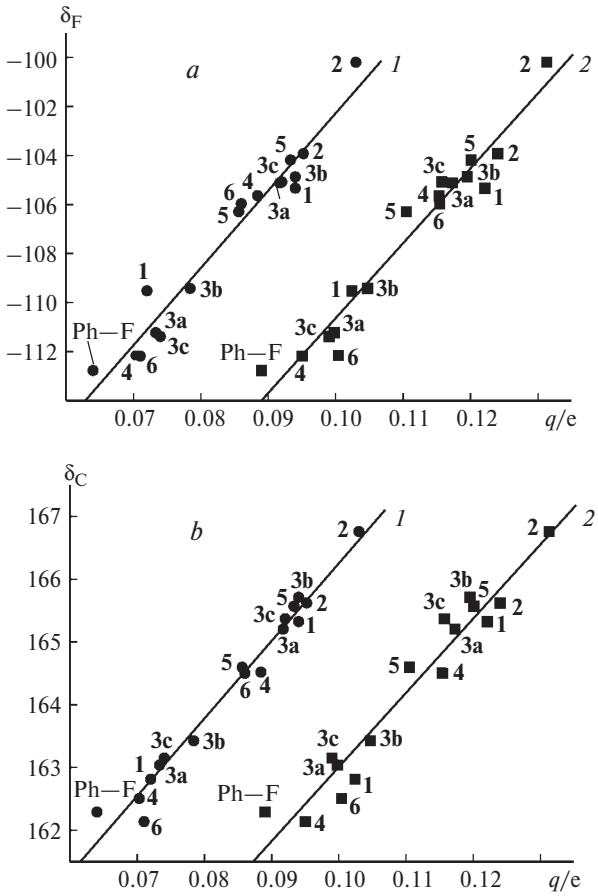



**Fig. 2.** Effect of the density charge ($q$) at the carbon atom ($C_{ipso}$—F), which was calculated by the PM3 (*1*) and AM1 (*2*) methods, on the chemical shifts in the $^{19}F$ ($\delta_F$) (*a*) and $^{13}C$ ($\delta_C$) (*b*) NMR spectra of difluoroaromatic compounds **1—6**. The figures at the points correspond to the ordinal numbers of the compounds.

possess higher positive charges. The calculated charge densities on $C_{ipso}$ for DFAC correlate linearly with the corresponding experimental values of $\delta_F$ and $\delta_C$ (Fig. 2). The PM3 method gave the better correlation ($R = 0.97766$ and 0.98752) than the AM1 method ($R = 0.97581$ and 0.96914).

Hence, the difluoroaromatic compounds obtained by us are of interest as monomers for the synthesis of polyarylene oxides with the controlled microstructure and properties.

## Experimental

The quantum-chemical PM3 and AM1 calculations were carried out using the GAMESS program.

The Raman and Fourier-transform IR spectra were recorded on a Perkin—Elmer 1720X spectrometer. The $^1H$ and $^{13}C$ NMR spectra were measured on a Bruker AMX-400 spectrometer operating at 400.13 and 100.61 MHz, respectively. The $^{19}F$ NMR spectra were recorded on a Bruker AC-200 instrument operating at 188.3 MHz with the use of $CCl_3F$ (δ 0.0) as the internal standard and $CDCl_3$ as the solvent.

The dynamics of thermal transformations was studied by TGA on a Perkin—Elmer TGA7 instrument (the rate of heating was 10 deg $min^{-1}$) and by DSC on a Perkin—Elmer DSC7 instrument (the rate of heating was 20 deg $min^{-1}$).

The starting fluoro- and bromobenzene (Lancaster), *p*-fluorophenylacetylene, $PdCl_2(Ph_3P)_2$, $Ph_3P$, and CuI (all from Aldrich), and chloral hydrate of high-purity grade were used without purification. The solvents were dried according to known procedures.

**4´-Fluoro-4-(phenylethynyl)benzophenone (7).** 4-Bromo-4´-fluorobenzophenone (2.79 g, 10 mmol), phenylacetylene (1.123 g, 11 mmol), $PdCl_2(Ph_3P)_2$ (0.07 g), $Ph_3P$ (0.07 g), CuI (0.035 g), and $Et_3N$ (80 mL) were placed in a 100-mL three-neck flask equipped with a stirrer, a reflux condenser, and a tube for supplying argon. The reaction mixture was refluxed for 10 h. After cooling, $Et_3N \cdot HBr$ that precipitated was filtered off and $Et_3N$ was distilled off from the filtrate to dryness. The residue was twice crystallized from $Me_2CO$ and dried in a vacuum desiccator at 100 °C for 3 h. The target product **7** was obtained in a yield of 2.89 g (94%) as a white crystalline compound, m.p. 150—152 °C. IR (KBr), ν/$cm^{-1}$: 2211 (C≡C); 1650 (C=O); 1225 (C—F). $^1H$ NMR ($CDCl_3$), δ: 6.80—7.80 (m, Ar—H). $^{13}C$ NMR ($CDCl_3$), δ: 194.34 (C=O); 165.28 (C—F); 136.44; 133.47; 132.45; 131.61; 129.79; 128.70; 128.33; 127.53; 122.47; 115.42; 92.44 (C≡C); 88.43 (C≡C). $^{19}F$ NMR ($CDCl_3$), δ: −105.89. Found (%): C, 83.84; H, 4.21; F, 6.09. $C_{21}H_{13}FO$. Calculated (%): C, 83.98; H, 4.36; F, 6.32.

**4´-Fluoro-4-(phenylglyoxalyl)benzophenone (8).** 4´-Fluoro-4-(phenylethynyl)benzophenone (**7**) (3.6 g, 12 mmol) and $Me_2CO$ (125 mL) were placed in a 200-mL two-neck flask equipped with a stirrer and a reflux condenser. Water (5 mL) and AcOH (1.9 mL) were added and then $KMnO_4$ (4.08 g, 0.026 mol) was added with stirring. The reaction mixture was refluxed for 2.5 h. The hot mixture was filtered and the residue was washed several times with hot $Me_2CO$. The filtrate was concentrated to 30 mL and diluted with water (600 mL). White needle-like crystals of 4´-fluoro-4-(phenylglyoxalyl)benzophenone (**8**) were obtained by crystallization from 95% EtOH. The yield was 3.62 g (91%), m.p. 112—114 °C. IR (KBr), ν/$cm^{-1}$: 1665 (C=O); 1652 (C=O); 1211 (C—F). $^1H$ NMR ($CDCl_3$), δ: 7.09—7.14 (m, 2 H, Ar—H); 7.46—7.50 (m, 2 H, Ar—H); 7.61—7.65 (m, 2 H, Ar—H); 7.78—7.82 (m, 2 H, Ar—H); 7.92—7.95 (d, 2 H, $J = 8.1$ Hz); 8.08—8.06 (d, 2 H, $J = 8.1$ Hz). $^{13}C$ NMR ($CDCl_3$), δ: 193.78 (C=O); 193.51 (C=O); 193.28 (C=O); 165.46 (C—F); 142.31; 135.02; 134.95; 132.56; 132.34; 129.75; 129.69; 129.55; 128.87; 115.51. $^{19}F$ NMR ($CDCl_3$), δ: −104.07. Found (%): C, 75.84; H, 3.91; F, 5.28. $C_{21}H_{13}FO_3$. Calculated (%): C, 75.89; H, 3.94; F, 5.71.

**4-Fluoro-4´-(4-fluorophenylethynyl)benzophenone (1).** 4-Bromo-4´-fluorobenzophenone (35.14 g, 0.126 mol), *p*-fluorophenylacetylene (15.13 g, 0.125 mol), $PdCl_2(Ph_3P_2)$ (0.44 g), $Ph_3P$ (0.44 g), CuI (0.29 g), and $Et_3N$ (700 mL) were placed in a 1-L three-neck flask equipped with a reflux condenser, a stirrer, and a tube for supplying argon. The reaction mixture was heated at 80 °C for 10 h (TLC control, $CHCl_3$—hexane, 3 : 1). After cooling, $Et_3N \cdot HBr$ that precipitated was filtered off and $Et_3N$ was distilled off from the filtrate. The residue was crystallized from $Me_2CO$ and dried *in vacuo*. Compound **1** was obtained in a yield of 35.7 g as white crystals, m.p. 176 °C (DSC). The characteristics of compound **1** are given in Tables 1 and 2.

**4-Fluoro-4´-(4-fluorophenylglyoxalyl)benzophenone (2).** Compound **1** (21.8 g, 0.068 mol), $KMnO_4$ (5.44 g), AcOH (20.25 mL), water (54 mL), and $Me_2CO$ (1.4 L) were placed in a 2-L two-neck flask equipped with a stirrer and a reflux condenser. The reaction mixture was refluxed for 2.5 h. In the course of the reaction, the color of the reaction mixture changed from crimson (characteristic of $KMnO_4$) to brown, which indicated that the reaction was brought to completion. The precipitate that formed was filtered off. The filtrate was concentrated to dryness *in vacuo* and the residue was carefully washed with water and dried *in vacuo* at 80 °C for 5 h. Compound **2** was obtained in a yield of 22.63 g as yellow crystals (crystallization from BuOH). The characteristics of compound **2** are given in Tables 1 and 2.

**4-Fluoro-4´-[3-(4-fluorophenyl)quinoxalin-2-yl]benzophenone (3a).** Compound **2** (3.5 g, 10 mmol), *o*-phenylenediamine (1.08 g, 10 mmol), $CHCl_3$ (45 mL), and MeOH (5 mL) were placed in a 100-mL two-neck flask equipped with a tube for supplying argon. The reaction mixture was kept at ~20 °C for ~24 h and then the solvents were distilled off on a rotary evaporator. The residue was recrystallized from 95% EtOH. White compound **3a** was obtained in a yield of 4.13 g. Compounds 4-fluoro-4´-[3-(4-fluorophenyl)-7(8)-nitroquinoxalin-2-yl]benzophenone (**3b**) and 4-fluoro-4´-[3-(4-fluorophenyl)-7(8)-methylquinoxalin-2-yl]benzophenone (**3c**) were prepared analogously. The characteristics of quinoxalines **3a—c** are given in Tables 1 and 2.

**4-[5-(4-Fluorophenyl)-2-(3-iodophenyl)imidazol-4-yl]-4´-fluorobenzophenone (4).** 4-Fluoro-4´-(4-fluorophenylglyoxalyl)benzophenone (**2**) (1.75 g, 5 mmol), *m*-iodobenzaldehyde (1.16 g, 5 mmol), $NH_4OAc$ (2.69 g), and AcOH (50 mL) were placed in a 100-mL two-neck flask equipped with a stirrer and a reflux condenser. The reaction mixture was refluxed for 7 h, cooled, and poured into water. The residue was filtered off, carefully washed with water, and dried *in vacuo* at 100 °C for 10 h to obtain colorless crystals. The characteristics of compound **4** are given in Tables 1 and 2.

**4´-(5,6-Dicyano-3-fluorophenylpyrazin-2-yl)-4-fluorobenzophenone (5).** Dinitrile of diaminomaleic acid (0.85 g, 7.8 mmol),

4-fluoro-4´-(4-fluorophenylglyoxalyl)benzophenone (2.35 g, 6.7 mmol), AcOH (10 mL), and AcOBu (50 mL) were placed in a 100-mL two-neck flask equipped with a stirrer and a reflux condenser. The reaction mixture was refluxed for 1 h. The solvent was distilled off and the residue was recrystallized from 95% EtOH. Compound **5** was obtained in a yield of 2.83 g as bright-yellow crystals. The characteristics of compound **5** are given in Tables 1 and 2.

**4-Fluoro-4´-[2-(4-fluorophenyl)-4-phenylimidazol-5-yl]benzophenone (6).** 4-Fluoro-4´-(fluorophenylglyoxalyl)benzophenone (3.32 g, 10 mmol), *p*-fluorobenzaldehyde (1.24 g, 10 mmol), $NH_4OAc$ (5.39 g, 70 mmol), and AcOH (30 mL) were placed in a 50-mL two-neck flask. The reaction mixture was refluxed with stirring for 10 h. After cooling, the reaction mixture was poured into ice water. The precipitate that formed was filtered off, carefully washed with water, and dried in a vacuum desiccator at 100 °C for 5 h. After recrystallization from a 5 : 1 mixture of 95% EtOH and $H_2O$, compound **6** was obtained in a yield of 3.62 g as yellow crystals. The characteristics of compound **6** are given in Tables 1 and 2.

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