Activated bis- and tetrafluoroaromatic compounds containing bis-phenylquinoxaline fragments

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New activated bis- and tetrafluoroaromatic compounds containing the bis-phenylquinoxaline fragments, *viz.*, methylene-bis-6(7),6′(7′)-{2-(*p*-fluoro)phenyl-3[4-(*p*-fluorobenzoyl)phenyl]quinoxalines}, were prepared according to multistep procedures with the use of chloral as the starting compound. The presence of the activating carbonyl groups in the *para* positions with respect to two fluorine atoms opens up the possibility of the use of these monomers for the synthesis of high-molecular-weight aromatic quinoxaline-containing polyether ketones.

Key words: quinoxalines, difluoroaromatic compounds, electron density, reactivity, ^{13}C and ^{19}F NMR spectroscopy, semiempirical quantum-chemical calculations, polyether ketones.

The insertion of the phenylquinoxaline fragments into macromolecules of aromatic polyethers (APE) has attracted considerable recent attention of researchers[1—6] because phenylquinoxaline systems are characterized by high thermal and chemical stability in combination with solubility in organic solvents and substantial intervals between the temperatures of their softening and destruction.[7—9] Phenylquinoxalyl-containing APE are generally prepared with the use of difluoroaromatic compounds (DFAC) bearing the phenylquinoxalyl fragments, for example, 2,3-bis(4-fluorophenyl)quinoxaline,[4,6,10,11] 1,4-bis[2(3-phenyl-6-fluoro)quinoxalinyl]benzene (mixture of isomers, which were not separated),[3] and 1,4-bis(6-fluoro-3-phenyl-2-quinoxalinyl)benzene.[2]

The efficiency of activation of the F atoms with the quinoxaline rings depends[1] on the positions of these atoms in DFAC. However, on the whole, the efficiency of the phenylquinoxaline rings as activators of the F atoms in DFAC is inadequate for high-molecular-weight APE to be prepared based on phenylquinoxaline-containing DFAC. With the aim of combining the wholesome effect of the phenylquinoxalyl groups in APE with a high molecular weight of the target polymers, we constructed activated DFAC bearing the bis-phenylquinoxalyl group. In this case, the DFAC molecules are activated due to the insertion of the carbonyl groups, which are among the most efficient activators of the fluorine atoms.[1,12,13]

Results and Discussion

Difluoroaromatic compounds were synthesized according to Scheme 1 starting from chloral, which is widely used for the preparation of condensation monomers and polymers.[14,15]

This scheme is based on the generation of 4′-bromo-4-fluorobenzophenone (**4**),[16] which was subjected to subsequent condensation with phenylacetylene or 4-fluorophenylacetylene followed by oxidation of the resulting compounds **5a**,**b** to diketones **6a**,**b** and the treatment of the latter with 3,3′,4,4′-tetraaminodiphenylmethane to obtain the target products, *viz.*, methylene-6(7),6′(7′)-bis{2-phenyl-3[4-(*p*-fluorobenzoyl)phenyl]quinoxaline} (**7a**) and methylene-6(7),6′(7′)-bis{2-(*p*-fluorophenyl)-3[4-(*p*-fluorobenzoyl)phenyl]quinoxaline} (**7b**), as a mixture of isomers. The structures of products **7a**,**b** were confirmed by the data from elemental analysis, IR spectroscopy, and NMR spectroscopy. The formation of these products as a mixture of isomers is consistent with the concepts known in the chemistry of bis- and polyphenylquinoxalines.[7—9] The ratio between the individual isomers of product **7a** was determined by ^{13}C NMR spectroscopy from the intensities of the signals for the methylene C atom at δ 42.033, 42.001, and 41.971. These signals belong to three possible isomers with the integral intensity ratio of 1 : 2 : 1. Attempts to identify individual

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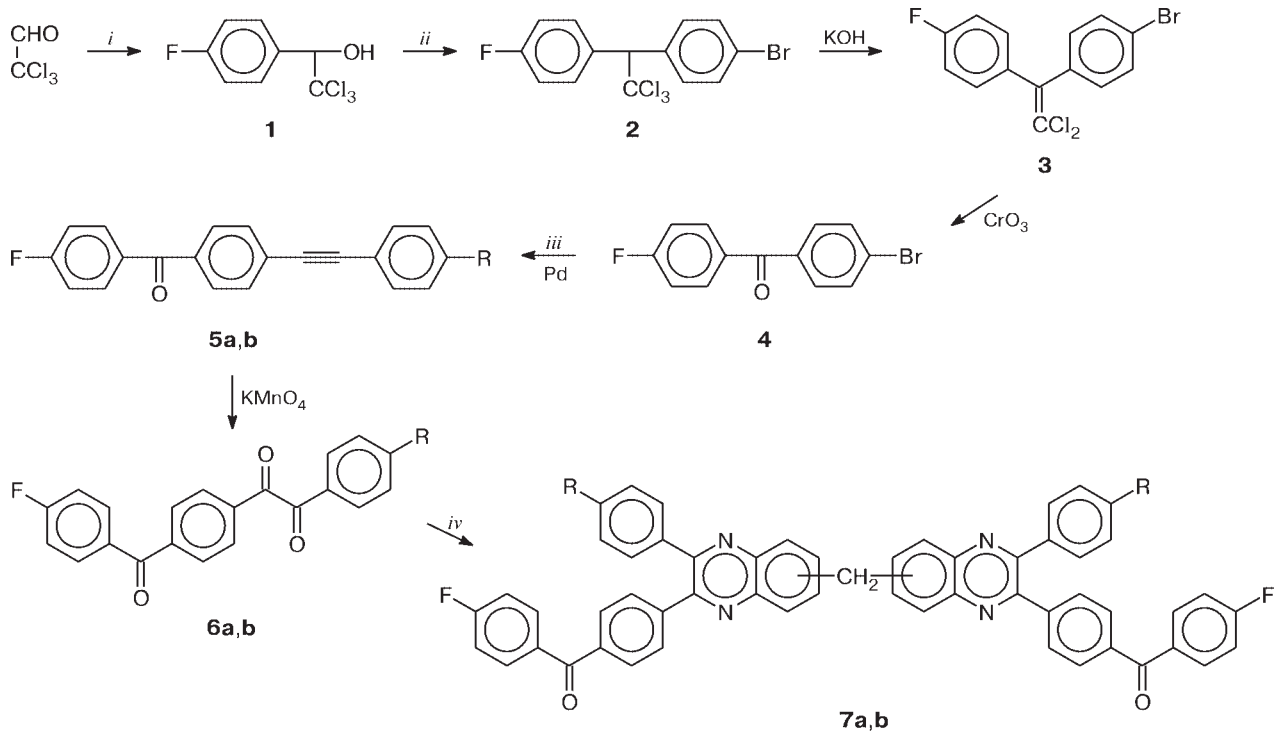
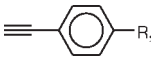
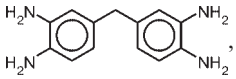
Scheme 1

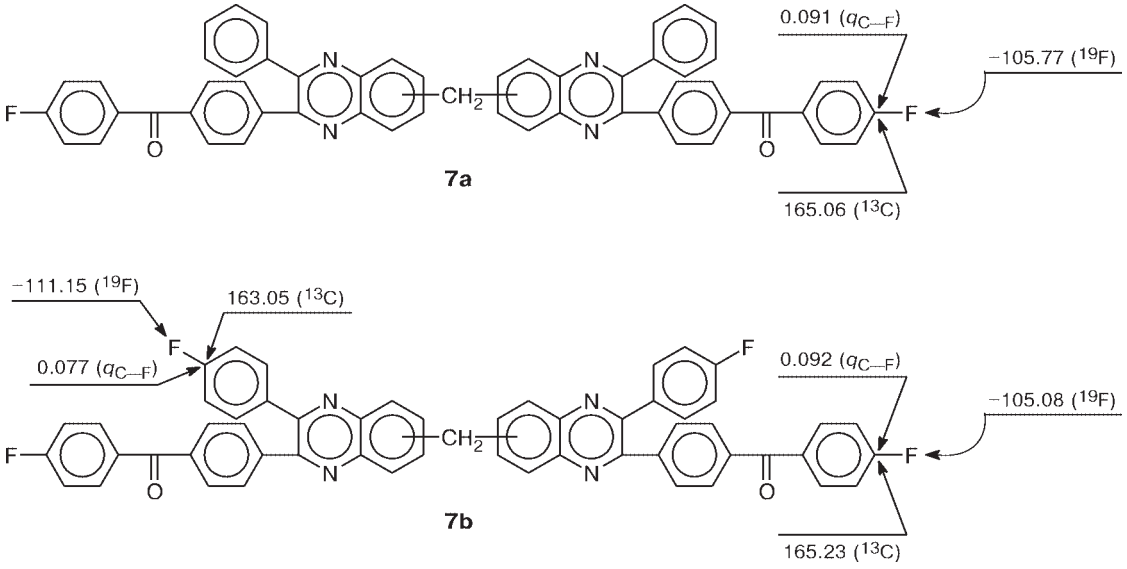


Reagents and conditions: *i*. PhF, 71%; *ii*. PhBr, 65%; *iii*.  , 78% (R = H), 81% (R = F);

iv.  , 92% (R = H), 94% (R = F).

isomers based on this region of the ^{1}H NMR spectrum, where the resonance absorption of the CH_2 group is manifested, failed. The ^{13}C NMR spectrum of product **7b** also has three signals in the absorption region of the methylene C atom (δ 41.98) with the integral intensity ratio of 1 : 2 : 1, which are assigned to three possible isomers of **7b**.

Scheme 2



The reactivities of the resulting fluoroaromatic compounds were estimated by semiempirical quantum-chemical calculations (PM3, q_{C-F} is the charge density) and by ^{13}C and ^{19}F NMR spectroscopy (Scheme 2). The F atoms in DFAC **7a** and **7b** were demonstrated to be sufficiently activated so that these compounds can be used for the preparation of high-molecular-weight APE.

The more complex situation was observed in the case of compound **7b**. Its molecule contains two nonequivalent pairs of the F atoms. The F atoms, which are located in the *para* positions with respect to the carbonyl groups, are sufficiently activated to be involved in the synthesis of high-molecular-weight APE. The F atoms, which are located in the *para* positions with respect to the quinoxaline fragment, are activated to a substantially lesser degree. This opens up the possibility of the synthesis of linear high-molecular-weight APE even based on tetrafluoroaromatic compound **7b**. At the same time, compound **7b** can be used in reactions of aromatic nucleophilic substitution under drastic conditions for the preparation of phenylquinoxaline-containing APE bearing very bulky substituents (treatment of **7b** with a twofold molar excess of phenols followed by the treatment of the reaction products with various bis-phenols). At the same time, compound **7b** is also of interest as a "core" in the synthesis of "dendrite" polymers.[17—20]

Experimental

Procedures for the synthesis of compounds **1**—**6** and their properties have been described previously.[16] The solvents were dried according to known procedures. The Raman and Fourier 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, with Me_4Si as the internal standard. The ^{19}F NMR spectra were recorded on a Bruker AC-200 instrument (188.3 MHz) with the use of CCl_3F (δ 0.0) and $CDCl_3$ as the internal standard and the solvent, respectively. The melting temperatures were determined on a Kofler stage.

Methylene-6(7),6′(7′)-bis{3-[4-(*p*-fluorobenzoyl)phenyl]-2-phenylquinoxaline} (7a). 4-Fluoro-4-(*p*-fluorophenylglyoxalyl)benzophenone (3.33 g, 10 mmol), 3,3′,4,4′-tetraaminodiphenylmethane (1.14 g, 5 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 stirred at ~20 °C for one day. The solvents were evaporated *in vacuo* and yellow compound **7a** was obtained in a yield of 3.78 g (92%), m.p. 160—168 °C (*n*-butyl alcohol). Found (%): C, 80.47; H, 4.11; F, 4.44; N, 6.84. $C_{55}H_{34}F_2N_4O_2$. Calculated (%): C, 80.47; H, 4.17; F, 4.63; N, 6.83. IR, ν/cm^{-1}: 1651 (C=O); 1217 (C—F). ^1H NMR, δ: 8.12—8.15 (m, 2 H, Ar); 8.07 (s, 2 H, Ar); 7.79—7.83 (m, 4 H, Ar); 7.70—7.73 (m, 6 H, Ar); 7.62—7.65 and 7.49—7.51 (both m, 4 H each, Ar); 7.25—7.38 (m, 6 H, Ar); 7.15—7.11 (t, 4 H, Ar); 4.50 (s, 2 H, CH_2). ^{13}C NMR, δ: 194.6 (C=O); 166.5, 163.9 (both C—F); 153.3; 152.9; 152.2; 151.7; 142.8; 142.7; 142.4; 141.3; 141.0; 140.2; 139.9; 138.3; 137.2; 137.1; 133.4; 132.5; 132.4; 132.0; 131.7; 129.6; 129.4; 128.2; 128.4; 128.4; 128.3; 115.4; 115.2; 42.0 (CH_2). ^{19}F NMR, δ: −105.17.

Methylene-6(7),6′(7′)-bis{3-[4-(*p*-fluorobenzoyl)phenyl]-2-(*p*-fluorophenyl)quinoxaline} (7b) was prepared analogously to compound **7a**, the yield was 94%, m.p. 147—158 °C (*n*-butyl alcohol). Found (%): C, 76.89; H, 3.65; F, 8.45; N, 6.52. $C_{55}H_{32}F_4N_4O_2$. Calculated (%): C, 77.09; H, 3.76; F, 8.86; N, 6.54. IR, ν/cm^{-1}: 1648 (C=O); 1221 (C—F). ^1H NMR, δ: 8.12—8.10 and 8.05—8.03 (both m, 2 H each, Ar); 7.82—7.78 (m, 4 H, Ar); 7.75—7.69 (m, 6 H, Ar); 7.64—7.61 (t, 4 H, Ar); 7.60—7.47 (m, 4 H, Ar); 7.14—7.10 (t, 4 H, Ar); 7.03—7.00 (m, 4 H, Ar); 4.48 (s, 2 H, $\underline{C}H_2$). ^{13}C NMR, δ: 194.4 (C=O); 166.5, 164.3, 164.0, 161.8 (all C—F); 152.2; 152.0; 151.7; 151.6; 142.8; 142.7; 142.5; 141.3; 141.1; 140.1; 139.9; 137.3; 137.3; 134.9; 133.3; 132.5; 132.4; 132.1; 131.8; 131.7; 131.6; 129.7; 129.6; 129.4; 129.3; 128.4; 128.4; 115.5; 115.4; 115.3; 115.2; 42.0 (CH_2). ^{19}F NMR, δ: −105.08; −111.15.

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