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New Activated Difluoroaromatic Compounds Containing Internal Acetylenic Moieties

M. L. Keshtov, S. V. Keshtova, M. M. Begretov, R. B. Tkhakakhov, and A. N. Shchegolikhin

Berbekov Kabardino-Balkar State University, Nalchik, Kabardino-Balkaria, Russia
Emanuel' Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

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Abstract — New activated difluoroaromatic compounds having an internal acetylenic moiety were synthesized by reaction of trichloroacetaldehyde with fluorobenzene, followed by reaction with iodobenzene and cross coupling with acetylene in the presence of palladium complexes. According to the results of quantum-chemical calculations and ^{19}F NMR data, the products are highly reactive compounds which can be used for the preparation of high-molecular-weight aromatic polyethers.

Aromatic polyethers containing acetylenic moieties attract interest due to their ability to harden at elevated temperature without evolution of low-molecular-weight volatile substances [1–3]. Such polymers are obtained most frequently by aromatic nucleophilic polysubstitution in acetylenic difluoroaromatic compounds, e.g., 4,4'-difluorodiphenylacetylene [2, 3] or 4,4'-bis(4-fluorophenylethynyl)benzophenone, under the action of aromatic bis-phenols [4]. In these reactions, acetylenic fragments activate fluorine atoms [1–4]; however, their activating effect is insufficient to obtain high-molecular-weight aromatic polyethers on the basis of such monomeric compounds.

In this connection, promising are difluoroaromatic compounds possessing both acetylenic moieties and sufficiently reactive fluorine atoms. It seemed to be the most reasonable to built up molecules having an internal acetylenic moiety in combination with carbonyl [5] and α-dicarbonyl fragments [6–12] in the *para* positions with respect to aromatic fluorine atoms. These fragments should effectively activate fluorine atoms to nucleophilic replacement. In continuation of our studies on the synthesis of new difluoroaromatic compounds and polyethers derived therefrom [13–15], we synthesized two new potential monomers, 4,4'-bis(4-fluorobenzoyl)diphenylacetylene (**VI**) and 4,4'-bis(4-fluorophenylglyoxyloyl)diphenylacetylene (**VII**), starting from trichloroacetaldehyde which is known as initial compound in the synthesis of condensation monomers and polymers [16]. The synthesis was carried out according to Scheme 1.

Successive treatment of trichloroacetaldehyde with fluorobenzene and iodobenzene afforded 1,1,1-trichloro-2-(*p*-fluorophenyl)-2-(*p*-iodophenyl)ethane (**I**) [17] which was then converted into 4-fluoro-4'-iododiphenylacetylene (**II**) [18], 4-fluoro-4'-iodobenzil (**III**) [19], 1,1-dichloro-2-(4-fluorophenyl)-2-(4-iodophenyl)ethene (**IV**) [17], and 4-fluoro-4'-iodobenzophenone (**V**) [17]. By reaction of 2 equiv of compounds **III** and **V** with acetylene, catalyzed by palladium complexes, we obtained the desired difluoroaromatic compounds, 4,4'-bis(4-fluorobenzoyl)diphenylacetylene (**VI**) and 4,4'-bis(4-fluorophenylglyoxyloyl)diphenylacetylene (**VII**).

The structure of products **VI** and **VII** was confirmed by the IR and NMR spectra and elemental analyses. In the ^{1}H NMR spectra of compounds **VI** and **VII** we observed multiplet signals typical of aromatic protons in the region δ 7.00–8.00 and 7.42–8.05 ppm, respectively. The ^{13}C NMR spectra are more informative. They contain characteristic signals at δ_C ~200 ppm, belonging to the carbonyl carbon atoms, a doublet at δ_C ~160–170 ppm ($^{1}J_{CF}$ = 257 Hz) from the aromatic carbon atom attached to fluorine, and a singlet at δ_C ~90 ppm due to equivalent carbon atoms at the triple bond. Compounds **VI** and **VII** show in the ^{19}F NMR spectra signals at δ_F –105.0 and –101.0 ppm, respectively. The IR spectra of **VI** and **VII** contain absorption bands due to stretching vibrations of the C≡C, C=O, and C–F bonds at 2210, 1709, and 1156 cm^{-1}, respectively.

The thermal stability of compounds **VI** and **VII** was studied by differential scanning calorimetry (DSC) and thermogravimetry. The DSC curve for compound **VI** (Fig. 1, *2*) is characterized by the presence of sharp endothermic peaks at 235 and

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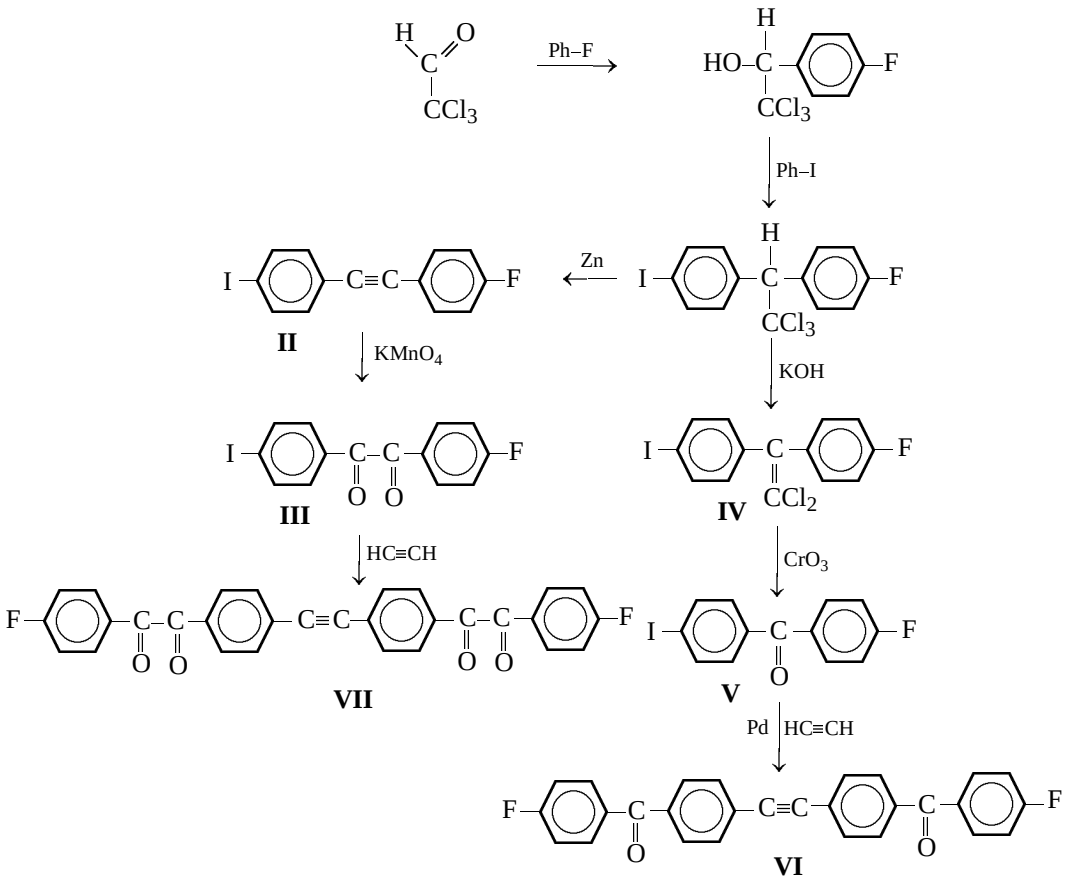
Scheme 1.



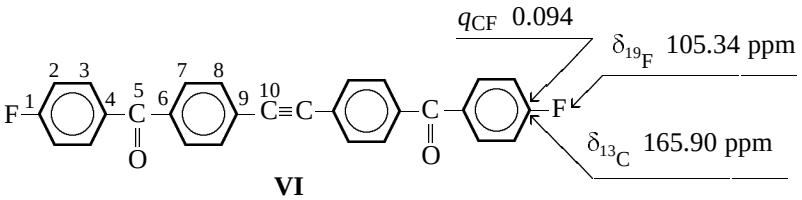
270°C (melting) and a fairly strong and broadened exothermic transition starting at 360°C and reaching its maximum at 410°C (which is typical of compounds having an internal triple bond). No exothermic transition was observed on the DSC curve on repeated heating of the same sample (Fig. 1, *3*). Presumably, in the first case reactions at the triple C≡C bonds occur [20]. After thermal treatment of compound **VI**, the Raman spectrum (Fig. 2) contained no peaks in the region 1900–2220 cm^{-1}, which are typical of C≡C bonds, and the product was insoluble in organic solvents. These data provide an additional support to the occurrence of reactions at the triple bond. As follows from the TGA curve, a large loss in the sample weight is observed in the temperature range preceding polymerization at the triple bonds (300–350°C. The rate of weight loss reaches its maximal value at the stage of exothermic polymerization at the triple bonds. Here, the released heat additionally raises internal temperature of the sample, thus favoring faster weight loss due to vaporization. As the sample becomes cross-linked (~400°C), the rate of weight loss sharply decreases and almost does not change on further heating. An analogous pattern is observed in the thermolysis of compound **VII** (Fig. 1, curves *4*, *5*).

The efficiency of the synthesis of high-molecular-weight aromatic polyethers is determined by the reactivity of difluoroaromatic monomers. Therefore, estimation of their reactivity attracts increased interest. We made an attempt to estimate the reactivity of compounds **VI** and **VII** by measuring chemical shifts in the ^{13}C and ^{19}F NMR spectra, as well as by calculating the charge density (q_{C-F}) on the carbon atom attached to fluorine by the PM3 semiempirical quantum-chemical method (Scheme 2). The greater the charge and the chemical shifts, the higher the reactivity in the synthesis of polyethers. As follows from Scheme 2, α-diketone fragments activate the fluorine atom to nucleophilic substitution to a greater extent, as compared with the carbonyl group.

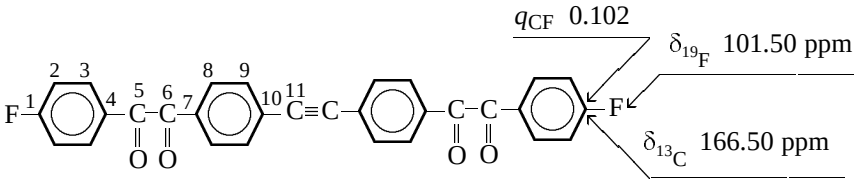
EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer-1720X Fourier spectrometer. The ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on Bruker AMX-400 and Bruker AC-200 spectrometers at 400.13, 100.61, and 188.3 MHz, respectively; chloroform-*d* was used as solvent. The dynamics of thermal transormations of compounds **VI** and **VII** were monitored by thermogravimetric analysis (Perkin–Elmer-TGA7) and dif-

Scheme 2.



VI



VII

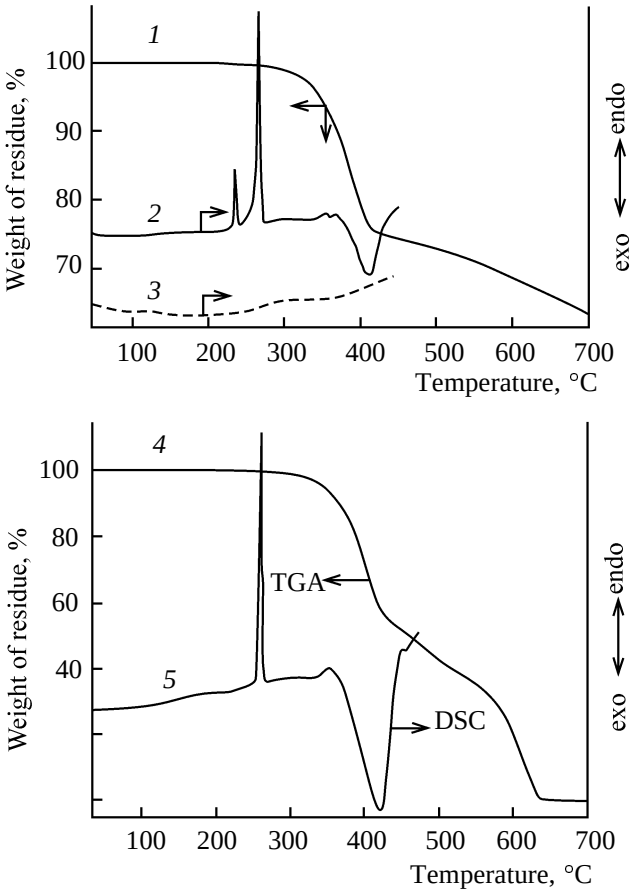


Fig. 1. TGA curves for compounds (*1*) **VI** and (*4*) **VII** and DSC curves for compounds (*2*, *3*) **VI** and (*5*) **VII.**

ferentsial scanning calorimetry (Perkin–Elmer-DSK7) at a heating rate of 10 deg/min.

4,4'-Bis(4-fluorobenzoyl)diphenylacetylene (VI). Acetylene was passed at a flow rate of 1.5 l/h through a mixture of 9.78 g of compound **V**, 0.21 g of palladium catalyst, 0.30 g of CuI, and 180 ml of diethylamine at 18–20°C over a period of 10 h. The product began to separate immediately after the reaction started. When the reaction was complete, the product was filtered off. Yield 4.94 g (78%), yellow crystals, mp 270–272°C (from *n*-butanol). IR spectrum, ν, cm^{-1}: 2210 (C≡C); 1658 (CO); 1182 (C–F). ^{1}H NMR spectrum, δ, ppm: 7.85 m (4H), 7.75 m (4H), 7.34 m (4H), 7.12 t (4H). ^{13}C NMR spectrum, δ_C, ppm: 116.4 d (C^2, $^2J_{CF}$ = 23 Hz), 129.8 d (C^3, $^3J_{CF}$ = 10 Hz), 127.7, 130.5, 136.6, 139.8, 140.5, 165.9 d ($^1J_{CF}$ = 256 Hz). ^{19}F NMR spectrum: δ_F –105.34 ppm. Found, %: C 79.45; H 3.70; F 8.89. $C_{28}N_{16}F_2O_2$. Calculated, %: C 79.60; H 3.82; F 9.00.

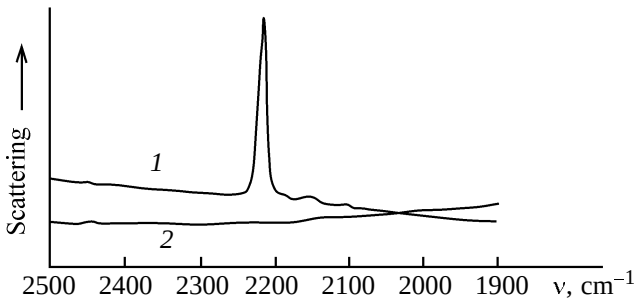


Fig. 2. Raman spectra of compound **VI** (*1*) before and (*2*) after thermolysis.

4,4'-Bis(4-fluorophenylglyoxyloyl)diphenylacetylene (VII) was synthesized in a similar way from 10.62 g of compound **III**. Yield 5.60 g (78%), yellow crystals, mp 262°C (DSC). IR spectrum, ν, cm^{-1}: 2208 (C≡C), 1664 (CO), 1179 (C–F). ^{1}H NMR spectrum, δ, ppm: 7.05–7.10 m (4H), 7.42–7.48 m (4H), 7.95–7.97 m (4H), 8.05–8.13 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 98.68 (C≡C), 116.92, 117.62, 125.99, 130.00, 131.49, 134.00, 134.21, 134.87, 135.27, 163.51, 170.01, 194.30, 196.00. ^{19}F NMR

spectrum: δ_F –101.50 ppm. Found, %: C 75.42; H 3.61; F 7.70. $C_{30}H_{16}F_2O_4$. Calculated, %: C 75.31; H 3.37; F 7.91.

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