New hexaarylbenzene-containing di- and tetrafluoroarenes

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New hexaarylbenzene-containing di- and tetrafluoroarenes were prepared by the Diels—Alder reactions of 1,4-bis(1-oxo-2,4,5-triphenylcyclopentadien-3-yl)benzene with 4-fluoro-4′-(phenylethynyl)- and 4-fluoro-4′-(4-fluorophenylethynyl)benzophenone, respectively.

Key words: di- and tetrafluoroarenes, poly(aryl ether ketones), ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, Diels—Alder reaction.

Condensation monomers containing tri- and tetraaryl-substituted benzene rings have attracted considerable attention because the polymers derived therefrom are characterized by a unique combination of high thermal characteristics and solubility in organic solvents. Such monomers belonging to diamines,[1—4] bisphenols,[5] bisphthalic anhydride,[6—10] bisnaphthalic anhydride,[10] and dicarboxylic acids[11,12] are generally prepared by the Diels—Alder reaction[13—16] of substituted cyclopentadienones with acetylenes.

As part of our continuing studies, we synthesized di- and tetrafluoroarenes containing hexaarylbenzene fragments as potential monomers for the preparation of poly(aryl ether ketones).[17,18]

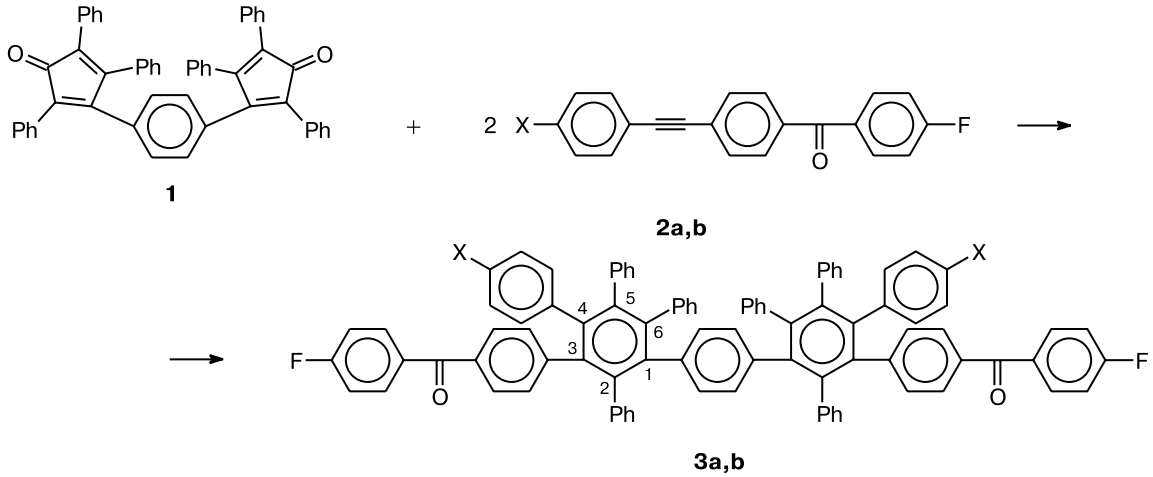
Results and Discussion

Condensation of 1,4-bis(1-oxo-2,4,5-triphenylcyclopentadien-3-yl)benzene (**1**)[19,20] with 2 mol.-equiv. of 4-fluoro-4′-(phenylethynyl)benzophenone (**2a**)[21] afforded compound **3a** (Scheme 1).

Analogously, the reaction of compound **1** with 4-fluoro-4′-(4-fluorophenylethynyl)benzophenone (**2b**)[21] resulted in tetrafluoroaromatic compound **3b** (Scheme 2).

Compounds **3a,b** were prepared as mixtures of isomers, one of which is shown in Scheme 1. Their structures were confirmed by elemental analysis, IR spectroscopy, and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

Scheme 1



X = H (**a**), F (**b**)

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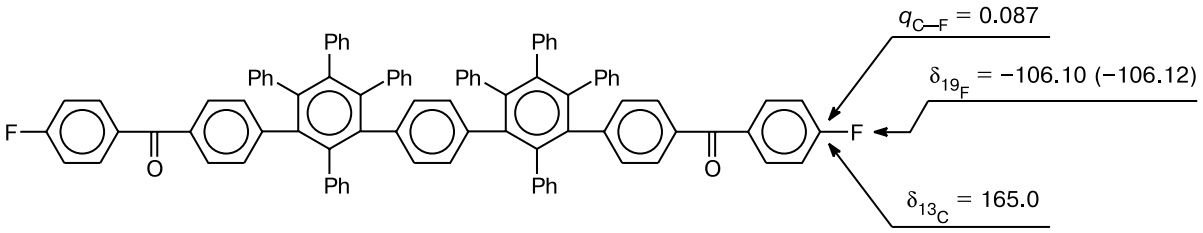
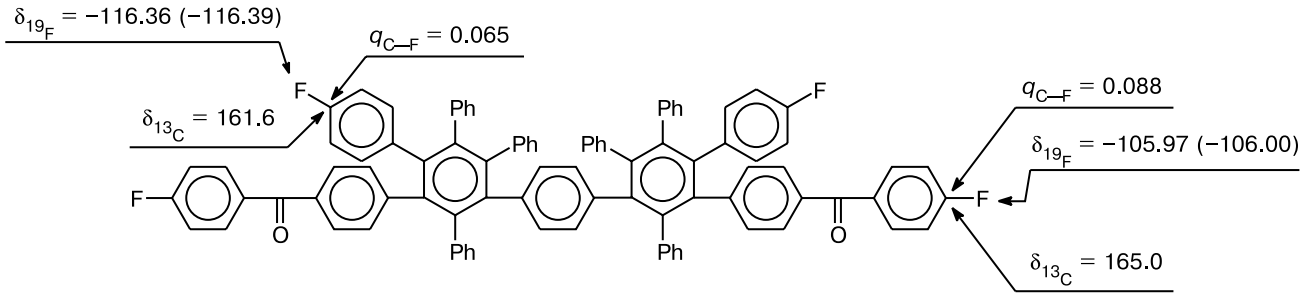
Scheme 2



3a



3b

In the ^{1}H NMR spectrum of compound **3a**, three close signals with the total intensity corresponding to four protons are observed in the region of resonances of protons of the central benzene ring. Apparently, these signals belong to isomers of **3a**. The ^{1}H NMR spectrum contains also three separate multiplets centered at δ 7.09, 7.25, and 7.59, each multiplet corresponding to four protons. In addition, there is a group of multiplets at δ 6.69—6.95 whose total intensity corresponds to 44 protons. The ^{13}C NMR spectrum of this compound contains, along with a low-field signal for the C atom of the carbonyl group at δ 195.2, two characteristic signals as doublets due to spin-spin coupling ^{13}C—^{19}F at δ 165.0 ($^1J_{C,F}$ = 254 Hz) and 115.1 ($^2J_{C,F}$ = 21.9 Hz). Signals for the ^{13}C nuclei bound to the aromatic protons are observed at δ 125—132, whereas signals for the ^{13}C atoms that are not bound to protons appear at δ 134—146. The ^{19}F NMR spectrum of compound **3a** has two close signals for ^{19}F nuclei at δ −106.10 and −106.12 belonging to the *p*-fluorophenyl groups due apparently to the presence of the isomers.

The ^{1}H NMR spectrum of compound **3b** shows a broadened singlet for four protons of the central benzene ring at δ 6.33, four individual poorly resolved multiplets centered at δ 6.57, 7.09, 7.27, and 7.59, each multiplet corresponding to four protons, and a group of multiplets at δ 6.70—6.95 whose total intensity corresponds to 38 protons. Along with a low-field signal for the C atom of the carbonyl group at δ 195.1, the ^{13}C NMR spectrum of this compound has characteristic doublets associated with the spin-spin coupling C—F at δ 165.0 ($^1J_{C,F}$ = 254 Hz), 161.6 ($^1J_{C,F}$ = 246 Hz), 115.2 ($^2J_{C,F}$ = 21.7 Hz), and 113.7 ($^2J_{C,F}$ = 21.3 Hz). The signals for the ^{13}C nuclei bound to the aromatic protons are observed at δ 125—132, whereas the signals for the ^{13}C nuclei that are not bound to protons appear at δ 134—145. The ^{19}F NMR spectrum of compound **3b** contains two close low-field signals at δ −105.97 and −106.00 assigned to the ^{19}F nuclei of the *p*-fluorophenyl groups bound to the electron-withdrawing carbonyl substituent and two close high-field signals at δ −116.36 and −116.39 belonging to the ^{19}F nuclei of the *p*-fluorophenyl groups attached to the central benzene ring.

The observed complication of the ^{19}F NMR spectrum is associated with the formation of isomeric addition products. To estimate the reactivities in nucleophilic substitution reactions, we calculated the charges (q_{C-F}) of the C atoms of the C—F bonds of difluoroarenes by the semiempirical quantum chemical PM3 method. A comparison of the ^{13}C and ^{19}F chemical shifts in the spectra of difluoroarenes with the calculated charges q_{C-F} reveals a correlation between these physical parameters and shows that difluoroarenes are more reactive than fluorobenzene.

The nonequivalence of the fluorine atoms (see Scheme 2) in tetrafluoride **3b** opens up the possibility of performing selective synthesis of a new type of fluorine-containing poly(aryl ether ketones). At the same time, if molecule **3b** is involved in aromatic nucleophilic substitution under drastic conditions, it can be considered as a "core" of dendritic polymers.

Experimental

The Fourier-transform IR spectra were recorded on a Perkin—Elmer-1720X spectrometer. The ^{1}H and ^{13}C NMR

spectra were measured on a Bruker AMX-400 spectrometer operating at 400.13 and 100.61 MHz, respectively, and the ^{19}F NMR spectra were recorded on a Bruker AC-200 instrument operating at 188.3 MHz with CCl_3F (δ 0.0) as the internal standard and $CDCl_3$ as the solvent.

1,4-Bis{3-[4-(4-fluorobenzoyl)phenyl]-2,4,5,6-tetraphenyl}benzene (3a). A mixture of compound **1** (1.3816 g, 2 mmol) and compound **2a** (1.2012 g, 2 mmol) in 1,2,4-trichlorobenzene (6 mL) was refluxed for 40 h. After cooling, the solution was poured into methanol (30 mL). The precipitate that formed was filtered off, dried, and recrystallized twice from *n*-butyl alcohol. A yellow compound was obtained, m.p. 315—321 °C, the yield was 2.2 g (89%). Found (%): C, 89.01; H, 4.61; F, 2.87. $C_{92}H_{60}F_2O_2$. Calculated (%): C, 89.40; H, 4.89; F, 3.07. IR (KBr), ν/cm^{-1}: 1645 (C=O).

1,4-Bis{3-[4-(4-fluorobenzoyl)phenyl]-4-(4-fluorophenyl)-2,5,6-triphenyl}benzene (3b) was prepared analogously; m.p. 321—329 °C (from *n*-butyl alcohol), the yield was 89%. Found (%): C, 86.45; H, 4.29; F, 4.16. $C_{92}H_{58}F_4O_2$. Calculated (%): C, 86.90; H, 4.59; F, 4.40. IR (KBr), ν/cm^{-1}: 1638 (C=O).

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