brium concentration and was found to be $2.7 \cdot 10^{-6}$ mole/liter. The experimentally determined [QH˙] value ($2.7 \cdot 10^{-6}$ mole/liter) agreed with the calculated value within experimental error.

The authors express their gratitute to Ya. S. Lebedev for a discussion of this work.

## CONCLUSIONS

3,6-Di-tert-butyl-2-hydroxyphenoxyl radicals (QH˙) were detected by EPR spectroscopy in a mixture of 3,6-di-tert-butylpyrocatechol ($QH_2$) and 3,6-di-tert-butyl-1,2-benzoquinone (Q in the polymerization of methyl methacrylate. The rate constant for the reaction $QH_2 + Q \rightleftarrows 2QH^{\cdot}$ and the rate contants for the forward and back reactions were determined at 60°C.

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# REACTION OF BIS-(N,N-DIMETHYL)-TEREPHTHALAMIDE WITH IMIDATES ON PERFLUOROHEXANECARBOXYLIC ACID

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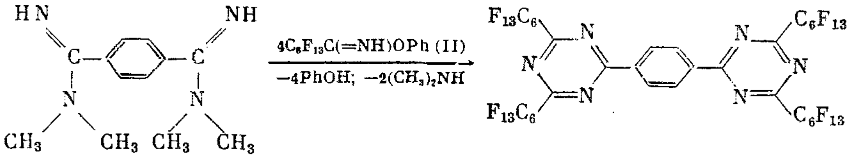
In a previous communication [1], we reported that substituted amidines of aromatic acids react under mild conditions with perfluorinated nitriles to give arylperfluoroalkyltriazines in high yields. On the other hand, no data are available on the reaction of perfluoroimidates with substituted aromatic amidines.

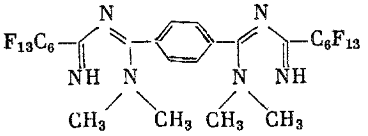
In the present work, we selected bis(N,N-dimethyl)terephthalamidine (I) and the phenylimidate of perfluorohexanecarboxylic acid (II) as the starting materials.

The reaction of these reagents in diethyl ether at room temperature gives aryleneperfluoroalkyltriazine (III) in high yield



(I) (III)

Substituted imidoylamidine (IV) is a likely intermediate as in the reaction with nitriles [1]



(IV)

The phenol and amine products formed upon condensation form a salt, which precipitates from the diethyl ether solution. The use of polar solvents such as chloroform and monoglyme, which facilitates the dissociation of the adduct of phenol with dimethylamine, lead to a sharp decrease in the yield of triazine (III) (from 95 to 30%).

Different behavior is observed upon carrying out the reaction with the methyl ester of iminoperfluorocarboxylic acid (V) in methanol. In this case, the final product is oligomeric azomethine (VI)

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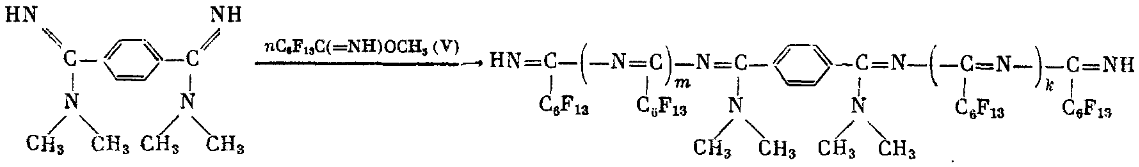

(VI)

n − (m + k) + 2 = 4, 10, 20 (mean values).

The formation of the azomethine structure is indicated by the $^{19}F$ and $^1H$ NMR spectra. The PMR spectra of (VI) show singlets at δ 8.33, 3.80, and 2.90 ppm, which correspond to signals for the protons of the aromatic ring, methyl groups at the nitrogen atom, and the NH group. The integral intensity ratio of these signals is 2:6:1. The $^{19}F$ NMR spectrum of (VI) not only supports this structure (δ 78.1 ($CF_3$), 123.0 ($CF_3$–$CF_2$), 118.5-119.5 ppm ($CF_2$–(–$CF_2$)$_3$–$CF_2$), but also permits determination of the mean extent of polymerization of the oligomer (k + m), since the chemical shifts of the difluoromethylene groups of the azomethine fragment and the terminal $CF_2$—C=NH group are quite distinguishable in the spectrum (113.5 and 113.0 ppm, respectively).

Further evidence for the formation of azomethine structures is found in the agreement of the molecular masses determined using the ratio of the integral intensities of the signals of the difluoromethylene groups at the azomethine and imine fragments in the $^{19}F$ NMR spectra.

A more detailed study of the formation of the oligomeric azomethines showed that the use of the perfluoroinated imidate is not required to obtain this structure. Analogous results are also obtained using the perfluorinated nitrile. This is attributed to the formation of (V) in methanol in the presence of (I) in the initial step at a high rate.

In this case, (I) is a reaction catalyst (pK*a* (I) = 10.5). This is supported by the data on the catalytic action of strong bases on the formation of imidates from perfluorinated nitriles and alcohols [2].

The observed course of the reaction between N,N-disubstituted aromatic amidines and perfluorinated imidates may be explained by the solvating effect of methanol, which hinders cyclization leading to the triazine ring. Support for this hypothesis is found in the formation of azomethine structure (VI) also when the phenyl ester of iminoperfluorocarboxylic acid is used.

Furthermore, steric factors related to the formation of the E-form of the products of the addition of the imidate to the aromatic acid amidine, which is incapable of cyclization, apparently also play a significant role. However, these proposals require further experimental support.

## EXPERIMENTAL

The $^{19}F$ and $^1H$ NMR spectra were taken on a WM-250 spectrometer at 235.2 and 250 MHz, respectively. The internal standards were $CFCl_3$ and HMDS, and $CDCl_3$ served as the solvent. The IR spectra were taken neat or in NaCl pellets on a Specord 75IR spectrometer. Freon-113 was distilled over $P_2O_5$ and stored in a sealed vessel. The methanol sample was dried over Mg + $I_2$ and stored in a sealed, dark vessel. The diethyl ether sample was distilled over $LiAlH_4$ and stored over sodium wire.

Bis-(N,N-dimethyl)tereophthalamidine (I) was obtained according to Pinner and Klein [3] from the dinitrile of terephthalic acid and subsequent dehydrochlorination of the amidine salt by aq. $K_2CO_3$.

Phenylimidate of perfluorohexanecarboxylic acid (II). A sample of 15 ml diethyl ether was added to a flask equipped with a stirrer and then, 4 g (42.6 mmoles) phenol and 0.5 g (4.31 mmoles) sodium phenolate were added. After 10 min, 17.62 g (51.1 mmoles) perfluorohexanecarboxylic acid nitrile was added and the mixture was stirred for 16 h. The volatile compounds were removed in vacuum to give 17.93 g (96%) (II) as a viscous liquid. Found: C 35.63; H 1.34; F 56.83; N 3.08%; mol. mass 435 (ebullioscopically in $C_6F_6$). Calculated for $C_{13}H_6F_{13}NO$: C 35.54; H 1.37; F 56.26; N 3.19%; mole. mass 439. IR spectrum (ν, $cm^{-1}$): 1695 (C=N), 1150-1250 (CF), 1080 (Ph-O), 1495-1595 (arom C=C), 3050 (Ph). $^{19}F$ NMR spectrum (δ, ppm): 80.8 ($CF_3$), 115.7 ($CF_2$–C=NH), 120.9, 121.2, 122.5 ($3CF_2$), 125.5 ($CF_3$–$CF_2$). PMR spectrum (δ, ppm): 6.93 (Ph), 8.70 (NH).

1,4-Bis(2, 4-perfluorohexyltriazinyl)benzene (III). A sample of 0.20 g (0.92 mmole) (I) and 15 ml diethyl ether were placed into a flask equipped with a magnetic stirrer. After complete dissolution of the amidine, 1.65 g (3.76 mmoles) (II) was added. Stirring was continued for 20 h. Then, the solvent was removed on a rotary evaporator and 100 ml ethanol was added to the residue. The mixture was stirred for 15 min. The precipitate of (III) was filtered off, washed with ethanol, and dried to give 1.31 g (95%) (III), mp 103.5-104.5°C (undecane). The purity of product (II) was confirmed by thin-layer chromatography on Silufol UV-254 plates with hexane as the eluent (Rf 0.35). Found: C 28.72; H 0.25; F 65.63; N 5.49%; mol. mass 1520 (ebullioscopically in $C_6F_6$). Calculated for $C_{36}H_4F_{52}N_6$: C 28.65; H 0.27; F 65.51; N 5.57%; mol. mass 1508. PMR spectrum (δ, ppm): 9.03 (Ph). $^{19}F$ NMR spectrum (δ, ppm): 80.8 ($CF_3$), 116.1 ($-CF_2-C\underline{\cdots}$), 120.9, 121.2, 122.5 ($3CF_2$), 125.9 ($CF_3-CF_2$). IR spectrum (δ, $cm^{-1}$): 720 (arom C-H); (ν, $cm^{-1}$): 1150-1250 (CF), 1515 and 1535 (arom C=C), 1558 (C=N). UV spectrum ($\lambda_{max}$, nm): 309 (ether), 303 (perfluorooctane).

Methylimidate of Perfluorohexanecarboxylic Acid (V). A sample of 10 ml methanol was added to a flask equipped with a magnetic stirrer and 0.03 g (1.45 mmoles) sodium was added. Stirring was continued until all the sodium dissolved. After cooling of the reaction mixture to about 20°C, 5.0 g (14.5 mmoles) perfluorohexanecarboxylic acid nitrile in 10 ml freon-113 was added. Stirring was continued for 7 h. The volatile components were removed in vacuum to give 5.14 g (94%) (V). Found: C 25.41; H 1.02; F 65.72; N 3.80%; mol. mass 370 (ebullioscopically in $C_6F_6$). Calculated for $C_8H_4F_{13}NO$: C 25.46; H 1.06; F 65.52; N 3.71%; mol. mass 377. IR spectrum (δ, $cm^{-1}$): 1380, 1455 ($CH_3$); (ν, $cm^{-1}$): 1150-1250 (CF), 2950 ($CH_3$), 3350 (NH), 1695 (C=N). $^{19}F$ NMR spectrum (δ, ppm): 80.8 ($CF_3$), 116.9 ($CF_2-C{=}NH$), 121.9, 122.3, 122.7 ($3CF_2$), 126.2 ($CF_3-CF_2$). PMR spectrum (δ, ppm): 3.85 ($CH_3$), 3.35 (NH).

Oligomeric Azomethine (VI) $(m + k) \simeq 2$. A sample of 15 ml methanol was placed into a flask equipped with a magnetic stirrer and then, 0.54 g (2.48 mmoles) (I) was added. After the amidine was fully dissolved, 3.74 g (9.91 mmoles) (V) in 15 ml freon-113 was added to the reaction mixture. At the completion of the reaction, the volatile components were removed at 0.01 mm to give 3.82 g (97%) (VI). Found: C 30.19; H 1.15; F 61.64; N 6.88%; mol. mass 1620 (ebullioscopically in $C_6F_6$), 1580 according to $^{19}F$ NMR spectroscopy. Calculated for $C_{40}H_{18}F_{52}N_8$: C 30.04; H 1.13; F 61.82; N 7.01%; mol. mass 1598. IR spectrum (δ, $cm^{-1}$): 1380, 1455 ($CH_3$); (ν, $cm^{-1}$): 1150-1250 (CF), 2950 ($CH_3$), 3050 (Ph), 3350 (NH), 1695 (C=N). The $^1H$ and $^{19}F$ NMR spectra are given in the text.

Oligomeric Azomethine (VI), $m + k \approx 18$. Experiments were conducted as above with the following quantities of reagents: amidine (I) – 0.72 g (3.30 mmoles), imidate (V) – 24.90 g (6.61 mmoles). Found: C, 25.79; H, 0.22; F, 69.52; N, 4.78%; mol. mass 7200 (ebullioscopically in $C_6F_6$), 7160 according to $^{19}F$ NMR spectroscopy. Calculated for $C_{152}H_{18}F_{260}N_{24}$: C, 25.63; H 0.25; F 69.40; N, 4.79%; mol. mass 7118. The IR, and $^1H$ and $^{19}F$ NMR spectra were analogous to those given above for (VI), $m + k \approx 2$.

Oligomeric azomethine (VI), $m + k \simeq 8$. A sample of 15 ml methanol and 0.37 g (1.70 mmole) (I) were added to a flask equipped with a magnetic stirrer. After the amidine was completely dissolved, 5.86 g (17.0 mmoles) perfluorohexanecarboxylic acid nitrile was added. After 15 min, the IR band for the nitrile group at 2270 $cm^{-1}$ had disappeared; a band for the imidate C=N group appeared at 1695 $cm^{-1}$. Removal of the volatile components in vacuum gave 6.02 g (97%) (VI). Found: C 27.12; H 0.47; F 67.48; N 5.28%; mol. mass 3650 (ebullioscopically in $C_6F_6$), 3690 according to $^{19}F$ NMR spectroscopy. Calculated for $C_{82}H_{18}F_{130}N_{14}$: C 26.83; H 0.49; F 67.34; N 5.34%; mole. mass 3668. The IR, $^1H$ NMR, and $^{19}F$ NMR spectra were analogous to those given above.

## CONCLUSIONS

1. The reaction of bis(N,N-dimethyl)terephthalamidine with imidates of perfluorohexanecarboxylic acid in diethyl ether gave 1,4-bis(2,4-perfluorohexyltriazinyl)benzene in high yield.

2. The reaction in methanol leads to the formation of fluorine-containing oligoarylenazomethines.

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