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α,ω-Bis(dimethylaminophenyl)polyfluoromethine dyes

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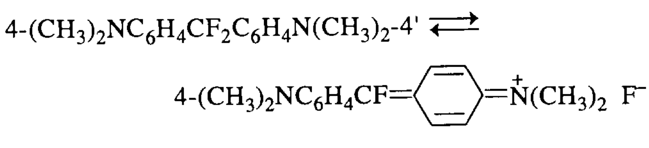
Abstract

The principles for constructing diarylpolyfluoromethine dyes with the $[4\text{-}(CH_3)_2NC_6H_4(CF{=}CF)_nCFC_6H_4N(CH_3)_2\text{-}4']^+ X^-$ structure from their difluorovinylene predecessors have been developed and their electronic and ^{19}F NMR spectra studied. The difluorovinylene shift in these dyes has been shown to be greater than that in their hydrogen analogues.

Introduction

We have found previously that polyfluoromethine systems with alternating double and single bonds constitute a new type of conjugated system which, due to the small size of the fluorine atoms, readily transmits conjugation. This was demonstrated with the synthesized series of α,ω-diarylperfluoropolyenes, α,β-difluorocinnamic acids and their difluorovinyl analogues, and with α,β-difluorochalcones [1]. One of us has synthesized the thiacarbocyanine dye with a completely fluorinated trimethine chain, which turned out to be a stable and deeply coloured compound with similar absorption intensity to the dye with an unsubstituted chain [2]. However, the simplest bis(dimethylaminophenyl)polyfluoromethine dyes have not been synthesized, and even the principles of their construction have not been developed.

In order to synthesize these compounds, we considered it necessary to prepare intermediates of the type $4\text{-}(CH_3)_2NC_6H_4(CF{=}CF)_nCF_2C_6H_4N(CH_3)_2\text{-}4'$, in which the difluorovinylene group should eliminate the fluoride ion due to effect of the donor dimethylamino group and the tendency of the molecule to convert into a conjugated system. Solution in polar solvents as well as treatment by Lewis acids facilitate this process. The possibility for the fluoride ion cleavage has been observed by one of us [3] in the first member of the series ($n=0$) of such polyfluoromethine dyes.



Results and discussion

1-(4-Dimethylaminophenyl)perfluoroprop-2-ene, $4\text{-}(CH_3)_2NC_6H_4CF_2CF{=}CF_2$ (**1**), on reaction with the lithium derivative $4\text{-}(CH_3)_2NC_6H_4\ (CF{=}CF)_nLi$ ($n=0$, 1, 2) should give polyfluoromethine dyes $[4\text{-}(CH_3)_2NC_6H_4\ (CF{=}CF)_nCF{=}C_6H_4N(CH_3)_2]^+\ X^-$ ($n=1, 2$) and hence provide a most convenient synthone for such dyes. In order to synthesize **1** it is possible to use copper or cadmium derivatives of 1-iodoperfluoroprop-2-ene (**2**) [4]. However, the copper derivative of this compound, which like its cadmium analogue is unstable at room temperature [5], does not react with 4-bromo- or 4-iodo-dimethylaniline at 25 °C even in the presence of the palladium catalyst $Pd[P(C_6H_5)_3]_4$. On heating $CF_2{=}CFCF_2Cu$ with 4-iodo-*N*-dimethylaniline, only a small amount (15%) of 1-(4-dimethylaminophenyl)perfluoroprop-1-ene (**3**) was obtained.

As the synthesis of arylperfluoropropene **1** via the reaction of the copper or cadmium derivatives of perfluoropropene **2** with 4-halogen-*N*-dimethylanilines was unsuccessful, 4-dimethylaminophenylzinc chloride was reacted with iodoperfluoroprop-2-ene in a 1:1 molar ratio in the presence of $Pd[P(C_6H_5)_3]_4$. Treatment of the resulting mixture with water followed by product isolation did not give the arylperfluoropropene **4** but rather 4-dimethylaminophenyl(1,2,2-trifluoroethylidene-4-dimethylaminophenyl)ketone (**5**) which is prob-

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ably the product of the hydrolysis of the diarylperfluoropropene **4**.

$$4\text{-}(CH_3)_2NC_6H_4Br \xrightarrow{Mg} 4\text{-}(CH_3)_2NC_6H_4MgBr \xrightarrow{ZnCl_2}$$

$$\xrightarrow{CF_2{=}CFCF_2I} 4\text{-}(CH_3)_2NC_6H_4CF{=}CFCF_2C_6H_4N(CH_3)_2\text{-}4' \xrightarrow{H_2O}$$

(4)

$$4\text{-}(CH_3)_2NC_6H_4COCFHCF_2C_6H_4N(CH_3)_2\text{-}4'$$

(5)

In order to synthesize the arylperfluoropropene **1**, the ratio of the reagents 4-dimethylaminophenylzinc chloride and iodoperfluoropropene (**2**) was changed to 1:2, resulting in a 9% yield of arylperfluoropropene **1** which rearranged into the arylperfluoropropene **3** within a few hours. ^{19}F NMR spectra first showed the presence of two CF_2 groups (−75.92 ppm) and a single fluorine atom (−152.04 ppm). However, with time, signals for the trifluoromethyl group and the two fluorine atoms of the (*E*)-difluorovinylene group appeared.

The rest of the reaction mass was treated with sodium perchlorate in acetonitrile after the extraction of arylperfluoropropene **1**, when the tris(fluoromethine) dye **6** precipitated as small crystals. The structure was confirmed by elemental analysis and ^{19}F NMR spectroscopy.

$$4\text{-}(CH_3)_2NC_6H_4CF{=}CFCF_2C_6H_4N(CH_3)_2\text{-}4' \xrightarrow{NaClO_4}$$

(4)

$$[4\text{-}(CH_3)_2NC_6H_4CF{=}CFCFC_6H_4N(CH_3)_2\text{-}4']^+\ ClO_4^-$$

(6)

Compound **6** was unstable towards atmospheric moisture and could only be stored under a layer of ether in an inert atmosphere. In methylene chloride solution, dye **6** decomposed within 10–15 h. The final product of its hydrolysis was ketone **5** which was isolated and identified.

The polyfluoromethine dye containing two α,β-difluorovinylene groups was prepared from 1,5-bis(4-dimethylaminophenyl)perfluoropenta-1,4-diene (**7**). This was obtained by the reaction of perfluoropenta-1,4-diene [6] with 4-dimethylaminophenyllithium.

$$4\text{-}(CH_3)_2NC_6H_4Li + CF_2{=}CFCF_2CF{=}CF_2 \longrightarrow$$

$$4\text{-}(CH_3)_2NC_6H_4CF{=}CFCF_2CF{=}CFC_6H_4N(CH_3)_2\text{-}4' \longrightarrow$$

(7)

$$[4\text{-}(CH_3)_2NC_6H_4CF{=}CFCF{=}CFCFC_6H_4N(CH_3)_2\text{-}4']^+\ F^-$$

(8)

In the nonpolar solvent hexane, the disubstituted perfluoropentadiene **7** exhibited an absorption maximum at 325 nm. In a polar solvent such as methylene chloride, the polyfluoromethine dye exhibited an absorption maximum at 860 nm. Dye **8** seems to exist in solution as an equilibrium mixture of the coloured ionic from **8** and a colourless non-ionic form **7**.

Attempts to replace the counterion F^- with other counterions such as ClO_4^- and BF_4^-, in order to isolate dye **8**, were unsuccessful and crystals could not be obtained. It should be noted that dye **8** only exists in solution and is much more unstable than the tris(fluoromethine) compound **6**. Within 30 min of preparing the solution in methylene chloride, the absorption maximum disappeared in conjunction with the appearance of a peak with a $\lambda_{max.}$ value of 620 nm, probably corresponding to the hydroxy derivative which then transforms into the ketone.

It was not possible to record the ^{19}F NMR fine structure of the perfluoropentadienyl cation **8** even on cooling to −80 °C. The ^{19}F NMR spectrum of the diarylperfluoropentadiene **7** showed three groups at −146.85 ppm ($F^{1,4}$) and −170.49 ppm ($F^{2,3}$), the coupling constants $J(F-F) = 127$ Hz being typical for the (*E*)-α,β-difluorovinylene groups, as was the signal at −99.87 ppm for the CF_2 group. On dissolving the diarylperfluoropentadiene **7** in methylene chloride, four more doublets of quartets, typical of the conjugated (*E*,*E*)-perfluorobutadiene system **9** appeared at −153.09 ppm (F^1), −140.32 ppm (F^2), −149.25 ppm (F^3) and −168.22 ppm (F^4), with the signal at −94.09 ppm corresponding to CF_2: $J(F^1-F^2)$ and $J(F^3-F^4) = 130$ Hz; $J(F^1-F^4) = 32.5$ Hz; and $J(F^2-F^3) = 36$ Hz. The two last coupling constants showed compound **9** to be in the (*S*)-*cis* conformation [7]. The ratio of the signals for diarylperfluoropentadiene **7** and diarylperfluoropentadiene **9** was 8:1, i.e. the equilibrium mixture contained more of the non-ionic form **7**:

$$4\text{-}(CH_3)_2NC_6H_4C\overset{1}{F}{=}C\overset{2}{F}CF_2C\overset{3}{F}{=}C\overset{4}{F}C_6H_4N(CH_3)_2\text{-}4' \rightleftharpoons$$

(7)

$$[4\text{-}(CH_3)_2NC_6H_4CF{\cdots}CF{\cdots}CF{\cdots}CF{\cdots}CF\text{-}$$

$$C_6H_4N(CH_3)_2\text{-}4']^+\ F^- \rightleftharpoons$$

$$4\text{-}(CH_3)_2NC_6H_4C\overset{1}{F}{=}\overset{2}{F}-\overset{3}{C}F{=}C\overset{4}{F}CF_2C_6H_4N(CH_3)_2\text{-}4'$$

(9)

The equilibrium conversion of the diarylperfluoropentadiene **7** into **9** via the perfluoropentadienyl cation and the reverse process are so rapid that the perfluoropentadienyl cation could not be detected by ^{19}F NMR spectroscopy. Attempts to stabilize the cation formed by treatment of the non-ionic form **7** with antimony pentafluoride in SO_2FCl at −60 °C, followed by generation of the perfluoropentadienyl cation from perfluoropenta-1,4-diene as described in ref. 8, resulted in the complete destruction of compound **7**.

1,9-Bis(4-dimethylaminophenyl)nonaperfluoro-1,3,6,8-tetraene (**10**) was obtained by the reaction of 4-dimethylamino-α,β-difluorostyryllithium [9], synthesized from 4-dimethylamino-α,β-difluoro-β-chlorostyrene, with perfluoropenta-1,4-diene.

$$4\text{-}(CH_3)_2NC_6H_4CF{=}CFCl \xrightarrow{C_4H_9Li}$$

$$[4\text{-}(CH_3)_2NC_6H_4CF{=}CFLi] \xrightarrow{CF_2{=}CFCF_2CF{=}CF_2}$$

$$4\text{-}(CH_3)_2NC_6H_4\overset{1}{CF}{=}\overset{2}{CF}\overset{3}{CF}{=}\overset{4}{CF}CF_2\overset{5}{CF}{=}\overset{6}{CF}\overset{7}{CF}{=}\overset{8}{CF}C_6H_4N(CH_3)_2\text{-}4'$$

(10)

The structure of compound **10** was confirmed by elemental analysis and ^{19}F NMR spectroscopy in which five groups of signals were observed, one corresponding to the CF_2 group and the four others in equivalent pairs to the fluorine atoms of the polymethine chain. The coupling constants of these atoms were equal to 127 Hz, indicating an all-(*E*) configuration for the polyene chain.

In contrast to the substituted compounds of perfluoropropene **4** and perfluoropentadiene **7**, when the perfluorononatetraene **9** was dissolved in polar solvents no elimination of fluoride anion occurred from the difluoromethylene group since the latter was well removed from the donor $(CH_3)_2N$ group and was thus less influenced by it than in compounds **4** and **7**.

A series of polymethine dyes with the structure $[4\text{-}(CH_3)_2NC_6H_4(CH{=}CH)_nCHC_6H_4N(CH_3)_2\text{-}4']^+\ ClO_4^-$ has been described previously [10]. These compounds were stable at 25 °C for 1 week. The bathochromic shift in the absorption maximum which occurred on the introduction of each subsequent vinyl group was 90–100 nm.

The first member of the polyfluoromethine dye had its absorption maximum shifted to shorter wavelength relative to the hydrogen analogue probably because of steric hindrance. The second and the third members exhibited longer wavelength absorption. The shift in the absorption maximum corresponding to the difluorovinylene group in the polyfluoromethine dye series was *c.* 1.5-times greater than that of the hydrogen analogue being 120–150 nm (see Table 1). On the basis of quantum chemical calculations, it has been shown that the shift corresponding to α,β-difluorovinylene in polymethine dyes exceeds that of the vinylene group [11].

TABLE 1. Absorption maxima of polymethine dyes[a] $[4\text{-}(CH_3)_2NC_6H_4(CY{=}CY)_nCYC_6H_4N(CH_3)_2\text{-}4']^+\ X^-$

n	Y=F		Y=H [6]	
	$\lambda_{max.}$ (nm)	$\Delta\lambda_{max.}$ (nm)	$\lambda_{max.}$ (nm)	$\Delta\lambda_{max.}$ (nm)
0	588 [3]	–	606	–
1	709	121	693	87
2	860	151	790	97

[a] All the absorption maxima were recorded in methylene chloride solution.

Experimental

^{19}F NMR spectra were taken with a Bruker WP-200 spectrometer at 188.28 MHz using methylene chloride solutions with CCl_3F as the external standard. UV spectra were recorded with Specord UV–vis and Specord M-40 spectrophotomers using methylene chloride solutions. IR spectra were obtained on a UR-20 instrument with KBr discs.

4-Dimethylaminophenyl(1,2,2-trifluoroethylidene-4-dimethylaminophenyl)ketone (5)

The Grignard reagent was obtained from 4-bromo-*N*-dimethylaniline (6 g) and magnesium (0.8 g) in THF (20 ml). Freshly melted zinc chloride (4.1 g) in THF (20 ml) was added with stirring. The mixture was stirred for a further 2 h, cooled to 0 °C and then $Pd[P(C_6H_5)_3]_4$ (0.5 g) and 1-iodoperfluoroprop-2-ene (**2**) (6 g) in THF (30 ml) was added. The reaction mixture was stirred for 4 h at 0 °C and for 16 h at 25 °C, and then filtered and poured into aqueous NH_4Cl plus ice. The organic layer was extracted with ether, the ether extract washed with water, dried over $MgSO_4$ and the solvent distilled off. Compound **5**: yield, 2.3 g (44%), m.p. 138–140 °C (from hexane). ^{19}F NMR δ: −75.78 (CF_2); −199.82 (F) ppm; *J*(F−H) = 50 Hz. IR (cm^{-1}): 1720 (CO). UV $\lambda_{max.}$: 319 nm (acetonitrile). Analysis: Found: F, 16.33, 16.43%. $C_{19}H_{21}F_3N_2O$ requires: F, 16.29%.

1-(4-Dimethylaminophenyl)perfluoroprop-2-ene (1) and 1,3-bis(4-dimethylaminophenyl)perfluoropropene-carbonium perchlorate (6)

4-Dimethylaminophenylzinc chloride was obtained via the procedure used for ketone **5** and $Pd[P(C_6H_5)_3]_4$ (0.5 g) and 1-iodoperfluoroprop-2-ene (**1**) (12 g) in THF (40 ml) added with stirring at 0 °C. The mixture was stirred for a further 4 h at 0 °C and for 16 h at 25 °C. Residual THF was distilled off *in vacuo* under argon. The solid residue was treated with hexane at 50–53 °C, the hexane extract evaporated and the residue distilled *in vacuo*. 1-(4-Dimethylaminophenyl)perfluoroprop-2-ene (**1**): yield, 1.1 g (14%), b.p. 121–123 °C/12 mmHg. From ^{19}F NMR spectroscopy, perfluoropropene **1** rearranged into fluoropropene **3** to 90% extent over 4–5 h. Compound **3**: b.p. 126–127 °C/12 mmHg. ^{19}F NMR δ: −66.52 (CF_3); −196.98 (F^1); −176.35 (F^2) ppm; $J(F^1\text{–}F^2) = 130$ Hz. Analysis: Found: F, 37.61, 37.64%. $C_{11}H_{10}F_5N$ requires: F, 37.85%.

The residue after treatment with hexane was dissolved in anhydrous acetonitrile (20 ml) and a solution consisting of $NaClO_4$ (2 g) in anhydrous acetonitrile (10 ml) added. Perchlorate **6** was isolated with anhydrous ether, filtered under argon and reprecipitated from methylene chloride with ether. Perchlorate **6**: yield, 0.9 g (13.9%), m.p. 120–121 °C (with decomposition). Analysis: Found: F, 13.60, 13.62%. $C_{19}H_{20}ClF_3N_2O_4$ requires: F, 13.20%.

(E,E)-1,5-bis(4-dimethylaminophenyl)perfluoropenta-1,4-diene (7)

To a solution consisting of 4-dimethylaminophenyllithium obtained from 4-bromo-*N*-dimethylaniline (6 g) and lithium (0.42 g) in ether (50 ml) was added perfluoropenta-1,4-diene (3.2 g) in ether (10 ml) with stirring at −60 °C. The mixture was stirred for a further 2 h and then poured into an aqueous solution of NH_4Cl plus ice. The organic layer was extracted with ether, the ether extract washed with water, dried over $MgSO_4$ and the solvent distilled off. Compound **7**: yield, 4.1 g (66%), m.p. 94–95 °C (from hexane). Analysis: Found: C, 60.43, 60.46; H, 4.67, 4.72; N, 6.51, 6.60%. $C_{21}H_{20}F_6N_2$ requires: C, 60.87; H, 4.83; N, 6.76%.

(E,E,E,E)-1,9-bis(4-dimethylaminophenyl)nonaperfluoro-1,3,6,8-tetraene (10)

To 4-dimethylamino-α,β-difluoro-β-chlorostyrene (6.5 g) in 1:1 anhydrous THF and ether (40 ml) was added 2 N butyllithium (15 ml) in hexane at −90 °C over 20 min. The mixture was stirred for 1 h at −90 °C to −100 °C when perfluoropenta-1,4-diene (3.2 g) in ether (10 ml) was added over 30 min. The reaction mixture was stirred for 2 h at −80 °C to −90 °C and then poured into aqueous NH_4Cl plus ice. The organic layer was extracted with water, dried over $MgSO_4$ and the solvent distilled off. Compound **10**: yield, 5.2 g (32%), m.p. 138–139 °C (from hexane). ^{19}F NMR δ: -103.93 (CF_2); -155.21 ($F^{1,8}$); -139.07 ($F^{2,7}$); -152.03 ($F^{3,6}$); -171.03 ($F^{4,5}$); $J(F^1\text{–}F^2) = J(F^7\text{–}F^8) = J(F^3\text{–}F^4) = J(F^5\text{–}F^6) = 127$ Hz. Analysis: Found: F, 35.05, 35.10; N, 5.09, 5.11%. $C_{25}H_{20}F_{10}N_2$ requires: F, 35.32; N, 5.20%.

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