

Substituent Shielding Parameters of Fluorine-19 NMR on Polyfluoroaromatic Compounds Dissolved in Dimethyl Sulphoxide- d_6

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High resolution fluorine-19 NMR spectra of polyfluoroaromatic compounds dissolved in deuterated dimethyl sulphoxide were measured and substituent shielding parameters were derived. These parameters were compared with the values observed in deuterated chloroform solutions and used to identify fluoroaromatic compounds related to perfluorinated polyimides and poly(amic acids). Average differences of $\Delta\delta$ between the solvents are 1.1, 1.0 and 2.1 ppm for *o*-, *m*- and *p*-fluorines of monosubstituted pentafluorobenzenes, respectively. The significant difference for *p*-fluorine of NH_2 is important in identifying perfluorinated diamines because they are source materials for perfluorinated polyimides. Substituent shielding parameters for *meta* and *para* substitution increase as the respective Hammett σ constants increase, which indicates that fluorine-19 NMR chemical shift is primarily determined by electron density.

KEY WORDS NMR; ^{19}F NMR; substituent shielding parameter; fluoroaromatic compounds; perfluorinated polyimides; Hammett σ constant

INTRODUCTION

We have recently reported the first synthesis of perfluorinated polyimides that have high optical transparency over the entire range of optical communication wavelengths (1.0–1.7 μm) and high glass transition temperatures, over 270 $^\circ\text{C}$.¹ Their optical transparency and high thermal stability are due to the absence of hydrogen atoms and to the fully aromatic molecular structure. In general, carbon-13 NMR spectra of these polymers are complicated because significant scalar couplings between carbons and directly bonded fluorine atoms make the carbon signals split into several peaks. We have shown that fluorine-19 NMR (^{19}F NMR) is very effective in examining the completion of the imidization reaction of perfluorinated poly(amic acid).¹

Substituent shielding parameters of ^{19}F NMR for fluoroaromatic compounds dissolved in deuterated chloroform (CDCl_3) have been reported by Bruce.² However, perfluorinated poly(amic acids), polyimides and related compounds do not dissolve in such non-polar organic solvents, and the substituent shielding parameters needed for calculating ^{19}F NMR chemical shifts of these compounds have not been reported. In order to examine the molecular structure of these compounds, substituent shielding parameters should be derived from NMR spectra measured in polar organic solvents, such as dimethyl sulphoxide, dimethylacetamide and *N*-methyl-2-pyrrolidinone. In this study, high-resolution ^{19}F NMR spectra of a series of polyfluoroaromatic compounds dissolved in deuterated dimethyl sulphoxide ($\text{DMSO}-d_6$) were measured, and the substituent shielding parameters derived from these compounds were elu-

cided by comparing the calculated and observed chemical shifts for model compounds of perfluorinated polyimides and poly(amic acids).

RESULTS AND DISCUSSION

Substituent shielding parameters

Structural formulae, ^{19}F NMR chemical shifts and substituent shielding parameters of the polyfluoroaromatic compounds used in this study are shown in Fig. 1. Substituent shielding parameters ($\Delta\delta$) were derived by relating the chemical shift of the *o*-, *m*- and *p*-fluorines to that of hexafluorobenzene. They are indicated in square brackets in the Fig. 1. The substituents, $\Delta\delta$ of *o*-, *m* and *p*-fluorines observed in CDCl_3 and in $\text{DMSO}-d_6$ and Hammett σ constants³ of the substituents are listed in Table 1. The signs of $\Delta\delta$ in CDCl_3 reported in Ref. 2 are reversed for compatibility with this study. Most of the $\Delta\delta$ values in $\text{DMSO}-d_6$ are within 2 ppm of those in CDCl_3 . The average differences of $\Delta\delta$ between the solvents are 1.1, 1.0 and 2.1 ppm for *o*-, *m* and *p*-fluorines, respectively. Relatively large differences (>3.0 ppm) in $\Delta\delta$ are observed for *p*-fluorine of OH (3.0 ppm), *p*-fluorine of NH_2 (4.7 ppm), *o*-, *m*- and *p*-fluorines of SO_2Cl (4.4, 5.0, 15.1 ppm) and *p*-fluorine of NHNH_2 (4.7 ppm). In particular, the significant difference at *p*-fluorine of NH_2 is important in identifying perfluorinated diamines because they are source materials for perfluorinated polyimides.

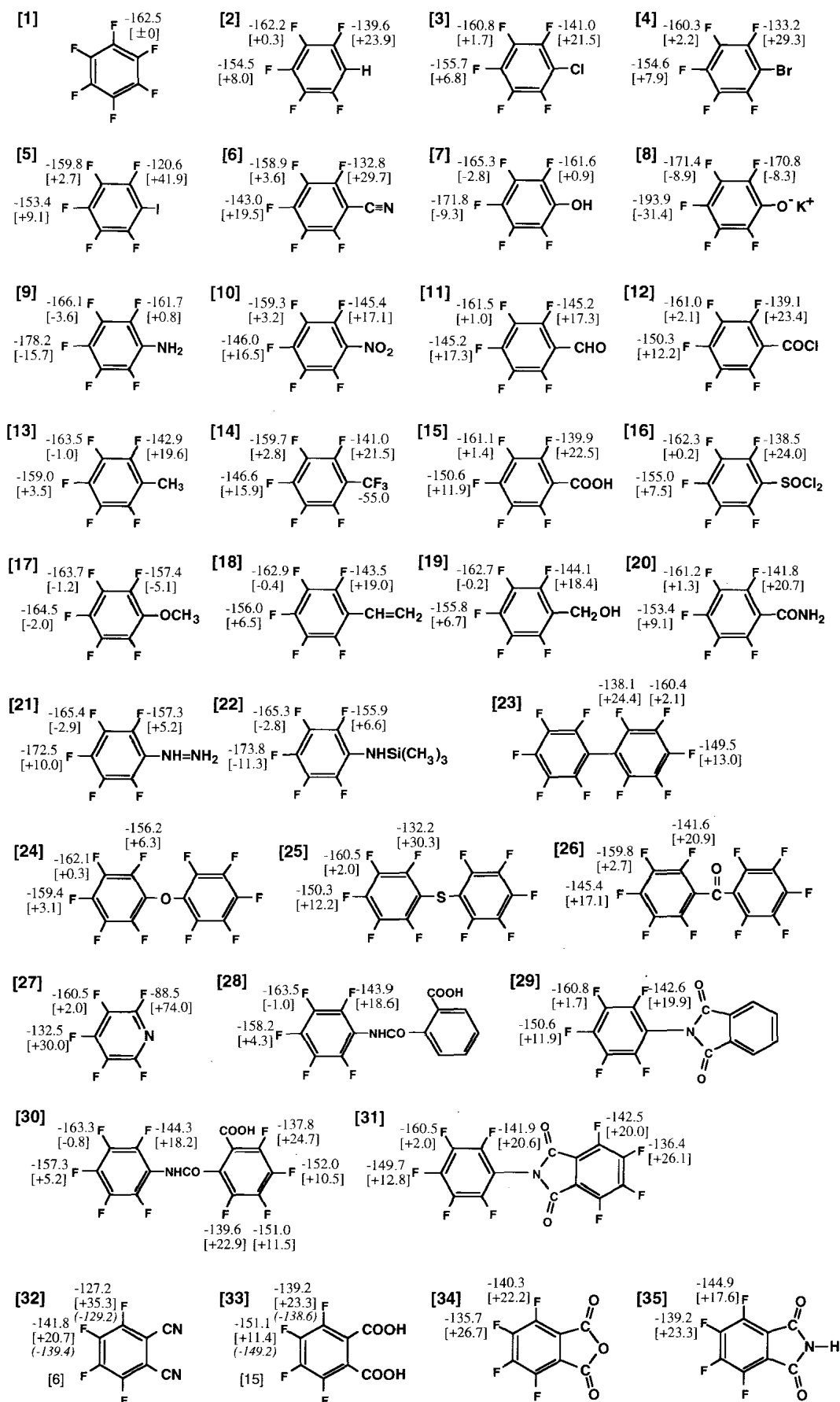


Figure 1. Structural formulae, ^{19}F NMR chemical shifts and substituent shielding parameters ($\Delta\delta$, in square brackets) of the polyfluoroaromatic compounds.

Table 1. Substituent shielding parameters ($\Delta\delta$) observed in CDCl_3 and $\text{DMSO}-d_6$ and the respective Hammett σ constants observed for monosubstituted pentafluorobenzenes

No.	Substituent	In CDCl_3			In $\text{DMSO}-d_6$			Hammett σ constant	
		$\Delta\delta_{ortho}$	$\Delta\delta_{meta}$	$\Delta\delta_{para}$	$\Delta\delta_{ortho}$	$\Delta\delta_{meta}$	$\Delta\delta_{para}$	σ_{meta}	σ_{para}
1	F	0.0	0.0	0.0	0.0	0.0	0.0	0.34	0.06
2	H	+23.7	+0.2	+8.4	+23.9	+0.3	+8.0	0.0	0.0
3	Cl	+21.6	+1.0	+6.2	+21.5	+1.7	+6.8	0.37	0.23
4	Br	+30.3	+1.7	+7.7	+29.3	+2.2	+7.9	0.39	0.23
5	I	+43.2	+3.0	+10.0	+41.9	+2.7	+9.1	0.35	0.18
6	CN	+30.7	+4.0	+19.8	+29.7	+3.6	+19.5	0.56	0.66
7	OH	-1.2	-1.4	-6.3	+0.9	-2.8	-9.3	0.12	-0.37
8	OK				-8.3	-8.9	-31.4		
9	NH_2	0.0	-2.6	-11.0	+0.8	-3.6	-15.7	-0.16	-0.66
10	NO_2	+17.1	+4.1	+16.4	+17.1	+3.2	+16.5	0.71	0.78
11	CHO				+17.3	+1.0	+17.3	0.36	0.22
12	COCl	+25.7	+3.9	+17.4	+23.4	+2.1	+14.4		
13	CH_3	+18.8	-1.5	+3.2	+19.6	-1.0	+3.5	0.07	-0.17
14	CF_3	+22.7	+2.4	+15.1	+21.5	+2.8	+15.9	0.43	0.54
15	COOH	+23.6	+1.0	+11.3	+22.5	+1.4	+11.9	0.37	0.45
16	SO_2Cl	+28.4	+5.3	+22.6	+24.0	+0.3	+7.5		
17	OCH_3	+4.5	-1.9	-1.9	+5.1	-1.2	-2.0	0.12	-0.27
18	$\text{CH}=\text{CH}_2$	+19.1	-1.0	+5.9	+19.0	-0.4	+6.5		
19	CH_2OH				+18.4	-0.2	+6.7		
20	CONH_2				+20.7	+1.3	+9.1	0.28	0.36
21	NHNH_2	+3.9	-1.5	-5.3	+5.2	-2.9	-10.0		
22	$\text{NHSi}(\text{CH}_3)_3$				+6.6	-2.8	-11.3		
23	C_6F_5	+25.0	+2.9	+14.2	+24.4	+2.1	+13.0		
24	OC_6F_5				+6.3	+0.3	+3.1		
25	SC_6F_5				+30.3	+2.0	+12.2		
26	COC_6F_5	+21.4	+3.1	+16.3	+20.9	+2.7	+17.1		

An extraordinarily large difference of 15.1 ppm between the two solvents is observed for *p*-fluorine of pentafluorosulphonyl chloride (**16**). Table 2 shows relative dielectric constants (ϵ_r) of seven solvents and the $\Delta\delta$ values of **16** observed in these solvents. The relative dielectric constant is an indicator of solvent polarity. Except for $\text{DMSO}-d_6$, the $\Delta\delta$ values are similar regardless of ϵ_r . Figure 2 shows ^{19}F NMR spectra of the mixture of **16** and $\text{DMSO}-d_6$ dissolved in nitromethane- d_3 and **16** dissolved in $\text{DMSO}-d_6$. The molar ratios of the compound to $\text{DMSO}-d_6$ are 1:0.1, 1:0.5, 1:1 and 1:2. Two sets of clearly separated signals are observed for the mixtures of **16** and $\text{DMSO}-d_6$. The chemical shifts of one set are close to those of **16** dissolved in $\text{DMSO}-d_6$ and those of the other are close to those in nitromethane- d_3 . The signal intensity of the

former signals increases with increasing amount of $\text{DMSO}-d_6$. This suggests the formation of a complex between the compound and $\text{DMSO}-d_6$, and the large differences in $\Delta\delta$ observed in $\text{DMSO}-d_6$ can be explained by the complex formation.

The model compounds **28** and **29** were prepared in order to derive $\Delta\delta$ for identifying poly(amic acid)s and polyimides synthesized from perfluorinated diamines and unfluorinated dianhydrides. Similarly, **30** and **31** were prepared for identifying perfluorinated poly(amic acid)s and perfluorinated polyimides. The changes in $\Delta\delta$ for fluorines in the amine moiety caused by perfluorination of the anhydride moiety are less than 1 ppm.

For **32** and **33**, the chemical shifts calculated using $\Delta\delta$ obtained from the monosubstituted pentafluorobenzenes are indicated in italics. The compound numbers whose $\Delta\delta$ were used for calculation are also indicated below the structural formulae in Fig. 1. The calculated chemical shifts are in good agreement with the observed values for **32** and **33**. The average difference between the calculated and the observed chemical shifts of these compounds is 1.7 ppm. Further, **34** can be synthesized by dehydration of **33**, while dehydration causes a significant downfield shift of 15.3 ppm in 4-fluorine. On the other hand, the chemical shifts of the 3- and 4-fluorines of the benzene ring attached to imide group in **31** are comparable to those of the respective fluorines in **31** and **32**. This indicates that the electronic structure of the imide group is very similar to that of the dicarboxylic anhydride group. This similarity can be used in assigning NMR signals of perfluorinated polyimide as described below.

Table 2. Relative dielectric constants of solvents and substituent shielding parameters (ppm) of pentafluorosulphonyl chloride in the solvents

Solvent	ϵ_r ^a	$\Delta\delta_{ortho}$	$\Delta\delta_{meta}$	$\Delta\delta_{para}$
Benzene- d_6	2.3	+27.3	+4.7	+21.5
Chloroform- d	4.8	+28.4	+5.5	+22.7
Acetone- d_6	19.8	+26.6	+3.6	+20.9
Methanol- d_4	32.6	+26.9	+3.6	+21.1
Nitromethane- d_3	35.0	+27.0	+4.0	+21.5
Dimethyl sulphoxide- d_6	46.0	+24.0	+0.2	+7.5
Water- d_2	80.1	+28.2	+4.3	+21.0

^a Relative dielectric constant at room temperature.

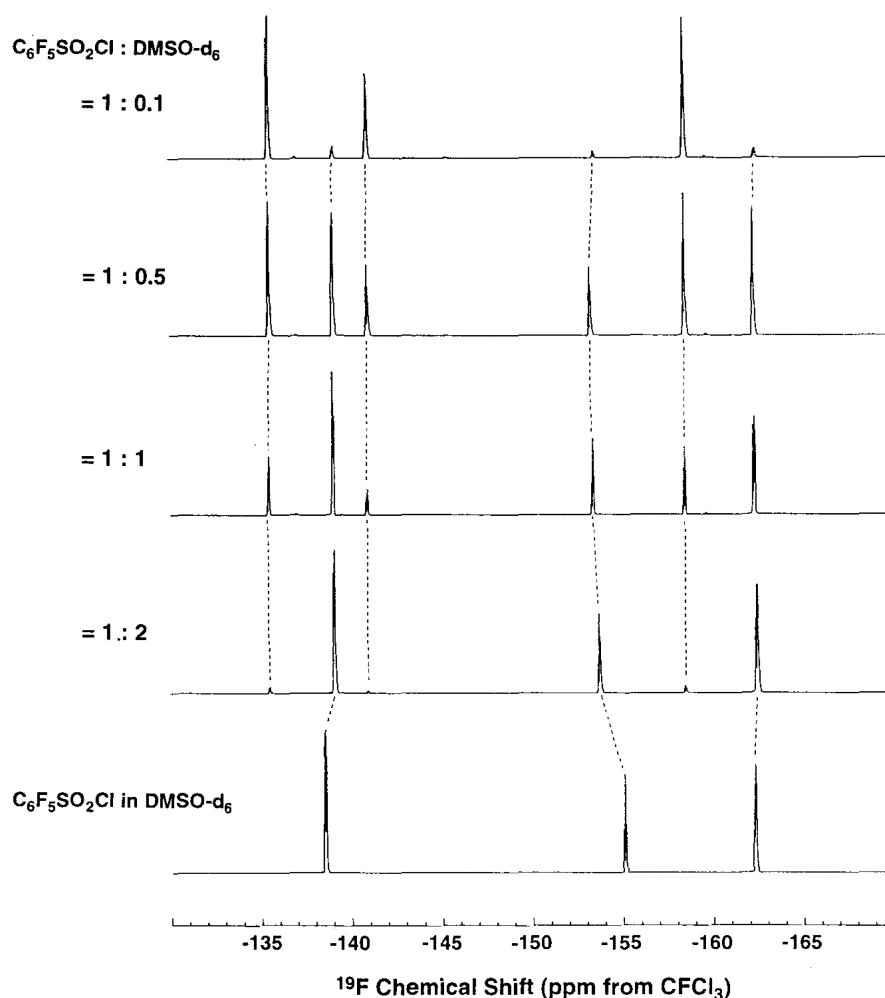


Figure 2. 376.49 MHz ^{19}F NMR spectra of a mixture of pentafluorosulphonyl chloride ($\text{C}_6\text{F}_5\text{SO}_2\text{Cl}$) and $\text{DMSO}-d_6$ dissolved in nitromethane- d_3 and $\text{C}_6\text{F}_5\text{SO}_2\text{Cl}$ dissolved in $\text{DMSO}-d_6$.

Figure 3 shows relationships between $\Delta\delta$ and Hammett σ constants³ for *m*- and *p*-fluorines of the monosubstituted pentafluorobenzenes. Despite the scatter of points, $\Delta\delta_{\text{meta}}$ and $\Delta\delta_{\text{para}}$ generally increase as σ_{meta} and σ_{para} increase, and the change in $\Delta\delta_{\text{para}}$ is

much larger than that in $\Delta\delta_{\text{meta}}$. The ^{19}F NMR chemical shift is displaced according to the electronic density, and σ_{para} can be estimated from $\Delta\delta_{\text{para}}$.

Identification of polyfluoroaromatic compounds using $\Delta\delta$

Structural formulae and observed and calculated ^{19}F NMR chemical shifts of polysubstituted fluoroaromatic compounds are shown in Fig. 4. Chemical shifts calculated using $\Delta\delta$ obtained from monosubstituted perfluorobenzenes are indicated in parentheses. These compounds are the source materials and/or model compounds of perfluorinated polyimides, or intermediates in synthesizing them. The compound numbers in Fig. 1 whose substituent shielding parameters are used for calculation are indicated below the formulae. As can be seen, comparisons of the observed and calculated values for di- and trisubstituted perfluorobenzenes (tetra- and trifluorobenzenes) show fair agreement. In particular, this method can predict very well the chemical shifts of the compounds consisting of two or three benzene rings. However, there are relatively large discrepancies (>3 ppm) between the observed and calculated chemical shifts for disubstitution of amino (NH_2) and *N*-(trimethylsilyl)amino [$\text{NHSi}(\text{CH}_3)_3$] groups (40–43). The large upfield displacements of -8.3 and -6.6 ppm from

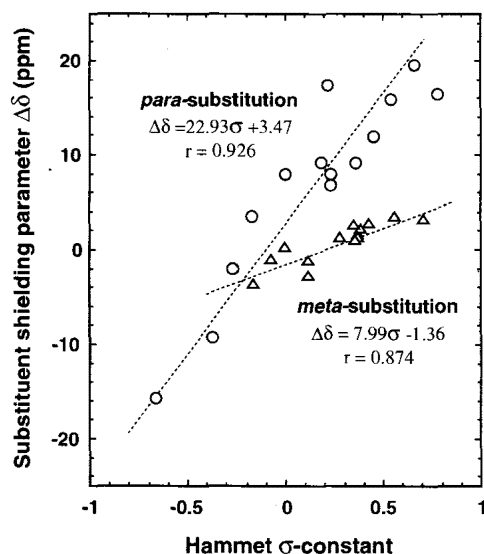


Figure 3. $\Delta\delta$ and Hammett σ constants for *m*- and *p*-fluorines of the monosubstituted pentafluorobenzenes.

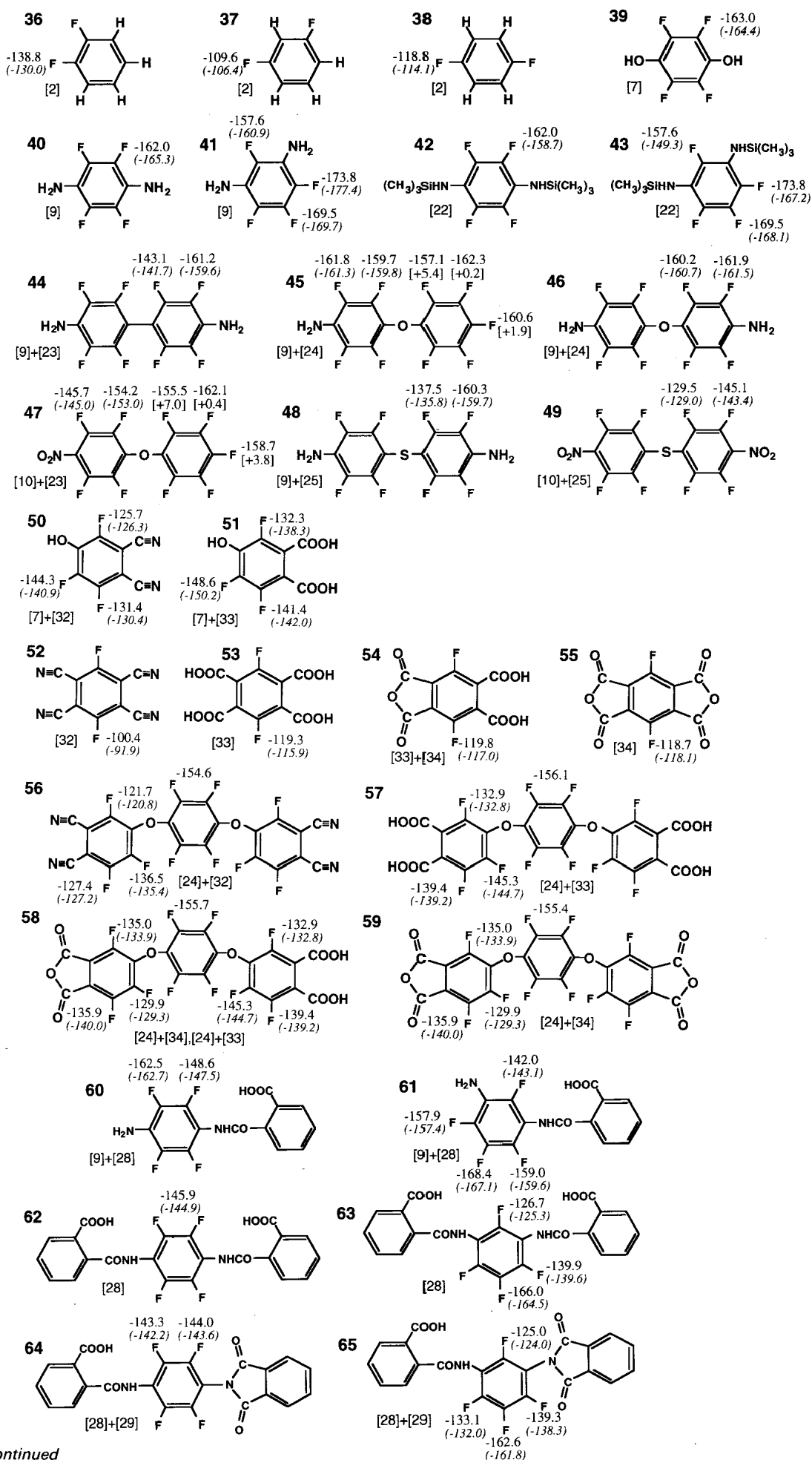


Figure 1—Continued

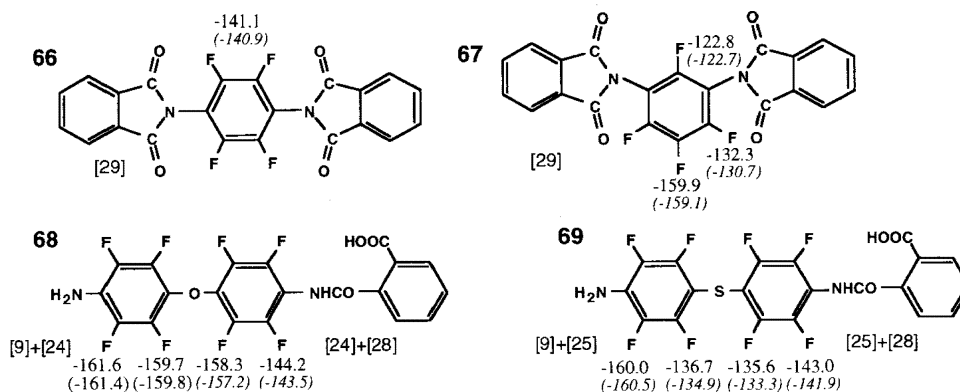


Figure 4. Structural formulae and observed and calculated ^{19}F NMR chemical shifts of polysubstituted fluoroaromatic compounds. Chemical shifts calculated using $\Delta\delta$ s are given in parentheses. The compound numbers in Fig. 1 whose $\Delta\delta$ are used for calculation are given below the formulae in square brackets. $\Delta\delta$ s obtained from polysubstituted fluoroaromatic compounds are given in square brackets.

the calculated values observed for 2- and 4-fluorines in *N,N'*-bis(trimethylsilyl)tetrafluoro-*m*-phenylenediamine (**43**) can be explained by the steric effect between the fluorines and the bulky $\text{NHSi}(\text{CH}_3)_3$ groups. Steric hindrance generally plays an important role in qualitative description of chemical shift effects. The upfield displacements of the γ shielding effect observed in carbon,⁴ nitrogen⁵ and phosphorus⁶ NMR has been explained in terms of steric compression resulting from repulsive interactions between non-bonded atoms.⁷ On the other hand, there is some uncertainty in the chemical shift calculation of tetrasubstituted difluorobenzenes, **36**, **37**, **38**, **52** and **53**. In particular, the discrepancies observed for **36** and **52** are larger than 8 ppm. This comes from the resonance effect caused by four substituents and from the accumulation of experimental errors in $\Delta\delta$.

Diamines **40**, **41**, **44**, **46** and **48** were used previously¹ to synthesize the perfluorinated polyimides. In addition, **42** and **43** can be used for the same purpose instead of **40** and **41**. Ohishi *et al.*⁸ reported that *N,N'*-bis(trimethylsilyl)-substituted aromatic diamines were more reactive than the parent diamines towards dicarboxylic chlorides in synthesizing polyamides. However, the very close chemical shifts of these compounds indicate that trimethylsilylation of amino groups does not cause a significant change in the electronic structure of aromatic diamines. This is also supported by the ^1H chemical shifts of amino hydrogens in **42** and **43** (4.84 and 5.09 ppm from tetramethylsilane) being very close to those in **40** and **41** (4.87 and 5.11 ppm), indicating the similarity of electron donation of amino groups by diamines and trimethylsilylated diamines. On the other hand, the calculated chemical shifts of the diamines and their derivatives that have two benzene rings (**44**–**49**) agree well with the experimental values.

The dianhydrides **55** and **59** have been used to synthesize perfluorinated polyimides.¹ For the dianhydrides and their derivatives **50**, **51** and **54**–**59**, the calculated chemical shifts show fairly good agreement with the experimental values, except for the fluorines just adjacent to the anhydride group in **58** and **59**. The reason for the 4.1 ppm discrepancy is not clear, but this fluorine can be distinguished from another fluorine adjacent to the anhydride group from the doublet splitting of its signal. The model compounds **60**–**67** were prepared to examine the imidization reaction of

poly(amic acid)s synthesized from perfluorinated diamines **40** and **41**. The calculated chemical shifts agree well with the experimental values within errors of 2 ppm.

Figure 5 shows the structural formula and observed and calculated ^{19}F NMR chemical shifts of a perfluorinated polyimide, 10FEDA/4FMPD, dissolved in $\text{DMSO}-d_6$. The polyimide film cured at 350°C was not soluble, but the film cured at 200°C was soluble in polar organic solvents.¹ All the signals are readily assigned using the $\Delta\delta$ derived from **24** and **31** and taking into account the similarity of the electronic structures of anhydride and imide groups. A relatively large discrepancy of 4.8 ppm is observed at the fluorine adjacent to the imide group. This coincides with the downfield displacement observed at the fluorine adjacent to anhydride group in **58** and **59**. In conclusion, the substituent shielding parameters derived in this study are very effective in identifying polyfluoroaromatic compounds and perfluorinated polyimides.

EXPERIMENTAL

High-resolution ^{19}F NMR spectra were measured at 376.49 MHz with a Bruker MSL-400 spectrometer at room temperature ($22 \pm 2^\circ\text{C}$). Samples were dissolved to a concentration of about 1 wt% in $\text{DMSO}-d_6$. The ^{19}F chemical shifts were read directly from internal trichlorofluoromethane (CFCl_3). ^{19}F NMR signals of monosubstituted pentafluorobenzenes can be easily assigned using signal intensity, splitting of the signals

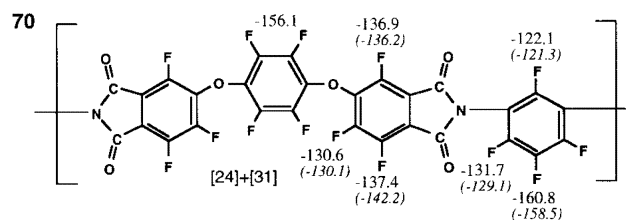


Figure 5. Structural formula and observed and calculated ^{19}F NMR chemical shifts of a perfluorinated polyimide, 10FEDA/4FMPD, cured at 200°C . Chemical shifts calculated using $\Delta\delta$ s are given in parentheses.

caused by fluorine-fluorine scalar coupling and substituent shielding parameters reported by Bruce.²

DMSO-*d*₆ (>99.5%, NMR grade) was purchased from Wako Pure Chemical Industries. Hexafluorobenzene (1), chloropentafluorobenzene (3), bromopentafluorobenzene (4), iodopentafluorobenzene (5), pentafluorobenzonitrile (6), pentafluorophenol (7), pentafluoroaniline (9), pentafluoronitrobenzene (10), octafluorotoluene (14), pentafluorobenzoic acid (15), pentafluorobenzenesulphonyl chloride (16), pentafluoroanisole (17), pentafluorostyrene (18), pentafluorobenzyl alcohol (19), pentafluorobenzamide (20), decafluorobiphenyl (23), pentafluoropyridine (27), tetrafluorophthalonitrile (32), tetrafluorobenzoic acid (33), tetrafluorophthalic anhydride (34), 1,2-difluorobenzene (36), 1,3-difluorobenzene (37) and 1,4-difluorobenzene (38) were purchased from Tokyo Kasei Kogyo, pentafluorobenzene (2), pentafluorobenzaldehyde (11), pentafluorobenzoylchloride (12) and pentafluorophenylhydrazine (21) from Kanto Chemical, 2,3,4,5,6-pentafluorotoluene (13), tetrafluorohydroquinone (39) and 4,4'-diaminooctafluorobiphenyl (44) from Aldrich Chemical, decafluorobiphenyl thioether (25) and decafluorobenzophenone (26) from Lancaster Synthesis, tetrafluorophthalimide (35) from Fluorochem, 1,4-

diaminotetrafluorobenzene (40) and 1,3-diaminotetrafluorobenzene (41) from Fuji Chemical and 1,2,4,5-tetracyanodifluorobenzene (52) from S.D.S. Biotech. The compounds obtained from commercial sources were used as received.

Potassium pentafluorophenoxide (8) was prepared by reaction of pentafluorophenol (7) and potassium hydroxide in ethanol. *N*-(Trimethylsilyl)pentafluoroaniline (22), *N,N'*-bis(trimethylsilyl)tetrafluoro-*p*-phenylenediamine (42) and *N,N'*-bis(trimethylsilyl)tetrafluoro-*m*-phenylenediamine (43) were synthesized from pentafluoroaniline (9), 1,4-diaminotetrafluorobenzene (40) and 1,3-diaminotetrafluorobenzene (41), respectively, according to the scheme of Ohishi *et al.*⁸ Decafluorobiphenyl ether (24) was synthesized by reaction of hexafluorobenzene (1) and potassium pentafluorophenoxide (8) in dimethylformamide. Figure 6 shows a scheme for synthesizing model compounds of perfluorinated poly(amic acids) (30) and perfluorinated polyimides (31) from an anhydride (34) and an amine (9). Compounds 28, 60–63, 68 and 69 were prepared in the same manner by reaction of the respective anhydrides and amines in dimethylacetamide (DMAc) at room temperature for 12 h. Compounds 64 and 65 were prepared by thermal imidization of the respective amic acids at 150 °C for 1 h. Compounds 29, 66 and 67 were prepared in the same manner as in Fig. 6 by thermal imidization of the respective amic acids at 250 °C for 2 h. The methods for preparing these compounds are described elsewhere.⁹

Perfluorinated diamines of bis(2,3,5,6-tetrafluoro-4-aminophenyl) ether (46) and bis(2,3,5,6-tetrafluoro-4-aminophenyl) sulphide (48) were prepared according to the schemes reported by Kobrina *et al.*¹⁰ and Furin *et al.*¹¹ Compounds 45, 47 and 49 are intermediates in synthesizing these perfluorinated diamines. The methods of synthesizing perfluorinated dianhydrides, namely 1,4-difluoro-2,3,5,6-benzenetetracarboxylic dianhydride (55), and 1,4-bis(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzene dianhydride (59), have been described elsewhere.^{1,12} Compounds 50, 51, 54, 56, 57 and 58 are intermediates in synthesizing these perfluorinated dianhydrides. The dianhydrides and diamines were purified by sublimation under reduced pressure.

Acknowledgement

We thank Dr Shigekuni Sasaki at NTT Interdisciplinary Research Laboratories for his helpful comments and the generous provision of intermediates of perfluorinated dianhydrides.

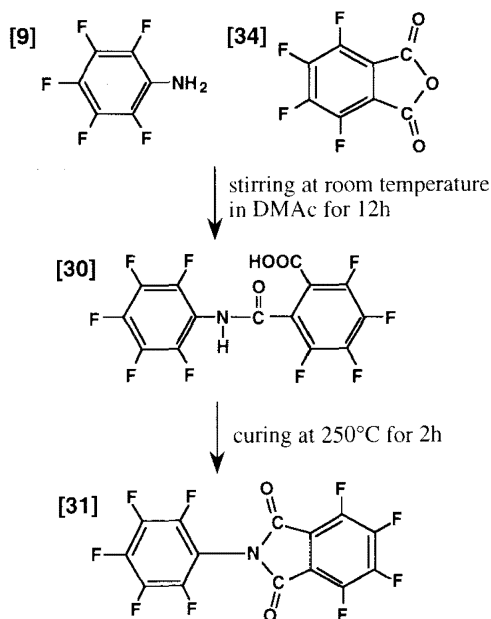


Figure 6. Scheme for synthesizing model compounds of perfluorinated poly(amic acids) and perfluorinated polyimides from an anhydride and an amine.

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