

^{19}F n.m.r. investigation of aromatic amic acid and imide model compounds. 1

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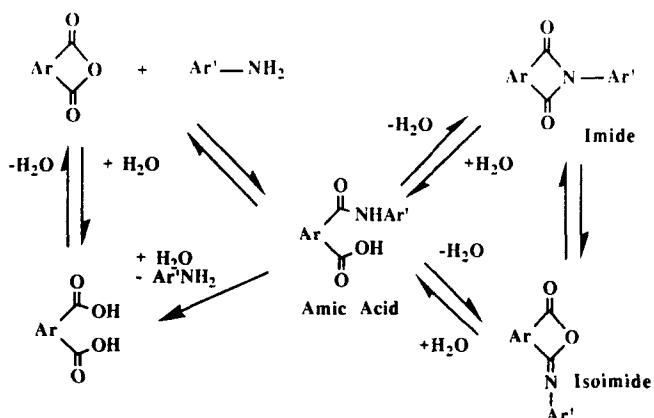
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Several fluorinated aromatic amic acid and imide model compounds and their intermediates were prepared and investigated in *N*-methylpyrrolidinone by ^{19}F and ^{13}C n.m.r. Starting materials included 4-fluoroaniline, 3-fluorophthalic anhydride, 2,2-bis(3,4-carboxyphenyl)hexafluoropropane dianhydride and 2,2-bis(4-aminophenyl)hexafluoropropane. The advantages of ^{19}F n.m.r. for studying amic acid and imide chemistry were numerous. Anhydride and amine starting materials, as well as amic acid, isoimide and imide compounds, were easily identified in the ^{19}F n.m.r. spectra. Isomeric contents of amic acid mixtures were directly measurable. Many unique aspects of polyimide chemistry, such as amic acid equilibria and imide interchange reactions, could be quantitatively identified. Data from ^{13}C n.m.r. and ^{19}F n.m.r. were related in many cases, as were the carbon-fluorine coupling constants.

(Keywords: polyimides; model compounds; ^{19}F n.m.r.)

INTRODUCTION

Polyimides have become attractive materials in many applications that demand high performance qualities of thermal, oxidative and chemical resistance¹⁻⁶. Since the discovery of a facile two-step synthetic method for the preparation of aromatic polyimides (PI) almost 30 years ago, concern has persisted due to the number of unknown variables associated with the chemistry of these polymers. The main reason for this concern has been the inability to distinguish between all of the possible species present in the reaction system (see *Scheme 1*). Thermal



Scheme 1 Possible reactions and equilibria for imide formation and/or degradation

or chemical conversion of the amic acid (AA) precursor results in a complex mixture of many different chemical species. Anhydride and amine starting materials reappear

due to AA equilibration and/or hydrolysis. Imide and isoimide groups begin forming with the liberation of water. Additionally, the anhydride formed may hydrolyse to the acid compound, which can eventually recycle to sufficiently high temperatures and again react with the free amine groups present. *Scheme 1* is in fact oversimplified in that all of the pathways illustrated are actually occurring on two sides of the macromolecular species, resulting in half imides/half amic acids, etc.

To better understand the chemical transformations taking place during imidization, several techniques have proved valuable. The main tool presently available for spectroscopically determining chemical species present in a poly(amic acid) (PAA) or PI reaction system is FTi.r.⁷⁻⁹. By the careful use of FTi.r., one can analyse the formation of anhydride or imide groups, and follow the imidization process; however, inconsistencies have arisen from the choice of observed FTi.r. bands and the effects of side reactions, solvent and other variables. Another tool available for imide and AA studies is u.v. spectroscopy¹⁰. Recently, u.v.-vis. absorption and fluorescence spectroscopy has shown the advantageous ability to follow several types of intermediates in the imidization process¹¹⁻¹⁵. Other promising analytical tools include potentiometric titration for calculating imidization conversion¹⁶ and high performance liquid chromatography (h.p.l.c.)¹⁷. Perhaps the most promising technique that has yet to find routine applications in the study of AA and imide chemistry is nuclear magnetic resonance (n.m.r.)¹⁸⁻²⁵. Reasons for its limited use include complex spectra for AAs, spectral interference due to the presence of solvents, uncertainties of peak identification and limited solubility of PIs.

The goal of this research was to shed further light on the solution chemistry of AA and imide materials using the technique of ^{19}F n.m.r. Several immediate advantages of this technique were obvious in advance. Studies could

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be performed in any solvent desired, with no spectral interference from the solvents. Industry has demonstrated a preference for *N*-methylpyrrolidinone (NMP) as solvent for PAA and, in the case of soluble PIs, for the final polymer. Utilization of an external lock solvent and fluorinated standards would allow the investigations to be carried out in an 'uncontaminated' NMP setting. ¹⁹F n.m.r. is a high-sensitivity technique (80–90% sensitivity of ¹H n.m.r.) where chemical shifts depend, to a large degree, on the chemical environment of the fluorine atoms²⁶. Although utilized in numerous studies, perhaps most notably in the well-known work of Taft *et al.* relating resonance and inductive effects in *p*- and *m*-substituted fluorobenzenes, respectively^{27,28}, surprisingly little has been published regarding use of this technique for the study of reaction mechanisms or pathways. Other studies have confirmed that ¹⁹F n.m.r. is uniquely suited for the study of isomer formation and other structural

information for nitrogen-substituted fluorobenzenes^{29–31}. Thus the fluorine atom can be viewed as 'a distant but sensitive observer removed from the confusion of the chemical battlefield by the rigid benzene ring'²⁷. We felt that by the careful selection of fluorinated aromatic model compounds and reaction conditions, AA equilibration and/or hydrolysis, imide hydrolysis and other possible side reactions could be identified. This initial report will discuss some of the model compounds prepared and their representative spectra. Applications of this technique will also be described.

EXPERIMENTAL

Instrumentation

Proton and ¹³C n.m.r. spectra were recorded on a Bruker AC 250 MHz instrument utilizing dimethylsulfoxide (DMSO-d₆) as solvent. Reported chemical shifts were

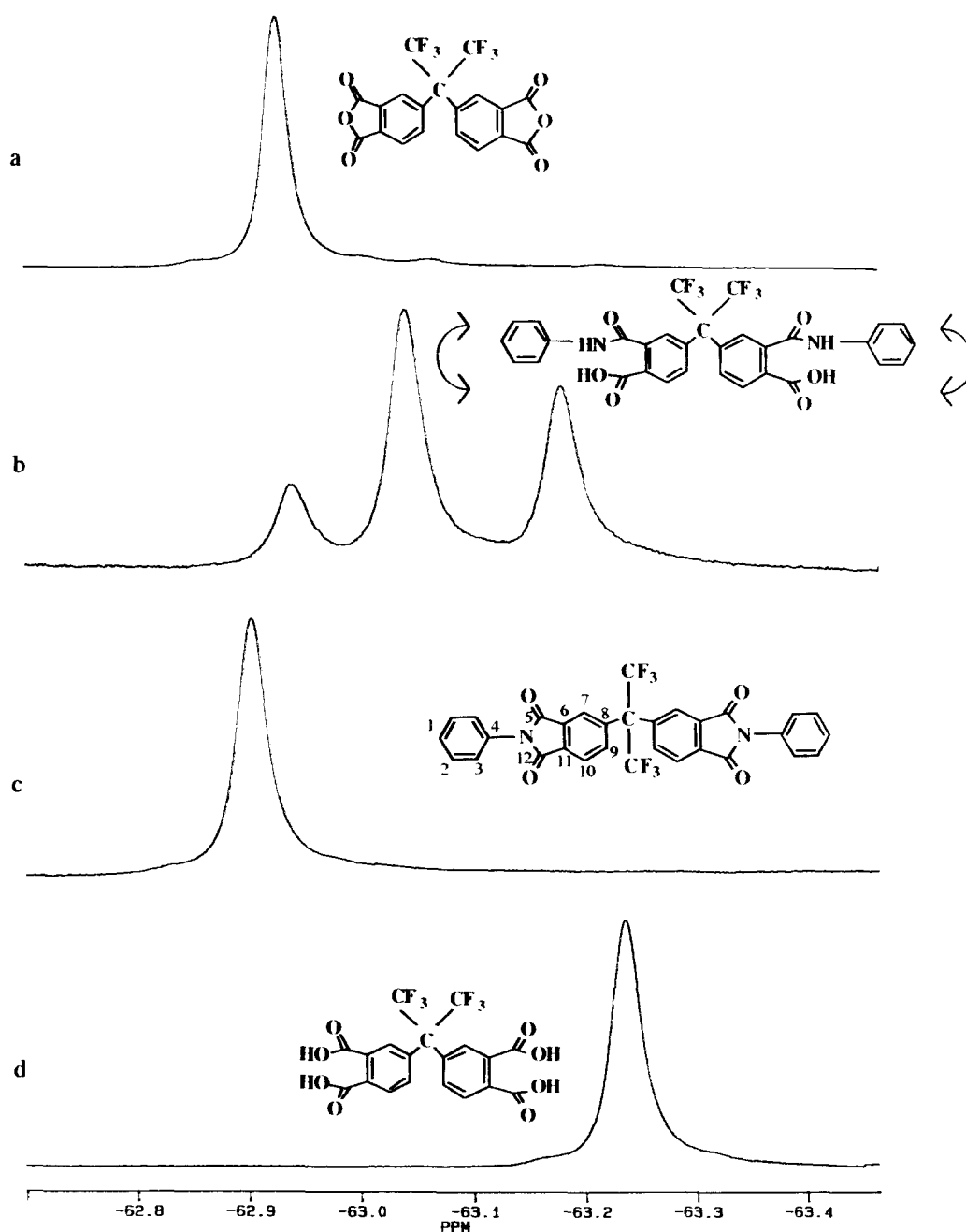


Figure 1 ¹⁹F n.m.r. spectra of 6FDA based model compounds: a, 6FDA; b, 6FDA/AN DAA; c, 6FDA/AN; d, 6FDA TA

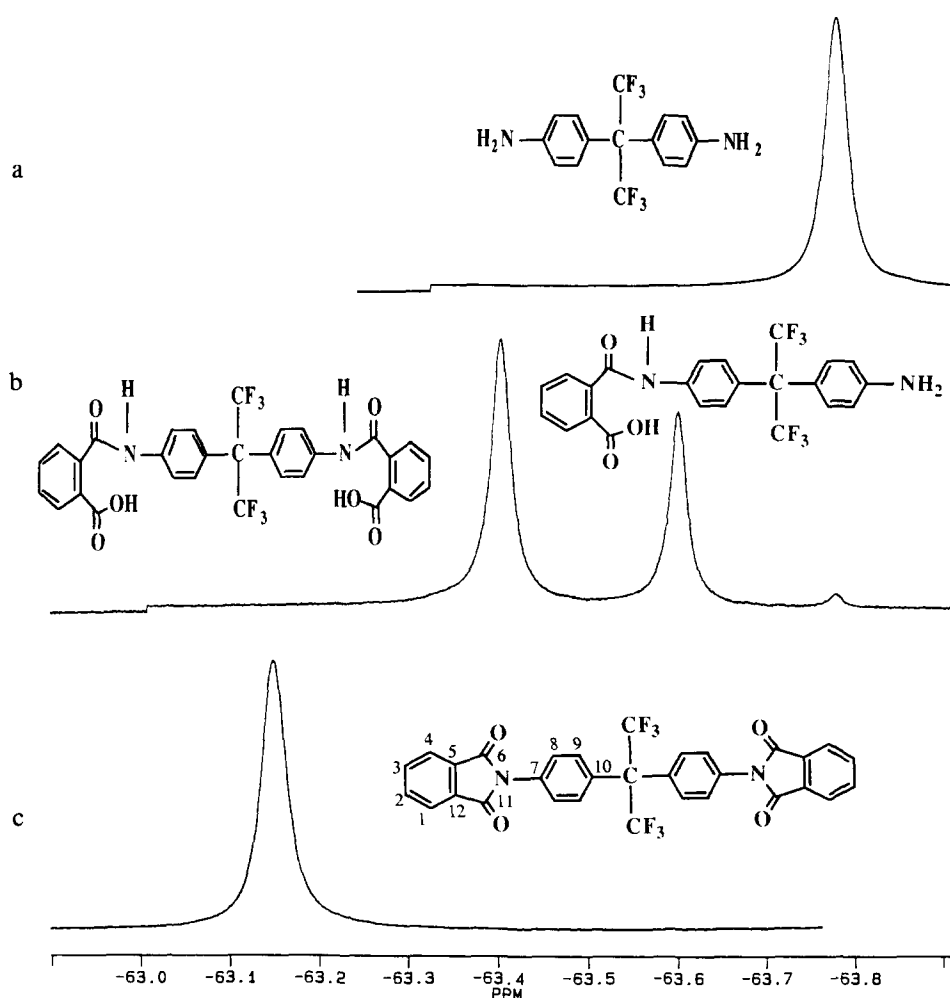


Figure 2 ¹⁹F n.m.r. spectra of 6FDM based model compounds: a, 6FDM; b, 6FDM/PA DAA mixture; c, 6FDM/PA

referenced to tetramethylsilane (TMS). Calculated chemical shifts were obtained by applying standard shift additivity rules and other data from simple models and from the literature³²⁻³⁸. Carbon numbers are indicated on the structures in Figures 1-4. ¹⁹F n.m.r. spectra were recorded on a Bruker AC 200 MHz instrument operating at 188 MHz using NMP as a sample solvent. All chemical shifts were referenced to CFCl₃. An external lock solvent (C₆D₆) was utilized by inserting a 4 mm n.m.r. tube containing the sample dissolved in NMP into a 5 mm n.m.r. tube containing a few drops of lock solvent. In all cases, a 90° (3.0 μs) pulse was applied 32 times with a delay of 2 s. Unless otherwise noted, 2% (weight/weight) solutions were utilized for study. Chemical shifts from ¹³C n.m.r. and ¹⁹F n.m.r. are listed in Tables 1 and 2 for the 4-fluoroaniline and 3-fluorophthalic anhydride models, respectively. Spin-spin coupling constants are given in Hz; ¹J(C, F) is normally taken to be a negative value³⁹.

Materials

All anhydride and amine compounds were of the highest quality commercially available. Aniline (AN) was distilled under reduced pressure; phthalic anhydride (PA) was sublimed and stored under anhydrous conditions. High quality NMP (BASF) was stored over molecular sieves. All other reagents were used as received from commercial sources as follows: 4-fluoroaniline (4-FA;

99%, Aldrich Chemical Co.); 3-fluorophthalic anhydride (3-FPA; Fluorochem Ltd); 2,2-bis(3,4-carboxyphenyl)-hexafluoropropane dianhydride (6FDA; monomer grade, Hoechst); 2,2-bis(4-aminophenyl)hexafluoropropane (6FDM; 99%, Chriskev Co., Inc.). Thin layer chromatography (t.l.c.) was performed on silica gel supported on glass plates with a mixture (1:1:1 by volume) of methanol, ethyl acetate and toluene. Imides were eluted with $R_f = 1$, half imide/half amic acids with $R_f \approx 0.75$ and (di)amic acids with $R_f = 0.33-0.50$.

Amic acids were prepared by two different methods. Stirring appropriate mixtures of amine and anhydride overnight in NMP yielded solutions of the desired AA suitable for ¹⁹F n.m.r. studies. For 4-FA/PA AA, 3-FPA/AN AA and 3-FPA/4-FA AA model compounds, the NMP synthesis was utilized as described above, and for ¹³C n.m.r. peak identification (Tables 1 and 2), the models were prepared in high yield (95%) in chloroform as described in the literature⁴⁰. Isomer composition for 3-FPA/AN AA and 3-FPA/4-FA AA was determined by ¹³C n.m.r. from measurement of peak heights of similar carbon atoms (Figure 5); from Figure 5a for 3-FPA/AN AA, it is clear that only one isomer was present, while the complexity of Figure 5b for 3-FPA/4-FA AA clearly indicated the formation of two isomers. Calculated shifts for the *m*-isomer of 3-FPA/AN AA are given below for reference and comparison with the *o*-isomer given in Table 2. Calculated

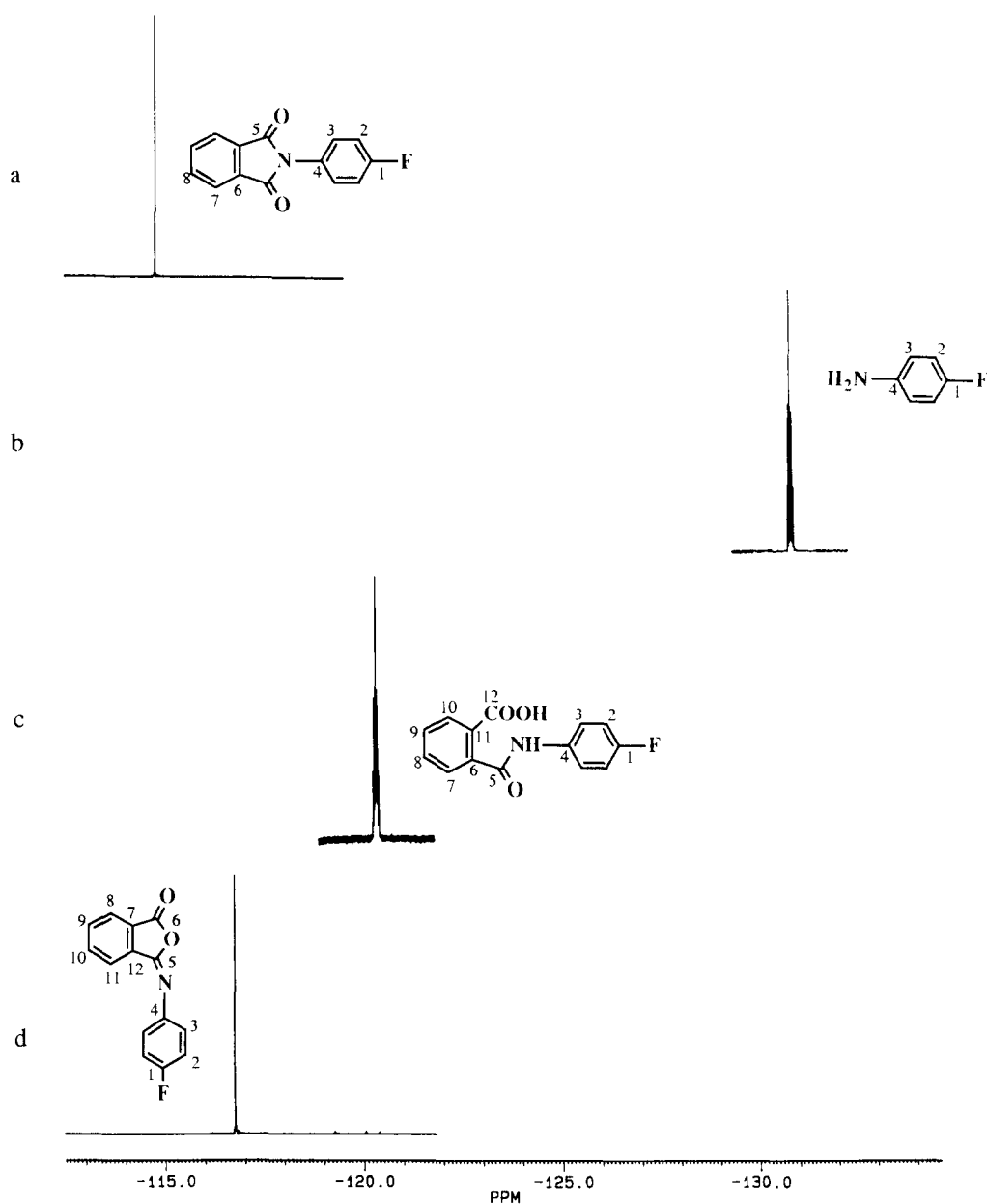


Figure 3 ¹⁹F n.m.r. spectra of 4-FA based model compounds: a, 4-FA/PA; b, 4-FA; c, 4-FA/PA AA; d, 4-FA/PA II

Table 1 ¹⁹F and ¹³C n.m.r. chemical shift data (ppm) for 4-fluoroaniline (4-FA) based models

Carbon no.	4-FA (-130.9) ^a			4-FA/PA AA (-120.3) ^a			4-FA/PA II (-116.8) ^a			4-FA/PA (-114.3) ^a		
	Calculated	Found	<i>J</i> (C, F)	Calculated	Found	<i>J</i> (C, F)	Calculated	Found	<i>J</i> (C, F)	Calculated	Found	<i>J</i> (C, F)
1	150.8	154.7	-230	158.3	158.2	-240	162.6	160.2	-243	163.0	161.5	-245
2	116.0	115.4	21.9	115.8	115.4	22.2	117.4	115.8	22.6	116.0	115.9	23.0
3	115.8	115.0	7.30	121.3	121.4	7.61	125.9	125.9	8.37	129.2	129.7	8.87
4	144.8	145.3	1.45	134.7	136.1	2.45	138.3	136.3	- ^b	128.3	128.3	2.58
5				167.6	167.5 ^c		144.8	140.6		167.2	167.1	
6				139.8	138.9		165.7	164.7		131.7	131.7	
7				128.0	128.0		129.3	127.7		123.6	123.6	
8				131.9	131.9		125.4	123.5		134.9	134.8	
9				129.5	129.6		134.3	133.9		134.9	134.8	
10				129.7	129.7		136.7	136.0		123.6	123.6	
11				130.1	130.1		127.0	125.4		131.7	131.7	
12				167.6	167.6 ^c		148.0	148.0		167.2	167.1	

^a Value in parentheses is ¹⁹F chemical shift

^b Not observed

^c Assignments possibly reversed

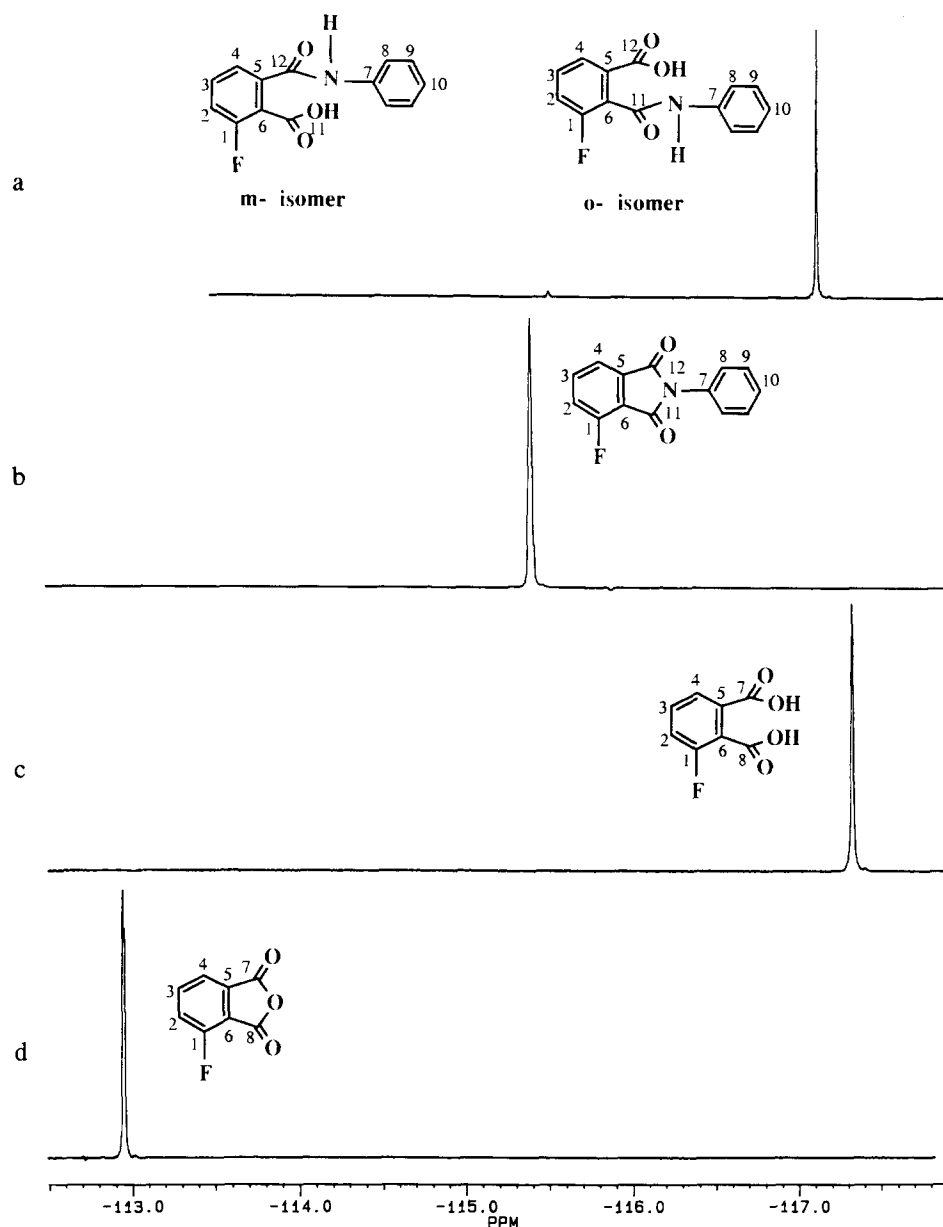


Figure 4 ¹⁹F n.m.r. spectra of 3-FPA based model compounds: a, 3-FPA/AN AA (*o*-isomer); b, 3-FPA/AN; c, 3-FPA DA; d, 3-FPA

Table 2 ¹⁹F and ¹³C n.m.r. chemical shift data (ppm) for 3-fluorophthalic anhydride (3-FPA) based models

Carbon no.	3-FPA (-112.9) ^a			3-FPA/AN (-115.4) ^a			3-FPA/AN AA (<i>o</i> -isomer) (-117.1) ^a			3-FPA DA (-117.3) ^a		
	Calculated	Found	<i>J</i> (C, F)	Calculated	Found	<i>J</i> (C, F)	Calculated	Found	<i>J</i> (C, F)	Calculated	Found ^b	<i>J</i> (C, F)
1	160.8	157.7	-264	158.4	157.1	-262	162.8	158.8	-245	163.4	158.4	
2	123.9	123.9	18.8	121.9	122.9	19.6	118.9	119.9	22.3	119.9	119.9	
3	138.5	139.7	8.18	136.5	137.9	7.92	131.1	131.0	8.49	134.5	125.8	
4	121.6	122.1	3.65	119.2	120.1	3.46	125.3	126.1	2.58	124.2	131.3	
5	133.7	133.7	- ^c	133.3	134.0	1.32	131.7	131.2	3.52	133.0	130.8	
6	119.1	118.2	13.3	118.7	117.6	12.3	126.8	127.3	20.5	118.4	124.8	
7				132.1	131.8		139.1	139.4				
8				127.6	127.6		119.7	119.5				
9				129.0	129.1		128.8	129.0				
10				128.2	128.5		123.8	123.8				
11				167.2	166.2 ^d		167.6	162.4 ^d				
12				167.2	164.0 ^d		167.6	166.1 ^d				

^a Value in parentheses is ¹⁹F chemical shift

^b Reference 36

^c Not observed

^d Assignments possibly reversed

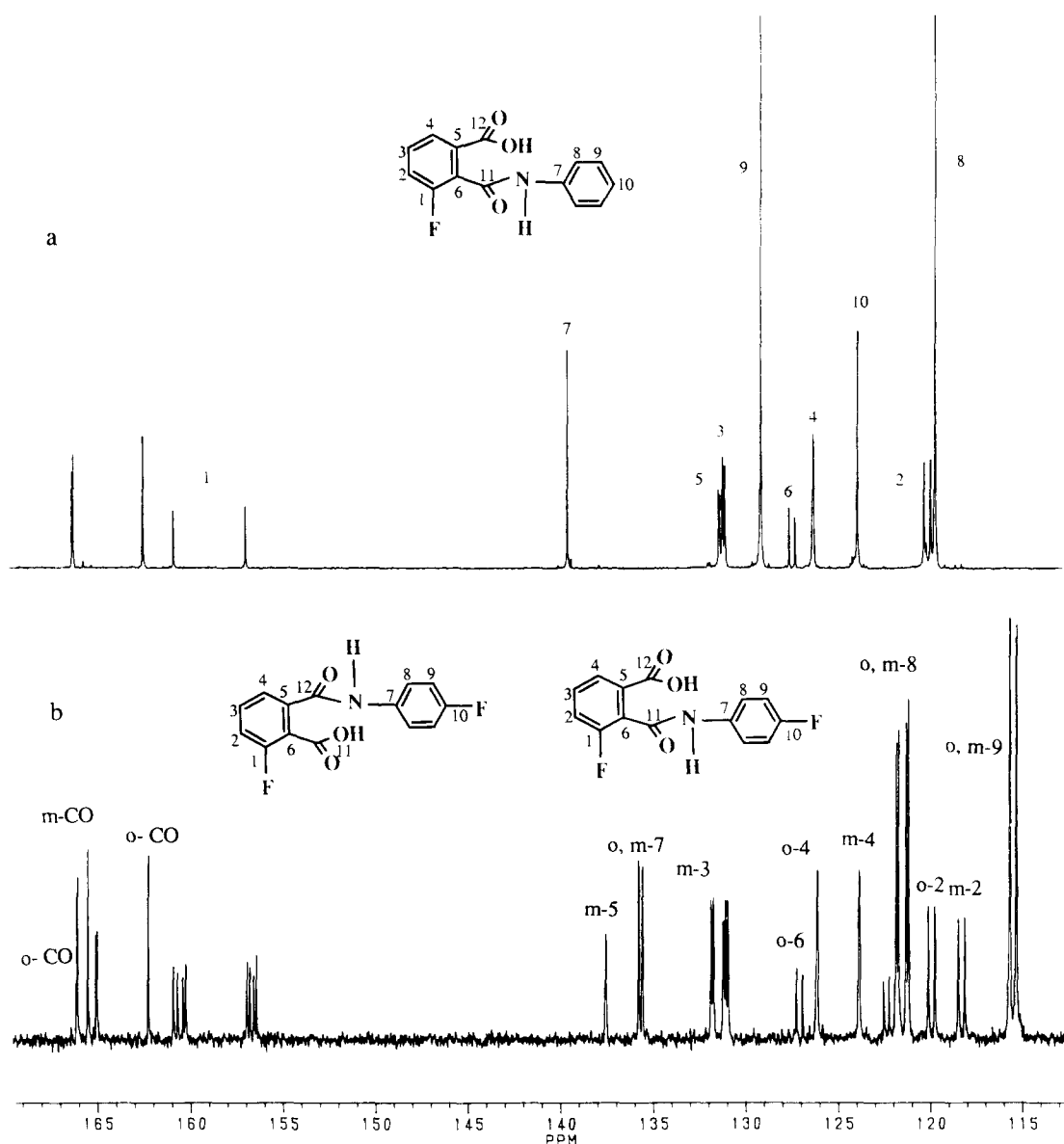


Figure 5 ¹³C n.m.r. spectra: a, 3-FP/AN AA (*o*-isomer); b, 3-FPA/4-FA AA isomer mixture

chemical shifts for 3-FPA/4-FA AA isomers were a composite of the 3-FPA/AN AA and 4-FA/PA AA values given in the tables and below.

3-FPA/AN AA (m-isomer). ¹³C n.m.r. calculated shifts: 1, (164.5); 2, (116.5); 3, (133.5); 4, (123.6); 5, (141.4); 6, (117.1); 7, (139.1); 8, (119.7); 9, (128.8); 10, (123.8); 11 and 12, (167.6).

Acid forms of the fluorinated anhydrides were prepared in NMP by stirring the anhydride overnight with excess water.

The isoimide of phthal(4-fluoro)anilic acid was prepared as described previously^{41,42}. It was isolated as an off-white solid with m.p. of 138–141°C. ¹H n.m.r. (DMSO-d₆): 8.00 (m, 4H); 7.35 (m, 4H).

A convenient method for the preparation of the imide models is outlined below. Into a three-neck round-bottom flask equipped with a nitrogen inlet, a magnetic stirrer, and a Dean–Stark trap with condenser were charged appropriate amounts of amine and anhydride dissolved in enough toluene for 10% (weight/volume) solids concentration. For the 6FDA/AN model imide,

azeotroping the mixture overnight was sufficient for complete conversion to imide by t.l.c. For all other imide models, heterogeneous solutions and little or no evolution of water were observed after refluxing for 1 h, thus, just enough dimethylacetamide (DMAC) was added to give homogeneous solutions. As soon as this point was reached (less than 1:5 DMAC:toluene by volume), immediate water evolution was noted in the Dean–Stark trap. Azeotroping was continued overnight or until no more AA was detected by t.l.c. For the 6FDA and 3-FPA models, the toluene solution was reduced to that volume where 50% solids existed, then cooled in the refrigerator overnight, yielding crystals of pure diimide. For PA/4-FA and PA/6FDM, the pure compound crystallized out of solution upon cooling. The models were collected by vacuum filtration and dried to constant weight at 120°C under reduced pressure. Typical yields were 80–90%. A summary of the imide models studied and characterization is given below.

6FDA/AN. M.p. 182–184°C (literature⁴³ 182.5–184.5°C). ¹H n.m.r.: 8.20 (d, 2H); 8.00 (d, 2H); 7.8 (s, 2H);

7.50 (m, 10H). ¹³C n.m.r.: 1, 128.5 (128.2); 2, 129.0 (129.1); 3, 127.7 (127.6); 4, 131.7 (131.9); 5 and 12, 166.2 and 166.3 (167.2); 6, 132.8 (131.9); 7, 124.5 (124.3); 8, 137.5 (137.5); 9, 136.0 (136.0); 10, 123.8 (123.8); 11, 133.2 (133.7); C-(CF₃)₂, 64.8 (septet); C-(CF₃)₂, 123.6 (quartet). ¹J(C, F) = -288 Hz, ²J(C, F) = 26 Hz. ¹⁹F n.m.r.: -63.32 (s). Analysis: calculated for C₃₁H₁₆F₆N₂O₄: C 62.63, H 2.71, F 19.18, N 4.71; found: C, 62.53, H 2.68, F 18.93, N 4.70.

PA/4-FA. M.p. 182.5–183.5°C (literature⁴⁴ 180–181.5). ¹H n.m.r. (DMSO-d₆): 7.90 (m, 4H); 7.50 (m, 2H); 7.30 (m, 2H). ¹⁹F n.m.r.: -114.27 (nonet). ¹J(H_o, F) = 8.7 Hz, ²J(H_m, F) = 5.0 Hz. Analysis: calculated for C₁₄H₈FNO₂: C 69.71, H 3.34, F 7.88, N 5.81; found: C 70.00, H 3.30, F 7.78, N 5.68.

PA/6FDM. M.p. 266–268°C. ¹H n.m.r.: 7.90 (d, 8H); 7.60 (q, 8H). ¹³C n.m.r.: 1 and 4, 123.0 (123.6); 2 and 3, 134.3 (134.9); 5 and 12, 131.1 (131.7); 6 and 11, 166.1 (167.2); 7, 133.0 (133.7); 8, 126.4 (127.9); 9, 129.8 (130.1); 10, 131.1 (130.8); C-(CF₃)₂, 65.1 (septet); C-(CF₃)₂, 124.4 (q). ¹⁹F n.m.r.: -63.72 (s). Analysis: calculated for C₃₁H₁₆F₆N₂O₄: C 62.63, H 2.71, F 19.18, N 4.71; found: C 62.73, H 2.87, F 19.05, N 4.70.

3-FPA/AN. M.p. 148–150°C (literature⁴⁵ 150–151°C). ¹H n.m.r.: 7.92 (m, 1H); 7.75 (m, 2H); 7.51 (m, 5H). Analysis: calculated for C₁₄H₈FNO₂: C 69.71, H 3.34, F 7.88, N 5.81; found: C 69.14, H 3.31, F 7.63, N 5.70.

RESULTS AND DISCUSSION

Model compound studies

Four types of fluorinated models were studied in NMP solution by ¹⁹F n.m.r. This section summarizes the results for each type of model, structures of which are illustrated in Figures 1–4. AA isomers are identified by the location of the amide groups with respect to the hexafluoroisopropyl or aryl fluoride moieties. Thus, the diamic acid (DAA) model of 6FDA with AN consists of three possible positional isomers (Figure 1c): *m,m*-, *p,p*- and *m,p*-, while for the AA model of 3-FPA with AN possibilities include *o*- and *m*-isomers (Figure 3b).

Models based on 6FDA. Four 6FDA-related compounds were studied. The dianhydride (6FDA), tetracarboxylic acid (6FDA TA) and AN based DAA (6FDA/AN DAA) and diimide (6FDA/AN) were prepared, and their respective ¹⁹F n.m.r. spectra measured (Figure 1). Each model, with the exception of DAA, displayed one signal, with the chemical shift moving upfield as those groups on the aryl rings became more polar in nature. Thus, the signal for the diimide appeared at -63.30 ppm and that for the tetracid at -63.63 ppm. One benefit of this technique is the ability to quantify the amounts of the three possible isomeric AA structures. Data from our ¹³C n.m.r. measurements and from current literature²⁵ suggest formation of the *p*-isomer in excess of the *m*-isomer, presumably due to the higher electrophilicity of the carbonyl group *para* to the 6F group. For the DAA model prepared in NMP at 2 wt% solids, the percentage of the three isomers from downfield to upfield was 14 (*m,m*): 39(*m,p*): 47(*p,p*), corresponding to 33% *m*- and 67% *p*-isomeric proportions.

Models based on 6FDM. Three models based on 6FDM species were studied in NMP solution. The diamine (6FDM) and PA based DAA (6FDM/PA DAA) and diimide (6FDM/PA) were synthesized and their ¹⁹F n.m.r. spectra measured (Figure 2). Both the diamine and the diimide spectra showed one peak as expected, but the DAA solution showed three peaks. Since only one signal was expected for this material, as only one isomeric species is formed, the peak furthest downfield (-64.40 ppm) was assigned to the DAA while the upfield signal (-63.18 ppm) was assigned as the half amic acid/half amine compound. The small signal at -64.35 ppm corresponded to the diamine remaining in solution. It is interesting to note that the hexafluoroisopropyl group is sufficiently deactivating to produce incomplete reaction with PA in NMP after 24 h at room temperature. The same chemical shift trend was noted as for the 6FDA series; specifically, as the groups *para* to the 6F group became less polar, the fluorine chemical shift moved downfield.

Models based on 4-FA. A series of four models related to 4-FA was studied. The amine (4-FA) and the PA based AA (4-FA/PA AA), imide (4-FA/PA) and isoimide (4-FA/PA II) were prepared and studied by ¹⁹F n.m.r. as illustrated in Figure 3. Well-separated chemical shifts were observed for this set of model compounds; a range of about 16 ppm between the amine and the imide was found. The chemical shift for each compound moved upfield as the group *para* to it became more electron-releasing in character. Decoupling of the fluorine signal from the aryl protons simplified each spectrum from a nonet (triplet of triplets, see Figures 3b and c) to a singlet (Figures 3a and d). The transmission of polar changes through bonds capable of transferring electron density (e.g. ether or in this case amide) resulting in large ¹⁹F n.m.r. shifts for aryl fluoride compounds has been recognized before³¹.

Such a large chemical shift range for these models compared to the 6F model compounds was expected, based on the electronic nature of the bonds through which electron density (as measured by ¹⁹F n.m.r. chemical shift changes) was being measured. For the 6F compounds, electron density is changing on the aryl carbon atom attached to the hexafluoroisopropyl group (carbon 8 for ¹³C n.m.r. values); however, no mechanism for the transferral of π electron density (the major contributor to ¹⁹F n.m.r. chemical shift changes) to the fluorine atoms is available. Thus only polar or inductive changes can be observed for the 6FDA system. On the other hand, for the 4-FA compounds, it is well known that ¹⁹F n.m.r. is a very sensitive tool for directly measuring electronic density changes brought about primarily by resonance effects for *p*-substituted fluorobenzenes, resulting in a broad array of ¹⁹F n.m.r. chemical shift values²⁷.

We have noted a trend between ¹³C n.m.r. and ¹⁹F n.m.r. chemical shifts, which becomes clear after reviewing Table 1. As the ¹⁹F n.m.r. chemical shift for each model moved downfield, the ¹³C n.m.r. chemical shifts for carbons 1 and 3 moved downfield as well, while carbons 4 moved increasingly upfield (with the exception of the isoimide). Such trends have been noted previously^{30,31}. The carbons 2, which cannot interact through resonance, were relatively unaffected by the change from amine through AA to imide. These data show the deshielding effects of acylation and imidization upon the nitrogen

lone pair. Interestingly, the carbon-fluorine coupling constants displayed trends for these transformations. The imide showed the highest coupling constants for all carbons, with decreasing values for each *J* value moving from isoimide to amine. Variation in *J* values increased with proximity to the carbon with which it was interacting.

Models based on 3-FPA. The final set of four models was based on 3-FPA. Included in this series of compounds were the anhydride (3-FPA), the diacid (3-FPA DA) and

the AN based AA (3-FPA/AN AA) and imide (3-FPA/AN). Similar to the 4-FA based models, a wide range of chemical shifts was observed for this sequence of models, with the ¹⁹F n.m.r. chemical shifts moving upfield with increasingly polar groups on the 3-FPA ring (Figure 4). A single signal was found in each decoupled spectrum. For the AA, two peaks were expected to be present since two different isomers were possible. Identification of each isomer was accomplished by preparing the AA from 3-FPA and AN and isolating it from chloroform. From the ¹³C n.m.r. spectrum, the

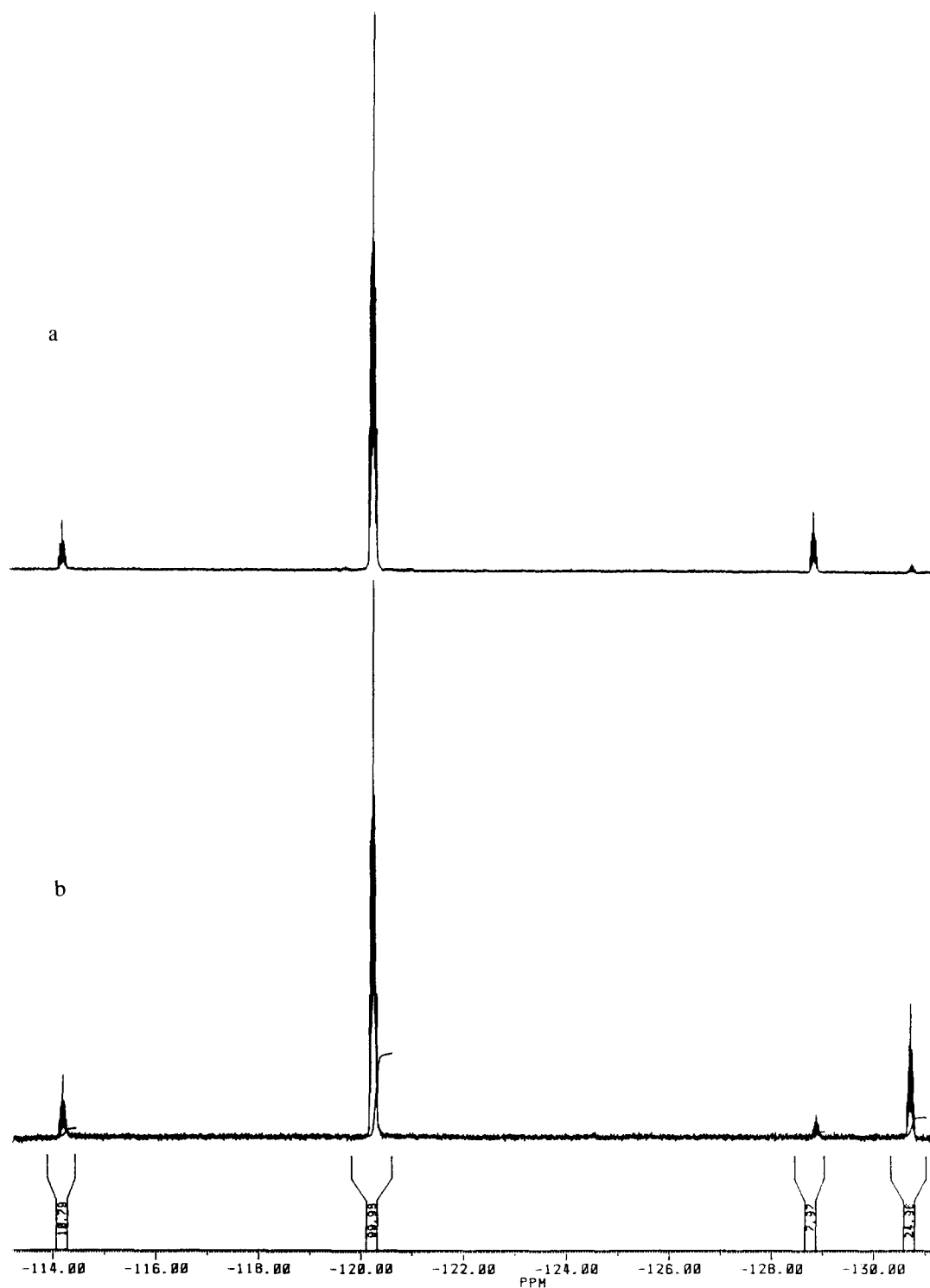


Figure 6 ¹⁹F n.m.r. spectra: a, 4-FA/PA AA heated in NMP at 90°C for 24 h; b, 4-FA/PA AA heated in NMP at 90°C for 24 h in the presence of 2% water

o-isomer was the sole isomer present (Figure 5a). Since fluorine is normally assumed to have electron releasing character (*ortho*, *para* director in electrophilic aromatic substitution), from simple resonance arguments the *m*-isomer should be present in excess. However, the ¹⁹F n.m.r. spectrum for the AA model synthesized in CHCl₃ was identical to the AA model prepared in NMP, indicating that the nature of electronic distribution in the 3-FPA part of the ring was such that *ortho* attack was highly favoured. A potential reason is the inductive electron withdrawing effect of the fluorine atom. We are presently investigating a range of 3- and 4-substituted PA starting materials and their AAs to further study the isomer distribution and its origin.

A correlation between ¹³C n.m.r. and ¹⁹F n.m.r. was not found for this set of model compounds. Since electronic density is being transferred through two sites (carbons 5 and 6), a mixture of effects can tend to enhance or eliminate normally observed trends. Steric and hydrogen-bonding phenomena can also interfere with any chemical shift correlations. Thus, unlike the 4-FA models, carbon 1 and the ¹⁹F chemical shifts showed no evident relationship.

Applications of ¹⁹F n.m.r. to imide and amic acid technology

Several phenomena unique to imide and AA chemistry are well suited for study by ¹⁹F n.m.r. Two representative applications are given below.

Amic acid equilibria. Several studies have recently confirmed the reversibility of the AA formation reaction^{14,17,46-53}; it has been known for some time that this reaction becomes quite important as the temperature of the system is raised^{54,55}. Thus upon heating a PAA solution, the multiple reactions shown in Scheme 1 become increasingly important. An important requirement for any technique studying these numerous reactions is the ability to quantify all of the species present simultaneously. Heating a 2% NMP solution of the 4-FA/PA AA model at 90°C overnight in air resulted in the coupled ¹⁹F n.m.r. spectrum shown in Figure 6a. Under these experimental conditions, a distribution of 83% AA, 2% amine and 6% imide resulted. The fourth peak in the spectrum at -128.9 ppm (9% of total signal) was due to a side reaction of the amine which was not eliminated by performing the reactions under nitrogen, suggesting that it is not a partially oxidized form of 4-FA. We have observed this same peak when solutions of AA based on 4-FA were reinvestigated after storage at room temperature in air for over 2 weeks. Since much less equilibration of AAs occur at room temperature, longer times were required for the observation of this peak at ambient conditions. This finding has implications for long-term storage of PAA materials, which we are currently investigating. Although it is known that equilibrated anhydride can hydrolyse to its acid form, thus shifting the equilibrium shown in Scheme 1 toward starting materials, side reactions of the liberated amine starting material can be another potential limiting reaction. The side reaction is possibly one with the solvent or an impurity in NMP, since we have observed this unknown compound in mixtures of NMP and 4-FA alone heated to 90°C for extended times.

An identical experiment to the above in the presence of water (2 wt%, corresponds to 13.4 mol water per AA group) gave significantly different results (Figure 6b). Both

more imide (10%) and more amine (16%) were formed, with the remaining composition 71% AA and 4% the unknown. The presence of much more amine than for the anhydrous sample can be explained by the rapid hydrolysis of any equilibrated anhydride. Formation of more imide than in the case of the anhydrous sample was probably due to catalysis of AA to imide transformation by the water present or by the hydrolysed product, phthalic acid. Organic aromatic and general acid catalysed imide formation is a known process⁵⁶.

Amic acid isomer composition. When a substituted anhydride or dianhydride is reacted with an amine (or diamine in the case of PIs), two or three isomeric species can be formed, respectively. In order to study the formation of different isomers and the factors that affect isomer distribution, several workers have studied AA formation by n.m.r. techniques^{17-23,25} or chromatography¹⁷. Quantitative analysis of such compositions is difficult by conventional ¹³C n.m.r. alone because of the complexity of the spectra, thus, isomer analysis is typically measured by ¹³C n.m.r. peak height measurements, which is not a particularly satisfying technique. While this technique has proved valuable for identifying the major isomer present in two isomer mixtures, only in certain cases has ¹³C n.m.r. proved valuable for quantifying three isomer compositions, due to the extreme complexity of the spectra.

Use of 6FDA model compounds allowed us to directly measure the composition of the three possible isomers in a dianhydride system, as discussed above. Although this is a valuable model study, quantitative analysis is somewhat difficult because of the lack of a suitable baseline between each signal in Figure 1b. Further studies on the 6FDA series of AAs will be reported in a future paper in this series.

The aromatic fluorine AA model compounds present a more attractive example for AA study. A brief discussion of the 3-FPA/4-FA AA synthesis is representative of this type of investigation.

Two possible isomers (structures shown in Figure 7) can be formed from the reaction of 3-FPA with 4-FA. Since only the *o*-isomer was formed for the 3-FPA/AN model compound, a single isomer was also expected in this, only slightly modified, case. However, upon formation of AA based on 3-FPA with 4-FA, two isomers were found in both NMP and chloroform reactions, as shown by the ¹⁹F n.m.r. spectra in Figures 7a and b, respectively. Two signals were observed for each type of fluorine atom, labelled as F₁ and F₂ for the anhydride and amine fluorine atoms, respectively. A 4.75:1 ratio of *o*- to *m*-isomers was formed in solution in NMP, while the ratio was 1.04:1 in chloroform where the product precipitated. The major isomer was the *o*-isomer in each case, as determined by ¹³C n.m.r. of the chloroform prepared AA (Figure 5b), and the location of the F₁ (*o*-isomer) peak which corresponded exactly to the ¹⁹F n.m.r. signal found for the 3-FPA/AN AA model compound *o*-isomer prepared in NMP, discussed previously. Note the complexity of this ¹³C n.m.r. spectrum compared to that in Figure 5a; peak identification was made simpler because chemical shifts of the pure *o*-isomer AA formed with AN were known from Figure 5a. Incidentally, the ¹⁹F n.m.r. chemical shift of the *m*-isomer F₁ for the 3-FPA/4-FA AA at -115.4 ppm was identical to the chemical shift for the

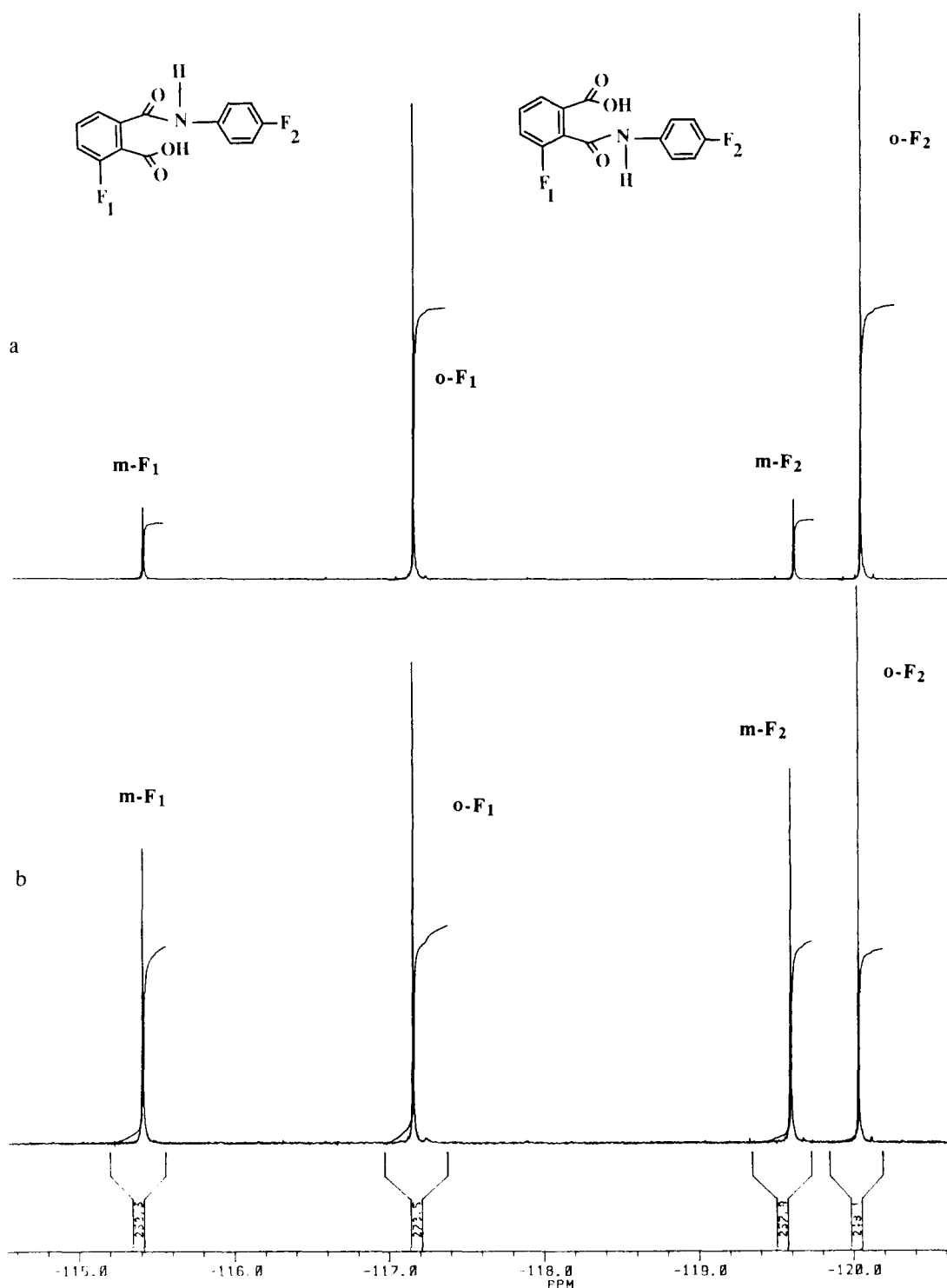


Figure 7 ¹⁹F n.m.r. spectra of 3-FPA/4-FA AA: a, prepared in NMP in homogeneous solution; b, prepared from precipitative reaction in chloroform

3-FPA/AN imide model compound; however, no signal was found corresponding to F₂ imide, and no imide was found to be present by ¹³C n.m.r. Since it has been reported that amine basicity does not affect isomer distribution^{21,22}, it was surprising to find that, in this case, the difference in amine basicity apparently did play a role, as did the solvent. We will present further data on this subject, as well as solvent role in isomer formation, in a forthcoming publication.

Other applications. Aside from following imide conversion from AA and isoimide starting materials, through the equilibrated species, this technique has

proved useful in our laboratories for a number of other applications. The isomer content of many fluorinated model and PAA materials in solution was directly measurable. Imide interchange has been observed in solution at high temperatures. Stability of imide and AA solutions under various conditions has also been studied by this technique. These and other uses of ¹⁹F n.m.r. will be described in a future paper of this series.

SUMMARY

¹⁹F n.m.r. has been found to be an extremely useful and versatile tool for the study of fluorinated imide and AA

model compounds in NMP solution. With the variety of types of possible fluorinated model compounds, and polymers as well, this technique is expected to yield many important results regarding AA and imide solution behaviour. The aromatic fluorine-containing models were especially important because of the ease of signal identification and separation of chemical shifts between chemically different starting materials, AA, imide and possible intermediates. The observed ¹⁹F n.m.r. chemical shifts changed with electronic differences at the aromatic carbon atoms; moreover, ¹⁹F n.m.r. and ¹³C n.m.r. data correlated in the 4-FA cases. Future reports from our laboratory will detail studies on many derivatives of related fluorinated AAs and imides.

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