ELSEVIER

Journal of Fluorine Chemistry 90 (1998) 39–46

JOURNAL OF FLUORINE CHEMISTRY

^{19}F NMR studies of the Diels–Alder adduct of *N*-pentafluorophenylmaleimide with phencyclone. Hindered rotation about a N–C_6F_5 bond

Kevin Bynum [a], Ron Prip [a], Ronald Callahan [b], Robert Rothchild [a,c,*]

[a] *The City University of New York, John Jay College of Criminal Justice, Science Department, 445 West 59th Street, New York, NY, USA*

[b] *New York University, Chemistry Department, Washington Place, New York, NY 10003, USA*

[c] *Doctoral Faculty, Graduate School and University Center, City University of New York, New York, NY, USA*

Received 4 December 1997; accepted 10 March 1998

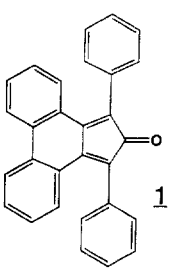
Abstract

N-pentafluorophenyl maleimide acts as an efficient Diels–Alder dienophile to form an adduct with phencyclone. The adduct was found to exhibit *five* distinct ^{19}F NMR signals (282 MHz, ambient temperature, $CDCl_3$) consisting of two gross doublets and three gross triplets. We interpret this as consistent with a severely hindered rotation about the N–C_6F_5 bond in the adduct, leading to a slow exchange limit (SEL) spectrum. The C_6F_5 group is thought to lie, on average, on the effective mirror plane of the adduct, perpendicular to the pyrrolidinedione ring system, to reduce steric interactions of the *ortho* fluorines with the imide $N(CO)_2$ carbonyls. ^{19}F–^{19}F COSY45 NMR allowed assignment of vicinal fluorines in the C_6F_5. Comparative data is presented for the precursors, *N*-pentafluorophenyl maleamic acid and *N*-pentafluorophenyl maleimide. Variable temperature ^{19}F NMR results for the maleamic acid are presented.

Keywords: Dynamic NMR; One- and two-dimensional NMR; ^{19}F–^{19}F COSY; Steric hindrance; Stereoisomers; Variable temperature NMR

1. Introduction

Recently, we have been investigating the ^1H, ^{13}C and ^{19}F NMR spectra for a series of Diels–Alder adducts derived from phencyclone, **1**, a potent diene for both normal and 'inverse electron demand' reactions [1]. We had observed that with medium field NMR (200 or 300 MHz for ^1H, 50 or 75 MHz ^{13}C), the *unsubstituted* bridgehead phenyls in the adducts exhibit slow exchange limit (SEL) spectra at ambient temperatures. Evidently, rotation about the $C(sp^2)$–$C(sp^3)$ bonds to the bridgehead C_6H_5 groups is considerably hindered. We have attributed most of this hindrance to non-bonded interactions between the *ortho* H-2′,6′ protons of the phenyls with the H-1,8 protons of the phenanthrenoid moiety in the adducts. We have described this for adducts of **1** with norbornadiene [2,3], 1,4-benzoquinone [4], maleic anhydride [5], *N*-*n*-propylmaleimide [6], *N*-*n*-butylmaleimide [7], *N*-carbamoylmaleimide [8], and 4-methyl-1,2,4-triazoline-3,5-dione [9]. These adducts not only exhibited SEL ^1H and ^{13}C NMR spectra, but also rather dramatic examples of magnetic anisotropy. For example, with *endo* stereochemistry in the adducts, some nuclei from the dienophile moiety were found to be strongly shielded, presumably the result of their location in the shielding region of the phenanthrenoid moiety. With the adduct from **1** and *N*-carbamoylmaleimide, we were also able to investigate potential hindered rotations of the carbamoyl group (N–CO–NH_2). We were interested in extending these NMR studies of anisotropic effects and hindered rotations to ^{19}F. The target compound that we selected would be obtained from Diels–Alder reaction of **1** with *N*-pentafluorophenylmaleimide, **2**. The preparation and ^{19}F NMR studies of the adduct, **3**, are the focus of this paper.



1

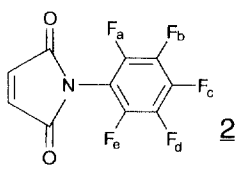
* Corresponding author. The City University of New York, John Jay College of Criminal Justice, Science Department, 445 West 59th Street, New York, NY 10019, USA.

0022-1139/98/$19.00
PII S0022-1139(98)00154-7

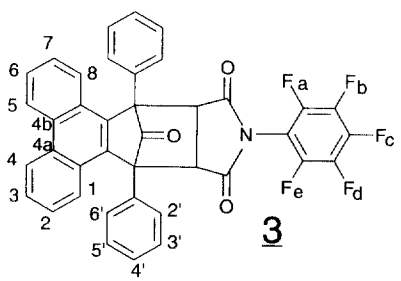
Table 1
Summary of 282 MHz ^{19}F NMR data

Nucleus				
a	b	c	d	e
Adduct, 3				
−143.51	−161.68	−151.22	−160.87	−143.86
dtd	tdd	tt	tdd	dtd
[22.3 ab; 6.8 ad,ae; 2.5 ac]	[21.9 ab,bc; 6.9 be; 1.6 bd]	[21.5 bc,cd; 2.6 ac,ce]	[22.0 cd,de; 6.7 ad; 1.6 bd]	[22.5 de; 7.0 ae,be; 2.8 ce]
N-pentafluorophenyl maleimide, 2				
−143.35	−161.14	−151.40	−161.14	−143.35
m	m	tt	m	m
		[21.5 bc,cd; 2.1 ac,ce]		
N-pentafluorophenyl maleamic acid, 5				
−144.14	−162.94	−157.46	−162.94	−144.14
m	m	t	m	m
		[22.9 bc,cd]		

For each compound, data are presented as: chemical shifts in ppm relative to $CFCl_3$ internal standard at 0.0 ppm (negative values); apparent multiplet structure in order of decreasing observed splittings (d = doublet, t = triplet, m = multiplet); apparent J values and assignments [in square brackets]. Couplings are believed accurate to within 0.2 Hz. Data for **2** and **3** were in $CDCl_3$; data for **5** were obtained in d_6-DMSO, all at ambient temperature. See Section 3. Data taken (in part) from Ref. [10] through the courtesy of Marcel Dekker.



2



3

2. Experimental

NMR data were obtained with a Bruker ACF300 spectrometer with Aspect A3000 data system and array processor using the 5-mm QNP 'quad' nuclear probe and B-VT 2000 temperature controller. ^{19}F NMR were acquired at an observe frequency of ca. 282 MHz. Standard Bruker microprograms were ordinarily used. For ^{19}F NMR, $CFCl_3$ was used as internal standard (at 0.00 ppm). Spectra were first acquired with a wide spectral window (low resolution) encompassing both $CFCl_3$ and sample resonances to accurately define ^{19}F sample shifts relative to the $CFCl_3$. The ^{19}F NMR spectra were then reacquired with a narrower spectral width, covering only the solute ^{19}F signals (not $CFCl_3$) to achieve fine digital resolution (ca. 0.5 Hz) and observe multiplet fine structure. Solvents and chemical reagents were obtained from Aldrich Chemical (Milwaukee, WI) and used without further purification. IR data were obtained on a Perkin-Elmer 1640 FTIR with DTGS detector at 2 cm^{-1} resolution, using 3M disposable type 61 polyethylene IR cards; selected peaks are reported. Melting points are uncorrected. Full extended details of syntheses, purification and characterization, particularly with respect to data for IR and one- and two-dimensional NMR (for ^1H and ^{13}C) appear elsewhere [10]. ^{19}F NMR data are presented in Table 1.

2.1. Synthesis of N-pentafluorophenyl maleamic acid, 5

To a solution of maleic anhydride (0.559 g) in 6 ml CH_2Cl_2 was added $C_6F_5NH_2$ (1.054 g) with stirring. More CH_2Cl_2 was added to a final volume of ca. 55 ml and the mixture was boiled for 5 min. Solvent removal gave a yellow oil that crystallized to an off-white solid of crude **5** (1.549 g, 97.7%) used directly for the next step. The mp (dec) 95–100°. IR: 1712.6, 1525.7, 1506.0, 1004.0, 965.6, 853.2.

2.2. Preparation of N-pentafluorophenylmaleimide, 2

A mixture of the crude maleamic acid, **5** (1.374 g), anhydrous sodium acetate (0.180 g) and acetic anhydride (2.01 g) was heated for 25 min in a boiling water bath, giving a dark red liquid which became semisolid on cooling to room temperature. After 1 week, the mixture was washed with dilute aqueous HCl and extracted into ether. The ether layer was washed with diluted HCl, saturated aqueous $NaHCO_3$, and H_2O, and dried (anhydrous Na_2SO_4).

Solvent removal gave crude tan solid **2** (1.079 g, 83%) with mp 79–85°, used without further purification. IR:

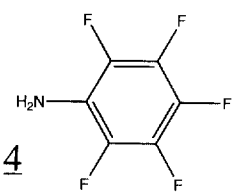
1734.2, 1525.3, 1374.1 (shldr), 1361.7, 1297.7, 1143.4, 1070.2, 1049.9, 985.8, 822.0, 726.8, 694.8, 641.9.

2.3. Preparation of Diels–Alder adduct, 3, from phencyclone and N-pentafluorophenyl maleimide

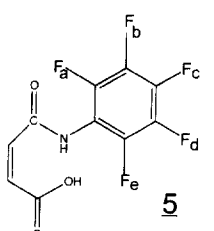
To 451 mg (nominal 1.71 mmol) crude **2** in 15 ml CH_2Cl_2 was added 158 mg **1** (0.413 mmol). The intense green–black phencyclone color was largely discharged after 2 h stirring, giving a clear yellow solution. After standing ca. 3.5 weeks, partial solvent removal and addition of hexane gave the adduct, **3**, 257 mg (0.398 mmol, 96% based on phencyclone) after filtration and drying, mp 214–216°. This material was used for spectral studies. IR: 1794.4 (bridging ketone CO), 1736.0 (shldr), 1732.6 (NCO), 1524.0 and 1519.5 (doublet), 1448.4, 1359.9, 1301.8, 1178.7, 993.7, 772.9, 754.6, 724.5, 698.0, 634.1.

3. Results and discussion

A straightforward synthetic route to the desired adduct, **3**, was employed, analogous to that followed for other phencyclone adducts. Pentafluoroaniline, **4**, was added to maleic anhydride to give the *N*-pentafluorophenyl maleamic acid, **5**. Cyclodehydration of **5** with acetic anhydride and sodium acetate gave the *N*-pentafluorophenylmaleimide, **2**. This maleimide added readily to phencyclone to generate the adduct, **3** (excess maleimide can be used to assure quick, complete consumption of **1** since unconsumed **2** is quite soluble and easily separated from the less soluble adduct).



4



5

The structure of the adduct, and the expected hindered rotation of the bridgehead phenyl groups for **3**, were confirmed by the SEL ^1H and ^{13}C NMR spectra at 300 and 75 MHz, respectively, at ambient temperatures. These data are presented separately [10]. However, we were surprised to find that the 282 MHz ^{19}F NMR spectrum for the adduct **3** exhibited *five* separate signals, as shown in Fig. 1. The low resolution ^{19}F spectrum (not shown) indicated two gross doublets at low field, attributed to the *ortho* fluorines of the C_6F_5 group in **3**, two gross triplets to high field, assigned to the *meta* fluorines, and a third triplet at intermediate shift, assigned to the *para* fluorine. The high resolution spectrum in Fig. 1 reveals the extensive fine structure of these multiplets. The presence of five fluorine resonances can be explained as a result of hindered rotation about the N–C_6F_5 bond due to non-bonded repulsions between the two imide carbonyls $N(CO)_2$ and the *ortho* fluorines of the pentafluorophenyl group, causing the C_6F_5 to exhibit an SEL ^{19}F NMR spectrum. Thus, the C_6F_5 ring could be considered to be, on average, perpendicular to the plane of the pyrrolidinedione ring, and would effectively lie on the mirror plane of the adduct. Because of the asymmetry in the adduct, one vicinal pair of fluorines, e.g., F(a) and F(b), would be in a different environment than the F(d) and F(e) pair, since one pair would be *syn* to the phenanthrenoid moiety and the other pair would be *anti*. (The ^1H and ^{13}C NMR spectra of adduct **3** were perfectly consistent with the presence of the mirror symmetry plane and with hindered rotations and SEL regimes due to slow bridgehead phenyl rotation. Note that the ^1H decoupled ^{13}C spectrum of **3** did not give detectable signals for the C_6F_5 carbons due to extensive splitting produced by the fluorines.) Our Referee has suggested that the pentafluorophenyl ring conformation may be 'canted' rather than truly perpendicular to the pyrrolidinedione ring. While this is true, it should be noted that a non-perpendicular orientation of the C_6F_5 ring (relative to the pyrrolidinedione ring) as a relative energy minimum would not produce a structure with a mirror plane of symmetry (sigma plane). The ambient temperature ^1H and ^{13}C NMR spectra for adduct **3** clearly indicate, by their simplicity, that a mirror plane must be present, *at least with respect to the effective NMR time scale* [10]. The presence of an *effective* mirror plane of symmetry in **3** could be consistent with a canted, non-perpendicular orientation of the C_6F_5 ring *only if there was rapid interconversion on the NMR time scale* between a pair of enantiomeric 'canted' conformations. Since an individual 'canted' conformation would be chiral, this required process would be equivalent to an enantiomerization. We simplistically may characterize the C_6F_5 ring conformation as being, effectively, a time-averaged perpendicular orientation. With this C_6F_5 conformation defined for **3**, we were interested in comparing ^{19}F shifts in **3** and the precursor maleimide **2**, as well as the maleamic acid **5**. *Endo* stereochemistry for adduct **3** would suggest that one of the vicinal *ortho*/*meta* pairs of fluorines *syn* to the phenanthrenoid moiety could be subject to anisotropic shielding.

To confirm assignments of vicinal fluorines in **3**, the 2D ^{19}F–^{19}F homonuclear chemical shift correlation experiment was performed as the COSY45 spectrum (Fig. 2).

Unexpectedly, the lower field *ortho* signal was found to correlate with the higher field *meta* signal (and the higher field *ortho* [gross doublet] correlated with the lower field *meta* [gross triplet] signals). This was surprising since it

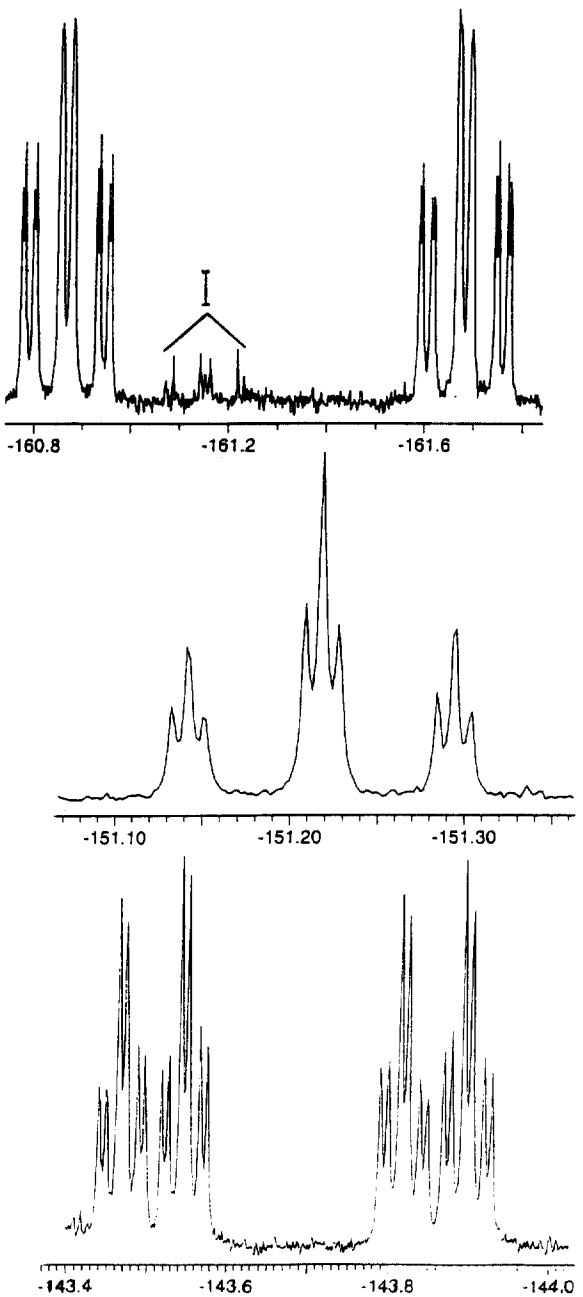


Fig. 1. The ^{19}F NMR spectrum of adduct **3** (282 MHz) in $CDCl_3$ at ambient temperature. Bottom trace: *ortho* fluorines, dtd, F(a) at left, F(e) on right; middle trace: *para* F(c), tt; top trace: *meta* fluorines, approx. tdd, F(d) at left, F(b) on right [I denotes impurities]. Note: Reprinted (in part) from Ref. [10] through the courtesy of Marcel Dekker.

suggested that the *syn* vicinal pair of fluorines were *not* both being anisotropically shielded, but that they were experiencing shifts in opposite directions. For **3**, the five fluorine signals were analyzed as a pseudo-first order ABCDE system. Key coupling constants (as apparent J values) were extracted from the *para* F(c) triplet of triplets to obtain the ^3J (vicinal) couplings F(b/c) and F(c/d), and the ^4J couplings F(a/c) and F(c/e). The vicinal couplings were assumed to be the largest for the C_6F_5 moiety. The shifts and observed couplings (apparent J values) are summarized in Table 1. For the pre-

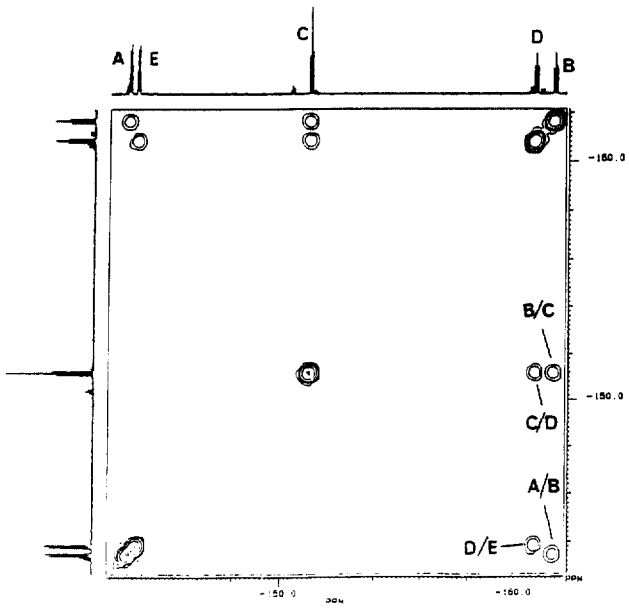


Fig. 2. The ^{19}F–^{19}F COSY45 spectrum of adduct **3** (consecutive letters for labeling of fluorines refer to vicinal fluorines on the C_6F_5 ring). A spectral width of 5556 Hz was used in F2. The magnitude mode spectrum was acquired with 64 increments in t_1, zero-filling once in both F1 and F2 to a final data matrix size of 128×256, using unshifted sine-bell apodization in both dimensions, and symmetrized. Crosspeaks are labeled to indicate correlated fluorines. See note in Fig. 1.

cursor maleimide **2**, with spectrum shown in Fig. 3, only three (complex) multiplets are seen in the ^{19}F NMR in 2:1:2 intensity ratios. Since steric factors between the C_6F_5 and the imide carbonyls should be similar in both **2** and **3**, we assume that slow C_6F_5 rotation is present in **2**, as well, but that high symmetry in **2** results in an AA'BB'C spectrum. Shifts for **2** are included in Table 1 for comparison with **3** since both compounds were adequately soluble in $CDCl_3$. Multiplet complexity for **2** did not allow full elucidation of F–F couplings. (The maleamic acid **5** had severely limited solubility in $CDCl_3$; shift data in Table 1 were acquired in different solvent and cannot be directly compared to the data for **2** and **3**.) The apparently simple multiplet structure for the signals of **3** allowed us to extract tentative observed coupling constant magnitudes (apparent J values). Thus, the *para* F(c) appeared as a triplet of triplets, suggesting near-isogamy (equal couplings) for the ^3J vicinal couplings bc and cd, of 21.5 Hz, and for the ^4J 'W' couplings ac and ce, of 2.6 Hz. Nucleus F(a) appeared as a dtd pattern, from which the ^3J ab coupling of 22.3 Hz was assigned. The narrower doublet subspectrum was assignable to ^4J (ac), ca. 2.5 Hz. This leaves us with accidental isogamy of ^4J (ae) and ^5J (ad) of 6.8 Hz to account for the triplet subspectrum. The F(b) appearance as a tdd multiplet is explained by essentially equal ^3J vicinal couplings, (ab) and (bc), of 21.9 Hz. Since the ^5J (ad) coupling of 6.8 Hz had been determined from the F(a) resonance, a ^5J (be) coupling of 6.9 Hz was attributed to the F(b) multiplet. This leaves only the ^4J coupling (bd) of 1.6 Hz to account for the narrow doublet subspectrum in the F(b)

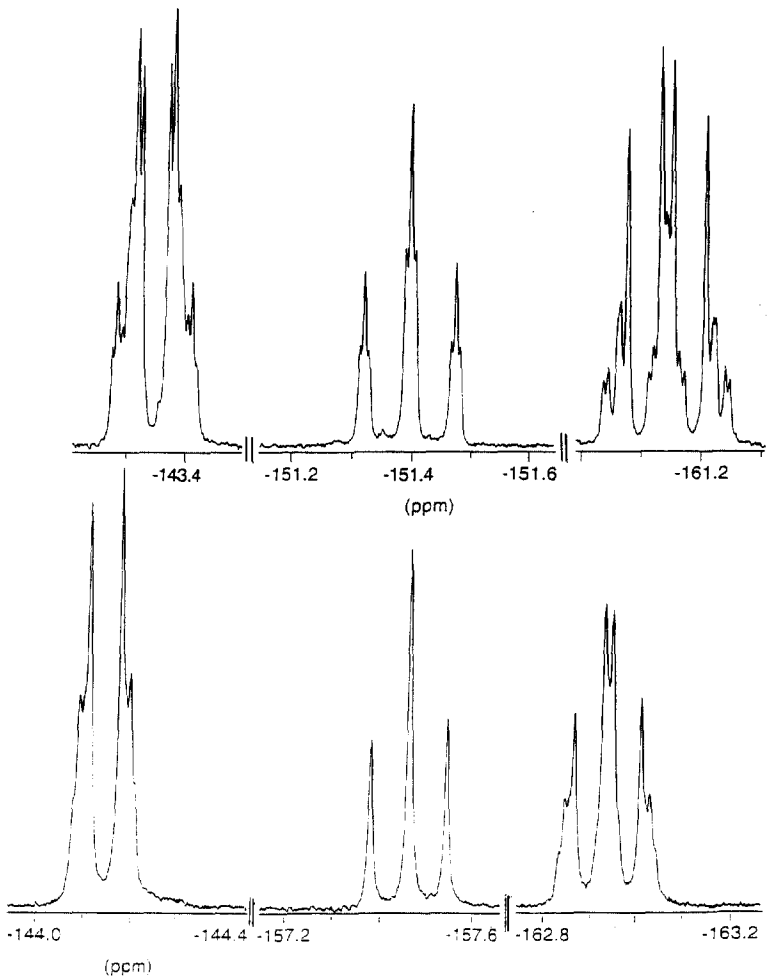


Fig. 3. (a) Upper trace: ^{19}F NMR spectrum of maleimide **2**, *ortho:para:meta* resonances (left to right) in 2:1:2 area ratios. Reprinted from Ref. [10] through the courtesy of Marcel Dekker. (b) Lower trace: ^{19}F NMR spectrum of maleamic acid **5** (in d_6-DMSO, 293 K), assignments as in Fig. 3a caption. Note: For each spectrum, chemical shift axes (ppm/cm) and vertical axes are uniform between the three expanded regions.

splitting pattern. Similar reasoning provides the remaining assignments, summarized in Table 1.

^{19}F shift comparisons of the adduct, **3**, with the maleimide, **2**, were surprising. We had expected that the vicinal *ortho/meta* pair *syn* to the phenanthrenoid moiety in the adduct might both be anisotropically shielded relative to the maleimide. The *para* F(c) of **3** was 0.18 ppm downfield of the corresponding signal in **2**, and the *meta* F(d) of **3** was 0.27 ppm downfield. However, the three remaining signals in **3** were all at higher field than in **2**, by 0.16 ppm for F(a), 0.51 ppm for F(e), and 0.54 ppm for F(b). The F(d,e) pair in **3**, shown to be vicinal by the F–F COSY45, were thus shifted in opposite directions. For the vicinal pair F(a,b), although both are shielded relative to **2**, the *ortho* F(a) shows a lower magnitude of shielding. If the a,b pair were *syn* to the phenanthrene group in **3**, F(a) might be expected to have the larger degree of shielding if it were positioned closer within the shielding cone of the central phenanthrene ring (see below). If the vicinal d,e pair were *syn*, the larger shielding magnitude for F(e) could be explained, but the deshielding of F(d) would seem to require critical anisotropic geometries, in which F(e) would be in the shielding cone and F(d) just outside the shielding cone, within the presumed deshielding region. Alternatively, we might suggest that F(a,b) are the *syn* fluorines, both anisotropically shielded, but with F(a) shielding partially cancelled due to close contact with the phenanthrenoid moiety. Figure 4 gives representations of **3** (via CS Chem3D) in which the *endo* adduct stereochemistry is shown, with a C_6F_5 conformation lying in the adduct mirror plane, perpendicular to the phenanthrene plane. The proximity of the *syn ortho* fluorine is quite clear. An approximate distance of ca. 3.17 Å from this fluorine to the closest quaternary phenanthrene carbons (C-4a,4b, phenanthrene numbering) was obtained from CS Chem3D, assuming that the C_6F_5 ring is essentially perpendicular to the pyrrolidinedione moiety. This calculated CF distance is actually close to the sum of the van der Waals radii for the fluorine and aromatic carbon. Thus, values of 1.35 Å for fluorine, and 1.70 or 1.85 Å for the 'half-thickness' of an aromatic ring (nucleus, molecule) have been given [11,12]. (The value for the aromatic carbon may be taken as half the distance separating the layers in graphite; an effective thickness for the ring in aromatic

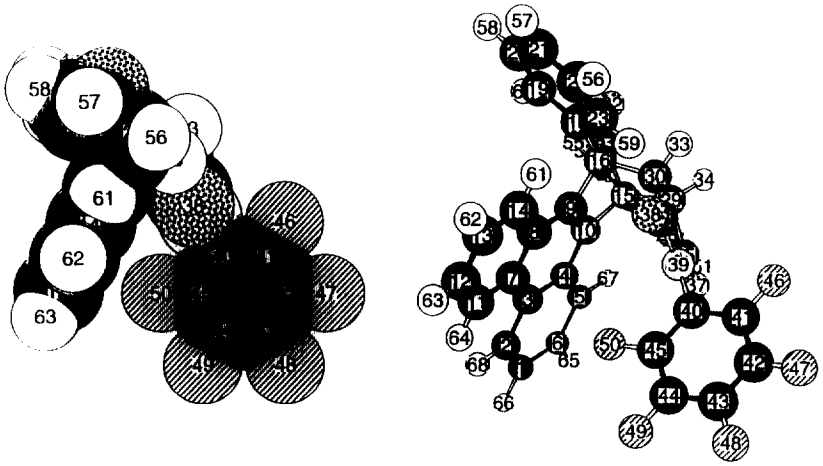


Fig. 4. Representative structure for adduct **3** (obtained from CS Chem3D) with C_6F_5 ring shown perpendicular to phenanthrenoid moiety, for *endo* stereochemistry (the bridgehead phenyls have arbitrarily been positioned roughly perpendicular to the phenanthrenoid portion). The *ortho* fluorine *syn* to the phenanthrene group (atom no. 50) is ca. 3.1 Å from the quaternary carbons 4a, 4b (phenanthrene system numbering; atom nos. 3 and 7 in illustrated structure). The space-filling representation shows a view along the axis perpendicular to the plane of the C_6F_5 ring, with the phenanthrene moiety seen 'edge-on'.

compounds [such as anthracene] of about 3.4 Å gives essentially the same value, 1.7 Å, for the van der Waals radii of the aromatic carbons [11].) The sum of these values for F and C, ca. 3.05–3.2 Å, is near that calculated for adduct **3**. It is, therefore, possible that this crowded *syn* ortho fluorine is subjected to deshielding from the van der Waals effect by steric compression [13], partially counteracting anisotropic shielding effects from the phenanthrenoid moiety.

The ^{19}F NMR spectra of the *N*-pentafluorophenyl maleamic acid, **5**, in d_6-DMSO (ambient temperature) showed rather broad signals, and variable temperature studies were performed from 293–353 K. Unusual temperature dependence in the NMR was noted. For each of the three resonances, i.e., gross doublet at lowest field, ca. −144 to −145 ppm [*ortho* F(a,e)], clean triplet at intermediate field, ca. −157.5 to −158.5 ppm [*para* F(c)], gross triplet at highest field, ca. −163 to −164 ppm [*meta* F(b,d)], the signals modestly broadened and then re-sharpened as temperature was increased from ambient. However, gross multiplicity (doublet vs. triplet structure) did not change, and the three resonances remained as three signals with unchanged area ratios. Each resonance moved slightly upfield, monotonically, with increasing temperature, with each 10° step moving the *ortho* signals ca. 0.10 ppm, the *para* signal ca. 0.18 ppm, and the *meta* signals ca. 0.17 ppm. From 293 to 353 K, the F(a,e) absorption moved from −144.14 to −144.76 ppm; F(c) moved from −157.46 to −158.53 ppm; F(b,d) moved from −162.94 to −164.02 ppm. Maximal broadening appeared to be around 313–323 K for F(c), around 313 K for F(b,d), and around 323–333 K for F(a,e). Results are shown in Fig. 5. A rigorous explanation for this phenomenon is not obvious to us. Because increasing temperature over the range studied produced *neither* coalescence from five fluorine signals to three, *nor* a monotonic sharpening of fluorine signals, we suggest that the rate process(es) being observed are *not* primarily associated with hindered rotation about the N–C_6F_5 bond. Originally, we thought that N–C_6F_5 rotation in **5** should have much lower energy barriers than in **2** or **3**, since the *ortho* fluorines in **5** are 'flanked' by only one amide carbonyl. Indeed, it is possible that the C_6F_5 may be coplanar with the amide system to benefit from resonance delocalization. If this were the case, and C_6F_5 rotation were slow, five fluorine signals might result. But if coplanarity of the C_6F_5NHCO system were accompanied by fast C_6F_5 rotation, the resulting FEL spectrum would show only three fluorine absorptions, and might not be distinguishable from the SEL regime with an energy minimum associated with orthogonal amide and C_6F_5. Our Referee has suggested that coplanarity of the amide with the C_6F_5 ring might be unrealistic for steric reasons. If the conformation corresponding to a relative energy minimum is neither coplanar nor perpendicular, but is skewed, five non-equivalent fluorines can result, particularly if the lifetime of the conformation is relatively long on the NMR time scale. For the non-planar skewed conformation, fast interconversion between chiral rotamers would be an enantiomerization (a process which could result in simplification to an AA'BB'C system for the fluorines, depending on magnitude and sense of C_6F_5 rotation in moving between skewed rotamers). We assume a preferred conformation for the secondary amide group of **5** in which the NH is *anti* to the amide CO. However, conformational dynamics in **5** might be extremely complex, with hindered rotations associated with the bonds from the alkene moiety to both the carboxamide and carboxylic acid carbonyls, in addition to N–C_6F_5 and possible HN–CO rotamers noted above. Intramolecular H-bonding may also play a role. An early review of NMR studies of amides and related compounds has presented useful discussions of amide conformations and anisotropy [14]. Several excellent recent treatises on general aspects of dynamic NMR and hindered rotations have appeared, such as Ref. [15].

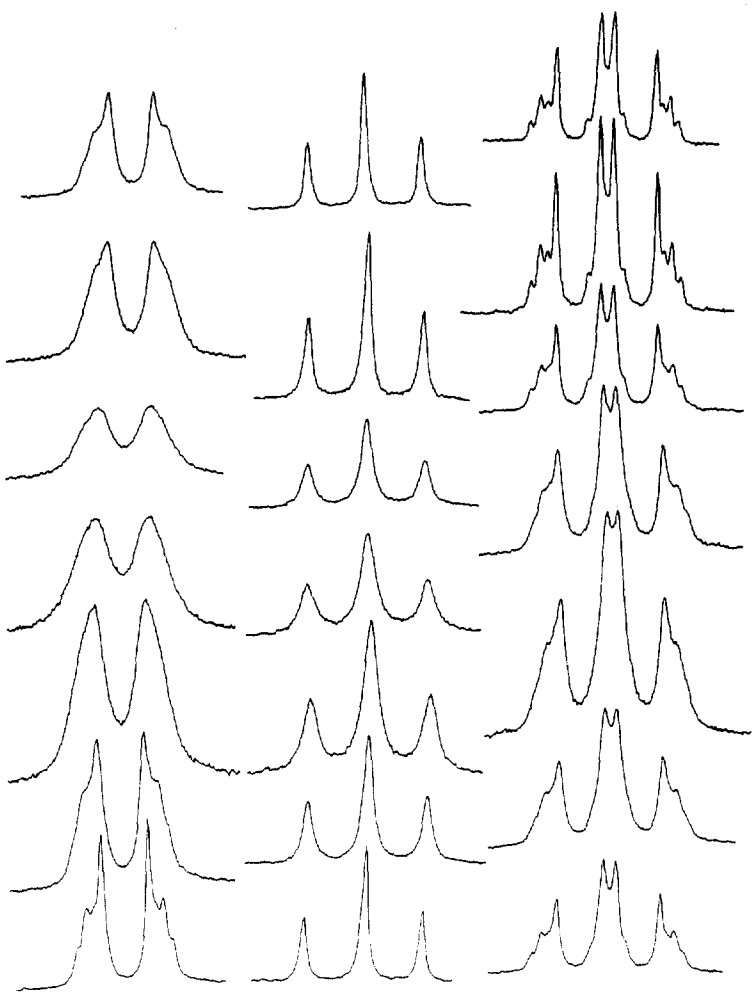


Fig. 5. Expansions of the ^{19}F NMR spectra of *N*-pentafluorophenyl maleamic acid, **5**, in d_6-DMSO, from 293 K (bottom traces) to 353 K (top traces) in 10 K increments. Absorptions for the *ortho* F(a,e) nuclei appear to the left (as gross doublets), the *para* F(c) clean triplets are shown in the center, and signals for the *meta* F(b,d) appear to the right (as gross triplets). The chemical shift scales are uniform for all traces, i.e., constant Hz/cm. Although signals were actually shifted to higher field with increasing temperature (see Section 3) traces are shown one above the other for clarity in comparisons. Actual shifts for F(a,e) were ca. −144 ppm; for F(c) ca. −157.5 to −158.5 ppm, and for F(b,d) about −163 to −164 ppm. See Section 3.

4. Conclusions

We have presented here data from ^{19}F NMR studies of *N*-pentafluorophenyl maleamic acid, **5**; *N*-pentafluorophenyl maleimide, **2**; and the Diels–Alder adduct, **3**, from addition of **2** to phencyclone. The *five* fluorine signals in the NMR of **3** imply hindered rotation about the N–C_6F_5 bond, with the SEL spectrum consistent with the C_6F_5 lying in the mirror plane of **3**. With *endo* stereochemistry in **3**, the *ortho* fluorine *syn* to the phenanthrene moiety is very close to quaternary phenanthrene carbons 4a, 4b, with calculated distances ca. 3.1–3.2 Å, but clear evidence of anisotropic shielding of fluorine is not apparent. ^{19}F–^{19}F COSY45 unambiguously allowed vicinal fluorine relationships in adduct **3** to be defined. The maleimide **2** and maleamic acid **5** each show only three ^{19}F NMR absorptions. Chemical shifts for **2** and **3** were compared and full F–F coupling data were obtained for **3**. Temperature dependence was seen for the ^{19}F NMR of **5** in d_6-DMSO over the range from 293–353 K, in which signals first broadened, then sharpened, as temperature was raised from ambient. Possible conformational processes in **5** were discussed. With the recent increase in studies of fluorine-containing compounds as potential pharmaceuticals [16], this present report may provide special interest concerning potential model compounds.

Acknowledgements

Partial support has been provided by the US Education Department Minority Science Improvement Program (Grant Nos. G008641165 and 1-132553815-A1), National Science Foundation (Grant Nos. DUE9750675 and USE9152822), The Forty-Five Foundation, and the Professional Staff Congress—City University of New York Research Award Program (to R.R.). We are grateful to the Referee for comments and suggestions, particularly regarding conformations in the adduct and precursors.

References

[1] T. Sasaki, K. Kanematsu, K. Iizuka, J. Org. Chem. 41 (1976) 1105.
[2] L.A. LaPlanche, Y. Xu, R. Benshafrut, R. Rothchild, E.A. Harrison Jr., Spectrosc. Lett. 26 (1993) 79.
[3] Y. Xu, L.A. LaPlanche, R. Rothchild, Spectrosc. Lett. 26 (1993) 179.
[4] R. Callahan, R. Rothchild, H. Wyss, Spectrosc. Lett. 26 (1993) 1681.
[5] R. Benshafrut, R. Callahan, R. Rothchild, Spectrosc. Lett. 26 (1993) 1875.
[6] K. Bynum, R. Rothchild, Spectrosc. Lett. 29 (1996) 1599.
[7] K. Bynum, R. Rothchild, Spectrosc. Lett. 29 (1996) 1621.
[8] K. Bynum, R. Rothchild, Spectrosc. Lett. 30 (1997) 727.
[9] K. Bynum, R. Rothchild, Spectrosc. Lett. 30 (1997) 1713.
[10] M.F. Amin, K. Bynum, R. Callahan, R. Prip, R. Rothchild, Spectrosc. Lett. 31 (1998) 673.
[11] L. Pauling, The Nature of the Chemical Bond, 3rd edn., Cornell Univ. Press, Ithaca, NY, 1960, esp. pp. 234–235 and pp. 257–262.
[12] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry: A Comprehensive Text, 3rd edn., Wiley-Interscience, New York, 1972, pp. 119–120.
[13] H. Gunther, NMR Spectroscopy: Basic Principles, Concepts and Applications in Chemistry, 2nd edn., Wiley, New York, 1994, pp. 94–97.
[14] W.E. Stewart, T.H. Siddall III, Chem. Rev. 70 (1970) 517.
[15] M. Oki, Applications of Dynamic NMR Spectroscopy to Organic Chemistry, VCH Publ., Deerfield Beach, FL, 1985.
[16] R. Filler, Y. Kobayashi, L.M. Yagupolskii (Eds.), Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications, Elsevier, Amsterdam, 1993.