# *In situ* Generation and Electrophilic Addition Reactions of the Elements of 'XF'[1]

L. D. HALL AND D. L. JONES
*Department of Chemistry, The University of British Columbia, Vancouver 8, British Columbia*

Received November 1, 1971[2]

Addition of the elements of 'IF' and of 'BrF' to alkenes can be effected by the *in situ* generation of these electrophiles from the halogen-AgF. For cyclohexene, 3,3,6,6-tetradeuterocyclohexene, methylenecyclohexane, styrene, and indene, these reactions are simple. However, for acenaphthylene, halogen–fluorine exchange and other reactions make the overall reaction quite complex. Electrophilic addition reactions for 1-fluoro-acenaphthylene are also described. The n.m.r. spectra of many of the products are given and discussed in some detail.

L'addition des éléments 'IF' et 'BrF' aux alcènes peut être effectuée par réaction in situ de ces électrophiles à partir de AgF-halogène. Pour le cyclohexène, tétradeutero-3,3,6,6 cyclohexène, méthylcyclohexane, styrène et indène, les réactions sont simples. Cependant pour l'acénaphtylène, l'échange halogène–fluor et d'autres réactions rendent la réaction globale complexe. Les réactions d'addition électrophile pour le fluoro-1 acénaphtylène ont été également décrites. Les spectres r.m.n. de plusieurs de ces produits ont été donnés et discutés de façon détaillée. [Traduit par le journal]

Can. J. Chem., 51, 2902 (1973)

A crucial aspect of our programme to develop fluorine as a structural probe has always been the synthesis of specifically fluorinated substrates. One of the methods which was found to be successful in the carbohydrate area involved the addition of the elements 'XF', where X = Cl, Br, or I, to an unsaturated sugar (2); the preferable source of the 'XF' electrophile was shown to be the generation *in situ* from halogen and silver monofluoride. In the present paper we describe the reaction of a variety of alkenes with the above source of the elements of 'XF'. As will be seen, the initial addition reaction may be followed by further halogen exchange reactions which are sometimes so fast that the initially formed adduct cannot be isolated.

It is appropriate to comment here that there had previously been some controversy in the literature concerning the efficacy of the $X_2$–AgF method for generating 'XF'. Schmidt and Meinert (3) reported that in acetonitrile solvent the elements of iodine monofluoride could be added across the double bond of cyclohexene, to form *trans*-1-fluoro-2-iodocyclohexane in 60% yield. However, Andreatta and Robertson (4), attempting to repeat this reaction, isolated only *N*-acetyl-2-iodocyclohexylamine in 17% yield; this work will show that the 'IF' addition reaction to cyclohexene is indeed a viable reaction, and can be extended to a variety of other alkenes, and also to 'BrF' additions.

## Results and Discussion

The compounds described in the first section of the following discussion were for the most part isolable in pure form and were fully characterized. In constrast, the acenaphthyl fluorides discussed subsequently were generally unstable and hence could only be characterized by their $^1$H and $^{19}$F n.m.r. spectra.

The reactions summarized in Scheme 1 are typical of those of aliphatic alkenes. Slow addition of a dilute solution of iodine in benzene to a stirred suspension of AgF in cyclohexene and benzene afforded as sole product 1-fluoro-2-iodocyclohexane (**1**). The stereochemistry of the product was shown to be *trans* by examination of the $^1$H n.m.r. spectrum of the product (**1**-$d_4$) obtained from 3,3,6,6-tetradeuterocyclohexene: it is noteworthy that neither the $^1$H nor the $^{19}$F n.m.r. spectra of the *crude* product arising from that reaction showed any detectable impurities.[3]

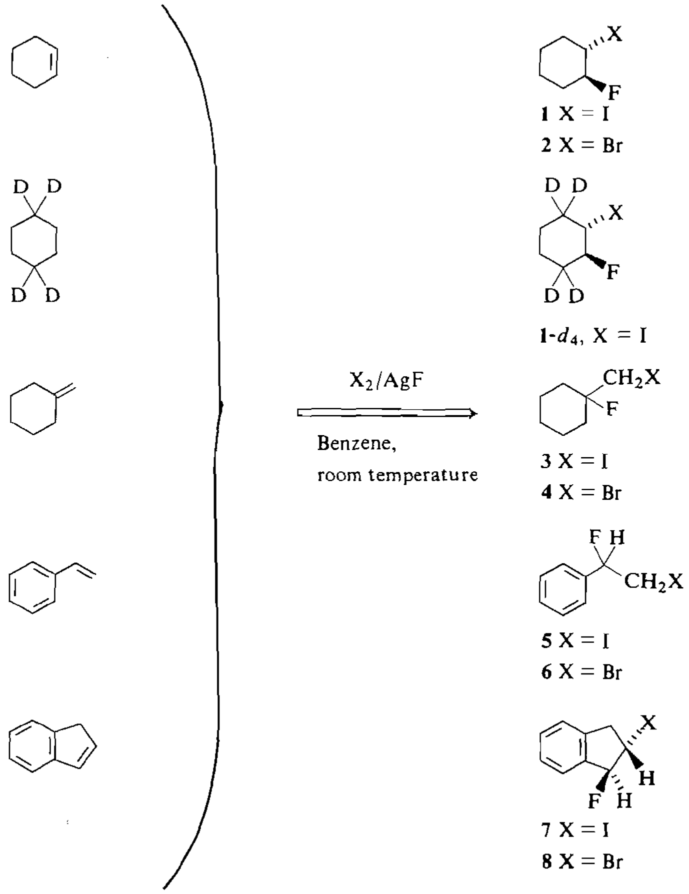
The addition of 'BrF' to cyclohexene was also successful, again producing a *trans*-product (**2**).

---

[1] For a preliminary communication see ref. 1. Presented in part at the 51st Canadian Chemical Conference of the Chemical Institute of Canada, Vancouver, British Columbia, June 3–5, 1968.

[2] Revision received February 23, 1973.

[3] The $^1$H n.m.r. spectrum of this deuterated compound is shown in the accompanying paper (5).



SCHEME 1

This reaction was more difficult to carry out and the AgF had to be absolutely dry, otherwise the 1,2-dibromide was formed.

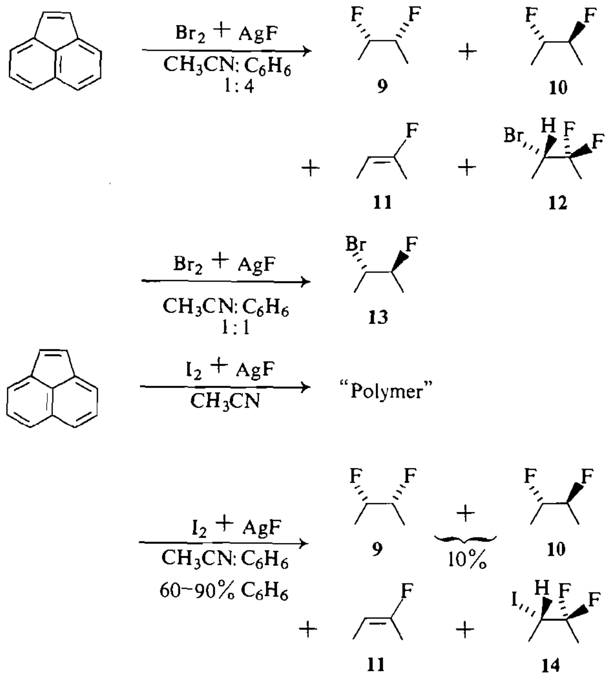
Direct extension of the 'IF' and 'BrF' addition reactions to methylene–cyclohexane, styrene, and indene produced in each instance the reaction product having the structure anticipated for the reaction of $X^+F^-$.

In marked contrast to the ease of the above addition reactions, attempts with acenaphthylene were at first unsuccessful. 'BrF' addition in benzene solution produced no 'BrF' adduct, but gave instead a low yield of the *cis*- and *trans*-difluorides (**9**, **10**) (see Scheme 2). The major product of the reaction contained no fluorine and was high melting. In addition to these products, there were also two others, both in trace quantities, which were observed in the $^{19}F$ n.m.r. spectrum of the crude product; one was later shown to be 1-fluoro-acenaphthylene (**11**) and the other 1-bromo-2,2-difluoro-acenaphthene (**12**) designated hereafter as the '$BrF_2$ adduct'.

If, however, the solvent was 50/50 benzene–acetonitrile,[4] the *trans*-'BrF' product (**13**) resulted. Increasing proportions of benzene in the solvent produced a mixture of all three products; *trans*-'BrF', *cis*- and *trans*-difluorides, as well as "polymeric" material; altering the time of the reaction seemed to have some effect on the relative amounts. Interestingly, it was not possible to convert the 'BrF' product to difluoride using AgF, with either benzene or acetonitrile as solvent. However, addition of $Br_2$ to acenaphthylene produced only *trans*-dibromide, confirming Cristols' result (6) and subsequent shaking with AgF yielded only *trans*-BrF (**13**).

---

[4] Acenaphthylene was dissolved in benzene–acetonitrile, but $Br_2$ added as a benzene solution.



SCHEME 2

Reactions of $I_2$ + AgF with acenaphthylene were performed as for the $Br_2$ + AgF reactions; however the experimental results were significantly different. Any 'IF' product, if it ever existed, was too unstable to be isolated and led to further products. In benzene, the major fluorinated products were once again the *cis*- and *trans*-difluorides (**9**, **12**) but in low yield. Trace quantities of fluoro-acenaphthylene (**11**) and the '$IF_2$' adduct (**14**) were also observed and isolated.

With increasing quantities of acetonitrile in the solvent, less of the above products were observed, and the best yields were obtained in 80–90% benzene.[5] Below 50% benzene none of these compounds were formed in substantial quantities but other fluorinated products were observed in the $^{19}F$ n.m.r. spectrum; however, they decomposed with every attempted isolation (such as column chromatography). From the chemical shift and multiplicity of the $^{19}F$ resonance it was evident that the unknown products could well contain a *trans*-'IF' adduct which would be expected to be very unstable indeed. The ratio of *cis*:*trans* difluorides was found to be close to 1:2, and essentially independent of solvent, in the range benzene–acetonitrile (40:60) to pure benzene. Finally it was observed that a number of other compounds were formed in trace quantities, and from the pattern of their $^{19}F$ resonances they appeared very similar in structure to the *trans*-difluoride.

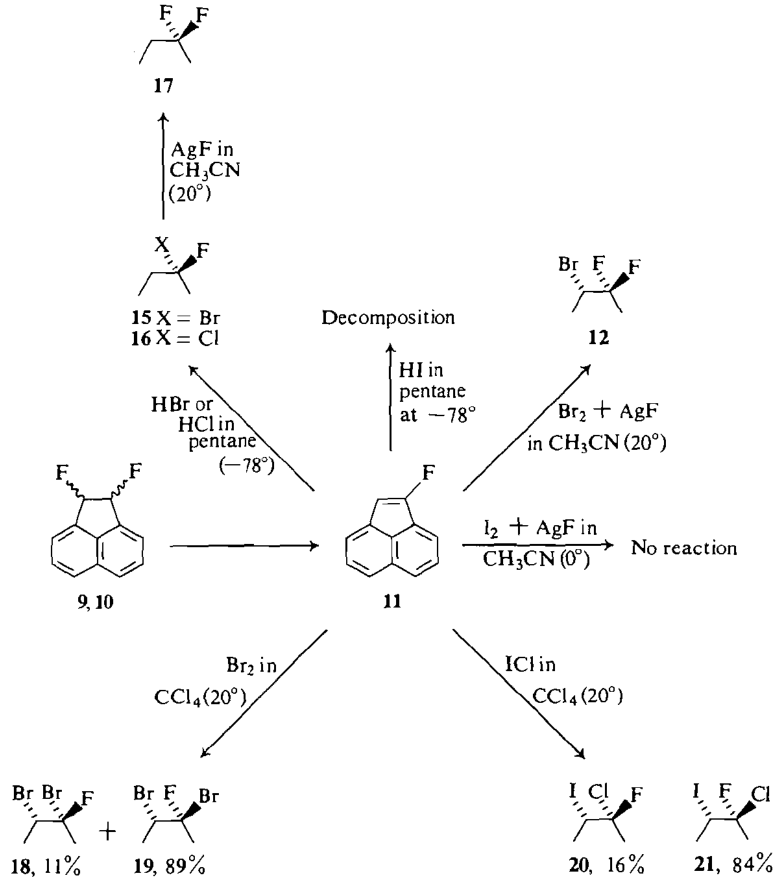
The unexpected results obtained with 'XF' additions to acenaphthylene can be attributed to the increased reactivity of the halogen 'X' of the 'XF' adduct. This reactivity is well illustrated by the effect of AgF on 1-bromo-acenaphthene, 1-bromo-indan and bromo-cyclohexane respectively. The acenaphthene derivative is converted to the fluoride in minutes; in contrast, the indan compound requires 24 h for the same reaction, and bromo-cyclohexane is unreactive.

The products obtained from the 'XF' reactions with acenaphthylene suggested that many acenaphthyl fluorides might be obtained by a series of simple reactions, chiefly utilizing 1-fluoro-acenaphthylene (**11**); such compounds would provide the necessary data to determine the effect of electronegativity on $^3J_{HF}$ couplings.

1-fluoro-acenaphthylene (**11**) was prepared by the method described by Merritt and Johnson (7), *i.e.*, elimination of HF, using a refluxing

---

[5] Volume measurement.



SCHEME 3

solution of KOH in ethanol, from either the *cis*- or the *trans*-1,2-difluoride of acenaphthene. The conversion obtained from this reaction was never quantitative, and it was necessary to recycle the recovered starting material. The reactions performed with **11** are summarized in Scheme 3. For convenience each of these reactions is listed separately below.

### *(a) Addition of HCl or HBr, Followed by AgF Exchange*

Addition of HBr or HCl gas to a solution of 1-fluoro-acenaphthylene (at −78°) yielded the corresponding '*gem*-BrF' (**15**) and '*gem*-ClF' (**16**) adducts; in neither case was any vicinal product observed. Shaking either of these compounds with AgF powder in acetonitrile solution at room temperature produced the *gem*-difluoride (**17**). Addition of HI, instead of HCl or HBr, produced only decomposition even at −78°.

### *(b) 'BrF' Addition*

Conditions identical with those used for acenaphthylene itself afforded as major product the expected '$BrF_2$' adduct spectroscopically identical with the trace material found in the reaction of acenaphthylene; two minor components were also formed, but these were not identified.

### *(c) 'IF' Addition*

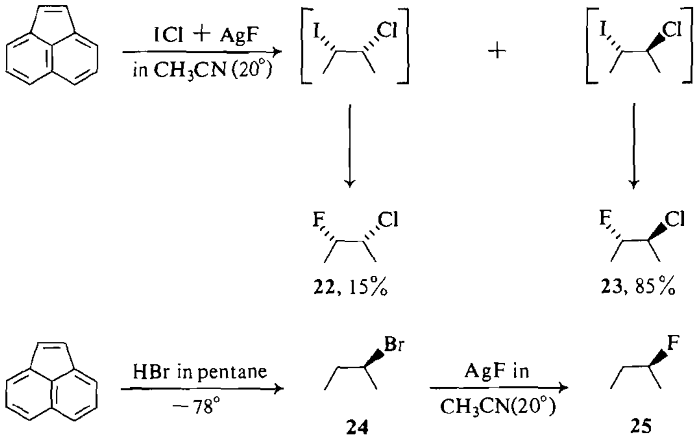
The analogous reaction between $I_2$, AgF, and 1-fluoro-acenaphthylene did not proceed.

### *(d) $Br_2$ Addition*

When elemental bromine was added to fluoro-acenaphthylene in either $CCl_4$ or $CH_3CN$ solution, both *cis*- and *trans*-products (**18, 19**) were observed; the ratio of *cis–trans* was 1:8.

### *(e) ICl Addition*

Analogous treatment of 1-fluoro-acenaphthylene with an ICl solution in $CCl_4$ gave similar



SCHEME 4

results, *i.e.* *cis*- and *trans*-products (**20**, **21**) in the ratio 1:5.

Some apparently anomalous additions have been previously observed with acenaphthylene by several other workers; thus $Cl_2$ addition can be made to add *cis* or *trans*, depending on reagents whereas only a *trans*-dibromide is known (6). Furthermore, HBr and HCl addition has been shown to go 75–90% *cis* (8). However, it is possible that earlier workers (6) might have missed a small quantity of a minor product, such as a *cis*-dibromide, for example.

The *cis*- and *trans*-'ClF' adducts (**22**, **23**) shown in Scheme 4 were prepared by 'XF' addition to acenaphthylene using ICl and AgF in $CH_3CN$ solution. Once again, the *trans*-adduct predominated (85%).

Following the procedure of Dewar and Fahey, 1-bromo-acenaphthene (**24**) was synthesized from acenaphthylene and HBr (8); this compound readily exchanged its bromine atom for a fluorine of AgF, in acetonitrile solution at room temperature. Unfortunately, this resulting fluoride was extremely unstable, and all attempts at purification or isolation resulted in decomposition; thus it was found impossible to run the compound on any available chromatographic apparatus (*i.e.* acid, neutral, or basic silica gel or alimina on either columns or plates). Additionally, it was decomposed by washing with a weakly basic aqueous solution, and also by warm chloroform.

## Summary

The reactions discussed above indicate that electrophilic addition of the elements of 'IF' and 'BrF' to alkene can be accomplished using the halogen-AgF reagent. Addition of 'IF' is more facile than that of 'BrF' and for aliphatic alkenes both are simple reactions. However, if the 'XF'-product has the bromine or iodine substituent in a benzylic position then further reactions can follow the initial addition and the overall reaction sequence is then extremely complex.

The reactions discussed here afforded a range of interesting substrates for n.m.r. studies and these are described in three accompanying papers (5, 10, 11).

## Experimental

All solutions were concentrated under reduced pressure. Benzene and acetonitrile were dried over calcium sulfate and light petroleum and dichloro-methane were fractionally distilled before use. Silver fluoride[6] was stored in a vacuum dessicator and ground to a fine powder just prior to a reaction. Cyclohexene was distilled before a reaction, but all other reagents were used as received.

Silica gel used for chromatographic columns was Mallinckrodt CC-7, a neutral high-purity grade.

### *trans-2-Iodocyclohexylfluoride (1)*

Cyclohexene (3.1 ml, 2.5 g) and silver monofluoride (12 g) were added to benzene (50 ml) and the resulting mixture stirred vigorously and cooled in an ice–bath. A solution of iodine (8 g) in benzene (80 ml) was then added over 0.5 h with continued stirring.

The reaction mixture was filtered and the filtrate washed successively with aqueous sodium bicarbonate, sodium thiosulfate, sodium bicarbonate, and finally with water. The organic layer was separated, dried ($MgSO_4$), and concentrated to a clear liquid whose $^1H$ n.m.r. spectrum was virtually indistinguishable from the distilled material. Distillation under reduced pressure gave **1** (4.4 g, 63%), b.p. 50° (2 mm) (lit. (9), 64° (9 mm)), $n_D^{23}$

---

[6] From Harshaw Chemical Co.

1.5310 (lit. (9), $n_D^{20}$ 1.5318). The $^{19}F$ chemical shift in $CHCl_3$ solution was +159.9 p.p.m. with respect to $CFCl_3$ as a reference.

Anal. Calcd. for $C_6H_{10}IF$: C, 31.59; H, 4.42; I, 8.32. Found: C, 31.76; H, 4.63; I, 8.11.

*trans-1-Bromo-2-fluoro-cyclohexane (2)*

The same procedure as for preparation of **1** was used except that bromine was substituted for iodine, and no thiosulfate washing was necessary in the work-up. Bromine (6.0 g) in benzene (25 ml) was added dropwise, and all other procedures and quantities remained the same. The n.m.r. spectra of crude and distilled material again were very similar, and also matched that of the product of the Bowers reaction (9). The product had a b.p. 58° (9 mm) (lit. (9), 30° (13 mm)[7]), $n_D^{25}$ 1.4825 (lit. (9) $n_D^{20}$ 1.4830).

Anal. Calcd. for $C_6H_{10}BrF$: C, 39.78; H, 5.56; F, 10.49. Found: C, 39.90; H, 5.65; F, 10.61.

*1-Iodomethyl-cyclohexyl Fluoride (3)*

Prepared in a similar procedure as used for **1**. Quantities used were; AgF (10 g); methylene cyclohexane (2.5 g) dissolved in benzene (35 ml); iodine (8.5 g) dissolved in benzene (85 ml). Reaction time was 90 min. Crude yield 6.0 g; distilled yield 4.4 g (70%), b.p. 61° (1 mm), $n_D^{25}$ 9.5175, $\phi_c$ 151.2 p.p.m.

Anal. Calcd. for $C_7H_{12}IF$: C, 34.73; H, 4.97. Found: C, 34.88; H, 5.02.

*1-Bromomethyl-cyclohexyl Fluoride (4)*

Similar procedure as for **2**; to methylene cyclohexane (2.5 g) and AgF (10 g) in benzene (40 ml) was added bromine (8 g) in benzene (40 ml) over 1 h at 0°. Distillation afforded 3.0 g of 4 (yield 59%), b.p. 47° (1 mm), $n_D^{25}$ 1.4825, $\phi_c$ 156.3 p.p.m.

Anal. Calcd. for $C_7H_{12}BrF$: C, 43.12; H, 6.15. Found: C, 42.89; H, 6.25.

The position of the substituents is obtained from the n.m.r. spectrum; the lack of an identifiable $^2J_{HF}$ coupling (characteristically about 50 Hz) located the fluorine at the tertiary position.

*2-Iodo-1-fluoro-1-phenylethane (5)*

Identical procedure as for preparation of **1**, except that styrene (2.5 g) was used as starting material. Distillation *in vacuo*, however, resulted in decomposition. Crude yield (after work-up and removal of solvent), 4.7 g (78%). The n.m.r. spectrum showed that the product was substantially pure and its similarity to that of the bromo-derivative **6**, which is discussed below; $\phi_c$ +166.8 p.p.m.

*2-Bromo-1-fluoro-1-phenylethane (6)*

Same procedure as for **2**, except that styrene (2.5 g) and bromine (5.0 g) in benzene (40 ml) were used; time of addition was 105 min.

Distillation under reduced pressure produced a clear liquid, 3.5 g (71%), b.p. 69° (1 mm), $n_D^{25}$ 1.5409, $\phi_c$ +174.5 p.p.m.

The n.m.r. spectra demonstrated the position of the substituents: the partial $^1H$ spectrum has two identifiable regions, an AB and M region of an ABMX spectra (where X = $^{19}F$). The 50 Hz $J_{MX}$ positions the fluorine in the secondary position.

*2-Iodo-1-fluoro-indan (7)*

Again, the same procedure was used as for **1**, (indene (2.8 g) was reacted with iodine (9.0 g) and AgF (13.0 g)). Although the product could not be distilled without decomposition, the crude product after work-up was a clear liquid, whose n.m.r. spectra showed no impurities. Crude yield was 4.8 g (66%), $\phi_c$ +155.2 p.p.m., $^2J_{HF}$ 5.6 Hz, $^3J_{HF}$ 18 Hz. The structure is derived from the n.m.r. spectra which are similar to those of the bromo-compound discussed below.

This compound was extremely unstable and the pure liquid, obtained by eluting off a neutral silica gel column with light petroleum at low temperatures, decomposed at room temperature in seconds. Elution down an alumina column produced indene. Solid $NaCO_3$ was effective in preventing decomposition.

*2-Bromo-1-fluoro-indan (8)*

Indene (2.8 g) was reacted with bromine (6.0 g) and AgF (13.0 g) over 90 min and worked-up in the usual way. Crude yield was 5.1 g (88%), $\phi_c$ 160.4 p.p.m., $^2J_{HF}$ 55 Hz, $^3J_{HF}$ 17 Hz. Distillation was not possible, but (in contrast to **7**) the material could be purified by elution down an alumina column with light petroleum.

In the $^1H$ spectra the proton next to the fluorine (identified by the characteristic $^2J_{HF}$ 55 Hz) has only one other coupling into it. Hence the fluorine must be in the 1-position. Furthermore, the proton to slightly higher field, which must be *geminal* to the bromine atom, is split into 16 lines (thus four couplings) and must be in the 2-position. The n.m.r. spectra and conformation of **8** are discussed more fully in the accompanying paper (10).

*cis- and trans-1,2-Difluoro-acenaphthene (**9**, **10**)*

Acenaphthylene (2.0 g) was dissolved in a stirred mixture of benzene (40 ml), acetonitrile (10 ml), and AgF (10 g). Iodine (4.0 g) was also dissolved in the same solvent mixture (40 ml) and this solution was then added dropwise to the acenaphthylene–AgF mixture over 1 h, with cooling (ice-bath) and stirring. The mixture was then poured into a larger volume of a saturated $NaHCO_3$ aqueous solution, mixed thoroughly, filtered, and the organic layer separated from the filtrate and washed with more water. Drying over $Na_2SO_4$ and $Na_2CO_3$ and removal of solvent produced a dark red viscous liquid, whose $^{19}F$ n.m.r. spectrum revealed the presence of at least two compounds.

This crude product mixture was then separated chromatographically by eluting down a neutral silica gel column with light petroleum (b.p. 37°). The column fractions were monitored by t.l.c., $^1H$ and $^{19}F$ n.m.r. First off the column was a small amount of starting material, quickly followed by fluoro-acenaphthylene (**11**) and 1-iodo-2,2-difluoro-acenaphthene (**14**), both in trace quantities; then came a major product, *trans*-1,2-difluoro-acenaphthene (**10**). Further elution with 20% $CH_2Cl_2$ in light petroleum produced *cis*-1,2-difluoro-acenaphthene (**9**), contaminated with some highly colored material. The fractions containing **9** and **10** were then purified by twice eluting them down silica gel columns as above.

---

[7] The literature value of the boiling point of **2** appears to be in error; a sample of **2** prepared by the literature method (9) had a boiling point in agreement with that reported here.

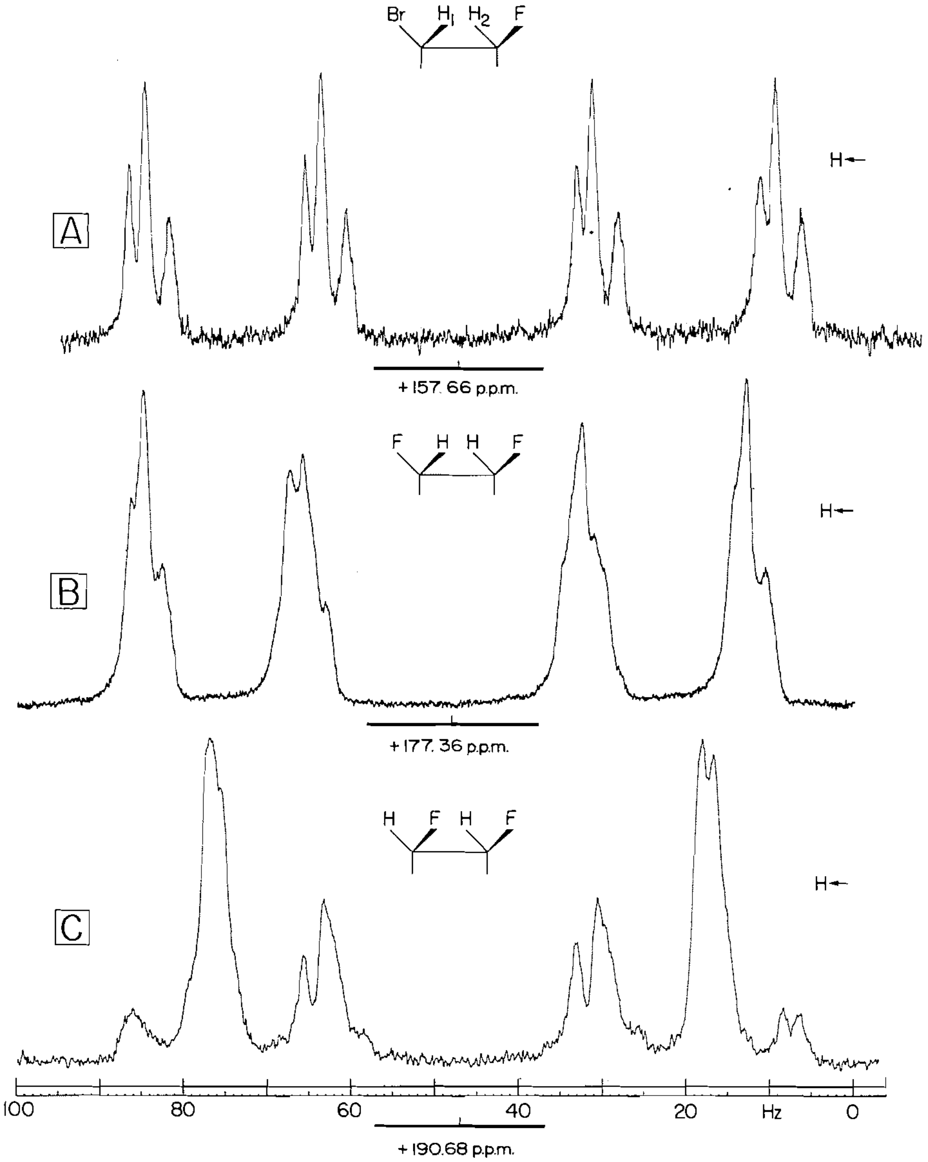


FIG. 1. $^{19}F$ n.m.r. (94.07 MHz) of the three major products of the 'XF' addition to acenaphthylene. A, *trans*-bromofluoride (**13**); B, *trans*-difluoride (**10**); C, *cis*-difluoride (**9**).

The $^1H$ spectrum of each is identical with its $^{19}F$ spectrum, which is a characteristic of $A_2X_2$ systems such as **9** and **10**; the $^{19}F$ spectra of each is shown in Figs. 1B and 1C and the $^1H$ spectra[8] in Figs. 2A and 2C. Decoupling of the aromatic protons of **10** produced a marked sharpening of the lines, as shown in Fig. 2B, but a similar decoupling experiment on **9** was a failure.

Crystalline samples of **9** and **10**, which were obtained by slow cooling of an ethanol–water solution, gave satisfactory elemental analyses.

Anal. Calcd. for $C_{12}H_{10}F_2$: C, 75.79; H, 4.21; F, 20.00. Found (*cis*): C, 75.95; H, 4.20; F, 19.80. Found (*trans*): C, 75.55; H, 4.00; F, 20.30.

Other physical data are:

| | *cis* (**9**) | *trans* (**10**) |
|---|---|---|
| M.p. (°C) | 113 | 47 |
| $^3J_{HF}$ (Hz) | 5.2 | 19.13 |
| $^3J_{HH}$ (Hz) | 5.1 | 1.23 |
| $^3J_{FF}$ (Hz) | 16.4 | 1.23 |
| $\phi_c$ (p.p.m.) | 190.68 | 177.36 |
| $\tau_H$ | 3.24 | 4.32 |

---

[8] Actually they are *partial* $^1H$ spectra, since the aromatic region is not shown.

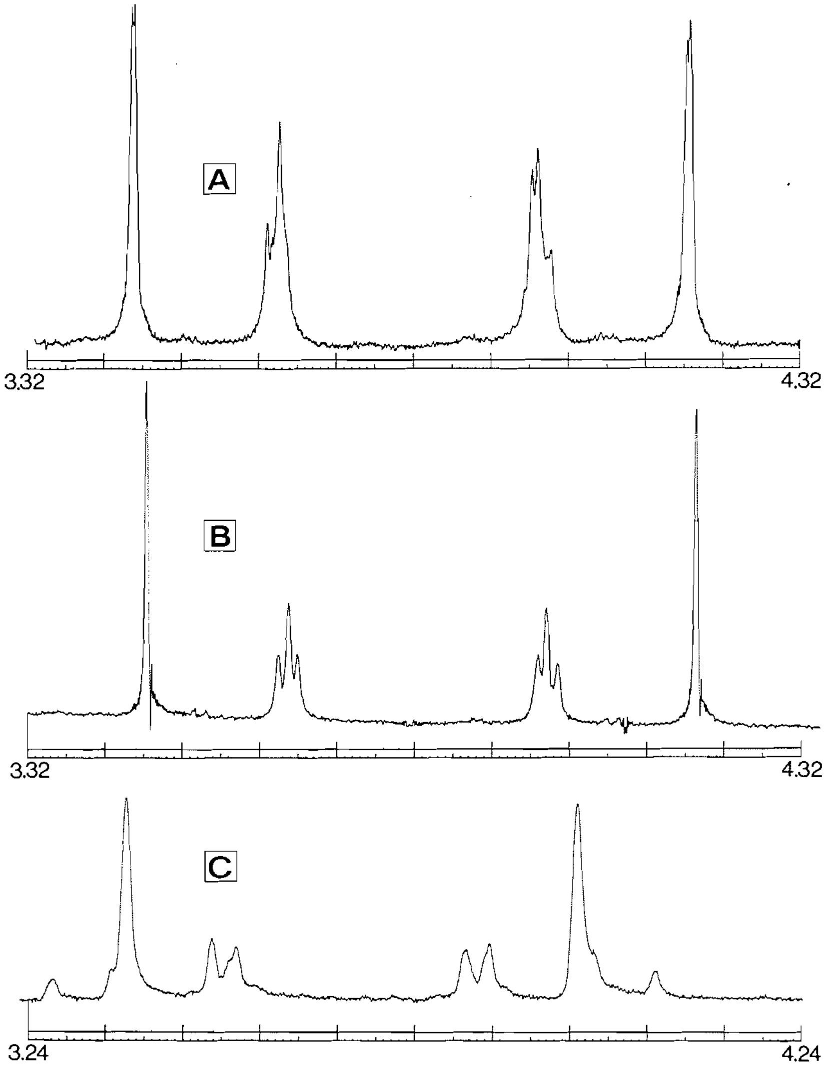


FIG. 2. Partial $^1$H n.m.r. spectra (100 MHz) of the difluorides of acenaphthylene. A, the normal spectrum of the *trans*-difluoride (**10**); B, the same spectrum but measured with simultaneous irradiation of the aromatic protons; C, the normal spectrum of the *cis*-difluoride (**9**).

Although quantitative values for the yields could not be obtained, subjective estimates are 10% for the *trans*-isomer (**10**) and 5% for the *cis* (**9**). A series of experiments were carried out to optimize the yield; the percentage of benzene in the solvent was varied from 50–100% and an optimum yield was obtained in the range 80–90% benzene. However, the ratio of *trans–cis* was constant at 2:1. The analysis of the $A_2X_2$ n.m.r. spectra was done by hand;[9] agreement with Merritt and Johnsons' values (7) is good for the *cis*-isomer but rather poorer for the *trans*. This is understandable since the previous analysis would have been carried out on a spectrum such as Fig. 2A rather than 2B.

*trans-1-Bromo-2-fluoro-acenaphthene (13)*

A solution containing $Br_2$ (2.5 g) and benzene (25 ml) was added dropwise to a vigorously stirred suspension of finely powdered AgF in 50:50 benzene–acetonitrile at 0°. Simultaneously, another solution containing acenaphthylene (2.0 g) in benzene (25 ml) was also added.

This addition was carried out over a period of 20 min, after which the reaction mixture was immediately filtered, washed with $NaHCO_3$ solution, and then dried over $Na_2SO_4$–$CaSO_4$. The resulting light yellow solution was evaporated under vacuum to 5–10 ml[10] and then eluted down an alumina column with light petroleum. Apart from a small quantity of starting material (which runs very fast) the only product was **13**; the $^{19}$F spectrum is

---

[9] $A_2X_2$ spectra consist of two unconnected sub-spectra and as such cannot be analyzed by an iterative computer procedure.

[10] Further concentration increases the possibility of decomposition.

shown in Fig. 1A and a partial $^1H$ spectrum in Fig. 3B. Decoupling of the aromatic protons revealed that this latter spectrum was the AB part of an ABX; this is shown above in Fig. 3A. Selective decoupling, not shown, of the left-hand doublet of $H_2$ collapsed the corresponding left-hand doublet in $H_1$. This confirms the analysis of spectra, and indicates that $^3J_{1F}$ has the same sign as $^2J_{2F}$. The small $^3J_{12}$, 1.0 Hz also indicates a *trans* relationship between Br and F.

The product **13** is very unstable and has to be kept well below 0° unless stabilized by solid $NaCO_3$. A concentrated pentane solution, cooled in Dry Ice deposited yellow crystals; however, they proved to have some solvent in them. A similar experiment with ethanol had the same result; however, the material deposited from this solution when warmed to −25° and pumped on for 4 h produced a crop of white–yellow crystals which had a sharp m.p. of 35° and whose $^1H$ n.m.r. showed no solvent present; they also gave satisfactory elemental analysis. The crystals were extremely unstable, being decomposed within minutes at room temperature.

Anal. Calcd. for $C_{12}H_{10}BrF$: C, 57.39; Br, 31.85; F, 7.57. Found: C, 57.16; Br, 31.59; F, 7.43.

$\tau_{H_1}$ 4.32; $\tau_{H_2}$ 3.52; $\phi_c$ 157.66 p.p.m.; $^3J_{HF}$ 21.4 Hz; $^3J_{HH}$ 1.0 Hz.

The product **13** could be distinguished from acenaphthylene with t.l.c.; the two compounds ran very close together (**13** last) but upon charring with concentrated $H_2SO_4$, acenaphthylene gives a green color whereas **13** turns brown.

### *1-Fluoro-acenaphthylene (11)*

Following the procedure of Merritt and Johnson (7), *cis*-difluoroacenaphthene (**9**) (1.0 g) was heated under reflux with KOH (3 g) in ethanol (50 ml) for 5 h. The $^{19}F$ n.m.r. spectrum of the crude product indicated that most of the starting material had reacted. The product mixture was worked-up by removing most of the ethanol *in vacuo*, dissolving in petroleum ether and washing with water. The organic layer was dried, filtered, and concentrated again, prior to separation on a neutral silica gel column with pentane–benzene (70:30). The product **11** ran ahead of the starting material (**9**) and gave a characteristic yellow color to the solution.

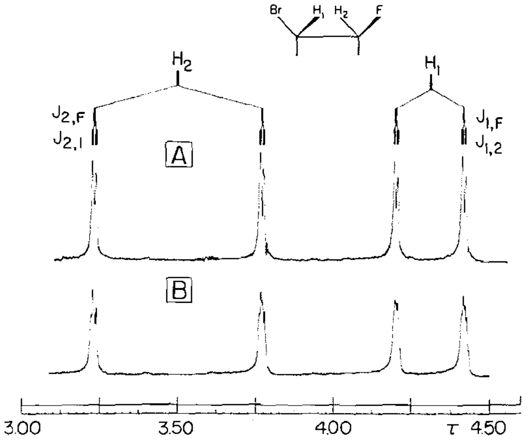


FIG. 3. Partial $^1H$ n.m.r. (100 Hz) of 1-bromo-2 fluoro-acenaphthene (**13**). A, the spectra measured with simultaneous irradiation of the aromatic protons; B, the normal spectrum.

Spectroscopically ($^1H$ and $^{19}F$ n.m.r.), this material appeared to be free of impurities; however, small amounts of acenaphthylene itself which were undetected in the n.m.r. spectrum were picked out on a t.l.c. plate (very slightly ahead of **11**). Therefore the material was rerun down an extra long column (60 in.) of neutral silica gel with pentane; this removed the residual acenaphthylene. The two compounds could be distinguished on a t.l.c. plate by the fact that fluoro-acenaphthylene (**11**) fluoresces under u.v. light whereas acenaphthylene does not.

A crystalline sample of **11** was obtained by cooling a pentane solution to −78°; m.p. 37°, yellow plates (previously reported as oil). $^1H$ n.m.r. singlet at τ 4.00 (besides aromatic region), $^{19}F$ n.m.r. singlet at $\phi_c$ 99.4 p.p.m.; no impurity peaks were detected.

The reaction yield was high (from $^{19}F$ n.m.r.) but not quantitative. Significant amounts of starting material remained even with long reaction times (24 h) or high alkalinity of the solution. Use of *trans*-difluoro-acenaphthene (**10**) lowered the yield somewhat.

### *1-Bromo-2,2-difluoroacenaphthylene (12)*

Bromine (0.4 g) in benzene (5 ml) was added over 20 min to a stirred solution of fluoro-acenaphthylene (**11**) (0.20 g) in acetonitrile (50 ml), containing powdered AgF (4.0 g). After the reaction, bicarbonate solution was added and the whole mixture filtered; the organic layer was separated, dried, filtered, and concentrated. $^{19}F$ n.m.r. of this material showed strong resonance which was evidently the AB-part of an ABX spectrum, and identified the main product as **12**; this was the same spectrum as that picked up weakly in the 'BrF' addition to acenaphthylene. This was analyzed (with TWOSUM) to give the following parameters: $J_{AB}$ 253.65 Hz ($^2J_{H_1F_2}$ (*gem*)), $J_{AX}$ 15.28 Hz ($^3J_{HF_1}$ (*cis*)), $J_{BX}$ 3.72 Hz ($^3J_{HF_2}$ (*trans*)), $\nu_{AB}$ = 237.14 Hz (2.52 p.p.m.), $\tau_H$ 4.23, $\phi_c(F_1)$ 88.3 p.p.m.; $\phi_c(F_2)$ 85.8 p.p.m.

### *1-Iodo-2,2-difluoroacenaphthene (14)*

'IF' did not react with 1-fluoro-acenaphthylene (**11**) under a variety of conditions, including as solvent acetonitrile, 60:40 benzene–acetonitrile, and benzene.

A small quantity of the desired product (**14**) was retrieved from the 'IF' reaction with acenaphthylene; after two chromatographic separations a spectroscopically pure sample was obtained, with a yield of only 0.2%. The large geminal F–F coupling (252 Hz) and the presence of only one other spin coupling into each $^{19}F$ resonance identified the product. The quartet in the $^1H$ spectrum confirmed this; $\phi_c(F_1)$ 75.8 p.p.m., $\phi_c(F_2)$ 87.5 p.p.m., $\tau_H$ = 4.24, $^2J_{FF}$ 252 Hz, $^3J_{HF_2}$ (*cis*) 16.26 Hz, $^3J_{HF_1}$ (*trans*) 4.24 Hz.

### *1-Bromo-1-fluoro-acenaphthene (15)*

Fluoro-acenaphthylene (**11**) (0.30 g) was dissolved in dichloromethane and cooled to −78°; HBr gas was then bubbled in slowly until the characteristic yellow color of **11** had disappeared (15 min), leaving a cream-colored solution. The solvent and excess HBr were then removed *in vacuo*, leaving a light brown solid. All chromatographic treatment of this material ended in decomposition.

The $^1$H spectrum showed only a single ABX spectrum (AB-part) in the methylene region; the $^{19}$F spectrum contained only a quartet at low field, with total width of 33 Hz, thus ruling out any *geminal* H–F coupling. The product must then be **15**: $\tau_{H_1}$ 6.14, $\tau_{H_2}$ 6.00, $\phi_c$ 79.8 p.p.m., $^2J_{HH}$ 18.3 Hz, $^3J_{HF}$ (*cis*) 22.8 Hz, $^3J_{HF}$ (*trans*) 10.3 Hz.

### *1-Chloro-1-fluoro-acenaphthene (16)*

The same reaction was performed as above, substituting HCl for HBr, with similar results; again no vicinal products were observed. Pentane was an equally good solvent for the reaction, which appeared (spectroscopically) to be quantitative: $\tau_{H_1} \simeq \tau_{H_2}$ 5.775, $\phi_c$ 81.3 p.p.m. ($^3J_{HF}$ (*cis*) + $^3J_{HF}$ (*trans*)) 32.8 Hz.

### *1,1-Difluoroacenaphthene (17)*

A solution of **15** (40 mg) in acetonitrile was shaken with AgF (0.20 g) at 20° for 20 min. The solid matter was filtered off and the acetonitrile removed *in vacuo*; t.l.c. showed two compounds both running fast, on silica gel. $^{19}$F n.m.r. of this material indicated two resonances; the weaker one was fluoro-acenaphthylene (**11**) and the other a triplet resonating at somewhat higher field than either **15** or **16**. $^1$H n.m.r. again showed the singlet at low field, characteristic of **11** and also a triplet at lower field than that for either **15** or **16**. Integration of this region showed it to contain two protons (by comparison with aromatic region). Integration of the $^{19}$F resonances gave the product ratio of 17:11 as 81%:19% (allowing for two fluorines in **17**).

Substituting **16** for **15** in this reaction and allowing 1 h reaction time gave substantially the same result, thus confirming that the new product **17** is the *gem*-difluoride. The identical triplets observed in both the $^1$H and $^{19}$F spectra are again characteristic of an AA′XX′ system; this time the large $J_{AA'}$ ($^2J_{FF}$ 250 Hz) effectively reduces the spectra to a true $A_2X_2$ (in which $J_{AX} = J_{A'X'}$ etc). This feature, which was verified by generating a theoretical spectrum using a reasonable set of parameters, is rather unfortunate since only the *sum* of the *vicinal* couplings may be extracted. The *geminal* couplings cannot be measured at all.

An attempt was made to get around this problem by selective deuteration; DBr was synthesized from $PBr_3$ (15 ml) according to the procedure in Shoemaker and Garland (12). This was then reacted with **11** in the same way as before to produce **15**-$d_1$, and exchanged with AgF to give **17**-$d_1$. This product was purified successfully by eluting down neutral silica gel with petroleum ether, but the $^1$H spectrum again showed a broad[11] triplet with shoulders which could not be decoupled from the aromatic region; the latter region itself was very broad (> 75 Hz). The only parameters which can be extracted therefore are: $\phi_c$ 84.5 p.p.m.; $\tau_H$ 6.52, ($^3J_{HF}$ (*cis*) + $^3J_{HF}$(*trans*)) 26.4 Hz.

### *cis-1,2-Dibromo-1-fluoro-acenaphthene (18) and trans-1,2-Dibromo-1-fluoro-acenaphthene (19)*

To fluoro-acenaphthylene (**11**) (0.20 g) was added $Br_2$ (0.20 g) as a $CCl_4$ solution, over 15 min at 20°. $^1$H and $^{19}$F n.m.r. showed that there were two products, of which the predominant one (89%) had a small $^3J_{HF}$ and was therefore assigned as the *trans* adduct. *cis* (**18**) (11%) $\phi_c$ 83.8 p.p.m., $\tau_H$ 4.30, $^3J_{HF}$ (*cis*) 18.9 Hz. *trans* (**19**) (89%) $\phi_c$ 89.7 p.p.m., $\tau_H$ 3.94, $^3J_{HF}$ (*trans*) 3.1 Hz (all in benzene solution). The reaction was performed in $CH_3CN$ with the same result.

### *cis-1,2-Iodochloro-1-fluoro-acenaphthene (20) and trans-1,2-Iodochloro-1-fluoro-acenaphthene (21)*

ICl (220 mg) was added to fluoro-acenaphthylene (**11**) in the same way as above. $^1$H and $^{19}$F n.m.r. again revealed two products; the predominant one having the smallest $^3J_{HF}$ was assigned the configuration with iodine and chlorine *trans*. The product ratio was also similar, 5:1 in favor of the *trans* (ICl) adduct. *cis* (**20**) (16%) $\phi_c$ 82.2 p.p.m., $\tau_H$ 3.67, $^3J_{HF}$ 19.7 Hz. *trans* (**21**) (84%) $\phi_c$ 74.9 p.p.m., $\tau_H$ 3.68, $^3J_{HF}$ 6.0 Hz (both in $CCl_4$ solution).

### *cis-1-Chloro-2-fluoro-acenaphthene (22) and trans-1-Chloro-2-fluoro-acenaphthene (23)*

Powdered AgF (8 g) was added to an acetonitrile solution (50 ml) of acenaphthylene (2.0 g) and the mixture cooled with an ice-bath. ICl (2.0 g), dissolved in acetonitrile (30 ml), was then added over 20 min to this mixture, with stirring. At the end of this period, the reaction was worked-up in the usual way. $^{19}$F n.m.r. of this crude product revealed two resonances in the ratio 85:15, and it was immediately eluted down a neutral silica gel column with petroleum ether – benzene.

Three compounds were separated; the first and major component contained no fluorine and showed a sharp singlet at τ 4.45, indicating that it was the *trans*-dichloride of acenaphthene; the mass spectrum, melting point and elemental analysis confirmed this.

The second compound, running close behind, gave $^{19}$F and $^1$H n.m.r. spectra almost identical with that of **13** (see Figs. 1A and 3A) and was assigned as the *trans*-chlorofluoride (**23**). The last component, a minor one, was evidently the *cis*-chlorofluoride (**22**), since there were two low-field protons with a coupling between them of 6.0 Hz (expected for $^3J_{HH}$, $\phi = 0°$), which were coupled to fluorine. The n.m.r. parameters in benzene solution are:

| | *cis* (**22**) | *trans* (**23**) |
|---|---|---|
| $^3J_{HF}$ (Hz) | 10.0 | 21.0 |
| $^2J_{HF}$ (Hz) | 53.7 | 53.5 |
| $^3J_{HH}$ (Hz) | 6.0 | 1.0 |
| $\tau_{H_1}$ | 4.87 | 4.53 |
| $\tau_{H_2}$ | 4.36 | 3.77 |
| $\phi_c$ (p.p.m.) | 173.3 | 162.5 |

### *1-Fluoro-acenaphthene (25)*

One gram of **24** was shaken with powdered AgF (2.0 g) for 20 min in acetonitrile at room temperature. The grey precipitate and excess AgF was filtered off and water and chloroform added to the solution. The organic layer was separated, dried, and concentrated down carefully without heating. The $^1$H spectrum showed a set of broad lines

---

[11] The spectrum of a deuterated compound such as **17**-$d_1$ has been thoroughly investigated by Kanazawa and Baldeschewieler (13) and as such is capable of analysis, provided that a reasonably well-resolved spectrum can be obtained. However, the extreme broadness of the lines prevents one from observing the weak transitions which are necessary to obtain the full analysis of the spectrum.

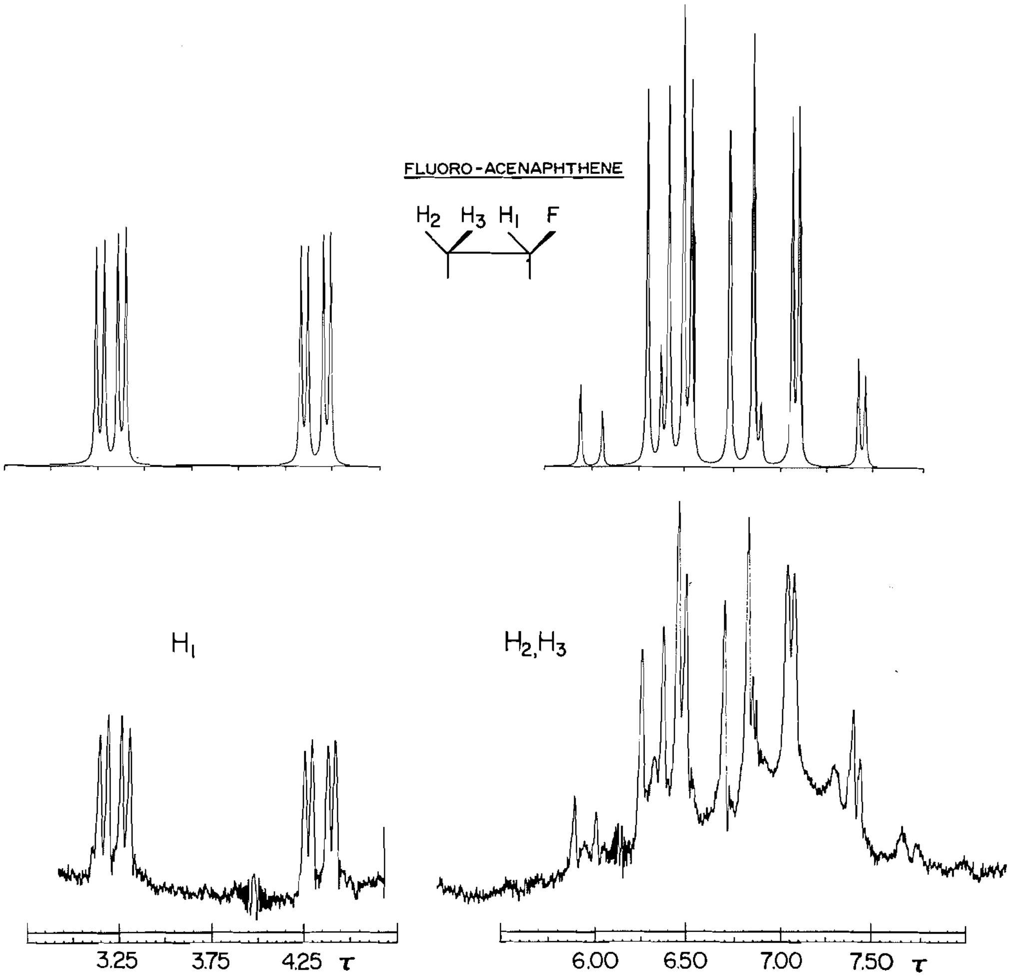


FIG. 4. Partial ${}^1H$ n.m.r. spectra of 1-fluoro-acenaphthene. The lower trace shows the spectrum measured with simultaneous irradiation of the aromatic protons. The upper trace is the computer simulation using the parameters listed in the text. The sample used could not be purified and hence contained some impurities.

in the methylene region and an octet at low field. By careful adjustment of the solvent, the complexity of the spectrum was reduced as much as possible (with 60% chloroform, 40% acetone). The lines were further sharpened by decoupling of the aromatic protons, and this double resonance (${}^1H$) spectrum is shown in Fig. 4, bottom.

The spectrum was then analyzed by hand as an ABMX system; values from this analysis were used as the input numbers for an iterative computer analysis of the spectrum using TWOSUM. The final computer spectrum, which is shown above in Fig. 4, top, had an average deviation of only 0.028 Hz from the experimental.

Some impurity lines are visible in Fig. 4; it was found impossible to purify **25** in any way at all, since it decomposed on alumina and silica gel, and with gentle heat, weak acid or base. N.m.r. parameters: ${}^3J_{H_3F}$ (*cis*) 29.52 Hz, ${}^3J_{H_1H_2}$ (*cis*) 6.68 Hz, ${}^3J_{H_2F}$ (*trans*) 21.39 Hz, ${}^3J_{H_1H_3}$ (*trans*) 1.485 Hz, ${}^2J_{H_2H_3}$ (*gem*) 18.30 Hz, ${}^2J_{H_1F}$ (*gem*) 55.59 Hz, $\tau_{H_1}$ 3.665, $\tau_{H_2}$ 6.458, $\tau_{H_3}$ 6.661, $\phi_c$ 158.8 p.p.m.

*Nuclear Magnetic Resonance Measurements*

All n.m.r. measurements were made with a modified Varian HA-100 instrument (14) operating in the locked modes of operation, using appropriate reference substances; all proton chemical shifts are given with respect to tetramethylsilane and fluorine shifts ($\phi_c$ values) are with respect to fluorotrichloromethane (freon 11).

Spectra for analysis purposes were run on appropriate sweep widths, usually 100 Hz, and were fully calibrated.

Analyses of the n.m.r. spectra were often performed by long-hand methods. Computer based analyses used the programme TWOSUM, kindly provided by Dr. John Martin of the University of Alberta, Edmonton, and the

IBM 7040 computer at the University of British Columbia Computer Centre. A plotting routine SMASH was written by Mr. John Coulthard of the U.B.C. Computer Centre and was used in conjunction with a Calcomp plotter.

It is a pleasure to thank the National Research Council of Canada and Imperial Oil Ltd. for their financial support of this work.

1. L. D. HALL, D. L. JONES, and J. F. MANVILLE. Chem. and Ind. (London), 991 (1965).
2. (*a*) L. D. HALL and J. F. MANVILLE. Chem. Commun. 35 (1968). (*b*) L. D. HALL and J. F. MANVILLE. Can. J. Chem. **47**, 361 (1969).
3. H. SCHMIDT and H. MEINERT. Angew. Chem. **71**, 126 (1959); **72**, 109 (1960); **72**, 493 (1960).
4. R. H. ANDREATTA and A. N. ROBERTSON. Aust. J. Chem. **19**, 1961 (1966).
5. L. D. HALL and D. L. JONES. Can. J. Chem. **51**, 2915 (1973).
6. S. J. CRISTOL, F. R. STERNITZ, and P. S. RAMEY. J. Am. Chem. Soc. **78**, 4939 (1956).
7. R. F. MERRITT and F. A. JOHNSON. J. Org. Chem. **31**, 1859 (1966).
8. M. J. S. DEWAR and R. C. FAHEY. J. Am. Chem. Soc. **85**, 2245 (1963).
9. A. BOWERS, L. C. IBANEZ, E. DENOT, and R. BECERRA. J. Am. Chem. Soc. **82**, 4001 (1960).
10. L. D. HALL and D. L. JONES. Can. J. Chem. **51**, 2925 (1973).
11. L. D. HALL and D. L. JONES. Can. J. Chem. **51**, 2930 (1973).
12. D. P. SHOEMAKER and C. W. GARLAND. Experiments in physical chemistry. McGraw-Hill, New York. 1963.
13. Y. KANAZAWA and J. D. BALDESCHWIELER. J. Mol. Spectrosc. **16**, 325 (1965).
14. R. BURTON and L. D. HALL. Can. J. Chem. **48**, 59 (1970).