*Anal.* Calcd for $C_8H_4N_2Br_2$: C, 33.36; H, 1.40; N, 9.73. Found: C, 33.39; H, 1.37; N, 9.63.

**3-Bromo-1,6-naphthyridine** (**7**) (372 mg, 18%) was recrystallized twice from cyclohexane giving white crystals, mp 125–126°.

*Anal.* Calcd for $C_8H_5N_2Br$: C, 45.96; H, 2.41; N, 13.40. Found: C, 45.95; H, 2.45; N, 13.23.

**8-Bromo-1,6-naphthyridine** (**8**).—Evaporation of the solvent gave 473 mg (22.6%) of fine cottony needles from cyclohexane, mp 84–86°.

*Anal.* Calcd for $C_8H_5N_2Br$: C, 45.96; H, 2.41; N, 13.40. Found: C, 45.96; H, 2.51; N, 13.12.

**1,6-Naphthyridine** (**2**).—A total of 160 mg (12%) of starting material was recovered.

**Bromo-1,7-naphthyridines.**—The same conditions were used as in the general procedure but the amounts were as follows: 1,7-naphthyridine (**3**), 343 mg (2.6 mmol); bromine, 700 mg (3.90 mmol); and pyridine, 240 mg (3.0 mmol).

**3,5-Dibromo-1,7-naphthyridine** (**11**).—White crystals [mp 149–151°, mass spectral molecular weight, 288, with the characteristic 1:2:1 ratio (two mass units apart) indicating the presence of two bromine atoms; P, *m/e* 288 (100%)], were obtained in a 27% (16 mg) yield.

*Anal.* Calcd for $C_8H_4N_2Br_2$: C, 33.36; H, 1.40; N, 9.73. Found: C, 33.06; H, 1.26; N, 9.48.

**5-Bromo-1,7-naphthyridine** (**10**).—The white solid was sublimed at 40° (0.1 mm) affording 140 mg (25%) of small fine needles, mp 69–70°.

*Anal.* Calcd for $C_8H_5N$ Br: C, 45.96; H, 2.41; N, 13.40. Found: C, 45.90; H, 2.57; N, 13.15.

**1,7-Naphthyridine** (**3**).—A total of 61 mg (18%) of starting material was recovered.

**Bromo-1,8-naphthyridines. 3-Bromo-1,8-naphthyridine** (**12**).—The white solid was sublimed at 100° (0.1 mm) giving 50 mg (4.8%), mp 155–156°, of the monobromo derivative.

*Anal.* Calcd for $C_8H_5N_2Br$: C, 45.96; H, 2.41; N, 13.40. Found: C, 45.90; H, 2.35; N, 13.30.

**3,6-Dibromo-1,8-naphthyridine** (**13**).—The material obtained from the chromatographic column was sublimed at 150° (0.1 mm) affording 6 mg (0.5%) of a white solid, mp 300°.

*Anal.* Calcd for $C_8H_4N_2Br_2$: C, 33.36; H, 1.40; N, 9.73. Found: C, 33.16; H, 1.30; N, 9.48.

**8-Amino-1,7-Naphthyridine** (**16**) **by the Skraup Reaction.**—The previously described procedure[1] for the preparation of 1,8-naphthyridines was employed except that 2,3-diamino- instead of 2-aminopyridine was used. The residue obtained on evaporation of the chloroform extract of the basic reaction mixture, on recrystallization from ethanol, gave 400 mg of a white solid (mp 168–169°). A mixture melting point of this solid with the amination product of 1,7-naphthyridine was not depressed.

# Fluorination of Nitroaromatic Amines in Liquid Hydrogen Fluoride and Acetonitrile[1]

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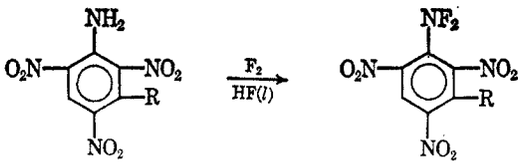
A general synthetic procedure has been found for the preparation of previously unreported nitroaromatic difluoramines. Nitroaromatic monoamines, such as picramide and its analogs, have been converted in high yield into the corresponding difluoramines in liquid hydrogen fluoride and in some cases in organic solvent, such as acetonitrile. Nitroaromatic diamines and triamines undergo similar fluorination reactions. Dinitro-substituted anilines fluorinate in good yield but the amine fluorination is accompanied by ring fluorination *ortho* to the difluoramino group. This reaction and general considerations of aromatic radical stabilization provide evidence for a radical mechanism operating in the fluorination reaction. In addition an unexpected product was obtained in the fluorination of 1,3-dinitro-2,4,6-triaminobenzene, which gave only a small amount of the corresponding trisdifluoramine and a major yield of 1,3-dinitro-2,4,6-tris(difluoramino)-1,2,3,4,5,6-hexafluorocyclohexane. Coupling rather than direct fluorination was obtained with pentafluoroaniline, which yielded bis(pentafluorophenyl)difluorohydrazine by a radical mechanism. The nitroaromatic difluoramino group between adjacent nitro groups was subject to attack by nucleophiles, such as ammonia and water. The synthesis, reaction, and properties of this novel class of compounds are discussed.

There have been relatively few reports of attempts to fluorinate amines by direct elemental fluorination.[2] Among the problems encountered in the direct fluorination of amines are the lack of a suitable solvent medium and decomposition of the reactants owing to the activity of the fluorine. At the least, formation of amine hydrogen fluoride salts can occur as fluorination proceeds, which has on several occasions effectively blocked further reaction. It was felt that, to circumvent these problems, weakly basic amines would be less susceptible to salt formation and, if already substituted with negative groups, they would be less susceptible to oxidation. It also appeared that fluorination in solution would work best, provided reasonable solvation of the starting material and product could be obtained. Since picramide did not form a salt with hydrogen fluoride, it was chosen as an example of a weak base and was fluorinated in liquid hydrogen fluoride, which is an excellent solvent for many nitroaromatic amines. 1-Difluoramino-2,4,6-trinitrobenzene was obtained in good yield, leading us to study the direct fluorination of a variety of nitroaromatic amines to the corresponding nitroaromatic difluoramines, a class of compounds not previously reported. Subsequent research revealed that some organic solvents, particularly acetonitrile, were useful in many cases and provided media for selective fluorinations in solution, a technique not often possible to use.




R = –H, $-CH_3$, $-OCH_3$, $-NO_2$

## Results and Discussion

The use of HF as a solvent for direct elemental fluorination of amines is unique and offers several advantages. Anhydrous HF is an excellent solvent for most amines

(1) Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(2) For reviews on fluorination of organic compounds, see R. Stephens and J. C. Tatlow, *Quart. Rev.* (London), **16**, 57 (1962); J. M. Tedder, *Advan. Fluorine Chem.*, 104 (1960).

and amides. Whereas the amines used in this work are not basic enough to allow salt formation, they are easily solvated. In addition HF allows the use of a much higher concentration of fluorine than that used with organic solvents. The low boiling point of HF (19°) provides for its easy removal during the reaction work-up.

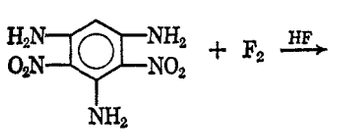
Fluorination of nitroaromatic amines can be carried out in acetonitrile, sulfuric acid, and acetic acid, as well as in HF. Anhydrous HF and acetonitrile are the preferred solvents since they give a cleaner reaction and high yields. Although acetonitrile and fluorine react, the products are volatile and are removed during the reaction work-up. The choice of solvent depends upon the nature of the amine to be fluorinated. Whereas 2,4,6-trinitroaniline and its derivatives can be fluorinated in HF, acetonitrile, or acetic acid without a significant variance in yield, 2,4- and 2,6-dinitroaniline must be fluorinated in acetonitrile, since fluorinations in HF result in complete decomposition. These compounds are basic enough so that partial or complete protonation of the amino group occurs in HF and attack on the aromatic ring occurs. The basic mononitroanilines and aniline cannot be fluorinated in any solvent; in all cases the starting material is destroyed. On the other hand, tetranitro- and pentanitroaniline must be fluorinated in HF; in acetonitrile they are not soluble and no reaction occurs. The solvent properties of HF probably account for its success in these cases. 1,5-Diamino-2,4-dinitrobenzene and 3,5-diamino-2,4,6-trinitrotoluene were consistent with these solvent correlations in that they were more soluble and were best fluorinated in acetonitrile. The only anomaly found was 1,3,5-triamino-2,4-dinitrobenzene, which could be fluorinated in HF but not in acetonitrile. This can be partially explained by the insolubility of the compound in acetonitrile; it is easily soluble in HF. In general, acetonitrile is suitable where solubility of the starting material presents no problem. Anhydrous HF can be used in cases where protonation of the amino group does not occur.

A typical reaction procedure consists of dissolving or suspending the nitroaromatic amine in a suitable solvent and passing a mixture of fluorine in nitrogen through the reaction solution until it becomes lightly colored, after first passing through a dark colored stage. In a few cases the product is insoluble and will precipitate. At this point the solvent is removed, leaving the difluoramino compound in crude state. Finally, purification is by recrystallization or by liquid chromatography using silica gel as the substrate.

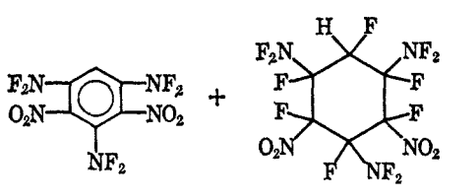
When HF is used as solvent, the fluorinations are carried out in a Kel-F apparatus. When the solvent is acetonitrile, either glass or Kel-F equipment can be used. The conditions for the fluorination of each compound vary, depending upon the solubility, ease of fluorination, etc., of the compound in question. Specific reaction conditions are given in the Experimental Section.

In most instances the desired difluoramino compounds were obtained in good yield. It can be seen from the Experimental Section that nitroaromatic monoamines were easily fluorinated and gave in all but one case stable difluoramino derivatives. Although difluoraminopentanitrobenzene was prepared and isolated in crystalline form, it decomposed in air or under nitrogen within a few minutes. Its structure was confirmed by nmr spectroscopy.

In contrast to nitroaromatic monoamines, the diamines and triamines gave only low yields of difluoramino compounds, along with decomposition products. 2,4-Bis(difluoramino)-1,5-dinitrobenzene could be prepared but had to be separated from its 3-fluoro and 6-fluoro derivatives. When this fluorination was run in acetonitrile both the 3- and 6-fluoro compounds were present; fluorination in HF yielded only the 6-fluoro product as a trace impurity. Fluorination of a compound with completely substituted positions, such as 3,5-diamino-2,4,6-trinitrotoluene, gave a low yield of the bisdifluoramino product. Fluorination of 1,3,5-trinitro-2,4-diaminobenzene and 1,3,5-trinitro-2,4,6-triaminobenzene provided only trace amounts of aromatic difluoramino products; these were detected by $^{19}F$ nmr spectra of the reaction products, but no compound could be isolated. 1,3,5-Triamino-2,4-dinitrobenzene (I) gave anomalous results not conforming to the patterns established by our other reactions. Fluorination of I was unsuccessful in acetonitrile. However, fluorination in HF gave a small amount of 1,3,5-tris(difluoramino)-2,4-dinitrobenzene (II) and, as the major product, the unexpected compound 1,3,5-tris(difluoramino)-2,4-dinitro-1,2,3,4,5,6-hexafluorocyclohexane (III). Since the more basic character of dinitroanilines was used as the rationale for their inability to be fluorinated in HF, it is surprising that I could be successfully fluorinated. Further, the occurrence of the cyclohexane compound (III) as the major product can only be explained as an addition reaction after initial fluorination. Fluorinated decomposition products often were present in reaction mixtures in this work, but this was the only case in which a stable ring-fluorinated compound was obtained. Although it is known that benzene can react with fluorine in the gaseous state to give perfluorocyclohexene,[3,4] and with $COF_3$ to give partially fluorinated cyclohexane,[5] the present case appears to be the first instance of ring saturation by fluorine in a liquid medium.



I



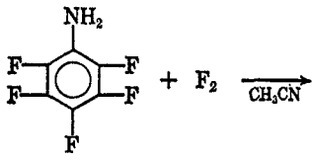
II III

2,2′4,4′,6,6′-Hexanitrodiphenylamine afforded an example of a nonbasic secondary amine. Fluorination in acetonitrile gave the desired 2,2′,4,4′,6,6′-hexanitrodiphenylfluoramine but the fluorination did not proceed in HF. It decomposes within a few days when stored

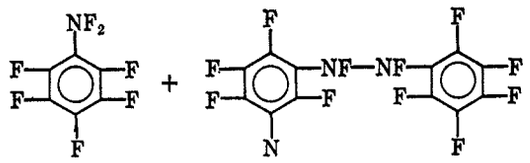
(3) N. Fukahara and L. A. Bigelow, *J. Amer. Chem. Soc.*, **63**, 2792 (1941).
(4) A. R. Gilbett and L. A. Bigelow, *ibid.*, **72**, 2411 (1950).
(5) J. A. Oliver and R. Stevens, *J. Chem. Soc.*, 5491 (1965).

at room temperature but is stable for several months at −18°.

Pentafluoroaniline provided an example of a nonbasic aromatic amine not containing a nitro group. Fluorination of this compound yielded as the major product the coupled compound bis(pentafluorophenyl)difluorohydrazine (VI) and a trace of pentafluorodifluoraminobenzene (V).



IV

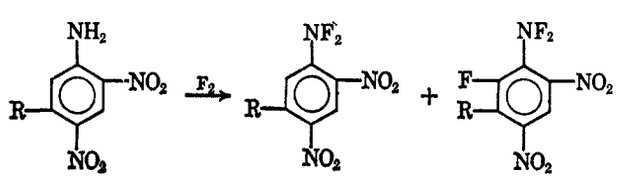


V VI

The fluorination of 2,4,6-trinitroacetanilide was studied briefly to determine whether substituted amines offered any advantage in yield and cleanliness of reaction over free bases. Fluorination in HF afforded 1-difluoramino-2,4,6-trinitrobenzene in 60–75% yield. The reaction proceeded in the same manner as with picramide and no special advantages were noted. However, it is believed that N-acetyl derivatives can be used in place of the parent amine with no loss of efficiency.

The rate and completeness of these fluorinations in solution have not permitted the isolation of intermediates for mechanism studies. Also, whether the fluorination reaction is a radical process or a direct attack of elemental fluorine by an ionic process has not been possible to determine definitely. However, since considerable evidence has been reported substantiating a radical mechanism for other fluorination reactions and satisfactorily answers all questions arising in the present work, we favor it at this time. For example, the fluorination of picramide and of other analogs would take place through abstraction of the amine hydrogen by fluorine radical, followed by fluorination, and a second hydrogen abstraction and fluorination.

Similarly ring fluorination always occurs by a radical reaction when the position *ortho* to the amino group is unsubstituted. Thus, VIIa–c when fluorinated gave the normal difluoramino derivatives, VIIIa–c, plus significant quantities of *o*-fluoro products, IXa–c.

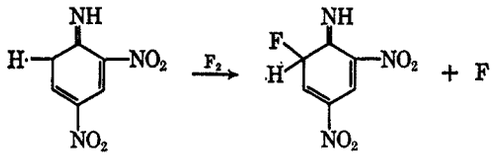


VIIa, R = H; b, R = F; c, R = $NH_2$

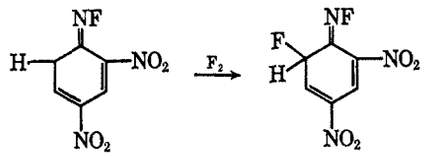
VIIIa, R = H; b, R = F; c, R = $NF_2$

IXa, R = H; b, R = F; c, R = $NF_2$

Fluorination of the *ortho* positions can occur through the reaction of intermediate stabilizing radicals such as X or XI shown below with fluorine followed by abstractions of the *ortho* hydrogen and continued fluorination of the amine group. The radical mechanism is further supported by the fact that bis(pentafluorophenyl)difluorohydrazine (VI) is the major product from the fluorination of pentafluoroaniline (IV). This product undoubtedly arises from coupling of two hexafluoroanilyl radicals. Although no coupling products were observed in nitroaromatic amine fluorinations, it seems reasonable that the greater stability of the corresponding radical intermediates, more delocalization of the radical site, and possible steric interferences would not favor the coupling reaction.

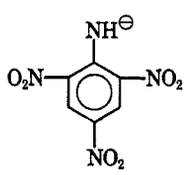


X



XI

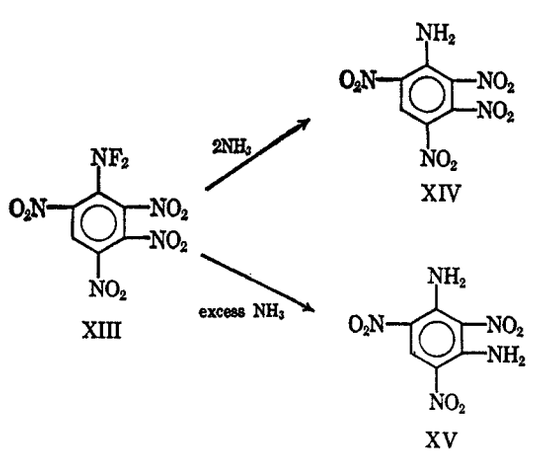
Whereas the radical mechanism is favored, the direct attack of elemental fluorine upon the amines giving rise to stable anions such as XII should not be discounted.



XII

A reaction scheme similar to that for the radical mechanism is quite possible. It is consistent with all questions arising from this work except for the presence of the one coupled product (VI).

A short study of the reactions of nitroaromatic difluoramino compounds was carried out using 1-difluoramino-2,3,4,6-tetranitrobenzene (XIII) as a model compound. When 2 equiv of ammonia were allowed to react, the product was tetranitroaniline (XIV). Addition of an excess of ammonia to XIII gave 1,3-diamino-2,4,6-trinitrobenzene (XV). Thus



XIII XIV XV

the difluoramino group is more easily displaced than nitro by nucleophilic attack. It was also found that the

nitroaromatic difluoramino groups were slowly hydrolyzed by water. When 1-difluoramino-2,4,6-trinitrobenzene was dissolved in 75% aqueous acetonitrile and the increase in picric acid was followed by ultraviolet analysis, it was found that at ambient temperature the difluoramino group was slowly hydrolyzed. Hydrolysis was essentially complete after 12 days.

The nmr spectra of the aromatic difluoramines have very sharp $NF_2$ peaks occurring in the $\varphi$ −60 to −68 region. The range of chemical shifts was found to be quite narrow, and substitution influenced the degree of shift only by a small amount. For comparison, the nmr data of the aromatic difluoramines is listed in the experimental section. It can be seen that when an $NF_2$ group occurs between two nitro groups, the range of chemical shift is $\varphi$ −61.3 to −63.5, whereas an $NF_2$ group between a fluoro and a nitro group gives shifts in the $\varphi$ −62.6 to −63.4 region. When the $NF_2$ group is flanked by a nitro group and a proton, the range is $\varphi$ −65.8 to −68.3. This generality, along with splitting patterns, has been found useful for the identification of mixtures of products from fluorination reactions involving nitroaromatic amines. Definite splitting patterns occur between difluoramino groups and *ortho* substituents. The coupling constant for difluoramino groups and fluorine atoms is about 21 cps and for protons about 2 cps. In one case, 1,3-bis(difluoramino)-2,4-dinitrobenzene, coupling occurs between difluoramino fluorines and a proton in the *meta* positions five bonds removed; a value of about 1 cps was determined for this interaction.

## Experimental Section

Melting points and boiling points are uncorrected. Elemental analyses were determined by Stanford University Microanalytical Laboratory. Infrared spectra were run on a Perkin-Elmer Infracord spectrophotometer, and nmr analyses were performed on a Varian HA-100 spectrometer. All $\tau$ and $\varphi$ values for the nmr spectra are reported with respect to tetramethylsilane and fluorotrichloromethane as internal standards. Since many of the compounds prepared in this work are derivatives of trinitrobenzene, they possess the characteristics of high explosives. Although no hazardous incidents have occurred in the present work, we advise that these compounds be handled with caution. The use of plastic in place of metal equipment is recommended.

**1-Difluoramino-2,4,6-trinitrobenzene.**—A 2.0-g sample of 2,4,6-trinitroaniline was dissolved in 50 ml of anhydrous HF in a Kel-F reactor and fluorinated by bubbling a stream of 60% $F_2$ in $N_2$ (62 cc/min) through the solution for 3 hr at −5–0°. As the fluorination proceeded a yellow solid precipitated from the reaction mixture. The solvent was removed by entrainment in $N_2$, leaving a yellow crystalline solid. This was immediately taken up in $CH_2Cl_2$ and treated with NaF; the solvent was removed, leaving 2.04 g of crude 1-difluoramino-2,4,6-trinitrobenzene (crude yield, 88%). This was further purified by means of a silica gel column using chloroform as eluent. Elution of the desired compound was detected by spraying a spot of eluate on filter paper with a 0.1% solution of N,N,N′,N′-tetramethyl-*p*-phenylenediamine dihydrochloride (TMPDA reagent) in 50% methylene chloride and ethanol.[6] The spot turned blue immediately and slowly changed to yellow over a 2-min period. Removal of solvent yielded 1.73 g of 1-difluoramino-2,4,6-trinitrobenzene as a light yellow crystalline solid, mp 69°, yield 75%. *Anal.* Calcd for $C_6H_2N_4O_6F_2$: C, 27.27; H, 0.77; N, 21.21. Found: C, 27.22; H, 0.89; N, 20.91.

Picramide can also be fluorinated in acetonitrile and acetic acid in yields of 74 and 64%, respectively.

**1-Difluoramino-2,6-dinitrobenzene.**—A 0.6-g sample of 2,6-dinitroaniline was dissolved in 15 ml of acetonitrile and was fluorinated at −10 to −5° with a stream of 15% fluorine in nitrogen for 55 min or until the color of the solution changed from orange to yellow. The reaction solution was then poured into 15 ml of diethyl ether and treated with activated charcoal, and the solvent was evaporated, leaving 0.81 g of an orange semisolid. This was taken up in 2 ml of chloroform and passed through a silica gel column using chloroform as solvent. The eluate collected gave a blue to yellow test with the TMPDA reagent.[6] The solvent was then removed *in vacuo*, leaving 0.39 g of a yellow crystalline solid, mp 76–80°. Recrystallization from a 50% chloroform–hexane mixture yielded light yellow needles, mp 91–93°. This compound was identified as 1-difluoramino-2,6-dinitrobenzene by nmr, infrared, and elemental analyses. *Anal.* Calcd for $C_6H_3F_2N_3O_4$: C, 32.86; H, 1.38; N, 19.18. Found: C, 32.61; H, 1.53; N, 19.19.

**3-Difluoramino-2,4,6-trinitrotoluene.**—A 0.50-g sample of 3-methyl-2,4,6-trinitroaniline dissolved in ~45 ml of anhydrous hydrogen fluoride was fluorinated with a stream of 46% fluorine in nitrogen (56 cc/min) for 30 min at −4 to −6°; a yellow solid precipitated during the fluorination. The solvent was removed, leaving a yellow crystalline solid. This was dissolved in chloroform, filtered to remove a small amount of insoluble material, and treated with sodium fluoride; the solvent was removed *in vacuo*, leaving 0.51 g of a yellow crystalline solid, mp 105–107°. Recrystallization from a chloroform–hexane mixture yielded 0.45 g (78% of theory) of a light yellow crystalline solid, mp 111°, which was identified as 3-difluoramino-2,4,6-trinitrotoluene by elemental analyses and infrared and nmr spectra. *Anal.* Calcd for $C_7H_4F_2N_4O_6$: C, 30.22; H, 1.45; 20.15. Found: C, 30.22; H, 1.35; N, 20.11.

When acetonitrile was used as solvent for this fluorination at −5°, the product was obtained in a 61% yield.

**1-Difluoramino-2,4-dinitrobenzene.**—Fluorination and isolation procedures were the same as for 1-difluoramino-2,6-dinitrobenzene. The product was a light yellow liquid which contained about 10% 1-difluoramino-6-fluoro-2,4-dinitrobenzene. *Anal.* Calcd for a 9:1 mixture: C, 32.60; H, 1.32; N, 19.02. Found: C, 32.72; H, 1.45; N, 18.90.

**1-Difluoramino-5-fluoro-2,4-dinitrobenzene.**—Preparative procedure was the same as for 1-difluoramino-2,6-dinitrobenzene. The product was a light yellow crystalline solid, mp 51°. An $^{19}F$ nmr spectrum showed the presence of a trace amount (<5%) of 1-difluoramino-5,6-difluoro-2,4-dinitrobenzene. *Anal.* Calcd for $C_6H_2F_3N_3O_4$: C, 30.37; H, 0.85; N, 17.73. Found: C, 30.09; H, 0.95; N, 17.80.

**3-Difluoramino-2,4,6-trinitroanisole.**—Reaction procedure was the same as that for 3-difluoramino-2,4,6-trinitrotoluene. The product was obtained in 77% yield as a yellow liquid. *Anal.* Calcd for $C_7H_4F_2N_4O_7$: C, 28.58; H, 1.36. Found: C, 28.03; H, 1.35.

**1-Difluoramino-2,3,4,6-tetranitrobenzene.**—Reaction procedure was the same as that for 1-difluoramino-2,4,6-trinitrobenzene except that no external cooling was used (bp HF, +19°). The product was obtained in 75% yield as a yellow crystalline solid, mp 84°. *Anal.* Calcd for $C_6HF_2N_5O_8$: C, 23.32; H, 0.33; N, 22.66. Found: C, 23.45; H, 0.60; N, 22.86.

When the fluorination was run in acetonitrile at 0° a yield of only 30% was obtained.

**Difluoraminopentanitrobenzene.**—Reaction procedure was the same as that for picramide except that no external cooling was used. The product was stable only in solution and could be detected by its nmr spectrum. When solvent was removed under nitrogen, large orange crystals appeared; however, after a few minutes these became an orange viscous oil.

**3,5-Bis(difluoramino)-2,4,6-trinitrotoluene.**—Reaction procedure was the same as that used for 1-difluoramino-2,6-dinitrobenzene. The product was obtained in 10% yield as a yellow crystalline solid, mp 143–145°. *Anal.* Calcd for $C_7H_3F_4N_5O_6$: C, 25.56; H, 0.91; N, 21.28. Found: C, 25.39; H, 1.00; N, 21.41.

**3-Difluoramino-5-chloro-2,4,6-trinitrotoluene.**—Reaction procedure was the same as that used for 1-difluoramino-2,6-dinitrobenzene. The product was obtained in 16% yield as a yellow crystalline solid, mp 149–153°. *Anal.* Calcd for $C_7H_3ClF_2N_4O_6$: C, 26.88; H, 0.97; N, 17.93. Found: C, 27.27; H, 1.19; N, 18.18.

**2,2′,4,4′,6,6′-Hexanitrodiphenylfluoramine.**—Reaction procedure was the same as that used for 1-difluoramino-2,6-dinitrobenzene. The product was obtained in 54% yield as an orange

(6) A method developed by M. J. Cziesla, Naval Ordnance Station, Indian Head, Md., private communication, Feb 21, 1964.

crystalline solid, mp 102–105° dec. *Anal.* Calcd for $C_{12}H_4FN_7O_{12}$: C, 30.26; H, 0.85. Found: C, 30.69; H, 0.98.

**Fluorination of 1,5-Diamino-2,4-dinitrobenzene.**—A 1.50-g sample of 1,5-diamino-2,4-dinitrobenzene was suspended in a 50 ml of acetonitrile and fluorinated at 0° with a stream of 20% fluorine in nitrogen (58 cc/min) for 105 min or until all of the solid starting material had dissolved and the solution turned light yellow. The reaction mixture was then poured into 100 ml of diethyl ether and treated with sodium fluoride, and the solvent was removed *in vacuo*, leaving 2.70 g of an orange liquid. This was dissolved in 1 ml of benzene and passed through a silica gel column using benzene as solvent. The eluate which was collected gave a positive difluoramino test with the TMPDA reagent. The solvent was removed, leaving 0.53 g of a light yellow semisolid. Recrystallization from a solution of 40% ether in hexane yielded 0.42 g of a yellow crystalline solid, mp 85° to 93°. An nmr spectrum of the solid showed that it consists of approximately 60% 1,5-bis(difluoramino)-2,4-dinitrobenzene, A, and 40% 1,5-bis(difluoramino)-2,4-dinitro-6-fluorobenzene, B. A trace of 1,5-bis(difluoramino)-2,4-dinitro-3-fluorobenzene was also present.

The two major components were separated and purified by passing the mixture through a silica gel column using a solution of 40% benzene in hexane as eluent. Product B eluted first, closely followed by A. However, they could be differentiated by using the TMPDA reagent, since product A gave a darker yellow spot than product B. Removal of solvent left pure samples of 0.24 g of A, mp 112°, and 0.16 g of B, mp 122°. Both products could be recrystallized from a 50% mixture of chloroform in hexane. *Anal.* Calcd for $C_6H_2F_4N_4O_4$ (A): C, 26.67; H, 0.75; N, 20.76. Found: C, 26.42; H, 0.75; N, 21.17. *Anal.* Calcd for $C_6HF_5N_4O_4$ (B): C, 25.02; H, 0.35; N, 19.45. Found: C, 25.01; H, 0.44; N, 19.59.

**Fluorination of 1,3,5-Triamino-2,4-dinitrobenzene.**—A 0.8 g sample of 1,3,5-triamino-2,4-dinitrobenzene was dissolved in 40 ml of anhydrous HF and fluorinated at −38° with a stream of 70% fluorine in nitrogen for 115 min or until the color of the reaction solution changed from orange to light yellow. The solvent was removed by entrainment in nitrogen, and the resulting green liquid was taken up in methylene chloride; this was treated with activated charcoal and the solvent was removed *in vacuo*, leaving 1.12 g of a light green liquid. This liquid was dissolved in chloroform and passed through a silica gel column using chloroform as solvent. The eluate was collected in two portions; one (A) gave a blue to yellow test with the TMPDA reagent, and the second portion (B) gave a spot which remained blue. Removal of solvent from A left 0.09 g of a light yellow solid, mp 46–53°. Recrystallization from a chloroform–hexane mixture gave a light yellow crystalline compound melting at 54–56°; this was 1,3,5-tris(difluoramino)-2,4-dinitrobenzene. *Anal.* Calcd for $C_6HF_6N_5O_4$: C, 22.44; H, 0.31; N, 21.82. Found: C, 22.18; H, 0.39; N, 22.20.

Evaporation of the solvent from fraction B left 1.02 g of a pale blue liquid which was tentatively identified as 1,3,5-tris(difluoramino)-2,4-dinitro-1,2,3,4,5,6-hexafluorocyclohexane arising from the saturation of the benzene ring of product A by fluorine. Elemental analysis and infrared and nmr spectra support this conclusion. *Anal.* Calcd for $C_6HF_{12}N_5O_4$: C, 16.56; H, 0.23; N, 16.10. Found: C, 16.91; H, 0.2; N, 15.57.

An $^{19}F$ spectrum of this product in $CDCl_3$ showed the data listed in Table I.

**Nmr Data for Aromatic Difluoramino Compounds.**—Listed below are the nmr data for the difluoramino nitroaromatic compounds synthesized in this work. The spectra were run on a Varian HA-100 spectrometer and all $\varphi$ and $\tau$ values are reported with respect to $CFCl_3$ and TMS, respectively. Where no designation of splitting pattern is mentioned, the signal is a singlet.

1-Difluoramino-2,4-dinitrobenzene showed an absorption at $\varphi$ −66.9 (−$NF_2$). 1-Difluoramino-2,4-dinitro-6-fluorobenzene had signals at $\varphi$ −62.6 (−$NF_2$), doublet, $J_{NF,F}$ = 22 cps; +102.3 (−F), triplet of doublets, $J_{F,NF}$ = 21 cps, $J_{F,H}$ = 10 cps. 1-Difluoramino-2,4-dinitro-5-fluorobenzene had signals at $\varphi$ −65.8 (−$NF_2$); +103.2 (−F), multiplet; $\tau$ 1.21 (−H, 3), doublet, 7 cps; 2.04 (−H, 6), doublet to triplets, $J_{H,F}$ = 10 cps, $J_{H,NF}$ = ~1.5 cps. 1-Difluoramino-2,4-dinitro-5,6-difluorobenzene had signals at $\varphi$ −62.7 (−$NF_2$), doublet, $J_{NF,F}$ = 21 cps; +126.5 (−F, 5), doublet, $J_{F,F}$ = 21 cps; +123.9 (F, 6), quartet, $J$ = 21 cps. 1-Difluoramino-2,6-dinitrobenzene showed absorptions at $\varphi$ −63.5 (−$NF_2$); $\tau$ 2.02 (H, ring). 1-Difluoramino-2,4,6-trinitrobenzene had signals at $\varphi$ −62.1 (−$NF_2$); $\tau$ 1.08 (H, ring). 1,5-Bis(difluoramino)-2,4-dinitrobenzene showed absorptions at $\varphi$ −68.3 (−$NF_2$); $\tau$ 1.51 (H, 3), quintet, $J_{H,NF}$ = ~1 cps; 1.35 (H, 6), quintet, $J_{H,NF}$ = ~2 cps. 1,5-Bis(difluoramino)-2,4-dinitro-6-fluorobenzene had signals at $\varphi$ −63.4 (−$NF_2$), doublet, $J_{NF,F}$ = 21.5 cps; +104.2 (−F), quintet, $J_{F,NF}$ = 21.5 cps; $\tau$ 2.72 (−H), singlet. 1,5-Bis(difluoramino)-2,4-dinitro-3-fluorobenzene had signals at $\varphi$ −67.4 (−$NF_2$), singlet; 102.6 (−F), singlet. 3-Difluoramino-2,4,6-trinitrotoluene had signals at $\varphi$ −62.8 (−$NF_2$); $\tau$ 7.42 (−$CH_3$); 1.48 (−H, ring). 3-Difluoramino-2,4,6-trinitroanisole showed absorptions at $\varphi$ −61.8 (−$NF_2$); $\tau$ 5.96 (−$CH_3$); 1.50 (−H, ring). 1-Difluoramino-2,3,4,6-tetranitrobenzene had signals at $\varphi$ −61.3 (−$NF_2$); $\tau$ 1.22 (−H, ring). 1-Difluoramino-2,3,4,5,6-pentanitrobenzene, 3-difluoramino-5-chloro-2,4,6-trinitrotoluene, and 3,5-bis(difluoramino)-2,4,6-trinitrotoluene had signals at $\varphi$ −62.0 (−$NF_2$), −62.5 (−$NF_2$), and −62.5 (−$NF_2$), respectively. 1,3,5-Tris(difluoramino)-2,4-dinitrobenzene showed absorptions at $\varphi$ −63.5 (−$NF_2$, 1); −68.2 (−$NF_2$, 3, 5). N-fluoro-1,1′,2,2′,3,3′-hexanitrodiphenylamine had a signal at $\varphi$ −15.4 (−NF).

TABLE I

| Peak, $\varphi$ | Assignment | Relative size |
|---|---|---|
| −23.9, multiplet | 1,3,5-$NF_2$ | 6 |
| 111.5, doublet of multiplets | 6-CF | 1 |
| 128.1, broad singlet | 1,5-CF | 2 |
| 151.0, triplet | 3-CF | 1 |
| 157.9, broad singlet | 2,4-CF | 2 |

**Registry No.**—Hydrogen fluoride, 7664-39-3; acetonitrile, 75-05-9; II, 15892-90-7; III, 15815-99-3; XIII, 15733-90-1; 1-difluoramino-2,4-dinitrobenzene, 15733-91-2; 1-difluoramino-2,4-dinitro-6-fluorobenzene, 15733-92-3; 1-difluoramino-2,4-dinitro-5-fluorobenzene, 15733-93-4; 1-difluoramino-2,4-dinitro-5,6-difluorobenzene, 15734-01-7; 1-difluoramino-2,6-nitrobenzene, 15733-94-5; 1-difluoramino-2,4,6-trinitrobenzene, 15733-96-7; 1,5-bis(difluoramino)-2,4-dinitrobenzene, 15733-95-6; 1,5-bis(difluoramino)-2,4-dinitro-6-fluorobenzene, 15733-97-8; 1,5-bis(difluoramino)-2,4-dinitro-3-fluorobenzene, 15733-98-9; 3-difluoramino-2,4,6-trinitrotoluene, 15734-02-8; 3-difluoramino-2,4,6-trinitroanisole, 15733-99-0; 1-difluoramino-2,3,4,5,6-pentanitrobenzene, 15734-00-6; 3-difluoramino-5-chloro-2,4,6-trinitrotoluene, 15735-52-1; 3,5-bis(difluoramino)-2,4,6-trinitrotoluene, 15816-00-9; 2,2′,4,4′,6,6′-hexanitrophenylfluoramine, 15816-01-0.

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