NEW COMPOUND SECTION

Synthesis, Spectral Data, and Physical Properties of Difluoraminopolynitroaromatic Compounds

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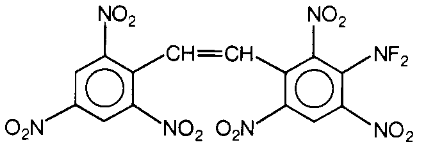
Three new classes of difluoraminopolynitroaromatic compounds (stilbene, biphenyl, and terphenyl derivatives) were prepared by adaptation of established procedures in treating the amino compound with elemental fluorine. A fourth class (azobenzene derivatives) was impossible to prepare by this method. Nmr and ir spectral data, as well as density and DTA results, are presented, and the syntheses are described.

A paucity of literature exists concerning the fluorination of amines with elemental fluorine (*13, 14*). Although the difficulties encountered in the fluorination of nitrogen compounds include lack of suitable solvents, decomposition, and salt formation, some progress in this area has been made, and the chemistry of organic nitrogen fluorides has been reviewed (*8*). Recently, we reported that weakly basic amines such as nitroaromatic amines could be successfully fluorinated in anhydrous hydrogen fluoride or acetonitrile, and the difluoramine derivatives isolated in good yield (*3*).

Our previous work (*3*) on primarily benzene derivatives has now been extended to higher analogs, i.e., stilbene, biphenyl, terphenyl, and azobenzene derivatives. The corresponding amino compounds were fluorinated to produce the following:



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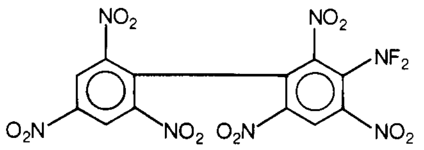

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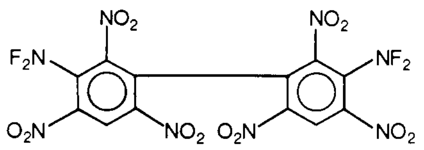

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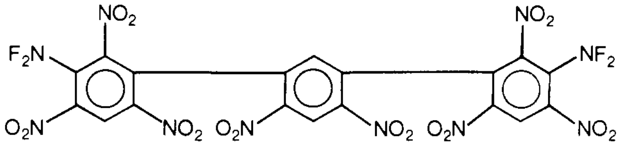

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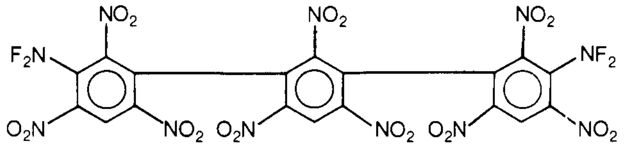

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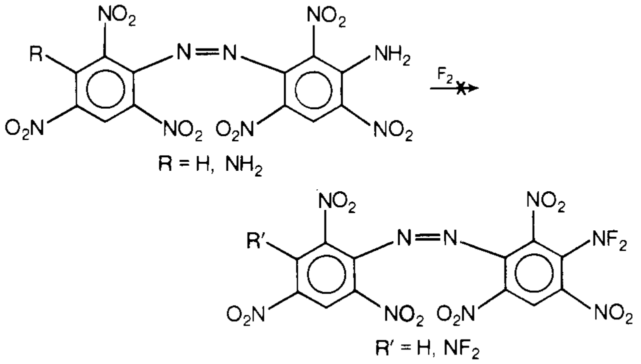
These compounds are high-melting (over 200°C), high-density (about 1.8 g/cc) yellow solids. Physical properties are summarized in Table I. The nmr spectra of the nitroaromatic difluoramines have sharp NF_2 peaks occurring usually as singlets in the 59.7–62.3-φ^* region. Compounds 3 and 4 each exhibited two peaks which were tentatively assigned to effects of rational barrier at the ring bonds. Table II slows both fluorine and proton nmr results.

Infrared spectra are summarized in Table III. The primary absorptions for Compounds 1–5 arose from the valence vibrations of the nitro groups and appeared as two peaks. Asymmetric stretching of the nitro groups appeared as a strong absorption in the 1540–1565 cm^{-1} range, and symmetric stretching appeared in the 1333–1348 cm^{-1} range.

The fourth class of compounds mentioned, azobenzene, eluded our attempts to fluorinate either of the aminohexanitroazobenzenes as shown:



R = H, NH_2

R′ = H, NF_2

Nonidentifiable products were formed in all attempts. From a synthesis point of view, this presented interesting

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Table I. Physical Properties and Purification of Difluoraminopolynitroaromatic Compounds[a]

Compd no.	Molecular formula	Mp, °C (dec)[b]	Column chromatography (silica gel),[c] eluant, vol %	Solvent of crystallization	Density, 25°C	DTA,[d] °C	
						Onset	Max
1	$C_{14}H_5F_2N_7O_{12}$	205–208	30% Ethyl acetate in chloroform	Nitromethane–chloroform	1.76	160	200
2	$C_{12}H_3F_2N_7O_{12}$	202–204	50% Methylene chloride in hexane	Chloroform	1.83	178	225
3	$C_{12}H_2F_4N_8O_{12}$	228–230	Chloroform	Chloroform	1.82	168	204 exploded
4	$C_{12}H_4F_4N_{10}O_{16}$	239[e,f]	10% Ethyl acetate in benzene[g,h] 10% Pentane in benzene	Ethyl acetate–chloroform	1.75	192	233
5	$C_{18}H_3F_4N_{11}O_{18}$	240[e]	10% Ethyl acetate in benzene[h]	Ethyl acetate–benzene	>1.75	...	...

[a] Elemental analyses (C, H, F, N) in agreement with theoretical values were obtained and submitted for review. [b] Preheated melting point apparatus to within 10° of the melting point. [c] Sample was placed on the column as an oil with minimum ethyl acetate. [d] Differential thermal analysis at 10°/min from 35°C. [e] Loosely packed in a capillary melting point tube. [f] Exploded. [g] Repeated chromatography was necessary. [h] Column was packed with 50% benzene–hexane.

Table II. Nmr Data for Difluoraminopolynitroaromatic Compounds[a]

Compd no.	Solvent	—NF_2, φ^*[b]	Aromatic C—H δ, ppm	—CH=CH—, ppm	J, Hz
1	Acetonitrile	61.9, s	9.15, s[c]	7.02, d; 7.44, d	$J_{AB} = 17$
2	Acetone-d_6	60.9, s	9.43, s; 9.50, t		$J_{FH} = 1$
3	Acetone-d_6	59.6, s; 59.8, s[d]	9.55, t		$J_{FH} = 1$
4	Acetone-d_6	62.2, s; 62.4, s[d]	8.28, s; 9.41, m		
5	Acetone-d_6	62.2, s	9.55, s; 9.60, s		

[a] s = singlet, m = multiplet, t = triplet. [b] Ref. 7. [c] Overlying a multiplet. [d] Occurrence of two NF_2 peaks instead of one peak is tentatively assigned to effects of rotational barrier at the aromatic rings.

Table III. Characteristic Ir Spectra of Difluoraminopolynitroaromatic Compounds[a]

Compd no.	NO_2, cm^{-1}, sym	NO_2, cm^{-1}, asym	C=C, cm^{-1}	=C—H, cm^{-1}
1	1348 s	1548 s	1587 w, 1605 w	3106 w
2	1333 s	1550 s	1600 m, 1618 m	3100 w
3	1339 s	1565 s	1613 w	3077 w
4	1340 s	1540 s	1605 m	3096 w
5	1340 s	1540 s	1600 m	3100 w

[a] Fluorolube mull. s = strong, m = medium, w = weak.

evidence that the azobenzene structure is unstable to the fluorination conditions. This is in contrast to the stilbene (Compound 1) prepared which is the carbon analog of the azobenzene compounds.

Experimental

Unless otherwise noted, chemicals were used as received from the manufacturer. Melting points reported are uncorrected and were obtained in a capillary with a Mel-Temp melting-point apparatus or a melting-point block. Elemental analyses were determined by Stanford University Analytical Laboratory and by E. McCarthy, SRI Analytical Services. Nmr data were obtained by L. Stietzel of SRI with a Varian HA-100 nmr spectrometer. Values for ^1H chemical shifts are given in φ units with respect to tetramethylsilane as internal reference, and values for the ^{19}F chemical shifts are given in φ^* units (7) with respect to trichlorofluoromethane as an internal reference. In nmr descriptions, s = singlet. Infrared spectra were run on a Perkin-Elmer Model 137 infracord spectrometer. Thin-layer chromatography was carried out on Eastman chromagram sheets of silica gel with fluorescent indicator. Densities were determined with a Fisher-Davidson gravitometer.

Caution: The difluoraminonitroaromatic compounds and their intermediates described in this paper are explosives and sensitive to initiation by impact, shock, friction, rapid heating, or other means. Many difluoramino and aromatic compounds are toxic in varying degrees and will cause stains and burns when brought into contact with the skin. Therefore, care should be taken when handling such compounds.

General fluorination procedure. Fluorine was obtained from the General Chemical Division of the Allied Chemical Corp. and was always diluted to ≤30% fluorine with nitrogen prior to fluorination (most organic materials burn in 50% fluorine). Undiluted fluorine was piped through copper tubing and when diluted, through Kel-F tubing. A Kel-F reaction cylinder (325-ml capacity) was used, and excess fluorine was destroyed by passing the exit gases through an aluminum column (3 ft × 3 in.) of whole charcoal briquets ($2F_2 + C \rightarrow CF_4$).

Dry acetonitrile (Nanograde) and the compound to be fluorinated were stirred magnetically in the Kel-F reactor (complete dissolution improved the reaction rate but was not required); air was removed by nitrogen; the reactor was immersed in a cooling bath; and a mixture of fluorine in nitrogen was bubbled through the reaction mixture until it darkened (red) and finally lightened to a clear yellow or orange color. The fluorine was shut off, and the system was flushed by a vigorous stream of nitrogen. Residual hydrogen fluoride was partially removed by adding anhydrous magnesium sulfate to the reaction mixture; column chromatography removed the last traces of HF. Also, methylene chloride was added to reduce the solubility of $MgSO_4$ in the acetonitrile.

The solvent was evaporated under vacuum, and the crude product was purified by column chromatography with silica gel. Elution of difluoraminonitroaromatic compounds in column chromatography was detected by spraying a spot of the eluate on filter paper with a 0.2% solution of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine dihydrochloride in 50% methylene chloride and ethanol (TMPDA reagent); thin-layer chromatograms were also sprayed with TMPDA reagent. The reagent turned blue in the presence of strong oxidizers such as NF_2-nitroaroma-

Table IV. Fluorination Conditions and Yield of Difluoramino Product

Amino compound		Acetonitrile, ml	Time, hr	Temp, °C^a	% Fluorine in nitrogen, vol	Flow rate of N_2+F_2, ml/min	NF_2 product	
No.	Wt, g						Yield, %	No.
1a	6.0	300	5.0	−15	30	60	45	1
2a	8.0	150	3.5	−15	25	80	43	2
3a	2.0	250	3.0	0	25	60	20	3
4b	5.0	250	5.0^b	−35	20	120	2	4
5d	1.5	300	4.0^b	−35	20	120	15	5

^{a} Ice bath (0°C). Salt, ice (—15°C). Dry Ice, ethylene dichloride slush (—35°C). ^{b} Unreacted amino compound was filtered from the reaction solution.

tic compounds. Often the blue color changed to yellow at or above ambient temperature.

The specific fluorination conditions and yields of Compounds 1-5 are shown in Table IV. Purification procedures, column chromatography and recrystallization of the five compounds, were described in Table I.

Aromatic Amine Intermediates

For Compound 1: 3-amino-2,2',4,4',6,6'-hexanitrostilbene, 1a. Compound 1a was prepared according to the method of Shipp (*11, 12*).

For Compound 2: 3-amino-2,2',4,4',6,6'-hexanitrobiphenyl, 2a. Anhydrous ammonia was bubbled from a coarse fritted glass tube through a magnetically stirred, boiling solution of 88 grams of 3-methoxy-2,2',4,4',6,6'-hexanitrobiphenyl (*6*) in 880 ml of anhydrous acetonitrile for 15 min. Excess ammonia was removed by boiling the clear red liquid an additional 15 min. Then 1 liter of hot ethanol was added with stirring to the hot reaction mixture. The flask was removed from the hot plate, and stirring was continued. Crystallization began after a few minutes. After the liquid had cooled to ambient temperature, the flask was placed in an ice water bath. Pure 2a was filtered, washed with cold ethanol, and dried in vacuo to give 62.4 grams of bright yellow crystals, mp 221–222°C lit (*5*) mp 217.5–218.5°C. A second fraction of 2a, 18.7 grams, mp 219–221°C was obtained by dissolving the residue from the mother liquor in 300 ml of boiling acetonitrile and adding 250 ml of hot ethanol to this hot solution, total 81 grams (95% yield).

For Compound 3: 3,3'-diamino-2,2'4,4',6,6'-hexanitrobiphenyl, 3a. Compound 3a was purchased from Northrop Carolina, Inc., Ashville, N.C.

For Compound 4: 3,3''-dimethoxy-2,2'',4,4',4'',6,6',6''-octanitro-m-terphenyl, 4a. Activated (*9*) copper powder (21.5 grams, 0.34 gram-atoms, Venus 44-F) in 50 ml of nitrobenzene was heated to 125°C. A solution of 1,3-dibromo-4,6-dinitrobenzene (*2*) (Reference is for the dichloro compound. We substituted with the dibromo compound.) (15.9 grams, 0.049 mole), 3-bromo-2,4,6-trinitroanisole (*3*) (Literature adaptation.) (39.3 grams, 0.012 mole) and warm nitrobenzene (100 ml was added in three portions. After the first 25-ml addition, no temperature rise was observed, and the slurry was warmed to 135°C. With the second 25-ml addition, an exothermic reaction occurred, and the temperature rose to 144°C. The metallic copper slowly took on a grey-brown color as copper bromide was formed. The remaining solution was added over 20 min at 135–140°C, and the slurry was stirred an additional 30 min at 135°C. The mixture was cooled to 60°C and filtered into a 1-liter, 3-necked flask.

The nitrobenzene was removed by steam distillation; this operation required approximately 5 hr. The yellow distillate was discarded, and the aqueous phase was decanted from the crude residual product, a dark gum. The gum was washed well with water, dissolved in 500 ml of boiling acetone, and treated with activated charcoal (Norit). The charcoal was removed, washed well with acetone, and the combined filtrates were concentrated to about 250 ml by use of reduced pressure. Hot methanol (500 ml) was added, and the solution was allowed to cool. A combined total of 16.8 grams (53% yield) crystalline 4a was obtained from the first crystallization and from the mother liquors, mp 267–270°C, reported (*10*) mp 265°C.

3,3''-Diamino-2,2'',4,4',4'',6,6',6''-octanitro-m-terphenyl, 4b. Compound 4a (11.0 grams, 0.017 mole) was dissolved in 110 ml of 1/1 tetrahydrofuran-methanol and treated with a slow stream of anhydrous ammonia for 0.5 hr with no external cooling. The yellow solution turned a red-orange color within 1 min, and an increase in temperature was observed (~20°C). Methanol (100 ml) was added, and the solution was carefully heated to boiling to remove excess ammonia. After cooling, 8.4 grams (80% crude yield) of 4b as a yellow product was obtained which was recrystallized by dissolving in 37 ml of hot dimethylformamide and adding methanol (15 ml). The yellow powder, 4b, 6.3 grams (60%) exploded at 352°C, reported (*4*) mp 355°C (exp).

For Compound 5: 1,3-dibromo-2,4,6-trinitrobenzene, 5a. Dry potassium nitrate, 92.2 grams (0.83 mole) was added portionwise during 20 min to 442.4 grams of 30% oleum (1.66 mole of SO_3). A resulting exotherm raised the temperature of the mixture to 120°C. With rapid stirring of this nitration mixture, 21.8 grams (0.092 mole) of *m*-dibromobenzene was added dropwise during 15 min at 120°C. A mild exotherm was observed during the addition; however, it was necessary to warm the reaction mixture with an oil bath to maintain a 120–130°C temperature range.

After the addition was complete, the mixture was stirred for 4 hr at 125°C, was cooled to 10°C, and was slowly quenched on 700 grams of crushed ice. The resulting aqueous mixture was extracted with four 300-ml portions of methylene chloride; the extracts were combined and then washed with two 500-ml portions of brine. The organic phase was filtered through anhydrous sodium sulfate and evaporated to give 32.3 grams (95%) of crude product as a yellow powder. Recrystallization of the yellow powder from 90 ml of chloroform gave 5a:23.4 grams of yellow prisms, mp 136–137°C (69%), lit. (*1*) mp 135°C.

3,3''-Dimethoxy-2',4',6'-trinitro-m-terphenyl, 5b. *m*-Bromoanisole (187 grams, 1 mole) and 1,3-dibromo-2,4,6-trinitrobenzene, 5a, (24 grams, 0.065 mole) were combined and slowly heated to 80°C. A yellow solution resulted. Activated copper (25 grams; 0.40 gram-atom) was added in 5-gram portions over a 25-min period, while raising the temperature slowly from 80° to 130°C. Within

15 min an exotherm of 8°C and production of copper bromide were observed. The gray slurry was heated at 125–130°C for 2.5 hr, cooled, and filtered to remove the unreacted copper and copper bromides. The precipitate was washed with 150 ml of acetone and 25 ml of benzene. The filtrates and washings were combined; the acetone and benzene were evaporated under reduced pressure.

Unreacted *m*-bromoanisole amounting to 154 grams was distilled from the crude product at 45–50°C (0.5 mm). Crude black residue, 30 grams (100% yield), was dissolved in 500 ml of hot, anhydrous acetone and treated twice with decolorizing carbon (10 grams). The resulting clear brown solution was concentrated to about 200 ml and 300 ml of hot methanol was added. On cooling 5b, an off-white powder was recovered, 15.3 grams (55% yield) with a melting point of 172–175°C. Reported (*4*) melting point is 178°C, (dec); ir (fluorolube and nujol) 3030 (w, aromatic CH), 2950 (CH_3O), 1550 (M, CNO_2), and 1350 cm^{-1} (w, CNO_2).

3,3''-Dimethoxy-2,2',2'',4,4',4'',6,6',6''-nonanitro-m-terphenyl, 5c. The nitration mixture was prepared in a 2-liter, 3-necked flask by adding 151 grams (1.5 mole) of dry potassium nitrate incrementally over 30 min to 800 grams of 30% oleum (3.0 mole of SO_3). The resulting exothermic reaction raised the temperature to 70°C. Potassium sulfate precipitated as the mixture was cooled to ambient temperature. After 5b (12.75 grams, 0.30 mole) was added quickly producing a temperature rise of 8°C, the slurry was cooled and stirred for 16 hr at 27°C. The slurry was then heated at 110–113°C for 4 hr (at this temperature foaming became severe), cooled to about 40°C, and slowly quenched in 1500 grams ice.

The resulting brown aqueous solution was extracted with ethyl acetate (5 × 200 ml) and the extracts were combined, washed with water (2 × 100 ml), and dried over anhydrous magnesium sulfate. The solvent was evaporated to give 5.2 grams (25%) as an off-white powder. Recrystallization of the crude solid from 1/4 acetone/methanol gave 4.0 grams of 5c as yellow needles; mp 310°C, (dec); ir (fluorolube and nujol) 3100 (w, aromatic CH); 1540 (m, CNO_2), 1340 cm^{-1} (m, CNO_2); nmr (dimethylsulfoxide-d_6); δ 3.94 (s, *6*, CH_3O), 8.90 (s, *2*, 5,5''-protons), 9.22 (s, *1*, 5'-proton).

3,3''-Diamino-2,2',2'',4,4',4'',6,6',6''-nonanitro-m-terphenyl, 5d. 5c (1.25 grams, 1.8 mole) was dissolved in 72 ml of a tetrahydrofuran–methanol–dimethylformamide (50/20/2-v/v/v). The solution was saturated with anhydrous ammonia and stirred for 30 min. The solution turned from a yellow to a blood-red within a few minutes, and a temperature rise of 10°C was observed. The solvents were removed with reduced pressure. Methanol (50 ml) was added, and the slurry was cooled and filtered. The wet, crude product, 1.3 grams, was recrystallized by dissolving in 5 ml of hot dimethylformamide and adding 50 ml of hot methanol.

On cooling, the yellow powder, 5d, that was recovered by filtration exploded at 355°C, 0.80 grams (66% yield); ir (fluorolube and nujol) 3400 (2, NH_2), 3100 (w, aromatic CH), 1360 cm^{-1}(m, CNO_2); nmr (dimethylsulfoxide-d_6), δ 8.74 (broad s, NH_2), 9.12 (s, *2*, 5,5''-protons); 0.42 (s, *1*, 5'-proton). The nmr spectrum also indicated the presence of a small amount of dimethylformamide. This solvent, which could not be removed by repeated drying with heat and vacuum, caused inaccurate elemental analysis.

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Alkyl 3-Pyridylmethyl Ketones and Derivatives

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Nine alkyl 3-pyridylmethyl ketones were prepared by the interaction of 3-picolylsodium and the requisite methyl ester. Physical properties were determined, and hydantoin and picrate derivatives of these ketones were prepared.

Recently, we had need of some alkyl 3-pyridylmethyl ketones. A careful perusal of the literature revealed that some of the required ketones had been prepared, but physical properties as well as derivatives were very sparse or lacking completely. Therefore, as the ketones were prepared, some of their physical constants were determined and derivatives prepared.

The synthesis of these ketones was patterned after the method of Raynolds and Levine (*4*) in which 3-picolylsodium was acylated with the requisite methyl ester. Typical carbonyl derivatives, i.e., oximes, semicarbazones, and 2,4-dinitrophenylhydrazones, proved to be difficult to prepare and recrystallize from these ketones; thus, hydantoin derivatives, which could be prepared with relative ease, were chosen. The hydantoin derivatives were prepared by the method of Henze and Speer (*3*).

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