Chemistry of Tetrafluorohydrazine. I. Reaction with Anthracenes[1]

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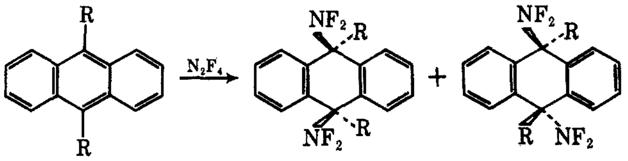
Anthracene and 9,10-dihaloanthracenes react with N_2F_4 very readily at low temperatures (40–70°) to give approximately *1:1* mixtures of the corresponding *cis-* and *trans-9,10-*bis(difluoramino)-9,10-dihydroanthracenes in excellent yields. Stereochemical differences between the *cis* and *trans* isomers are discussed.

Although nitrogen trifluoride, the parent binary N–F compound, has been synthesized by Ruff[2] in 1928, the over-all development of the field of nitrogen–fluorine chemistry has been accelerated only recently.[3,4] A major opportunity for further development in this field came with the discovery of tetrafluorohydrazine, N_2F_4.[5] A number of workers have since described the utilization of this compound as a source of NF_2 radicals for the synthesis of new organic and inorganic monodifluoramines.[6–23]

It was of interest, therefore, to attempt the synthesis of N,N-difluoramino aromatic compounds by treating aromatic hydrocarbons with N_2F_4. No reaction occurred with benzene, naphthalene, phenanthrene, mesitylene, or pyrene; however, anthracene and 9,10-substituted anthracenes reacted very smoothly[24] to give compounds containing NF_2 groups. Anthracenes, with their very reactive 9,10 positions, behave very much like conjugated dienes in Diels–Alder type reactions,[25] addition of halogens,[26] and addition of free radicals.[27]

The N_2F_4 reaction with anthracenes was run in an autoclave, using benzene as solvent under mild conditions (40–70°). Anthracene itself gave two isomeric 1:1 adducts (total yield 70–80%) in about equal amounts which were separated into the pure components by fractional crystallization. From ultraviolet, infrared, and F^{19} nmr spectra and by analogy to previous work on the addition of free radicals to anthracenes,[27,28] it is concluded that attack occurred in the 9,10 position and that the two isomers are the *cis-* and *trans-*9,10-bis(difluoramino)-9,10-dihydroanthracenes (IIa and IIIa). The infrared spectra show strong absorption peaks between 10.00 and 12.00 μ, characteristic of the N–F stretching vibration.[7,12,23,29] The F^{19} nmr spectra of these compounds show peaks at about −4000 to −8000 cps from $CFCl_2CFCl_2$, typical for the fluorine resonance of the NF_2 group.[6–23]



I II III

a, R=H
b, R=F

c, R=Cl
d, R=Br

From X-ray crystallographic data, 9,10-dihydroanthracene was shown[30] to have a nonplanar middle ring in a boat conformation, IV. A *cis*-9,10-disubstituted 9,10-dihydroanthracene may have the substituents in the diequatorial (e,e) or the diaxial (a,a) positions. Models show that the steric requirements are greater in the equatorial than the axial positions

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(7) J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960).

(8) R. K. Pearson and J. W. Frazer, *ibid.*, **21**, 188 (1961).

(9) J. W. Frazer, B. E. Holder, and E. F. Worden, *ibid.*, **24**, 45 (1962).

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(19) M. Lustig, C. L. Bumgardner, F. A. Johnson, and J. K. Ruff, *ibid.*, **3**, 1165 (1964).

(20) M. Lustig, C. L. Bumgardner, and J. K. Ruff, *ibid.*, **3**, 917 (1964).

(21) M. Lustig and G. H. Cady, *ibid.*, **2**, 388 (1963).

(22) R. K. Pearson and R. D. Dresdner, *J. Am. Chem. Soc.*, **84**, 4743 (1962).

(23) T. E. Stevens and J. P. Freeman, *J. Org. Chem.*, **29**, 2279 (1964).

(24) These aromatic compounds and many others were found to give very little significant reaction with *t*-butoxy radicals, formed by thermal decomposition of di-*t*-butyl peroxide, while anthracene gives both 9-methylanthracene and 9,9,10,10-tetrahydro-10,10-dimethyl-9,9-dianthryl: A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1956).

(25) O. Diels and K. Alder, Ann., **486**, 191 (1931); E. Clar, *Ber.*, **64**, 1676 (1931); **64**, 2194 (1931); W. E. Bachmann and M. C. Kleotzel, *J. Am. Chem. Soc.*, **60**, 481 (1938); W. E. Bachmann and L. B. Scott, *ibid.*, **70**, 1458 (1948).

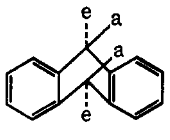
(26) E. de B. Barnett and J. W. Cook, *J. Chem. Soc.*, **125**, 1084 (1924); E. de B. Barnett and M. A. Matthews, *Rec. Trav. Chim.*, **43**, 530 (1924); E. de B. Barnett, J. W. Cook, and M. A. Matthews, *ibid.*, **44**, 217 (1925); **44**, 728 (1925); **44**, 818 (1925); **45**, 68 (1926).

(27) (a) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1956); (b) A. L. J. Beckwith and W. A. Waters, *ibid.*, 1001 (1957); (c) A. L. J. Beckwith, R. O. C. Norman, and W. A. Waters, *ibid.*, 171 (1958); (d) R. O. C. Norman, and W. A. Waters, *ibid.*, 167 (1958); (e) A. F. Bickel and E. C. Kooyman, *Rec. Trav. Chim.*, **71**, 1137 (1952); (f) J. W. Engelsma, E. Farenhorst, and E. C. Kooyman, *ibid.*, **73**, 878 (1954); (g) E. Farenhorst and E. C. Kooyman, *ibid.*, **81**, 816 (1962); (h) C. Dufraisse, *et al.*, *Compt. Rend.*, **256**, 548 (1963).

(28) Addition of chlorine or bromine to anthracenes gives a mixture of *cis-* and *trans-*9,10-dihydroanthracenes, but they are very unstable and aromatize readily.[26] More recently, 2-cyano-2-propyl radicals, from the thermal decomposition of 2,2′-azoisobutyronitrile, were added to anthracenes[27e–g] to give a mixture of *cis-* and *trans-*9,10-bis(2-cyano-2-propyl)-9,10-dihydroanthracenes along with a considerable amount of 9,9′,10,10′-tetrahydro-10,10′-bis(2-cyano-2-propyl)-9,9′-dianthryl. The assignment of the right isomer to the right structure in this case has been questioned by A. H. Beckett and J. Walker, *Tetrahedron*, **19**, 545 (1963).

(29) Stretching vibrations in the infrared of compounds that contain the N–F band appear between 10 and 12 μ: (a) J. R. Durig and R. C. Lord, *Spectrochim. Acta*, **19**, 1877 (1963); E. N. Moskuitina, *et al.* [*Chem. Abstr.*, **61**, 6533*e* (1964)], for N_2F_4; (b) R. H. Sanborn [*J. Chem. Phys.*, **33**, 1855 (1960)] for N_2F_2; (c) E. A. Lawton and E. F. C. Cain [*J. Inorg. Nucl. Chem.*, **17**, 188 (1961)] for $H_2NC(=O)NF_2$; (d) R. C. Petry [*J. Am. Chem. Soc.*, **82**, 2400 (1960)] for $ClNF_2$; and (e) C. L. Bumgardner and M. Lustig [*Inorg. Chem.*, **2**, 662 (1963)] for FSO_2NF_2.

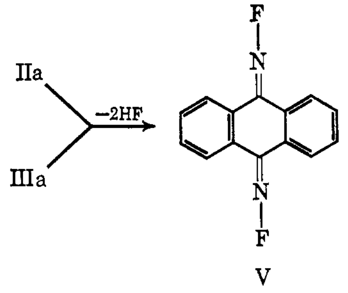
(30) W. G. Ferrier and J. Iball, *Chem. Ind.* (London), 1296 (1954).



IV

because of the interaction of the substituents with the perihydrogens. On this basis, *cis*-9,10-disubstituted 9,10-dihydroanthracenes are assigned mainly in a diaxial (a,a) rather than diequatorial (e,e) conformation, while the *trans* isomers exist in a relatively strained equatorial-axial (e,a) conformation.[31] It has been shown that equilibration of many 9,10-disubstituted 9,10-dihydroanthracenes results in the formation of the thermodynamically more stable *cis* isomer in predominating amounts.[32,33] Thus, the more stable 9,10-bis(difluoramino)-9,10-dihydroanthracene [mp 203–204°; $\lambda_{\max}^{\text{EtOH}}$ 256 mμ (sh) (ϵ 400), 261 (490), 267 (460), and 273 (326)] has been assigned the *cis* structure IIa, while the less stable isomer [mp 125–127°, $\lambda_{\max}^{\text{EtOH}}$ 255 mμ (ϵ 2620)] which decomposes slowly at 25° with evolution of hydrogen fluoride has been assigned the *trans* structure.[34] This assignment, derived purely from conformational analysis, is supported by the dipole moments of the two stereoisomers, 4.97 D. for the *cis* and 2.70 D. for the *trans* adduct. Moreover, in *meso*-substituted 9,10-dihydroanthracenes like the *cis* and *trans* isomers of 9,10-dimethyl,[35] 9,10-diphenyl,[36] and 9,10-dihydroxy,[37] whose structures have been proven, the *cis* isomer is the higher melting. It was also shown that in the ultraviolet spectra of many *cis* and *trans* isomers, without exception the *trans* isomer has a larger extinction coefficient.[38–42]

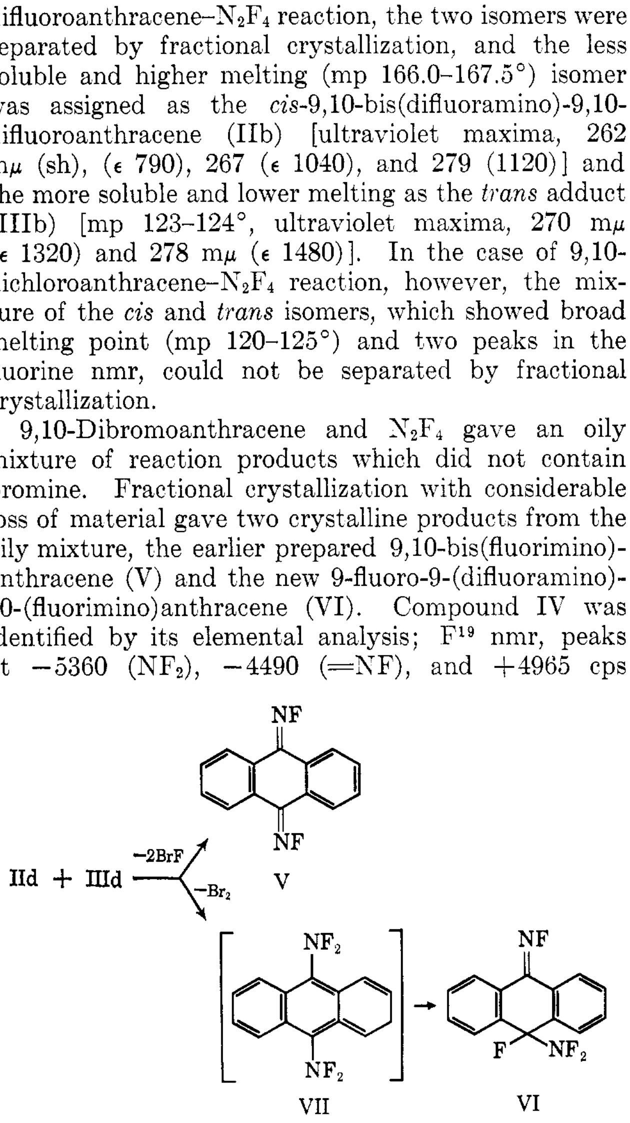
Both *cis*- and *trans*-9,10-bis(difluoramino)9,10-dihydroanthracene (IIa and IIIa) eliminate 2 moles of hydrogen fluoride to give 9,10-bis(fluorimino)dihydroanthracene (V). Evidence for structure V are the elemental analyses; infrared spectra, 6.33, 6.40 (C=N), and 11.26, 11.50 μ (=N-F); and ultraviolet spectra, 243 mμ (ϵ 29,000). In accordance with their stabilities pointed out earlier, IIIa reacts very readily using a relatively weak base, sodium fluoride in refluxing acetonitrile, whereas IIa is inert to sodium fluoride and requires sodium carbonate in refluxing acetonitrile. The presence of two fluorine resonances in low field in the nmr spectrum of V (singlets at −4525 and −4515 cps) indicates that it exists as a mixture of *syn* and *anti* isomers.



V

Similarly, 9,10-difluoroanthracene (Ib) and 9,10-dichloroanthracene (Ic) when treated with N_2F_4 gave two isomeric 1:1 adducts. In the case of the 9,10-difluoroanthracene–N_2F_4 reaction, the two isomers were separated by fractional crystallization, and the less soluble and higher melting (mp 166.0–167.5°) isomer was assigned as the *cis*-9,10-bis(difluoramino)-9,10-difluoroanthracene (IIb) [ultraviolet maxima, 262 mμ (sh), (ϵ 790), 267 (ϵ 1040), and 279 (1120)] and the more soluble and lower melting as the *trans* adduct (IIIb) [mp 123–124°, ultraviolet maxima, 270 mμ (ϵ 1320) and 278 mμ (ϵ 1480)]. In the case of 9,10-dichloroanthracene–N_2F_4 reaction, however, the mixture of the *cis* and *trans* isomers, which showed broad melting point (mp 120–125°) and two peaks in the fluorine nmr, could not be separated by fractional crystallization.

9,10-Dibromoanthracene and N_2F_4 gave an oily mixture of reaction products which did not contain bromine. Fractional crystallization with considerable loss of material gave two crystalline products from the oily mixture, the earlier prepared 9,10-bis(fluorimino)-anthracene (V) and the new 9-fluoro-9-(difluoramino)-10-(fluorimino)anthracene (VI). Compound IV was identified by its elemental analysis; F^{19} nmr, peaks at −5360 (NF_2), −4490 (=NF), and +4965 cps



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(31) A. H. Beckett and B. A. Mulley, *J. Chem. Soc.*, 4159 (1955).

(32) J. Rigaudy and K. V. Thang, *Bull. Soc. Chim. France*, 1628 (1959).

(33) A. H. Beckett and J. Walker, *Tetrahedron*, **19**, 545 (1963).

(34) It is reported[27g] that *cis*-9,10-bis(2-cyano-2-propyl)-9-cyano-9,10-dihydroanthracene is more stable than the *trans* isomer. The addition of benzyl radicals to anthracene gave only one isomer of H-9,10-dibenzyl-9,10-dihydroanthracene in 21% yield among other products[27b,c] which is assigned the *cis* structure; the *trans* isomer was assumed to be too unstable to be isolated.[32]

(35) A. H. Beckett and R. G. Lingard [*J. Chem. Soc.*, 2409 (1959)] and L. M. Jackman and J. W. Lown [*ibid.*, 3776 (1962)] report a melting point of 129–130° for the *cis* and 101.8–101.5° for the *trans* isomer.

(36) C. K. Ingold and P. G. Marshall [*ibid.*, 3080 (1926)] report mp 227° for the *cis* and W. Schenk and E. Bergmann, report mp 199° for the *trans* isomer.

(37) C. Dufraisse, G. Rio, and Y. Lepage, *Compt. Rend.*, **247**, 1928 (1958); Y. Lepage [*Ann. Chim.*, **4**, 1137 (1959)] reports mp 190–195° for the *cis* and 151–152° for the *trans* isomer.

(38) N. H. Cromwell and M. A. Graff [*J. Org. Chem.*, **17**, 414 (1952)] showed that for 1-methyl- and 1-cyclohexyl-2-phenyl-3-(p-phenylbenzoyl)-ethylenimines the *trans* isomer has the larger extinction coefficient.

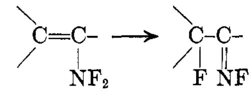
(39) L. P. Kuhn, R. E. Lutz, and C. R. Bauer [*J. Am. Chem. Soc.*, **72**, 5058 (1950)] report the ultraviolet spectra of a number of *cis*- and *trans*-dibenzoylethylenes among which the *trans* isomer always has the larger extinction coefficient.

(40) N. H. Cromwell and R. A. Setterquist [*ibid.*, **76**, 5752 (1954)] report that *cis*-*o*-nitrobenzalacetophenone oxide absorbs at 252 mμ (ϵ 18,760) and the *trans* isomer at 253 mμ (ϵ 20,110).

(41) C. L. Stevens and V. J. Traynelis [*J. Org. Chem.*, **19**, 533 (1954)] report that α-chlorodiphenacyl oxime (*cis*) absorbs at 245.0 mμ (ϵ 10,800) and the β-chlorophenacyl oxime (*trans*) at 246.5 mμ (ϵ 13,300).

(42) Of the available ultraviolet spectra of 9,10-disubstituted 9,10-dihydroanthracenes, C. La Lau [*Rec. Trav. Chim.*, **73**, 931 (1954)] reports that *cis*- and *trans*-9,10-dimethyl show almost identical absorption. *cis*- and *trans*-9,10-bis(2-cyano-2-propyl)-9,10-dihydroanthracene, however, show a number of differences: *cis* isomer, mp 163–169°; $\lambda_{\max}^{\text{dioxane}}$, 265.3 m$\mu$ (ϵ 550), 274.0 mμ (ϵ 480); *trans* isomer, mp 189.0–189.5°; $\lambda_{\max}^{\text{dioxane}}$ 264 mμ (ϵ 400, 274 (sh) (~280), and 283 (sh) (~54). This assignment of the isomers should be reversed, however, on the arguments given in the text, and this has also been pointed out by Beckett and Walker.[32,33]

(CF); infrared spectra, 6.01 (C=N), 10.27, 10.33, 10.84, 11.00, 11.40, and 11.55 μ (N-F); and ultraviolet spectra, 248 mμ (ε 11,800). It appears, therefore, that the initially formed 9,10-dibromoanthracene–N_2F_4 1:1 adduct (mixture of IId and IIId) is unstable and either eliminates the elements of 2BrF to give V or a molecule of Br_2 to give 9,10-bis(difluoramino)anthracene (VII), which also is unstable and rearranges to VI. A similar rearrangement of vinyl $-NF_2$ compounds has been

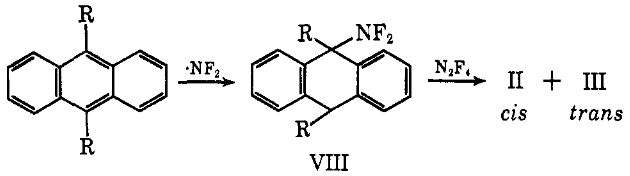


postulated by Bumgardner in the photochemical reaction of difluoramino radicals with acetylenes.[12]

9,10-Dichloro-9,10-bis(difluoramino)anthracene at its melting point undergoes a smooth thermal reaction, giving back a quantitative yield of N_2F_4 and 9,10-dichloroanthracene. This reaction occurs at a slower rate in solvents like benzene, or hexane under reflux. Thus, one can safely store N_2F_4 as the stable 9,10-dichloranthracene adduct (IIc and IIIc) and can generate a small amount upon demand.

This addition reaction appears to proceed by way of difluoramino radical ($\cdot NF_2$), and not by any concerted process involving molecular N_2F_4. The ready dissociation of N_2F_4 into NF_2 radicals[43] suggests this path.

$$N_2F_4 \rightleftharpoons 2\cdot NF_2$$



I

VIII

The 9,10 positions of the anthracene I are very susceptible to radical attacks[27] and thus intermediate VIII is formed, which then reacts with N_2F_4 to yield a mixture of II and III. That no 9,9,10,10-tetrahydro-10,10-bis-(difluoramino)-9,9-dianthryl derivatives were formed as a result of coupling of VIII as shown to occur in the case of other radical addition reactions,[27] indicates that N_2F_4 is an excellent radical trap.

Experimental Section[44]

General Procedure.—The reactions with N_2F_4 (obtained from Air Products, Inc., and from Explosives Department of E. I. du Pont de Nemours and Co.) were run in 80- or 240-ml Hastelloy-lined shaker tubes. *Caution is essential in handling N_2F_4 and most N-F compounds.* They are oxidizers and react vigorously sometimes with organic compounds. Adequate shielding is absolutely required during work-up of the products as explosions may occur. Liquid or solid reactants were placed in the tube under a nitrogen atmosphere, the head was screwed into place, the tube was cooled to −78° and evacuated with a vacuum pump. The tube was placed behind a barricade and the specified amount of N_2F_4 was condensed into it by remote control. It is recommended that tetrafluorohydrazine be stored at −78° in previously fluorinated cylinders fitted with a "Monel" valve. The temperature of the tube was raised until reaction occurred (pressure drop) and kept at this temperature until pressure remained constant. The tube was allowed to cool to room temperature, the gaseous products were vented, the tube was removed from the barricade, and the products were recovered.

9,10-Bis(difluoramino)-9,10-dihydroanthracene.—Into a 240-ml tube containing 16.0 g (0.09 mole) of anthracene and 50 g of benzene was condensed 11.0 g (0.105 mole) of N_2F_4. The tube was sealed and shaken at 30° for 12 hr. The benzene-insoluble, solid adduct (10.0 g) was removed by filtration and recrystallized from benzene to give 7.0 g (28%) *cis*-9,10,bis-(difluoramino)-9,10-dihydroanthracene (IIa) as colorless needles: mp 203–204°; infrared maxima (KBr), 10.24 (m), 10.55 (m), 10.77 (s), 10.93 (s), 11.17 (s), 11.56 (m) (N-F), and 13.17 (s) μ (aromatic); ultraviolet absorption (EtOH), 273 mμ (ε 326), 267 (460), 261 (490), 256 (sh) (400) dipole moment, 4.97 D. (benzene) F^{19} nmr (nitrobenzene), −6790 cps (doublet, J_{F-H} = ~30 cps).

Anal. Calcd for $C_{14}H_{10}F_4N_2$: C, 59.54; H, 3.59; F, 26.93; N, 9.92. Found: C, 59.88; H, 3.72; F, 26.88; N, 9.26.

The benzene solution was evaporated *in vacuo* to give 14.0 g of a solid residue which was recrystallized from hexane to give 10 g (40%) of *trans*-9,10-bis(difluoramino)-9,10-dihydroanthracene (IIIa) as white needles: mp 125–127°; infrared maxima at 10.22 (s), 10.40 (s), 10.76 (s), 10.94 (m), 11.14 (s), 11.45 (s), 11.75 (s) (N-F_2), and 13.30 μ (s) (aromatic); ultraviolet absorption (EtOH), 255 mμ (ε 2620) F^{19} nmr (nitrobenzene), −5987 cps (doublet, J_{F-H} = ~30 cps); dipole moment, 2.70 D. (benzene). This material should be stored in the cold because it slowly evolves HF on standing at 25°.

Anal. Calcd for $C_{14}H_{10}F_4N_2$: C, 59.54; H, 3.59; F, 26.93; F, 26.93; N, 9.92. Found: C, 59.61; H, 3.79; F, 26.76; N, 9.90.

9,10-Bis(difluorimino)anthracene (V). A. From *trans*-9,10-Bis(difluoramino)-9,10-dihydroanthracene (IIIa).—A well-stirred mixture of 0.5 g of *trans*-9,10-bis(difluoramino)9,10-dihydroanthracene, 2.5 g of sodium fluoride powder, and 5.0 ml of acetonitrile was refluxed for 16 hr. The sodium fluoride was removed by filtration, the acetonitrile was evaporated *in vacuo*, and the residual solid was recrystallized from hexane to give 0.3 g of bis(fluorimino)anthracene (V): mp 213–214°; infrared maxima (KBr), 6.33 (m), 6.40 (m) (-C=N-), 11.26 (s), 11.50 (s) (=N-F), 12.77 (s), and 12.91 (s) μ (aromatic); ultraviolet absorption (EtOH), 243 mμ (ε 29,000), 265 (sh) (13,700), and 300 (sh) (3420); F^{19} nmr (nitrobenzene), two peaks at −4525 and −4515 cps.

Anal. Calcd for $C_{14}H_8F_2N_2$: C, 69.42; H, 3.33; F, 15.68; N, 11.57. Found: C, 68.99; H, 3.55; F, 15.64; N, 11.56.

B. From *cis*-9,10-Bis(difluoramino)-9,10-dihydroanthracene (IIa).—A well-stirred mixture of 1.0 g of *cis*-9,10-bis(difluoramino)-9,10-dihydroanthracene, 15 ml of acetonitrile, and 4.0 g of anhydrous sodium carbonate powder was refluxed for 10 hr. The sodium carbonate was removed by filtration, the acetonitrile was evaporated *in vacuo*, and the solid residue was recrystallized from hexane to give 0.79 g of bis(fluorimino)anthracene, mp 212–213°, identical in all respects with the sample prepared above.

Reaction of 9,10-Dibromoanthracene with N_2F_4.—In a 240-ml tube containing 20 g (0.06 mole) of dibromoanthracene and 26 g of benzene was condensed 6.7 g (0.064 mole) of N_2F_4, and the tube was sealed and shaken at 70° for 1 hr. The solvent was evaporated *in vacuo* to give a dark oil which on trituration with heptane gave 3–4 g of a solid. The solid was recrystallized from heptane, mp 180–200°, and proved to be impure bis(fluorimino)-anthracene (V) (see above) by comparison of its infrared, ultraviolet, and nmr spectra.

The rest of the oil (8–10 g) crystallized with difficulty from heptane and after repeated recrystallizations gave a small amount of 9-fluoro-9-difluoramino-10-fluoriminoanthracene (VI): mp 91–93°; infrared maxima (KBr), 6.01 (w) (C=N), 10.27 (m), 10.33 (m), 10.84 (m), 11.00 (s), 11.40 (s), 11.55 (s) (N-F), and 13.65 (s) μ (aromatic); ultraviolet absorption (EtOH), 248 mμ (ε 11,800); F^{19} nmr (nitrobenzene), −5360 (NF_2), −4490 (=NF), and +4965 cps (CF).

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(43) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961); F. A. Johnson, K. A. Booman, and C. B. Colburn [*J. Chem. Phys.*, **35**, 1481 (1961)] have shown that the equilibrium $N_2F_4 \rightleftharpoons 2NF_2\cdot$ exists.

(44) All melting points were taken on a Fisher-Johns block and are not corrected. Fluorine nmr spectra were obtained with a high-resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates operating at 56.4 Mc/sec and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (cps) from the F^{19} resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane ("Freon-112") as external reference. One should add +3826 cps in order to get frequencies with respect to $CFCl_3$ ("Freon-11"). Negative frequency displacements are for resonances at lower field than the reference. The infrared spectra were determined with a Perkin-Elmer spectrophotometer, Model 21. Only the peaks relative to structural arguments are recorded as weak (w), medium (m), or strong (s).

Anal. Calcd for $C_{14}H_8F_4N_2$: C, 60.05; H, 2.88; N, 10.01. Found: C, 61.51; H, 2.96; N, 9.89.

9,10-Dichloro-9,10-bis(difluoramino)-9,10-dihydroanthracene (IIc and IIc).—In a 240-ml tube containing 30 g (0.12 mole) of 9,10-dichloroanthracene and 60 g of benzene was condensed 14.0 g (0.135 mole) of N_2F_4, and the tube was sealed and shaken at 71° for 1 hr. The benzene-insoluble solid was unreacted 9,10-dichloroanthracene and was removed by filtration. The benzene solution was evaporated *in vacuo* to give 23.0 g (54%) of 9,10-dichloro-9,10-bis(difluoramino)anthracene as a mixture of *cis* and *trans* isomers. It was carefully recrystallized from petroleum ether (40–60°)-benzene with the minimum of heating to give 20 g of white, cubic crystals: mp 120–125° dec; infrared maxima (Nujol), 10.17 (m), 10.57 (s), 11.32 (s), 11.57 (sh) (m), 11.72 (sh) (m) (NF_2), and 13.40 (s) μ (aromatic); ultraviolet absorption (EtOH), 273 mμ (ϵ 1600), 280 (1490), 298 (157), 309 (100), 332 and (42.5); F^{19} nmr (nitrobenzene), -6175 cps and -6075 cps (NF_2) in about 2:1 ratio.

Anal. Calcd for $C_{14}H_8Cl_2F_4N_2$: C, 47.90; H, 2.30; Cl, 20.20; F, 21.65; N, 7.98. Found: C, 48.39; H, 2.59; Cl, 20.16; F, 22.15; N, 7.72.

9,10-Difluoroanthracene (Ib).—A mixture of 75 g of commercial steel wool (washed with CCl_4) and 55 g of 9,9,10,10-tetrafluoroanthracene[45] was heated in a shaker tube for 6 hr at 260°. The shaker tube contents were extracted with hot benzene, and the benzene was evaporated to give a dark green residual solid. The solids of two such runs were combined and passed through a chromatographic column packed with Woelm basic alumina using hexane as the eluent. There was obtained 5.0 g of 9,10-difluoroanthracene as yellow needles: mp 170–172°; infrared maxima (KBr), 6.13 (m) (C=C), 9.56 (s) (C–F), and 13.2 (s) μ (aromatic); ultraviolet absorption (EtOH), 245 mμ (ϵ 88,000), 253 (208,000), 320 (sh) (1080), 375 (2140), 352 (5250), 368 (sh) (6740), 370 (8270), 385 (435) and 391 (6200); F^{19} nmr (benzene), +3880 (singlet) cps.

Anal. Calcd for $C_{14}H_8F_2$: C, 78.50; H, 3.77; F, 17.74. Found: C, 78.18; H, 3.82; F, 18.65.

9,10-Difluoro-9,10-bis(difluoramino)-9,10-dihydroanthracene.—In an 80-ml tube containing 4.0 g (0.019 mole) of 9,10-difluoroanthracene (Ib) and 10 ml of benzene was condensed 3.0 g (0.029 mole) of N_2F_4, and the tube was sealed and heated to 35–40° for 2 hr. On evaporation of the solvent there was obtained 5.0 g of solid which was recrystallized from hexane to give as an initial crop of crystals 1.8 g (30%) of colorless needles, mp 166–167.5°, assigned as the *cis*-9,10-difluoro-9,10-bis(difluoroamino)anthracene (IIb): infrared maxima (KBr), at 10.37 (m), 10.85 (s), 11.29 (s), 11.49 (s) (NF_2), and 13.27 (s) μ (aromatic); ultraviolet absorption (ethanol), 262 (sh) mμ (ϵ 790), 267 (1040), and 274 (1120); F^{19} nmr (nitrobenzene), -5270 cps (doublet, $J = \sim 7$ cps, NF_2) and +4650 cps (triplet, $J = \sim 7$ cps, C–F).

Anal. Calcd for $C_{14}H_8F_6N_2$: C, 52.84; H, 2.53; F, 35.83; N, 8.81. Found: C, 53.23; H, 2.78; F, 34.81; N, 9.01.

On concentration of the mother liquor, there was obtained another crop of crystals which were recrystallized from petroleum ether (bp 40–60°) to give 1.7 g (28%) of white needles, mp 123–124°, assigned as the *trans*-9,10-difluoro-9,10-bis(difluoramino)-anthracene (IIIb): ultraviolet absorption (ethanol), 270 mμ (ϵ 1320), and 278 mμ (ϵ 1480); F^{19} nmr (benzene), -5310 cps (doublet, $J = \sim 15$ cps, NF_2) and +3495 cps (triplet, $J = \sim 16$ cps C–F); infrared maxima (KBr), at 10.29 (m), 10.36 (m), 10.86 (s), 11.25 (s), 11.49 (s) (NF_2), and 13.02 (s) μ (aromatic).

Anal. Calcd for $C_{14}H_8F_6N_2$: C, 52.84; H, 2.53; F, 35.83; N, 8.81. Found: C, 53.37; H, 2.70; F, 35.09; N, 9.01.

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Chemistry of Tetrafluorohydrazine. II. Reaction with Olefins to Give N-Fluoriminonitriles[1]

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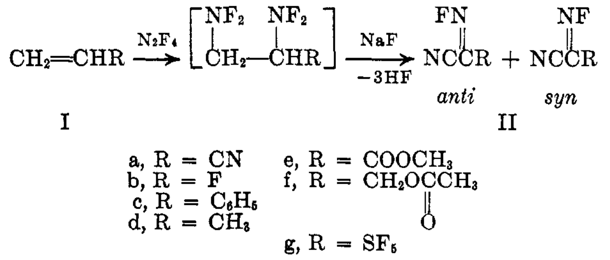
In the reaction of N_2F_4 with terminal olefins in the presence of sodium fluoride, addition of N_2F_4 to the double bond occurred first, followed by elimination of hydrogen fluoride to give N-fluoriminonitriles. *syn* and *anti* Isomerism was observed with these compounds by nmr and in the case of 1-cyano-N-fluoroformimidoyl fluoride (IIb), the two isomers were separated by gas chromatography.

The addition of N_2F_4[2] to anthracenes to give 1:1 adducts has been reported in the preceding paper[3] of this series. When the difluoramino group is attached to hydrogen-substituted carbon, there is the possibility of eliminating HF from the adducts. This suggests that the addition of N_2F_4 to an olefin could be carried out in the presence of an anhydrous base in an appropriate solvent, and that the 1:1 adduct formed initially could lose hydrogen fluoride to give in one step an N-fluorimino derivative. In this paper the synthesis and reactions of a number of novel N-fluoriminonitriles prepared by this method are described.

Reactions of the terminal olefins Ia–g with N_2F_4 were run in an autoclave containing a solvent and powdered sodium fluoride, taking the precautions outlined in the Experimental Section. The products IIa–g (obtained in 30–70% yield) were purified either by distillation or gas chromatography with precautions appropriate to the handling of potentially explosive compounds. Their structures were assigned on the basis of analytical data and infrared, mass, proton, and fluorine nmr spectra. The infrared spectra of these compounds contain strong absorption peaks between 10.00 and 12.00 μ, characteristic of the N–F stretching vibration.[3] In many cases, especially when NF_2 groups are present, this absorption appears as a number of peaks,



$$\underset{\mathrm{I}}{CH_2{=}CHR} \xrightarrow{N_2F_4} \left[\begin{array}{cc} NF_2 & NF_2 \\ | & | \\ CH_2 & \!\!-\!\!\; CHR \end{array}\right] \xrightarrow[-3HF]{NaF} \underset{anti}{NC\overset{\overset{FN}{\|}}{C}R} + \underset{syn}{NC\overset{\overset{NF}{\|}}{C}R}$$

II

a, R = CN
b, R = F
c, R = C_6H_5
d, R = CH_3
e, R = $COOCH_3$
f, R = $CH_2O\underset{\underset{O}{\|}}{C}CH_3$
g, R = SF_5

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[3] A. L. Logothetis, *J. Org. Chem.* **31**, 3686 (1966).