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POLYFLUOROHETEROCYCLIC COMPOUNDS PART XX*. PREPARATION AND NUCLEOPHILIC SUBSTITUTION OF HEXAFLUOROQUINOXALINE

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SUMMARY

Hexachloroquinoxaline has been prepared in three stages from *o*-phenylenediamine, and converted into hexafluoroquinoxaline with potassium fluoride. Nucleophilic attack on hexafluoroquinoxaline by hydrazine or hydroxide ion occurs readily at positions 2 and 3 to give disubstituted derivatives, while methoxide ion gave the corresponding mono- and di-methoxy compounds and, under forcing conditions, the 2,3,6-trimethoxy derivative. Oxidation of 2,3-dihydrazino-5,6,7,8-tetrafluoroquinoxaline with cupric sulphate gave 5,6,7,8-tetrafluoroquinoxaline, and with cupric chloride the corresponding 2,3-dichloro-5,6,7,8-tetrafluoroquinoxaline was obtained. 5,6,7,8-Tetrafluoro-2,3-dihydroxyquinoxaline, which was also obtained from hexafluoroquinoxaline by hydrolysis in sulphuric acid, exists as the 1*H*,4*H*-quinoxalin dione tautomer, but diazomethane converts it specifically into the unsymmetrical *O*,*N*-dimethyl derivative.

INTRODUCTION

Polyfluoroaryl nitrogen heterocyclic compounds present interesting problems of orientation for nucleophilic aromatic substitution, as the hydrocarbon analogues pose for electrophilic aromatic substitution. Earlier studies have shown that acid-induced[2] nucleophilic aromatic substitution, which is not a common process, can occur readily in these systems, as well as the more usual attack by nucleophiles on the neutral heterocyclic systems[3]. It has been established that, in the absence of acid catalysis, fluorine atoms *para* to ring nitrogen are generally very reactive towards nucleophilic displacement[3]. Perfluoro-1,4-diazine[3] and its derivatives

* For Part XIX see ref. 1.

provide systems in which this strong activating influence is absent, facilitating investigation of the chemistry of fluorine at other positions relative to ring nitrogen, and of the effect of an initial substituent on subsequent reactions. From the preparative viewpoint, polyhalo-heterocyclic compounds are receiving increasing attention as potential herbicidal and fungicidal agents. We now report[4] our studies of hexafluoroquinoxaline.

RESULTS AND DISCUSSION

The most widely used preparation of perfluoro nitrogen heterocyclic compounds is the halogen-exchange reaction between the perchloro compound and potassium fluoride at high temperature and without a solvent[3,5], and we find that this method provides a convenient route to hexafluoroquinoxaline. Newbold and his co-workers have obtained hexachloroquinoxaline (3)[6] from tetrachloro-*o*-phenylene diamine, but we prepared it on a larger scale by chlorination of 2,3-dichloroquinoxaline (1)[7], readily available from *o*-phenylene diamine, with phosphorus pentachloride under autogenous pressure in a nickel-lined autoclave at 300°. The yield was 60% based on the diamine.

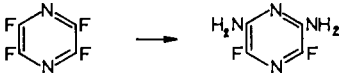
Fluorination of hexachloroquinoxaline (3) was achieved with anhydrous potassium fluoride at 380°, and the product was separated from a small amount of 5-chloropentafluoroquinoxaline (5) by fractional distillation, or by recrystallisation from benzene, to give hexafluoroquinoxaline (4) as colourless needles m.p. 142–144°, b.p. 197°/760 mm. Like tetrafluoropyrazine[3], but unlike all the other perfluorodiazines[2,8] and benzodiazines[5], hexafluoroquinoxaline is perfectly stable to atmospheric moisture.

The by-product (5) of fluorination was shown, by ^{19}F NMR spectroscopy, to have retained chlorine at C-5, since only one fluorine shows a large downfield shift compared with hexafluoroquinoxaline, which is characteristic[3,9] of fluorine *ortho* to chlorine. The spectrum also revealed $J(2,3)$ as 30 Hz compared with various fluoropyrazines[3] which have $J(ortho)$ *ca.* 16 Hz. In contrast to the conditions needed for complete fluorination of hexachloroquinoxaline, 2,3-dichloroquinoxaline (1) was readily converted into 2,3-difluoroquinoxaline (2) by potassium fluoride in sulpholan at 190°.

Nucleophilic attack on hexafluoroquinoxaline by methoxide and hydroxide ions, or by hydrazine, occurred first at positions 2 and 3, *ortho* to nitrogen. Thus, one molecular proportion of sodium methoxide reacted with hexafluoroquinoxaline at −20° to give the monomethoxy compound (7), while the dimethoxy derivative (8), obtained at 20°, was not further substituted by methanolic sodium methoxide at reflux temperature. Only under forcing conditions (sealed tube at 120°) was fluorine displaced from the carbocyclic ring, methoxide ion then giving the 2,3,6-trimethoxy derivative (12). Excess hydrazine hydrate converted hexafluoroquinoxaline to the 2,3-dihydrazino derivative (6) under mild conditions, and the

structure of this compound, whose insolubility and poor stability made it unsuitable for direct NMR study, was confirmed by oxidation with aqueous cupric sulphate to give 5,6,7,8-tetrafluoroquinoxaline (10), and with cupric chloride to the 2,3-dichloro derivative (11). Similarly, potassium hydroxide in t-butanol gave the 2,3-dihydroxy compound (9).

The formation of these *ortho*-disubstituted derivatives of hexafluoroquinoxaline contrasts with the behaviour of the tetrafluoropyrazine system[3], in which strongly deactivating (w.r.t. *nucleophilic* attack) substituents such as hydroxy, hydrazino, or amino give only mono-substituted derivatives under these conditions. Indeed, prolonged reaction between tetrafluoropyrazine (14) and concentrated aqueous ammonia gives the *meta* diamino compound (15).



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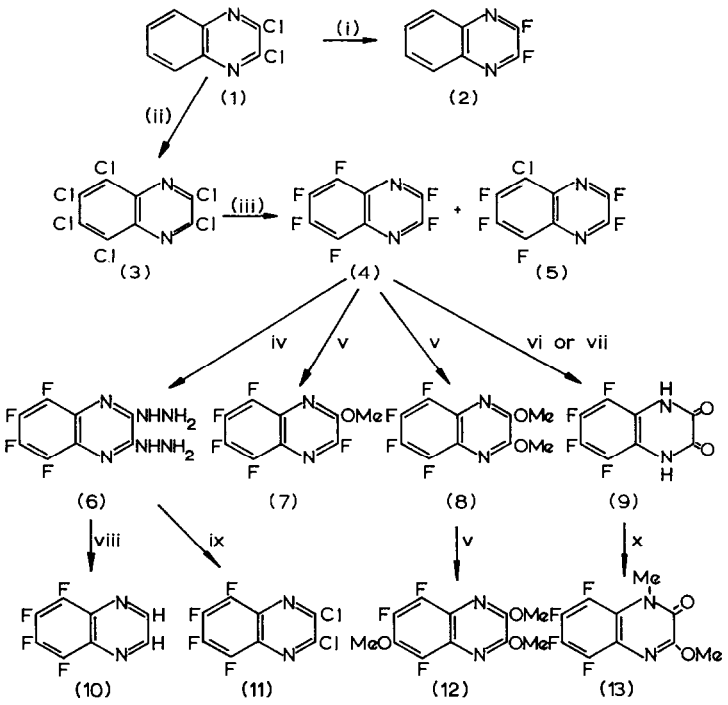
Hexafluoroquinoxaline did not give a simple derivative with ammonia and further investigation of this system is in hand.



Reagents: i, KF–sulpholan; ii, PCl_5; iii, KF–380°; iv, $N_2H_4 \cdot H_2O$–EtOH; v, NaOMe–MeOH; vi, KOH–t-BuOH; vii, H_2O–H_2SO_4; viii, $CuSO_4$–H_2O; ix, $CuCl_2$–HCl; x, CH_2N_2–Et_2O.

Nucleophilic attack on hexafluoroquinoxaline also occurred under acidic conditions; addition of water to its solution in sulphuric acid gave the 2,3-dihydroxy derivative (9), identical with that obtained with potassium hydroxide.

5,6,7,8-Tetrafluoro-2,3-dihydroxyquinoxaline probably exists as the dicarbonyl tautomer (9) since its IR spectrum (solid in KBr) shows strong absorption between 1730 and 1667 cm^{-1} (C = O) and its ^{19}F NMR (in *N*-methyl-2-pyrrolidone at 60°) consists of two absorptions at −3.5 and +7.1 ppm (from hexafluorobenzene). The UV spectrum (ethanol) of the dihydroxy compound (9) differs distinctly from that of the corresponding dimethoxy derivative (8). Methylation of the dihydroxy compound (9) with ethereal diazomethane gave a single dimethyl derivative, assigned the unsymmetrical structure (13) since its ^{19}F NMR spectrum shows four distinct resonances at −10.8, −2.9, +1.4 and +2.9 ppm.

EXPERIMENTAL

IR spectra were measured on either a Grubb–Parsons Spectromaster or GS2A spectrophotometer, UV spectra on a Unicam SP800, and NMR spectra on a Perkin–Elmer R10 operating at 56.46 MHz, using hexafluorobenzene as an internal standard (downfield shifts are quoted as negative). Molecular weights were determined by mass spectrometry with an A.E.I. MS9 instrument. Ether solutions were dried over magnesium sulphate. Sulpholan was re-distilled *in vacuo*, and dried over a molecular sieve.

Hexachloroquinoxaline (3)

2,3-Dichloroquinoxaline[8] (100 g) and phosphorus pentachloride (600 g) were closed *in vacuo* in a nickel-lined autoclave (1.5 l capacity) and heated to 300° for 17 h. The autoclave was cooled, vented, and its contents were added to ice. The mixture was extracted with ether, the extract was washed with water, dried, and evaporated. The residue was recrystallised from benzene to give hexachloroquinoxaline (152 g, 90%), m.p. 200–201° (lit., 207–209°)[6] (Found: C, 27.9; Cl, 63.8%; Mol. wt., 334. Calc. for $C_8Cl_6N_2$: C, 28.5; Cl, 63.2; Mol. wt., 334), $\nu_{max.}$ (KBr) 1538, 1408–1399 (doublet), 1364, 1287, 1259, 1250, 1156, 1038, 1000, 988, 820 (w), 775, 671, 617 (w), and 550 cm^{-1}, $\lambda_{max.}$ (ethanol) 266.5, 323, 337.5, and 351 nm.

Hexafluoroquinoxaline (4) and 5-chloro-2,3,6,7,8-pentafluoroquinoxaline (5)

Hexachloroquinoxaline (60 g) and freshly dried potassium fluoride (400 g) were closed *in vacuo* in a stainless steel autoclave (700 ml capacity) and heated to 380° for 19 h. The contents of the autoclave were pumped out into a cold trap and the condensate was distilled through a column (1 × 90 cm) of Dixon gauze-rings to give *hexafluoroquinoxaline* (nc) (20.2 g, 50%) as colourless needles b.p. 196–198°/760 mm, m.p. 142–144° (Found: C, 40.2; F, 48.5%; Mol. wt., 238.

$C_8F_6N_2$ requires C, 40.3; F, 47.9%; Mol. wt., 238), $\nu_{max.}$ (KBr) 1667, 1515–1471 (multiplet), 1346, 1316 (sh), 1261, 1232, 1218, 1199, 1170, 1095, 1080, 1053, 1017 (vs), 816, 799, 654, 593 (w), and 521 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 239, 305.5, 312.5, and 318 nm (log ε 4.47, 3.61, 3.61, and 3.57). ^{19}F NMR (ether) showed absorption at −10.3, −13.4, and −84.9 ppm. The material remaining in the fractionating column was recrystallised from benzene to give a further crop (14.0 g) of hexafluoroquinoxaline (total 34.2 g, 80%), and the residue from the distillation flask was dissolved in acetone and filtered; the solvent was evaporated and the residue was sublimed *in vacuo* and recrystallised from ether to give the *monochloro derivative* (nc) (1.9 g, 5%) m.p. 119–120° (Found: C, 38.0; F, 37.4%; Mol. wt., 254. $C_8ClF_5N_2$ requires C, 37.7; F, 37.3%; Mol. wt., 254), $\nu_{max.}$ (KBr) 1645, 1592 (w), 1515–1449 (multiplet), 1326, 1247, 1232, 1217, 1200, 1167, 1107, 1081 (w), 1038, 1020 (w), 909, 797, 787, 680 (w) and 639 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 242, 308, 314.5, and 320 nm (log ε 4.43, 3.70, 3.71, and 3.67). ^{19}F NMR (acetone) showed absorption at −10.6, −18.5, −36.3, −83.3, and −85.5 ppm. The low field (AB) signal gave $J(2,3)$ as 30 Hz.

2,3-Difluoroquinoxaline (2)

2,3-Dichloroquinoxaline[8] (20 g) and freshly dried potassium fluoride (36·5 g) in sulpholan (150 ml) were heated to 190° with stirring for 24 h. The mixture was cooled, poured into water, and extracted with ether. The extract was washed with water, dried, and evaporated; the residue was twice sublimed at 20°/0.01 mm to give 2,3-*difluoroquinoxaline* (nc) (9.8 g, 60%) m.p. 94–95° (Found: C, 57.5; H, 2.40; F, 22.7%; Mol. wt., 166. $C_8H_4F_2N_2$ requires C, 57.8; H, 2.40; F, 22.9%; Mol. wt. ,166), $\nu_{max.}$ (KBr) 3015 (w), 1449, 1389, 1346, 1330, 1282 (w), 1242, 1190, 1167, 1145, 1012, 915, 887, 772, 763 (vs), 732, 675 (w), 612 (sh), and 609 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 238.5, 242, 246.5, 307, 313, 320.5, 327, and 335.5 nm (log ε 4.39, 4.50, 4.45, 3.78, 3.83, 3.91, 3.87, and 3.98). ^{19}F NMR (acetone) showed absorption at −80.5 ppm.

5,6,7,8-Tetrafluoro-2,3-dihydrazinoquinoxaline (6)

Hexafluoroquinoxaline (1.0 g) in ethanol (10 ml) was treated dropwise with ethanolic hydrazine hydrate (1.0 g, 4.8 mole) during 5 min with stirring at *ca.* 20°. The mixture was stirred for a further 30 min and poured into water; the resulting precipitate was recrystallised from ethyl acetate to give the *dihydrazino derivative* (nc) (1.05 g, 95%) m.p. *ca.* 280° (decomp.) (Found: C, 36.1; H, 2.20; F, 29.4%; Mol. wt., 262. $C_8H_6F_4N_6$ requires C, 36.6; H, 2.30; F, 29.0%; Mol. wt., 262), $\nu_{max.}$ (KBr) 3413, 3268–2985 (br) (multiplet), 1637, 1570, 1464 (br), 1418 (sh), 1339, 1282, 1250, 1190, 1163, 1136 (w), 1057, 1018, 848, 807, 773, 746, and 667 cm^{-1}.

2,3-Dichloro-5,6,7,8-tetrafluoroquinoxaline (11)

5,6,7,8-Tetrafluoro-2,3-dihydrazinoquinoxaline (1.0 g) was added slowly to a solution of copper (II) chloride (10 g) in conc. hydrochloric acid (40 ml) with stirring at *ca.* 20°. The mixture was stirred for a further 30 min and then distilled; the distillate (*ca.* 20 ml) was diluted with water and extracted with ether, the organic layer was washed with water, dried, and evaporated. The residue was sublimed at 20°/0.01 mm to give the *dichloro derivative* (nc) (850 mg, 80%, m.p. 80–82° (Found: C, 35.9; F, 28.0%; Mol. wt., 270. $C_8Cl_2F_4N_2$ requires C, 35·45; F, 28.05%; Mol. wt., 270), $\nu_{max.}$ (KBr) 1656, 1546, 1511–1497 (doublet), 1453, 1351, 1269, 1188, 1164, 1117 (w), 1068, 1010, 968, 683, 651, and 629 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 222.5, 250, 253.5, 310.5, 318, 323.5, 331, and 338.5 nm (log ε 4.05, 4.63, 4.63, 3.65, 3.73, 3.81, 3.78, and 3.82). ^{19}F NMR (acetone) showed absorption at −11.9 and −12.9 ppm.

5,6,7,8-Tetrafluoroquinoxaline (10)

5,6,7,8-Tetrafluoro-2,3-dihydrazinoquinoxaline (2.0 g) was added to a solution of hydrated copper sulphate (10 g) in water (40 ml) with stirring at *ca.* 20° as in the previous experiment. The product, similarly isolated and purified, was *5,6,7,8-tetrafluoroquinoxaline* (nc) (1.01 g, 65%), m.p. 90–91° (Found: C, 47.8; H, 0.90; F, 37.8%; Mol. wt., 202. $C_8H_2F_4N_2$ requires C, 47.5; H, 1.00; F, 37.6%; Mol. wt., 202), $\nu_{max.}$ (KBr) 1681 (sh), 1661, 1570 (w), 1504, 1401, 1376 (w), 1339, 1290 (w), 1250 (w), 1220 (w), 1200, 1152, 1114–1105 (w) (doublet), 1053 (vs), 970, 913, 896 (w), 870, 741, and 643 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 236.5, 305, and 313.5 nm (log ε 4.59, 3.53, and 3.55). ^{19}F NMR (acetone) showed absorption at −13.7 and −15.4 ppm.

2,5,6,7,8-Pentafluoro-3-methoxyquinoxaline (7)

Hexafluoroquinoxaline (1.0 g) in methanol (20 ml) was treated dropwise with methanolic sodium methoxide (7.3 ml, 1.0 mole; 1.0 *M*) at −20° during 30 min. The mixture was stirred for a further 10 min at −20°, allowed to reach room temperature during 10 min, poured into water and extracted with ether. The extract was washed with water, dried, and evaporated. The residue was sublimed at 20°/0.001 mm to give the *monomethoxy derivative* (nc) (810 mg, 80%), m.p. 70–72° (Found: C, 43.5; H, 1.10; F, 38.6%; Mol. wt., 250. $C_9H_3F_5N_2O$ requires C, 43.2; H, 1.2; F, 38.0%; Mol. wt., 250), $\nu_{max.}$ (KBr) 2941 (w), 1658, 1600 (w), 1515–1462 (multiplet), 1410, 1351 (sh), 1326, 1266, 1235, 1190, 1075 (w), 1046, 1020, 973, 814, 801, 714 (w), 667 (w), and 647 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 243.5 and 312 nm (log ε 4.48 and 3.70). ^{19}F NMR (acetone) showed absorption at −4.0, −6.9, −10.6, and −86.6 ppm.

5,6,7,8-Tetrafluoro-2,3-dimethoxyquinoxaline (8)

Hexafluoroquinoxaline (1.0 g) in methanol (15 ml) was treated, at 18°, with methanolic sodium methoxide (2.0 mole) as in the previous experiment, and the product, similarly isolated, was sublimed at 60°/0·001 mm to give the *dimethoxy derivative* (nc) (860 mg, 85%) as colourless needles, m.p. 146–148° (Found: C, 45.6; H, 2.0; F, 28.6%; Mol. wt., 262. $C_{10}H_6F_4N_2O_2$ requires C, 45.8; H, 2.3; F, 29.0%; Mol. wt., 262), $\nu_{max.}$ (KBr) 3003 (w), 2959 (w), 2874 (w), 2326–2299 (w) (doublet), 1661 (w), 1595, 1497, 1453, 1435, 1412, 1335, 1294–1282 (doublet), 1266, 1205 (sh), 1190, 1049, 1022, 995 (sh), 981, 807, 745 (w), 646, and 545 (w) cm^{-1}, $\lambda_{max.}$ (cyclohexane) 222.5, 246, 284.5, 291, 296, 303, 309, 316.5, and 323 nm (log ε 4.14, 4.42, 3.47, 3.54, 3.68, 3.73, 3.90, 3.76, and 3.91). ^{19}F NMR (acetone) showed absorption at −1.3 (6 and 7*F*) and −8.4 ppm (5 and 8*F*).

5,6,8-Trifluoro-2,3,7-trimethoxyquinoxaline (12)

5,6,7,8-Tetrafluoro-2,3-dimethoxyquinoxaline (1·0 g) and methanolic sodium methoxide (2.5 ml, 1.07 mole; 1.63 *M*) were sealed in a Carius tube and heated to 120° for 18 h. The tube was cooled, its contents were added to water, and extracted with ether. The extract was washed with water, dried, and evaporated; the residue was sublimed at 60°/0·001 mm to give the *trimethoxy derivative* (nc) (900 mg, 85%), m.p. 132–134° (Found: C, 42.7; H, 3.0; F, 21.0%; Mol. wt., 274. $C_{11}H_9F_3N_2O_3$ requires C, 42.6; H, 2.90; F, 20.8%; Mol. wt., 274), $\nu_{max.}$ (KBr) 3003 (w), 2959 (w), 1656 (w), 1600, 1493, 1435, 1414, 1339, 1282 (sh), 1261, 1205, 1190 (sh), 1163 (w), 1066, 1028, 997 (sh), 983, 942, 802, 745 (w), and 646 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 245 and 311 nm (log ε 4.34 and 3.60). ^{19}F NMR (acetone) showed absorption at −7.2 and −7.8 (5 and 6*F*) and at −14.8 ppm (8*F*).

5,6,7,8-Tetrafluoro-1H,4H-quinoxalin-2,3-dione (9)

(*a*) Hexafluoroquinoxaline (1.0 g), potassium hydroxide (2.0 g), and t-butanol (40 ml) were heated under reflux for 15 h. The solution was evaporated to *ca.* 20 ml, and water was added. The remaining t-butanol was evaporated, the mixture was acidified with conc. hydrochloric acid (15 ml), and the resulting precipitate was recrystallised from ethanol to give the *quinoxalin-dione* (nc) (550 mg, 55%), which decomposed without melting at *ca.* 300° (Found: C, 41.0; H, 0.80; F, 32.7%; Mol. wt., 234. $C_8H_2F_4N_2O_2$ requires C, 41.0; H, 0.85; F, 32.5%; Mol. wt., 234), $\nu_{max.}$ (KBr) 3165–2857 (br) (multiplet), 1730, 1686, 1667 (sh), 1550, 1527, 1481 (w), 1435, 1381, 1290, 1147, 1042–1020 (multiplet), 833, 791 and 612 cm^{-1}, $\lambda_{max.}$ (ethanol) 227, 253.5, 260, 303, 314 (infl.), and 332 (infl.) (log ε 4.00, 3.89, 3.94, 3.84, and 3.39). ^{19}F NMR (*N*-methyl-2-pyrrolidone, 60°) showed absorptions of equal intensity at −3.5 and +7.1 ppm.

(*b*) Hexafluoroquinoxaline (1.0 g) in conc. sulphuric acid (10 ml) was treated dropwise with water (40 ml) during 45 min with vigorous stirring; the addition was regulated to keep the temperature below 60°. The mixture was stirred for a further

3 h at 20°. The resulting precipitate (866 mg) was washed with water, dried (100°) and recrystallised from ethanol to give 5,6,7,8-tetrafluoro-1*H*,4*H*-quinoxaline-2,3-dione, identical (IR) with that obtained in the previous experiment.

5,6,7,8-Tetrafluoro-2-methoxy-4-methylquinoxaline-3-one (13)

5,6,7,8-Tetrafluoro-1*H*,4*H*-quinoxaline-2,3-dione (1.0 g), suspended in ether (150 ml), was treated dropwise with ethereal diazomethane with stirring at *ca.* 20° until there was no further effervescence and the pale yellow colour persisted. The resulting clear solution was stirred for a further 3 h at 20°, concentrated, and shown by GLC (silicone elastomer at 230°) to contain a single product. The remaining ether was evaporated and the residue was sublimed at 40°/0.01 mm to give the *O,N-dimethyl derivative* (nc) (950 mg, 85%) m.p. 134–136° (Found: C, 45·7; H, 2.25; F, 29.4%; Mol. wt., 262). $\nu_{max.}$ (KBr) 2959 (w), 1695, 1667 (sh), 1631, 1613 (sh), 1515, 1449, 1412, 1377, 1340, 1299, 1282, 1232, 1159, 1124, 1101 (w), 1060, 1029, 983, 917, 824, 807, 794, 753, 645 and 610 cm^{-1}, $\lambda_{max.}$ (ethanol) 230, 240 (infl.), 252 (infl.), 264 (infl.), 306.5, 314 (infl.), and 332 (infl.) (log ε 4.15, 4.12, 4.06, 3.87, 3.86, 3.83 and 3.45). ^{19}F NMR (*N*-methyl-2-pyrrolidone) showed absorption at −10.8, −2.9 + 1.4 and +2.9 ppm.

2,6-Diamino-3,5-difluoropyrazine (15)

Tetrafluoropyrazine[3] (5.15 g) and aqueous ammonia (d. 0.880, 54 ml) were stirred together in a tightly stoppered flask at *ca.* 25° for 14 days; the flask was then opened and stirred for 2 h. The crystals which separated were washed with water and twice recrystallised from acetone (charcoal) to give colourless prisms of the *diamino derivative* (nc) (1.7 g) m.p. *ca.* 243° with sublimation and decomposition. (Found: C, 33.1; H, 2.6; N, 37.3; Mol. wt., 146. $C_4H_4F_2N_4$ requires C, 32.9; H, 2.75; N, 38.4; Mol. wt., 146), $\nu_{max.}$ (KBr) 3472, 3310, 3226, 3185 (sh), 1645, 1555 (m), 1515, 1401 (s), 1325, 1294 (m), 1168, 116 (m), 1095 (m), 909, 720, 650 (br), *ca.* 600 (v.br), 540, 481 (m), 463, $\lambda_{max.}$ (ethanol) 233.5 and 339 nm. ^{19}F NMR (ethanol/acetone 1:1) showed absorption at −44.1 ppm (s).

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