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THE ELECTROCHEMICAL OXIDATION OF POLYFLUOROAROMATIC AMINES—II

THE SYNTHESIS OF SUBSTITUTED POLYFLUOROPHENAZINES

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Abstract—1- and 2-Methoxy-heptafluorophenazine and 1- and 2-bromoheptafluorophenazine have been obtained by anodic oxidation of appropriately substituted 2-amino-octafluorodiphenylamines, the synthesis of which is described. By reaction of octofluorophenazine with suitable nucleophiles, 2-methoxy-, 2-hydroxy and 2-N.N[1]-dimethylamino-heptafluorophenazine were formed; some of their reactions are described.

A PREVIOUS paper[1] described the synthesis of a number of highly fluorinated phenazine compounds by the electrochemical oxidation of polyfluoroaromatic amines. We now report the synthesis of some 1- and 2-substituted polyfluorophenazines by a similar method, and some nucleophilic substitution reactions of octafluorophenazine.

By the electrochemical oxidation of 2-amino-3-methoxy- and 2-amino-5-methoxy-octafluorodiphenyl-amine (see below), 1-methoxy- and 2-methoxy-heptafluorophenazine respectively, were obtained in good yield. The position of the substituent in each case follows unequivocally from the structure of the starting material, but was confirmed by ^{19}F NMR spectroscopy. The electrolysis of solutions of *p*-methoxy-tetrafluoroaniline gave unequivocally 2,7-dimethoxy-hexafluorophenazine, the structure of which was confirmed by ^{19}F NMR spectroscopy; 4,4′-dimethoxy-octafluoroazobenzene was also obtained from the electrolysis product.

2-Methoxy-heptafluorophenazene has also been obtained by the nucleophilic attack of methoxide ion on octafluorophenazine, a reaction which gave a product identical with that from the electrochemical oxidation of 2-amino-5-methoxy-octafluoro-diphenylamine. Likewise using potassium hydroxide in t-butanol at 80° as the nucleophile, afforded 2-hydroxy-heptafluorophenazine as a yellow solid, slightly soluble in water to give a yellow solution, becoming red in the presence of alkali. Treatment of the phenazinol with diazomethane gave 2-methoxy-heptafluorophenazine, identical with the samples prepared by the alternative routes. 2-Hydroxy-heptafluorophenazine was also obtained by the demethylation of 2-methoxy-heptafluorophenazine with aqueous hydriodic acid. Substitution also occurred in the reaction of dimethylamine with octafluorophenazine and by analogy yielded 2-dimethylamino-heptafluorophenazine. Attempts were made to prepare 1-hydroxy-heptafluorophenazine by the demethylation of 1-methoxy-heptafluorophenazine using a variety of conditions, but without success.

Electrochemical oxidation of 2-amino-3-bromo- and 2-amino-5-bromo-octafluorodiphenylamine gave 1-bromo- and 2-bromo-heptafluorophenazine respectively, with correct ^{19}F NMR spectra. The position of the bromo-substituent follows, as in the cases of the methoxypolyfluorophenazines, from the structures of the starting materials. The

preparation of 2-bromo-heptafluorophenazine from 2-*H*-heptafluorophenazine[1] using Br_2/glacial acetic acid and Br_2/H_2SO_4 was unsuccessful, starting material being recovered. An alternative synthesis from 2-*H*-heptafluorophenazine by formation of a lithio-derivative (using lithium methyl) followed by addition of bromine was also unsuccessful, and, in the presence of a sufficient excess of lithium methyl, no starting material could be recovered. It was observed in other experiments using octafluorophenazine and lithium methyl at 50° that no identifiable products or starting material could be obtained from the reaction mixture.

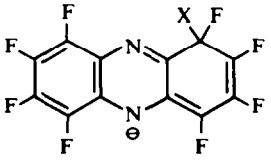
The preparation of Grignard reagents from 1-bromo- and 2-bromo-heptafluorophenazine was also attempted. In the case of the 1-bromo-derivative, only starting material could be recovered from the reaction mixture. From 2-bromo-heptafluorophenazine a mixture of 2-bromo- and 2-*H*-heptafluorophenazine (approx 5:1 by weight) was obtained, indicating only a slow formation of a Grignard reagent.

The preparation of the amino-diphenylamine compounds used for electrochemical oxidation was as previously described.[1] n-Butyllithium was added slowly to pentafluoroaniline to give the lithium anilide, which was added to the appropriate methoxy- or bromo-tetrafluoro-nitrobenzene. From 3-methoxy- and 3-bromo-6-nitrotetrafluorobenzene substitution of fluorine is limited to the position *ortho* to the nitro group but, in the 5-methoxy- and 5-bromo-analogues also, only the fluorine *ortho*- to the nitro group was replaced, in accordance with previous observations.[6]

The 3-methoxy- and 5-methoxy-6-nitrooctafluorodiphenylamine derivatives were then reduced with hydrogen using a Pd/charcoal catalyst to yield 2-amino-5-methoxy- and 2-amino-3-methoxyoctafluoro-diphenylamine respectively. In order to avoid reduction of the aromatic bromine atom 3-bromo- and 5-bromo-6-nitrodiphenylamine were reduced with stannous chloride, giving 2-amino-5-bromo-and 2-amino-3-bromooctafluorodiphenylamine respectively.

The results we have obtained show that nucleophilic attack on octafluorophenazine occurs at the 2- position. Nucleophilic attack on heptafluoro-quinoline and isoquinoline[2] results in substitution at the 2- and 4- positions in the former and the 1- position in the latter, showing that the ring nitrogen is dominant in controlling the orientation of attack, presumably by effective delocalization of the negative charge of the intermediate carbanion. This conclusion is confirmed by studies on polyfluoropyridines.[3]

With these results in mind among the most important resonance contributors to the Wheland intermediate for nucleophilic substitution in octafluorophenazine are structures I and II respectively.



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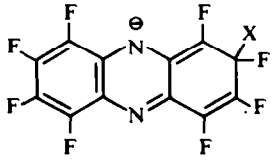

II

It has frequently been argued in our work on nucleophilic substitution on aromatic fluorocarbon derivatives[4] that *p*-quininoid structures (analogous to II) are more important than *o*-quininoid structures (analogous to I). The position of substitution in octafluorophenazine is in agreement with this.

EXPERIMENTAL

NMR spectra were recorded on samples dissolved in acetone d_6 unless otherwise stated. All data are quoted on the delta scale with high field (low frequency) shifts negative. The reference standards ($\delta = 0{\cdot}0$) are TMS and CCl_3F for ^1H and ^{19}F spectra respectively.

The techniques used for electrochemical oxidations and extraction of product were similar to those previously described.[1] The electrolyte employed was a potassium acetate: acetone: water mixture and the anode was of platinum. At the end of the oxidation the anolyte was distilled to remove acetone, and the solid residue sublimed and recrystallized as appropriate.

Electrolysis of 2-*amino*-3-*methoxyoctafluorodiphenylamine*

The amine (0·9 g) was anodically oxidized at 1·4–1·5V as previously descibed, and 380 coulombs passed. The soln from the anode compartment was evaporated to give a product (1·0 g) which, after being dried in a vacuum dessicator, was sublimed at 100–110° under reduced pressure to give a yellow solid (0·45 g). Recrystallization from light petroleum (b.p. 40–60°) afforded 1-*methoxyheptafluorophenazine* m.p. 141·5–143°, (0·36 g). (Found: C, 46·4; H, 1·3; N, 8·4. $C_{13}H_3F_7N_2O$ requires C, 46·4; H, 0·9; N, 8·3%); mass spectrometry gave a top mass peak of 336 ($C_{13}H_3F_7N_2O$). The ^1H NMR spectrum consisted of one signal at δ4·18 (doublet). The ^{19}F NMR spectrum had five signals of intensity ratio 1 : 1 : 2 : 2 : 1. The chemical shifts of these signals were δ −145·8 (doublet), −149·7 (triplet), −151·3 (doublet), 152·2 (multiplet) and −154·4 (doublet) respectively, consistent with 1-methoxyheptafluorophenazine.

Electrolysis of 2-*amino*-5-*methoxyoctafluorodiphenylamine.*

The amine (1·0 g) was electrolysed at an anode potential of 1·4–1·5V, in the standard electrolyte (500 ml), and approximately 250 coulombs passed. The soln was evaporated to remove acetone and the brown residue (1·23 g) filtered. Recrystallization from light petroleum (b.p. 40–60°) gave 2-*methoxyheptafluorophenazine* (0·98 g), m.p. 131–132° (Found: C, 46·5; H, 0·9. $C_{13}H_3F_7N_2O$ requires C, 46·4; H, 0·9%). The proton NMR spectrum showed one signal, chemical shift δ4·53, which was a doublet of doublets ($J = 3{\cdot}6$ and 0·8 Hz), due to the methyl hydrogen atoms. The ^{19}F NMR spectrum showed five signals with chemical shifts δ − 144·3, − 151·1, − 152·8, − 154·0, and − 156·0 in the ratio 1 : 1 : 2 : 2 : 1, consistent with the proposed structure.

Electrolysis of p-*methoxy-tetrafluoroaniline*

The amine (2·0 g) prepared as previously described,[5] was electrochemically oxidized at an anode potential of 1·2–1·3V, a total of 1,990 coulombs being passed. The soln from the anode compartment was distilled to remove acetone and a black ppt (1·67 g) filtered off. A sample (0·85) of the solid was fractionally sublimed to give 4,4′-dimethoxy-octafluoroazobenzene (0·18 g, 17%) m.p. and mixed m.p. 150°, having an IR spectrum identical with that of an authentic sample,[5] and (ii) a yellow solid (0·12 g). This, after recrystallization from CCl_4, was identified as 2,7-*dimethoxyhexafluorophenazine* (0·10 g), m.p. 218·5–219·5° (Found: C, 48·5; H, 2·0; N, 8·1. $C_{14}H_6F_6N_2O_2$ requires: C, 48·3; H, 1·7; N, 8·0%). The ^1H NMR spectrum showed one signal, chemical shift δ4·46, and the ^{19}F NMR spectrum three signals in the ratio 1 : 1 : 1, with chemical shifts δ −137·4, −149·6, and −152·1, consistent with the proposed structure.

Reactions of octafluorophenazine

(i) *Sodium Methoxide.* NaOMe soln (12·5 ml, 0·209 gNa/100 ml MeOH) was added slowly to a stirred soln of octafluorophenazine[1] (0·36 g) in dry MeOH at room temp and the mixture stirred for 2½ h. The soln was then evaporated to dryness under reduced pressure, the solid washed with water and dissolved in Et_2O. The ethereal soln was dried over $MgSO_4$ and evaporated to yield a yellow solid (0·38 g) which was shown by thin layer chromatography to contain three components. Separation by column chromatography (SiO_2; C_6H_6 eluant) gave (i) octafluorophenazine (0·022 g) and (ii) 2-methoxyheptaflourophenazine (0·236 g), both of which were identified by m.p., mixed m.p. and IR spectroscopy. The remaining component could not be separated in sufficient quantity to be identified.

(ii) *Potassium hydroxide in t-butanol.* To a soln of octafluorophenazine (0·5 g) in t-butanol (160 ml) was added KOH (0·2 g) and the mixture heated (80°) for 3h. The red soln was poured into water (400 ml) and the t-butanol distilled off. The aqueous residue was extracted with Et_2O (3 × 50 ml) and then acidified with 4N HCl. The acidified soln was re-extracted with Et_2O (3 × 100 ml) and the ether extract dried ($MgSO_4$) and evaporated to give a brown solid (0·4 g). Sublimation of this gave a yellow product (0·37 g) which was recrystallized (C_6H_6) to give 2-*hydroxy-heptafluorophenazine* (0·28 g), m.p. 272–273° (Found:

C, 44·7; H, 0·3; N, 8·7: $C_{12}HF_7N_2O$ requires C, 44·7; H. 0·3; N, 8·7%). Mass spectrometry gave a top mass peak 322 (correct for $C_{12}HF_7N_2O$). The ^1H NMR spectrum consisted of a broad singlet at δ6·5–6·8 and the ^{19}F spectrum of four signals in the intensity ratio 1 : 1 : 3 : 2 with chemical shifts δ −144·3, −151·4, −152·5 and −155·1 respectively, in accord with the assigned structure.

(iii) *Dimethylamine.* Dimethylamine (0·25 g, 33% w/v in EtOH) in EtOH (10 ml) was added over 5 min to a stirred soln of octafluorophenazine (0·3 g) in EtOH (150 ml), and the mixture stirred for a further 2 h. The soln was evaporated to dryness under reduced pressure to yield a red solid which was washed with water and dissolved in CH_2Cl_2. The soln was dried ($MgSO_4$) and evaporated to leave a residue (0·313 g). A TLC examination of the residue showed the presence of one major and three minor components in the mixture. Separation of the product by column chromatography (SiO_2, C_6H_6 eluant) gave (i) octafluorophenazine (0·03 g), identified by m.p. and IR spectrum and (ii) a red solid (0·21 g), which after recrystallization was identified as *2-dimethylaminoheptafluorophenazine* (0·16 g), m.p. 148·5–151° (Found: C, 47·8; H, 1·8. $C_{14}H_6F_7N_3$ requires C, 48·2; H, 1·7%). The ^1H NMR spectrum (in CF_3COOH, C_6H_{12} internal standard) consisted of one signal, δ 2·32, which was a triplet $J_{NMe-F} = 2·0$ Hz. The ^{19}F NMR spectrum showed five signals in the ratio 1 : 2 : 1 : 2 : 1 with chemical shifts δ −133·9, −139·6, −143·6, −146·2 and −151·2 respectively consistent with the proposed structure. The remaining two minor components could not be isolated in sufficent quantity for identification.

Reaction of 2-hydroxyheptafluorophenazine with diazomethane

A soln of CH_2N_2 in Et_2O (5 ml, 0·25M) was added to 2-hydroxyheptafluorophenazine (50 mg) in dry Et_2O (40 ml) at 0°. The soln was stirred for 2 h, when the Et_2O was evaporated to leave a yellow product (50 mg) which was shown by TLC to be a single component. Recrystallization from light petroleum (b.p. 60–80°) gave 2-methoxyheptafluorophenazine, m.p. 131°, with an IR spectrum identical with that of a sample prepared by an alternative route.

Demethylation of 2-methoxyheptafluorophenazine

A mixture of 2-methoxyheptafluorophenazine (0·1 g) and aqueous HI (4 ml, 54% w/w) was heated under reflux for 2 h and the cooled soln treated with sodium metabisulphite. The reaction mixture was made alkaline and extracted with Et_2O (3 × 40 ml). The ethereal extracts were dried ($MgSO_4$) and evaporated to give 2-methoxyheptafluorophenazine (0·02 g), identified by m.p. and IR spectrum. The aqueous soln was acidified and extracted with Et_2O (4 × 40 ml), and the Et_2O layer dried ($MgSO_4$) and evaporated to yield a residue (0·05 g). Sublimation of the residue gave 2-hydroxyheptafluorophenazine (0·04 g) identified by IR spectrum.

Attempted demethylation of 1-methoxyheptafluorophenazine

(i) The methoxyphenazine (0·25 g) and anhydrous $AlCl_3$ (0·4 g) were heated at 140° for 4 h when water was added to the cooled reaction mixture. After isolation, only a red oil (0·02 g) was obtained from which no identifiable components could be isolated. After reaction at 80° for 1h 1-methoxyheptafluorophenazine (0·09 g) was recovered, together with a trace of an orange solid, the IR spectrum of which showed a peak at 1700 cm^{-1} and a broad peak between 2500–2500 cm^{-1}.

(ii) The methoxyphenazine (0·1 g) and aqueous HI (4 ml, 54% w/w) was heated under reflux for 2h and the cooled soln treated with sodium metabisulphite. After isolation 1-methoxyheptafluorophenazine (0·03 g) was obtained, and also a red yellow-residue (0·03 g), which could not be purified but had an IR spectrum showing absorptions at 1700 and at 2800–3500 cm^{-1}.

Electrolysis of 2-amino-5-bromooctafluorodiphenylamine

The amine (1·05 g) was electrochemically oxidized at potential of 1·55–165V, as previously described, and 260 coulombs passed. The anolyte was evaporated to remove acetone and the aqueous residue filtered. The solid filtered off was dried in vacuum and the residue (0·96 g) sublimed at 140°–150° under reduced pressure to give a yellow sublimate (0·58 g).

Recrystallization from light petroleum (b.p. 60–80°) gave *2-bromo-heptafluorophenazine* (0·41 g), m.p. 191–192° (Found: C, 37·3; H, 0·5; N, 7·3. $C_{12}BrF_7N_2$ requires C, 37·4; H, 0·0; N, 7·3%). Mass spectrometry (386 and 384) and the IR spectrum were in agreement with the proposed structure. The ^{19}F NMR spectrum (in THF) showed four signals in the intensity ratio 1 : 1 : 2 : 3 with chemical shifts δ −117·1 (doublet), −124·7 (doublet), −149·6 (multiplet) and −151·8 (multiplet) respectively, in accord with the structure.

Electrolytic oxidation of 2-amino-3-bromooctafluorodiphenylamine

The amine (1·1 g) was electrolytically oxidized at 1·55–1·60 as previously described, 385 coulombs being consumed during the electrolysis. The anolyte was worked up in the standard way to give a residue (0·9 g), which was sublimed at 140° under reduced pressure to give a yellow product (0·64 g), shown by TLC to contain two components. Separation by column chromatography (silica gel, benzene solvent) afforded 2-amino-3-bromooctafluorodiphenylamine (0·09 g), identified by a comparison of IR spectra and a yellow solid (0·54 g) which after recrystallization gave *1-bromoheptafluorophenazine* (0·35 g), m.p. 221–222° (Found: C, 37·8; H, 0·5; N, 7·0. $C_{13}BrF_7N_2$ requires C, 37·4; H, 0·0; N, 7·3%). Mass spectrometry (384 and 386) and the IR spectrum were consistent with the proposed structure. The ^{19}F NMR spectrum showed five signals in the ratio 1 : 1 : 1 : 2 : 2 with chemical shifts δ −113·0 (doublet of doublets), −146·4 (doublet of doublets), −148·3 (doublet of doublets), −149·6 (doublet) and −151·6 (doublet) respectively, in agreement with the proposed structure.

Attempted bromination of 2-H-heptafluorophenazine

(i) *Br_2 Glacial AcOH.* Br_2 (0·16 g) in glacial AcOH (10 ml) was added slowly to a solution of the phenazine (0·30 g) in glacial AcOH (50 ml) and the mixture heated for 1h at 80°. After isolation, only 2H-heptafluorophenazine (0·26 g) was obtained.

(ii) *Br_2/Fuming H_2SO_4.* Br_2 (6·0 g) was added slowly to a soln of 2*H*-heptafluorophenazine (0·3 g) in fuming H_2SO_4 (15 ml, 20% SO_3), and the mixture heated at 70° for 3 h; only 2*H*-heptaflurorphenazine (0·28 g) was found.

(iii) *Lithium Methyl.* A solution of 2*H*-heptafluorophenazine (0·8 g) in dry 1,2-dimethoxyethane (60 ml) under N_2 was cooled to −65° and LiMe (3·0 ml, 0·86N) in Et_2O added. After stirring for 2h at −50°, Br_2 (0·4 ml) was added and the soln warmed to room temp. The mixture was then poured into water and worked up. Only 2*H*-heptafluorophenazine (0·6 g) was obtained. A repeat experiment at −40° and in the presence of a threefold excess of LiMe gave no identifiable product or starting material.

Preparation of Grignard reagents

(i) *1-Bromoheptafluorophenazine.* A soln of the phenazine (0·20 g) in Et_2O (40 ml) was refluxed and stirred with an excess of Mg for 1·5h; no apparent reaction occurred. $C_2H_4Br_2$ (1 ml) was added and the mixture refluxed for a further 3h when dilute HCl was added and the Et_2O layer separated. Isolation yielded 1-bromoheptafluorophenazine (0·12 g) only.

(ii) *2-bromoheptafluorophenazine.* A soln of the phenazine (0·3 g) in dry Et_2O (50 ml) was refluxed and stirred with an excess of Mg for 2h. No reaction was observed and $C_2H_4Br_2$ (1 ml) was added and the soln refluxed for a further 2h. Dilute aq HCl was added, the Et_2O layer separated and the aqueous residue extracted with Et_2O (2 × 50 ml). The combined ethereal solutions were dried ($MgSO_4$) and evaporated to give a yellow solid (0·27 g). Separation of the mixture by column chromatography (Alumina, benzene: light petroleum (b.p. 40–60°) = 2 : 1 eluant) afforded 2-bromoheptafluorophenazine (0·17 g) and 2-*H*-heptafluorophenazine (0·03 g), both identified by m.p., mixed m.p. and comparison of IR spectra.

Preparation of 3-methoxy-6-nitrooctafluorodiphenylamine

n-Butyllithium (3·8 ml, 0·14 g, nBuLi/ml), in dry Et_2O (20 ml) was added over 5 min to a stirred soln of pentafluoroaniline (1·47 g) in dry Et_2O (100 ml), and the soln stirred for a further 20 min. The soln was then added slowly (20 min) to a stirred soln of 1,2,4,5-tetrafluoro-3-methoxy-6-nitrobenzene[6] (1·8 g) in dry Et_2O (50 ml), and the mixture refluxed for 23 h. The Et_2O soln was then washed with 4N HCl (3 × 100 ml), dried ($MgSO_4$) and evaporated to give a product (3·2 g). Separation by column chromatography (alumina) using light petroleum (b.p. 40–60°) and benzene (3 : 1) as eluant afforded a product (1·5 g), which after recrystallization gave *3-methoxy-6-nitrooctafluorodiphenylamine* (1·17 g), m.p. 61-63°, (Found: C, 40·5; H, 1·3; N, 7·5; $C_{13}H_4F_8N_2O_3$ requires C, 40·2; H, 1·0; N, 7·2%). The ^1H NMR spectrum (in CCl_4) showed two signals in the ratio 1 : 3 with chemical shifts δ 7·3 (ascribed to > NH) and δ 4·13, which was a triplet with $J_{OMe\text{-}F}$ = 2·0 Hz (ascribed to —O—CH_3). The ^{19}F NMR spectrum consisted of six signals in the ratio 1 : 1 : 2 : 1 : 1 : 2, with chemical shifts δ −145·8 (doublet of doublets J = 22·5 and 8·6 Hz), −146·7, −152·7, −159·2 (a multiplet), −161·4 and −162·9 respectively in agreement with the structure proposed.

Preparation of 2-amino-5-methoxyoctafluorodiphenylamine

3-methoxy-6-nitrooctafluorodiphenylamine (1·2 g) was dissolved in EtOH (50 ml) and Pd/C (0·1 g 10% Pd) added. The mixture was hydrogenated, then filtered, and the EtOH evaporated to leave a product (1·1 g).

Recrystallization from light petroleum (b.p. 40–60°) gave *2-amino-5-methoxyoctafluorodiphenylamine* (0·88 g) m.p. 88–89°. (Found: C, 43·6; H, 1·9; N, 7·9. $C_{13}H_6F_8N_2O$ requires 43·6; H, 1·7; N, 7·8%).

Preparation of 5-methoxy-6-nitrooctafluorodiphenylamine

n-Butyllithium (5·7 ml, 0·16 g n-BuLi/ml) was added slowly (10 min) to a stirred soln of pentafluoroaniline (2·68 g) in dry Et_2O (150 ml). The soln was stirred under N_2 for 40 min, and then slowly added (30 min) to a solution of 1,2,3,4-tetrafluoro-5-methoxy-6-nitrobenzene[6] (3·3 g) in dry Et_2O (100 ml), and the mixture stirred for 20 h at room temp. The soln was then washed with 4N HCl, the ether layer separated and dried ($MgSO_4$), and evaporated to give a product (6·0 g). This was then separated on an alumina column (light petroleum (b.p. 40–60°): benzene = 2 : 1 as eluant) to give a trace of 2-methoxy-3,4,5,6-tetrafluoronitrobenzene and a yellow product (2·9 g). After recrystallization from light petroleum (b.p. 40–60°) this was identified as *5-methoxy-6-nitrooctafluorodiphenylamine* (2·3 g) m.p. 46–47° (Found: C, 40·1; H, 1·2; N, 7·4; F, 39·4. $C_{13}H_4F_8N_2O_3$ requires C, 40·2; H, 1·0; N, 7·2; F, 39·2%) Mass spectrometry gave a top mass peak at 388 ($C_{13}H_4F_8N_2O_3$). The ^1H NMR spectrum consisted of two signals of intensity ratio 1 : 3 with chemical shifts δ 7·53 (singlet) and 4·2 (doublet) respectively. The ^{19}F spectrum showed five signals in the intensity ratio 1 : 1 : 2 : 1 : 3 with chemical shifts δ −150·7 (triplet) −151·8 (doublet), −153·4 (multiplet), −155·6 (doublet of quartets) and −162·1 (complex multiplet). The spectra are consistent with the proposed structure.

Preparation of 2-amino-3-methoxyoctafluorodiphenylamine

To 5-methoxy-6-nitrooctafluorodiphenylamine (1·3 g) in EtOH (70 ml) was added Pd C (0·1 g. 10% Pd) and the suspension hydrogenated. The mixture was filtered, and the ethanolic solution evaporated to give a yellow product (1·1 g), which after recrystallization from light petroleum (b.p. 60–80°) gave *2-amino-3-methoxyoctafluorodiphenylamine* (0·88 g) m.p. 103·5–104·5° (Found: C, 43·4; H, 2·0; N, 7·6. $C_{13}H_6F_8N_2O$ requires C, 43·6; H, 1·7; N, 7·8%); mass spectrometry gave a top mass peak at 358 ($C_{13}H_6F_8N_2O$). The ^1H NMR spectrum showed 2 signals at δ 6·2 (a singlet) and 3·85 (a singlet between a doublet) in the intensity ratio 1 : 5. The ^{19}F spectrum consisted of six signals at δ −151·7 (a doublet), −155·7 (a doublet), −159·0 (a multiplet), −164·8 (doublet of triplets), −170·4 (a triplet of triplets) and −176·0 (a triplet) in the intensity ratio 1 : 1 : 2 : 2 : 1 : 1. The spectra are in agreement with the assigned structure.

Preparation of 3-bromo-6-nitrooctafluorodiphenylamine

n-Butyllithium (3·0 ml, 0·159 g n-BuLi/ml) in dry Et_2O (20 ml) was added over a period (20 min) to pentafluoroaniline (1·34 g) in dry Et_2O (140 ml) with stirring. The soln was stirred (20 min) under N_2 and the mixture added slowly (30 min) to 1-bromo-2,3,5,6-tetrafluoro-4-nitrobenzene[7] (2·0 g) in dry Et_2O (100 ml) with stirring, and the mixture refluxed for 20 h. The ethereal soln was then washed with 4N HCl (3 × 100 ml), dried ($MgSO_4$) and the ether evaporated to give a product (3·8 g) which was shown by TLC to contain two components. Separation by column chromatography on alumina (light petroleum (b.p. 40–60°); benzene–2 : 1 eluant) gave a trace of 4-bromotetrafluoronitrobenzene and a yellow solid (1·2 g), which after recrystallization (light petroleum (b.p. 60–80°)) was shown to be *3-bromo-6-nitrooctafluorodiphenylamine* (0·89 g) m.p. 97–98° (Found: C, 33·3; H, 0·6; N, 6·4. $C_{12}HBrF_8N_2O_2$ requires C, 33·0; H, 0·2; N, 6·4%). Mass spectrometry gave top mass peaks at 436 and 438, correct for the named compound. The ^1H NMR spectrum consisted of one signal at δ 7·95 with a ^{19}F spectrum containing five signals of intensity ratio 1 : 1 : 1 : 2 : 3 with chemical shifts of δ −119·3 (doublet of doublets), −134·1 (doublet of doublets), −148·1 (quartet) − 152·9 (multiplet) and − 164·3 (multiplet) respectively, consistent with the proposed structure.

Reduction of 3-bromo-6-nitrooctafluorodiphenylamine

The compd (1·0 g) was dissolved in a mixture of EtOH (50 ml), conc H_2SO_4 (10 ml) and water (10 ml). $SnCl_2 2H_2O$ (3·0 g) was added and the soln heated at 45° for 2·5h. After neutralizing the soln with 4N NaOH it was extracted with Et_2O (3 × 100 ml), and the ethereal extracts washed with water (3 × 50 ml), dried ($MgSO_4$) and evaporated to give a product (0·7 g). The product was sublimed under reduced pressure, and the sublimate recrystallized from light petroleum (b.p. 40–60°) to give *2-amino-5-bromooctafluorodiphenylamine* (0·57 g) m.p. 75–76° (Found: C, 35·6; H, 0·9; N, 7·0; $C_{12}H_3BrF_8N_2$ requires C, 35·4; H, 0·7; N, 6·9%). The ^1H NMR spectrum consisted of two signals, chemical shifts δ 6·32 and 5·83 in the intensity ratio 1 : 2. The ^{19}F spectrum showed six signals at δ −121·8, (a doublet), −133·3 (a doublet), −159·1 (doublet of triplets), −160·8 (a quartet), −165·0 (a multiplet), and −168·2 (triplet of triplets) in the intensity ratio 1 : 1 : 2 : 1 : 1 : 2 respectively. These spectra are consistent with the proposed structure.

Preparation of 5-bromo-6-nitrooctafluorodiphenylamine

n-Butyllithium (7·8 ml, 0·127 g/ml) in dry Et_2O (15 ml) was added slowly to a stirred soln of pentafluoroaniline (0·67 g) in dry Et_2O (100 ml). The mixture was stirred under N_2 for a further 15 min and then added to a stirred soln of 1-bromo-2,3,4,5-tetrafluoro-6-nitrobenzene[8] (1·0 g) in dry Et_2O (120 ml) and the mixture refluxed for 16 h. The ethereal mixture was then washed with 4N HCl (3 × 50 ml), dried ($MgSO_4$) and evaporated to give a black oil (2·0 g), which was shown by TLC to contain two components. The mixture was separated by column chromatography (alumina with light petroleum (b.p. 40–60°): benzene = 2:1 as eluant) to give 1-bromo-2,3,4,5-tetrafluoro-6-nitrobenzene (0·17 g), identified by a comparison of IR spectra and a yellow solid (0·7 g). Recrystallization of the solid from light petroleum (b.p. 40–60°) gave *5-bromo-6-nitrooctafluorodiphenylamine* (0·63 g) m.p. 75·5–76·5° (Found: C, 32·7; H, 0·5; N, 6·3. $C_{12}HBrF_8N_2O_2$ requires C, 33·0; H, 0·2; N, 6·4%). Mass spectrometry gave top mass peaks at 438 and 436, correct for $C_{12}HBrF_8N_2O_2$. The ^1H NMR spectrum (in CCl_4) showed one signal at δ 6·2 and the ^{19}F NMR spectrum 5 signals in the intensity ratio 1:1:1:2:3 with chemical shifts δ −127·2 (doublet of doublets) −142·8 (doublet of doublets), −149·5 (quartet), −153·8 (doublet) and −161·9 (multiplet) respectively, in agreement with the proposed structure.

Preparation of 2-amino-3-bromooctafluorodiphenylamine

5-Bromo-6-nitro-octafluorodiphenylamine (1·6 g) was dissolved in a mixture of EtOH (40 ml), conc HCl (6 ml) and water (3 ml). $SnCl_2 \cdot 2H_2O$ (3 g) was added and the mixture stirred for 12 h. The soln was then neutralized with 4N NaOH and extracted with Et_2O (3 × 100 ml). The ethereal soln was washed with water (150 ml), dried ($MgSo_4$) and evaporated to leave a product (1·6 g) which was sublimed under reduced pressure to give *2-amino-3-bromooctafluorodiphenylamine* (1·4 g), m.p. 97–98°. (Found: C, 35·7; H, 1·0; N, 6·6. $C_{12}H_3BrF_8N_2$ requires C, 35·4; H, 0·7; N, 6·9%). The mass spectrum showed top mass peaks at 408 and 406 correct for $C_{12}H_3BrF_8N_2$. The ^1H NMR spectrum consisted of two signals, both singlets at δ 4·9 and 4·5, in the intensity ratio of 1:2 attributed to > NH and $>NH_2$ respectively. The ^{19}F spectrum showed six signals of intensity ratio 1:1:2:2:1:1 at δ −126·9 (doublet of doublets), −144·7 (doublet of doublets) −158·1 (multiplet), −162·9 (doublet of triplets), −166·4 (triplets) and −170·9 (triplet) respectively, consistent with the proposed structure.

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