A Benzoquinone Di-imine from the Oxidation of Pentafluoroaniline by Hypochlorite. *X*-Ray Crystal Structure and Possible Formation *via* Pentafluorophenylnitrene

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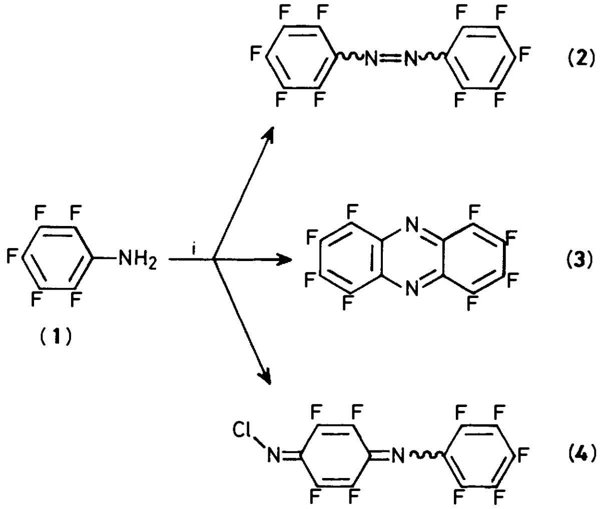
Oxidation of pentafluoroaniline by aqueous sodium hypochlorite under phase-transfer conditions gave decafluoroazobenzene (**2**), octafluorophenazine (**3**), and the dark red *N*-chloro-*N'*-(pentafluorophenyl)-2,3,5,6-tetrafluorobenzo-1,4-quinone di-imine (**4**) as a mixture of *Z*- and *E*-isomers. *X*-Ray diffraction studies revealed that this chloro imine gives crystals containing both isomers, the structures of which have been solved. Singlet pentafluorophenylnitrene is proposed to be an intermediate in the oxidation reaction whereby compounds (**2**), (**3**), and (**4**) are formed following nucleophilic attack by pentafluoroaniline on the nitrogen atom, and the *ortho*- and *para*-positions respectively. A convenient, albeit not high yielding, procedure for the preparation of decafluoroazobenzene is described.

Decafluoroazobenzene (**2**) was required by us as a precursor of its hydroxylated derivatives that we wished to evaluate as inhibitors of steroid hormone biosynthesis. It has been prepared by the oxidation of pentafluoroaniline by Burdon *et al.* with aqueous sodium hypochlorite[1] (25% yield), and by Birchall *et al.* with bleaching powder in tetrachloromethane[2] (51% yield). In our hands, the application of the latter method led to the requirement for a chromatographic purification of the product. In an attempt to find a more convenient procedure for preparing the multigram quantities of decafluoroazobenzene that we required for our studies, we chose to invesigate the oxidation with sodium hypochlorite under conditions of phase-transfer catalysis. We report that by such a procedure, decafluoroazobenzene is indeed formed readily, but the moderate yield obtained is accounted for by the abundant formation of octafluorophenazine and a hitherto undescribed benzoquinone di-imine.



Scheme 1. *Reagents:* i, NaOCl(aq), CH_2Cl_2 or EtOAc, $Bu_4N^+HSO_4^-$.

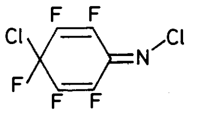
Results and Discussion

Oxidation of Pentafluoroaniline.—The oxidation of pentafluoroaniline by aqueous sodium hypochlorite is slow and complicated by the poor solubility of the pentafluoroaniline and insolubility of the products in the reaction mixture. Addition of an organic solvent immiscible with the aqueous phase (*e.g.* dichloromethane) slows the reaction further, presumably since solubilisation of pentafluoroaniline in the aqueous phase is inhibited. However, the addition of tetrabutylammonium hydrogen sulphate strongly catalysed the oxidation. Products obtained (see Scheme 1) were, in order of increasing polarity on silica gel t.l.c., (*i*) the desired decafluoroazobenzene as a *ca.* 10:1 mixture of geometric isomers, (*ii*) a deep-red solid, and (*iii*) octafluorophenazine.

Elemental analysis and mass spectrometry revealed the molecular formula $C_{12}ClF_9N_2$ for the deep-red solid. Fluorine-19 n.m.r. spectroscopy (Figure 1) showed that the product consisted of a 3:2 ratio of two similar components. Each retained a pentafluorophenyl ring but the remaining fluorine resonances to higher frequency were all non-equivalent, and not borne on an aromatic ring since no fluorine–fluorine coupling of >9 Hz was present. Connectivities between the fluorine atoms were established from a COSY-90 experiment (Figure 1) which revealed in each component a coupling from the *ortho*-fluorine atoms of the pentafluorophenyl ring to one of the remaining fluorine atoms. Structural elucidation of the product as the chloro imine (**4**) was however made from a single crystal *X*-ray diffraction study (see below).

Relationship of (**4**) *to Known Compounds.*—Although the chloro imine (**4**) has not been described previously, stable fluorinated chloro imines have been reported including compound (**5**) which is obtained by iodine-induced rearrangement of *N,N*-dichloropentafluoroaniline (**6**),[3] and the (*Z*) and (*E*)-benzoquinone di-imines (**7**) and (**8**) which are obtained by oxidation of tetrafluoro-*p*-phenylenediamine with *t*-butyl hypochlorite.[4] In the ^{19}F n.m.r. spectra of these latter compounds, a greater spread of ^{19}F chemical shifts is observed in the *Z*-isomer (**7**) than in the *E*-isomer (**8**). By analogy we can tentatively assign the major isomer obtained of the chloro imine (**4**) as *Z*. Interestingly, the isomer ratio obtained in the preparation of (**7**) and (**8**) of 3:2 is identical with that obtained by us for the chloro imine (**4**).

Crystal Structure of (**4**).—The crystal was formed in a space



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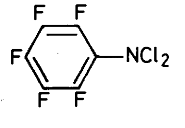

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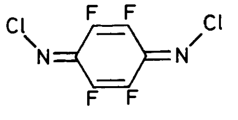

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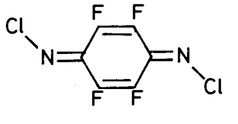


(8)

group containing both *Z*- and *E*-geometric isomers, designated A and B, in an equimolar ratio. Structural representations of these isomers are given in Figure 2. Isomer A has the C(8)–C(3)–N(2)–Cl(1) torsion angle at −179(2)°. Bond distances and angles for the two molecules are given in Table 2. Apart from the orientation of the chloro imine function, there are few differences of significance in the geometry of the two molecules, and these are most probably accounted for by the low ratio of parameters to observations in the least-squares, as well as by the extensive crystal decay. A comparison of the C(3)–N(2) exocyclic bond length and angles around C(3) and N(2) with those reported for the *N*-chloro imine rearrangement product (**5**) of *N*,*N*-dichloropentafluoroaniline from a gas-phase electron-diffraction study,[5] shows significant differences. The equivalent C–N bond length in the latter is 1.224(10) Å which is shorter than the C(3)–N(2) distance of 1.345(25) Å in compound (**4**). This difference indicates that the benzoquinone di-imine ring system in (**4**) is comparatively more delocalised than that in (**5**) and may possess some degree of aromatic character. Nevertheless, the trends in bond distances in Table 2 concur well with the assignment of the compound as a

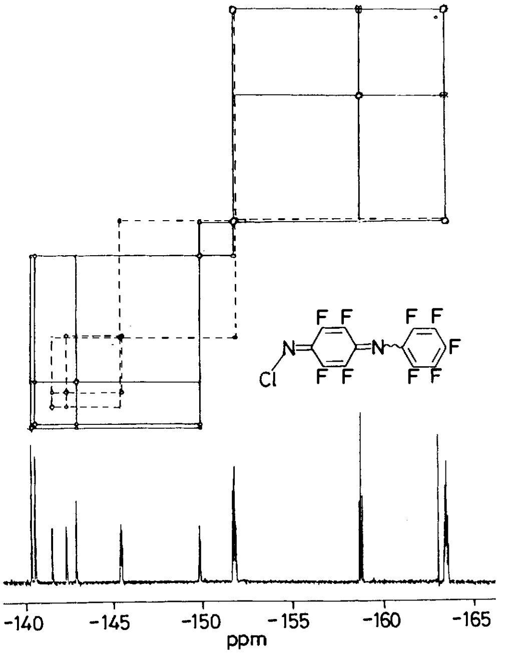


Figure 1. ^{19}F N.m.r. spectrum (235 MHz in $CDCl_3$) of a mixture of *Z*- and *E*-isomers of the chloro imine (**4**). Inter-relationships between fluorine atoms are revealed by the 2D COSY-90 experiment (above).

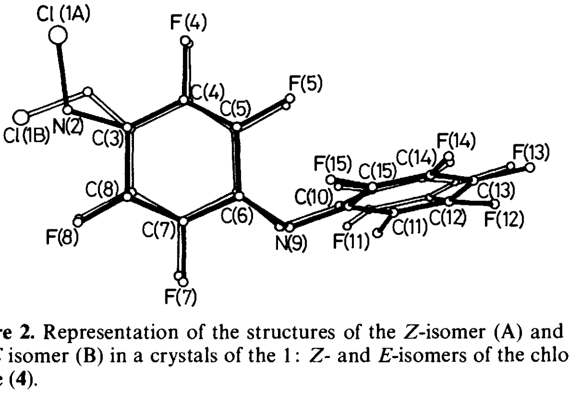


Figure 2. Representation of the structures of the *Z*-isomer (A) and of the *E* isomer (B) in a crystals of the 1 : *Z*- and *E*-isomers of the chloro imine (**4**).

Table 1. Positional parameters and their estimated standard deviations.

Atom	*x*	*y*	*z*
Molecule A			
Cl(1A)	1.131 6(4)	0.838 1(5)	0.594 9(4)
N(2A)	1.025(1)	0.827(1)	0.748(1)
C(3A)	0.898(2)	0.808(1)	0.783(1)
C(4A)	0.823(2)	0.803(1)	0.714(1)
F(4A)	0.889 0(8)	0.814 6(9)	0.592 6(6)
C(5A)	0.694(2)	0.780(1)	0.773(1)
F(5A)	0.630 7(8)	0.773 3(9)	0.709 0(6)
C(6A)	0.612(1)	0.766(1)	0.911(1)
C(7A)	0.684(2)	0.777(1)	0.974(1)
F(7A)	0.616 3(8)	0.768 2(9)	1.097 5(6)
C(8A)	0.816(2)	0.801(2)	0.919(1)
F(8A)	0.877 7(8)	0.812(1)	0.981 9(7)
N(9A)	0.489(1)	0.739(1)	0.954(1)
C(10A)	0.396(1)	0.726(1)	1.085(1)
C(11A)	0.355(1)	0.607(1)	1.162(1)
F(11A)	0.406(1)	0.502 7(9)	1.124 8(7)
C(12A)	0.253(2)	0.580(1)	1.290(1)
F(12A)	0.218(1)	0.461(1)	1.361 8(8)
C(13A)	0.198(1)	0.680(1)	1.328(1)
F(13A)	0.108 8(9)	0.658(1)	1.449 5(7)
C(14A)	0.239(2)	0.800(2)	1.253(1)
F(14A)	0.184(1)	0.899 1(9)	1.291 6(8)
C(15A)	0.335(2)	0.818(1)	1.131(1)
F(15A)	0.375(1)	0.939 4(9)	1.054 1(8)
Molecule B			
Cl(1B)	1.001 7(6)	0.497 6(5)	0.803 8(4)
N(2B)	0.873(1)	0.493(1)	0.949(1)
C(3B)	0.823(2)	0.376(1)	1.025(1)
C(4B)	0.850(1)	0.257(1)	1.014(1)
F(4B)	0.940 2(8)	0.243 4(9)	0.901 7(6)
C(5B)	0.792(2)	0.155(1)	1.102(1)
F(5B)	0.819 0(9)	0.043 6(9)	1.085 5(7)
C(6B)	0.686(1)	0.160(1)	1.231(1)
C(7B)	0.658(1)	0.279(1)	1.236(1)
F(7B)	0.560 4(9)	0.290(1)	1.348 4(7)
C(8B)	0.715(2)	0.388(2)	1.148(1)
F(8B)	0.682(1)	0.495 7(9)	1.161 8(8)
N(9B)	0.621(1)	0.064(1)	1.325(1)
C(10B)	0.647(1)	−0.059(1)	1.330(1)
C(11B)	0.766(1)	−0.142(1)	1.342(1)
F(11B)	0.868 4(8)	−0.084 6(9)	1.323 7(8)
C(12B)	0.799(2)	−0.266(1)	1.365(1)
F(12B)	0.893 8(9)	−0.335 4(9)	1.373 4(7)
C(13B)	0.670(2)	−0.325(1)	1.380(1)
F(13B)	0.693(1)	−0.450(1)	1.403 8(8)
C(14B)	0.560(2)	−0.246(2)	1.373(1)
F(14B)	0.463(1)	−0.314(1)	1.386 5(8)
C(15B)	0.543(2)	−0.126(1)	1.349(1)
F(15B)	0.428 6(9)	−0.063(1)	1.347 8(8)

Table 2. Bond distances Å and bond angles°.

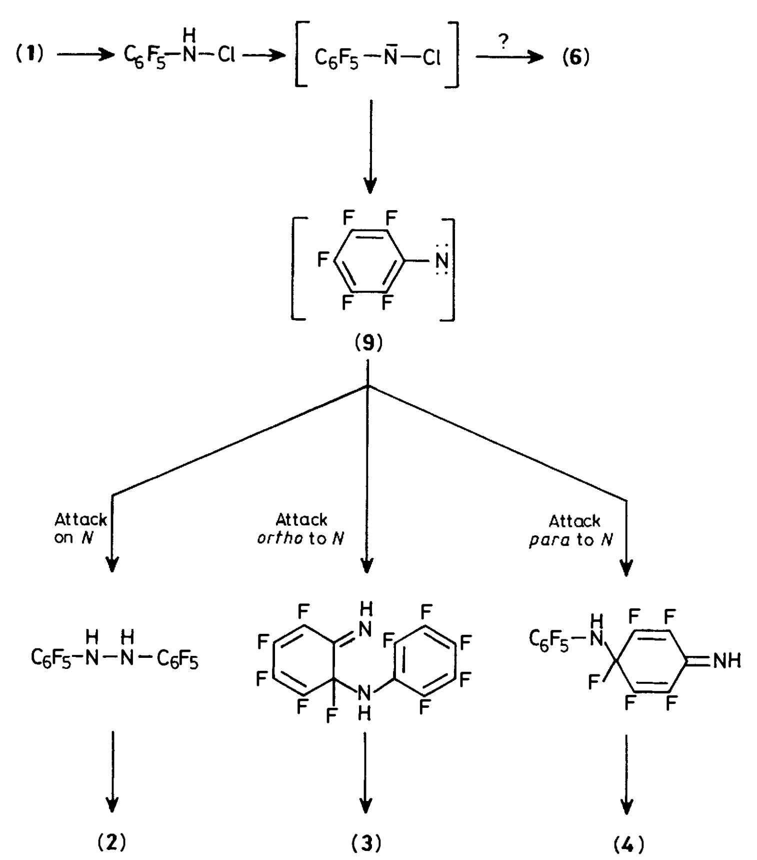
	Molecule A	Molecule B
Bond distances		
Cl(1)–N(2)	1.699(12)	1.718(12)
N(2)–C(3)	1.32(2)	1.37(2)
C(3)–C(4)	1.46(3)	1.51(2)
C(3)–C(8)	1.50(2)	1.39(2)
C(4)–F(4)	1.32(2)	1.27(2)
C(4)–C(5)	1.32(2)	1.35(2)
C(5)–F(5)	1.31(2)	1.364(15)
C(5)–C(6)	1.50(2)	1.36(2)
C(6)–C(7)	1.40(3)	1.52(2)
C(6)–N(9)	1.29(2)	1.295(15)
C(7)–F(7)	1.35(2)	1.33(2)
C(7)–C(8)	1.35(2)	1.29(2)
C(8)–F(8)	1.31(3)	1.349(14)
N(9)–C(10)	1.46(2)	1.36(2)
C(10)–C(11)	1.36(2)	1.44(2)
C(10)–C(15)	1.31(2)	1.43(3)
C(11)–F(11)	1.38(2)	1.35(2)
C(11)–C(12)	1.43(2)	1.32(2)
C(12)–F(12)	1.33(2)	1.34(2)
C(12)–C(13)	1.33(2)	1.44(3)
C(13)–F(13)	1.342(13)	1.33(2)
C(13)–C(14)	1.37(2)	1.34(2)
C(14)–F(14)	1.33(2)	1.40(3)
C(14)–C(15)	1.37(2)	1.28(2)
C(15)–F(15)	1.38(2)	1.29(2)
Bond angles		
Cl(1)–N(2)–C(3)	116(1)	114(1)
N(2)–C(3)–C(4)	134(1)	107(2)
N(2)–C(3)–C(8)	111(2)	136(1)
C(4)–C(3)–C(8)	115(1)	117(1)
C(3)–C(4)–F(4)	118(1)	120(1)
C(3)–C(4)–C(5)	122(1)	115(1)
F(4)–C(4)–C(5)	120(2)	125(1)
C(4)–C(5)–F(5)	120(1)	115(1)
C(4)–C(5)–C(6)	123(2)	130(1)
F(5)–C(5)–C(6)	117(1)	116(1)
C(5)–C(6)–C(7)	114(1)	113(1)
C(5)–C(6)–N(9)	115(2)	122(1)
C(7)–C(6)–N(9)	131(1)	125(1)
C(6)–C(7)–F(7)	118(1)	117(1)
C(6)–C(7)–C(6)	125(1)	120(2)
F(7)–C(7)–C(8)	117(2)	123(1)
C(3)–C(8)–C(7)	120(2)	125(1)
C(3)–C(8)–F(8)	118(1)	119(1)
C(7)–C(8)–F(8)	123(1)	116(1)
C(6)–N(9)–C(10)	121(2)	126(1)
N(9)–C(10)–C(11)	116(1)	126(1)
N(9)–C(10)–C(15)	127(1)	120(1)
C(11)–C(10)–C(15)	117(1)	113(1)
C(10)–C(11)–F(11)	123(1)	116(1)
C(10)–C(11)–C(12)	123(2)	124(2)
F(11)–C(11)–C(12)	114(1)	120(1)
C(11)–C(12)–F(12)	120(2)	120(2)
C(11)–C(12)–C(13)	116(1)	120(2)
F(12)–C(12)–C(13)	124(1)	120(1)
C(12)–C(13)–F(13)	118(1)	115(1)
C(12)–C(13)–C(14)	123(1)	115(2)
F(13)–C(13)–C(14)	119(2)	130(2)
C(13)–C(14)–F(14)	122(1)	109(2)
C(13)–C(14)–C(15)	117(2)	128(2)
F(14)–C(14)–C(15)	120(1)	123(2)
C(10)–C(15)–C(14)	125(1)	121(2)
C(10)–C(15)–F(15)	118(1)	119(1)
C(14)–C(15)–F(15)	118(2)	121(2)

benzoquinone di-imine with a non-delocalised ring system and alternating single and double bonds. Both the quinonoid and perfluorophenyl rings are planar in both molecules within experimental error. The dihedral angles between the rings are 74(2)° in molecule A and 67(2)° in molecule B, indicating some slight flexibility about the linkage between the rings. These values are some 20° greater than have been found for the situation where two naphthalene molecules and a quinone ring are linked by imines.[6] Here, the values of the dihedral angles are 45 and 53°. The increased values in the present compound are most probably due to the influence of the fluorine atoms, with their slightly greater van der Waals radii compared with hydrogen atoms.

Mechanistic Considerations.—The formation of the products observed in the oxidation of pentafluoroaniline can be readily explained by invoking singlet pentafluorophenylnitrene (**9**) as a common intermediate (Scheme 2). This nitrene would form from pentafluoroaniline by chlorination of the nitrogen atom followed by base-induced α-elimination of the elements of hydrogen chloride. Singlet pentafluorophenylnitrene is anticipated to be an ambident electrophile since the electron-deficiency of the nitrogen can be neutralised by attack of a nucleophile not only on nitrogen but also on the *ortho*- or *para*-position of the aromatic ring. Nucleophilic attack by remaining pentafluoroaniline on nitrogen would give decafluorohydrazobenzene which would further oxidise to form decafluoroazobenzene. Consistent with this mechanism is the observation that decafluorohydrazobenzene, independently prepared by reduction of decafluorazobenzene with zinc,[2] reverts to decafluoroazobenzene under our oxidation conditions. Attack on the *ortho*-carbon atom of the nitrene, elimination of the elements of hydrogen fluoride (HF), electrocyclic ring closure, and a further elimination of HF would give octafluorophenazine. Attack on the *para*-position followed by elimination of HF and chlorination of the imine nitrogen atom would lead to the observed chloro imine (**4**). Consistent with the proposed intermediacy of pentafluorophenylnitrene in our reaction is the reported formation of both decafluoroazobenzene and octafluorophenazine in the thermal decomposition of azidopentafluorobenzene in the presence of pentafluoroaniline where singlet pentafluorophenylnitrene is considered to be an intermediate.[7]

A second possibility for the formation of the chloro imine is *via N,N*-dichloropentafluoroaniline (**6**) which is the product when pentafluoroaniline is oxidised by t-butyl hypochlorite.[3] The chloro imine (**4**) could be derived by nucleophilic attack on (**6**) by pentafluoroaniline *para* to the dichloroamino substituent. This substituent has been shown, by analysis of ^{19}F n.m.r. spectra[8] to be about as electron-withdrawing as a nitrile function and we have shown that pentafluorobenzonitrile readily undergoes displacement of the *para*-fluorine under phase-transfer conditions.[9] Evidence against the intermediacy of (**6**) in general is that neither it nor its rearrangement product was observed in the product mixture. Additionally, compound (**6**) is in too high an oxidation state to lead to the formation of octafluorophenazine and would not be expected to be a precursor of decafluoroazobenzene. We cannot exclude the possibility that the effective electrophile is the arylnitrenium radical ($ArNH^{\bullet}$) formed by way of hydrogen-atom transfer from pentafluoroaniline to the electron-deficient nitrene. However, it is noteworthy that addition of the radical scavenger 2,6-di-t-butyl-4-methylphenol had no influence on the oxidation reaction. Whatever the electrophilic species involved in the oxidation, the presence of products obtained by attack *ortho* and *para* to the nitrogen atom is in contrast with pentafluoroaniline itself which undergoes attack by nucleophiles *meta* to the nitrogen atom.[10]

We have investigated the product compositions obtained in the preparations of decafluoroazobenzene from pentafluoroaniline by the reported methods[1,2] and have observed the by-



Scheme 2.

products (**3**) and (**4**) in both cases. Our observation of octafluorophenazine from the oxidation of pentafluoroaniline with calcium hypochlorite in tetrachloromethane is in contrast with the results of Birchall *et al.* who did not observe this product by this method, but did observe it from the oxidation of pentafluoroaniline with lead tetra-acetate. Our results indicate that all of the methods give rise to decafluoroazobenzene by the same mechanism.

Procedure for the Preparation of Decafluoroazobenzene.—In keeping with observations of Lee and Freedman[11] who have made a detailed study of phase-transfer catalysed oxidations by hypochlorite, the reaction rate for the oxidation of pentafluoroaniline was increased when ethyl acetate was used in place of dichloromethane as the organic phase. There was also some improvement in the yield of decafluoroazobenzene when using this solvent. In a convenient procedure for the preparation of decafluoroazobenzene amenable to scale-up, the organic layer from the phase-transfer-catalysed reaction using ethyl acetate was concentrated and the decafluoroazobenzene isolated by crystallisation from an ethanol solution of the residue. However, the yield obtained by this procedure (28%) was still not significantly better than that in the procedure of Burdon *et al.*[1] In order for a high yielding overall conversion of pentafluoroaniline to decafluoroazobenzene to be achieved it is advisable to employ a method that avoids perfluorophenylnitrene or equivalent as the electrophile *e.g* by preparing first the *N,N*-dichloro derivative[3] which can undergo reductive nitrogen–nitrogen coupling with selenium.[12]

Experimental

^{19}F N.m.r. spectra were recorded in $CDCl_3$ at 235.3 MHz on a Bruker AC250 spectrometer with 32 K data points over 7042 Hz to give a digital resolution of 0.43 Hz. Chemical shift values are calibrated relative to hexafluorobenzene at δ −163. The COSY-90 spectrum (Figure 1) was acquired to give 1 K and 2 K data points in the two dimensions to give, after symmetrisation, a digital resolution of 13.8 Hz. Mass spectra were recorded on a VG7070H spectrometer with a direct insertion probe and VG2235 data system. M.p.s (uncorrected) were determined on a Kofler hot-stage except for that of octafluorophenazine which was sealed in a capillary and heated by silicone oil bath.

Oxidation of Pentafluoroaniline under Phase-transfer Conditions.—(*a*) *Isolation of* N-*chloro*-N′-(*pentafluorophenyl*)-2,3,5,6-*tetrafluorobenzo*-1,4-*quinone di-imine.* To a stirred solution of pentafluoroaniline (300 mg, 1.64 mmol) in dichloromethane (2 cm^3) containing tetrabutylammonium hydrogen sulphate (90 mg, 0.26 mmol) was added aqueous sodium hypochlorite (5% available chlorine, 2 cm^3, 2.8 mmol). After 3 h at ambient temperature the mixture was partitioned between dichloromethane (50 cm^3) and water (50 cm^3). The organic phase was dried with sodium sulphate and concentrated. The residue was applied to a column of silica gel (Merck art. 15111, 10 g). Elution with light petroleum, b.p. 60–80 °C applied at a positive pressure of 0.5 atm gave decafluoroazobenzene (**2**) as orange crystals comprising a *ca.* 10:1 mixture of *E*- and *Z*-isomers (61 mg, 21%) m.p. 142–143 °C (lit.,[2] 142–143 °C). Elution with light petroleum (b.p. 60–80 °C)–dichloromethane (50:1) gave a mixture of *Z*- and *E*-isomers of *N*-chloro-*N′*-(pentafluorophenyl)-2,3,5,6-tetrafluorobenzo-1,4-quinone di-imine (**4**) as deep red crystals (30 mg, 10%), m.p. 78–80 °C (from cold light petroleum, b.p. 30–40 °C) (Found: C, 37.9; H, 0.16; N, 7.37; Cl, 9.55; F, 44.95. $C_{12}ClF_9N_2$ requires C, 38.1; N, 7.4; Cl, 9.4; F, 45.2%); $\delta_F(CDCl_3)$ (see Figure 1), 3:2 mixture of components; major component: −163.5 (2 F, m, 3- and 5-F of C_6F_5), −158.7 (1 F, t, J 21.2 Hz; 4-F of C_6F_5), −151.7 (2 F, m, 2- and 6-F of C_6F_5), − 149.8 (1 F, m), −142.9 (1 F, ddd, *J* 1.9, 4.3, 6.9 Hz), −140.5 (1 F, t, *J* 7 Hz), and −140.3 (1 F, t, *J* 4 Hz); minor component: −163.4 (2 F, m), −158.7 (1 F, t, *J* 21.2 Hz), −151.8 (2 F, m), −145.4 (1 F, dd, *J* 3.4, 8.8 Hz), −145.4 (1 F, m), −142.3 (1 F, dd, *J* 6.9, 8.8 Hz), and −141.5 (1 F, dd, *J* 1.6, 6.9 Hz); *m/z* 378 and 380 (100 and 36%, $M^{+\cdot}$), 343 (41, $M^+ - Cl$), 324 (5, $M^+ - Cl - F$), 293 (31), 167 (34), 150 (44) and 117 (56). Elution of the column with light petroleum (b.p. 60–80 °C)–dichloromethane (1:1) gave octafluorophenazine (**3**) (34 mg, 13%) as a yellow solid, m.p. 236 °C (lit.,[2] 230–232 °C).

When the reaction was carried out as above but using ethyl acetate instead of dichloromethane and a reaction time of 2 h, the products were: decafluorobenzene (116 mg, 39%), the chloro imine (**4**) (80 mg, 26%), and octafluorophenazine (**3**) (20 mg, 7.5%).

(*b*) *Procedure for the preparation of decafluoroazobenzene.* To a gently stirred solution of pentafluoroaniline (24.5 g, 134 mmol) in ethyl acetate (220 cm^3) cooled by means of a water bath at 18 °C was added a solution of sodium hypochlorite (5% available chlorine; 300 cm^3, 213 mmol) containing tetrabutylammonium hydrogen sulphate (1.0 g, 3 mmol). After 2 h, the aqueous phase was discarded, the deep red organic phase was concentrated and the residue dissolved in ethanol. Cooling gave crystals of decafluoroazobenzene (6.01 g, 28%), m.p. 140–143 °C (lit.,[2] 142–143 °C).

X-*Ray Crystal-structure Determination of the Chloro Imine* (**4**).—*Crystal data*: $C_{12}N_2F_9Cl$, $M = 378.59$. Triclinic, $a = 11.067(2)$, $b = 11.580(3)$, $c = 12.437(3)$ Å, $\alpha = 64.72(2)$, $\beta = 63.47(2)$, $\gamma = 75.05(2)°$, $V = 1\,285.0$ Å^3, space group $P\bar{1}$, $Z = 4$, D_x 1.946 Mg m^{-3}, $\lambda(\text{Cu-}K_\alpha) = 1.5418$ Å, $\mu = 38.07$ cm^{-1}, $F(000) = 736$, $T = 298$ K.

Dark red crystals of compound (**4**) were grown from ethanol. The crystal density was shown to be greater than 1.910 Mg m^{-3} at 20 °C by the flotation method using caesium chloride. A rectangular crystal of dimensions 0.5 × 0.1 × 1.0 mm was used.

Data Collection and Processing.—Cell dimensions were obtained from least-squares refinement of 25θ values measured on an Enraf–Nonius diffractometer; Ni-filtered Cu-K_α radiation was used ($\lambda = 1.5417\,8$ Å). Intensity data were collected with an $\omega/2\theta$ scan technique and a maximum scan time of 100 s per reflection, for $1.5 \leqslant \theta \leqslant 60°$ and $0 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-13 \leqslant l \leqslant 13$, 3445 unique reflections, were measured of which 1382 had $I \geqslant 1.0\sigma(I)$. Two intensity standards were monitored every 1800 s during the data collection, which showed a loss in intensity of 31.3% during a total exposure time of 68.8 h. This was corrected for by means of a linear decay relationship. An empirical absorption correction was applied to the data set.[13]

Structure Analysis and Refinement.—The structure was solved by direct methods with MULTAN82.[14] Positional and anisotropic thermal parameters for Cl, F and N, and positional and isotropic thermal parameters for C atoms were refined on F by full-matrix least-squares methods, for the two molecules in the asymmetric unit. The refinement of carbon atom types with isotropic thermal parameters only was due to the paucity of intensity data. The final *R* was 0.1103 and R_w was 0.0945; a non-Poisson distribution weighting scheme of the form $1/[\sigma^2(F) + (PF)^2]^{\frac{1}{2}}$ was found appropriate with *P* set at 0.040. Scattering factors were taken from ref. 15. Calculations were performed on a VAX 11/750 computer using the SDP system.[16] Final positional and isotropic thermal parameters are given in Table 2 for the two independent molecules in the asymmetric unit. Tables of anisotropic temperature factors are available as supplementary data from the Cambridge Crystallographic Data Centre.*

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References

1 J. Burdon, C. J. Morton, and D. F. Thomas, *J. Chem. Soc.*, 1965, 2621.
2 J. M. Birchall, R. N. Haszeldine, and J. E. G. Kemp, *J. Chem. Soc. C*, 1970, 449.
3 R. E. Banks and T. J. Noakes, *J. Chem. Soc., Perkin Trans. 1*, 1976, 143.
4 R. E. Banks, M. G. Barlow, J. C. Hornby, and T. J. Noakes, *J. Fluorine Chem.*, 1978, **13**, 179.
5 T. J. Noakes, B. Beagley, and A. Foord, *J. Mol. Struct.*, 1976, **35**, 115.
6 Z. P. Povet'eva, K. L. A. Chetkina, and V. V. Nopylov, *Zh. Strukt. Khim.*, 1980, **21**, 118.
7 R. E. Banks and A. Prakash, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1365.
8 R. E. Banks, M. G. Barlow, T. J. Noakes, and M. M. Saleh, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1746.
9 M. Jarman and R. McCague, *J. Chem. Res.* 1985, (*S*) 116; (*M*) 1342.
10 J. G. Allen, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 6329.
11 G. A. Lee and H. H. Freedman, *Isr. J. Chem.*, 1985, **26**, 229.
12 G. N. Dolenko, A. V. Zibarev, S. A. Krupoder, L. N. Mazalov, O. Ch. Poleschuk, G. G. Furin, G. F. Khudorozhko, and G. G. Yakobson, *J. Fluorine Chem.*, 1981, **17**, 1.
13 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
14 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, MULTAN82, A system of Computer Programs for the Automatic Solution of Crystal Structures from *X*-ray Diffraction Data, Universities of York, England, and Louvain, Belgium, 1982.
15 International Tables for *X*-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974 (Present distributor D. Reidel, Dordrecht, The Netherlands).
16 B. A. Frenz, Enraf–Nonius Structure Determination Package. Version 17. College Station, Texas, U.S.A., 1980.

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* *Supplementary data:* see 'Instructions for Authors' (1989), *J. Chem. Soc., Perkin Trans. 2*, January issue.