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N-HALOGENO-COMPOUNDS. PART 9 [1]. AZOXY- AND AZO-ARENES DERIVED FROM 4-(DICHLOROAMINO)TETRAFLUOROPYRIDINE; CRYSTAL STRUCTURE OF trans-2,3,5,6-TETRAFLUORO-4-(2,4,6-TRIMETHYLPHENYL-ONN-AZOXY)PYRIDINE

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SUMMARY

The nitrosoarenes ArNO (Ar = C_6H_5, 2-MeC_6H_4, 2,4,6-$Me_3C_6H_2$ and C_6F_5) have been condensed with 4-(dichloroamino)-tetrafluoropyridine to provide the azoxy-compounds $\mathrm{py_FN{=}\overset{+}{N}(\bar{O})Ar}$ ($\mathrm{py_F}$ = 2,3,5,6-tetrafluoro-4-pyridyl); de-oxygenation of the first three with triphenylphosphine or triethyl phosphite gave the corresponding azo-compounds, and the reverse reaction was achieved in the case of $\mathrm{py_FN{=}NC_6H_2Me_3}$-2,4,6 using peroxytrifluoroacetic acid. Thermolysis of 4-azidotetrafluoropyridine in the presence of pentafluoronitrosobenzene provided the perfluorinated azoxy-compound $\mathrm{py_FN{=}\overset{+}{N}(\bar{O})C_6F_5}$. X-Ray methods have been used to determine the molecular geometry of $\mathrm{py_FN{=}\overset{+}{N}(\bar{O})C_6H_2Me_3}$-2,4,6.

INTRODUCTION

Azoxy-compounds do not feature in the host of functionalized polyfluoropyridines synthesised since pentafluoropyridine was first prepared twentyfive years ago [2]. Thus,

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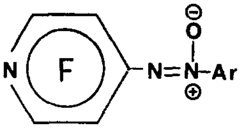
having prepared the first NN-dichloro-derivatives of fluoroaromatic amines [3,4], we decided [5] to subject 4-(dichloroamino)tetrafluoropyridine to the Kovacic condensation reaction, viz. $RNCl_2 + R'NO \longrightarrow RN{=}\overset{+}{N}(\bar{O})R'$ [6]. Hitherto, reports on this synthetic methodology have been restricted to the use of non-aromatic NN-dichloroamines of the hydrocarbon class.

DISCUSSION



(I) Ar = C_6H_5
(II) Ar = $2\text{-}MeC_6H_4$
(III) Ar = $2,4,6\text{-}Me_3C_6H_2$
(IV) Ar = C_6F_5

CuCl-Promoted [6b] reaction of 4-(dichloroamino)tetrafluoropyridine with nitrosobenzene, 2-methylnitrosobenzene, and 2,4,6-trimethylnitrosobenzene in acetonitrile proceeded smoothly to give the expected azoxy-compounds (I), (II) and (III), respectively, in 30-56% yield (after isolation chromatographically). No attempts were made either to optimize conditions or to determine the fate of material unaccounted for. Base-promoted [6a] condensation of the dichloroamine with nitrosobenzene occurred exothermically, giving azoxy-compound (I) in 35% yield (49% based on C_6H_5NO converted) together with 4-aminotetrafluoropyridine and octafluoro-4,4'-azopyridine. In the absence of a promoter, 4-(dichloroamino)tetrafluoropyridine attacked 2-methylnitrosobenzene in acetonitrile to give azoxy-compound (II) in 16% yield, 4-aminotetrafluoropyridine, and much tarry material.

Azoxy-compounds (I)-(III) were characterised by elemental analysis, spectroscopic methods (n.m.r. and mass), and deoxygenation with triethyl phosphite or triphenylphosphine to provide good yields (76-85%) of the unsymmetrical azo-compounds $py_FN{=}NAr$ (py_F = tetrafluoro-4-pyridyl; Ar = C_6H_5, 2-MeC_6H_4, 2,4,6-$Me_3C_6H_2$). As expected, N-oxidation of the 2,4,6-trimethylphenylazo-compound with peroxytrifluoroacetic acid occurred at the site of greatest electron availability, regenerating tetrafluoro-4-(2,4,6-trimethylphenyl-ONN-azoxy)-pyridine (III; 75% yield). That the azoxy-compounds were of the type predicted from their mode of synthesis, *i.e.* (aryl-ONN-azoxy)pyridines [$py_FN{=}\overset{+}{N}(\bar{O})Ar$] not (aryl-NNO-azoxy)-pyridines [$py_F\overset{+}{N}(\bar{O}){=}NAr$], was supported by the mass spectral data: the base peak in each spectrum corresponded to the ion Ar^+, which was assumed to arise from C-N cleavage alpha to the N-oxide group [*cf.* 7]. X-Ray analysis of the 2,4,6-trimethyl-compound (III) (see below) coupled with the invariability of the ^{19}F n.m.r. chemical shift data for the series (I)-(III) clinched the structural assignments. Resonances of 3,5-fluorines in the azoxy-compounds were shifted towards lower field by *ca.* 10 p.p.m. compared with those in the corresponding azo-compounds.

CuCl-Promoted condensation of 4-(dichloroamino)tetrafluoropyridine with pentafluoronitrosobenzene gave, in 21% yield, perfluoro[(phenyl-ONN-azoxy)pyridine](IV), the first mixed azoxyarene of the fluorocarbon class. Structure $py_FN{=}\overset{+}{N}(\bar{O})C_6F_5$ was assigned in preference to $py_F\overset{+}{N}(\bar{O}){=}NC_6F_5$ on the following grounds: (1) method of synthesis; (2) comparison of the compound's ^{19}F n.m.r. chemical shift data with those of the tetrafluoro-4-(aryl-ONN-azoxy)pyridines (I)-(III) [$\delta^{IV}_{3(5)F}$ -64.3, $\delta^{III}_{3(5)F}$ -65.5 p.p.m. (TFA)] and the corresponding diazene $py_FN{=}NC_6F_5$ [$\delta_{3(5)F}$ -73.6 p.p.m.]; (3) mass spectral data, the relative intensities of *m/z* 167 ($C_6F_5{}^+$, 41%) and 150 ($py_F{}^+$, 9%)(base peak *m/z* 181 , $C_6F_5N^+$) allowing [7] the deduction to be made that the bond alpha to the $\overset{+}{N}{-}\bar{O}$ group is attached to the pentafluorophenyl moiety; and (4) the same compound was obtained (21% yield) by heating 4-azidotetrafluoropyridine under nitrogen in the presence of an excess of pentafluoronitrosobenzene, *i.e.* a method which, judging from work on hydrocarbon systems [8], might well be expected to yield only the isomer $py_FN{=}\overset{+}{N}(\bar{O})C_6F_5$.

X-Ray Crystallographic Analysis of 2,3,5,6-Tetrafluoro-4-(2,4,6-trimethylphenyl-ONN-azoxy)pyridine (III)*

Crystal data Compound (III), $C_{14}H_{11}F_4N_3O$, M_r = 313.25, monoclinic, space-group = P2(1)/c, *a* = 7.474(4), *b* = 15.921(4), *c* = 13.036(4) Å, β = 114.22(4)°, V = 1414.66 $Å^3$, Z = 4, D_c = 1.471 Kg dm^{-3}, graphite monochromatised Mo-kα radiation, λ = 0.71069 Å, mμ (Mo-K_α) = 0.144 mm^{-1}.

Structure solution and refinement The structure was solved by direct methods using MULTAN80 [9] and refined by full matrix least-squares using SHELX 76 [10] to a final R of 0.061 for 1635 unique structure factors [F > 3s.d.(F)] [R_w = 0.056, w = 5.73/s.d.$(F)^2$]. All the non-hydrogen vibrational parameters were treated anisotropically while the hydrogen atoms were maintained isotropic.

Fluctuations in the final difference map ≤ 0.33 e $Å^{-3}$. Scattering factors were taken from International Tables for X-ray Crystallography [11]. All computations were carried out on the joint CDC 7600/ICL 1906A system of the University of Manchester Regional Computing Centre. The Cambridge Crystallographic Database was surveyed using the Crystal Structure Search and Retrieval [12] interactive system accessed via the UMIST link to the DEC10 at Edinburgh.

RESULTS AND DISCUSSION

- Final atomic coordinates are given in Table 1, and some details of molecular geometry are presented in Table 2. Figure 1 is a labelled view of the title molecule and Figures 2 and 3 show the molecular packing. Figure 4 is a composite Newman projection of the azoxy region.

The bond lengths and angles show little deviation from expected values. Fluorination has shortened the average pyridyl C-N bond length to 1.298 Å† relative to unsubstituted pyridine; 1.336(3) Å [13], which is in agreement with other fluorinated

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*Lists of structure factors, hydrogen co-ordinates and anisotropic vibrational parameters are available on request (from R.E.B.).

†Note that the C-N bonds are of unequal length owing to a packing effect (see later).

TABLE 1. Fractional atomic coordinates ($x10^4$) and vibrational parameters ($Å \times 10^4$) for heavier atoms

	x	y	z	Ueq[24]
C(1)	5658(6)	3102(2)	3882(3)	521
C(2)	5835(6)	3962(3)	3962(3)	691
C(3)	4634(7)	4409(3)	3004(4)	731
C(4)	3346(6)	4021(3)	2037(4)	744
C(5)	3259(6)	3157(3)	2023(3)	666
C(6)	4430(6)	2659(2)	2945(3)	582
C(7)	7297(9)	4416(4)	4974(5)	911
C(8)	2047(11)	4508(5)	1028(5)	1069
C(9)	4326(10)	1711(4)	2878(6)	967
C(10)	7847(6)	2141(3)	6632(3)	671
C(11)	7743(7)	1274(3)	6660(4)	768
C(12)	8954(9)	854(3)	7607(5)	995
C(13)	10342(7)	2035(4)	8480(4)	859
C(14)	9178(7)	2519(3)	7588(4)	728
N(1)	10250(7)	1235(4)	8501(4)	1043
N(2)	6538(5)	2625(2)	5723(3)	655
N(3)	6923(5)	2596(2)	4862(3)	599
O(1)	8260(5)	2191(2)	4781(3)	1165
F(1)	6478(4)	853(2)	5777(2)	1070
F(2)	8853(5)	24(2)	7644(3)	1532
F(3)	11686(4)	2413(2)	9384(2)	1194
F(4)	9350(4)	3356(2)	7618(2)	1057

TABLE 2. Bond lengths (Å) and angles (°) with esd in brackets

C(2)-C(1)	1.375(5)	C(6)-C(1)	1.383(5)
N(3)-C(1)	1.477(4)	C(3)-C(2)	1.398(5)
C(7)-C(2)	1.508(6)	C(4)-C(3)	1.378(6)
C(5)-C(4)	1.376(6)	C(8)-C(4)	1.493(7)
C(6)-C(5)	1.406(5)	C(9)-C(6)	1.512(6)
C(11)-C(10)	1.383(6)	C(14)-C(10)	1.374(6)
N(2)-C(10)	1.416(5)	C(12)-C(11)	1.369(6)
F(1)-C(11)	1.333(5)	N(1)-C(12)	1.318(6)
F(2)-C(12)	1.326(5)	C(14)-C(13)	1.368(6)
N(1)-C(13)	1.277(6)	F(3)-C(13)	1.338(5)
F(4)-C(14)	1.338(5)	N(3)-N(2)	1.268(4)
O(1)-N(3)	1.230(4)	C(6)-C(1)-C(2)	125.7(4)
N(3)-C(1)-C(2)	118.0(3)	N(3)-C(1)-C(6)	116.3(3)
C(3)-C(2)-C(1)	115.6(4)	C(7)-C(2)-C(1)	123.8(4)
C(7)-C(2)-C(3)	120.4(4)	C(4)-C(3)-C(2)	122.7(4)
C(5)-C(4)-C(3)	118.1(4)	C(8)-C(4)-C(3)	122.1(5)
C(8)-C(4)-C(5)	119.8(5)	C(6)-C(5)-C(4)	122.9(4)
C(5)-C(6)-C(1)	115.0(4)	C(9)-C(6)-C(1)	124.1(4)
C(9)-C(6)-C(5)	121.0(4)	C(14)-C(10)-C(11)	116.1(4)
N(2)-C(10)-C(11)	122.6(4)	N(2)-C(10)-C(14)	121.0(4)
C(12)-C(11)-C(10)	119.2(5)	F(1)-C(11)-C(10)	120.4(4)
F(1)-C(11)-C(12)	120.4(5)	N(1)-C(12)-C(11)	123.1(5)
F(2)-C(12)-C(11)	119.6(6)	F(2)-C(12)-N(1)	117.3(5)
N(1)-C(13)-C(14)	124.0(5)	F(3)-C(13)-C(14)	118.7(6)
F(3)-C(13)-N(1)	117.2(5)	C(13)-C(14)-C(10)	119.7(5)
F(4)-C(14)-C(10)	119.2(4)	F(4)-C(14)-C(13)	121.1(5)
C(13)-N(1)-C(12)	117.8(5)	N(3)-N(2)-C(10)	113.0(3)
N(2)-N(3)-C(1)	116.6(3)	O(1)-N(3)-C(1)	117.7(3)
O(1)-N(3)-N(2)	125.6(3)		

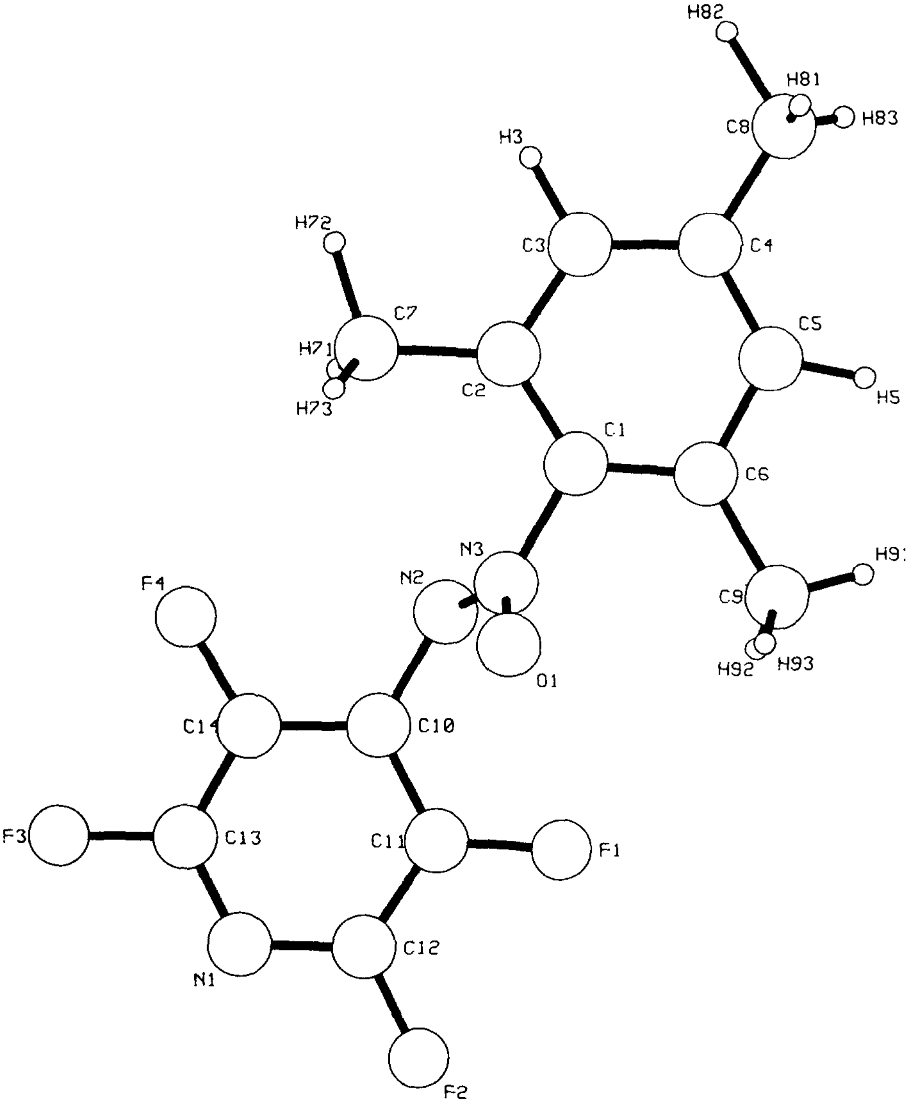

Fig. 1. Labelled molecular stereoformula of *trans*-2,3,5,6-tetrafluoro-(2,4,6-trimethylphenyl-*ONN*-azoxy)pyridine (III) produced using PLUTO [18].

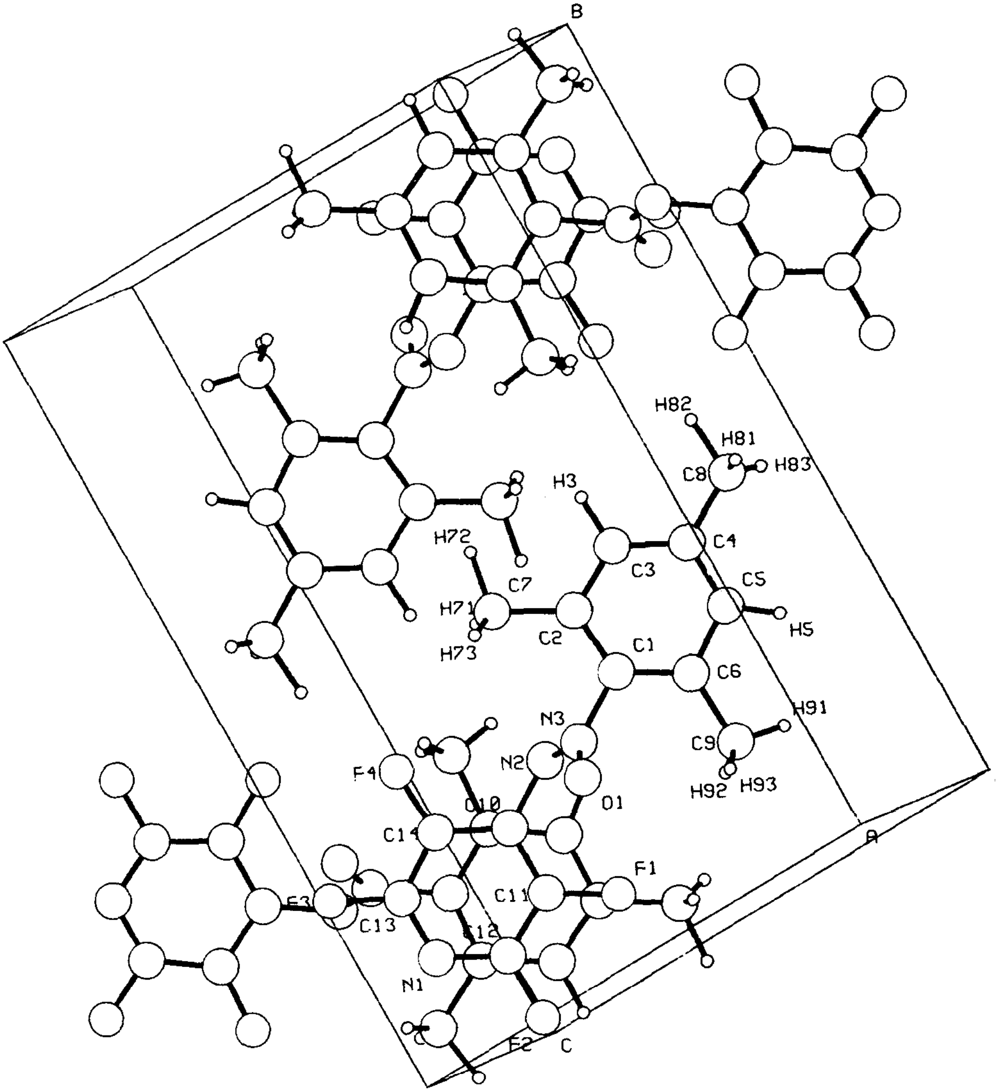

Fig. 2. View of the unit cell showing the overlapping aromatic rings.

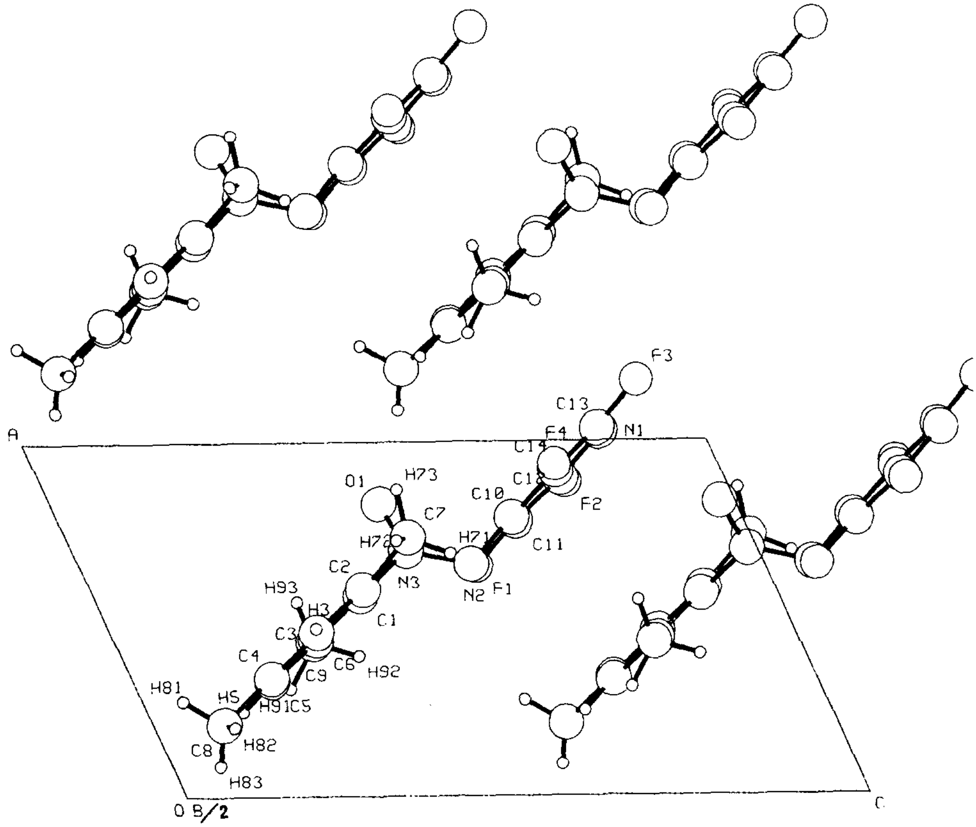

Fig. 3. Cell projection on the <u>ac</u> plane.

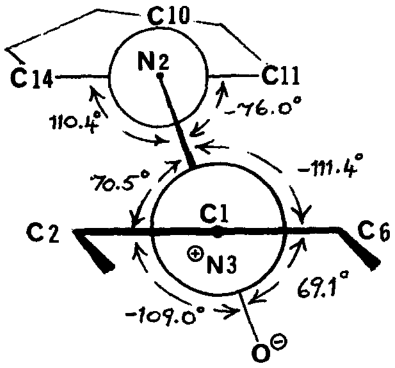

Fig. 4. Composite Newman projection of the azoxy region (e.s.d. 0.8°). Torsion angle C1-N3-N2-C10 = -178.5°.

compounds {1.28(2) Å [14] and 1.302(6) Å [15]}. Several non-planar <u>trans</u>-azoxybenzenes have been studied whose dimensions encompass those of the title molecule (III) [16]. Although the molecule of (III) is not planar, the pyridyl and mesityl groups are almost parallel to one another and to the *b* axis (Figures 3 and 4) so that all the rings within the crystal, including those generated by crystallographic symmetry operations, are approximately parallel. Figures 2 and 3 show how the tetrafluoropyridyl moiety in one molecule overlaps the mesityl group in a *c*-glide generated adjacent molecule to form stacks of π-bonded aromatic rings along the *a* axis at distances approximating the sum of the van der Waals radii [C(2)...C(12) 3.47(1), C(3)...C(12) 3.50(1), C(5)...C(13) 3.44(1), C(6)...C(13) 3.44(1) Å]. The molecules thus form corrugated sheets in the *ac* plane within which there is further interaction due to the close approach of an azoxy oxygen atom to a fluoro-pyridyl ring in an adjacent molecule [O(1)...C(13) 3.00(1) Å, F(3)...O(1) 2.88(1) Å]. The azoxy-oxygen/carbon atom interaction is reminiscent of the weak carbonyl interaction in chloranil and may account for the significant asymmetry about N(1) in the pyridyl ring [N(1)-C(12) 1.318(6), N(1)-C(13) 1.277(6) Å].

EXPERIMENTAL

Spectroscopic Analysis

N.m.r. and mass spectra were obtained with a Perkin-Elmer R32 instrument (^{1}H at 90, ^{19}F at 84.6 MHz; compounds were examined as solutions in $CDCl_3$; ext. TMS or TFA were used as references, and shifts to high field have been designated negative) and a Kratos MS45 spectrometer (ionising voltage 70 eV), respectively.

X-Ray Measurements

The *X*-ray analysis was performed on a 0.3 x 0.3 x 0.2 mm crystal using an Enraf Nonius CAD4 diffractometer. Cell dimensions and crystal orientation were determined from 25 reflexions followed by the measurement of 1975 unique reflexions having $0 \leqq \theta \leqq 25$ °, $0 \leqq \underline{h} \leqq 8$, $0 \leqq \underline{k} \leqq 18$, $-15 \leqq \underline{l} \leqq 15$ using the $\omega/2\theta$ scan mode. Standard reflexion measurements showed the crystal to be stable during data collection. Lorentz and polarization corrections were applied to the data but no absorption correction was made.

Starting Materials

4-(Dichloroamino)tetrafluoropyridine was prepared by chlorination of 4-aminotetrafluoropyridine [3], pentafluoronitrosobenzene [19] and 2,4,6-trimethylnitrosobenzene [20] were obtained by oxidation of the corresponding amino-compounds, and nitrosobenzene and its 2-methyl analogue were made *via* reduction ($Zn-NH_4Cl$ aq.) of the appropriate nitrosoarenes and dichromate oxidation of the hydroxylamines thus produced [21]. 4-Azidotetrafluoropyridine was prepared by nucleophilic azidation of pentafluoropyridine [22].

Reaction of 4-(Dichloroamino)tetrafluoropyridine with Nitrosoarenes

(a) With nitrosobenzene

A. *In the presence of base* - 4-(Dichloroamino)tetrafluoropyridine (5.0 g, 21.3 mmol) was added dropwise to a stirred mixture of nitrosobenzene (2.2 g, 20.6 mmol), benzyltriethylammonium chloride (0.1 g), and petroleum ether (b.p. 60-80 °C); the temperature of the mixture was then raised to 35 °C before 50% aqueous potassium hydroxide solution (6.5 cm^3) was added dropwise during 30 minutes, causing an exothermic reaction to take place. The dark brown product was poured on to crushed ice (*ca*. 30 g) and the aqueous mixture was neutralized (H_2SO_4 aq.) before being extracted with diethyl ether (3 x 30 cm^3). The extracts were combined, washed (H_2O), dried ($MgSO_4$) and evaporated to provide a brown solid that was worked-up by dry-column flash chromatography [silica; petroleum ether (b.p. 60-80 °C)-dichloromethane] to provide nitrosobenzene (0.6 g, 5.6 mmol, 27% recovery), 2,3,5,6-tetrafluoro-4-(phenyl-*ONN*-azoxy)pyridine (2.0 g, 7.4 mmol, 49% based on C_6H_5NO consumed) (I; nc) [Found: C, 48.9; H, 1.5;

N, 15.2%; M (mass spec.), 271. $C_{11}H_5F_4N_3O$ requires C, 48.7; H, 1.8; N, 15.5%; M, 271), m.p. 74-75 °C, δ_F -11.1 (m; 2-,6-F) and -65.1 (m; 3-,5-F) p.p.m., δ_H 7.6 (m; 3-,4-,5-H) and 8.0 (m; 2-, 6-H) p.p.m., m/z 271 ($M^{+\cdot}$, 19%), 231 (77%), 105 ($C_6H_5N_2^+$, 31%), 91 ($C_6H_5N^+$, 71%), 77 ($C_6H_5^+$, 100%), 4-aminotetrafluoropyridine (0.35 g, 2.1 mmol, 10%), and octafluoro-4,4'-azopyridine (0.8 g, 2.4 mmol, 22%). The first, third and fourth products possessed correct melting points, and their i.r. spectra were identical with those of authentic samples.

B. In the presence of cuprous chloride - 4-(Dichloroamino)-tetrafluoropyridine (2.0 g, 8.5 mmol) was added dropwise during 15 minutes to a stirred mixture of nitrosobenzene (0.9 g, 8.4 mmol), copper(I) chloride, and acetonitrile (50 cm^3); after 12 hours had elapsed (stirring was continued), the reaction mixture was poured into water (500 cm^3) and organic material was extracted with diethyl ether (4 x 50 cm^3). The ether extract was dried ($MgSO_4$) and evaporated, leaving a solid residue (1.4 g) which was chromatographed [silica; petroleum ether (b.p. 60-80 °C)-dichloromethane] to provide tetrafluoro-4(phenyl-ONN-azoxy)pyridine (0.9 g, 3.3 mmol, 39.5%), m.p. 74-76 °C, with the same spectroscopic properties (i.r., n.m.r.) as the material obtained by method A.

(b) With 2-methylnitrosobenzene

Treatment of 2-methylnitrosobenzene (5.0 g, 41.3 mmol) in acetonitrile (100 cm^3) with 4-(dichloroamino)tetrafluoropyridine (9.5 g, 40.4 mmol) in the presence of copper(I) chloride (5.0 g), as in experiment (a)B above followed by the same work-up procedure, provided 2,3,5,6-tetrafluoro-4-(2-methylphenyl-ONN-azoxy)pyridine (II; nc)(3.5 g, 12.3 mmol, 30%) [Found: C, 50.8; H 2.3; F, 26.4; N, 14.7%; M (mass spec.), 285. $C_{12}H_7F_4N_3O$ requires C, 50.5; H, 2.5; F, 26.7; N, 14.7%; M, 285], a white solid, m.p. 76-77 °C (pale yellow when liquified), δ_F -11.0 (m; 2-,6-F) and -65.5 (m; 3-,5-F) p.p.m., δ_H 2.53 (s; CH_3), 7.44 (m; 3-,4-,5-H), and 7.84 (m; 6-H) p.p.m., m/z 285 ($M^{+\cdot}$, 14%), 268 ($M^{+\cdot}$ -HO·, 15%), 119 ($C_7H_7N_2^+$, 36%), 105 ($C_6H_5N_2^+$, 33%), 104 (40%), 91 ($C_7H_7^+$, 100%).

When the reaction was repeated (by A.C. ALTY) using 1.0 g (8.3 mmol) of 2-methylnitrosobenzene in 50 cm^3 of acetonitrile and 1.9 g (8.1 mmol) of 4-(dichloroamino)tetrafluoropyridine but no copper(I) chloride, an exothermic reaction occurred (the temperature rose from 24 to 29°C during 5 minutes). After the brownish-orange reaction mixture had been stirred for 20 hours at ambient temperature, it was worked-up as in experiment (*a*)B except that dichloromethane was used as extractant, to provide tetrafluoro-4-(2-methylphenyl-*ONN*-azoxy)pyridine (II) (0.4 g, 1.4 mmol, 16%), m.p. 75-77 °C, 4-aminotetrfluoropyridine (0.2 g), and a brown tar (*ca*. 1 g).

(c) With 2,4,6-trimethylnitrosobenzene

Experiment (*b*) above was repeated, using 2,4,6-trimethylnitrosobenzene (1.3 g, 8.7 mmol), 4-(dichloroamino)tetrafluoropyridine (2.0 g, 8.5 mmol), copper(I) chloride (1.7 g), and acetonitrile (50 cm^3). Work-up, as before, provided 2,3,5,6-tetrafluoro-4-(2,4,6-trimethylphenyl-*ONN*-azoxy)pyridine (III; nc) (1.5 g, 4.8 mmol, 56%) [Found: C, 53.7; H, 2.2; F, 24.4; N, 13.4%; *M* (mass spec.), 313. $C_{14}H_{11}F_4N_3O$ requires C, 53.7; H, 3.5; F, 24.3; N, 13.4%; *M*, 313], a white solid, m.p. 118-119 °C (pale yellow when liquefied), δ_F -11.0 (m; 2-,6-F) and -65.5 (m; 3-,5-F) p.p.m., δ_H 2.15 (s; 2-,4-,6-CH_3) and 6.80 (s; 3-,5-H) p.p.m. (rel. int. 9:2), *m/z* 313 ($M^{+\cdot}$, 14%), 296 ($M^{+\cdot}$-HO·, 67%), 148 (82%), 119 ($C_9H_{11}^+$, 100%).

(d) With pentafluoronitrosobenzene

Experiment (*b*) was repeated, using pentafluoronitrosobenzene (5.0 g, 25.4 mmol), 4-(dichloroamino)tetrafluoropyridine (6.0 g, 25.5 mmol), copper(I) chloride (5.0 g) and acetonitrile (150 cm^3), to provide 2,3,5,6-tetrafluoro-4-(pentafluorophenyl-*ONN*-azoxy)pyridine (IV; nc) (1.9 g, 5.3 mmol, 21%), which was recrystallised from ethanol to provide a pure sample [Found: C, 36.3; F, 47.4; N, 11.4%; *M* (mass spec.), 361. $C_{11}F_9N_3O$ requires C, 36.6; F, 47.4; N, 11.6%; *M*, 361], a white solid, m.p. 46-47 °C (pale yellow when liquefied), δ_F -10.1 (m, AA'XX' type; 2-,6-F), -64.3 (m, AA'XX' type; 3-,5-F), -67.9 (m; 2'-,6'-F), -68.9 (tt, *J* 21 and 4 Hz; 4'-F), and -79.5 (m; 3'-,5'-F) p.p.m. (rel. int. 2:2:2:1:2), *m/z* 361 ($M^{+\cdot}$, 17%), 195 ($C_6F_5N_2^+$, 20%), 181 ($C_6F_5N^+$, 100%), 167 ($C_6F_5^+$, 41%), 150 ($C_5F_4N^+$, 9%).

Deoxygenation of Tetrafluoro-4-(aryl-ONN-azoxy)pyridine

(a) Tetrafluoro-4-(phenyl-ONN-azoxy)pyridine

A mixture of the azoxy-compound (0.5 g, 1.8 mmol) and triethyl phosphite (0.35 g, 2.1 mmol) was heated at 160-170 °C (oil bath) under nitrogen for 2 h. The red product was evaporated to dryness, in vacuo, and the residue was chromatographed [dry-column flash method; silica eluted with light petroleum (b.p. 40-60 °C)/dichloromethane] to provide orange 2,3,5,6-tetrafluoro-4-(phenylazo)pyridine (nc) (0.35 g, 1.38 mmol, 76%) [Found: C, 50.0; H, 1.4; N, 15.9%; M, 255. $C_{11}H_5F_4N_3$ requires C, 51.8; H, 2.0; N, 16.5; M, 255], m.p. 89-91 °C, δ_F -10.1 (m; 2-,6-F) and -74.5 (m; 3-,5-F) p.p.m., δ_H 7.62 (m; 3-,4-,5-H) and 8.00 (m; 2-,6-H) p.p.m., m/z 255 ($M^{+\cdot}$, 21%), 105 ($C_6H_5N_2^+$, 21%), and 77 ($C_6H_5^+$, 100%).

(b) Tetrafluoro-4-(2-methylphenyl-ONN-azoxy)pyridine

A solution of the azoxy-compound (0.5 g, 1.75 mmol) and triphenylphosphine (0.9 g, 3.4 mmol) in dichloromethane (15 cm^3) was heated under reflux in a nitrogen atomosphere for 2 h (the progress of the reaction was followed by TLC). The red product was evaporated to dryness, in vacuo, and the residue was subjected to dry-column flash chromatography [silica eluted with petroleum ether b.p. 40-60 °C)]; the red fraction collected was recrystallized from petroleum ether to provide 2,3,5,6-tetrafluoro-4-(2-methylphenylazo)pyridine (nc) (0.4 g, 1.5 mmol, 85%), m.p. 60-62 °C, m/z 269 ($M^{+\cdot}$, 19%), 119 ($C_7H_7N_2^+$, 11%), 91 ($C_7H_7^+$, 100%).

(c) Tetrafluoro-4-(2,4,6-trimethylphenyl-ONN-azoxy)pyridine

This azoxy-compound (1.0 g, 3.2 mmol) was deoxygenated with triethyl phosphite (0.6 g, 3.6 mmol) for 2.5 h as described above for its phenylazoxy analogue. Chromatographic work-up of the product followed by a recrystallisation (ethanol) provided the known azo-compound tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine (0.8 g, 2.7 mmol, 84%)(Found: C, 56.7;

H, 3.6; N, 14.3. Calc. for $C_{14}H_{11}F_4N_3$: C, 56.6; H, 3.7; N, 14.1%), m.p. 143-144 °C (lit. [23], 140-143 °C), with correct spectroscopic (i.r., n.m.r., mass) properties.

Oxidation of Tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine

A sample of the azo-compound (1.0 g, 3.4 mmol) was added to a stirred mixture of trifluoroacetic anhydride (15 cm^3), 85% hydrogen peroxide (6 cm^3), and chloroform (100 cm^3) sited behind a blast screen (the reddish colour of the azo-compound changed to lemon yellow almost immediately). The reaction mixture was heated under reflux for 2 h then cooled, washed with water and extracted with diethyl ether to provide tetrafluoro-4-(2,4,6-trimethylphenyl-ONN-azoxy)pyridine (III)(0.8 g 2.6 mmol, 75%), m.p. 118-119 °C (after recrystallisation from ethanol), with a correct i.r. spectrum.

Reaction of 4-Azidotetrafluoropyridine with Pentafluoronitrosobenzene

A mixture of 4-azidotetrafluoropyridine (1.0 g, 5.2 mmol) and pentafluoronitrosobenzene (5.0 g, 25.4 mmol) was heated to *ca*. 170 °C (oil bath) under nitrogen in apparatus sited behind a blast screen. After 6 h, the deep brown reaction mixture was cooled and worked-up chromatographically [flash method; silica eluted with petroleum ether (b.p. 60-80 °C)/dichloromethane] to provide, after a final recrystallization [petroleum ether (b.p. 40-60 °C)] tetrafluoro-4-(pentafluorophenyl-ONN-azoxy)pyridine (IV)(0.4 g, 1.1 mmol, 21%), m.p. 46-47 °C, with the same i.r. spectrum as the material prepared from 4-(dichloroamino)tetrafluoropyridine.

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