

***N*-Fluoro-compounds. Part VI.¹ Preparation and Some Reactions of Perfluoro-*NN'*-difluoropiperazine; Cross-linking of a Nitroso Rubber**

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Perfluoro-*NN'*-difluoropiperazine, prepared by electrochemical fluorination of piperazine, reacts with aqueous potassium iodide to give oxalic acid and with perfluorocyclobutene in the presence of u.v. light to yield perfluoro- (*N*-cyclobutyl-*N'*-fluoropiperazine). Photolysis of the *NN'*-difluoro-compound in silica, either alone or in the presence of oxygen, produces a polymeric wax that yields a nitroxide-containing, purplish-blue liquid when heated and can be used to cross-link elastomeric trifluoronitrosomethane-tetrafluoroethylene-hexafluorobutadiene copolymers.

THE development of a satisfactory cross-linking procedure for the special-purpose, alternating copolymer of trifluoronitrosomethane with tetrafluoroethylene, $[-N(CF_3) \cdot O \cdot CF_2 \cdot CF_2 -]_n$,² known as 'nitroso rubber,' has been thwarted by its chemical inertness.³ Attempts to overcome this handicap by use of a termonomer system to introduce reactive sites have led to the development of 'carboxy nitroso rubber,'^{3,4} a copolymer containing units derived from trifluoronitrosomethane, tetrafluoroethylene, and the nitroso-acid $HO_2C \cdot [CF_2]_3 \cdot NO$; the pendant carboxy-functions provided by the last monomer enable the rubber to be cured by treatment with, for example, chromium trifluoroacetate or the bis-epoxide derived from cyclopentadiene dimer. Following the dis-

covery⁵ that trifluoronitrosomethane copolymerises with perfluorobuta-1,3-diene to yield a nitroso rubber built up from units of the type $-N(CF_3) \cdot O \cdot CF_2 \cdot CF(CF_2) -$ and $-N(CF_3) \cdot O \cdot CF_2 \cdot CF \cdot CF \cdot CF_2 -$, we embarked on a study of the preparation and vulcanisation of unsaturated copolymers based on the $CF_3 \cdot N \cdot O \cdot CF_2 \cdot CF_2 \cdot CF \cdot CF \cdot CF_2$ termonomer system, the ultimate goal being to introduce cross-links of the same chemical type (and therefore stability) as the backbone, *i.e.* to produce a perfect 'nitroso rubber' network.⁶ The object of the work now described was to investigate the synthesis of the potential cross-linking agent perfluoropiperazine-*NN'*-dioxyl (1) from the corresponding bis- (*N*-fluoro)-compound (2).

⁴ N. B. Levine, *Rubber Age (New York)*, 1969, **101**, 45.

¹ Part V, R. E. Banks, A. J. Parker, M. J. Sharp, and G. F. Smith, *J.C.S. Perkin I*, 1972, 5.

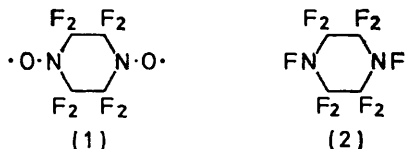
² D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1955, 1881, 2532.

³ For a recent review of nitroso rubbers see M. C. Henry and C. B. Griffis, *Fluorine Chem. Rev.*, 1967, **1**, 1.

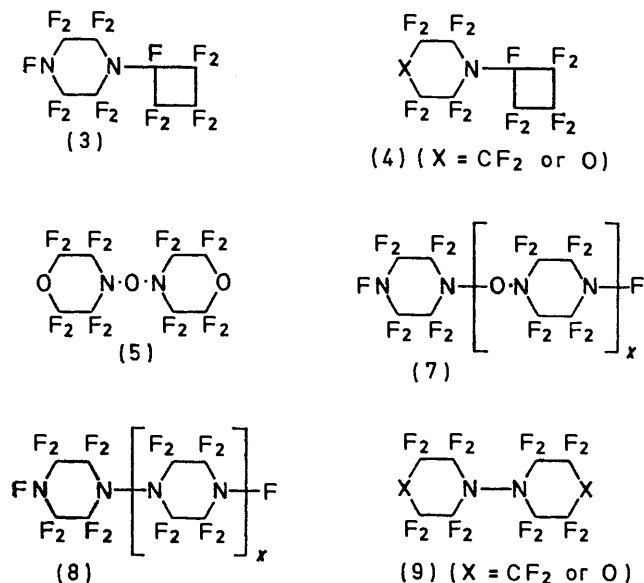
⁵ R. E. Banks, M. G. Barlow, and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 6149; R. E. Banks, R. N. Haszeldine, and V. Matthews, unpublished results.

⁶ R. E. Banks, K. C. Eapen, R. N. Haszeldine, P. Mitra, T. Myerscough and S. Smith, *J.C.S. Chem. Comm.*, 1972, 833.

Synthesis and Properties of Perfluoro-NN'-difluoropiperazine.—Electrochemical fluorination (Simons' process⁷) of piperazine gave a low yield (ca. 8%) of perfluoro-NN'-difluoropiperazine (2), a colourless, dense, volatile



(b.p. 44 °C) liquid with a musty odour. This apparently new perfluorinated heterocycle liberated iodine almost quantitatively from aqueous sodium iodide (diagnostic $>\text{NF}$ test⁸), the ring being degraded to oxalic acid, as expected, and combined photochemically with perfluorocyclobutene to give perfluoro-(*N*-cyclobutyl-*N'*-fluoropiperazine) (3). Once formed, the *N*-cyclobutylpiperazine (3) (b.p. 124 °C) accumulated at the bottom of the vapour-phase reactor, and its conversion into perfluoro-[*NN'*-di(cyclobutyl)piperazine] was not detected.



Formation of (3) can be explained in terms of the free-radical sequence proposed to account for 1 : 1 adduct formation (4) from perfluoro-*N*-fluoropiperazine⁹ or -morpholine¹ and perfluorocyclobutene under similar circumstances. It seemed, therefore, that u.v. irradiation of perfluoro-*NN'*-difluoropiperazine in the presence of oxygen and silica might serve as a route to perfluoropiperazine-*NN'*-dioxy (1), just as similar treatment of perfluoro-*N*-fluoromorpholine leads to perfluoromorpholine-*N*-oxy via the N-O-N compound (5).¹

U.v. irradiation of perfluoro-*NN'*-difluoropiperazine in the presence or absence of oxygen gave silicon tetrafluoride and a white wax, which collected on the silica lamp house of the photochemical reactor. The wax was

apparently insoluble in common hydrocarbon-type solvents and in trichlorofluoromethane, 1,1,2-trichlorotrifluoroethane, trifluoroacetic acid, trifluoroacetic anhydride, and perfluoro-*N*-fluoropiperidine, and could not be milled with Nujol or hexachlorobutadiene. When heated above 223 °C, it changed quickly into a liquid possessing the deep purple colour characteristic of perfluorinated nitroxides; the colour faded rapidly when the liquid was shaken with an excess of toluene (cf. bistrifluoromethyl nitroxide¹⁰ and perfluoropiperidine-*N*-oxyl,⁹ which quickly abstract benzylic hydrogen from toluene to give the corresponding colourless hydroxylamines), but disappeared only slowly (1 week) when the liquid was stored at room temperature in glass. E.s.r. spectroscopy confirmed that the purple liquid contained stable radicals, but the complex spectrum defied analysis owing to lack of symmetry, which may have been caused by the presence of several different species.¹¹ Thermal decomposition of the wax in the presence of a copolymer of trifluoronitrosomethane with tetrafluoroethylene and perfluorobutadiene containing both pendant $-\text{CF}(\text{F})\text{CF}_2$ and backbone $-\text{CF}(\text{F})\text{CF}-$ units⁵ caused the copolymer to become cross-linked, a conversion which can be effected with the bis-nitroxide $\text{CF}_3\cdot\text{N}(\dot{\text{O}})\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{N}(\dot{\text{O}})\cdot\text{CF}_3$ (6)⁶ but not to any marked degree with the mono-nitroxides $\text{CF}_2\cdot\text{CF}_2\cdot\text{O}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{N}\cdot\text{O}\cdot$ and $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot$.

Mass spectrometric examination of the wax revealed that it was macromolecular in nature, low-intensity peaks occurring at *m/e* values approaching 900. The breakdown pattern is consistent with a mixture of two oligomers of type (7) and (8), and the possibility of material composed of the two types of units present in such oligomers cannot be discounted; the formation of type (8) material is analogous to the production of N-N compounds (9) during photolysis of perfluoro-*N*-fluoropiperidine⁹ and -morpholine.¹ At this stage, lack of material, the low yield and intense electrode corrosion problems in the electrochemical fluorination of piperazine at a time when sheet nickel was almost unobtainable, and the successful synthesis and use in polymer cross-linking studies of perfluoro-2,5-diazahexane-2,5-dioxy (6)⁶ led to the abandonment of further structural investigations, including attempts to isolate the bis-nitroxide (1) presumed to be present in the thermolysis product from the polymeric wax.

Cross-linking of a Trifluoronitrosomethane-Tetrafluoroethylene-Hexafluorobuta-1,3-diene Copolymer.—The vulcanisate obtained by heating at 220 °C under pressure a 10 : 1 w/w mixture of a nitroso copolymer of overall composition $[(\text{CF}_3\text{NO})_{1.0}(\text{C}_2\text{F}_4)_{0.7}(\text{C}_4\text{F}_6)_{0.3}]_n$ and the polymeric wax was a tough fawn rubber having the appearance of a common 'elastic band.' Unlike the raw copolymer, this product was insoluble in (but slightly

⁹ R. E. Banks, K. Mullen, and G. E. Williamson, *J. Chem. Soc. (C)*, 1968, 2608.

¹⁰ R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc. (C)*, 1966, 901.

¹¹ A. J. Parker and M. J. Sharp, personal communication.

⁷ For reviews, see J. Burdon and J. C. Tatlow, *Adv. Fluorine Chem.*, 1960, 1, 129; S. Nagase, *Fluorine Chem. Rev.*, 1967, 1, 77.

⁸ R. E. Banks, 'Fluorocarbons and their Derivatives,' Macdonald, London, 1970, 2nd edn., p. 133.

swollen by) 1,1,2-trichlorotrifluoroethane, perfluoro-n-pentane, or perfluorotributylamine at 20–40 °C. When subjected to thermogravimetric analysis (nitrogen atmosphere; heating rate 15 °C per min) both the raw and vulcanised copolymer began to lose weight just below 200 °C, but whereas the former had completely disappeared by the time the temperature reached 400 °C, the vulcanised material had suffered only *ca.* 25% weight loss. The cross-linking mechanism is envisaged as a process involving radical formation through thermolysis of the waxy agent to yield diradicals *via* N–O bond homolysis, and subsequent involvement of the unsaturated sites along the copolymer backbone.

EXPERIMENTAL

I.r., ¹⁹F n.m.r., and mass spectra were obtained with a Perkin-Elmer spectrophotometer model 257, a Perkin-Elmer R10 instrument (56.46 MHz; positive chemical shift values are to high field of the reference signal), and an A.E.I. MS/2H spectrometer, respectively. Thermogravimetric analyses were performed with a Du Pont analyser model 900/950.

Preparation of Perfluoro-NN'-difluoropiperazine.—A solution of piperazine (120 g) in anhydrous hydrogen fluoride (*ca.* 4 l) was subjected to electrochemical fluorination at 25 A and 6 V (current density *ca.* 0.025 A cm⁻²) in a cell of the type described previously;¹² after an induction period of 48 h, product began to collect in the cold trap, which was kept at –78 °C. The fluorination was run continuously, piperazine (total 840 g) and hydrogen fluoride being replenished during a period of 4 months, during which time the nickel anodes became so corroded that they had to be thrown away. The product (412 g) gave eight peaks on a gas-liquid chromatogram (10 m silicone MS550 oil–Celite; 20 °C), some appearing as ‘shoulders’; the material causing the eighth peak had a retention time similar to that of perfluoro-*N*-fluoropiperidine and proved (after collection using preparative g.l.c.) to be *perfluoro-NN'-difluoropiperazine* (estimated yield 8%) [Found: C, 18.4; N, 10.9%; *M* (mass spec.), 266. C₈F₁₆N₂ requires C, 18.1; N, 10.5%; *M*, 266], b.p. (isoteniscope) 44 °C, λ_{max} (vapour) 7.52s, sh, 7.59s, 7.78s, 8.16vs, 8.47vs, 8.77s (C–F str.), 10.42vs, and 10.58vs, sh (N–F str.) μm, δ_F (ext. CF₃·CO₂H) +31.1 (CF₂, appears as a broad complex absorption with two sharply defined maxima of unequal height at +31.06 and +31.14 p.p.m.) and +34.6br (NF, s) p.p.m. (rel. int. 4:1), *m/e* 266 (C₄F₁₀N₂⁺, 10%), 247 (C₄F₉N₂⁺, 100%; CF₃⁺, *m/e* 69, also occurred in 100% abundance), 214 (C₄F₈N₂⁺, 20), 209 (C₄F₇N₂⁺, 14), 164 (C₃F₆N⁺, 87), 114 (C₂F₄N⁺, 71), 100 (C₂F₄⁺, 41), and 64 (CF₂N⁺, 10).

Reactions of Perfluoro-NN'-difluoropiperazine.—(a) *With potassium iodide.* The *NN'*-difluoropiperazine (0.54 g, 2.03 mmol) was shaken with an excess of 2*M*-sodium iodide (10 ml) at 70 °C for 3 days. The solution was neutralised (NaHCO₃) and shown by titration (0.05*M*-sodium thio-sulphate) to contain 3.73 mmol of free iodine (92%). Oxalic acid was isolated from the iodine-free solution as its di-(*S*-benzylthiuronium) salt (0.15 g, 0.17 mmol, 43%), m.p. and mixed m.p. 199 °C, by standard techniques.

(b) *With perfluorocyclobutene.* A gaseous mixture of perfluoro-*NN'*-difluoropiperazine (3.10 g, 11.7 mmol) and perfluorocyclobutene (3.78 g, 23.4 mmol) was irradiated for 20 h in a 1 l u.v. reactor as described previously.⁹ The

volatile product, containing silicon tetrafluoride, carbonyl fluoride, perfluorocyclobutene (2.90 g, 17.9 mmol, 77% recovery), and perfluoro-*NN'*-difluoropiperazine (2.30 g, 8.65 mmol, 74% recovery) was pumped out of the vessel, leaving an oil, which was subjected to preparative g.l.c. (3 m silicone MS550 oil–Celite; 50 °C) to give perfluorobicyclobutyl (0.18 g, 0.50 mmol; 4%) (i.r. spectrum), and *perfluoro-(N-cyclobutyl-N'-fluoropiperazine)* (1.21 g, 2.83 mmol, 93% based on perfluoro-*NN'*-difluoropiperazine consumed) (Found: C, 22.3; N, 6.7. C₈F₁₆N₂ requires C, 22.4; N, 6.5%), b.p. 124 °C at 753 mmHg (Siwoloboff), *n*_D²⁵ 1.310, λ_{max} (film) 7.19m, 7.23w, sh, 7.64vs, 7.69vs, sh, 7.78s, 7.83s (doublet), 7.92s, 7.97s (doublet), 8.23vs, 8.69s, 8.81s, 9.01s, 9.80m, 10.26s (N–F str.), 10.51w, 10.80s, and 12.61s μm, δ_F (ext. CF₃·CO₂H; *ca.* 60% w/w soln. in CFCl₃) +16.0vbr [s, CF₂·N(cyclo-C₄F₇)·CF₂], +32.0br (s, NF), +33.3 (s, CF₂·N·CF₂), +51.3br (ABq, J_{AB} *ca.* 230 Hz, N·CF·CF₂·CF₂·CF₂), +54.7 (ABq, J_{AB} 226 Hz, N·CF·CF₂·CF₂·CF₂), and +60.4br (s, N·CF·CF₂·CF₂·CF₂) p.p.m. (rel. int. 4:1:4:4:2:1), *m/e* 428 (C₈F₁₆N₂⁺, <1%), 324 (65%), 145 (C₃F₅N⁺, 100%), 114 (C₂F₄N⁺, 61%), 100 (C₂F₄⁺, 61%), and 69 (CF₃⁺, 91%). The presence of an N–F bond in the last product was confirmed by the rapid liberation of iodine when it was shaken with a solution of potassium iodide in wet acetone at room temperature.

(c) *Photolysis.* In a 5 l reactor of the type described previously,¹³ a mixture of perfluoro-*NN'*-difluoropiperazine vapour (3.43 g, 12.9 mmol) and oxygen (0.41 g, 12.8 mmol) was irradiated with u.v. light for 1 week. After this period, the silica insert was coated almost completely with a waxy solid (2.50 g) [Found: C, 18.8; F, 58.9; N, 10.8. Calc. for (7; *x* = 2): C, 19.0; F, 65.4; N, 11.1%], m.p. 223 °C (decomp.), and the volatile product comprised oxygen, silicon tetrafluoride contaminated with carbonyl fluoride (0.26 g, 2.50 mmol), and perfluoro-*NN'*-difluoropiperazine (0.60 g, 2.26 mmol, 17.5% recovery). The mass spectrum of the wax showed *m/e* 751 (C₁₂F₂₅N₆O₃⁺, <1%), 735 (C₁₂F₂₅N₆O₂⁺, 1), 722 (C₁₂F₂₆N₆⁺, 2), 703 (C₁₂F₂₅N₆⁺, 9), 684 (C₁₂F₂₄N₆⁺, <1), 665 (C₁₂F₂₃N₆⁺, 1), 653 (C₁₁F₂₃N₆⁺, 1), 646 (C₁₂F₂₂N₆⁺, 1), 627 (C₁₂F₂₁N₆⁺, 2), 615 (C₁₁F₂₁N₆⁺, 1), 608 (C₁₂F₂₀N₆⁺, 4), 589 (C₁₂F₁₉N₆⁺, 1), 570 (C₁₂F₁₈N₆⁺, 2), 558 (C₁₁F₁₈N₆⁺, 2), 556 (C₁₂F₁₈N₅⁺, 2), 507 (C₈F₁₇N₄O₂⁺, 2), 491 (C₈F₁₇N₄O⁺, 11), 475 (C₈F₁₇N₄⁺, 20), 456 (C₈F₁₆N₄⁺, 2), 453 (C₇F₁₅N₆⁺, 1), 437 (C₈F₁₅N₄⁺, 2), 425 (C₈F₁₅N₄⁺, 1), 418 (C₈F₁₄N₄⁺, <1), 399 (C₈F₁₃N₄⁺, 2), 396 (C₆F₁₄N₃O⁺, 2), 387 (C₇F₁₃N₄⁺, 2), 380 (C₈F₁₂N₄⁺, 2), 361 (C₈F₁₁N₄⁺, 1), 342 (C₈F₁₀N₄⁺, 3), 330 (C₇F₁₀N₄⁺, 3), 313 (C₆F₁₁N₂O⁺, 2), 292 (C₇F₉N₄⁺, 11), 275 (C₅F₉N₂O⁺, 1), 263 (C₄F₉N₂O⁺, 69), 261 (C₅F₉NO⁺, 2), 247 (C₄F₉N₂⁺, 4), 228 (C₄F₈N₂⁺, 7), 225 (C₄F₇NO₂⁺, 3), 218 (C₃F₆N₂O⁺, 1), 209 (C₄F₇N₂⁺, 13), 197 (C₃F₇N₂⁺, 2), 190 (C₄F₆N₂⁺, 3), 180 (C₃F₆NO⁺, 18), 171 (C₄F₅N₂⁺, 1), 168 (C₂F₆NO⁺, 11), 164 (C₃F₆N⁺, 73), 159 (C₃F₅N₂⁺, 9), 152 (C₄F₄N₂⁺, 1), 145 (C₂F₅N⁺, 63), 130 (C₂F₄NO⁺, 20), 128 (C₂F₄N₂⁺, 1), 126 (C₃F₄N⁺, 2), 123 (C₃F₃NO⁺, 2), 119 (C₂F₅⁺, 30), 114 (C₂F₄N⁺, 100), 100 (C₂F₃⁺, 37), 95 (C₄FN₂⁺, 14), 92 (C₂F₂NO⁺, 4), 81 (C₂F₃⁺, 3), 69 (CF₃⁺, 83), 47 (COF⁺, 5), 44 (CO₂⁺, 4), 32 (O₂⁺, 4), 30 (NO⁺, 73), 28 (CO⁺, N₂⁺, 26), and low intensity peaks (<1%) in the region *m/e* 751–882.

Cross-linking of Nitroso Rubber.—Trifluoronitrosomethane (23.5 g, 238 mmol), tetrafluoroethylene (16.7 g, 167 mmol),

¹² R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 1956, 2684.

¹³ A. H. Dinwoodie and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 1675.

and hexafluorobutadiene (11.6 g, 71.4 mmol) were condensed separately into a cold (-196°C) stainless steel autoclave (1 l) equipped with a high-speed stirrer and containing a degassed mixture of lithium bromide (400 g), magnesium carbonate (21.4 g) and water (700 ml). The autoclave was warmed to -25°C (CaCl_2 -ice) and kept at that temperature while the stirrer was operated at 1500 rev. min^{-1} for 20 h. The autoclave was then allowed to warm slowly to room temperature, unchanged monomers were pumped away, and the aqueous suspension was acidified with dilute hydrochloric acid. The raw copolymer was washed with distilled water, then acetone (10 ml), and dried at 30°C *in vacuo*, to give a white elastomeric gum (33 g) {Found: C, 19.6; N, 6.6. Calc. for

$[(\text{CF}_3\text{NO})_{1.0}(\text{C}_2\text{F}_4)_{0.7}(\text{C}_4\text{F}_6)_{0.3}]_n$: C, 19.9; N, 6.4%}, which was soluble in perfluoro(tributylamine) and showed C:C str. i.r. absorption at $5.61\mu\text{m}$ and $5.81\mu\text{m}$. A sample of this copolymer (1.0 g) was vulcanised by mixing it thoroughly with the wax (0.1 g) from the perfluoro-*NN'*-difluoropiperazine-oxygen reaction, pressing the mixture between polished stainless steel plates in a polymer press (400 lb in^{-2}), and then raising the press temperature to 220°C during 15 min and maintaining it for 5 min.

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