

Reactions Involving Fluoride Ion. Part 36.¹ Aromatic Amines as Carbon Nucleophiles in Reactions with Unsaturated Fluorocarbons

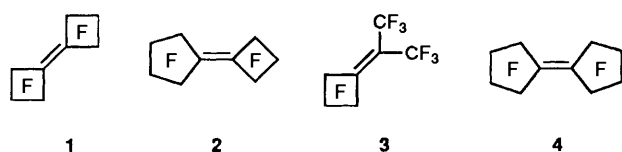
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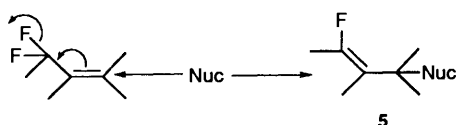
N,N-Dimethylaniline and *N*-methylindole react as carbon nucleophiles with perfluorocycloalkene derivatives, giving products **6a** and **6b** arising from allylic displacement. 1,8-Bis(dimethylamino)naphthalene **7**, reacts through the 4,5-positions as a difunctional nucleophile, giving a novel annelation. Reactions with **2** and **3** are regiospecific leading to products **8** and **9**, respectively. Reaction of perfluorobicyclopentylidene **4** with **7** gives first, through defluorination, the diene **19** and then by annelation of this the product **14**. The colours of the products are evidence of extensive charge separation.

In previous parts of this series of papers involving fluoride ion-induced reactions, we have described syntheses of unusual perfluorocycloalkene derivatives, e.g. **1-4**.²⁻⁴ These are



especially interesting because they each involve four electron-withdrawing groups attached to the double bond, thereby activating the system towards nucleophilic attack. Nevertheless, each system, **1-4**, must react *via* allylic displacement processes because there is no group attached to the double bond that can be directly displaced.

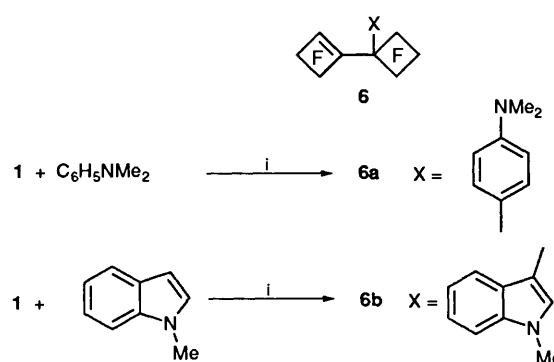
Consequently, the resultant system **5** is often very susceptible



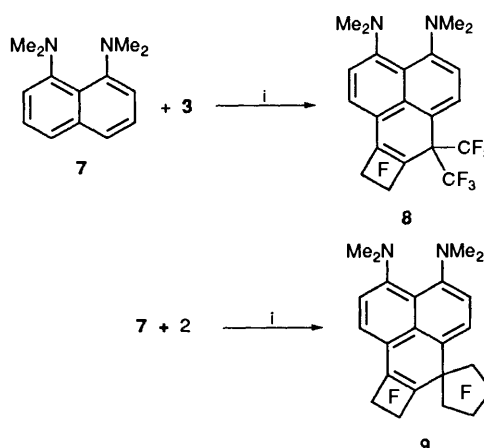
to further attack and, therefore, these systems frequently act as difunctional electrophiles.⁵ There is a vast literature concerning processes which involve nucleophilic attack on perfluoroalkenes⁶ but there is limited information concerning reactions of tertiary aromatic amines with these systems. Such amines are, of course, extremely reactive towards electrophilic aromatic substitution but, surprisingly, there have not been any reported examples, to our knowledge, of perfluorinated alkenes acting as electrophiles in reactions with these systems.

However, we have now discovered some examples of nucleophilic attack on fluorinated alkenes by aromatic amines reacting through carbon of the aromatic ring. For example, *N,N*-dimethylaniline reacted with perfluorobicyclobutylidene **1** to give **6a** by nucleophilic attack, accompanied by allylic displacement of fluoride ion; *N*-methylindole reacted in an analogous way to give **6b**.

We have also found that 1,8-bis(dimethylamino)naphthalene **7** reacts as a difunctional nucleophile with some of these systems leading to a novel annelation. Reaction with **3**, gave product **8** through electrophilic attack at the 4- and 5-positions in the 1,8-bis(dimethylamino)naphthalene and, similarly, reaction of **7** with **2** gave the analogous product **9** (Scheme 1). At first sight it is surprising that these annelations are regiospecific.



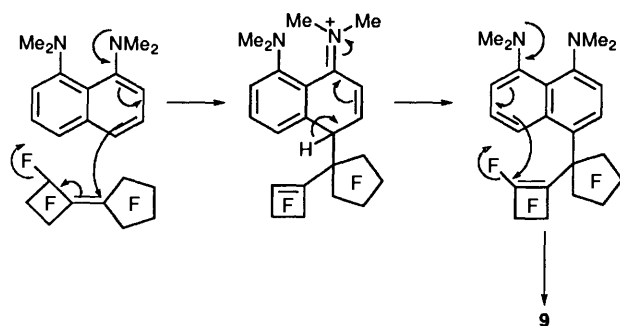
Reagents and conditions: i, MeCN, room temp., overnight



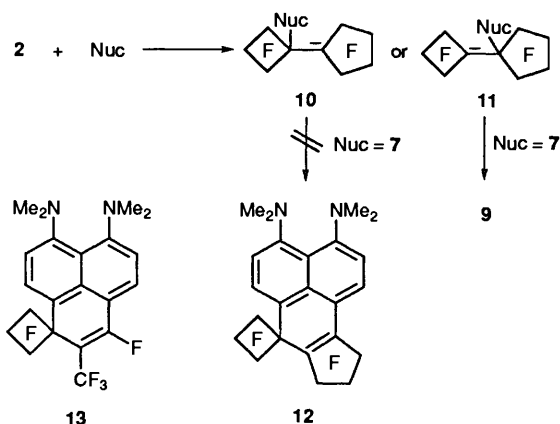
Reagents and conditions: i, MeCN, reflux, overnight

However, in each case, this specificity can be rationalised on the basis of the initial nucleophilic attack on the perfluorocycloalkene derivative **2** or **3**. For example, reaction with **2** could take two different initial courses giving **10** or **11** as intermediates. Obviously, the product **9** derives entirely from **11** rather than **10** and this specificity is understandable on the basis of the stability of the developing carbanions **10** and **11**. The carbanion **11** would be the more stable since the charge develops on a carbon atom contained in the more strained ring: this happens because the carbon of the four-membered ring must have more s-character in the orbital containing the developing charge.

Structures of **8** and **9** were derived from NMR data. First,

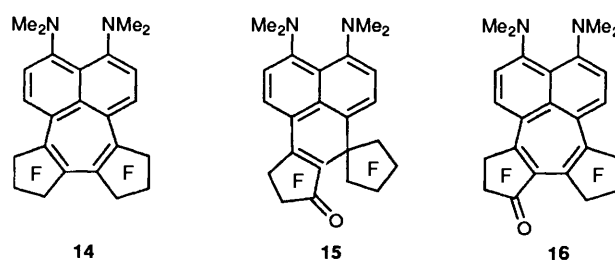


Scheme 1



the pattern of the proton chemical shifts *etc.*, were entirely consistent with a variety of data for other 4,5-disubstituted derivatives of 1,8-bis(dimethylamino)naphthalene **7**.⁸ The ¹⁹F NMR data for **8**, clearly indicated trifluoromethyl groups attached to a saturated site, and two difluoromethylene groups, consistent with the unsaturated four-membered ring in **8**. Obviously, these data are quite inconsistent with structure **13** which would be obtained by alternative regiochemistry of nucleophilic attack on **3**. Similar arguments led to the structure **9**; the ¹⁹F NMR spectrum showed four resonances in the difluoromethylene region, with shifts in the cyclobutene ring similar to those observed in **8**. In contrast, structure **12**, which would arise from alternative regiochemistry, would be expected to show five distinguishable resonances in the difluoromethylene region.

Reaction of 1,8-bis(dimethylamino)naphthalene **7** with perfluorobicyclopentylidene **4** was more complex. In concentrated solutions in acetonitrile, a dark green solid was obtained, which was sparingly soluble but could be recrystallised from acetonitrile. However, no NMR signals could be obtained, suggesting a paramagnetic system, reminiscent of the classical Würster salts.⁹ However, it was shown by elemental analysis and mass spectrometry to be a product which had lost two fluorine atoms from the starting material **4** as well as further reaction with **7**. A possible structure is **14**. Nevertheless, in high dilution in acetonitrile, some products were obtained that could be characterised. As before, the product was a dark solid but chromatography over alumina gave three fractions: (a) a solid identical (MS, IR, m.p.) with the above **14**; (b) yellow-green crystals with a metallic lustre **15** which gave a dark purple solution; (c) a bright purple solid **16**, that gave a green solution! The fraction (b) was identified as the ketone **15** by NMR spectroscopy. In particular, a 2-D ¹⁹F COSY spectrum confirmed difluoromethylene groups in a saturated cyclopentane ring, *i.e.* shifts similar to product **9**, as well as difluoromethylene groups in the unsaturated ring. The structure



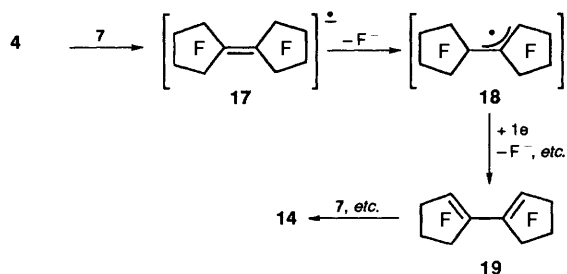
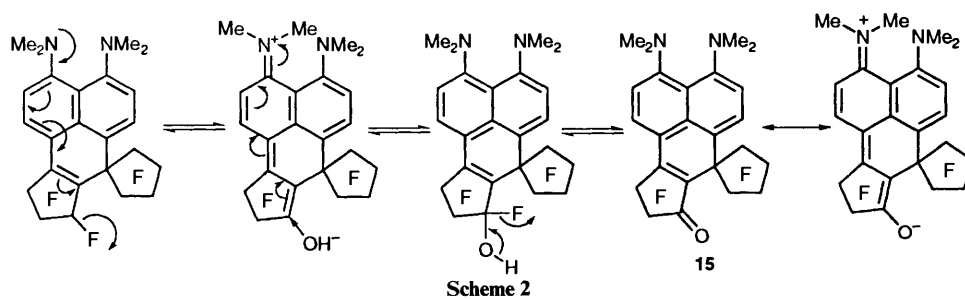
15 is advanced, over the other possible positions of carbonyl because only in this structure do we obtain maximum charge separation, which would account for the remarkable colour changes with phase. The acetonitrile used was anhydrous and therefore hydrolysis must occur during chromatography. Fraction (c), was also shown to be a hydrolysis product apparently derived from **14**. The structure **16** again was derived from NMR data and, particularly, a 2-D ¹⁹F COSY experiment, from which we could deduce (i) the presence of five difluoromethylene groups, (ii) the shifts derived from difluoromethylene groups in the cyclopentenone ring showed close similarity to those in **15**, and (iii) the remaining three difluoromethylene groups are consistent with those in a variety of similar perfluorocyclopentene derived systems.^{3,4} The most reasonable mechanism for formation of these unusual systems is contained in Scheme 2, where the opportunities for significant charge separation suggests the basis of the remarkable colour changes that occur. The opportunities for charge transfer in the solid state could also account for the metallic appearance.

It is curious, that system **2** reacts by an initial two-electron transfer, *i.e.* nucleophilic attack, whereas **4** obviously undergoes a one-electron transfer, leading to defluorination prior to subsequent nucleophilic attack by 1,8-bis(dimethylamino)naphthalene. We have previously shown that defluorination of **4** by sodium amalgam may be achieved¹⁰ but initial defluorination by **7** is surprising. However, we can envisage a one-electron transfer process leading to **17** (Scheme 3), followed by loss of fluoride ion giving **18** and then the process repeated leading to the diene **19**. The latter was not observed but reacted with **7** to give the product **14**. In a separate experiment, **7** reacted with the diene **19** to give the same product **14**. The most obvious explanation of the different mode of attack of **1** and **4** in reactions with **7** stems from activation by strain in the four-membered ring system. For example, **1** is of greatly enhanced reactivity over **4** in reactions with neutral ethanol¹¹ and, consequently, **2** is much more reactive than **4** towards nucleophilic attack.

Experimental

All materials were either obtained commercially (Aldrich) or prepared by literature procedures.²⁻⁴ All solvents were dried prior to use by literature procedures. NMR spectra were recorded on either a Varian VXR400S or a Bruker AC250 Spectrometer. In ¹⁹F NMR spectra, upfield shifts are quoted as negative. *J* Values are given in Hz. Mass spectra were recorded on a Varian VG 7070E spectrometer, IR spectra on a Perkin-Elmer 577 Grating Spectrophotometer and UV spectra on a Perkin-Elmer Lambda 3 spectrophotometer using standard techniques. Elemental analyses were obtained on either a Perkin-Elmer 240 or a Carlo Erba Elemental Analyser. Melting points were recorded at atmospheric pressure and are uncorrected.

Reactions of Perfluorobicyclobutylidene 1.—(a) *With N,N-dimethylaniline.* A mixture containing *N,N*-dimethylaniline (0.5 g, 4.1 mmol) and perfluorobicyclobutylidene **1** (1.1 g, 3.4 mmol)



was stirred at room temperature overnight in acetonitrile (5 cm³). Water (15 cm³) was added to the mixture to precipitate the solid product which was filtered off, recrystallised from aqueous ethanol and vacuum sublimed to yield 1-[1'-(*p*-dimethylaminophenyl)perfluorocyclobutyl]perfluorocyclobut-1-ene **6a** (1.05 g, 73%) as white needles; m.p. 84–85 °C (Found: C, 45.0; H, 2.3; N, 3.2 C₁₆H₁₀F₁₁N requires C, 45.2; H, 2.3; N, 3.3%); $\nu_{\max}/\text{cm}^{-1}$ 1715 (C=C); δ_{H} (250 MHz, CD₃CN, Me₄Si) 2.96 (6 H, s, NMe₂), 6.76 and 7.16 (4 H, AA'XX', J_{AX} 8.7, 3- and 2-ArH); δ_{F} (235 MHz, CD₃CN, CFCl₃) –101.2 (1 F, s, 2-CF), –114.0 (2 F, s, 4-CF₂), –119.0 (2 F, s, 3-CF₂), –117.0 and –120.9 (4 F, AB, J_{AB} 214, 2'-CF₂), –128.0 and –133.9 (2 F, AB, J_{AB} 222, 3'-CF₂); m/z (EI⁺) 425 (M⁺, 100%).

(b) *With N-methylindole*. A mixture containing *N*-methylindole (0.4 g, 3 mmol) and perfluorobicyclobutylidene **1** (1.0 g, 3 mmol) was refluxed in acetonitrile (5 cm³) overnight. On cooling, the reaction mixture was diluted with water (15 cm³) to precipitate the solid product which was filtered off, dried and purified by vacuum sublimation (oil-bath temp. 100 °C, <0.1 mmHg) to give white crystals of 1-[1'-(*N*-methylindol-3''-yl)perfluorocyclobutyl]perfluorocyclobut-1-ene **6b** (0.60 g, 46%); m.p. 59–60 °C (Found: C, 47.25; H, 1.8; N, 3.1. C₁₇H₈F₁₁N requires C, 46.9; H, 1.85; N, 3.2%); $\nu_{\max}/\text{cm}^{-1}$ 1720 (C=C); δ_{H} (400 MHz, CD₃CN, Me₄Si) 3.85 (3 H, s, N-Me), 7.20 (1 H, t, $J_{5'',6''}$ 7.6, 6''-H), 7.33 (1 H, t, $J_{5'',6''}$ 7.6, 5''-H), 7.39 (1 H, d, $J_{6'',7''}$ 8.0, 7''-H), 7.51 (1 H, d, $J_{4'',5''}$ 8.3, 4''-H), 7.56 (1 H, s, 2''-H); δ_{F} (376 MHz, CD₃CN, CFCl₃) –100.6 (1 F, s, 2-CF), –114.7 (2 F, s, 4-CF₂), –119.3 (2 F, s, 3-CF₂), –117.2 and –120.4 (4 F, AB, J_{AB} 215, 2'-CF₂), –128.2 and –130.4 (2 F, AB, J_{AB} 221, 3'-CF₂); m/z (CI⁺, NH₃) 436 (M⁺ + 1, 28%).

Reactions of 1,8-Bis(dimethylamino)naphthalene 7.—(a) *With perfluoroisopropylidencyclobutane 3*. A mixture containing 1,8-bis(dimethylamino)naphthalene **7** (0.7 g, 3.2 mmol), the fluoroalkene **3** (1.0 g, 3.2 mmol) and acetonitrile (10 cm³) was heated at reflux overnight. Water was added to the mixture to precipitate an orange solid which was filtered off and shown by TLC to contain two components. The solid was evaporated onto chromatographic alumina elution of which with light petroleum afforded 3,4-bis(dimethylamino)-8,8,9,9-tetrafluoro-5,5-(trifluoromethyl)-8,9-dihydro-7H-cyclobuta[a]phenalene **8** (1.1 g, 21%) as orange crystals; R_{F} 0.5; m.p. 128 °C (from aqueous ethanol) (Found: C, 52.2; H, 3.4; F, 38.0; N, 5.6. C₂₁H₁₆F₁₀N₂ requires C, 51.9; H, 3.3; F, 39.0; N, 5.8%);

λ_{\max} (MeCN)/nm 273.6 (log ϵ 3.78), 367.6 (3.45) and 451.2 (3.78); $\nu_{\max}/\text{cm}^{-1}$ 1680 (C=C); δ_{H} (250 MHz, CD₃CN, Me₄Si) 2.81 (6 H, s, 3-NMe₂), 2.88 (6 H, s, 4-NMe₂), 6.79 and 7.45 (2 H, AX, J_{AX} 8.3, 1-H and 2-H), 6.98 and 7.85 (2 H, AX, J_{AX} 8.8, 5-H and 6-H); δ_{F} (235 MHz, CD₃CN, CFCl₃) –67.2 (6 F, s, CF₃), –105.1 (2 F, s, 9-CF₂), –112.5 (2 F, s, 8-CF₂); δ_{C} (100 MHz, CD₃CN, Me₄Si) 43.5 (s/br, N-Me), 107.7 (s, C-6a), 108.9 (s, C-2), 111.5 (s, C-5), 115–120 (many overlapping peaks, CF₂ and CF₃), 116.7 (s, C-9b), 121.4 (s, C-3a), 123.7 (s, C-9a), 126.0 (s, C-7a), 126.9 (s, C-1), 130.4 (s, C-6), 134.1 (s, C-9c), 152.9 (s, C-3), 153.0 (m, C-7) and 156.1 (s, C-4); m/z (CI⁺, NH₃) 487 (M⁺ + 1, 20%). A red solid was also isolated (0.05 g) as yet unidentified; $\nu_{\max}/\text{cm}^{-1}$ 1790 (C=O); δ_{F} (235 MHz, CD₃CN, CFCl₃) –68.9 (s, 6 F) and –110.5 (s, 2 F); m/z (EI⁺) 464 (M⁺, 83%).

(b) *With fluoroalkene 2*. A mixture containing 1,8-bis(dimethylamino)naphthalene **7** (0.6 g, 2.8 mmol) and fluoroalkene **2** (1.0 g, 2.7 mmol) was refluxed overnight in acetonitrile (5 cm³). The solvent was removed to leave an orange solid which was washed with water, collected and dried. The solid was evaporated onto chromatographic alumina from which light petroleum (b.p. 40–60 °C) eluted 3,4-bis(dimethylamino)-2',2',3',3',4',4',5',5',8,8,9,9-dodecafluorospiro[8,9-dihydro-7H-cyclobuta[a]phenalene-7-cyclopentane] (**0.2 g, 13%**) as orange crystals; m.p. 137–139 °C; R_{F} 0.5 (Found: C, 50.4; H, 3.9; N, 4.4%; M⁺, 548.11762. C₂₃H₁₆F₁₂N₂ requires C, 50.3; H, 2.9; N, 5.1%; M⁺, 548.11219); λ_{\max} (MeCN)/nm 273.6 (log ϵ 4.06), 365.6 (3.74) and 452.8 (4.10); $\nu_{\max}/\text{cm}^{-1}$ 1673 (C=C); δ_{H} (400 MHz, CD₃CN, Me₄Si) 2.88 (6 H, s, 3-NMe₂), 2.94 (6 H, s, 4-NMe₂), 6.86 and 7.33 (2 H, AX, J_{AX} 8.4, 2-H and 1-H), 7.04 and 7.52 (2 H, AX, J_{AX} 8.8, 5-H and 6-H); δ_{F} (376 MHz, CD₃CN, CFCl₃) –104.9 (2 F, s, 9-CF₂), –112.8 and –116.0 (4 F, AB, J_{AB} 249.1, 2'-CF₂), –114.6 (2 F, s, 8-CF₂), –135.2 (4 F, s, 3'-CF₂); δ_{C} (100 MHz, CD₃CN, Me₄Si) 43.0 (s/br, NMe₂), 109.4 (s, C-2), 111.4 (s, C-5), 115.4 (s, C-3a), 115–120 (many overlapping peaks, CF₂), 128.6 (s, C-1), 134.0 (s, C-9c), 135.8 (s, C-6), 151.9 (m, C-7), 154.4 (s, C-3) and 158.2 (s, C-4); m/z (CI⁺, NH₃) 549 (M⁺ + 1, 37%).

(c) *With perfluorobicyclopentylidene 4*. (i) At low dilution. A mixture containing 1,8-bis(dimethylamino)naphthalene **7** (1.1 g, 5.1 mmol) and perfluorobicyclopentylidene **4** (1.0 g, 2.3 mmol) was stirred overnight at room temperature in acetonitrile (5 cm³) to form a dark olive green precipitate. Water was added to the mixture and the solid was collected by filtration. The solid was adsorbed onto chromatographic alumina from which light petroleum–dichloromethane (4 : 1) eluted 3,4-bis(dimethylamino)-7,7,8,8,9,9,10,10,11,11,12,12-dodecafluoro-8,9,11,12-tetrahydro-7H,10H-dicyclopenta[4,5:6,7]cyclohepta[1,2,3-ij]-naphthalene **14** (0.54 g, 42%); m.p. 243–45 °C (decomp.) (from acetonitrile); R_{F} 0.65 (Found: C, 51.3; H, 2.8; F, 40.0; N, 4.9. C₂₄H₁₆F₁₂N₂ requires C, 51.4; H, 2.8; F, 40.7; N, 5.0%); no NMR data could be recorded; m/z (EI⁺) 560 (M⁺, 100%).

(ii) At high dilution. A mixture containing 1,8-bis(dimethylamino)naphthalene **7** (0.5 g, 2.5 mmol) and perfluorobicyclopentylidene **4** (1.0 g, 2.3 mmol) was stirred overnight at room temperature in acetonitrile (120 cm³). Evaporation of the

mixture under reduced pressure left a solid residue, which was adsorbed onto chromatographic alumina and from which light petroleum-dichloromethane (4:1) eluted compound **14** (0.23 g, 18%), as above; 3,4-bis(dimethylamino)-2',2',3',3',4',4',5',5',9,9,10,10-dodecafluoro-10H-spiro(cyclopenta[a]phenylene-7-cyclopentan)-8(9H)-one **15** (0.14 g, 10%) as bright green metallic-looking flakes; m.p. > 280 °C; R_F 0.45 (Found: C, 48.4; H, 2.75; N, 4.50. $C_{24}H_{16}F_{12}N_2O$ requires C, 50.0; H, 2.75; N, 4.5%). $C_{24}H_{16}F_{12}N_2O \cdot H_2O$ requires C, 48.5; H, 3.0; N, 4.7%; ν_{max}/cm^{-1} 1720 (C=O); δ_H (400 MHz, CD_3CN , Me_4Si) 2.16 (12 H, s, NMe_2), 6.95 and 7.25 (2 H, AX, J_{AX} 8.8, 1-H and 2-H), 7.05 and 7.92 (2 H, AX, J_{AX} 8.8, 5-H and 6-H); δ_F (376 MHz, CD_3CN , $CFCl_3$) -111.0 and -113.4 (4 F, AB, J_{AB} 246.7, 2'-CF₂), -117.8 [s(pseudo AB), 2F, 10-CF₂], -131.4 [2 F, s(pseudo AB), 9-CF₂], and -132.3 [4 F, s(pseudo AB), 3'-CF₂]; m/z (Cl^- , NH_3) 576 (M^+ , 72%); and 3,4-bis-(dimethylamino)-7,7,8,8,9,9,11,11,12,12-decafluoro-8,9,11,12-tetrahydro-7H-dicyclopenta[4,5:6,7]cyclohepta[1,2,3-ij]-naphthalen-10-one **16** (0.12 g, 9%) as bright purple metallic-looking flakes; m.p. > 280 °C; R_F 0.3 (Found: C, 53.2; H, 3.05; N, 4.75%; M^+ , 538.1100900. $C_{24}H_{16}F_{10}N_2O$ requires C, 53.5; H, 2.95; N, 5.2%; M^+ , 538.110295); ν_{max}/cm^{-1} 1720 (C=O); δ_H (400 MHz, CD_3CN , Me_4Si) 2.16 (12 H, s, NMe_2), 6.49 and 6.92 (2 H, AX, J_{AX} 8.8, 5-H and 6-H), 6.51 and 7.33 (2 H, AX, J_{AX} 8.8, 2-H and 1-H); δ_F (376 MHz, CD_3CN , $CFCl_3$) -106.5 and -128.8 (2 F, AB, J_{AB} 278, 12-CF₂), -109.3 and -133.1 (2 F, AB, J_{AB} 262, 7-CF₂), -119.4 and 128.0 (2 F, AB, J_{AB} 260, 9-CF₂), -128.8 and -136.0 (2 F, AB, J_{AB} 283, 11-CF₂), -133.4 and -143.3 (2 F, AB, J_{AB} 240, 8-CF₂); m/z (Et^+) 538 (M^+ , 100%).

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Paper 3/04874H

Received 11th August 1993

Accepted 20th September 1993