Photolysis of fluorodiphenylamines

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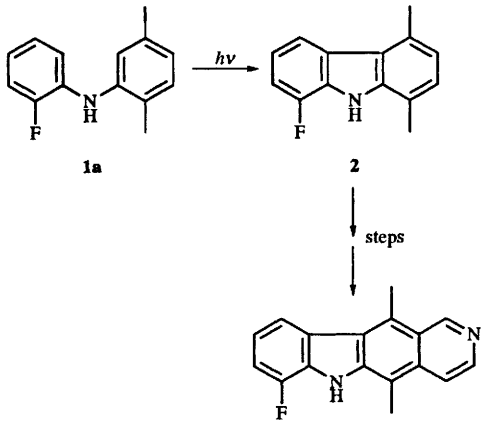
PERKIN 1

Photolysis of 2-fluoro-2′,5′-dimethyldiphenylamine 1a, in ethanol with a medium-pressure mercury lamp, gave a mixture of 1,4-dimethylcarbazole 7 (53%), 8-fluoro-1,4-dimethylcarbazole 2 (11%) and 6-ethoxy-2-fluoro-2′,5′-dimethyldiphenylamine 8 (19%). Photolysis of 4-fluoro-2′,5′-dimethyldiphenylamine 1b gave 6-fluoro-1,4-dimethylcarbazole 25 (35%) and 1,4-dimethylcarbazole 7 (47%).

As part of our attempts to prepare 7-fluoroellipticine **3** for studies of the cellular binding sites of fluorinated derivatives of anti-cancer agents we wished to prepare 8-fluoro-1,4-dimethylcarbazole **2** as an intermediate for conversion into 7-fluoroellipticine **3** by way of a modified Cranwell–Saxton route. It was hoped that the carbazole **2** could be obtained from the photolysis of the 2-fluoro-2′,5′-dimethyldiphenylamine **1a** (Scheme 1).



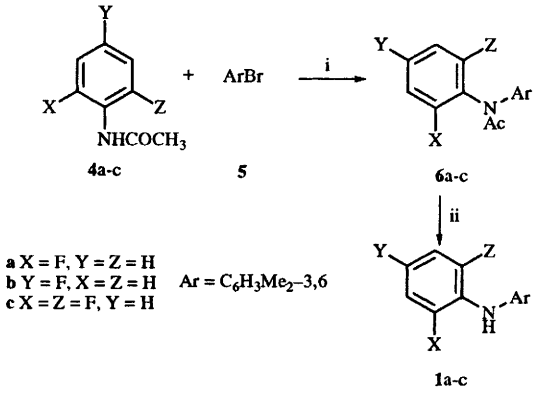
Scheme 1

The photocyclisation of diphenylamines has long been known[1] but most studies have prepared the carbazoles by photolysis of *N*,*N*-diarylsulfonamides,[2] during which the *p*-tolylsulfonyl protecting group is removed and the diphenylamine moiety cyclised. Other methods of carbazole synthesis include the palladium(II) acetate oxidation of diphenylamines. Photochemical conversion of diphenylacetamides has also been attempted,[3] but the carbazoles were minor components and were accompanied by larger amounts of photo-Fries products.

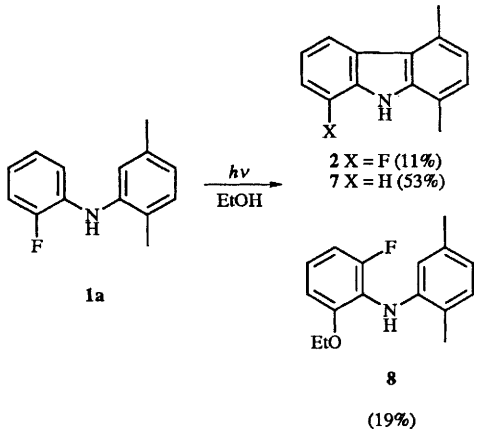
Results and discussion

The halogenodiphenylamines **1** used in this study were prepared by the Goldberg coupling of the corresponding halogenoacetanilides **4** with 2-bromo-1,4-dimethylbenzene **5**, followed by base-catalysed hydrolysis of the amides **6** to the free amines (Scheme 2).

Photolysis of 2-fluoro-2′,5′-dimethyldiphenylamine **1a** gave a mixture containing 1,4-dimethylcarbazole **7** (53%), 8-fluoro-1,4-dimethylcarbazole **2** (11%) and an unknown product, the mass and ^{1}H NMR spectra of which indicated that it had arisen from the substitution of an ethoxy group onto one of the phenyl rings. Decoupling experiments showed that the substitution had taken place into the 2-fluorophenyl ring at the 6-position (*ortho*) to give the 6-ethoxy-2-fluoro-2′,5′-dimethyldiphenylamine **8** (19%), (Scheme 3); this was confirmed by an X-ray crystal structure (Fig. 1).



Scheme 2 *Reagents and conditions:* i, Cu bronze, 160 °C, K_2CO_3; ii, EtOH, KOH



Scheme 3

The dehydrogenative photocyclisation of diphenylamines proceeds *via* an oxygen-sensitive intermediate, with yields varying according to the particular diphenylamine used, which could be due to an alteration in the dominant photochemical pathway.[4] The reaction proceeds initially *via* an excited triplet state, forming a radical cation which could presumably then react with either the ethoxy radical formed by irradiation of ethanol[5] or ethanol itself to give the observed ethoxylated fluorodiphenylamine. This product does not seem to be an intermediate in the formation of the fluorocarbazole **2** since irradiation of 6-ethoxy-2-fluoro-2′,5′-dimethyldiphenylamine **8** in ethanol for 24 h gave *ca.* 1% of the ethoxycarbazole **9**, with no loss of ethoxy substituent (this is not surprising when

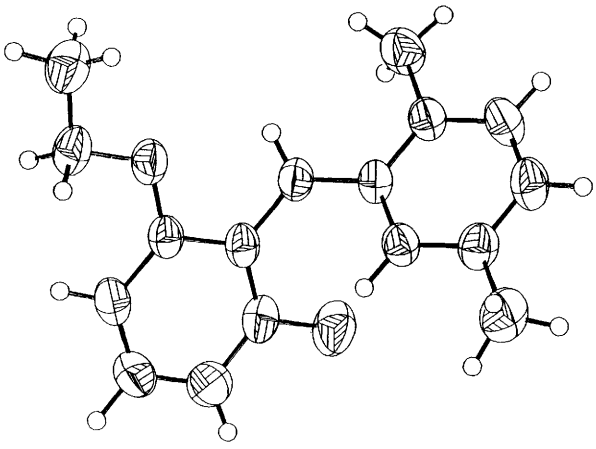
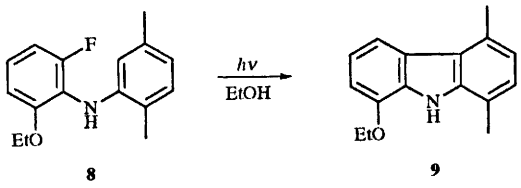


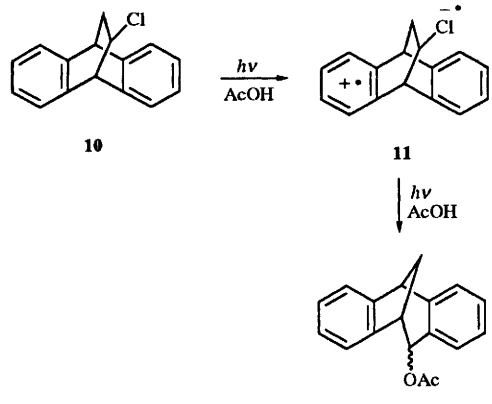
Fig. 1 X-Ray crystal structure of 6-ethoxy-2-fluoro-2′,5′-dimethyldiphenylamine **8**



8 **9**

considered in conjunction with the fact that photolysis of the mono-*ortho*-fluorodiphenylamine **1a** proceeds preferentially with loss of the fluorine atom); nor is the ethoxy compound **8** formed from the fluorocarbazole, since irradiation of 8-fluoro-1,4-dimethylcarbazole **2** for 24 h in ethanol gave no reaction.

Such photosolvolyses are rare but acetoxylation of the bridged tricyclic species **10**, to give **12**, is suspected to proceed *via* a zwitterionic biradical **11** from the photo-induced electron transfer from the π-system to the anti-bonding σ C-Cl orbital (Scheme 4).[6] A further rare example of photosolvolysis is the

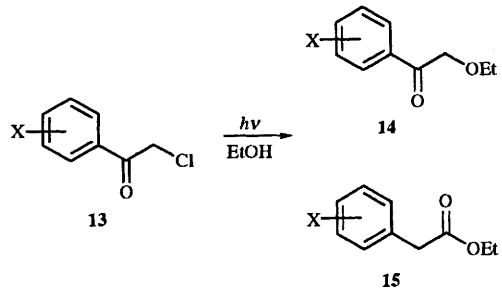


10 **11** **12**

Scheme 4

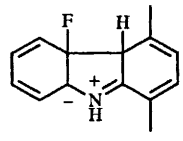
reaction of the phenacyl chlorides **13** with ethanol to give the ethoxy ketones **14** and phenylacetic esters **15**.[7]

The loss of an *ortho* fluorine atom in the photocyclisation of 2-fluoro-2′,5′-dimethyldiphenylamine **1a** to give 1,4-dimethylcarbazole **7** may either be occurring as a spontaneous homolytic cleavage of the C–F bond of the radical cation of the diphenylamine, or it may be lost as a consequence of cyclisation to the carbazole **7**; if the latter is the case, the preferential loss of fluorine is presumably due to the fluoride ion acting as a better leaving group than hydrogen in the rearomatisation step from the well established reaction intermedate **16**.[1,5] Another example of the loss of a fluorine atom occurs during the Fischer indole cyclisations in refluxing in tetralin of acetophenone 1,3,4,5,6,7,8-heptafluoro-2-naphthylhydrazone **17** and aceto-



13 **14** **15**

phenone pentafluorophenylhydrazone **19** to give 4,5,6,7,8,9-hexafluoro-2-phenylbenz[*e*]indole **18** and 4,5,6,7-tetrafluoro-2-phenylindole **20**, respectively. These two compounds are typical Fischer products, but are formed by the loss of an *ortho*-fluorine atom rather than an *ortho*-hydrogen atom.[8] The reaction giving the indole **20** was originally carried out using acetophenone 2,3,4,5-tetrafluorophenylhydrazone **21**, *i.e.* the starting material contained both an *ortho* fluorine and an *ortho* hydrogen atom. The hydrogen atom was lost, giving 4,5,6,7-tetrafluoro-2-phenylindole **20** (15%). The displacement of an *ortho* fluorine atom in the reaction of **19** occurs on a comparable scale, with a 12% yield of product.[8b]



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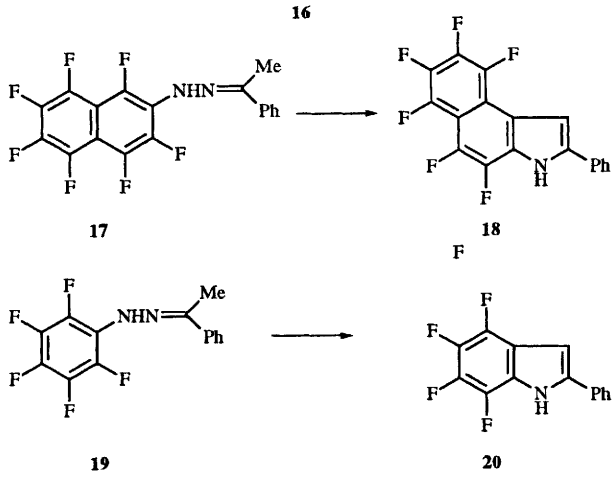
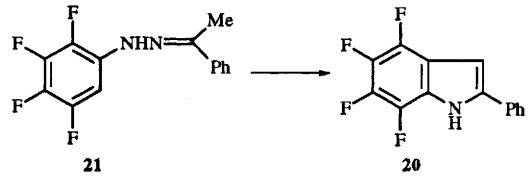


17 **18** **19** **20**

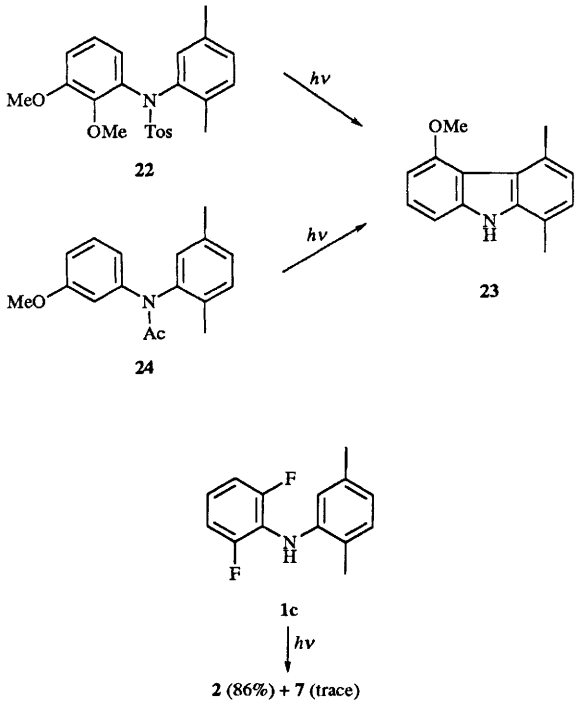
Other work within this department reveals the loss of an *ortho* methoxy substituent when the *N*-tosyldimethoxydiphenylamine **22** was subjected to photochemical irradiation to give the methoxycarbazole **23** in low yield.[9] This, however, appears



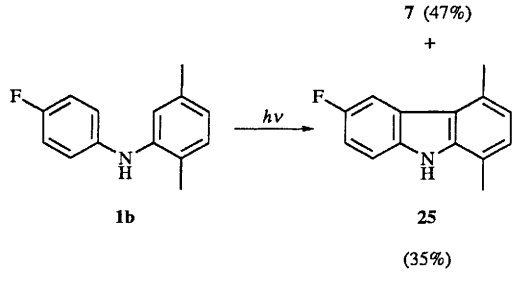
21 **20**

to be more a function of the effect of a *meta* methoxy substituent on the position of cyclisation than of the tendency of an *ortho* methoxy group to favour cyclisation to the *ipso* position, since on photoirradiation the diphenylamine **24** cyclised to the position *ortho* to the methoxy group rather than *para* to it, to give the carbazole **23**.

Irradiation of 2,6-difluoro-2′,5′-dimethyldiphenylamine **1c** gave 8-fluoro-1,4-dimethylcarbazole **2** (86%) along with a trace of 1,4-dimethylcarbazole **7**. The 8-fluoro-1,4-dimethylcarbazole was then converted into 7-fluoroellipticine **3**.[10]



Finally, irradiation of 4-fluoro-2′,5′-dimethyldiphenylamine **1b** gave 6-fluoro-1,4-dimethylcarbazole **25** and 1,4-dimethylcarbazole **7**; possibly the non-fluorinated derivative originated from homolysis of the C–F bond in the diphenylamine radical cation.



Experimental

Mps were determined using a Gallenkamp apparatus and are uncorrected. Elemental analyses were recorded on a Perkin-Elmer 240C. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer using sodium chloride plates. Solid samples were run as Nujol mulls and liquid samples as thin films. ^{1}H NMR and ^{13}C NMR spectra were acquired on a Bruker WM360 spectrometer at 360 and 90 MHz, respectively, and run in deuteriochloroform unless stated otherwise. ^{1}H NMR coupling constants are given in Hz and all chemical shifts are relative to an internal standard of tetramethylsilane. Low resolution electron impact mass spectra were obtained on a Varian CH5-D spectrometer (Cardiff) or Fisons VG Platform II (Cardiff) and high resolution spectra on a VG ZAB-E spectrometer (SERC Mass Spectrometry Service Centre, Swansea). UV absorption spectra were recorded on a Uvikon 930 spectrophotometer. Thin layer chromatography was performed on Merck silica gel $60F_{254}$ and dry-column flash chromatography on Merck silica 60H. Tetrahydrofuran and 1,4-dioxane were refluxed over sodium wire with a small amount of benzophenone until a blue colour developed and then distilled. Pyridine was distilled and stored over potassium hydroxide pellets. Potassium carbonate for the Goldberg reactions was dried at 180 °C overnight prior to use. Copper bronze was activated by treatment with a 2% (w/v) solution of iodine in acetone and stirred at room temperature for 15 min. The activated copper was filtered off, washed with concentrated hydrochloric acid in acetone (1 : 1, v/v) and finally with acetone before being dried *in vacuo*.

2-Fluoro-2′,5′-dimethyldiphenylamine 1a

(i) 2-Fluoroacetanilide 4a. Acetic anhydride (30 cm^3, 0.32 mol) was added slowly with stirring to 2-fluoroaniline (25 g, 0.225 mol) on ice. White crystals formed to which water (50 cm^3) was added. The crystals were filtered off and recrystallised from toluene to give *2-fluoroacetanilide* **4a** (30.35 g, 88%), mp 76–78 °C (Found: C, 63.0; H, 5.4; N, 9.3. C_8H_8FNO requires C, 62.7; H, 5.3; N, 9.2%); δ_H 2.17 (3 H, s, Me), 6.98–7.12 (3 H, m, 3-H, 4-H, 5-H), 7.90 (1 H, br s, NH) and 8.18 (1 H, t, *J* 9, 6-H) *m*/*z* 153 (M$^+$, 20%), 111 (100), 83 (14) and 57 (11); ν_{max}/cm^{-1} 3248 (NH) and 1669 (C=O).

(ii) *N*-Acetyl-2-fluoro-2′,5′-dimethyldiphenylamine 6a. 2-Fluoroacetanilide **4a** (10 g, 65.3 mmol), potassium carbonate (4 g), pre-treated copper bronze (10 g) and 2-bromo-1,4-dimethylbenzene (24 g, 0.13 mol) were heated together at 180 °C under dry N_2 for 7 h. On cooling, the mixture was diluted with ethyl acetate (200 cm^3) and stirred overnight. The solids were filtered off and washed with ethyl acetate. The combined filtrate and washings were evaporated under reduced pressure to give a brown solid which was recrystallised from ethanol to afford pale brown needles of the *title compound* **6a** (9.83 g, 59%), mp 94 °C (Found: C, 74.9; H, 6.0; N, 5.6. $C_{16}H_{16}FNO$ requires C, 74.7; H, 6.2; N, 5.5%); δ_H 2.00 (3 H, s, COMe), 2.11 (3 H, s, 2′-Me), 2.35 (3 H, s, 5′-Me) and 6.93–7.34 (7 H, m, ArH); *m*/*z* 257 (M$^+$, 34%), 216 (16), 215 (100), 194 (10) and 136 (18); ν_{max}(Nujol)/cm^{-1} 1680 (C=O).

(iii) The diphenylamine 1a. The diphenylamide **6a** (4 g, 5.5 mmol) was refluxed with potassium hydroxide pellets (9 g, 0.16 mol) in ethanol (35 cm^3) for 2 h, after which the reaction mixture was cooled, poured into water (100 cm^3) and extracted with ethyl acetate (3 × 20 cm^3). The combined extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a brown oil which crystallised when scratched to give a light brown solid which was recrystallised from aqueous ethanol to yield buff needles of the *title compound* **1a** (3.25 g, 97%); mp 38 °C (Found: C, 77.9; H, 6.7; N, 6.4. $C_{14}H_{14}FN$ requires C, 78.1; H, 6.5; N, 6.5%); δ_H 2.24 (3 H, s, 2′-Me), 2.30 (3 H, s, 5′-Me), 5.47 (1 H, br s, NH), 6.76–6.83 (1 H, m, 6-H), 6.81 (1 H, dd, *J* 8, 2 Hz, 4′-H), 6.99 (1 H, qd, *J* 8, 2 Hz, 4-H), 7.00 (1 H, td, *J* 8, 2 Hz, 3-H), 7.05 (1 H, d, *J* 2, 6′-H), 7.05 (1 H, td, *J* 8, 2, 5-H) and 7.11 (1 H, d, *J* 8, 2 Hz, 3′-H); δ_F −134.0; *m*/*z* 216 (15%), 215 (M$^+$, 100), 214 (11), 194 (12), 176 (12), 161 (24) and 120 (12); λ_{max}/nm 273 (ε/dm^3 mol^{-1} cm^{-1} 7483); ν_{max}(Nujol)/cm^{-1} 3442 (NH).

4-Fluoro-2′,5′-dimethyldiphenylamine 1b

(i) *N*-Acetyl-4-fluoro-2′,5′-dimethyldiphenylamine 6b. 4-Fluoroacetanilide **4b** (5.23 g, 34 mmol), potassium carbonate (4 g), pre-treated copper bronze (4 g) and 2-bromo-1,4-dimethylbenzene (10.88 g, 59 mmol) were heated together at 180 °C under dry N_2 for 7 h. On cooling, the mixture was diluted with ethyl acetate (150 cm^3) and stirred overnight. The solids were filtered off and washed with ethyl acetate, and the combined filtrate and washings were evaporated to dryness under reduced pressure. The residual solid was purified by column chromatography on silica using light petroleum (bp 40–60 °C)–ethyl acetate as eluent to give two solids, one of which was unchanged 4-fluoroacetanilide (1.10 g). The other was recrystallised from aqueous ethanol to give white crystals of the *title compound* **6b** (5.16 g, 74% corr.), mp 128 °C (Found: C, 74.5; H, 6.3; N, 5.4. $C_{16}H_{16}FNO$ requires C, 74.7; H, 6.2; N, 5.5%); δ_H 1.97 (3 H, s, COMe), 2.17 (3 H, s, 2′-Me), 2.34 (3 H, s, 5′-Me), 6.95 and 6.98 (2 × 1 H, 2 × dd, *J* 8, 2, 2-H, 6-H), 7.08 (1 H, d, *J* 8, 3′-H), 7.26 and 7.28 (2 × 1 H, 2 × dd, *J* 8, 2, 3-H,

5-H); *m/z* 257 (M^+, 54), 215 (100), 214 (36), 198 (25), 136 (61), 77 (23) and 43 (52); ν_{max}(Nujol)/cm^{-1} 1673 (C=O).

(ii) The diphenylamine 1b. The diphenylamide **6b** (4.84 g, 19 mmol) was hydrolysed with potassium hydroxide (9 g, 0.16 mol) in ethanol, as described above, to give a green oil which was purified by column chromatography on silica using light petroleum (bp 40–60 °C)–ethyl acetate as eluent to give the *diphenylamine* **1b** as a pale green oil (2.71 g, 65%) (Found: C, 77.9; H, 6.5; N, 6.4. $C_{14}H_{14}FN$ requires C, 78.1; H, 6.5; N, 6.5%); δ_H 2.20 (3 H, s, 2′-Me), 2.25 (3 H, s, 5′-Me), 5.23 (1 H, br s, NH), 6.71 (1 H, dd, *J* 8, 2, 4′-H), 6.89–6.99 (5 H, m, 2-H, 3-H, 5-H, 6-H, 6′-H) and 7.06 (1 H, d, *J* 8, 3′-H); *m/z* 215 (M^+, 43%), 119 (86), 105 (66), 90 (100), 83 (67), 63 (85) and 51 (48); λ_{max}/nm 275 (ε/dm^3 mol^{-1} cm^{-1} 5382); ν_{max}/cm^{-1} 3413 (NH).

Photolysis of the diphenylamine 1a

The diphenylamine **1a** (0.65 g, 3.02 mmol) was irradiated in ethanol (100 cm^3) for 96 h using a medium-pressure mercury lamp. Removal of the ethanol under reduced pressure and column chromatography on silica using light petroleum (bp 40–60 °C)–ethyl acetate as eluent gave the following products: 1,4-dimethylcarbazole **7** (0.31 g, 53%), mp 96–98 °C (lit.,[11] 97–98 °C); δ_H 2.54 (3 H, s, 1-Me), 2.85 (3 H, s, 4-Me), 6.94 (1 H, d, *J* 8, 3-H), 7.13 (1 H, d, *J* 8, 2-H), 7.25 (1 H, t, *J* 8, 6-H), 7.41 (1 H, t, *J* 8, 7-H), 7.48 (1 H, d, *J* 8, 8-H), 8.01 (1 H, br s, NH) and 8.17 (1 H, d, *J* 8, 5-H); *m/z* 196 (17%), 195 (M^+, 100), 194 (39), 180 (33), 98 (13); λ_{max}/nm 369 (ε/dm^3 mol^{-1} cm^{-1} 533), 335 (1953), 323 (1775), 289 (9763), 278 (7278) and 263 (3195); ν_{max}(Nujol)/cm^{-1} 3408 (NH), 1615 and 1589 (C=C); 8-fluoro-1,4-dimethylcarbazole **2** (0.07 g, 11%); mp 99–102 °C (lit.,[12] 102–104 °C) (Found: C, 78.7; H, 5.9; N, 6.5. Calc. for $C_{14}H_{12}FN$: C, 78.9; H, 5.6; N, 6.6%); δ_H 2.55 (3 H, s, 1-Me), 2.83 (3 H, s, 4-Me), 6.95 (1 H, d, *J* 8, 3-H), 7.13 (3 H, m, 2-H, 6-H, 7-H), 7.91 (1 H, dd, *J* 7, 3, 5-H), 8.14 (1 H, br s, NH, exchanges with D_2O); δ_F −135.6; *m/z* 214 (MH^+, 16%), 213 (100), 198 (34) and 107 (15); λ_{max}/nm 333 (ε/dm^3 mol^{-1} cm^{-1} 9241), 320 (8056), 283 (25 828), 273 (16 113) and 264 (10 900); ν_{max}(Nujol)/cm^{-1} 3465 (NH) and 6-*ethoxy*-2-*fluoro*-2′,5′-dimethyldiphenylamine **8** (0.15 g, 19%), mp 69–70 °C (Found: C, 74.1; H, 7.1; N, 5.6; $C_{16}H_{18}FNO$ requires C, 74.1; H, 7.0; N, 5.4%); δ_H 1.37 (3 H, t, *J* 7, CH_3), 2.23 (3 H, s, 2′-Me), 2.32 (3 H, s, 5′-Me), 4.06 (2 H, q, *J* 7, CH_3CH_2), 5.38 (1 H, br s, NH), 6.45 (1 H, dd, *J* 5, 2, 6′-H), 6.64 (1 H, dd, *J* 8, 2, 4′-H), 6.71 (1 H, dt, *J* 8, 2, 5-H), 6.78 (1 H, td, *J* 8, 2, 3-H), 6.96 (1 H, q, *J* 8, 4-H) and 7.00 (1 H, d, *J* 8, 3′-H); δ_C 14.91 (2′-Me), 17.54 (5′-Me), 21.57 (CH_2CH_3), 64.75 (CH_2CH_3), 107.95 (C-7), 108.85 (C-9), 109.08 (C-11), 115.39 (C-6), 121.04 (C-4), 122.21 (C-2), 122.99 (C-10), 130.21 (C-3), 136.24 (C-5), 142.66 (C-12), 152.79 (C-1) and 152.86 (C-8); δ_F −119.0; *m/z* 260 (17%), 259 (M^+, 100), 245 (8), 231 (8), 230 (19), 216 (9), 215 (54), 214 (9), 212 (14), 210 (19) and 77 (8); λ_{max}/nm 275 (ε/dm^3 mol^{-1} cm^{-1} 15 819); ν_{max}(Nujol)/cm^{-1} 3392 (NH), 1610 and 1580 (C=C).

Photolysis of the diphenylamine 8

The diphenylamine **8** (61.5 mg) was irradiated for 24 h in ethanol (30 cm^3); although the starting material was largely unchanged a little (1.2%; calculated from ^{1}H NMR of reaction mixture) 8-*ethoxy*-1,4-*dimethylcarbazole* **9** was produced [Found: *m/z* (HRMS): 239.1310. $C_{16}H_{18}NO$ requires *m/z* 239.1310]; δ_H 1.57 (3 H, t, *J* 7, CH_3), 2.58 (3 H, s, 1-Me), 2.86 (3 H, s, 4-Me), 4.29 (2 H, q, *J* 7, CH_3CH_2), 7.79 (1 H, d, *J* 8, 5-H) and 8.24 (1 H, br s, NH); aromatics obscured by peaks from the diphenylamine **8**; *m/z* 239 (M^+, 100%), 210 (97), 182 (43) and 167 (15).

Photolysis of 8-fluoro-1,4-dimethylcarbazole 2

The carbazole **2** (68.3 mg) was irradiated for 24 h in ethanol (30 cm^3) to give recovery of unchanged starting material.

Photolysis of the diphenylamine 1b

The diphenylamine **1b** (1 g, 4.6 mmol) was irradiated in ethanol (100 cm^3) for 48 h with samples being taken at regular intervals. The samples were evaporated under reduced pressure to give a dark-green gum which was column chromatographed to give the diphenylamine **1b** (0.21 g); 6-fluoro-1,4-dimethylcarbazole **25** (0.27 g, 35% corr.), mp 89–91 °C (lit.,[13] 91–92 °C); δ_H 2.55 (3 H, s, 1-Me), 2.81 (3 H, s, 4-Me), 6.95 (1 H, d, *J* 7, 3-H), 7.17 (1 H, d, *J* 7, 2-H), 7.18 (1 H, td, *J* 9, 2, 7-H), 7.39 (1 H, dd, *J* 9, 4, 8-H), 7.84 (1 H, dd, *J* 10, 2, 5-H) and 7.93 (1 H, br s, NH), *m/z* 213 (M^+, 50%), 210 (51), 198 (86), 184 (84), 106 (59), 105 (100), 99 (69), 92 (76) and 63 (86); λ_{max}/nm 345 (ε/dm^3 mol^{-1} cm^{-1} 4265), 332 (2986), 293 (18 553) and 283 (11 729); and 1,4-dimethylcarbazole **7** (0.34 g, 47% corr.); mp 96–98 °C (lit.,[11] 97–98 °C); δ_H 2.54 (3 H, s, 1-Me), 2.85 (3 H, s, 4-Me), 6.94 (1 H, d, *J* 8, 3-H), 7.13 (1 H, d, *J* 8, 2-H), 7.25 (1 H, t, *J* 8, 6-H), 7.41 (1 H, t, *J* 8, 7-H), 7.48 (1 H, d, *J* 8, 8-H), 8.01 (1 H, br s, NH) and 8.17 (1 H, d, *J* 8, 5-H); *m/z* 196 (17%), 195 (M^+, 100), 194 (39), 180 (33) and 98 (13); λ_{max}/nm 369 (ε/dm^3 mol^{-1} cm^{-1} 533), 335 (1953), 323 (1775), 289 (9763) and 278 (7278); ν_{max}(Nujol)/cm^{-1} 3408 (NH), 1615 and 1589 (C=C).

Crystal data

$C_{16}H_{18}FNO$, M = 259.31. Monoclinic, a = 7.8580(10), b = 18.7510(10), c = 9.538(4) Å, $\alpha = \beta = \gamma = 90°$, V = 1405.4 (6) Å^3, space group $P2_1/c$, Z = 4, D_M = 1.226 g cm^{-3}. White crystals. Crystal dimensions 0.10 × 0.10 × 0.08 mm, μ(Mo-Kα) = 0.085 mm^{-1}.

Data collection and processing

FAST TV Area detector diffractometer following previously described procedures.[14] From the ranges scanned, 4369 data were recorded ($2.17 \leqslant \theta \leqslant 25°$), 2114 unique ($R_{int}$ = 0.0546).

Structure analysis and refinement

Direct methods and refined on F_o^2 by full-matrix least-squares (SHELXL-93)[15] using all 2114 data to final wR (on F_o^2) and R (on F) values of 0.1756 and 0.0642 for 244 parameters (non-hydrogen atoms anisotropic; hydrogens in idealised positions with U_{iso}s tied to the U_{eq}s of the parents). The corresponding R-values for data with $I > 2\sigma(I)$ are 0.1008 and 0.0391, respectively. Full details of data collection and structure refinements, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

Acknowledgements

We thank the EPSRC for the award of a studentship to R. L.

† For details, see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1

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Paper 5/06000A
Received 11*th September* 1995
Accepted 19*th October* 1995