

Polyhalogenoheterocyclic Compounds. Part 40.¹ Tertiary Aromatic Amines As Carbon-Nucleophiles With Activated Perfluorinated Aromatic Compounds

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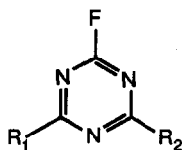
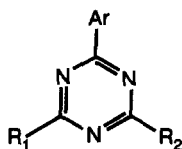
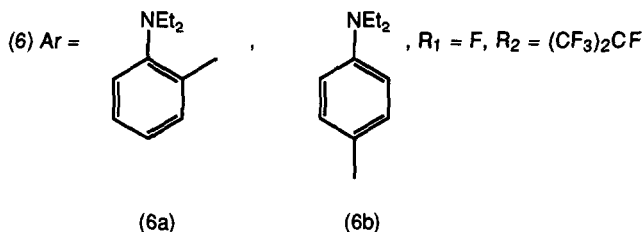
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Dedicated to Professor C.W. Rees on the occasion of his 65th. birthday.

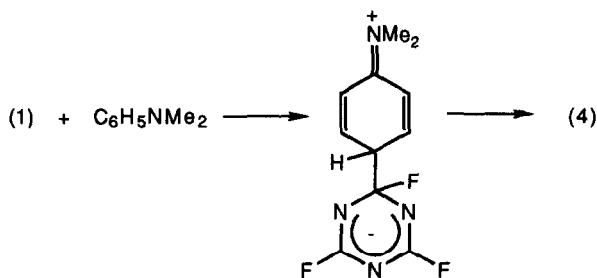
Abstract: *The first examples illustrating that aromatic amines may act as carbon nucleophiles, in reactions with fluorinated aromatic compounds, are described. Products with potential for considerable charge separation are described.*

Due to activity in the field of non-linear optics, synthesis of simple molecules with high dipole moments has become of interest² and the work described in this paper involves products with the potential for considerable charge-separation. In this series of papers we have been describing synthesis and reactions of a whole class of new highly-fluorinated heterocyclic compounds and many of these systems are very reactive towards nucleophiles. It has been emphasised recently, that reactions of acyclic tertiary amines with activated aromatic systems are rare.³ Although reactions of trichloro-1,3,5-triazine with a variety of tertiary aromatic amines have, indeed, been explored⁴ it is surprising that analogous reactions of fluorinated heterocyclic compounds have not been reported, in spite of the normally greater reactivity of carbon-fluorine than carbon-chlorine bonds in nucleophilic aromatic substitution. Here, however, we describe a series of such processes.

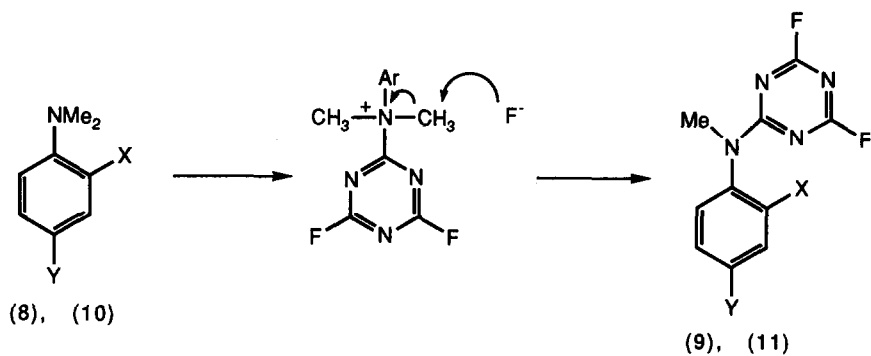
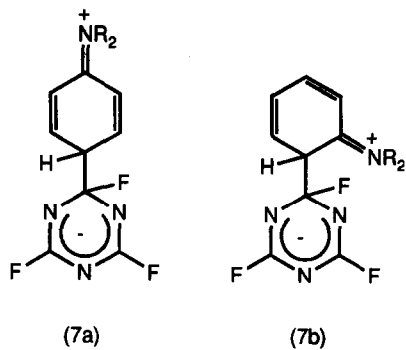
We have used, essentially, trifluoro-1,3,5-triazine (1) and the corresponding perfluoroisopropyl derivatives (2,3) prepared by now standard perfluoroalkylation procedures.⁵ Addition of N,N-dimethylaniline to a solution of (1) in acetonitrile gave an immediate blue colouration, due presumably to charge-transfer interaction, of some type, but on heating under reflux the colour changed gradually to dark red. Work-up gave the mono-substituted derivative (4) whose structure followed simply from n.m.r. data. Clearly, the N,N-dimethylaniline reacts through carbon as a nucleophile, according to Scheme 1. Using the same procedure, reaction of dimethyl- or diethyl-aniline with (2) gave a mixture of

(1) $R_1 = R_2 = F$ (2) $R_1 = F, R_2 = (CF_3)_2CF$ (3) $R_1 = R_2 = (CF_3)_2CF$ (4) $Ar = NMe_2C_6H_4-, R_1 = R_2 = F$ (5) $Ar = NMe_2C_6H_4-, R_1 = F, R_2 = (CF_3)_2CF$ 

mono-substituted products, (5), (6a), (6b) respectively, where the diethylaniline reacts both through positions which are ortho- and para- to the dialkylamino group. This is a surprising difference and, consequently, the crude products (5) arising from reaction with dimethylamine were examined carefully by n.m.r., to determine whether an isomer had been lost on work-up and recrystallisation. Nevertheless, only one isomer could be detected in that case. Intuitively, we would have anticipated *less* of the product arising from the intermediate (7b) than (7a), when we change R from Me to Et, simply on the basis of steric arguments but what we have observed is actually the *reverse* and, at this stage, we have no convincing argument to explain this difference. It is probable that charge separation is lower in (7b) than (7a), but it is not clear why the importance of this factor should alter from Me to Et.

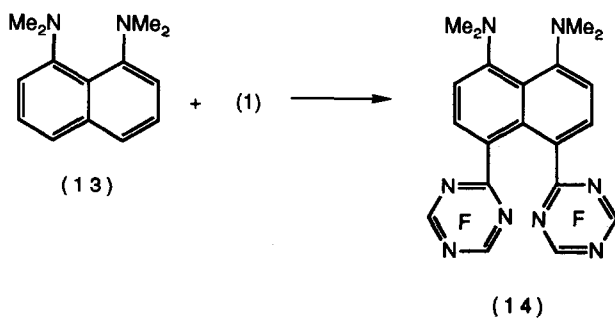
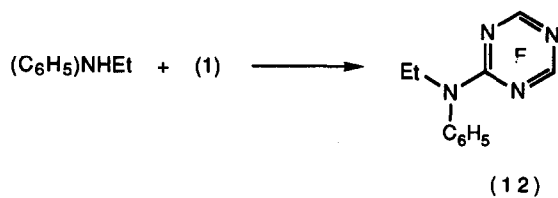


Scheme 1.



(8), (9) X = OMe, Y = H

(10), (11) X = H, Y = NMe₂



Reaction of trifluorotriazine (1) with ortho-methoxydimethylaniline (8) took a different route. In this case, reaction occurred through nitrogen as the nucleophile, giving the triazine derivative (9). It could be argued that the ortho-methoxy group inhibits conjugation of the dimethylamino group with the ring, but we also found that the para-dimethylaminobenzene (10) gave an analogous product (11). Consequently, the different behaviour must stem from the fact that increasing the electron density in the ring, by introducing another dimethylamino group or the methoxy group, also makes the nitrogen a better nucleophile. Secondary amines generally react through nitrogen and, in this case, N-methylaniline, gave the corresponding product (12).

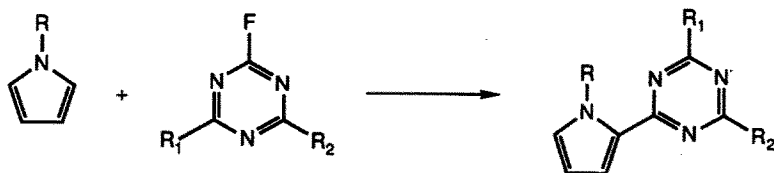
Proton sponge (13) presents an interesting example of a difunctional aromatic amine and electrophilic substitution at the 4,5-positions is known.⁶ In this case, reaction with trifluorotriazine (1) gave the analogous di-substituted derivative (14) as red crystals, consistent with other electrophiles..

Both pyrrole and N-methylpyrrole, as well as N-methylindole, act like N,N-dimethylaniline in reacting exclusively through carbon and these systems are, of course, very susceptible to electrophilic attack in general. It is interesting that in these examples, the products (15)-(23) were isolated as pale yellow crystals.

Thus, these reactions of fluorinated triazines with tertiary aromatic amines, provide examples of nucleophilic attack of aromatic amines, through carbon centres. It is clear that these processes only occur with the most activated systems because N-methylindole reacted in a similar way with tetrafluoropyrimidine (24) giving (25) under more vigorous conditions, but we were unable to achieve reactions with pentafluoropyridine, even after heating in a sealed tube for prolonged periods. There is, however, strong interaction between these systems because a solid is formed instantly on mixing pentafluoropyridine with N-methylindole, as neat liquids, but examination of a solution of this solid revealed only starting materials. Therefore, formation of the solid can only involve relatively weak intermolecular interactions of a type that has been investigated previously with other perfluoroaromatic systems.⁷

NMR-Data

One of the interesting questions, is the degree of charge-separation that occurs in the simple products, for example (4,4a) and a useful model is the σ -complex (26) obtained by adding cesium fluoride to trifluorotriazine (1).⁸ Comparing chemical shift data for the ring fluorines in these systems, Table 1., it is clear that the shifts for ring fluorines in (4) and (6b) are significantly to a higher field than (1), but mid-way between the values for (1) and the sigma complex (26). This is a clear demonstration of the charge separation represented by (4,4a).



(15) R = H, R₁ = R₂ = F

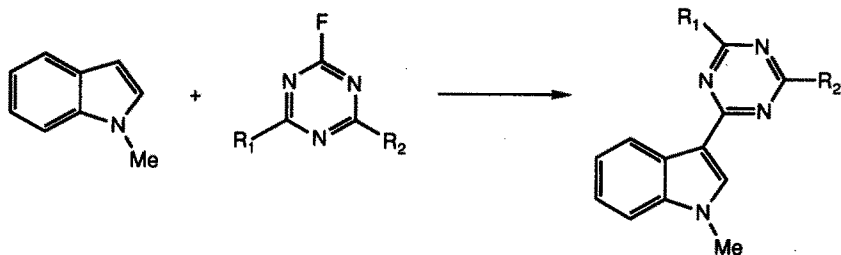
(16) R = H, R₁ = F, R₂ = (CF₃)₂CF

(17) R = H, R₁ = R₂ = (CF₃)₂CF

(18) R = Me, R₁ = R₂ = F

(19) R = Me, R₁ = F, R₂ = (CF₃)₂CF

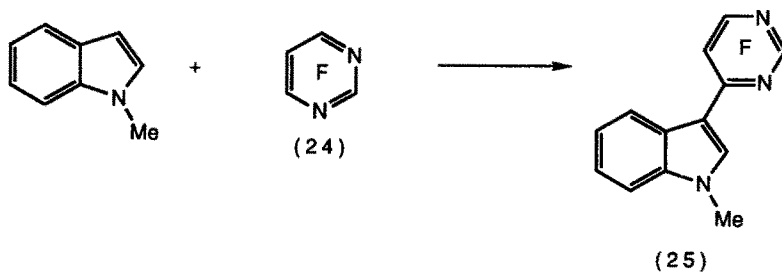
(20) R = Me, R₁ = R₂ = (CF₃)₂CF

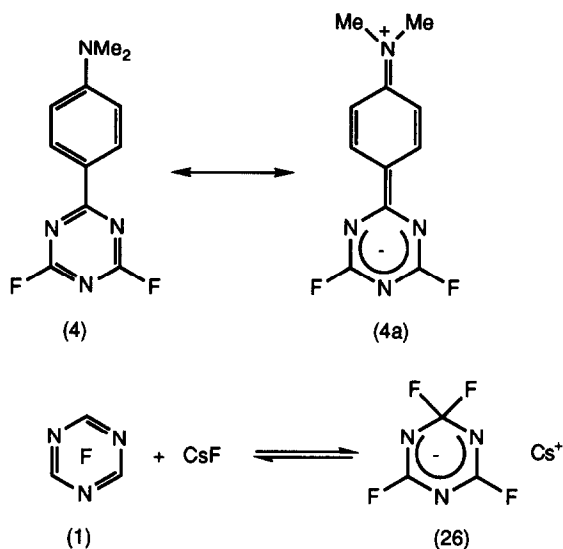


(21) R = Me, R₁ = R₂ = F

(22) R = Me, R₁ = F, R₂ = (CF₃)₂CF

(23) R = Me, R₁ = R₂ = (CF₃)₂CF

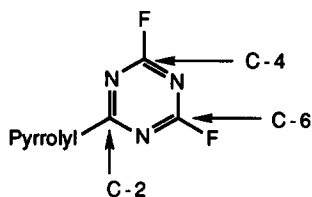




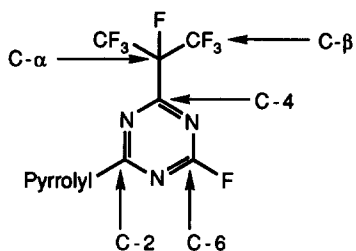
Surprisingly, there is comparatively little C-13 data for polyfluorinated aromatic compounds recorded in the literature. Problems often arise because of the extensive long-range coupling which can occur and the difficulties associated with broad-band fluorine decoupling which preclude simple solutions to this problem and some of our data is recorded in Table 2

Table 1. ¹⁹F Chemical Shifts (ppm from CFC1₃)

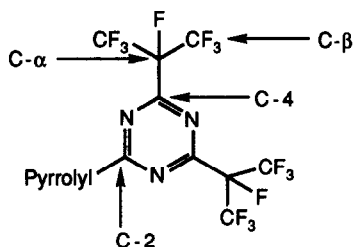
Compound	Ring F	QE	QE ₃
(1)	- 3.3		
(2)	- 3.2	- 8.3	- 7.4
(26)	- 5.1		
(4)	- 4.0		
(5)	- 3.7	- 8.4	- 7.4
(6b)	- 4.3	- 18.8	- 7.8

Table 2. C-13 NMR shifts.**Monosubstituted Triazine (15)**

<u>Compound</u>	<u>C-2</u>	<u>C-4</u>
	t (3J)	d d (1J , 3J)
(15)	172.3 (14)	172.0 (226, 19)

Disubstituted Triazines (16) and (19)

<u>Compound</u>	<u>C-2</u>	<u>C-4</u>	<u>C-6</u>	<u>C-α</u>	<u>C-β</u>
	dd (3J , 4J)	dd (2J , 3J)	dd (1J , 4J)	d sept (1J , 2J)	qd (1J , 2J)
(16)	170.4 (13, 3)	169.2 (22, 12)	171.2 (229, 3)	90.9 (211, 33)	121.3 (288, 27)
(19)	170.2 (13, 3)	168.2 (21, 12)	170.3 (228, 3)	90.3 (211, 35)	120.8 (288, 27)

Table 2 continuedTrisubstituted Triazines (17) and (20)

<u>Compound</u>	<u>C-2</u>	<u>C-4</u>	<u>C-α</u>	<u>C-β</u>
	t (4 J)	dd (2 J, 3 J)	d sept (1 J, 2 J)	qd (1 J, 2 J)
(17)	166.5 (3)	165.9 (22, 4)	90.4 (211, 33)	120.8 (288, 27)
(20)	166.6 (3)	165.5 (22, 3)	90.2 (218, 33)	120.7 (288, 27)

EXPERIMENTAL**Reactions of Pyrroles with Fluorinated Triazines**

General Procedure - A mixture containing a pyrrole and the corresponding fluorinated triazine was refluxed in acetonitrile (5ml) for two hours. On cooling, water (15ml) was added to the reaction mixture to precipitate the solid product, which was collected by filtration, dried in a desiccator and purified by vacuum sublimation (Oil bath temperature 130°C, <0.1mm Hg). All yields are quoted for pure, isolated products.

Reaction of Pyrrole with Trifluoro-s-triazine. Pyrrole (0.5g, 7.4mmol) and trifluoro-s-triazine (1.0g, 7.4mmol) gave 2-(pyrrol-2-yl)-4,6-difluoro-s-triazine (15) (0.87g, 65%) as white crystals; m.p. 156-160°C; Anal. Calc. for C₇H₄N₄F₂: C, 46.15; H, 2.2; N, 30.75. Found: C, 46.0; H, 2.1; N, 30.8. λ_{max} (CH₃CN) 310.1nm (log₁₀ε 4.48); ν_{max} 3420cm⁻¹ (N-H); m/z (EI⁺) 182 (M⁺, 100%).

Reaction of Pyrrole with Perfluoroisopropyl-s-triazine. Pyrrole (0.80g, 12mmol) and perfluoroisopropyl-s-triazine (2) (2.5g, 9mmol) gave 2-(pyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (16) (2.05g, 71%) as pale yellow needles; m.p. 112-115°C. Anal. Calc. for C₁₀H₄N₄F₈: C, 36.1; H, 1.2; N, 16.85; Found: C, 35.7; H, 1.2; N, 16.5. λ_{max} (CH₃CN) 336.0nm (log₁₀ε 4.41); ν_{max} 3480cm⁻¹ (N-H); m/z (EI⁺) 332 (M⁺, 100%).

Reaction of Pyrrole with Perfluorodi-isopropyl-s-triazine.- Pyrrole (0.27g, 4.0mmol) and perfluorodi-isopropyl-s-triazine (1.46g, 3.3mmol) gave 2-(pyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (17) (1.1g, 68%) as pale yellow needles; m.p. 64-66°C. Anal. Calc. for $C_{13}H_4N_4F_{14}$: C, 32.4; H, 0.8; N, 11.6; Found: C, 32.2; H, 0.75; N, 11.5. $\lambda_{\max}$ (CH_3CN) 344.8nm ($\log_{10}\epsilon$ 4.58); $\nu_{\max}$ 3470 cm^{-1} (N-H); m/z (El^+) 482 (M^+ , 100%).

Reaction of N-methylpyrrole with Trifluoro-s-triazine.- N-methylpyrrole (1.0g, 12mmol) and trifluoro-s-triazine (1.6g, 12mmol) gave 2-(N-methylpyrrol-2-yl)-4,6-difluoro-s-triazine (18) (1.06g, 45%) as pale yellow needles; m.p. 117-118°C. Anal. Calc. for $C_8H_6N_4F_2$: C, 49.0; H, 3.1; N, 28.6. Found: C, 48.5; H, 3.0; N, 28.4. $\lambda_{\max}$ (CH_3CN) 314.6nm ($\log_{10}\epsilon$ 4.44); m/z (El^+) 196 (M^+ , 75%).

Reaction of N-methylpyrrole with Perfluoroisopropyl-s-triazine.- N-methylpyrrole (0.30g, 3.7mmol) and perfluoroisopropyl-s-triazine (1.05g, 3.7mmol) gave 2-(N-methylpyrrol-2-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (19) (0.69g, 54%) as pale yellow needles; m.p. 110-111°C. Anal. Calc. for $C_{11}H_6N_4F_8$: C, 38.15; H, 1.7; N, 16.2; F, 43.95; Found: C, 38.2; H, 1.5; N, 15.9; F, 43.4. $\lambda_{\max}$ (CH_3CN) 324.5nm ($\log_{10}\epsilon$ 4.38); m/z (Cl^+ , NH_3) 346 (M^+-1 , 100%).

Reaction of N-methylpyrrole with Perfluorodi-isopropyl-s-triazine.- N-methylpyrrole (0.3g, 3.7mmol) and perfluorodi-isopropyl-s-triazine (1.5g, 3.5mol) gave 2-(N-methylpyrrol-2-yl)-4,6-perfluorodi-isopropyl-s-triazine (20) (0.73g, 48%) as pale yellow needles; m.p. 88-89°C. Anal. Cal. for $C_{14}H_6N_4F_{14}$: C, 33.9; H, 1.2; N, 11.3; F, 53.6. Found: C, 33.9; H, 1.1; N, 11.3; F, 53.9. $\lambda_{\max}$ (CH_3CN) 349.4nm ($\log_{10}\epsilon$ 4.33); m/z (El^+) 496 (M^+ , 100%).

Reactions of N-methylindole with Fluorinated Triazines

General Proceedure - A mixture containing N-methylindole and the corresponding fluorinated triazine was refluxed in acetonitrile (5ml) for 30mins. On cooling, water (15ml) was added to precipitate the solid product which was dried and purified by vacuum sublimation (Oil bath temperature 150°C, <0.1mm Hg).

Reaction of N-methylindole with Trifluoro-s-triazine.- N-methylindole (1.0g, 7.6mmol) and trifluoro-s-triazine (1.0g, 7.4mmol) gave 2-(N-methylindol-3-yl)-4,6-difluoro-s-triazine (21) (1.43g, 78%) as white crystals (from acetone); m.p. 244°C. Anal. Calc. for $C_{12}H_8N_4F_2$: C, 58.5; H, 3.25; N, 22.75 Found: C, 58.25; H, 3.25; N, 22.6. m/z (Cl^+ , NH_3) 247 (M^++1 , 100%).

Reaction of N-methylindole with Perfluoroisopropyl-s-triazine.- N-methylindole (0.7g, 5.3mmol) and perfluoroisopropyl-s-triazine (1.5g, 5.3mmol) gave 2-(N-methylindol-3-yl)-4-perfluoroisopropyl-6-fluoro-s-triazine (22) (1.76g, 90%) as pale yellow needles; m.p. 190-194°C.

Anal. Calc. for $C_{15}H_8N_4F_8$: C, 45.45; H, 2.0; N, 14.1; F, 38.4. Found: C, 45.7; H, 2.0; N, 14.2; F, 38.1. $\lambda_{\max}$ (CH_3CN) 262.4nm ($\log_{10}\epsilon$ 4.12), 355.3 (4.31); m/z (El^+) 396 (M^+ , 57%).

Reaction of N-methylindole with Perfluorodi-isopropyl-s-triazine .- N-methylindole (0.3g, 2.3mmol) and perfluorodi-isopropyl-s-triazine (1.0g, 2.3mmol) gave **2-(N-methylindol-3-yl)-4,6-perfluorodi-isopropyl-s-triazine** (23) (1.1g, 87%) as yellow crystals; m.p. 205-206°C. Anal. Calc. for $C_{18}H_8N_4F_{14}$: C, 39.55; H, 1.45; N, 10.25; F, 48.7. Found: C, 39.25; H, 1.45; N, 9.9; F, 48.9. $\lambda_{\max}$ (CH_3CN) 213.0nm ($\log_{10}\epsilon$ 4.56), 246.0 (4.02), 265.0 (4.23), 276.0 (4.14), 365.0 (4.53); m/z (El^+) 546 (M^+ , 100%).

Reaction of N-methylindole with Tetrafluoropyrimidine

A mixture containing N-methylindole (0.8g, 6mmol) and tetrafluoropyrimidine (1.0g, 6.5mmol) was refluxed overnight in acetonitrile (5ml). On cooling, water (15ml) was added to the reaction mixture to precipitate the solid product which was collected by filtration, dried, recrystallised from acetone as yellow plates and identified as **6-(N-methylindol-3-yl)-2,4,5-trifluoropyrimidine** (25) (0.58g, 36%); m.p. 231°C. Anal. Cal. for $C_{13}H_8N_3F_3$: C, 59.3; H, 3.05; N, 15.95; F, 21.7. Found: C, 59.35; H, 3.0; N, 15.9; F, 22.0. $\lambda_{\max}$ (CH_3CN) 214.0nm ($\log_{10}\epsilon$ 4.75), 263.0 (4.35), 344.0 (4.78); m/z (El^+) 263 (M^+ , 100%).

Reaction of N,N-Dimethylaniline with Trifluoro-s-triazine

A mixture containing N,N-Dimethylaniline (1.75g, 14mmol) and trifluoro-s-triazine (2.0g, 15mmol) was refluxed overnight in acetonitrile (5ml). On cooling a red/brown solid precipitated which was collected by filtration, washed with water and recrystallised from acetonitrile to yield pure **2-(4-N,N-dimethylaminophenyl)-4,6-difluoro-s-triazine** (4) (0.96g, 28%); m.p. 234-237°C. Anal. Cal. for $C_{11}H_{10}N_4F_2$: C, 55.9; H, 4.25; N, 23.7%. M^+ , 236.08735amu. Found: C, 55.6; H, 4.05; N, 23.5. M^+ , 236.08416. $\lambda_{\max}$ (CH_3CN) 364.0nm ($\log_{10}\epsilon$ 4.51); m/z (El^+) 236 (M^+ , 100%).

Reaction of N,N-Dimethylaniline with Perfluoroisopropyl-s-triazine

A mixture containing N,N-Dimethylaniline (0.5g, 4.1mmol) and perfluoroisopropyl-s-triazine (1.2g, 4.2mmol) was refluxed in acetonitrile (5ml) for 2 hr. On cooling, water (15ml) was added to precipitate the solid product which was collected by filtration and dried. Vacuum sublimation yielded pure **2-(4-N,N-dimethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine** (5) (0.62g, 36%) as a yellow solid; m.p. 168-170°C. Anal. Calc. for $C_{14}H_{10}N_4F_8$: C, 43.5; H, 2.6; N, 14.5. Found: C, 42.8; H, 2.5; N, 14.2. $\lambda_{\max}$ (CH_3CN) 368.8nm ($\log_{10}\epsilon$ 4.40); m/z (El^+) 386 (M^+ , 100%).

Reaction of N,N-Diethylaniline with Perfluoroisopropyl-s-triazine

A mixture containing N,N-Diethylaniline (0.5g, 3.4mmol) and perfluoroisopropyl-s-triazine (1.0g, 3.5mmol) was refluxed in acetonitrile (5ml) for 2 hr. On cooling, water (15ml) was added to precipitate the solid product which was collected by filtration and dried. Vacuum sublimation yielded a mixture of the two isomers, 2-(4-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (6b) and 2-(2-N,N-diethylaminophenyl)-4-perfluoroisopropyl-6-fluoro-s-triazine (6a) (0.63g, 45%) as a yellow solid. Anal. Calc. for $C_{16}H_{14}N_4F_8$: C, 46.35; H, 3.4; N, 13.5. Found: C, 46.0; H, 3.5; N, 13.6. $\lambda_{\max}$ (CH₃CN) 228.0nm (log₁₀ε 3.86), 260.9 (3.93), 405.3 (4.39); m/z (Cl⁺, NH₃) 415 (M⁺+1, 13%).

Reaction between Proton Sponge and Trifluoro-s-triazine

A mixture containing proton sponge (2.1g, 10mmol) and trifluoro-s-triazine (1.5g, 11mmol) was stirred at room temperature overnight in acetonitrile (5ml). The solution turned orange immediately and gradually red crystals precipitated which were collected by filtration and recrystallised from acetonitrile to yield pure 1,8-bis(dimethylamino)-4,5-bis(difluoro-s-triaz-1-yl)-naphthalene (14) (2.3g, 53%); m.p. 258-260°C. Anal. calc. for $C_{20}H_{16}N_8F_4$: C, 54.0; H, 3.6; N, 25.2%. M⁺, 444.1434amu. Found: C, 53.7; H, 3.6; N, 24.9. M⁺, 444.1272. m/z (Cl⁺, NH₃) 445 (M⁺+1, 100%). The ¹H NMR spectrum consists of a singlet at δ 3.09 (int. 6, NCH₃), and two AX systems in the aromatic region, 7.02-8.36 ppm, (each having intensity 2). These assignments are consistent with those reported earlier, for 4,5-disubstituted proton-sponge derivatives.⁹ One ¹⁹F resonance at δF -40.2 ppm was observed.

Reaction of N-ethylaniline with Trifluoro-s-triazine

A mixture containing N-ethylaniline (0.9g, 7.4mmol) and trifluoro-s-triazine (1.0g, 7.4mmol) was refluxed in acetonitrile (5ml) for 3 hr. The solvent was removed under reduced pressure to leave an off-white solid which was washed with water and collected by filtration. Vacuum sublimation yielded pure 2-(ethylphenylamino)-4,6-difluoro-s-triazine (12) (1.2g, 69%) as white needles; m.p. 63.5-64°C. Anal. Calc. for $C_{11}H_{10}N_4F_2$: C, 55.9; H, 4.2; N, 23.7. Found: C, 55.6; H, 4.0; N, 24.0. $\lambda_{\max}$ (CH₃CN) 236.0nm (log₁₀ε 4.26); m/z (EI⁺) 236 (M⁺, 47%).

Reaction of N,N-Dimethylamino-2-methoxybenzene (8) with Trifluoro-s-triazine

A mixture containing N,N-Dimethylamino-2-methoxybenzene (1.0g, 6.6mmol) and trifluoro-s-triazine (1.2g, 8.8mmol) was refluxed overnight in acetonitrile (5ml). Water (15ml) was added to the mixture to precipitate the solid product which was collected by filtration. Vacuum sublimation yielded pure 2-methyl(2-methoxyphenyl)-amino-4,6-difluoro-s-triazine (9) (0.51g, 31%) as white crystals;

m.p. 139°C. Anal. calc. for $C_{11}H_{10}N_4OF_2$: C, 52.4; H, 3.95; N, 22.2. Found: C, 52.25; H, 3.85; N, 22.35. m/z (El^+) 252 (M^+ , 9%), 221 (100, M^+-OMe).

Reaction of N,N,N',N'-tetramethyl-1,4-diaminobenzene (10) with Trifluoro-s-triazine

A mixture containing N,N,N',N'-tetramethyl-1,4-diaminobenzene (0.6g, 3.6mmol) and trifluoro-s-triazine (0.4g, 3.0mmol) was refluxed overnight in acetonitrile (5ml). Water was added to the mixture to precipitate the solid product which was collected by filtration. Vacuum sublimation yielded pure 2-methyl(4-N,N-dimethylaminophenyl)amino-4,6-difluoro-s-triazine (11) (0.12g, 15%) as white crystals. Anal. calc. for $C_{12}H_{13}N_5F_2$: C, 54.3; H, 4.9; N, 26.4. Found: C, 54.5; H, 5.1; N, 26.7. m/z (El^+) 265 (M^+ , 100%).

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