Synthesis of a series of dichloroamino- and dihalosulfonamido-1,3,5-triazines and investigation of their hindered rotation and stereodynamic behaviour by NMR spectroscopy

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Mono-substituted 1,3,5-triazines (*s*-triazines) have been prepared and characterised by NMR spectroscopy. The room temperature ^{13}C NMR spectra of dichloroamino-*s*-triazines show three signals for the triazine ring, clearly indicating that C(2) and C(3) are in inequivalent environments. At elevated temperatures, two of the signals broaden and coalesce. Conversely, a number of dihalosulfonamido-*s*-triazine compounds were found to display only one signal for C(2) and C(3), indicating that the degree of π-bonding in the exocyclic C–N bond in these compounds is less significant. The low temperature exchange limits for the dihalosulfonamido-*s*-triazine compounds are reported.

Introduction

Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) is an extremely important compound that finds widespread application in dye chemistry,[1] agriculture[2] and the textile industry.[3] Displacement of the chlorine atoms by nucleophiles such as amines, alcohols and phenols has been well documented[4] and a wide range of substitution products may be prepared. Considering the simplicity and widespread application of these compounds, it is somewhat surprising that so little has been reported on their stereodynamics. All studies to date have investigated restricted rotation in the more complicated di- and tri-amino-substituted *s*-triazines[5] (*s*-triazine = 1,3,5-triazine) and to our knowledge no reference has been made to the simpler mono-amino derivatives. During the course of our research on low surface energy textile treatments for cellulose, a number of dichloroamino-*s*-triazine derivatives were required. We now report their synthesis and stereodynamics as studied by NMR spectroscopy.

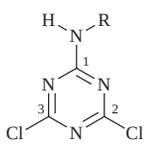
Results and discussion

Dichloroamino-s-triazine compounds, **1**, **2** and **3** were prepared by the treatment of cyanuric chloride with the corresponding alkylamine. Mono-substitution can be attained at 0 °C owing to electron-donation from the exocyclic nitrogen atom in the product increasing the electron density of the ring, which stabilises the remaining C–Cl bonds. The dichlorosulfonamido-*s*-triazine derivatives are prepared by the reaction of cyanuric chloride with the sodium salt of the corresponding sulfonamide. However, unlike the mono-amino derivatives, considerable care is needed in the preparation of the mono-sulfonamido analogues. The C–Cl bonds in these compounds remain labile to further substitution owing to the electron-withdrawing effect of the sulfonamide group[6] and low temperatures are required to avoid formation of the di- and tri-substituted derivatives. The degree of π-bonding in the exocyclic C–N bond in these compounds was therefore predicted to be much less than that in the mono-amino derivatives. Evidence for this is clearly discernible from the NMR data.

The room temperature proton decoupled ^{13}C NMR spectrum of **1**, **2** and **3** displayed three distinct signals for the triazine ring (Table 1) indicating inequivalence of C(2) and C(3). Increasing the temperature revealed that for **1** and **2**, the C(2) and C(3) resonances coalesce at approximately 120 °C. The fast exchange spectrum could not be recorded owing to the temperature limitation of the instrument. The fluorinated analogue **3** displays a lower coalescence temperature and the fast exchange limit for this compound was observed at 120 °C. The fluxional behaviour exhibited by these triazines is indicative of restricted rotation about the exocyclic C–N bond, due to π-bonding, and is comparable to that displayed by amides. In the case of **3**, the lower coalescence temperature indicates that the inductive effect of the perfluoroalkyl chain is sufficient to diminish the degree of double-bond character, despite the presence of the methylene spacer group (*cf.* $CH_3CH_2NH_2$, $K_b = 4.5 \times 10^{-4}$, $CF_3CH_2NH_2$, $K_b = 5.0 \times 10^{-9}$).[7]

The room temperature proton decoupled ^{13}C NMR data for the sulfonamide derivatives **4**, **5**, **8**† and **9** displayed only two resonances for the triazine ring, indicating that C(2) and C(3) are equivalent owing to free rotation of the sulfonamide group about the exocyclic C–N bond (fluorine coupling in **8** and **9** causes C(2)/C(3) to appear as a doublet of doublets and C(1) as a triplet). Therefore, in contrast to the amino analogues, relatively little double bond character exists between the sulfonamide nitrogen and the triazine ring. The free energies of activation for rotation ($\Delta G^{\ddagger}$) were estimated and are presented in Tables 1 and 2. The $\Delta G^{\ddagger}$ values for the sulfonamide derivatives were significantly lower than those obtained for the amino-triazines.

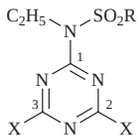
Table 1 ^{13}C NMR data for dichloroamino-*s*-triazine compounds and estimated values of the free energy of rotation ($\Delta G^{\ddagger}$)



No.	R	Solvent	*T*/°C	δ_C/ppm (proton decoupled) C(1)	δ_C/ppm (proton decoupled) C(2)/C(3)	$\Delta G^{\ddagger}$/kJ mol^{-1}
1	C_8H_{17}	$CDCl_3$	26	166.5	170.2, 171.3	78
2	C_2H_5	$CDCl_3$	20	165.4	169.2, 170.8	—
3	$CH_2C_7F_{15}$	$CDCl_3$	29	166.8	170.6, 171.6	79
		$C_6D_5NO_2$	120	167.5	171.2	

† A pure sample of triazine **8** could not be obtained, however the signals corresponding to the impurities were remote from the area of interest.

Table 2 ^{13}C NMR data for dihalosulfonamido-*s*-triazine compounds (b: broad, t: triplet, dd: doublet of doublets) and estimated values of the free energy of rotation ($\Delta G^{\ddagger}$)



					δ_C/ppm (proton decoupled)		
No.	R	X	Solvent	T/°C	C(1)	C(2)/(3)	$\Delta G^{\ddagger}$/kJ mol^{-1}
4	C_8H_{17}	Cl	d_8-THF	0	166.1	171.3	44
				−70	165.9	171 (b), 172 (b)	
				−90	165.8	170.2, 171.4	
5	$C_6H_4CH_3$	Cl	d_8-THF	24	165.1	171.1	—
				−50	164.8	170 (b), 172 (b)	
				−90	164.6	169.8, 171.2	
6	C_8F_{17}	Cl	d_8-THF	24	166.2	172.1	—
				−70	166.1	171.8	
7	C_8F_{17}	F	d_8-THF	2	170.6 (t)	172.4 (dd)	—
				−60	170.5 (t)	172.2 (dd)	
8	C_8H_{17}	F	d_8-THF	20	170.3 (t)	172.0 (dd)	44
				−50	170.0 (t)	173 (b), 170 (b)	
				−90	170.0 (t)	171.2 (dd), 172.1 (dd)	
9	$C_6H_4CH_3$	F	d_8-THF	24	169.3 (t)	171.8 (dd)	44
				−60	168.9 (t)	170 (b), 173 (b)	
				−90	168.8 (t)	171.0 (dd), 171.9 (dd)	

In an attempt to observe the fluxional behaviour of the sulfonamide group, low-temperature ^{13}C NMR spectra were recorded. The C(2)/C(3) resonance in **4**, **5**, **8** and **9** broadens as the temperature decreases and almost disappears at approximately −50 °C. At −70 °C, C(2) and C(3) appear as two individual resonances and slow exchange is observed at approximately −90 °C.

The perfluoroalkyl derivatives **6** and **7** displayed a similar trend to that observed for **3**, where the coalescence temperature of the respective class of triazine was lowered by the strong electron-withdrawing capacity of the perfluoroalkyl group.[6,8] Unfortunately, the solution became gelatinous on further cooling and the slow exchange spectrum of **6** and **7** could not be recorded.

In conclusion, the syntheses and stereodynamic behaviour of various dichloroamino-*s*-triazines and dihalosulfonamido-*s*-triazines are reported. The ^{13}C NMR data provides useful information about the distribution of electron density in a range of *s*-triazines. The data correlate well with the greater reactivity of the C–Cl bond in dichlorosulfonamido-*s*-triazines relative to dichloroamino-*s*-triazines. Surprisingly, although difluoro-*s*-triazines display greater reactivity relative to the dichloro-analogues, significant differences in their fluxional NMR behaviour were not observed. A more detailed study of coalescence temperature is therefore required. The dihalo-*s*-triazines containing a perfluorosulfonamido-group exhibited the lowest coalescence temperature of the compounds investigated.

Experimental

Instrumentation

NMR spectra were measured using a JEOL Lambda 300 (^{1}H 300.4 MHz; ^{13}C 75.45 MHz), a JEOL 400 GXD (^{1}H 399.65 MHz; ^{13}C 100.4 MHz) and a JEOL Lambda 500 (^{1}H 500 MHz; ^{13}C 125.65 MHz; ^{19}F 470.4 MHz) spectrometer. All spectra were measured at ambient temperature (294 K) unless otherwise noted. Typical acquisition parameters were 8 scans for ^{1}H spectra collected into 32768 data points, 500 scans for ^{13}C spectra collected into 32768 data points and 16 scans for ^{19}F collected into 65536 data points. The free energies of activation for rotation ($\Delta G^{\ddagger}$/kJ mol^{-1}) were calculated using the following equation: $\Delta G^{\ddagger} = RT_c[23 + 2.3\log_{10}(T_c/\Delta\nu)]$ where T_c = coalescence temperature (K), $\Delta\nu$ = frequency separation (Hz) and R = gas constant (J mol^{-1}).[9] Mass spectra were obtained by positive liquid secondary ion mass spectrometry (LSIMS) using a Micromass Autospec SQ Mass Spectrometer. Melting points are uncorrected.

Solvents and reagents

Analytical grade solvents were used as supplied. Cyanuric chloride (Aldrich) was recrystallised from chloroform. Cyanuric fluoride and *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonamide (Fluorochem) were used as supplied. 4-Methylbenzenesulfonyl chloride and octanesulfonyl chloride (Aldrich) were used as supplied. *N*-Ethyloctane-1-sulfonamide and *N*-ethyl-4-methylbenzenesulfonamide were prepared from the corresponding sulfonyl chloride and ethylamine gas in dichloromethane.

***N*-Octyl-4,6-dichloro-1,3,5-triazin-2-amine 1.** Cyanuric chloride (2.86 g, 15.5 mmol), dissolved in chloroform (100 cm^3), was added to a solution of sodium carbonate (1.64 g, 15.5 mmol) dissolved in water (40 cm^3). The two-phase mixture was stirred vigorously and cooled to 0–5 °C. Octylamine (2.00 g, 15.5 mmol) dissolved in chloroform (5 cm^3) was added dropwise. The reaction mixture was stirred vigorously for 1 h at 0–5 °C and then allowed to warm to room temperature. The organic layer was separated and washed with water (3 × 10 cm^3) and dried over sodium sulfate. Filtration and removal of the chloroform by evaporation under reduced pressure afforded *N*-octyl-4,6-dichloro-1,3,5-triazin-2-amine **1** (3.66 g, 85%) as a white solid, mp 58–60 °C (Found: C, 47.7; H, 6.6; N, 20.2; $C_{11}H_{18}N_4Cl_2$ requires C, 47.7; H, 6.5; N, 20.2%); δ_H (300 MHz; $C_6D_5NO_2$) 0.78 (3H, t, J 7 Hz, CH_3), 1.16 [10H, m, $(CH_2)_5$], 1.60 (2H, m, CH_2CH_2N), 3.44 (2H, m, CH_2N), 6.90 (1H, t, J 5.85 Hz, NH); δ_C (75 MHz; $C_6D_5NO_2$) 14.4 (CH_3), 23.3, 27.3, 29.5, 29.8, 29.9 and 32.4 (CH_2), 42.2 (CH_2N), 166.5 (triazine C–NH), 170.2 (triazine C–Cl), 171.3 (triazine C–Cl); *m*/*z* 277 [$(M + H)^+$, 100%], 305 [$(M + C_2H_5)^+$, 20], 291 [$(M + CH_3)^+$, 6], 241 [$(M - Cl)^+$, 54], 219 [$(M - C_4H_9)^+$, 6], 205 [$(M - C_5H_{11})^+$, 6], 191 [$(M - C_6H_{13})^+$, 8], 177 [$(M - C_7H_{15})^+$, 38].

***N*-Ethyl-4,6-dichloro-1,3,5-triazin-2-amine 2.** Cyanuric chlor-

ide (1.00 g, 5.42 mmol), dissolved in chloroform (40 cm^3), was added to a solution of sodium hydrogen carbonate (1.37 g, 16.3 mmol) dissolved in water (15 cm^3). Ethylamine hydrochloride (1.30 g, 15.9 mmol) dissolved in water (5 cm^3) was added dropwise and the two-phase mixture was stirred vigorously for 3 h at ambient temperature. The organic layer was separated and washed with water (3 × 10 cm^3) and dried over sodium sulfate. Filtration and removal of the chloroform by evaporation under reduced pressure afforded *N*-ethyl-4,6-dichloro-1,3,5-triazin-2-amine **2** (0.89 g, 85%) as a white solid: δ_H (400 MHz; $CDCl_3$) 1.23 (3H, t, *J* 7.27 Hz, $NHCH_2CH_3$), 3.53 (2H, quintet, *J* 6.66 Hz, $NHCH_2CH_3$), 7.24 (1H, br, $NHCH_2CH_3$); δ_C (100 MHz; $CDCl_3$) 14.30 (CH_3), 36.43 (CH_2), 165.4 (triazine C–NH), 169.2 (triazine C–Cl), 170.8 (triazine C–Cl).

***N*-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctyl)-4,6-dichloro-1,3,5-triazin-2-amine 3.** Cyanuric chloride (0.93 g, 5.00 mmol), dissolved in chloroform (20 cm^3), was added to a solution of sodium hydrogen carbonate (0.46 g, 5.50 mmol) dissolved in water (10 cm^3). The two-phase mixture was stirred vigorously and cooled to 0–5 °C. *N*-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctyl)amine (2.00 g, 5.00 mmol) dissolved in chloroform (5 cm^3) was added dropwise. The reaction mixture was stirred vigorously for 1 h at 0–5 °C and then allowed to warm to room temperature. The organic layer was separated and washed with water (3 × 10 cm^3) and dried over sodium sulfate. Filtration and removal of the chloroform by evaporation under reduced pressure afforded an oil, which on trituration with cyclohexane yielded a white solid. Evaporation of the cyclohexane gave *N*-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-4,6-dichloro-1,3,5-triazin-2-amine **3** (2.30 g, 84%) as a white solid, mp 79–80 °C (Found: C, 24.1; H, 0.5; N, 10.4; $C_{11}H_3N_4Cl_2F_{15}$ requires C, 24.2; H, 0.55; N, 10.2%); δ_H (500 MHz; $CDCl_3$) 4.31 (2H, dt, *J* 6.41 Hz, *J* 14.95 Hz, CH_2), 6.93 (1H, t, *J* 6.41 Hz, NH); δ_C (126 MHz; $CDCl_3$) 41.1 (t, *J* 23.8 Hz, CH_2N), 110.7–118.4 [$CF_3(CH_2)_6$], 166.8 (triazine C–NH), 170.6 (triazine C–Cl), 171.6 (triazine C–Cl); δ_F (470 MHz; $CDCl_3$; $CFCl_3$) −79.9 (CF_3), −116.8, −120.8, −121.0, −121.8, −122.2 and −125.2 (CF_2); *m/z* 574 [$(M + H)^+$, 64%], 575 [$(M + C_2H_5)^+$, 6], 561 [$(M + CH_3)^+$, 6], 527 [$(M - F)^+$, 100], 177 [$(M - C_7F_{15})^+$, 14].

***N*-(4,6-Dichloro-1,3,5-triazin-2-yl)-*N*-ethyloctane-1-sulfonamide 4.** Sodium (0.13 g, 5.65 mmol) was dissolved with stirring in ethanol (20 cm^3) and *N*-ethyloctane-1-sulfonamide (1.19 g, 5.38 mmol) was added portion-wise. The resulting solution was stirred for 30 min and then evaporated to dryness. The resulting solid was dissolved in acetone (60 cm^3), cooled to −60 °C and added to a cold (−60 °C) solution of cyanuric chloride (1.00 g, 5.42 mmol) dissolved in acetone (20 cm^3). The temperature of the reaction mixture did not rise above −55 °C during the addition. After the addition, the reaction mixture was allowed to warm to room temperature. Sodium chloride was removed by filtration and the acetone was removed by evaporation under reduced pressure. The resulting sticky solid was purified by column chromatography on silica gel (hexane : diethyl ether; 7 : 1) to afford *N*-(4,6-dichloro-1,3,5-triazin-2-yl)-*N*-ethyloctane-1-sulfonamide **4** (1.30 g, 65%) as a white solid, mp 68–69 °C (Found: C, 42.5; H, 6.1; N, 15.3; $C_{13}H_{22}N_4Cl_2O_2S$ requires C, 42.3; H, 6.0; N, 15.2%); δ_H (300 MHz; $CDCl_3$) 0.87 (3H, t, *J* 7.0 Hz, CH_3), 1.28 [8H, m, $(CH_2)_4$], 1.35 (3H, t, *J* 7.0 Hz, CH_3), 1.44 (2H, m, CH_2), 1.80 (2H, m, CH_2CH_2S), 3.70 (2H, m, CH_2S), 4.12 (2H, q, *J* 7.0 Hz, CH_2N); δ_C (75 MHz; $CDCl_3$) 14.0 (CH_3), 14.5 (CH_3), 22.5, 23.2, 27.9, 28.8 and 31.6 (CH_2), 42.6 (CH_2N), 55.3 (CH_2S), 165.1 (triazine C–NSO_2), 171.0 (triazine C–Cl); *m/z* 369 [$(M + H)^+$, 100%], 397 [$(M + C_2H_5)^+$, 6], 333 [$(M - Cl)^+$, 16].

4,6-Dichloro-2-(*N*-ethyl-4-methylbenzenesulfonamido)-1,3,5-triazine 5. Sodium (0.09 g, 3.96 mmol) was dissolved with stirring in ethanol (20 cm^3) and *N*-ethyl-4-methylbenzenesulfonamide (0.79 g, 3.96 mmol) was added portion-wise. The resulting solution was stirred for 30 min and then evaporated to afford a sticky solid. Tetrahydrofuran (20 cm^3) was added and the suspension was cooled to −10 °C under argon. Cyanuric chloride (0.73 g, 3.96 mmol) dissolved in tetrahydrofuran (5 cm^3) was added to the reaction mixture dropwise. After the addition, the reaction mixture was allowed to warm to room temperature over a 1 h period. The solvent was removed by evaporation and the resulting residue was dissolved in dichloromethane (40 cm^3). The solution was filtered through a pad of Celite® and the solvent was removed by evaporation under reduced pressure. Purification of 0.51 g of the crude material by chromatography on silica gel (chloroform) afforded 4,6-dichloro-2-(*N*-ethyl-4-methylbenzenesulfonamido)-1,3,5-triazine **5** (0.45 g, 88%) as a white solid (Found: C, 41.6; H, 3.4; N, 16.1; $C_{12}H_{12}N_4Cl_2O_2S$ requires C, 41.5; H, 3.5; N, 16.1%); δ_H (300 MHz; $CDCl_3$) 1.43 (3H, t, *J* 7 Hz, CH_3), 2.44 (3H, s, $CH_3C_6H_4$), 4.26 (2H, q, *J* 7 Hz, CH_2N), 7.33 (2H, d, *J* 8.4 Hz, Ar CH), 8.00 (2H, d, *J* 8.4 Hz, Ar CH); δ_C (75 MHz; $CDCl_3$) 14.5 (CH_3), 21.6 ($CH_3C_6H_4$), 42.6 (CH_2N), 129.1 (8-C and 4-C), 129.6 (Ar 7-C and 5-C), 135.3 (Ar 6-C), 145.4 (Ar 9-C), 163.8 (triazine C–NSO_2), 170.5 (triazine C–Cl); *m/z* 347 [$(M + H)^+$, 100%], 375 [$(M + C_2H_5)^+$, 6], 361 [$(M + CH_3)^+$, 6], 311 [$(M - Cl)^+$, 18].

***N*-(4,6-Dichloro-1,3,5-triazin-2-yl)-*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonamide 6.** Sodium (5.00 g, 0.22 mol) was dissolved with stirring in ethanol (210 cm^3) and *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonamide (114 g, 0.22 mol) was added portion-wise. The resulting solution was stirred for 30 min and then evaporated to dryness. The resulting sticky solid was dissolved in acetone (200 cm^3) and cooled to −78 °C under argon. Cyanuric chloride (39.9 g, 0.22 mol) dissolved in acetone (300 cm^3) was added to the reaction mixture dropwise such that the temperature did not rise above −75 °C (1 h). After the addition, the reaction mixture was allowed to warm to room temperature over a 1 h period. The precipitated solid was removed by filtration and the orange solution dried over sodium sulfate. Filtration and evaporation under reduced pressure afforded *N*-(4,6-dichloro-1,3,5-triazin-2-yl)-*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonamide **6** (125 g, 86%). The product can be purified by precipitation from a chloroform–industrial methylated spirit (IMS) solvent mixture. In a typical purification procedure, the crude product (58.6 g) was dissolved in chloroform (150 cm^3) and then precipitated into IMS (400 cm^3). The precipitate was collected by filtration and dried under vacuum at 25 °C to afford triazine **6** (42.3 g, 72%) as a fine white solid, mp 92–93 °C (Found: C, 23.2; H, 0.7; N, 8.3; $C_{13}H_5N_4Cl_2F_{17}O_2S$ requires C, 23.1; H, 0.75; N, 8.3%); δ_H (300 MHz; THF-d_8) 1.42 (3H, t, *J* 7.0 Hz, CH_3), 4.26 (2H, q, *J* 7.0 Hz, CH_2N); δ_C (75 MHz; THF-d_8) 14.7 (CH_3), 47.0 (CH_2N), 110–118 (m, C_8F_{17}), 166.4 (triazine C–NSO_2), 172.2 (triazine C–Cl); *m/z* 675 [$(M + H)^+$, 100%], 703 [$(M + C_2H_5)^+$, 4], 689 [$(M + CH_3)^+$, 6], 193 [$(M - SO_2C_8F_{17})^+$, 98].

***N*-(4,6-Difluoro-1,3,5-triazin-2-yl)-*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonamide 7.** Sodium (0.85 g, 37.0 mmol) was dissolved with stirring in methanol (30 cm^3) and *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonamide (19.5 g, 37.0 mmol) was added portion-wise. The resulting solution was stirred for 1 h and then evaporated to dryness. Cyanuric fluoride (5.00 g, 37.0 mmol) was dissolved in acetone (40 cm^3) and cooled to −78 °C under an atmosphere of argon. The sodium salt of the sulfonamide prepared above, was dissolved in acetone (20 cm^3) and added slowly to the cyanuric fluoride solution over a 1 h period. After 2 h, the reaction mixture was allowed to warm to room tem-

perature and the solvent was removed by evaporation under reduced pressure. Distillation (200 °C, 0.3 mbar) of 4.85 g of the crude product afforded *N*-(4,6-difluoro-1,3,5-triazin-2-yl)-*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonamide **7** (1.50 g, 31%) as a white solid, mp 72 °C (Found: C, 24.1; H, 0.95; N, 8.4; $C_{13}H_5N_4F_{19}O_2S$ requires C, 24.3; H, 0.8; N, 8.7%); δ_H (500 MHz; acetone-d_6) 1.45 (3H, t, *J* 7.0 Hz, CH_3), 4.34 (2H, t, *J* 7.0 Hz, CH_2N); δ_C (126 MHz; acetone-d_6) 14.3 (CH_3CH_2), 47.3 (CH_3CH_2), 170.3 (triazine C–NSO_2), 172.0 (dd, *J* 19.6 Hz, *J* 231 Hz, triazine C–F); δ_F (470 MHz; acetone-d_6; $CFCl_3$) −35.9 (triazine C–F), −80.6 (CF_3), −119.6, −120.0, −121.2, −121.4, −122.2 and −125.8 (CF_2); *m*/*z* 643 [$(M + H)^+$, 100%], 671 [$(M + C_2H_5)^+$, 4], 657 [$(M + CH_3)^+$, 10], 159 [$(M - SO_2C_8F_{17})^+$, 56].

***N*-(4,6-Difluoro-1,3,5-triazin-2-yl)-*N*-ethyloctane-1-sulfonamide 8.** Sodium (0.037 g, 1.60 mmol) was dissolved with stirring in ethanol (10 cm^3) and *N*-ethyloctane-1-sulfonamide (0.39 g, 1.76 mmol) was added portion-wise. The resulting solution was stirred for 30 min and then evaporated to dryness. Cyanuric fluoride (0.44 g, 3.30 mmol) was dissolved in acetone (10 cm^3) and cooled to −78 °C under an atmosphere of argon. The sodium salt of the sulfonamide prepared above, was dissolved in acetone (10 cm^3) and added slowly to the cyanuric fluoride solution. The reaction mixture was allowed to warm to room temperature and after a 2 h period, the solvent was removed by evaporation under reduced pressure. Distillation (220 °C, 0.3 mbar) of the crude product afforded a mixture containing *N*-(4,6-difluoro-1,3,5-triazin-2-yl)-*N*-ethyloctane-1-sulfonamide **8** (0.23 g, 48%) as a pale yellow oil. Further attempts at purification by chromatography on silica gel led to decomposition of the product: δ_H (500 MHz; $CDCl_3$) 0.88 (3H, t, *J* 7 Hz, CH_3), 1.30 (8H, m, $(CH_2)_8$), 1.36 (3H, t, *J* 7 Hz, CH_3), 1.45 (2H, m, CH_2), 1.80 (2H, m, $CH_2CH_2SO_2$), 3.71 (2H, m, CH_2SO_2), 4.14 (2H, q, *J* 7 Hz, CH_2N); δ_C (126 MHz; $CDCl_3$) 14.2 (CH_3), 14.7 (CH_3), 22.8, 23.4, 28.2, 29.1 and 31.9 (CH_2), 43.2 (CH_2N), 55.4 (CH_2SO_2), 169.4 (t, *J* 17.1 Hz, triazine C–NSO_2), 171.3 (dd, *J* 19.7 Hz, *J* 233 Hz, triazine C–F); δ_F (470 MHz; $CDCl_3$; $CFCl_3$) −32.6 (triazine C–F).

2-(*N*-Ethyl-4-methylbenzenesulfonamido)-4,6-difluoro-1,3,5-triazine 9. Cyanuric fluoride (2.00 g, 14.8 mmol) and *N*-ethyl-4-methylbenzenesulfonamide (1.50 g, 7.50 mmol) were dissolved in acetone (10 cm^3). 2,4,6-Trimethylpyridine (1.80 g, 14.9 mmol) was added and the reaction mixture was stirred at ambient temperature for 2 d. Diethyl ether (100 cm^3) was added and the solution was washed with 2 M HCl (2 × 50 cm^3), water (2 × 50 cm^3) and saturated aqueous sodium chloride (1 × 50 cm^3). The organic layer was separated, dried over sodium sulfate, filtered and the solvent was removed by evaporation under reduced pressure to afford 2-(*N*-ethyl-4-methylbenzenesulfonamido)-4,6-difluoro-1,3,5-triazine **9** (1.41 g, 60%). Further purification of the product (0.90 g) was achieved by chromatography on silica gel (diethyl ether) to give 2-(*N*-ethyl-4-methylbenzenesulfonamido)-4,6-difluoro-1,3,5-triazine **9** (0.85 g, 95%) as a pale yellow liquid: δ_H (300 MHz; $CDCl_3$) 1.44 (3H, t, *J* 7 Hz, CH_3), 2.44 (3H, s, $CH_3C_6H_4$), 4.29 (2H, q, *J* 7 Hz, CH_2N), 7.33 (2H, d, *J* 8.4 Hz, Ar 3,5-H_2), 7.98 (2H, d, *J* 8.4 Hz, Ar 2,6-H_2); δ_C (75 MHz; $CDCl_3$) 14.5 (CH_3), 21.7 (CH_3), 43.2 (CH_2N), 129.3, 129.5 (Ar 2,3,5,6-C_4), 135.2 (Ar 4-C), 145.5 (Ar 1-C), 168.4 (t, *J* 16.8 Hz, triazine C–NSO_2), 170.7 (dd, *J* 19.6 Hz, *J* 231 Hz, triazine C–F); δ_F (470 MHz; $CDCl_3$; $CFCl_3$) −33.6 (triazine C–F); *m*/*z* 315 [$(M + H)^+$, 100%], 343 [$(M + C_2H_5)^+$, 8], 295 [$(M - F)^+$, 12].

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