Synthesis of substituted 2-amino-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazines

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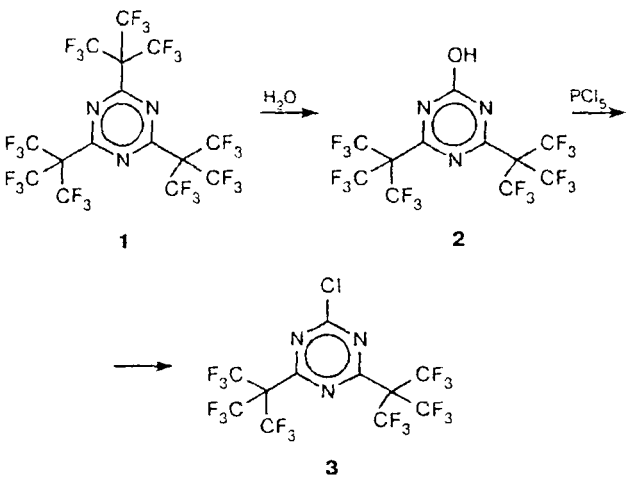
A procedure was developed for the synthesis of substituted 2-amino-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazines from 2-chloro-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazine and aliphatic and aromatic amines. The data of ^{19}F NMR spectroscopy are indicative of the presence of a barrier to internal rotation.

Key words: 2-chloro-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazine, 2-(alkylamino)-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazines, nucleophilic substitution, hindered rotation, NMR spectra.

Substituted 2-amino-4,6-bis(perfluoroalkyl)-1,3,5-triazines may be of practical interest as perfluoroalkyl analogs of herbicides of the triazine series,[1] components of high-temperature lubricants used in aerospace industry,[2] water- and oil-repellent agents, and surfactants.[3] The aim of the present work is to develop procedures for the synthesis of substituted 2-amino-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazines based on 2,4,6-tris(nonafluoro-*tert*-butyl)-1,3,5-triazine (**1**). The reactivities of 2,4,6-tris(*n*-perfluoroalkyl)-1,3,5-triazines were characterized by their hydrolysis and alcoholysis[4,5] as well as by their reactions with ammonia and methylamine, which require rather drastic conditions.[6] It was expected that the replacement of the nonafluoro-*tert*-butyl group in compound **1** by aliphatic and aromatic amines would proceed rather readily due to formation of a stable nonafluoro-*tert*-butyl anion.[7] However, control experiments demonstrated that the reactions of compound **1** with aliphatic amines afforded mixtures of products, which were difficult to separate (apparently, due to the reaction of perfluoroisobutylene, which was formed as a result of decomposition of the nonafluoro-*tert*-butyl anion, with amines[8]), while the reactions of **1** with anilines containing electron-withdrawing substituents proceeded either very slowly or did not proceed at all. An insignificantly modified version of a known procedure for the synthesis[9] of triazine **1** made it possible to obtain 2-hydroxy-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazine (**2**) without isolation of **1**. Subsequent chlorination of compound **2** afforded 2-chloro-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazine (**3**) (Scheme 1).

We studied the reactions of compound **3** with ammonia and aliphatic and aromatic amines (**4**). The molecule of triazine **3** contains two groups capable of nucleophilic replacement, *viz.*, the Cl atom and the *tert*-C_4F_9 group.

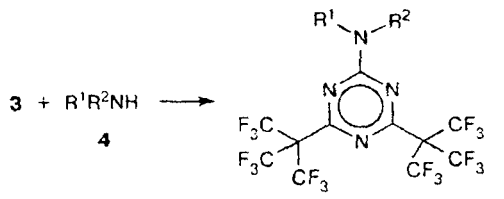
Scheme 1



1 **2** **3**

Nevertheless, the reactions of compound **3** with amines were accompanied by only the nucleophilic replacement of the Cl atom to give the corresponding substituted 2-amino-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazines (**5a—bb**) as the major products (Scheme 2, Table 1).

Scheme 2



5a—bb

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Table 1. Physicochemical characteristics of compounds **5a—bb**

Compound	R^1	R^2	Yield (%)	M.p./°C*	Found / Calculated (%)			Molecular formula
					C	H	N	
5a	H	H	91	98—99	24.26 24.82	0.54 0.38	10.89 10.52	$C_{11}H_2F_{18}N_4$
5b	H	Me	94	36—37	26.18 26.39	0.95 0.74	10.52 10.25	$C_{12}H_4F_{18}N_4$
5c	H	Pr^i	91	82—83	29.40 29.28	1.53 1.40	9.83 9.76	$C_{14}H_8F_{18}N_4$
5d	Me	Me	93	75—76	27.90 27.87	1.23 1.08	10.12 10.00	$C_{13}H_6F_{18}N_4$
5e	H	Allyl	94	52—53	29.58 29.38	1.22 1.05	9.90 9.79	$C_{14}H_6F_{18}N_4$
5f	H	Bu^t	95	62—63	30.89 30.62	1.90 1.71	9.59 9.52	$C_{15}H_{10}F_{18}N_4$
5g	Et	Et	89	77—78	30.79 30.63	1.82 1.71	9.56 9.52	$C_{15}H_{10}F_{18}N_4$
5h	Pr	Pr	85	75—76	33.59 33.13	2.52 2.29	9.12 9.09	$C_{17}H_{14}F_{18}N_4$
5i	$R^1+R^2=(CH_2)_2O(CH_2)_2$		90	103—104	30.09 29.92	1.47 1.34	9.34 9.30	$C_{15}H_8F_{18}N_4O$
5j	$R^1+R^2=(CH_2)_5$		86	91—92	32.14 32.01	1.74 1.67	9.35 9.33	$C_{16}H_{10}F_{18}N_4$
5k	$R^1+R^2=(CH_2)_6$		85	66—67	33.52 33.24	2.09 1.97	9.14 9.12	$C_{17}H_{12}F_{18}N_4$
5l	H	CH_2Ph	91	91—92	35.26 34.74	1.43 1.29	9.02 9.00	$C_{18}H_8F_{18}N_4$
5m	H	Ph	95	135—136	33.97 33.57	1.08 0.99	9.24 9.21	$C_{17}H_6F_{18}N_4$
5n	H	4-MeC_6H_4	93	95—96	35.05 34.74	1.37 1.30	9.01 9.00	$C_{18}H_8F_{18}N_4$
5o	H	2-MeC_6H_4	91	107—108	35.36 34.74	1.45 1.30	9.02 9.00	$C_{18}H_8F_{18}N_4$
5p	H	4-$MeOC_6H_4$	92	154—155	34.23 33.87	1.36 1.26	8.78 8.78	$C_{18}H_8F_{18}N_4O$
5q	H	4-ClC_6H_4	93	137—138	32.15 31.77	0.89 0.78	8.71 8.72	$C_{17}H_5ClF_{18}N_4$
5r	H	4-BrC_6H_4	92	168—169	29.88 29.72	0.82 0.73	8.10 8.15	$C_{17}H_5BrF_{18}N_4$
5s	H	4-IC_6H_4	94	193—194	27.82 27.81	0.76 0.69	7.56 7.63	$C_{17}H_5IF_{18}N_4$
5t	H	4-$NO_2C_6H_4$	91	147—148	31.33 31.26	0.79 0.77	10.76 10.72	$C_{17}H_5F_{18}N_5O_2$
5u	H	3-$NO_2C_6H_4$	92	122—123	31.55 31.26	0.86 0.77	10.87 10.72	$C_{17}H_5F_{18}N_5O_2$
5v	H	2-$NO_2C_6H_4$	93	91—92	31.41 31.26	0.82 0.77	10.80 10.72	$C_{17}H_5F_{18}N_5O_2$
5w	H	4-$MeCOC_6H_4$	92	170—171	35.68 35.09	1.37 1.24	8.61 8.62	$C_{19}H_8F_{18}N_4O$
5x	H	4-$EtOCOC_6H_4$	93	154—155	35.87 35.31	1.60 1.48	8.24 8.24	$C_{20}H_{10}F_{18}N_4O_2$
5y	H	2,6-$Me_2C_6H_3$	89	98—99	—	—	—	$C_{19}H_{10}F_{18}N_4$
5z	H	2,4,6-$Me_3C_6H_2$	89	120—121	36.68 36.93	1.56 1.85	—	$C_{20}H_{12}F_{18}N_4$
5aa	H	2-NH_2Ph	89	131—132	32.90 32.76	1.17 1.13	11.31 11.24	$C_{17}H_7F_{18}N_5$
5bb	Ph	Ph	67	135—136	40.96 40.37	1.56 1.47	8.16 8.19	$C_{23}H_{10}F_{18}N_4$

* From heptane.

Table 2. Spectral characteristics of compounds **5a—bb**

Compound	NMR ($CDCl_3$, δ, J/Hz)		Δδ ^{19}F	m/z (I_{rel}(%))*
	^1H	^{19}F		
5a	6.00 (s, 2 H, NH_2)	14.855	0	532 (42), 513 (27), 271 (9), 246 (8), 69 (100), 42 (50)
5b	3.12 (d, 3 H, CH_3, J = 8.0); 6.07 (br.s, 1 H, NH)	14.695	0	546 (11), 527 (10), 158 (10), 138 (14), 82 (28), 69 (100), 55 (56), 53 (20)
5c	1.34 (d, 6 H, CH_3, J = 6.0); 4.18 (m, 1 H, CH); 5.90 (br.s, 1 H, NH)	14.674; 14.727	0.053	574 (9), 559 (100), 555 (14), 158 (15), 138 (11), 69 (95), 42 (20)
5d	3.27 (s, 6 H, CH_3)	14.570	0	560 (58), 559 (13), 545 (42), 541 (42), 531 (12), 471 (14), 69 (100), 55 (37), 44 (86)
5e	4.12 (m, 2 H, CH_2); 5.30 (m, 2 H, CH_2=C); 5.86 (m, 1 H, CH=C); 6.16 (br.s, 1 H, NH)	14.713; 14.730	0.018	572 (2), 312 (12), 246 (11), 183 (11), 158 (29), 138 (23), 108 (33), 81 (58), 69 (100), 56 (52), 55 (41), 54 (21), 53 (12), 41 (37)
5f	1.48 (s, 9 H, CH_3); 6.03 (br.s, 1 H, NH)	14.781; 14.802	0.021	588 (1), 573 (100), 513 (16), 158 (14), 83 (53), 69 (57), 57 (27), 42 (29)
5g	1.24 (t, 6 H, CH_3, J = 7.0); 3.65 (q, 4 H, CH_2, J = 7.0)	14.638	0	588 (35), 574 (18), 573 (100), 569 (27), 545 (25), 246 (11), 158 (12), 138 (13), 69 (77), 55 (28)
5h	0.93 (m, 6 H, CH_3, J = 8.0); 1.65 (m, 4 H, CH_2); 3.53 (m, 4 H CH_2, J = 7.0)	14.665	0	616 (12), 597 (16), 588 (11), 587 (59), 545 (29), 69 (33), 55 (18), 43 (100), 42 (16), 41 (36)
5i	3.81 (m, 4 H, CH_2O); 3.89 (t, 4 H, CH_2N, J = 4.0)	14.724	0	602 (18), 583 (17), 559 (10), 545 (17), 513 (17), 272 (28), 203 (16), 183 (16), 158 (11), 138 (22), 82 (13), 69 (100), 56 (27), 53 (49)
5j	1.72 (m, 6 H, CH_2); 3.86 (m, 4 H, CH_2N)	14.457	0	600 (12), 511 (24), 246 (12), 183 (12), 158 (15), 138 (12), 136 (10), 84 (31), 69 (100), 55 (55)
5k	1.62 (m, 4 H, CH_2); 1.82 (m, 4 H, CH_2); 3.77 (t, 4 H, CH_2N, J = 6.0)	14.683	0	614 (9), 545 (22), 525 (23), 158 (15), 136 (13), 84 (15), 83 (13), 82 (15), 81 (30), 69 (100), 55 (64)
5l	4.68 (d, 2 H, CH_2, J = 6.0); 6.36 (br.t, 1 H, NH, J = 6.0); 7.34 (m, 5 H, H arom.)	14.858; 14.882	0.024	622 (37), 603 (16), 534 (15), 533 (71), 158 (20), 136 (10), 131 (47), 106 (88), 104 (37), 91 (100), 77 (14), 69 (54)
5m	6.24 (m, 1 H, H arom.); 6.42 (m, 2 H, H arom.); 6.56 (m, 2 H, H arom.); 6.80 (s, 1 H, NH)	14.861; 14.897	0.035	608 (50), 214 (12), 158 (12), 118 (100), 117 (10), 91 (17), 69 (46)
5n	1.36 (s, 3 H, CH_3); 6.22 (d, 2 H, H arom., J = 8.0); 6.44 (d, 2 H, H arom., J = 8.0); 6.74 (s, 1 H, NH)	14.852; 14.882	0.030	622 (100), 603 (27), 533 (10), 246 (10), 158 (28), 132 (67), 131 (68), 104 (20), 91 (41), 77 (19), 69 (70)
5o	1.34 (s, 3 H, CH_3); 6.26 (m, 3 H, H arom.); 6.52 (br.s, 1 H, NH); 6.72 (m, 1 H, H arom.)	14.769; 14.894	0.125	622 (56), 603 (26), 553 (21), 158 (80), 132 (39), 131 (100), 106 (30), 105 (10), 104 (36), 77 (25), 69 (68)
5p	3.82 (s, 3 H, CH_3); 6.98 (d, 2 H, H arom., J = 8.0); 7.44 (d, 2 H, H arom., J = 8.0); 7.74 (s, 1 H, NH)	14.873; 14.919	0.046	638 (56), 623 (36), 619 (26), 246 (22), 158 (22), 148 (17), 133 (100), 105 (25), 78 (11), 69 (73)
5q	7.38 (d, 2 H, H arom., J = 8.0); 7.53 (d, 2 H, H arom., J = 8.0); 7.88 (s, 1 H, NH)	14.885; 14.921	0.036	642 (100), 623 (15), 246 (15), 158 (15), 154 (28), 153 (10), 152 (87), 125 (10), 90 (10), 69 (72)
5r	7.44 (d, 2 H, H arom., J = 8.0); 7.54 (d, 2 H, H arom., J = 8.0); 7.84 (s, 1 H, NH)	14.962; 14.998	0.036	686 (66), 669 (10), 667 (12), 246 (18), 198 (62), 197 (10), 196 (64), 158 (20), 117 (22), 116 (11), 90 (32), 69 (100)
5s	7.50 (d, 2 H, H arom., J = 10.0); 7.72 (d, 2 H, H arom., J = 10.0); 10.20 (s, 1 H, NH)	14.522; 14.546	0.024	734 (78), 715 (10), 362 (12), 273 (11), 246 (12), 244 (75), 158 (16), 117 (57), 116 (16), 90 (66), 76 (14), 69 (100), 65 (13), 64 (14), 63 (21)
5t	8.00 (d, 2H, H arom., J = 10.0); 8.35 (d, 2 H, H arom., J = 10.0); 10.75 (s, 1 H, NH)	14.537; 14.570	0.033	653 (23), 634 (10), 623 (19), 158 (17), 133 (51), 117 (63), 116 (13), 105 (12), 91 (10), 90 (64), 69 (100), 65 (14), 64 (11), 63 (19)

(to be continued on next page)

Table 2. (*Continued*)

Compound	NMR ($CDCl_3$, δ, J/Hz) ^{1}H	^{19}F	Δδ ^{19}F	m/z (I_{rel}(%))*
5u	7.63 (m, 1 H, H arom.); 8.05 (m, 2 H, H arom.); 8.75 (m, 1 H, H arom.); 10.48 (s, 1 H, NH)	14.614; 14.656	0.042	653 (64), 634 (21), 362 (21), 117 (100), 116 (17), 91 (10), 90 (58), 76 (10), 69 (79), 65 (13), 63 (15)
5v	7.40 (m, 1 H, H arom.); 7.80 (m, 1 H, H arom.); 8.30 (m, 1 H, H arom.); 8.55 (m, 1 H, H arom.); 10.85 (s, 1 H, NH)	14.855	0	653 (44), 634 (15), 363 (13), 362 (100), 274 (10), 273 (10), 120 (10), 117 (42), 116 (13), 105 (12), 91 (13), 90 (70), 69 (94), 63 (12)
5w	2.63 (s, 3 H, CH_3); 7.85 (d, 2 H, H arom., J = 10.0); 8.05 (d, 2 H, H arom., J = 10.0); 10.43 (s, 1 H, NH)	14.611; 14.650	0.039	650 (15), 636 (17), 635 (82), 631 (11), 362 (10), 145 (32), 144 (20), 143 (10), 117 (69), 116 (18) 91 (15), 90 (75), 69 (100), 63 (16), 43 (72)
5x	1.40 (t, 3 H, CH_3, J = 10.0); 4.41 (q, 2 H, CH_2, J = 10.0); 7.80 (d, 2 H, H arom., J = 10.0); 8.10 (d, 2 H, H arom., J = 10.0); 10.20 (s, 1 H, NH)	14.635; 14.671	0.036	680 (22), 652 (20), 636 (15), 635 (66), 362 (11), 162 (13), 158 (13), 145 (46), 144 (20), 143 (12), 118 (11), 117 (83), 116 (19), 91 (13), 90 (86), 69 (100), 63 (17), 45 (18)
5y	2.17 (s, 6 H, CH_3); 7.17 (m, 4 H, NH and H arom.)	14.630; 14.910	0.280	636 (56), 617 (24), 567 (18), 173 (10), 172 (87), 158 (15), 146 (29), 145 (100), 144 (25), 143 (18), 131 (38), 130 (15), 129 (10), 118 (30), 117 (14), 116 (11), 106 (23), 105 (10), 104 (11), 103 (19), 91 (27), 78 (11), 77 (24), 69 (78)
5z	2.12 (s, 6 H, CH_3); 2.32 (s, 3 H, CH_3); 6.98 (s, 2 H, H arom,); 7.18 (br.s, 1 H, NH)	14.608; 14.849	0.241	—
5aa	3.53 (br.s, 2 H, NH_2); 6.88 (m, 2 H, H arom.); 7.30 (m, 1 H, H arom.); 7.53 (m, 1 H, H arom.); 8.20 (br.s, 1 H, NH)	14.858; 15.007	0.149	623 (8), 404 (14), 159 (79), 158 (21), 133 (100), 132 (21), 118 (11), 106 (15), 105 (41), 90 (14), 79 (11), 78 (10), 68 (66)
5bb	7.30 (m, H arom.)	14.722	0	684 (84), 665 (17), 322 (12), 220 (14), 194 (16), 193 (40), 192 (18), 168 (13), 167 (50), 166 (32), 158 (16), 138 (10), 117 (14), 83 (11), 77 (100), 69 (85), 65 (12)

* The molecular ion peak and the most intense peaks of fragmentation ions are given.

The yields of substitution products **5a—aa** were 85—95%. Only in the case of low reactive diphenylamine, was the yield of the corresponding aminotriazine **5bb** 67%. The characteristics of compounds **5a—bb** are given in Tables 1 and 2.

The data of ^{1}H NMR spectroscopy and mass spectrometry are consistent with the suggested structures. The characteristic features of the ^{19}F NMR spectra call for a separate discussion. In the ^{19}F NMR spectra of triazines **5a,b,d,g—k,v** and **5bb**, the signals of the *tert*-C_4F_9 group are observed as singlets at δ 14—15. In the spectra of compounds **5c,e,f,l—u,w—aa**, these signals are observed as two singlets with equal intensities in the same region (the difference between the chemical shifts (Δδ) varies from 0.018 to 0.280 depending on the nature of the R^2 substituent). An increase in the number of signals in the ^{1}H, ^{13}C, and ^{14}N NMR spectra of substituted amino-1,3,5-triazines, which is associated with the presence of the barrier to internal rotation, was reported in the literature.[10,11] It was demonstrated[11] that the presence of nonequivalent substituents at the exocyclic N atom ($R^1 \neq R^2$) as well as the presence of electron-withdrawing substituents in the triazine ring are necessary for this phenomenon (hindered rotation) to be observed in NMR spectra. For compounds **5c,e,f,l—u,w—aa**, these conditions are fulfilled and the nonequivalence of the *tert*-C_4F_9 groups observed in the ^{19}F NMR spectra is attributable to the absence of free rotation about the $R^1R^2N—C(2)$ bond of the triazine. Note two exceptions, *viz.*, compounds **5b** and **5v**, in which the *tert*-C_4F_9 groups are equivalent (Δδ = 0) in spite of the presence of the different R^1 and R^2 substituents, which may be associated either with a low barrier to internal rotation or to the accidentally close values of the ^{19}F chemical shifts of the *tert*-C_4F_9 groups in these compounds.

Experimental

The ^{1}H and ^{19}F NMR spectra were recorded on a CXP-200 instrument (200 and 188.22 MHz, respectively) with Me_4Si and CF_3COOH as the internal and external standards, respec-

tively. The mass spectra were obtained on a Finnigan MAT instrument (EI, the ionizing voltage was 70 eV). In the mass spectra of compounds **3**, **5q**, and **5r**, the molecular ion peaks of the chlorine- and bromine-containing fragments correspond to the ^{35}Cl and ^{79}Br isotopes, respectively. The course of the reactions was monitored by TLC on Silufol UV-254 plates (hexane—chloroform, 1 : 1).

2-Hydroxy-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazine (2). A solution of cyanuric chloride (90 g, 0.49 mol) in 1,2-dimethoxyethane (150 mL) was added to a mixture of perfluoroisobutylene (300 g, 1.5 mol) and CsF (228 g, 1.5 mol) in 1,2-dimethoxyethane (1 L). The reaction mixture was stirred at ~20 °C for 6 h and then water (500 mL) was added. After completion of the exothermic reaction, the mixture was extracted with hexane (1 L), the organic layer was separated and dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. Compound **2** was obtained in a yield of 142 g (55%), m.p. 29—31 °C. ^1H NMR ($CDCl_3$), δ: 5.53 (s, 1 H, OH). ^{19}F NMR ($CDCl_3$), δ: 14.725 (s, *t*-C_4F_9). MS, *m/z* (I_{rel} (%)): 534 $[M + H]^+$ (15), 533 $[M]^+$ (5), 514 $[M - F]^+$ (32), 464 $[M - CF_3]^+$ (4), 314 $[M - C_4F_9]^+$ (8), 69 $[CF_3]^+$ (100). Found (%): C, 24.77; H, 0.18; N, 7.82. $C_{11}HF_{18}N_3O$. Calculated (%): C, 24.78; H, 0.19; N, 7.88.

2-Chloro-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazine (3). A mixture of compound **2** (142 g, 0.266 mol) and PCl_5 (61 g, 0.28 mol) was kept at ~20 °C for 48 h. Then $POCl_3$ that formed was distilled off and the residue was distilled *in vacuo*. Compound **3** was obtained in a yield of 85 g (57.9%), b.p. 65 °C (1 Torr), m.p. 20—22 °C. ^{19}F NMR ($CDCl_3$), δ: 14.254 (s, *t*-C_4F_9). MS, *m/z* (I_{rel} (%)): 551 $[M]^+$ (100), 532 $[M - F]^+$ (75), 306 $[M - C_4F_9CN]^+$ (13), 271 $[M - C_4F_9CN - Cl]^+$ (87), 69 $[CF_3]^+$ (82). Found (%): C, 23.95; N, 7.82. $C_{11}ClF_{18}N_3$. Calculated (%): C, 23.95; N, 7.62.

2-Alkylamino-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazines (5a—l). The corresponding amine (or an aqueous solution of the amine) (2.2 mmol) was added to a solution of chlorotriazine **3** (552 mg, 1 mmol) in acetone (5 mL). The reaction mixture was stirred for 10 min and poured into water (100 mL). The precipitate that formed was filtered off, washed with water and a dilute HCl solution (1—5%), dried on a filter, dissolved in a 1 : 1 hexane—chloroform mixture (20 mL), and passed through a small pad of silica gel L 40/100. The solvents were evaporated.

2-Arylamino-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazines (5m—aa). The corresponding aniline (1.1 mmol) and $NaHCO_3$ (168 mg, 2 mmol) were added to a solution of chlorotriazine **3** (552 mg, 1 mmol) in acetone (5 mL). The reaction mixture was stirred for 2 h and poured into water (100 mL). The precipitate that formed was filtered off, washed with water and dilute HCl (1—5%), dried on a filter, dissolved in a 1 : 1 hexane—chloroform mixture (20 mL), and passed through a small pad of silica gel L 40/100. The solvents were evaporated.

2-(Diphenylamino)-4,6-bis(nonafluoro-*tert*-butyl)-1,3,5-triazine (5bb). Diphenylamine (186 mg, 1.1 mmol) and finely ground LiH (16 mg, 2 mmol) were added to a solution of chlorotriazine **3** (552 mg, 1 mmol) in dry THF (5 mL). The reaction mixture was stirred for 3 h and poured into water (100 mL). The precipitate that formed was filtered off, dried on a filter, and isolated by chromatography on a column with silica gel (hexane as the eluent).

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