4,6-Bis- and 2,4,6-tris-(*N*,*N*-dialkylamino)-*s*-triazines: synthesis, NMR spectra and restricted rotations

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Syntheses of various symmetrically and non-symmetrically trisubstituted triazines are reported. Dynamic NMR (^1H and ^{13}C) experiments demonstrate that 2,4,6-tris(dialkylamino)-*s*-triazines show correlated rotations of the alkyl groups in the dialkylamino moieties. Unsymmetrical 2-chloro-, 2-alkoxy- and 2-aryloxy-4,6-bis(di-*n*-alkylamino)-*s*-triazines display two non-equivalent *n*-alkyl groups, due to the restricted rotation around the Ar–N bonds.

Cyanuric chloride and various di- and mono-chloro-*s*-triazines have frequently been used as precursors of diverse substituted 1,3,5-triazines (*s*-triazines), accessible *via* displacement of the chlorine atoms by various carbon, nitrogen and oxygen nucleophiles.[1] We now report the synthesis of some symmetrical and unsymmetrical triazines (Scheme 1) and an investigation of their stereodynamics by NMR. For several previously described compounds, improved preparative procedures are presented.

Results and discussion

Symmetrical trisubstituted 1,3,5-triazine derivatives prepared directly from cyanuric chloride (5)

2,4,6-Tris-(dialkylamino)-*s*-triazines **1a**, **1b**, **1d**, **3a**, **3b**, **4**, **6a** and **6b** were prepared directly by refluxing cyanuric chloride **5** with varying excesses of the corresponding dialkylamine in an appropriate solvent for 12 to 24 h (Scheme 1). 2,4,6-Tris-(di-*n*-butylamino)-*s*-triazine **1c** and 2,4,6-(tris-di-*n*-pentylamino)-*s*-triazine **1e** were prepared by refluxing cyanuric chloride **5** with di-*n*-butylamine and di-*n*-pentylamine, respectively, in aqueous sodium carbonate (5%) for 24 h. Reaction of cyanuric chloride with neat diisopropylamine under reflux gave 2-chloro-4,6-bis-(diisopropylamino)-*s*-triazine **2a**; subsequent treatment with further diisopropylamine at 200 °C for 3 days, gave 2,4,6-tris(diisopropylamino)-*s*-triazine **3a** in high yield (98%). Refluxing cyanuric chloride **5** with di-*n*-octylamine (1 : 10 ratio) in dioxane and aqueous sodium carbonate (5%) for 72 hours gave 2-chloro-4,6-bis-(di-*n*-octylamino)-*s*-triazine **2b**. Refluxing **5** in neat di-*n*-octylamine gave the same product. 2,4,6-Tris-(di-*n*-octylamino)-*s*-triazine **3b** was also prepared by heating 2-chloro-4,6-bis(di-*n*-octylamino)-*s*-triazine **2b** with di-*n*-octylamine (1 : 3 ratio) at 135–140 °C for 8 h.

Unsymmetrical trisubstituted *s*-triazines prepared from bis(di-*n*-butylamino)chloro- and from (di-*n*-butylamino)dichloro-triazine

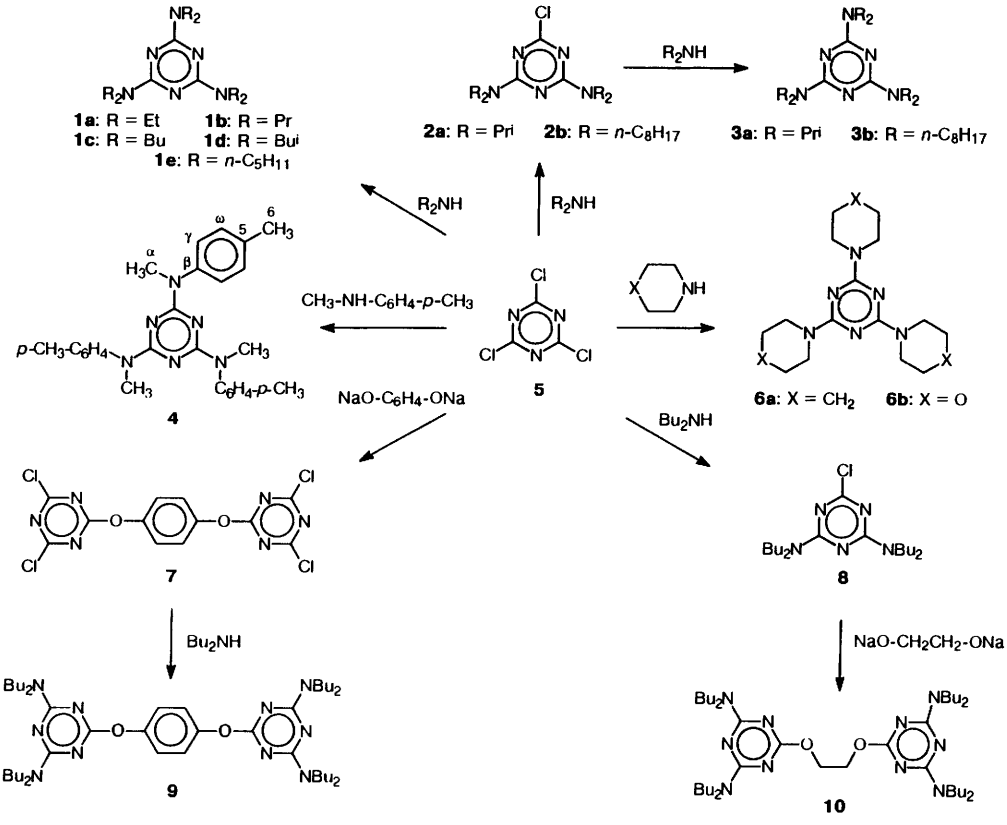
This pathway relies on the reactivity of the chlorine in 2-chloro-4,6-bis-(di-*n*-alkylamino)-*s*-triazines towards nitrogen and oxygen nucleophiles.[2–4] 2-Chloro-4,6-bis-(di-*n*-butylamino)-*s*-triazine **8**, frequently previously employed in the preparation of non-symmetrical trisubstituted *s*-triazines, was synthesized according to the literature procedures[5] from cyanuric chloride **5** and di-*n*-butylamine. 2-Chloro-4,6-bis(di-*n*-butylamino)-*s*-triazine **8** was heated for 4 h at 140–150 °C with disodium ethylene glycoxide (obtained by refluxing sodium with a tenfold excess of ethyleneglycol) in an equimolar ratio to give 2,2'-ethane-1,2-diyldioxybis[4,6-bis(dibutylamino)-*s*-triazine] **10**. However, a similar procedure using disodium 1,4-hydroquinone failed to give 2,2'-*p*-phenylenedioxybis[4,6-bis(dibutylamino)-*s*-triazine] **9**. In an alternative approach, cyanuric chloride **5** and 1,4-hydroquinone (2 : 1 molar ratio) in methanol were treated with equimolar aqueous 5% sodium hydroxide at room temperature for 2 h to give 2,2'-*p*-phenylenedioxybis(4,6-dichloro-*s*-triazine) **7**. Subsequent nucleophilic displacement of the four chlorine atoms of **7**, by treatment with neat di-*n*-butylamine under reflux for 10 h, gave compound **9** in 25% yield.

NMR spectroscopy of tetrakisalkyldiaminotriazines

Proton spectral assignments for the tetrakisalkyldiaminotriazines **2a**, **2b**, **8**, **9** and **10** are given in Table 1. At high temperatures, all of the alkyl groups are equivalent. Each type of proton in the butyl groups gives rise to a clear signal. In the *n*-octyl groups, the α, β and ω protons are resolved, the others forming a broad multiplet. The chemical shifts of the α protons (3.30–3.60 ppm) occur at lower field than those of a methylene group on an aromatic amine (*ca.* 3.00 ppm),[6] due to the electron-withdrawing effect of the triazine ring. The coupling constants are typical for freely rotating alkyl chains.[7]

At low temperatures, the proton spectra are significantly different. The straight chain alkyl compounds **2b**, **8**, **9** and **10** show one decoalescence, clearly visible at the α-protons, due to restricted rotation around the Ar–NR_2 bond. Hindered internal rotation of dialkylamino groups bonded to electron-deficient aromatic rings has been shown to be due to an increased bond-order of the Ar–NR_2 linkage. For example, it was demonstrated that the pyrimidine ring is electron-deficient enough for a decoalescence of the 4-dimethylaminopyrimidine methyl signal to occur at −40 °C.[8] However, to our knowledge, this phenomenon has not previously been reported for amino-*s*-triazines. The low-temperature spectra of different tetrakisalkyldiaminotriazines show significant differences: the decoalescence is noticeable for all protons in the *n*-butyl chain of **9** and also for the α, γ and ω protons in **10**, while only a broadening of the lines is seen for protons other than at the α positions in **2b** and **8**. A possible explanation is the greater difference between the chemical shifts of the isochronous sites in **9** and **10** due to the deshielding effect of the oxygen atom (**9** and **10**) and the phenylene ring (**9**).

Compound **2a**, with isopropyl side chains, shows two decoalescences: the first one, occurring at about −60 °C, splits the α and β proton resonances into two broad signals. The second, noticeable at −65 °C, causes a second splitting of the signals, leaving multiplets for the α protons and two pairs of doublets for the β protons. One of these decoalescences is assumed to result from the restricted rotation around the Ar–



Scheme 1

NR_2 bond, as in the previous case. The other is presumably due to the restricted rotation of the isopropyl groups around the C_α–N bond; the two isopropyl groups are now non-equivalent, as illustrated in Fig. 1A.

The ^{13}C NMR spectral data are shown in Table 2. At high temperatures there are two triazine ring signals in a 2:1 ratio, at chemical shifts in the range previously encountered for other 1,3,5-triazines.[9] The alkyl chain carbons show one signal for each position, at a chemical shift close to that typical for the corresponding position in an aliphatic amine.[10]

At low temperatures, compounds **2b**, **8**, **9** and **10** show two triazine ring signals in a 2:1 ratio and a pair of equally intense signals for each position in the aliphatic chain, due to restricted rotation of the dialkylamino groups around the Ar–N bond (Table 2).

Compound **2a** shows a different pattern at −60 °C: three equally intense signals for the triazine ring, and four equally intense signals for each position of the aliphatic chain. This behaviour is in agreement with the freezing (on the NMR timescale) of the rotation around the C_α–N bond. Furthermore, the non-equivalence of the carbons in positions 4 and 6 of the triazine ring suggests that this freezing leaves the four C_α–H bonds pointing in the same rotational direction, as illustrated in Fig. 1B.

NMR spectroscopy of 2,4,6-trisdialkylamino-*s*-triazines

The proton spectra of 2,4,6-tris(dialkylamino)-*s*-triazines are presented in Table 3. At high temperatures all compounds show one signal for each position in the aliphatic chain. Chemical shifts are similar to those of the tetrakisalkyldiaminotriazines (presented in Table 1) and the coupling constants are again typical for a freely rotating alkyl chain.

The low-temperature proton spectra show behaviour of different types for the various symmetrical hexakisalkyltriaminotriazines. Thus, compound **3a** exhibits a clear decoalescence of all proton signals; at the other extreme, compounds **1a** and **1e** show no tendency towards decoalescence, retaining their narrow multiplets at −60 °C. The remaining compounds (**1b**, **1c**, **1d**, **3b**, **4**, **6a**, **6b**) show broadening of some signals on lowering the temperature.

The carbon spectral assignments of 2,4,6-trisdialkylamino-*s*-triazines are presented in Table 4. For all compounds, there is only one triazine ring signal and one signal for each position in the alkyl chain at high temperatures. The chemical shifts are similar to those of the tetrakisalkyldiaminotriazines, presented in Table 2.

Lowering of the temperature (−60 °C) causes the ^{13}C spectra of the 2,4,6-tris-(dialkylamino)-*s*-triazines again to show varied behaviour: compounds **1a**, **1b**, **1d**, **1e**, **3b**, **6a** and **6b** preserve the pattern encountered at high temperatures; compound **1c** displays a first decoalescence showing one signal for the triazine ring and two signals for each position in the aliphatic chain. A second decoalescence shows three equally intense triazine ring signals and four equally intense signals for each of the first three positions in the butyl chain (Fig. 2). Compounds **3a** and **4** display only one decoalescence, which leaves the triazine carbons equivalent and doubles some signals of the amino group substituents.

The diverse spectral behaviour of the tris-(dialkylamino)-triazines (summarized in Table 5) can be explained by a unified pattern of conformational behaviour: on lowering of the temperature, rotations around both the Ar–N bond and the N–C_α bond become restricted. The energy barriers for each process and the lowest-energy geometry depend on the structure. Thus, the lowest-energy geometry for tris-(diisopropylamino)triazine **3a**, presented in Fig. 1C, has all of the C_α–H bonds pointing in the same rotational direction, as for **2a**. This lowest energy conformation is perhaps due to the

Table 1 ^{1}H NMR assignments for 4,6-bis(dialkylamino)-*s*-triazines

				Position in substituent															
				α				β				Other				ω			
NR_2	Compound	Solvent	T/° C	δ_H[a]	m	J/Hz	H[b]	δ_H	m	J/Hz	H	δ_H	m	J/Hz	H	δ_H	m	J/Hz	H
i-C_3H_7	**2a**	$CDCl_3$	−65	5.10	m		2	1.48	d	7	6								
				3.60	m		2	1.44	d	7	6								
								1.18	d	7	6								
								1.16	d	7	6								
		$CDCl_3$	−60	5.10	br		2	1.46	br		12								
				3.60	br		2	1.17	br		12								
		$(CD_3)_2SO$	120	4.25	h	8	6	1.29	d	8	36								
n-C_8H_{17}	**2b**	$CDCl_3$	−60	3.46	br t	7.5	4	1.53	br		8	1.24	br		40	0.87	br t	7.5	12
				3.40	br t	7.5	4												
		$(CD_3)_2SO$	120	3.49	t	7.5	8	1.60	br		8	1.29	br		40	0.89	br t	7.5	12
n-C_4H_9	**8**	$C_2D_2Cl_4$	−40	3.40	br		4	1.46	br		8	1.22	br		8	0.84	br		12
				3.33	br		4												
		$C_2D_2Cl_4$	100	3.55	t	7.5	8	1.65	c	7.5	8	1.40	x	7.5	8	1.00	t	7.5	12
n-C_4H_9	**9**	$CDCl_3 + C_2Cl_4$	40	3.46	t	7.5	4	1.59	c	7.5	4	1.32	x	7.5	4	0.94	t	7.5	6
				3.37	t	7.5	4	1.49	c	7.5	4	1.22	x	7.5	4	0.87	t	7.5	6
												7.09	s		4				
		$(CD_3)_2SO$	120	3.41	t	7.5	8	1.51	c	7.5	8	1.25	x	7.5	8	0.87	t	7.5	12
												7.09	s		4				
n-C_4H_9	**10**	$CDCl_3 + C_2Cl_4$	24	3.48	t	7.5	4	1.56	br		8	1.31	x	7.5	8	0.93	t	7.5	6
				3.44	t	7.5	4					4.60	s		4	0.90	t	7.5	6
		$CDCl_3 + C_2Cl_4$	60	3.47	t	7.5	8	1.58	c	7.5	8	1.32	x	7.5	8	0.92	t	7.5	12
												4.57	s		4				

[a] br = broad, s = singlet, t = triplet, q = quartet, c = quintet, x = sextet, h = septet. [b] Integration.

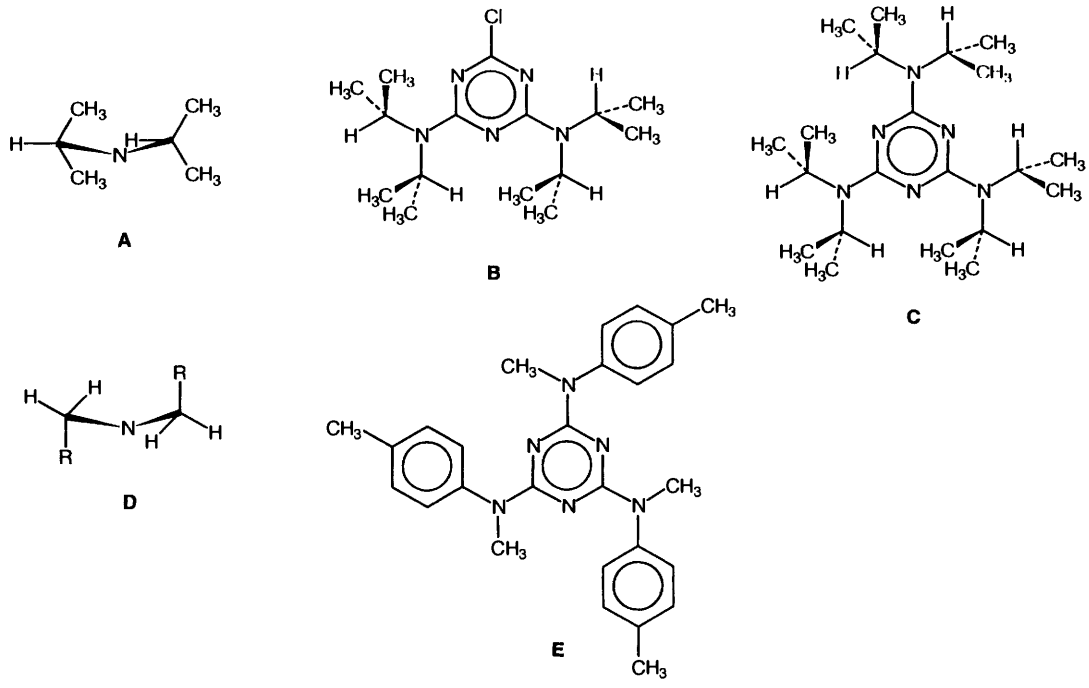


Fig. 1

Table 2 ^{13}C NMR assignments for 4,6-bis(dialkylamino)-*s*-triazines

				δ_C(substituent)					δ_C(triazine ring)	
NR_2	Compound	Solvent	*T*/° *C*	α	β	γ	ω	Other	C-2	C-4,6
i-C_3H_7	**2a**	CD_2Cl_2	−60	46.1 45.6 44.9 44.9	20.6 20.0 19.95 19.72	—	—	—	166.9	163.0 162.5
		$CDCl_3$	20	45.7	18.4 18.3 18.1 18.0	—	—	—	167.0	161.4
		$(CD_3)_2SO$	120	45.1	19.6	—	—	—	166.2	162.9
n-C_8H_{17}	**2b**	CD_2Cl_2	−60	47.5 46.7	29.9 29.6	28.0 24.7	14.2	*a*	168.3	163.5
		$(CD_3)_2SO$	120	46.3	28.2	28.0	12.8	*b*	167.5	162.6
n-C_4H_9	**8**	$CDCl_3$	−40	46.8 46.3	29.8 29.2	20.0 19.7	13.8	—	168.0	163.3
		$C_2D_2Cl_4$	100	46.6	29.6	19.7	13.2	—	168.5	164.5
n-C_4H_9	**9**	$CDCl_3 + C_2Cl_4$	40	47.1 46.8	30.3 30.1	20.3 20.0	13.8	149.5 122.0	170.7	166.0
		$(CD_3)_2SO$	120	45.8	29.0	18.8	12.6	148.5 121.0	169.2	165.0
n-C_4H_9	**10**	$(CD_3)_2SO$	35	47.2 46.8	30.5 30.2	20.5 20.3	14.0	64.1	170.3	166.0
		$CDCl_3 + C_2Cl_4$	60	46.8	30.5	20.4	14.0	64.1	170.2	166.0

[a] C-4: 32.08 + 31.97; C-5: 27.23 + 27.03; C-6: 27.00 + 26.85; C-7: 22.91 + 22.84. [b] C-4: 30.6; C-5: 26.8; C-6: 26.0; C-7: 21.3.

interactions between the different dialkylamino groups. In this arrangement, all of the triazine carbons are equivalent, while the isopropyl groups fall into two non-equivalent groups, both in the proton and carbon spectra.

'Frozen structures' presented in Fig. 1D can explain the spectral behaviour of compounds **1b**, **1d** and **3b**. The α-hydrogens are non-equivalent and the β-protons, coupled to them, show a complex multiplet. Meanwhile, the two alkyl chains are equivalent, so no decoalescence is to be expected in the carbon spectrum. Since complete decoalescence is not observed, but merely a broadening of the signals of the protons in the α and β positions, it is likely that the barrier to rotation around the C_α–N bond in these compounds is rather low. The same might be the case for the other normal-chain compounds, **1a** and **1e**, in which the barrier could be even lower. Compounds **6a** and **6b** demonstrate the same spectral behaviour. However, in these cases the broadening of the proton signals is due to slowing of the six-membered ring inversion.

Table 3 ^{1}H NMR assignments for 2,4,6-tris(dialkylamino)-*s*-triazines

				Position in substituent															
				α				β				Other				ω			
NR_2	Compound	Solvent	T/° C	δ_H	m[a]	J/Hz	H[b]	δ_H	m	J/Hz	H	δ_H	m	J/Hz	H	δ_H	m	J/Hz	H
C_2H_5	**1a**	CD_2Cl_2	−60	3.53	q	8	12									1.14	t	8	18
n-C_3H_7	**1b**	$CDCl_3$	−60	3.42	br t	8	12	1.62	br x	8	12					0.90	t	8	18
		$CDCl_3$	60	3.41	t	8	12	1.61	x	8	12					0.88	t	8	18
i-C_3H_7	**3a**	CD_2Cl_2	−60	5.26	br h	7	3	1.50	d	7	18								
				3.57	br h	7	3	1.16	d	7	18								
		CD_2Cl_2	20	4.40	br		6	1.37	br		36								
		$(CD_3)_2SO$	100	4.37	h	7	6	1.27	d	7	36								
n-C_4H_9	**1c**	CD_2Cl_2	−60	3.48	br		12	1.56	br		12	1.33	br		12	0.91	t	8	18
		c	60	3.41	t	8	12	1.50	c		12	1.36	x	8	12	0.84	t	8	18
i-C_4H_9	**1d**	$CDCl_3$	−60	3.25	br d	7	12	2.14	br n	7	6	0.86	d	7	36				
		$(CD_3)_2SO$	120	3.32	d	8	12	2.12	n	8	6	0.87	d	8	36				
n-C_5H_{11}	**1e**	$CDCl_3$	−60	3.43	t	8	12	1.57	c	8	12	1.29	m		24	0.89	t	8	18
n-C_8H_{17}	**3b**	$CDCl_3$	−60	3.42	br t	8	12	1.58	br		12	1.29	m		60	0.89	t	8	18
		c	80	3.33	t	8	12	1.56	c	8	12	1.29	m		60	0.88	t	8	18
$-CH_3$	**4**	CD_2Cl_2	−60	3.32	br s		9	7.03	d	8	6	7.12	d	8	6	2.30	s		9
$-C_6H_4CH_3$-*p*																			
		d	60	3.33	s		9	7.01	d	8	6	7.12	d	8	6	2.30	s		9
$-(CH_2)_5-$	**6a**	$CDCl_3$	−60	3.75	br		12	1.60	br		12	1.60	br		6				
		$CDCl_3$	60	3.69	t	5	12	1.53	m		12	1.60	m		6				
$-(CH_2)_2-O-(CH_2)_2-$	**6b**	$CDCl_3$	−60	3.77	br		12	3.77	br		12								
		$CDCl_3$	60	3.73	m		12	3.78	m		12								

[a] br = broad, s = singlet, t = triplet, q = quartet, c = quintet, x = sextet, h = septet, n = nonet. [b] Integration. [c] $CDCl_3$ + C_2Cl_4. [d] $CDCl_3$ + $(CD_3)_2SO$.

Table 4 ^{13}C NMR assignments for 2,4,6-tris(dialkylamino)-*s*-triazines

NR_2	Compound	Solvent	*T*/°C	δ_C(substituent) α	β	γ	ω	Other	δ_C(triazine ring)
C_2H_5	**1a**	CD_2Cl_2	−60	44.1	14.2				164.9
n-C_3H_7	**1b**	CD_2Cl_2	−60	48.6	21.3	11.3			164.2
i-C_3H_7	**3a**	CD_2Cl_2	−60	44.6 43.9	20.8 19.9				163.1
		CD_2Cl_2	20	44.9	21.0				164.1
n-C_4H_9	**1c**	CD_2Cl_2	−40	48.35 47.49 46.82 46.60	30.21 30.12 30.07 29.71	20.39 20.25 20.22 19.61	14.03		164.2 160.1 155.7
		CD_2Cl_2	10	48.1 47.2	30.6	20.7 20.4	14.2		160.3
		$CDCl_3$	60	47.6	30.4	20.3	13.8		159.6
i-C_4H_9	**1d**	$CDCl_3$	−60	56.1	27.3	20.5			164.4
n-C_5H_{11}	**1e**	$CDCl_3$	−60	47.1	29.5	28.1	22.7	14.1	164.9
n-C_8H_{17}	**3b**	$CDCl_3$	−60	47.7	29.0	27.9	14.4	*a*	165.5
$-CH_3$ $-C_6H_4CH_3$-*p*	**4**	CD_2Cl_2	−60	37.1 36.7	141.2 141.7	125.5	128.2	*b*	163.6
		d	60	35.5	140.6	124.3	127.0	*c*	163.6
$-(CH_2)_5-$	**6a**	$CDCl_3$	−60	43.5	25.6	24.8			164.6
$-(CH_2)_2-O-(CH_2)_2-$	**6b**	$CDCl_3$	−60	43.0	66.8				164.5

[a] C-4: 32.5; C-5: 30.2; C-6: 30.0; C-7: 23.2. [b] C-5: 134.1; C-6: 20.7 (for positions labelling, see Scheme 1). [c] C-5: 133.9; C-6: 20.8. [d] $CDCl_3$ + $(CD_3)_2SO$.

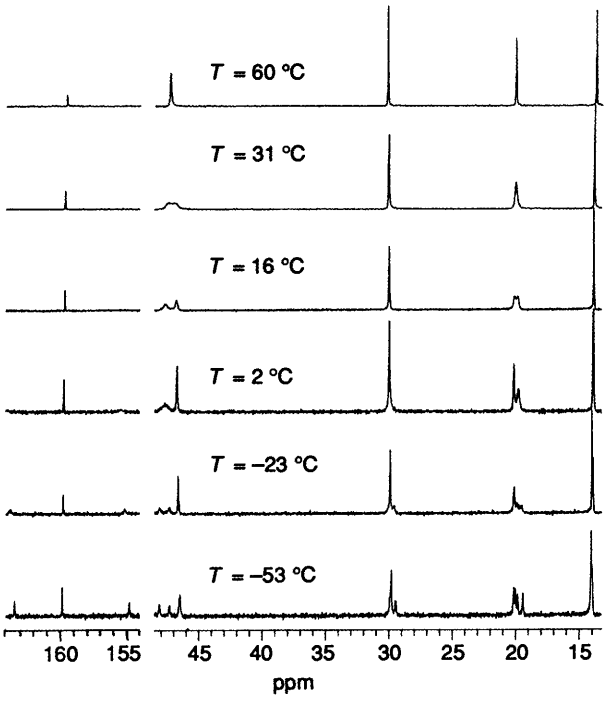


Fig. 2

Compound **4** is the only structure which contains different groups on the amino nitrogen. The lowest-energy structure, implying restricted rotation around the Ar–N bonds, presented in Fig. 1E, should give rise to one signal for each of the α, β, 5 and 6 positions (Scheme 1) and two signals for each of the γ and ω positions. Decoalescences of the α and β carbon signals

Table 5 Spectral behaviour (number of decoalescences) of tris(dialkylamino)triazines

Compound	^1H spectrum	^{13}C spectrum
1a, 1e	none	none
1b, 1d, 3b, 6a, 6b	(partial)	none
4	(partial)	one
3a	one	one
1c	(partial)	two

suggest that not all of the dialkylamino groups are in the same plane as the triazine ring.

A satisfactory explanation is still being sought for the spectral behaviour of compound **1c**. It might be that in this case, van der Waals associations between alkyl chains, or CH/π interactions[11] between the alkyl chains and the highly polarizable triaminotriazine moiety play a role. A better understanding of the processes that govern the spectral behaviour of tris(dialkylamino)triazines is expected to be gained by the results of X-ray spectroscopy and by consideration of the barriers measured by NMR spectroscopy in conjunction with the results of molecular mechanics modelling; we hope to provide this later.

Experimental

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. ^1H and ^{13}C spectra were obtained on either a Varian VXR 300 MHz or a General Electric QE 300 MHz spectrometer with tetramethylsilane as the internal standard. *J* values are given in Hz. The dynamic ^1H and ^{13}C NMR experiments were performed on a Varian VXR 300

Table 6 Analytical data for bis- and tris-(dialkylamino)-*s*-triazines

Compound (Formula)	Yield (%)	Mp/° C	Lit. mp/° C	Lit. ref.	Recryst. solvent	Found (%) (required) C	H	N	M^+ Found (required)
1a	80	oil	47	2, *a*	—	—	—	—	—
1b ($C_{21}H_{42}N_6$)	80	75	68	4, *b*	EtOH	66.93 (66.67)	11.36 (11.11)	21.97 (21.97)	—
1c	45	112	4	4	EtOH	—	—	—	463.441[c] (462.448)
1d ($C_{27}H_{54}N_6$)	80	105–106	91	4	EtOH	70.07 (70.13)	11.95 (11.69)	18.35 (18.18)	—
1e	55	oil	—	12	—	—	—	—	547.527[c] (546.530)
2a	80	111	—	13	EtOH	—	—	—	—
2b ($C_{35}H_{68}N_5Cl$)	75	oil		14		70.83 (70.83)	11.88 (11.88)	11.26 (11.26)	—
3a ($C_{21}H_{42}N_6$)	98	154–188			EtOH	66.36 (66.67)	11.37 (11.11)	22.48 (22.17)	—
3b ($C_{51}H_{102}N_6$)	70	35–36	32	4	EtOH	76.19 (76.19)	13.33 (13.04)	10.45 (10.51)	—
4 ($C_{27}H_{30}N_6$)	45	160–161			Pr^iOH	73.81 (73.97)	6.96 (6.85)	19.30 (19.18)	—
				3					
6a ($C_{18}H_{30}N_6$)	80	288–232	210–221		EtOH	65.46 (65.45)	9.29 (9.09)	25.65 (25.45)	—
				3					
6b ($C_{15}H_{24}N_6O_3$)	80	276	284–289		EtOH	53.43 (53.57)	7.22 (7.15)	25.28) (25.03)	—
				12					
8	70	oil			—	—	—	—	—
				—					
9 ($C_{44}H_{76}N_{10}O_2$)	25	>350	—		C_2Cl_4	67.49 (67.79)	9.84 (9.74)	18.02 (17.95)	—
				—					
10 ($C_{40}H_{76}N_{10}O_2$	65	35	—		EtOH	68.46 (68.38)	11.13 (10.83)	20.08 (19.94)	—

[a] Lit.,[4] 12 °C. [b] Products were purified by distillation. [c] HRMS (POS FAB GLY, M + 1).

instrument, and the temperature was that indicated by the VT unit. High resolution mass spectra were recorded on a Kratos AEI 30 mass spectrometer. TLC was carried out on pre-coated plates (silica gel G60) purchased from Fisher. Cyanuric chloride and secondary amines were purchased from Aldrich and used without further purification. THF, toluene and diethyl ether were distilled from sodium–benzophenone under nitrogen prior to use. NMR data are given in Tables 1–4. Other analytical and experimental data are given in Table 6.

General procedure for the preparation of compounds 1a and 1d

The corresponding amine (82 mmol) was added dropwise to cyanuric chloride **5** (2.0 g, 11 mmol) in DMF (50 cm^3) at 0–5 °C. When the addition was complete, the mixture was heated under reflux for 8 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (2 × 50 cm^3). The organic layer was dried over $MgSO_4$ and the solvent removed *in vacuo* to give the crude product.

General procedure for the preparation of compounds 1b and 2a

The corresponding amine (100 mmol) in acetone (50 cm^3) was treated with cyanuric chloride **5** (2.0 g, 11 mmol) in acetone (50 cm^3) at 0 °C. When the addition was complete the mixture was heated under reflux for 8 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (2 × 50 cm^3). The organic layer was washed with water (5 × 100 cm^3), dried over $MgSO_4$ and the solvent removed *in vacuo* to give a yellow oil, which was precipitated with ethanol.

General procedure for the preparation of compounds 1c and 1e

Cyanuric chloride **5** (5.0 g, 27 mmol) in THF (40 cm^3) was added dropwise to a solution containing the corresponding di-*n*-alkylamine (77 mmol) and 5% aqueous sodium carbonate (200 cm^3). The mixture was refluxed for 24 h, and then allowed to stand at room temperature to effect complete precipitation (**1c**) or separation (**1e**) of the product. The crude product was washed with a mixture of EtOH–water (1 : 1).

2-Chloro-4,6-bis(di-*n*-octylamino)-*s*-triazine (2b)

Cyanuric chloride **5** (5.0 g, 27 mmol) in aqueous 5% sodium carbonate (200 cm^3) was treated with di-*n*-octylamine (10.0 g, 41 mmol) and the mixture refluxed for 8 h. The solution was cooled to room temperature and the organic layer was extracted with CH_2Cl_2 (80 cm^3), washed with water (3 × 150 cm^3) and dried over $MgSO_4$. The solvent was removed *in vacuo* to yield the title compound in a pure state.

2,4,6-Tris-(diisopropylamino)-*s*-triazine (3a)
2-Chloro-4,6-bis(diisopropylamino)-*s*-triazine **2a** (0.54 g, 2 mmol) and diisopropylamine (0.30 g, 3 mmol) were heated in a stainless steel bomb (Swagelok, 4 cm^3) for 72 h at 200 °C. The reaction mixture was cooled, dissolved in dichloromethane and washed with water (3 × 50 cm^3). The organic layer was dried ($MgSO_4$), the solvent removed *in vacuo*, and the residue recrystallized.

2,4,6-Tris-(di-*n*-octylamino)-*s*-triazine (3b)
Di-*n*-octylamine (7.23 g, 30 mmol) was added dropwise to the chlorotriazine **2b** (12 g, 20 mmol) at 25 °C and the mixture refluxed for 8 h. The reaction mixture was allowed to cool to room temperature to effect complete precipitation of the product. The precipitate was filtered and washed with EtOH–water (9:1) to give the title compound as white crystals.

2,4,6-Tris-(*N*-methyl-*p*-tolylamino)-*s*-triazine (4)
N-Methyl-*p*-toluidine (6 g, 50 mmol) was added dropwise to cyanuric chloride **5** (2.0 g, 11 mmol) in DMF (50 cm^3) and the mixture refluxed for 8 h. The reaction mixture was allowed to cool to room temperature, and triazine **4** was precipitated with EtOH. The precipitate was filtered and washed with EtOH–water (9:1) to give the title compound as white crystals.

General procedure for the preparation of compounds 6a and 6b
The corresponding amine (200 mmol) in acetone (50 cm^3) was treated with cyanuric chloride **5** (2.0 g, 11 mmol) in acetone (50 cm^3) at 0 °C. When the addition was complete the mixture was heated under reflux for 8 h. Any insoluble material was removed by filtration and the acetone was distilled off. The filtrate and the residue were dissolved in an additional quantity of amine (100 mmol). The mixture was heated under reflux for 8 h, then allowed to cool to room temperature, poured into water and extracted with CH_2Cl_2 (2 × 50 cm^3). The organic layer was washed with water (5 × 100 cm^3), dried over $MgSO_4$ and the solvent removed *in vacuo* to give the crude product.

2,2′-*p*-Phenylenedioxybis(4,6-dichloro-*s*-triazene) 7
A mixture of cyanuric chloride **5** (4 g, 22 mmol) and 1,4-hydroquinone (1.1 g, 10 mmol) in methanol (40 cm^3) was treated with aqueous 8% NaOH (40 cm^3) at room temperature for 3 h to give the crude product as a white precipitate. The precipitate was filtered and washed with methanol (3 × 20 cm^3), then dried *in vacuo* to give the title compound as a white solid, yield 75%.

4,6-Bis(di-*n*-butylamino)-2-chloro-*s*-triazine (8)
A solution of cyanuric chloride **5** (2.0 g, 11 mmol) in THF (5 cm^3) was added to a stirred solution of dibutylamine (9.7 g, 75 mmol) in THF (25 cm^3) at 20 °C over 15 min, and the reaction mixture stirred for an additional 90 min. The solvent was removed *in vacuo* and the oily residue was dissolved in chloroform (50 cm^3), then washed with water until the aqueous phase remained neutral. The organic layer was dried over Na_2SO_4, and the solvent evaporated *in vacuo* to give the title compound.

2,2′-*p*-Phenylenedioxybis[4,6-bis(dibutylamino)-*s*-triazine] (9)
A mixture of the dichlorotriazine **7** (6.6 g, 18 mmol) and di-*n*-butylamine (11.5 g, 89 mmol) was heated at 150 °C for 10 h. The reaction mixture was cooled to room temperature to give a white precipitate which was extracted with C_2Cl_4 (3 × 30 cm^3). The organic layer was washed successively with 5% aqueous hydrochloric acid (3 × 25 cm^3), 5% aqueous Na_2CO_3 (2 × 30 cm^3) and water (25 cm^3), then dried over Na_2SO_4. The solvent was removed *in vacuo* and the solid residue was triturated with EtOH and dried to give the title compound as white crystals.

2,2′-Ethane-1,2-diyldioxybis[4,6-bis(dibutylamino)-*s*-triazine (10)
The dichlorotriazine **7** (6.6 g, 18 mmol) was added to a solution of sodium ethylene glycolate in ethylene glycol, prepared from sodium (0.41 g, 11 mmol) and dry ethylene glycol (10 cm^3). The mixture was heated at 150 °C for 4 h, until no starting material **7** remained (TLC). The reaction mixture was cooled to room temperature to yield a white precipitate which was filtered and recrystallized from EtOH to give the title compound as a white solid.

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