Restricted rotations in 4,6-bis- and 2,4,6-tris-(*N*,*N*-dialkylamino)-*s*-triazines

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Barriers to rotation have been measured in some 4,6-bis- and 2,4,6-tris-(*N*,*N*-dialkylamino)-*s*-triazines. X-Ray crystal structures are reported for 2-chloro-4,6-bis(diisopropylamino)-*s*-triazine 1, 2,4,6-tris(diisopropylamino)-*s*-triazine 6, 2,4,6-tris(diisobutylamino)-*s*-triazine 8 and the tetrakis(dibutylamino) derivative 12. In the isopropyl compounds 1 and 6, the structures are precisely ordered with all the isopropyl groups in the same direction: the dynamic NMR behaviour is in good agreement and barriers for rotation around the N–Ar and N–C_α bonds in 1 were assigned as 15.6 and 12.1 kcal mol^{-1}, respectively.

Introduction

We have previously described[1] the variable temperature ^{1}H and ^{13}C NMR spectra of the bis(dialkylamino)-*s*-triazines **1**–**3**, **11**, **12** and tris(dialkylamino)-*s*-triazines **4**–**10**. The temperature dependence of the spectral behaviour of these compounds is summarized in Table 1. We found[1] that all the bis(dialkylamino)-*s*-triazines with normal chains (**2**, **3**, **11**, **12**) displayed, in the ^{13}C spectrum, a single decoalescence which doubled the signals of each carbon in the chain. In the proton spectrum a decoalescence was observed which doubled the signals for the α-positions in compounds **2** and **3** and for all the positions in compounds **11** and **12**. The tris(dialkylamino)-*s*-triazines with normal and branched chains displayed varied spectral behaviour. Compound **1** showed two decoalescences in both the ^{1}H and ^{13}C spectra.

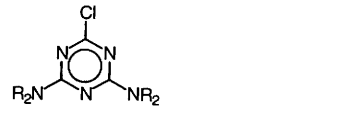
We now offer a detailed explanation of the spectral behaviour of these compounds and support this by X-ray data. The values of the barriers to rotation, determined by dynamic NMR spectroscopy, are also presented.

Results and discussion

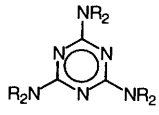
The barriers to rotation were measured in the ^{13}C NMR spectra for compounds displaying decoalescences, using the relation $\Delta G^{\ddagger}_c = aT_c$ [9.972 + log($T_c/\Delta\nu_c$)], where $\Delta G^{\ddagger}_c$ is the free enthalpy of activation at the coalescence temperature, T_c, $\Delta\nu_c$ is the frequency separation of the isochronous sites (extrapolated to T_c), and $a = 4.575 \times 10^{-3}$ for $\Delta G^{\ddagger}_c$ in kcal mol^{-1}.† This relation[2] is valid for exchange between equally populated sites, which is the case for the molecules under consideration. Whenever possible, more than one signal was used for the measurement of the same barrier. The measured free enthalpies of activation ($\Delta G^{\ddagger}_c$) for the rotations in dialkylamino-*s*-triazines are given in Table 2. The reliability of these values is ±0.04 kcal mol^{-1}, which corresponds to an uncertainty of ±1 °C in the temperature measurement. The δ_C value is given for the coalesced signal.

The lowest energy structures of the dialkylamino-*s*-triazines will be discussed assuming that all of the N–C_α bonds are in the plane of the triazine ring due to the partial double-bond character of the ring C–NR_2 (N–Ar) bonds, which is due to the conjugation of the lone pair on the amino nitrogen with the highly electron-deficient triazine ring. It was previously demonstrated that the less electron-deficient pyrimidine ring is electron-withdrawing enough to induce restricted rotation in dialkylaminopyrimidines.[3] Furthermore, the X-ray data show that all the crystalline dialkylamino-*s*-triazines display this planar framework together with significant double-bond character in the exocyclic N–Ar bonds.

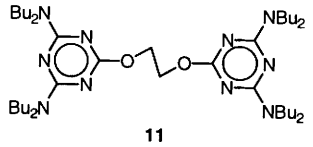
The structures of **1**, **6**, **8** and **12** have all been determined by single crystal X-ray crystallography. Figs. 1–4 show perspective views and atom labelling of these structures. Table 3 lists



1: R = Pr^i
2: R = Bu
3: R = C_8H_{17}



4: R = Et
5: R = Pr
6: R = Pr^i
7: R = Bu
8: R = Bu^i
9: R = C_5H_{11}
10: R = C_8H_{17}



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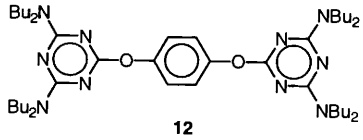

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Table 1 Number of decoalescences of the signals of bis- and tris-(dialkylamino)-*s*-triazines

Compound	^{1}H spectrum	^{13}C spectrum
1	two	two
2, **3**, **11**, **12**	one	one
4, **9**	none	none
5, **8**, **10**	(partial)[a]	none
6	one	one
7	(partial)	two

[a] A partial decoalescence means that merely a broadening of the lines was observed.

† 1 cal = 4.184 J.

Table 2 Barriers to rotation in dialkylamino-*s*-triazines

Compound	Solvent	δ_C	Position[a]	T_c/K	$\Delta G^{\ddagger}_c$/kcal mol^{-1}
1	$CDCl_3$	162.7	arom.	243	12.09
		19.8	β	252	12.08
		20.3	β	310.5	15.61[b]
6	$CDCl_3$	44.8	α	266.5	13.01
		20.8	β	269.5	13.04
7	$CDCl_3$	48.2	α	270	13.14
		47.5	α	305	14.88[b]
		19.7	γ	258	12.94
		20.5	γ	297	15.08[b]
2	$C_2D_2Cl_4$	46.5	α	348	17.6
		29.5	β	349.5	17.8
		19.8	γ	345	17.8
3	$C_2D_2Cl_4$	47.1	α	353	17.92
		29.8	β	346	18.01
		27.1	ε	356	17.95
11	$C_2D_2Cl_4$	46.9	α	335	17.18
		30.3	β	341	17.13
		20.4	γ	326.5	17.12
12	$C_2D_2Cl_4$	46.9	α	337.5	17.36
		30.2	β	338	17.15
		20.1	γ	336	17.38

[a] Nature of the C-atom of which the signal undergoes coalescence: arom. indicates ring carbon; α, β, γ, ε indicate various alkyl carbons. [b] Values for the second barrier to rotation.

Table 3 Selected bond lengths (Å) and angles (°)

	1	**6**	**8**	**12**
N(1)–C(2)	1.299(3)	1.345(2)	1.339(2)	1.319(6)
N(1)–C(6)	1.367(3)	1.343(2)		1.375(7)
C(2)–X(2)[a]	1.759(2)	1.366(2)	1.363(2)	1.370(6)
C(2)–N(3)	1.311(3)	1.330(2)	1.341(2)	1.300(6)
N(3)–C(4)	1.364(3)	1.346(2)	1.345(2)	1.362(6)
C(4)–N(4)	1.349(3)	1.362(2)	1.359(3)	1.333(6)
C(4)–N(5)	1.337(3)	1.341(2)		1.335(6)
N(5)–C(6)	1.330(3)	1.336(2)		1.339(7)
C(6)–N(6)	1.346(3)	1.372(2)		1.344(6)
C(6)–N(1)–C(2)	112.0(2)	113.9(1)	113.4(2)[a]	111.3(5)
N(3)–C(2)–N(1)	131.6(2)	126.0(1)	126.8(2)	129.4(5)
N(3)–C(2)–X(2)[b]	114.3(2)	117.3(1)	116.6(1)	118.1(5)
N(1)–C(2)–X(2)[b]	114.1(2)	116.7(1)	116.6(1)	112.4(5)
C(2)–N(3)–C(4)	111.6(2)	114.3(1)	113.3(2)	114.4(5)
N(5)–C(4)–N(3)	124.3(2)	125.5(1)	126.5(2)[a]	123.9(6)
N(5)–C(4)–N(4)	118.0(2)	117.1(1)		119.9(5)
N(3)–C(4)–N(4)	117.8(2)	117.5(1)	116.8(1)	116.2(5)
C(6)–N(5)–C(4)	116.4(2)	114.4(1)		115.1(5)
N(5)–C(6)–N(1)	124.2(2)	125.9(1)		125.7(5)
N(5)–C(6)–N(6)	118.8(2)	117.5(1)		117.7(5)
N(1)–C(6)–N(6)	117.0(2)	116.6(1)		116.6(6)

[a] C(6) and N(5) generated from C(2) and N(3) by the transformation: $-x, y, \frac{3}{2} - z$. [b] X(2) = Cl for **1**; X(2) = N(2) for **6** and **8**; X(2) = O(1) for **12**.

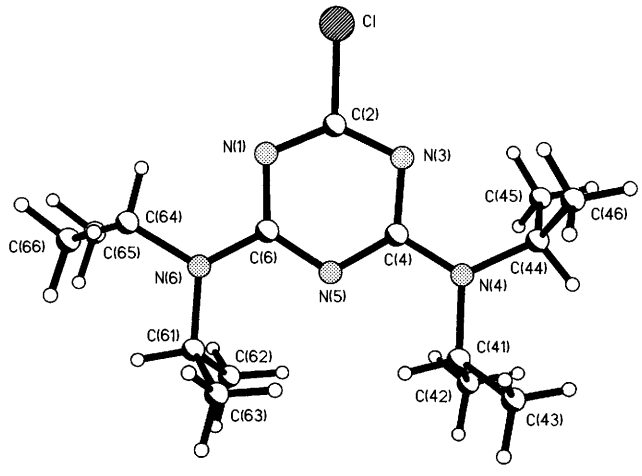

Fig. 1 Perspective view and atom labelling of X-ray structure of **1**

selected bond lengths and angles for the triazine rings of the structures. In all structures the triazine rings are close to planar, the maximum deviation from planarity being 0.026 Å for N(1′) of **12**. The geometries of the triazine rings deviate significantly from idealised hexagons. Specifically, the internal angles at the nitrogen atoms are more acute than 120° (mean value, 113.6°), while the angles at the carbons are more obtuse (mean value 126.3°). This is characteristic of other triazines in the literature.[4–11] The attached amino substituents show clear evidence of partial double bonding to the triazine carbons, with a mean value for the N–C bond length of 1.355 Å, as compared with the C–N bond length in methylamine of 1.474 Å. Consequently, all attached α carbons lie approximately in the plane of the triazine ring; Table 4 lists the deviations, in Å, of selected atoms from the mean triazine ring planes.

Dynamic behaviour of diisopropylamino-*s*-triazines 1 and 6

Polyisopropyl systems in which several isopropyl groups are attached to a planar skeleton (*e.g.* hexaisopropylbenzene[12] and tetraisopropylethylene[13]) have been shown to exist in a 'tongue and groove' ('statistically geared') conformation in which all the isopropyl groups are bisected by the central plane and are oriented in the same direction. We will show that the spectral

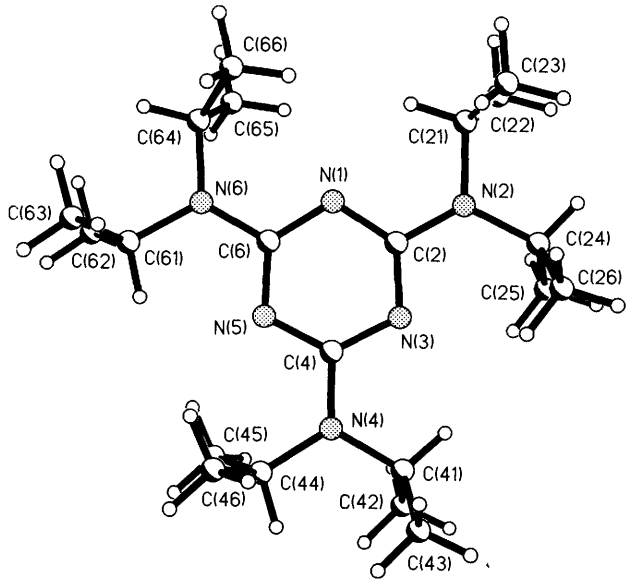

Fig. 2 Perspective view and atom labelling of X-ray structure of **6**

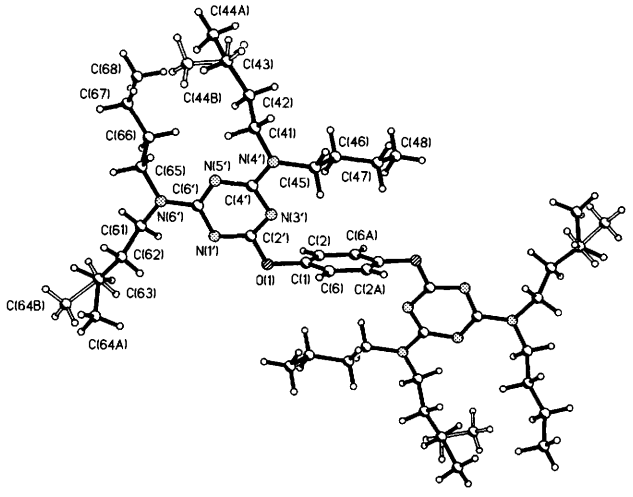

Fig. 3 Perspective view and atom labelling of X-ray structure of **12** (multiple drawing of the same methyl group represents disorder)

behaviour of compounds **1** and **6** are in perfect agreement with similarly geared, homodirectionally oriented structures, presented in Fig. 5 and that this interpretation is further supported by X-ray data.

Unlike any other previously described structure with isopropyl groups attached to a planar framework, in compound **1**, (*i*) correlated rotations around the N–Ar bond and (*ii*) correlated rotations around the N–C_α bond can both interconvert isochronous sites. For rotations around the N–C_α bonds the isochronous sites are 1 with 4 and 2 with 3, while for rotations around the N–Ar bond the isochronous sites are 1 with 3 and 2 with 4. The spectral behaviour of compound **1** proves that both rotations occur, but since the NMR signals for positions 1–4 could not be assigned, it was not possible from the behaviour of **1** alone to determine which of the two barriers is due to a particular rotation. However, in compound **6** correlated rotations around the N–Ar bond do not exchange isochronous sites, thus the barrier to rotation (13.0 kcal mol^{-1}) can be assigned to the rotation around the N–C_α bonds. It is likely that the two isopropyl groups in the diisopropylamino moiety are less compressed in **1** than in **6**; hence the barriers to rotation in compound **1** were assigned as follows: $\Delta G^{\ddagger}_{c}$ = 12.1 kcal mol^{-1} to rotation around the N–C_α bonds and $\Delta G^{\ddagger}_{c}$ = 15.6 kcal mol^{-1} to rotation around the N–Ar bonds.

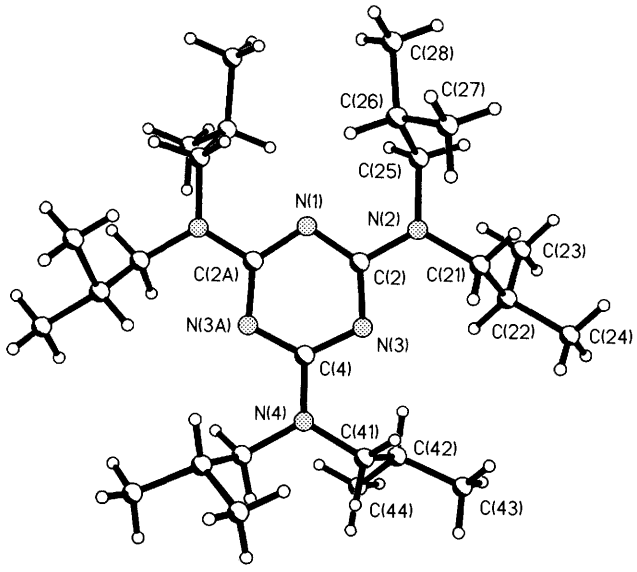

Fig. 4 Perspective view and atom labelling of X-ray structure of the major conformer of **8**

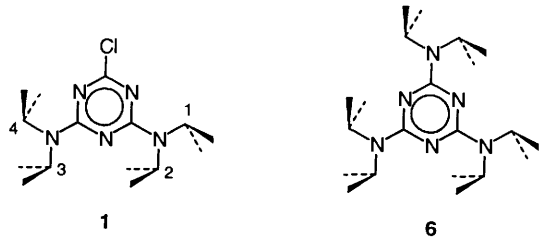

Fig. 5 Frozen structures for diisopropylamino-*s*-triazines

The solid-state structure (Fig. 1) of 2-chloro-4,6-bis(diisopropylamino)-*s*-triazine **1** has the four isopropyl substituents in the lowest energy conformation discussed above. This 'geared' conformation has all the isopropyl groups oriented in the same direction. The internal angle at C(2) is particularly large (Table 3) and correlates with the C–Cl bond length according to the relationship recently proposed by Glowka and Iwanicka for other chlorotriazines.[9] There is no evidence for the N • • • Cl intermolecular interactions observed in some chlorotriazines,[10,11] presumably as a result of the steric bulk of the isopropyl substituents. 2,4,6-Tris-(diisopropylamino)-*s*-triazine **6** also exists in the solid state as the most stable conformer with all substituents geared in the same direction (Fig. 2). There is no disorder of these substituents, in contrast to the structures of hexaisopropylbenzene[12] and the pentaisopropylcyclopentadienyl radical.[14]

Dynamic behaviour of dialkylamino-*s*-triazines with normal chains

Lowest energy structures for both bis- and tris-(dialkylamino)-*s*-triazines with normal alkyl chains will be discussed, assuming that the two alkyl groups bonded to each nitrogen are on different sides of the planar skeleton of the molecule, as shown in Figs. 6 and 7 for the bis- and tris-compounds, respectively. In a similar way, an opposite orientation of the alkyl groups in *N*,*N*-dialkylamides has been documented[15] and explained by their repulsive van der Waals interaction.

Dynamic behaviour of bis(dialkylamino)-*s*-triazines with normal chains

There are two lowest energy conformations for bis(dialkylamino)-*s*-triazines with normal chains that are in agreement with the spectral behaviour of these compounds, one with a symmetry axis, the other with a symmetry plane, as presented in Fig. 6. For both the C_2 and the C_s conformations, the

Table 4 Selected atomic displacements (Å) from the plane of the triazine ring

	1	6	8	12
Ar–X	−0.009 (Cl)	0.030 N(2)	−0.023 N(2)	−0.047 O(1)
	0.028 N(4)	−0.018 N(4)	0.000 N(4)	−0.050 N(4')
	−0.001 N(6)	0.006 N(6)		−0.057 N(6')
N–Cα	0.089 C(41)	0.108 C(21)	−0.066 C(21)	0.024 C(41)
	−0.069 C(44)	0.089 C(24)	−0.043 C(25)	0.027 C(45)
	−0.013 C(61)	−0.100 C(41)	0.167 C(41)	−0.120 C(61)
	0.010 C(64)	0.015 C(44)		−0.273 C(65)
		0.030 C(61)		
		−0.141 C(64)		

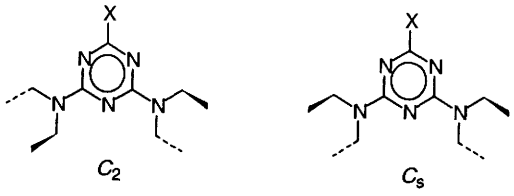

Fig. 6 Frozen structures of bis(di-*n*-alkylamino)-*s*-triazines

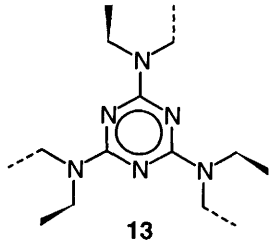

Fig. 7 Frozen structures of tris(di-*n*-alkylamino)-*s*-triazines

alkyl groups close and remote to the X moiety are non-equivalent and are interconverted by rotation around the N–Ar bond. The barriers to rotation should not depend on the alkyl group, and indeed, for compounds **2** and **3** which both have X = Cl, the difference is the same as the error in measurement (0.2 kcal mol^{-1}). Compounds having X = Cl present barriers to rotation *ca.* 0.4 kcal mol^{-1} higher than compounds having X = O (**11** and **12**) and this can be explained by the decrease in the electron-withdrawing power of the triazine ring when the Cl atom is replaced by the more electron-donating oxygen atom. The barrier to rotation in the isopropyl chain compound **1** is *ca.* 2.2 kcal mol^{-1} lower than in the similar butyl chain compound **2**. This is consistent with the repulsive nature of the interaction between the diisopropylamino groups in **1**, that destabilises the ground state.

X-Ray data in this series, available as yet for compound **12** only (Fig. 3), suggest that conformations with adjacent alkyl chains on different dialkylamino groups situated on the same side of the planar framework (conformations C_s in Fig. 6) are possible and even conformations with the alkyl groups bonded to the same nitrogen situated on the same side of the triazine ring might be a possibility.

The hydroquinone derivative **12** crystallises about a crystallographic centre of inversion. Two of the terminal methyl groups are disordered, with approximately equal site occupancies (Fig. 3). In this case the butyl substituents do not exist in the lowest energy conformation. In fact, three of the four butyl groups attached to each triazine ring lie on the same side of the triazine plane. This is likely to be a consequence of the dissymmetry introduced by the aryl group in combination with crystal packing forces.

Dynamic behaviour of tris(dialkylamino)-*s*-triazines with normal chain

'Frozen conformation' **13**, with D_3 symmetry, which explains the spectral behaviour of compounds **5**, **8** and **10** is presented in Fig. 7. The N–Ar bond is a C_2 axis of the dialkylamino group and the alkyl chains are alternately on one side or the other of the planar framework, in a propeller shape. In this structure all carbons corresponding to the same position in the alkyl chains are equivalent, while the two protons are not. Exchange between isochronous sites occurs, as in compound **6**, by rotations around the N–C_α bonds. When these rotations become slow on the NMR time-scale, a broadening of the proton signals, clearly visible for the α-positions in compounds **5**, **8** and **10**, occurs. Compounds **4** and **9** should present similar frozen structures, but possess lower rotational barriers **4** or lower frequency separation between isochronous sites **9**.

2,4,6-Tris(diisobutylamino)-*s*-triazine **8** has a crystallographic C_2 axis of symmetry, but does not exist in the highest symmetry conformation **13**. Specifically, the orientation of one of the three crystallographically independent isobutyl substituents [at N(4)] is the opposite of that expected in the lowest energy conformation. Inspection of intra- and inter-molecular contact distances failed to explain this observation. However one of the isobutyl substituents is disordered over two orientations of its isopropyl component in a 2:1 ratio (only the major contributor is shown in Fig. 4).

No explanation can as yet be provided for the spectral behaviour of compound **7**. Further information is expected from its X-ray crystal structure.

Conclusion

We have demonstrated that through-space interaction between substituents in a *meta* relationship can determine the solid-state equilibrium conformation and the solution conformation and the dynamic NMR behaviour in a series of bis(dialkylamino)- and tris(dialkylamino)-*s*-triazines. The results described in our paper significantly expand our knowledge of such long-range interactions.

Experimental

Materials

Compounds **1**–**12** were prepared as described in our previous work.[1]

Dynamic NMR

The dynamic ^1H and ^{13}C NMR experiments were performed on a Varian VXR 300 instrument. The $\Delta G^{\ddagger}_c$ values depend critically on the accurate measurement of T_C,[16] hence an internal probe (neat methanol for temperatures in the range −60–50 °C or neat ethylene glycol for temperatures in the range 20–80 °C) was employed. The probe was placed in a 1 mm OD tube concentrically inserted in the 5 mm OD NMR tube containing the sample. The temperature was measured using a four transients proton spectrum with a total acquisition time of 4 s. The heating of the sample due to the irradiation used for decoupling was monitored by means of a queue of alternating

Table 5 Crystal data, collection and refinement parameters

	1	6	8	12
Formula	$C_{15}H_{28}ClN_5$	$C_{21}H_{42}N_6$	$C_{27}H_{54}N_6$	$C_{44}H_{76}N_{10}O_2$
M	313.87	378.61	462.76	777.15
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
a/Å	12.368(1)	19.157(2)	17.041(3)	12.201(4)
b/Å	13.796(1)	11.160(1)	12.191(2)	20.260(5)
c/Å	11.820(1)	12.101(1)	14.273(2)	9.386(3)
β/°	117.612(6)	113.98(1)	90	101.04(2)
V/Å^3	1789.7(2)	2363.8(4)	2965.2(8)	2277(1)
Space group	$P2_1/c$	Cc	$Pbcn$	$P2_1/c$
Z	4	4	4	2
D_x/g cm^{-3}	1.165	1.064	1.037	1.133
Crystal colour	Colourless	Colourless	Colourless	Colourless
Dimensions/mm	0.54 × 0.40 × 0.18	0.68 × 0.61 × 0.48	0.79 × 0.48 × 0.35	0.83 × 0.24 × 0.18
μ/cm^{-1}	2.16	0.65	0.62	0.72
Temperature/K	130	130	130	132
2θ-range/°	4–50	4–52	4–54	4–48
Data collected	$\pm h, +k, +l$	$\pm h, +k, \pm l$	$+h, +k, +l$	$\pm h, +k, +l$
No. measured	3009	4032	3244	3536
No. with $I > 2\sigma(I)$	1858	3396	1625	1320
a	0.0547	0.0552	0.0491	0.0678
Parameters	190	245	174	274
R_w (all data)	0.102	0.085	0.097	0.190
$R1$ [$I > 2\sigma(I)$]	0.043	0.035	0.043	0.084
Esd (distances)/Å	0.002–0.004	0.002–0.003	0.002–0.005	0.006–0.02
Esd (angles)/°	0.2–0.2	0.12–0.2	0.1–0.4	0.4–0.9

carbon and proton experiments. After about 100 transients the temperature stabilised within a range of 0.5 °C, so the ^{13}C NMR spectra were run using a sequence of 100 dummy transients followed by 1000 normal transients. Near the coalescence temperature, spectra were run at an interval of 1 °C, thus the expected error for the T_c measurements is ± 1 °C, which corresponds to a maximum error in $\Delta G^{\ddagger}_c$ of 0.04 kcal mol^{-1}.

X-Ray crystallography. Data collections, structure solutions and refinements

The crystal data, collection and refinement parameters for the four structures are listed in Table 5. All measurements were made with a Nicolet P4s diffractometer using graphite monochromatised Mo-Kα (λ = 0.710 73 Å) radiation. Cell parameters were determined by least-squares refinement on diffractometer angles for at least 30 centred reflections with $2\theta > 20°$. Throughout data collections (ω scan mode) the intensities of three standard reflections were monitored at regular intervals and in no case showed variations of > 5%. Intensities were corrected for Lorentz and polarisation effects, but not for absorption.

The structures were solved by direct methods using SHELXS,[17] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-93.[18] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. The site occupancies of disordered atoms were obtained by refinement. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2]^{-1}$ where $P = [\max(F_o)^2 + 2F_c^2]/3$. All calculations were performed with an IBM RS6000 computer.

Full tables of atom coordinates, bond lengths and angles, anisotropic displacement parameters and calculated hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.‡

‡ For details of the CCDC deposition scheme see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1.

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Paper 5/03323C
Received 22nd *May* 1995
Accepted 5th *October* 1995