The Chemistry of *N*-Substituted Benzotriazoles. Part 7.† The Isomeric Composition and Mechanism of Interconversion of Some *N*-(Aminomethyl)benzotriazole Derivatives

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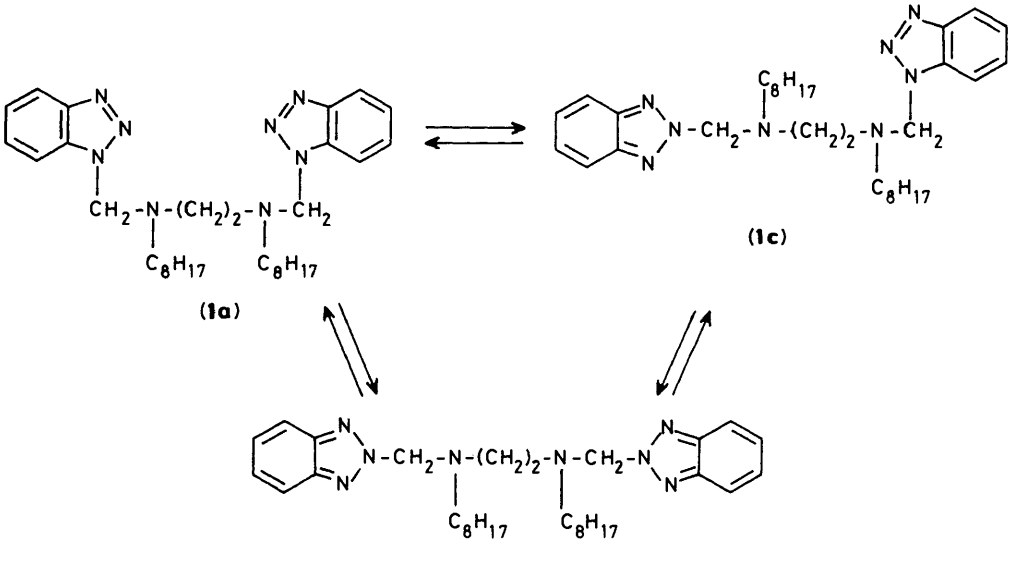
A variety of *N*-(dialkylaminomethyl)benzotriazoles are shown by ^1H and ^{13}C n.m.r., i.r., and *X*-ray crystallography to exist solely in the 1-substituted form in the crystalline phase, but as an equilibrium mixture of the 1- and 2-isomers in the liquid, melt, solution and argon matrix phases. The 1- and 2-isomers equilibrate by an intermolecular mechanism as proven by cross-over experiments.

N,N-Disubstituted aminomethylbenzotriazole derivatives exist in solution as an equilibrium mixture of the corresponding 1-(*N,N*-disubstituted aminomethyl)- and 2-(*N,N*-disubstituted aminomethyl)-benzotriazoles.[1] While the 1-isomer normally predominates, the position of this equilibrium depends strongly on the polarity of the solvent and also on the substrate structure.[1] Thus, as the polarity of the medium increases so does the amount of the 1-isomer relative to the 2-isomer, whereas increased bulkiness in the *N*-aminomethyl substituents favours 2-substitution.[1]

Work related to a different area[2] required the preparation of the *N*-(aminomethyl)benzotriazole derivative (**1**). During the characterization of compound (**1**) significant differences in its spectral properties were observed depending on whether it was in a solid or liquid phase. The data showed that (**1**) existed as a single isomer (**1a**) in the solid state whereas a rapid equilibrium was established upon dissolution to afford a mixture of the isomeric *N,N'*-bis(benzotriazol-1-ylmethyl)-, *N,N'*-bis(benzotriazol-2-ylmethyl)-, and *N*-(benzotriazol-1-ylmethyl)-*N'*-(benzotriazol-2-ylmethyl)-*N,N'*-dioctylethylenediamines (**1a**), (**1b**), and (**1c**), respectively (Scheme 1). Previous reports on the isomerizaton of simpler *N,N*-disubstituted aminomethylbenzotriazoles had implied that these compounds existed as single isomers in the solid state[1] and an ionic dissociative mechanism was proposed for the isomerization in solution; however, no evidence for these conclusions was presented. The results obtained with compound (**1**) prompted us to begin a detailed study on the inter- and intra-molecular equilibria of a



Scheme 1.

representative set of *N,N*-disubstituted aminomethylbenzotriazoles (**2**)—(**6**) (Scheme 2) in the solid, liquid, and vapour phases. Our aim was to compare the properties of these compounds in different phases, as well as to elucidate the mechanism of their isomerization.

Results and Discussion

Solution Phase.—The structure of compounds (**1**)—(**6**) in solution was examined by i.r., ^1H and ^{13}C n.m.r. spectroscopy.

^1H n.m.r. data are recorded in Table 1. Deuteriochloroform

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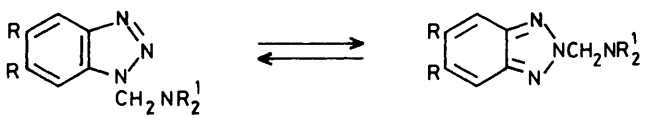


	R	R^1
(2)	H	CH_3
(3)	H	$-(CH_2)_2-$
(4)	CH_3	$-CH_2CH_3$
(5)	H	$-CH_2CH_3$
(6)	CH_3	$-(CH_2)_2-$

Scheme 2.

solutions of compounds (**2**)—(**6**) exhibited, in all cases, two singlets in the region 5.70—5.40 p.p.m., corresponding to the NCH_2N protons, indicating the presence of both the benzotriazol-1-yl and -2-yl isomers. Compound (**1**) (see the Experimental section) displayed three such singlets corresponding to the 1,1-, 2,2-isomers and also to the unsymmetrical *N*-(benzotriazol-2-ylmethyl)-*N'*-(benzotriazol-1-ylmethyl)-*N,N'*-dioctylethylenediamine (**1c**). The aromatic regions were characteristic and the resonances were readily assigned[3,4] to ring protons of the individual isomers. Thus, doublets at δ 8.01 and 7.60 were assigned to 4-H and 7-H, respectively, in the ring-unsubstituted-1-substituted isomers, whereas a multiplet at about δ 7.60 was due to the same protons in the 2-substituted isomers. The 5,6-dimethylbenzotriazoles (**4**) and (**6**) showed 4-H and 7-H as two singlets at δ 7.8 and 7.35, respectively, in the 1-isomers, and as one singlet at δ 7.30 in the 2-isomers. These assignments were based on chemical shifts and coupling constants reported for 1- and 2-(*N*-methylbenzotriazole) derivatives.[3,4]

Also consistent with literature reports[1] is the observation (see ratios in Table 1) that increasing bulkiness in the *N,N*-dialkyl substituents (*i.e.* changing from NMe_2 or pyrrolidino to NEt_2) results in increasing amounts of the 2-substituted isomers. As expected,[1] the change from $CDCl_3$ to the more polar solvent dimethyl sulphoxide (DMSO) resulted in increased amounts of the major 1-substituted isomers at the expense of the 2-substituted ones (Table 1). Indeed, the concentration of the 2-substituted isomers in DMSO was so low that their ^1H n.m.r. signals were frequently obscured: in such cases the ratio of isomers was estimated as >9 favouring the 1-isomer. A noticeable downfield shift was observed for 7-H in the 1-isomer, resonating in DMSO at about δ 7.90 and 7.70 for ring-unsubstituted- and 5,6-dimethyl substituted-1-isomers, respectively.

The ^{13}C n.m.r. spectra of compounds (**1**)—(**6**) in both $CDCl_3$ and DMSO also clearly demonstrated the presence of isomeric mixtures. Thus, more than six aromatic carbon signals were observed in all cases and two NCH_2N absorptions appeared in the region 77.52—64.70 p.p.m. [see Table 2 for compounds (**2**)—(**6**) and Experimental section for compound (**1**)]. The assignments are concordant with data reported for bisbenzotriazolylmethanes.[5]

I.r. spectroscopy has been used previously to distinguish between 1- and 2-substituted benzotriazolyl derivatives.[6,7] The 1-isomers typically display two weak absorptions in the region 1 630—1 550 cm^{-1} (where the C=C and C=N stretching vibrations are most probably located), whereas the 2-isomers show instead one weak absortion in the same region. The i.r. spectra of bromoform or chloroform solutions of compounds (**1**)—(**6**) (Table 3, Figure 1) displayed in all cases all three of these absorption bands supporting the presence of both the 1- and the 2-(*N,N*-dialkylaminomethyl)benzotriazole derivatives in compounds (**2**)—(**6**) [and of 1,1-, 1,2-, and/or 2,2-bisbenzotriazolyl derivatives in (**1**)].

Compound (**5**) is a liquid at 25 °C: the i.r. spectrum of an undiluted film shows in the region 1 630—1 550 cm^{-1} three absorptions at 1 625, 1 588, and 1 569 cm^{-1}, indicating that in the liquid state, just as in solution, *N*-aminomethylbenzotriazoles exist as mixtures of benzotriazol-1-yl and -2-yl isomers. Furthermore, the i.r. spectrum of a sample of melted (**1**) also displayed all of the three absorptions characteristic of the presence of 1- and 2-substituted benzotriazoles.

Solid Phase.—Examination of compound (**1**) in a KBr disc, or in a Nujol dispersion, showed the presence of only two weak

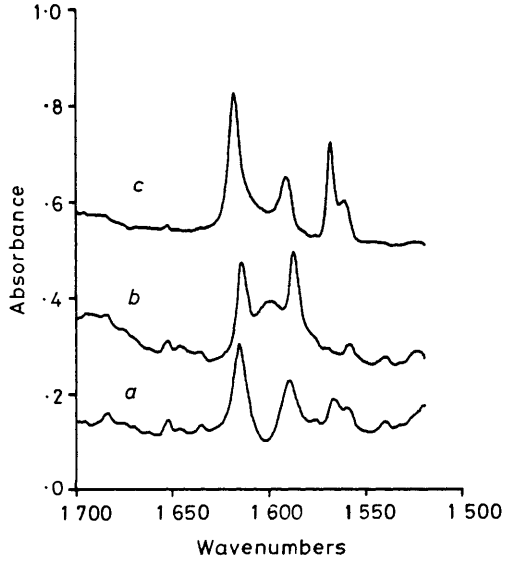


Figure 1. FT-IR spectrum of *N,N*-dimethylaminomethylbenzotriazole (**2**): (*a*) 0.3M solution in $CHCl_3$; (*b*) KBr pellet; (*c*) Ar matrix spectrum

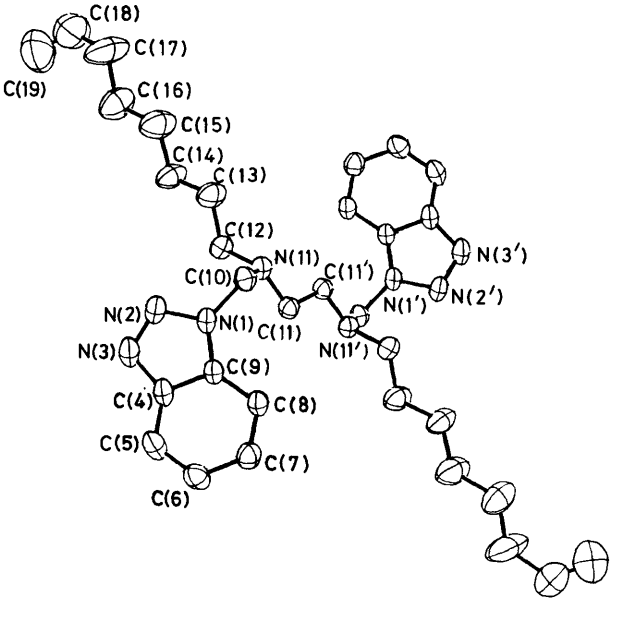


Figure 2. The conformation of *N,N'*-bis(benzotriazolylmethyl)-*N,N'*-dioctylethylenediamine (**1**) with the atom numbering scheme used

Table 1. ^{1}H N.m.r. spectra of the 1- and 2-aminomethylbenzotriazoles (**2**)—(**6**)

		1-Isomer						2-Isomer				
Compound	Solvent	4-H	5-H	6-H	7-H	NCH_2N[a]	R^1	4-, 7-H	5-, 6-H	NCH_2N[a]	R^1	Ratio[b]
(**2**)	$CDCl_3$	8.07[c]	7.49[d]	7.41[d]	7.62[c]	5.40	CH_3 2.40[a]	7.90[d]	*e*	5.51	CH_3 2.46[c]	4.3
(**2**)	DMSO	8.03[c]	7.54[f]	7.38[f]	7.97[c]	5.53	CH_3 2.29[a]	*e*	*e*	*e*	*e*	
(**3**)	$CDCl_3$	8.01[c]	7.44[f]	7.30[f]	7.60[c]	5.51	NCH_2CH_2 2.75[d] NCH_2CH_2 1.72[d]	7.87[d]	*e*	5.70	N-CH_2 2.87 *e*	5.5
(**3**)	DMSO	8.01[c]	7.53[g]	7.37[g]	7.92[c]	5.68	NCH_2CH_2 2.61[d] NCH_2CH_2 1.57[d]	*e*	*e*	*e*	*e*	>9
(**4**)	$CDCl_3$	7.77[a]	CH_3 2.42[a]	CH_3 2.39[a]	7.35[a]	5.44	CH_2CH_3 2.66[h] CH_2CH_3 1.14[f]	7.62[a]	CH_3 2.39[a]	5.57	CH_2CH_3 2.68[h] CH_2CH_3 1.16[f]	2.5
(**4**)	DMSO	7.77[a]	CH_3 2.39[a]	CH_3 2.04[a]	7.67[a]	5.52	CH_2CH_3 2.59[d] CH_2CH_3 1.05[a]	7.67[a]	CH_3 2.04[a]	5.56	CH_2CH_3 2.59[d] CH_2CH_3[e]	
(**5**)	$CDCl_3$	8.05[c]	7.48[g]	7.36[g]	7.62[c]	5.52	CH_2CH_3 2.68[h] CH_2CH_3 1.15[f]	7.91[h]	*e*	5.64	*e*	2.2
(**5**)	DMSO	7.77[c]	7.59[g]	7.44[g]	7.91[c]	5.62	CH_2CH_3 2.59[h] CH_2CH_3 1.05[f]	*e*	*e*	*e*	*e* *e*	>9
(**6**)	$CDCl_3$	7.79[a]	CH_3 2.43[a]	CH_3 2.40[a]	7.37[a]	5.51	NCH_2CH_2 2.75[d] NCH_2CH_2 1.72[d]	7.62[a]	CH_3 2.84[a]	5.63	NCH_2 2.84[d] NCH_2CH_2[e]	5.1
(**6**)	DMSO	7.76[a]	CH_3 2.39[a]	CH_3 2.36[a]	7.70[a]	5.57	NCH_2CH_2 2.63[a] NCH_2CH_2 1.60[a]	*e*	CH_3 2.36[a]	5.57	NCH_2 2.68 NCH_2CH_2[e]	

[a] Singlet. [b] 1-Isomer/2-isomer. [c] Doublet, *J* 8 Hz. [d] Multiplet. [e] Obscured by signals of the 1-isomer. [f] Triplet, *J* 7 Hz. [g] Triplet, *J* 8 Hz. [h] Quartet, *J* 7 Hz.

Table 2. ^{13}C N.m.r. spectra of the 1- and 2-aminomethylbenzotriazoles (**2**)—(**6**)

Compd.	Solvent	C-3a	C-4	C-5	C-6	C-7	C-7a	NCH_2N	$ArCH_3$	R^1
(**2a**)	$CDCl_3$	145.4	119.4	123.5	127.1	109.7	133.6	69.7	—	CH_3 42.1
(**2a**)	DMSO	144.8	118.9	123.8	127.3	111.1	134.0	69.2	—	CH_3 41.9
(**3a**)	$CDCl_3$	145.6	119.6	123.6	127.2	109.8	133.8	65.0	—	NCH_2CH_2 50.1
										NCH_2CH_2 23.6
(**3a**)	DMSO	144.8	118.9	123.8	127.3	110.9	133.9	64.1	—	NCH_2CH_2 49.4
										NCH_2CH_2 23.2
(**4a**)	$CDCl_3$	144.9	118.7	137.4	136.4	109.3	133.4	65.1	20.9	NCH_2CH_3 45.4
									20.2	NCH_2CH_3 12.6
(**4a**)	DMSO	144.1	117.8	137.0	136.1	110.0	133.0	64.5	20.3	NCH_2CH_3 44.7
									19.7	NCH_2CH_3 12.5
(**5a**)	$CDCl_3$	145.1	119.0	123.1	126.7	109.6	133.2	64.8	—	NCH_2CH_3 44.8
										NCH_2CH_3 12.1
(**5a**)	DMSO	144.9	118.8	123.5	127.0	110.8	133.6	64.7	—	NCH_2CH_3 44.7
										NCH_2CH_3 12.4
(**6a**)	$CDCl_3$	144.8	118.6	137.5	136.5	109.1	133.3	64.7	20.6	NCH_2CH_2 50.1
									20.2	NCH_2CH_2 23.6
(**6a**)	DMSO	144.0	117.8	137.2	133.1	110.0	132.9	63.9	20.3	NCH_2CH_2 49.5
									19.8	NCH_2CH_2 23.2
(**2b**)	$CDCl_3$	143.7	117.9	126.0	126.0	117.9	143.7	77.5	—	CH_3 41.7
(**2b**)	DMSO	*a*	118.1	126.3	126.3	118.1	*a*	77.4	—	*a*
(**3b**)	$CDCl_3$	144.0	118.1	126.4	126.4	118.1	144.0	72.5	—	NCH_2CH_2 49.3
										NCH_2CH_2 23.9
(**3b**)	DMSO	*a*	117.8	126.1	126.1	117.8	*a*	71.9	—	NCH_2CH_2 48.6
										NCH_2CH_2 *b*
(**4b**)	$CDCl_3$	143.4	116.6	132.8	132.8	116.6	143.4	71.6	20.7	NCH_2CH_3 45.7
										NCH_2CH_3 12.8
(**4b**)	DMSO	142.8	116.3	132.7	132.7	116.3	142.8	71.0	20.2	NCH_2CH_3 45.2
										NCH_2CH_3 12.8
(**5b**)	$CDCl_3$	143.5	117.7	125.5	125.5	117.7	143.5	71.4	—	NCH_2CH_3 45.2
										NCH_2CH_3 12.4
(**5b**)	DMSO	*a*	117.9	126.0	126.0	117.9	*b*	71.4	—	NCH_2CH_3 45.2
										NCH_2CH_3 *b*
(**6b**)	$CDCl_3$	143.4	116.5	136.5	136.5	116.5	143.4	72.1	20.6	NCH_2CH_2 49.4
									20.2	NCH_2CH_2 23.8
(**6b**)	DMSO	*b*	116.4	*b*	*b*	116.4	*b*	71.6	20.3	NCH_2CH_2 48.7
									19.8	NCH_2CH_2 23.6

[a] Too weak to be detected. [b] Obscured by signals of the 1-isomer.

Table 3. I.r. spectra of benzotriazole derivatives (**1**), (**2**), (**5**), and (**6**) in the region 1 650—1 550 cm^{-1}

	ν/cm^{-1}			
Phase	Solution ($CHCl_3$)	Neat or Melt	Argon[a] Matrix	KBr disc
(**1**)	1 610, 1 590, 1 565[b]	1 610, 1 590, 1 565	—	1 610, 1 590
(**2**)[a]	1 618, 1 592, 1 519	—	1 616, 1 590, 1 517	1 615, 1 587
(**5**)[a]	1 625, 1 590, 1 570	1 625, 1 588, 1 569	—	—
(**6**)[a]	1 627, 1 582, 1 552	—	—	1 631, 1 585

[a] FT spectra. [b] Bromoform solution.

absorptions at 1 610 and 1 590 cm^{-1} in the diagnostic region 1 630—1 550 cm^{-1}, as expected for a bis(benzotriazol-1-yl) derivative.[6,7] In particular, no absorption was found in the region 1 570—1 550 cm^{-1} confirming the absence of benzotriazol-2-yl groups.

Similarly, the i.r. spectra of the aminomethylbenzotriazoles (**2**), (**3**), (**4**), and (**6**) in KBr discs (Table 3, Figure 1) each displayed only two absorptions at 1 630—1 550 cm^{-1} in agreement with their 1-(*N*,*N*-dialkylaminomethyl)benzotriazole structures.

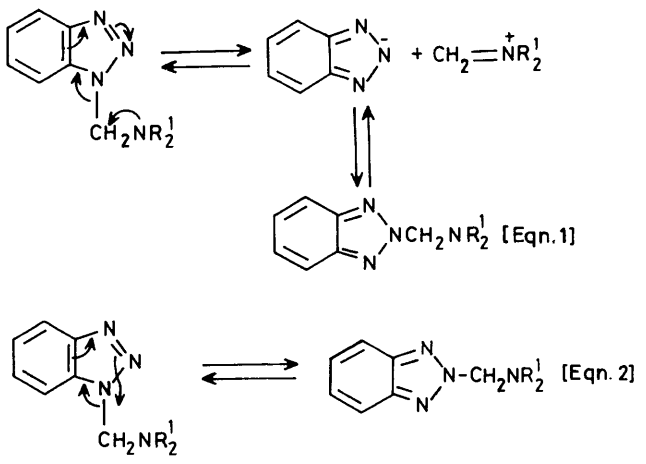
The i.r. results agree with the structure of *N*,*N*′-bis(benzotriazol-1-ylmethyl)-*N*,*N*′-dioctylethylenediamine (**1a**) determined by *X*-ray analysis (Figure 2). Comparison of the geometry of the benzotriazole ring system (Tables 4 and 5) with that of other benzotriazol-1-yl and -2-yl derivatives[8–16] showed bond delocalization patterns very similar to those observed in the benzotriazol-1-yl group.[8–14]

The solid state ^{13}C n.m.r. spectra of compounds (**2**), (**3**), and (**4**) were also examined. The spectrum of compound (**4**) showed a simple 1:1 correspondence between peaks and carbons. The spectra of compounds (**2**) and (**3**) showed asymmetric splitting in the peaks attributable to C-3a and methyl [compound (**2**)], and C-5 or C-6 [compound (**3**)]. The lack of correlation of carbon types for which splittings were observed suggests that these features are due to crystallographic factors and do not indicate the presence of two isomers. Thus, the solid state n.m.r. results also support the existence of only the 1-isomer.

Inert Gas Matrix Phase.—I.r. spectroscopy in a matrix prepared at reduced pressure was used as an approximation for the study of the properties of compound (**2**) in the gas phase. Thus, the i.r. spectra of (**2**) in an argon matrix showed the presence of the characteristic three bands diagnostic of both the benzotriazol-1-yl and -2-yl isomers (Figure 1).

Mechanistic Studies.—The most likely mechanism for the isomerization observed in the liquid and solution phases is a dissociation-recombination process, Equation (1),[1] but a concerted mechanism, Equation (2), had not previously been ruled out (Scheme 3). To distinguish between these two possibilities, a cross-over experiment was carried out by mixing together $CDCl_3$ or DMSO solutions of compounds (**3**) and (**4**) and analysing the mixtures by ^1H (Table 6) and ^{13}C (Table 7) n.m.r. These spectra revealed the presence of eight compounds that could be readily assigned as both the 1- and 2-isomers of each of (**3**), (**4**), (**5**), and (**6**), by direct comparison with the spectra of the individual pairs. The relative intensities (Tables 6 and 7) are also consistent with these assignments. As expected, the 1-isomers predominate even in $CDCl_3$ and more so in the more polar DMSO. The ^1H n.m.r. spectrum ($CDCl_3$) of the mixture (Table 6) showed only seven of the expected eight peaks in the NCH_2N region of 5.70—5.30 p.p.m. The missing signal is apparently hidden under the rather broad peak at δ 5.60. In DMSO the NCH_2N signals for the 2-isomers are obscured by the corresponding 1-isomer signals (see above), and only four signals corresponding to the 1-isomers are observed.

The ^{13}C n.m.r. spectrum (Table 7) provided more widely separated peaks. The NCH_2N carbons appeared in $CDCl_3$ as two groups of four singlets each at 71.70—70.50 and 64.60—



Scheme 3.

Table 4. Atomic co-ordinates ($\times 10^4$) for compound (**1**)

	x	*y*	*z*
N(1)	−203(4)	2 708(2)	643(2)
N(2)	1 899(5)	2 669(3)	966(3)
N(3)	3 061(5)	3 257(3)	230(3)
C(4)	1 710(5)	3 696(3)	−589(3)
C(5)	2 161(6)	4 398(3)	−1 528(4)
C(6)	468(7)	4 704(3)	−2 186(3)
C(7)	−1 667(6)	4 340(3)	−1 920(4)
C(8)	−2 136(5)	3 669(3)	−989(3)
C(9)	−396(5)	3 342(3)	−330(3)
C(10)	−1 876(5)	2 095(3)	1 342(3)
N(11)	−2 824(4)	809(2)	1 113(2)
C(11)	−4 101(5)	577(3)	5(3)
C(12)	−1 305(6)	7(3)	1 396(3)
C(13)	−885(8)	−244(4)	2 607(4)
C(14)	747(8)	−1 008(4)	2 901(4)
C(15)	1 299(11)	−1 261(5)	4 095(5)
C(16)	2 996(10)	−1 993(5)	4 476(5)
C(17)	3 397(14)	−2 276(7)	5 681(5)
C(18)	4 899(17)	−3 194(12)	6 038(9)
C(19)	6 466(16)	−3 111(13)	5 651(11)

Table 5. Bond lengths (Å) and angles (°)

N(1)–N(2)	1.360(4)	N(1)–C(9)	1.358(4)
N(1)–C(10)	1.486(4)	N(2)–N(3)	1.303(5)
N(3)–C(4)	1.375(5)	C(4)–C(5)	1.384(5)
C(4)–C(9)	1.394(5)	C(5)–C(6)	1.356(6)
C(6)–C(7)	1.415(6)	C(7)–C(8)	1.362(5)
C(8)–C(9)	1.390(5)	C(10)–N(11)	1.430(4)
N(11)–C(11)	1.462(4)	N(11)–C(12)	1.471(5)
C(11)–C(11′)	1.505(6)	C(12)–C(13)	1.481(5)
C(13)–C(14)	1.497(8)	C(14)–C(15)	1.471(7)
C(15)–C(16)	1.521(10)	C(16)–C(17)	1.480(8)
C(17)–C(18)	1.573(16)	C(18)–C(19)	1.153(17)
N(1)–N(1)–C(9)	110.2(3)	N(2)–N(1)–C(10)	119.5(3)
C(9)–N(1)–C(10)	130.3(3)	N(1)–N(2)–N(3)	108.8(3)
N(2)–N(3)–C(4)	108.3(3)	N(3)–C(4)–C(5)	130.6(3)
N(3)–C(4)–C(9)	108.5(3)	C(5)–C(4)–C(9)	120.8(3)
C(4)–C(5)–C(6)	117.2(4)	C(5)–C(6)–C(7)	121.7(4)
C(6)–C(7)–C(8)	122.0(4)	C(7)–C(8)–C(9)	115.9(3)
N(1)–C(9)–C(4)	104.3(3)	N(1)–C(9)–C(8)	133.3(3)
C(4)–C(9)–C(8)	122.4(3)	N(1)–C(10)–C(11)	115.7(3)
C(10)–N(11)–C(11)	113.5(3)	C(10)–N(11)–C(12)	113.8(2)
C(11)–N(11)–C(12)	114.0(3)	N(11)–C(11)–C(11′)	111.3(4)
N(11)–C(12)–C(13)	113.5(3)	C(12)–C(13)–C(14)	113.5(4)
C(13)–C(14)–C(15)	116.5(5)	C(14)–C(15)–C(16)	120.3(6)
C(15)–C(16)–C(17)	117.8(6)	C(16)–C(17)–C(18)	117.1(7)
C(17)–C(18)–C(19)	120.4(12)		

Table 6. ^1H N.m.r. data for the NCH_2N group of benzotriazoles (**3**)—(**6**) from the cross-over experiment

	2-Isomers			1-Isomers			
Assignment	(**3**)	(**5**), (**6**)	(**4**)	(**3**)	(**6**)	(**5**)	(**4**)
δ($CDCl_3$)	5.66	5.60	5.55	5.53	5.47	5.45	5.40
Area (%)	4	9	6	23	23	18	17
δ(DMSO)				5.70	5.60	or 5.64	5.54
Area (%)				37	25	or 24	15

Table 7. ^{13}C N.m.r. data for the NCH_2N groups of benzotriazoles (**3**)—(**6**) from the cross-over experiment

	2-Isomers				1-Isomers			
Assignment	(**3**)	(**6**)	(**4**)	(**5**)	(**4**)	(**5**)	(**3**)	(**6**)
δ($CDCl_3$)	71.7	71.2	71.0	70.6	64.4	64.2	64.1	63.9
Area (%)	4	4	5	5	18	17	24	22
δ(DMSO)					64.5	64.8	64.1	64.0
Area (%)					25	29	25	21

Table 8. Preparation of the aminomethylbenzotriazoles (**2**)—(**6**)

Compd.	R	R^1	Yield (%)	M.p. (°C) or b.p. (mmHg)	Found (%) C	H	N	Molecular Formula	Required (%) C	H	N
(**2**)	H	Me	97	95—98				*a*			
(**3**)[b]	H	$-(CH_2)_2-$	98	79—81	65.65	7.3	27.9	$C_{11}H_{14}N_4$	65.32	6.98	27.70
(**4**)[b]	Me	$-(CH_2)_2-$	91	99.5—101	68.0	8.45	24.45	$C_{13}H_{18}N_4$	67.80	7.88	24.33
(**5**)[c]	H	Et	96	120—124(0.65)	64.15	7.75	27.8	$C_{11}H_{16}N_4$	64.68	7.89	27.43
(**6**)[d]	Me	Et	88	39—41	67.0	9.0	24.15	$C_{13}H_{20}N_4$	67.21	8.68	24.11

[a] Lit.,[1] m.p. 98—100 °C (from diethyl ether). [b] Recrystallizes from diethyl ether. [c] See ref. 20. [d] Recrystallizes from low boiling light petroleum.

63.80 p.p.m., corresponding to the 2- and 1-isomers, respectively. The ratios were measured by integration of these signals in a quantitative experiment. In DMSO the signals for the 2-isomers were too weak to allow precise measurements. An identical equilibrium mixture as regards both chemical shifts and ratios was obtained by mixing together solutions of (**5**) and (**6**).

Temperature Effect.—The ^1H n.m.r. spectra of (**4**), (**5**), and (**6**) were also recorded at −50 °C and at 40 °C in $CDCl_3$ and the ratios of isomers measured. The results indicate no significant change in the isomer distribution with respect to the data obtained at 25 °C.

Conclusions

It can be concluded from our studies that (*N,N*-disubstituted aminomethyl)benzotriazoles exist as a single benzotriazol-1-yl isomer in the solid phase. However, in liquid, solution and vapour phases these compounds undergo isomerization and mixtures of the benzotriazol-1-yl and -2-yl isomers are observed. Our studies prove that the isomerism process is intermolecular and are consistent with a dissociative pathway to iminium ions and a benzotriazole anion. The subsequent recombination of these two species furnishes equilibrium mixtures of benzotriazol-1-yl and -2-yl isomers where the 1-isomer always predominates.

Experimental

M.p.s were determined on a Kofler hot-stage microscope, and are uncorrected. I.r. spectra were recorded either on a Perkin-Elmer 283B spectrophotometer or on a FT-IR Nicolet 7000 Series; measurements were done on 0.3M $CHCl_3$ or $CHBr_3$ solutions, or on a 1% KBr pellet; the spectrum of (**2**) in an argon matrix was recorded at 24 K and 10^{-7} mmHg. ^1H (200 MHz) and ^{13}C (50 MHz) n.m.r. spectra were recorded on a Varian XL200 (FT mode) spectrometer. Cross-over experiments were carried out by mixing equimolar solutions of both substrates.

Solid state ^{13}C n.m.r. spectra were acquired on a modified Varian XL 200 n.m.r. spectrometer using Cross polarization and magic angle spinning (CPMAS). Cross polarization contact times were 1 ms whereas delays between successive applications of the CPMAS sequence were 1 or 2 s. Resolution enhancement of the spectra was utilized to improve the peak separation. The interrupted decoupling scheme of Opella and Frey[17] was used to assist the peak assignment.

N,N′-*Bis*(*benzotriazol*-1-*ylmethyl*)-N,N′-*dioctylethylenediamine* (**1**).—A mixture of 1-hydroxymethylbenzotriazole[18] (5.66 g, 38 mmol), acetic acid (1.14 g, 19 mmol), and *N,N*′-dioctylethylenediamine (5.68 g, 20 mmol) in ethanol (50 ml) was refluxed for 3 min and, after being cooled, was poured onto ice–water. The mixture was extracted with chloroform (3 × 50 ml) and the organic extracts washed with water and dried ($MgSO_4$). Evaporation of the solvent afforded compound (**1**) (8.4 g, 82%) as a solid, m.p. 63—65 °C (from methanol) (Found: C, 70.4; H, 9.6; N, 20.55. $C_{32}H_{50}N_8$ requires C, 70.29; H, 9.22; N, 20.49%); $\nu_{max.}$($CHBr_3$) 2 925, 2 850, 1 610, 1 585, 1 560, 1 460, 1 450, 1 375, 1 285, 1 265, 1 000, 820, and 740 cm^{-1}; δ_H($CDCl_3$) 8.06 (d, *J* 8 Hz, 4-H, 1,1-isomer), 7.90 (m, 4-, 7-H, 1,2- and 2,2-isomers), 7.70—7.30 (m, all isomers), 5.69 (s, NCH_2N, 2,2-isomer), 5.63 and 5.58 (s, NCH_2N, 1,2-isomer), 5.51 (s, NCH_2N, 1,1-isomer), 3.0—2.50 (8 H, m, all isomers), 1.52 (4 H, m, all isomers), 1.25 (20 H, br s, all isomers), and 0.87 (6 H, t, all isomers); δ_C($CDCl_3$) 145.6, 144.0, 133.6, 127.2, 126.0, 123.7, 119.6, 118.1, 109.8, 73.3, 66.4, 52.4, 49.6, 49.2, 31.7, 29.3, 29.1, 27.5, 27.0, 22.5, and 13.95. The ratio of 1,1-to 1,2-isomers was 1.8.

N,N-*Dialkylaminomethylbenzotriazoles* (**2**)—(**6**).—These were prepared according to a general literature procedure[19] from a secondary amine, formaldehyde, and benzotriazole. Physical and spectroscopic data for compounds (**2**)—(**6**) are given in Tables 1—3 and 8.

Crystal Data for N,N′-*Bis*(*benzotriazol*-1-*ylmethyl*)-N,N-*dioctylethylenediamine* (**1**).—The compound, $C_{32}H_{50}N_8$, M = 546.9, crystallizes in the triclinic space group $P\bar{1}$, with the crystal lattice parameters a = 6.421(2), b = 11.104(2), c = 12.108(1) Å, α = 88.11(1), β = 98.39(1), γ = 103.88(2)° and V = 829.0(3) Å^3, Z = 1, D_x = 1.10 g cm^{-3}, D_m = 1.09 g cm^{-3} (by flotation in KI solution), μ(Mo-K_α) = 0.7 cm^{-1}.

Data Collection and Solution of the Structure.—*X*-Ray diffraction data were measured on a Nicolet R3m diffractometer, using a colourless crystal of dimensions 0.34 × 0.57 × 0.57 mm, graphite-monochromatized Mo-K_α radiation (λ = 0.710 73 Å), and the $\theta - 2\theta$ scan technique. Two standard reflections showed the intensity variation $< \pm 3\%$. In the h, k, l range 0,12,13 −7,12,13 ($1.5 < 2\theta < 47.0°$), 2 793 reflections were collected, of which 2 159 unique observed [$F_o/\sigma(F_o) > 2.5$] were used in calculations. The measured density indicates one molecule in the unit cell, and because of this the structure was solved in the space group $P\bar{1}$. Direct methods and Fourier synthesis were applied to find the molecular model. The molecule appeared to be centrosymmetric with both benzotriazole fragments substituted at *N*-1. The least-squares refinement of 181 parameters (half of the chemical formula in the asymmetric part) was carried out in the space group $P\bar{1}$. Of a total of 25 hydrogen atoms, 12 were located in the difference map, the positions of 6 were calculated from the geometry of the molecule, and atoms bonded to three terminal carbon atoms of the aliphatic chain were not taken into account. The H-atom parameters were fixed and included in the structure-factor calculations. The final refinement of positional and anisotropic thermal parameters for non-hydrogen atoms using 2 152 reflections gave R = 0.085 and R_w = 0.081 ($w = 1/\sigma^2$).

The SHELXTL system[21] on a DG Desktop computer was used for all calculations.

The final positional and equivalent thermal parameters of non-hydrogen atoms are given in Table 4. Bond distances and angles are collected in Table 5. The conformation of the molecule and the atom numbering scheme are shown in Figure 2. Lists of anisotropic thermal parameters, H-atom parameters and structure factors are available on request from the Cambridge Crystallographic Data Centre.*

* See 'Instructions for Authors (1987),' paragraph 5.6.3 in *J. Chem. Soc., Perkin Trans. 1*, 1987, Issue 1.

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