Mannich/Friedel–Crafts Preparations of 1-(Arylmethyl)benzotriazoles and Synthetic Transformations of Their Lithio Derivatives

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The synthesis of 1-(arylmethyl)benzotriazoles by Mannich type reactions of benzene, toluene, *p*-xylene and chlorobenzene with 1-chloromethylbenzotriazole in the presence of aluminium halides is reported. Alkylation of their lithio derivatives followed by the cleavage of benzotriazole from the resulting 1-(α-arylalkyl)benzotriazoles upon reduction with $LiAlH_4$–$AlCl_3$ or elimination by AcOH are shown to be useful procedures for the preparation of substituted arenes. An oxidative coupling of lithiated 1-(arylmethyl)benzotriazoles gave 1,2-diaryl-1,2-di(benzotriazol-1-yl)ethanes. Novel heterocyclic ring fissions of the lithio derivatives of 1-(arylmethyl)benzotriazoles afforded 1,2,4-benzotriazine and 1,2-bis(*N*-methylanilino)ethene derivatives.

The significant role of iminium salts in many reactions has long been recognized.[1] Thus, the Mannich reaction is one of the most familiar and powerful of synthetic methods. Common substrates for the Mannich reaction are active methylene compounds, amines, thiols, alcohols, alkynes, hydrogen cyanide and electron-rich aromatic systems such as pyrroles, indoles, phenols[2] and aromatic amines.[3]

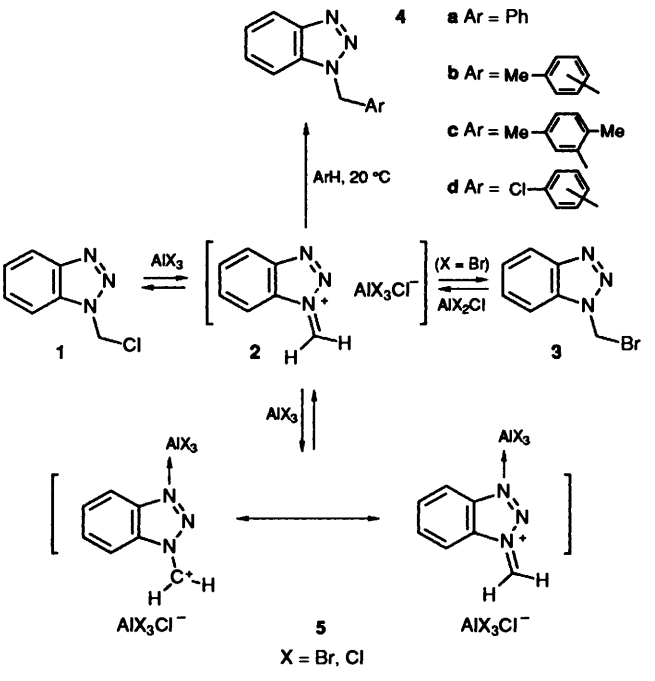
Recently, we reported the synthesis of methylenebisanilines from 1-hydroxymethylbenzotriazole.[4] We now disclose the first examples of an electrophilic substitution of non-activated aromatic hydrocarbons, related to both the Mannich and Friedel–Crafts reactions.

Reaction of Arenes with Methylenebenzotriazolium Cation.— The methylenebenzotriazolium salt **2**, generated *in situ* from 1-chloromethylbenzotriazole and an appropriate Lewis acid, reacts with aromatic substrates which are inert both under standard Mannich reaction conditions, and to the action of several other types of iminium salts.[1] Specifically, benzene, toluene, *p*-xylene or chlorobenzene with 1-chloromethylbenzotriazole **1** in the presence of aluminium bromide or chloride under mild conditions afford the respective 1-(arylmethyl)-benzotriazoles **4** in high yields (Scheme 1).

The aluminium bromide catalysed reactions with toluene and chlorobenzene yielded mixtures of the *o*-, *m*- and *p*-isomers in ratios which were determined by gas chromatography and ^1H NMR spectroscopy as 33, 19 and 48% for **4b** and 21, 15 and 53% for **4d**, respectively.

The mild reaction conditions and the relatively low selectivity of the process indicate the high reactivity of the methylene-benzotriazolium cation **2** which exceeds that of the usual Mannich intermediates: methylene- and dichloromethylene-iminium salts do not react with electron-rich-substituted aromatics such as anisole even on heating in the presence of Friedel–Crafts catalysts.[1]

The high electrophilicity of the methyelenebenzotriazolium cation in this reaction (Scheme 1) may be attributed partly to the π-deficient nature of the benzotriazole ring, but there is probably additional activation of the cation due to coordination with an excess of the Lewis acid, and formation of the mesomeric system **5** which has a close structural relationship with Friedel–Crafts electrophilic species.[5] Indeed, the best yields of compounds **4** were achieved using 1.5 equiv. of the aluminium halide. Less strong Lewis acid such as $ZnBr_2$, $ZnCl_2$ and $TiCl_4$ failed to catalyse the reaction of 1-chloromethylbenzotriazole with *p*-xylene under similar conditions (*cf.* ref. 5).



Scheme 1

o- and *p*-Dichlorobenzene, nitrobenzene, *N*-methylpyrrole, anisole and thiophene failed to yield products **4** under the conditions of Scheme 1. From the reaction mixtures with dichlorobenzene or *N*-methylpyrrole and aluminium bromide, 1-bromomethylbenzotriazole was isolated in good yield, indicating the reversible formation of the methylenebenzotriazolium salt **2** (Scheme 1). No such halogen exchange was observed on heating in nitrobenzene; instead, the compound **1** was recovered in high yield. The latter result, as well as our unsuccessful attempted reactions with *N*-methylpyrrole, anisole and thiophene may be accounted for by complex formation from aluminium halides and these potential substrates which result in the deactivation of both the Lewis acid and the aromatic substrates. Previously it has been reported[5] that (i) the normal activating effect of electron-donor groups in the course of an electrophilic aromatic substitution is often replaced by a strong deactivating effect due to coordination with the Lewis acid, and (ii) the activity of aluminium halides can be depressed by

complexation with nitrobenzene. Attempted reactions with anisole and thiophene results in the formation of complex mixtures: it is reported[5] that anisole can undergo cleavage of the methyl group by a Lewis acid which leads to complications in the course of Friedel–Crafts transformations, and that thiophene is difficult to alkylate by Friedel–Crafts reactions because of polymerization. Biphenyl and naphthalene gave the expected products of type **4** with **1** and $AlCl_3$; however, these products were obtained as mixtures and in low yields (*ca.* 20–30% by ^1H NMR spectroscopy) along with considerable amounts of higher aromatic hydrocarbons. Biphenyl and naphthalene can undergo Scholl reactions with aluminium halides to give coupled and other products.[5]

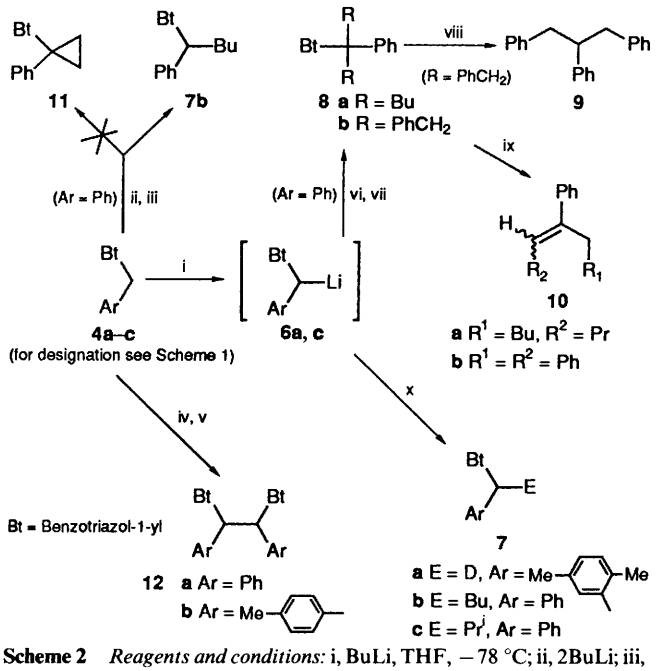
The reaction of 1-chloromethylbenzotriazole **1** with aromatic compounds in the presence of aluminium halides is a process which, because of the key intermediate—the iminium salt **2**—can be classified as Mannich reaction while possessing certain of the features and limitations of a Friedel–Crafts transformation.

1-(Arylmethyl)benzotriazoles are of considerable interest due to their herbicidal activity.[6] Compounds of this type have also been patented for use in printing synthetic fabrics.[7] Previously known methods for the preparation of 1-(arylmethyl)benzotriazoles were based on the *N*-alkylation of various benzotriazole derivatives such as alkali metal salts,[8] and N^1-tributyltin-[9] and N^1-trimethylsilylbenzotriazoles.[10] These methods are restricted by the availability of the arylmethyl halides and often complicated by the formation of mixtures with the isomeric 2-substituted benzotriazoles (*cf.* refs. 8, 11). In spite of the drawbacks of the presently described procedure (reminiscent of those of Friedel–Crafts transformations; see above), reactions of a methylenebenzotriazolium salt with aromatic hydrocarbons can provide a convenient alternative for the preparation of 1-(arylmethyl)benzotriazoles using the readily available 1-chloromethylbenzotriazole **1**.[12]

Lithiation of 1-*(Arylmethyl)benzotriazoles* **4** *and Reactions of the Lithio Derivatives with Electrophiles.*—Previous publications from our laboratory have shown that methylene or methine groups α to benzotriazol-1-yl substituents can undergo smooth lithiation. Reactions of these lithiated derivatives have enabled the preparation of aromatic ketones,[13] carboxylic acids,[14] aldehydes,[15] and various other derivatives.[16,17] When BuLi or lithium diisopropylamide (LDA) acted on compounds **4a–c** (the pure *p*-isomer of **4b** was used[18]) in THF, the lithiated intermediates formed easily as deep blue solutions. These were quenched with electrophiles (deuterium oxide, 1-iodobutane or 2-iodopropane) to yield the respective products **7a–c** in high yields (Scheme 2).

A similar procedure, using 2 equiv. of BuLi and 2 equiv. of electrophile, allowed the preparation of the tetrasubstituted methanes **8**, in quantitative yields. The benzotriazole group can be easily cleaved from compound **8b** by reduction with $LiAlH_4$–$AlCl_3$ (1:1) in boiling toluene. In this way, 1,2,3-triphenylpropane **9** was obtained in 98% yield (Scheme 2). This product was previously prepared in low yields by (i) the action of 1,2,3-trichloropropane on benzene in the presence of aluminium chloride,[19] (ii) the reduction of phenyldibenzylcarbinol with red phosphorus and hydroiodic acid[20] or (iii) heating α-benzyl-α-phenylethyleneglycol with aqueous oxalic acid.[21] The elimination of benzotriazole from compounds **8a, b** on heating with acetic acid (140 °C, sealed tube) gave olefins **10a, b** in high yields. The products **10a, b** were obtained as mixtures of *E*- and *Z*-isomers in ratios of 4:1 and 5:1, respectively. Thus, the transformation of 1-(arylmethyl)benzotriazoles into lithio derivatives, along with our new reductive and eliminative cleavages of the benzotriazole auxiliary group, provide novel and convenient routes to substituted arenes.

Attempted bis-alkylation of the lithiated compound **5a** with



Scheme 2 *Reagents and conditions:* i, BuLi, THF, −78 °C; ii, 2BuLi; iii, $BrCH_2CH_2Br$, −78→20 °C; iv, LDA; v, $BrCH_2CH_2Br$ or I_2, −78→20 °C; vi, BuLi; vii, 2RI, −78→20 °C; viii, $LiAlH_4$–$AlCl_3$, toluene, heat; ix, AcOH, heat; x, E^+, −78→20 °C

1,2-dibromoethane did not afford the expected cyclopropane **11** (Scheme 2). Instead, the butyl product **7b** was obtained in 60% yield. Obviously, the formation of **7b** resulted from an exchange process between BuLi and 1,2-dibromoethane, followed by the reaction of the butyl bromide with the lithiated compound **5a**. When LDA was used instead of BuLi, 1,2-dibromoethane yielded the oxidatively coupled products—1,2-di(benzotriazol-1-yl)-1,2-diarylethanes **12a** (66%) and **12b** (73%) (Scheme 2). Similar results were obtained with either 1 or 2 equiv. of LDA (lithium diisopropylamine). Products **12a, b** were obtained as mixtures of racemic and meso-forms in ratios of *ca.* 3:1 and 2:1, respectively. Both diastereoisomers of **12a** were isolated by column chromatography, and the major diastereoisomer of **12b** was isolated by washing with diethyl ether. The structures of compounds **12** were supported by elemental analyses and spectral data. The ^1H NMR spectra of the products displayed doublets for the benzotriazole 4-H protons at δ_H 7.9–8.4 (*J* 8.0–8.3 Hz; *cf.* ref. 22) together with the resonances of other aromatic protons and CH singlets in the δ_H 7.1–7.7 region. Under electron impact, compounds **12** did not form stable molecular ions; instead intense fragment ion peaks $[M - N_2]^+$ were observed. Finally, an X-ray crystallographic study (below) confirmed the structure of the racemic modification of compound **12a** (Fig. 1).

Oxidative couplings of metalated organic species have received increasing attention in recent years for their synthetic utility. The common reagents are metal salts, especially those of copper and silver,[23] and in certain cases, molecular iodine.[24] Thus, in the aforementioned reaction 1,2-dibromoethane acts as a specific oxidative coupling agent and, as in transformations using metal salts, both radical and non-radical mechanisms could be suggested.[23] Compounds **12a, b** were also obtained from lithio derivatives of **4a, b** and molecular iodine (Scheme 2).

Previously, successful oxidative coupling has been reported for carbanionic species stabilized with carbonyl,[25] alkoxycarbonyl,[23] and phosphoryl[26] and thioamidyl[27] groups. Our new reaction of lithiated 1-(arylmethyl)benzotriazoles is the first example of an oxidative coupling of a benzotriazole-stabilized carbanion.

Recently it was shown in our laboratory[28] that benzotriazol-1-yl carbanions may lose nitrogen to afford *o*-carbiminophenyl

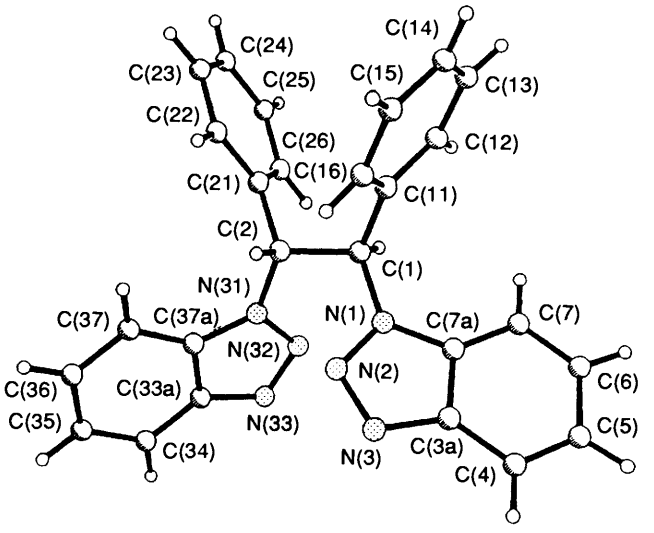


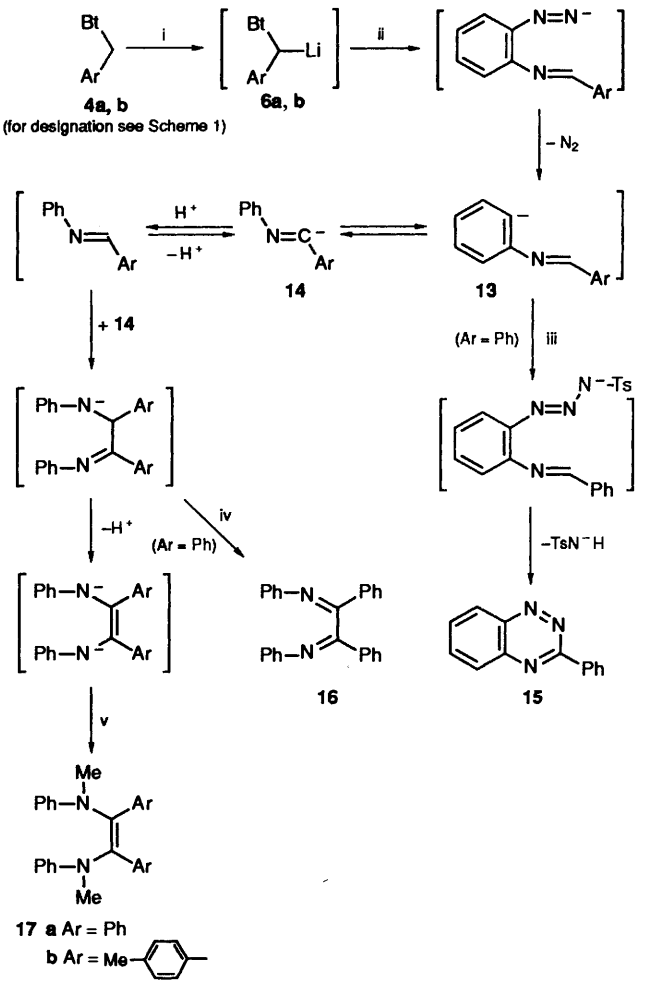
Fig. 1 Perspective view and atom labelling of the X-ray structure of compound **12a** (benzene solvate not shown)

anions. We now report the analogous benzotriazole ring fragmentation of lithiated 1-arylmethylbenzotriazoles (Scheme 3). The reaction proceeds slowly at temperatures above −20 °C, and is rapid at 0–5 °C (when the evolution of nitrogen was observed). Quenching the reaction of **4a** with water followed by work-up in the presence of air gave benzil dianyl **16** in 60% yield. Alternatively, benzotriazole ring-fission products from **4a** were trapped with tosyl azide to yield 3-phenyl-1,2,4-benzotriazine **15** (10%) along with compound **16** (49%). Both dimerization of aromatic aldimines[29] and the oxidation of α,α′-dianilinostilbene with gaseous oxygen into benzyl dianyl **15** have been reported previously.[30] A compound of this type was also isolated in our earlier studies[28] of the thermal (−78–25 °C) reaction of lithiated 1-(4-dimethylaminobenzyl)benzotriazole (no detailed explanation for its formation was suggested). The new benzotriazine ring formation in the reaction with tosyl azide clearly indicates the presence of the intermediate anion **13** (or its proton transfer-derived isomer **14**) in the reaction medium.

Quenching the reactions of **4a, b** and LDA with methyl iodide resulted in the stereospecific formation of 1,2-bis(*N*-methylanilino)-1,2-diarylethenes **17a, b**. Compound **17a** was previously obtained by the methylation of the disodium derivative of α,α′-dianilinostilbene.[30] Evidently, dianions of this type are also responsible for the formation of compounds **17** (Scheme 3). It is noteworthy, that as with the solution of the disodium derivative of α,α′-dianilinostilbene in THF,[30] our reaction mixtures of **4** (prior to the addition of the electrophile) were deep red.

The structures of compound **15–17** were supported by spectral data and (for **15**, **16** and **17a**) by comparison with reported m.p.s (see Experimental section). An X-ray crystallographic study (below) confirmed the structure of the compound **17a**.

The *Z*-structures have previously been suggested for a series of dianilinostilbenes which includes **17a**.[30] It should be noted, however, that two methyl singlets in the ^{1}H NMR spectrum of **17a** in $CDCl_3$ (δ_H 2.62 and 3.0) were assigned to 'nonequivalent methyls', although only one 6-proton signal at δ_H 2.67 was observed in a C_6D_6 solution of **17a**.[30] The ^{1}H and ^{13}C NMR spectra of the freshly prepared samples of our compounds **17a, b** both in $CDCl_3$ and in C_6D_6 displayed only one set of signals each. We observed the appearance of additional signals in the solutions in $CDCl_3$ on standing due to spontaneous isomerization at 25 °C. After 1 day, the ratio of the *E*- to *Z*-isomers was *ca.* 1:1 in each case. *E.g.*, in the ^{1}H NMR spectrum of **17a** a singlet at δ_H 3.05 appeared and increased while the initially



Scheme 3 *Reagents and conditions:* i, LDA, THF, −78 °C; ii, −78→15 °C; iii, TsN_3; iv, H^+, [O]; v, 2MeI

observed resonance at δ_H 2.67 decreased until the two signals were of equal intensity. Therefore, these signals should be assigned to *E*- and *Z*-isomers, rather than to nonequivalent methyl groups. On the contrary, no changes were observed in C_6D_6 solutions of **17a, b**. Obviously, the isomerization could be catalysed by traces of acid (which is commonly present in $CDCl_3$) and proceed *via* a *C*-protonated form of **17**. Indeed, the addition of catalytic amounts of trichloroacetic acid (*ca.* 7.3 mol% in respect to **17a**) to the C_6D_6 solution of **17a** resulted in the appearance of a singlet at δ_H 2.86. The intensity of this signal increased with time, while the initially observed methyl resonance at δ_H 2.56 decreased until the ratio of the two signals was *ca.* 1:1.3 (after 40 h). No further change was observed during the next 40 h.

Crystal Structure of **12a** *and* **17a**.—Fig. 1 shows a perspective view and atom labelling of the crystal structure of **12a**. Final atom coordinates are listed in Table 1 and selected bond lengths and angles in Table 2. The X-ray determination reveals the structure of **12a** to be the racemic isomer of 1,2-di(benzotriazol-1-yl)-1,2-diphenylethane. The asymmetric unit comprises one molecule of substrate and half a molecule of benzene, the centre of which lies on a crystallographic centre of inversion. The molecule exists in a staggered conformation with the pairs of phenyl rings and benzotriazole rings mutually gauche. The potential C_2 symmetry of the molecule is destroyed in the solid state by small torsion angle differences. For example, relative to the plane described by H(1)–C(1)–C(2)–H(2) the two phenyl ring mean planes are inclined at angles of 56.3(3)° and 117.3(3)°,

Table 1 Atomic coordinates (× 10^4) with esds in parentheses

Atom	*x*	*y*	*z*
N(1)	219(3)	6443(1)	4464(2)
N(2)	787(3)	5748(2)	4558(2)
N(3)	2040(3)	5835(2)	4865(2)
C(3A)	2282(3)	6602(2)	4991(2)
C(4)	3436(3)	6985(2)	5337(3)
C(5)	3362(4)	7755(2)	5412(3)
C(6)	2179(4)	8149(2)	5148(3)
C(7)	1032(4)	7786(2)	4809(3)
C(7A)	1112(3)	6998(2)	4741(2)
C(1)	−1205(3)	6541(2)	4194(3)
C(11)	−1889(3)	6730(2)	5101(3)
C(12)	−2478(3)	7434(2)	5186(3)
C(13)	−3071(4)	7622(3)	6031(3)
C(14)	−3095(4)	7110(3)	6785(3)
C(15)	−2514(4)	6406(3)	6714(3)
C(16)	−1906(3)	6216(2)	5875(3)
C(2)	−1795(3)	5830(2)	3674(2)
C(21)	−3256(3)	5941(2)	3363(2)
C(22)	−4173(3)	5508(2)	3792(2)
C(23)	−5516(3)	5618(2)	3536(3)
C(24)	−5937(3)	6162(2)	2853(3)
C(25)	−5023(3)	6592(2)	2410(3)
C(26)	−3681(3)	6475(2)	2655(3)
N(31)	−1066(3)	5620(1)	2833(2)
N(32)	−382(3)	6127(2)	2336(2)
N(33)	188(3)	5767(2)	1646(2)
C(33A)	−144(3)	5006(2)	1699(3)
C(34)	220(3)	4386(2)	1142(3)
C(35)	−259(4)	3690(2)	1387(3)
C(36)	−1081(4)	3603(2)	2149(3)
C(37)	−1449(3)	4207(2)	2698(3)
C(37A)	−950(3)	4909(2)	2456(2)
C(1B)[a]	1157(5)	317(2)	5411(4)
C(2B)[a]	984(5)	184(3)	4415(4)
C(3B)[a]	−173(6)	−135(3)	4009(3)

[a] Benzene solvate.

Table 2 Selected bond lengths (Å) and angles (°) with esds in parentheses

N(1)–N(2)	1.357(4)	N(1)–C(7A)	1.366(4)
N(1)–C(1)	1.475(4)	N(2)–N(3)	1.316(4)
N(3)–C(3A)	1.383(4)	C(3A)–C(7A)	1.397(5)
C(1)–C(11)	1.514(5)	C(1)–C(2)	1.538(5)
C(2)–C(21)	1.523(4)	C(2)–N(31)	1.471(4)
N(31)–N(32)	1.355(4)	N(31)–C(37A)	1.365(4)
N(32)–N(33)	1.315(4)	N(33)–C(33A)	1.388(5)
C(33A)–C(37A)	1.390(5)		
N(2)–N(1)–C(7A)	110.7(3)	N(2)–N(1)–C(1)	122.1(2)
C(7A)–N(1)–C(1)	126.9(3)	N(1)–N(2)–N(3)	108.5(2)
N(2)–N(3)–C(3A)	108.1(3)	N(3)–C(3A)–C(7A)	108.7(3)
N(1)–C(7A)–C(3A)	104.0(3)	N(1)–C(1)–C(11)	109.7(3)
N(1)–C(1)–C(2)	110.7(3)	C(11)–C(1)–C(2)	111.6(3)
C(1)–C(2)–C(21)	110.7(3)	C(1)–C(2)–N(31)	111.2(3)
C(21)–C(2)–N(31)	111.4(2)	C(2)–N(31)–N(32)	123.0(3)
C(2)–N(31)–C(37A)	126.4(3)	N(32)–N(31)–C(37A)	110.6(3)
N(31)–N(32)–N(33)	108.8(3)	N(32)–N(33)–C(33A)	107.7(3)
N(33)–C(33A)–C(37A)	108.8(3)	N(31)–C(37A)–C(33A)	104.2(3)

and the two benzotriazole ring means planes inclined at angles of 58.9(3)° and 126.2(3)°. The phenyl and benzotriazole rings are all planar to within 0.009 Å and exhibit normal bonding geometries. There are no unusually short intermolecular contacts between non-hydrogen atoms of less than 3.2 Å.

Fig. 2 shows a perspective view and atom labelling of the crystal structure of **17a**. Final coordinates are listed in Table 3 and selected bond lengths and angles in Table 4. The structure is confirmed as the *Z*-isomer of 1,2-di(*N*-methylanilino)-1,2-diphenylethylene. The *N*-methylanilino substituents exist in

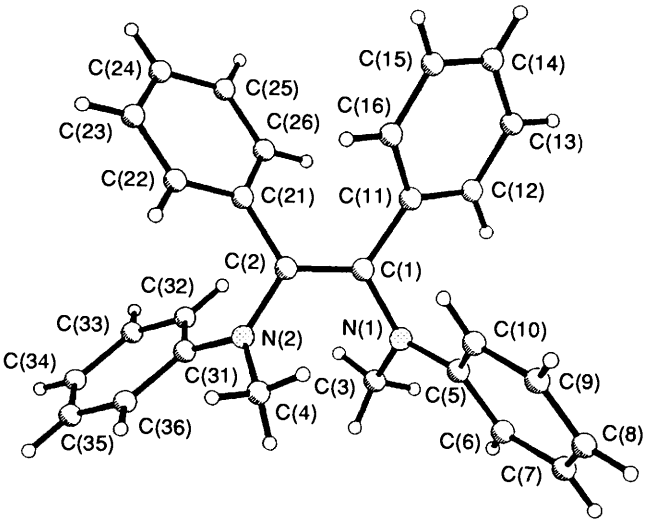


Fig. 2 Perspective view and atom labelling of the X-ray structure of compound **17a**

Table 3 Atomic coordinates (× 10^4) for **17** with esds in parentheses

Atom	*x*	*y*	*z*
N(1)	328(2)	1857(1)	−60(2)
N(2)	606(2)	963(1)	1830(2)
C(1)	1546(2)	1416(1)	362(2)
C(2)	1787(3)	1056(1)	1401(2)
C(3)	146(3)	2268(1)	883(2)
C(4)	−916(3)	774(1)	924(2)
C(5)	−797(3)	1869(1)	−1319(2)
C(6)	−1838(3)	2364(1)	−1768(2)
C(7)	−2979(3)	2361(1)	−3001(3)
C(8)	−3123(3)	1873(1)	−3815(2)
C(9)	−2100(3)	1383(1)	−3385(2)
C(10)	−946(3)	1378(1)	−2159(2)
C(11)	2601(2)	1408(1)	−299(2)
C(12)	2968(3)	1960(1)	−755(2)
C(13)	4061(3)	1965(1)	−1266(2)
C(14)	4790(3)	1423(1)	−1351(2)
C*(15)	4391(3)	868(1)	−957(2)
C(16)	3294(3)	859(1)	−450(2)
C(21)	3292(3)	755(1)	2179(2)
C(22)	3350(3)	151(1)	2638(2)
C(23)	4746(3)	−120(1)	3399(2)
C(24)	6107(3)	207(1)	3734(2)
C(25)	6073(3)	809(1)	3295(2)
C(26)	4676(3)	1083(1)	2530(2)
C(31)	899(3)	1015(1)	3128(2)
C(32)	2146(3)	1372(1)	3964(2)
C(33)	2423(3)	1431(1)	5238(2)
C(34)	1474(3)	1145(1)	5718(2)
C(35)	246(3)	798(1)	4906(2)
C(36)	−44(3)	727(1)	3624(2)

Table 4 Selected bond lengths (Å) and angles (°) for **17a** with esds in parentheses

N(1)–C(1)	1.421(3)	N(1)–C(3)	1.465(4)
N(1)–C(5)	1.403(3)	N(2)–C(2)	1.415(4)
N(2)–C(4)	1.450(3)	N(2)–C(31)	1.408(3)
C(1)–C(2)	1.365(3)	C(1)–C(11)	1.487(4)
C(2)–C(21)	1.487(4)		
C(1)–N(1)–C(3)	118.6(2)	C(1)–N(1)–C(5)	122.1(2)
C(3)–N(1)–C(5)	118.9(2)	C(2)–N(2)–C(4)	119.2(2)
C(2)–N(2)–C(31)	121.4(2)	C(4)–N(2)–C(31)	119.3(2)
N(1)–C(1)–C(2)	120.0(2)	N(1)–C(1)–C(11)	117.3(2)
C(2)–C(1)–C(11)	122.5(2)	N(2)–C(2)–C(1)	121.1(2)
N(2)–C(2)–C(21)	115.6(2)	C(1)–C(2)–C(21)	123.3(2)

conformations that minimise steric interactions. An interesting feature of the structure is the significant twisting of the double bond in order to relieve steric interactions between adjacent substituents. For example the mean planes described by N(1)–C(1)–C(11) and N(2)–C(2)–C(21) are mutually inclined at an angle of 19.7(2)° and the N(1)–C(1)–C(2)–N(2) and C(11)–C(1)–C(2)–C(21) torsion angles are 20.4(3)° and 16.8(3)° respectively. The bonding geometries of the nitrogen atoms are closer to trigonal than to tetrahedral. Again the potential C_2 symmetry of the molecule is destroyed in the solid state by torsion angle differences. For example, relative to the plane of the double bond the C(1) and C(2) phenyl rings are inclined at angles of 41.3(3)° and 48.9(3)° respectively, and the N(1) and N(2) phenyl rings are inclined at angles of 109.83(3)° and 68.4(3)° respectively. The four phenyl rings are all planar to within 0.014 Å and there are no unusually short intermolecular contacts between non-hydrogen atoms of less than 3.49 Å.

Experimental

General.—M.p.s were determined on a Fisher-Johns hot-stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively on a Varian XL300 or General Electric QE300 spectrometer in $CDCl_3$ referenced to Me_4Si for the proton spectra and the solvent for the carbon spectra. *J* Values are given in Hz. High resolution mass spectra were recorded on a Kratos AEI MS30 spectrometer. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. Tetrahydrofuran (THF), benzene and toluene were distilled under nitrogen from sodium–benzophenone immediately before use. All reactions with water-sensitive compounds were carried out in dry nitrogen atmospheres.

1-Chloromethylbenzotriazole was prepared according to a literature procedure.[12]

General Procedure for the Preparation of 1-(*Arylmethyl*)*benzotriazoles* **4**.—1-Chloromethylbenzotriazole **1** (0.45 g, 2.67 mmol) was added portionwise with stirring to a solution of $AlBr_3$ (1.07 g, 4.01 mmol) in the aromatic hydrocarbon (16.00 mmol). The mixture was stirred at *ca.* 20 °C over 3 h (in the syntheses of **4a–c**) or 8 h (in the preparation of **4d**). Ice–water (20 cm^3) was added, followed by extraction with chloroform (3 × 20 cm^3). The combined extracts were washed with 10% NaOH (20 cm^3), water (20 cm^3) and dried ($MgSO_4$), and the solvent was evaporated off to yield crude products, purified by silica gel column chromatography (eluent: chloroform–hexanes, 1:3).

1-*Benzylbenzotriazole* **4a**. Yield 0.49 g, 88%, colourless plates, m.p. 114–115 °C (from methanol) (lit.,[18] 115 °C).

1-[(o-, m- *and* p-*Tolyl*)*methyl*]*benzotriazoles* **4b**. Yield 0.52 g, 88%, pale-yellow oil (Found: M^+, 223.1112. $C_{14}H_{13}N_3$ requires *M*, 223.1111); δ_H 2.30 (1.5 H, s, *p*-Me), 2.31 (0.7 H, s, *m*-Me), 2.34 (0.8 H, s, *o*-Me), 5.80 (s, *m*- and *p*-CH_2), 5.86 (s, *o*-CH_2) (2 H), 7.02–7.44 (7 H, m) and 8.03–8.11 (1 H, m, 4-H Bt).* The pure *p*-isomer (0.09 g, 15%) was isolated by recrystallization from methanol, colourless prisms, m.p. 108–109 °C (lit.,[18] 107 °C).

1-[(2,5-*Dimethylphenyl*)*methyl*]*benzotriazole* **4c**. Yield 0.52 g, 82%, colourless prisms, m.p. 75–76 °C (from hexanes) (Found: C, 76.0; H, 6.4; N, 17.5. $C_{15}H_{15}N_3$ requires C, 75.9; H, 6.4; N, 17.7%); δ_H 2.25 (3 H, s, Me), 2.29 (3 H, s, Me), 5.81 (2 H, s, CH_2), 6.89 (1 H, s, 6-H of aryl), 6.97–7.42 (5 H, m) and 8.07 (1 H, d, *J* 8.3, 4-H Bt); δ_C 18.77 (Me), 20.90 (Me), 50.68 (CH_2), 109.86 (C-7 Bt), 119.97 (C-4 Bt), 123.80 (C-5 Bt), 127.26, 129.21 (C-6 Bt), 129.32, 130.83, 132.33 (C-7a Bt), 132.99, 133.29, 135.96 and 146.22 (C-3a Bt).

* Bt = benzotriazole.

1-[(o-, m- *and* p-*Chlorophenyl*)*methyl*]*benzotriazole* **4d**. Yield 0.51 g, 79%, pale-yellow oil (Found: M^+, 243.0565. $C_{13}H_{10}ClN_3$ requires *M*, 243.0565); δ_H 5.82 (s, *m*- and *p*-CH_2), 5.98 (s, *o*-CH_2) (2 H), 7.12–7.43 (7 H, m) and 8.06–8.13 (1 H, m, 4-H Bt); δ_C 49.13 and 51.44 (CH_2), 109.45, 109.54 and 109.61 (C-7 Bt), 120.07 and 120.01 (C-4 Bt), 146.12 and 146.29 (C-3a Bt).

1-*Bromomethylbenzotriazole* **3**.—The title compound was obtained by the reaction of compound **1** with $AlBr_3$ in *o*-dichlorobenzene analogously to the procedure described above for the preparation of compounds **4**. The combined chloroform extracts were washed with water (20 cm^3) and dried ($MgSO_4$), and the solvent was evaporated to a volume of *ca.* 3 cm^3. Hexanes (30 cm^3) were added, and the solution was left at 20 °C over *ca.* 7 h to yield pale-yellow crystals of pure compound **3**. Yield 0.44 g, 77%, m.p. 113–114 °C (lit.,[31] 113–115.5 °C).

General Procedure for the Preparation of 1-(*Arylalkyl*)*benzotriazoles* **7** *and* **8**.—To a solution of the appropriate compound **4** (4.00 mmol) in THF (25 cm^3) at −78 °C, BuLi [2.5 mol dm^{-3}; solution in hexanes, 1.76 cm^3 (4.40 mmol) in the preparation of **7** or 3.52 cm^3 (8.80 mmol) in the preparation of **8**] was added dropwise with stirring. After 15 min the electrophile (4.00 mmol in 5 cm^3 of THF or 8.00 mmol in 10 cm^3 of THF for the preparation of **7** and **8**, respectively) was added at −78 °C dropwise with stirring. The mixture was allowed to warm to 20 °C over *ca.* 5 h, and ice water (20 cm^3) was added followed by extraction with diethyl ether (4 × 15 cm^3). The combined extracts were washed with water (40 cm^3) and dried ($MgSO_4$). Evaporation of the solvent yielded pure **7a, 8**, or crude products **7b, c**. The latter were purified by silica gel column chromatography (eluent: chloroform–hexanes, 1:10).

1-[1-*Deuterio*-1-(2,5-*dimethylphenyl*)*methyl*]*benzotriazole* **7a**. Yield 0.89 g, 94%, m.p. 77–78 °C (from hexanes) (Found: C, 75.9; H + D, 6.5; N, 17.6. $C_{15}DH_{14}N_3$ requires C, 75.6; H + D, 6.8; N, 17.6%); δ_H 2.25 (3 H, s, Me), 2.29 (3 H, s, Me), 5.79 (1 H, m, CHD), 6.90 (1 H, s, 6-H of aryl), 7.02–7.42 (5 H, m) and 8.07 (1 H, d, *J* 8.4, 4-H Bt); δ_C 18.16 (Me), 20.30 (Me), 49.81 (t, *J* 21.0, CHD), 109.34 (C-7 Bt), 119.23 (C-4 Bt), 123.33 (C-5 Bt), 126.74, 128.65 (C-6 Bt), 128.75, 130.23, 131.66, 132.40 (C-7a Bt), 132.70, 135.33 and 145.48 (C-3a Bt).

1-(*Benzotriazol*-1-*yl*)-1-*phenylpentane* **7b**.—Yield 0.87 g, 82%, m.p. 72–73 °C (from hexanes) (Found: C, 76.9; H, 7.2; N, 15.7. $C_{17}H_{19}N_3$ requires C, 76.95; H, 7.2; N, 15.8%); δ_H 0.89 (3 H, t, *J* 7.2, Me), 1.34 (4 H, m, CH_2CH_2), 2.45 (1 H, m, CH), 2.77 (1 H, m, CH), 5.78 (1 H, dd, *J* 6.3 and 6.4, NCH), 7.20–7.45 (8 H, m) and 8.05 (1 H, d *J* 7.9, 4-H Bt); δ_C 13.83 (Me), 22.28 (CH_2), 28.71 (CH_2), 34.50 (CH_2), 63.83 (NCH), 109.83 (C-7 Bt), 119.99 (C-4 Bt), 123.77 (C-5 Bt), 126.82, 127.01, 128.18 (C-6 Bt), 128.81, 132.79 (C-7a Bt), 139.42 and 146.24 (C-3a Bt).

1-(1-*Isopropyl*-1-*phenylmethyl*)*benzotriazole* **7c**. Yield 0.80 g, 80%, m.p. 101–102 °C (from methanol) (Found: C, 76.1; H, 6.8; N, 16.7. $C_{16}H_{17}N_3$ requires C, 76.5; H, 6.8; N, 16.7%); δ_H 0.92 (3 H, d, *J* 6.5, Me), 0.99 (3 H, d, *J* 6.6, Me), 3.25 (1 H, m, CH), 5.24 (1 H, d, *J* 10.5, NCH), 7.24–7.58 (8 H, m) and 8.04 (1 H, d, *J* 8.3, 4-H Bt); δ_C 20.29 (Me), 20.39 (Me), 32.65 (CH), 70.81 (NCH), 109.55 (C-7 Bt), 119.91 (C-4 Bt), 123.75 (C-5 Bt), 127.05, 127.80, 128.24 (C-6 Bt), 128.70, 133.27 (C-7a), 138.32 and 145.80 (C-3a Bt).

5-(*Benzotriazol*-1-*yl*)-5-*phenylnonane* **8a**. Yield 1.28 g, 100%, m.p. 82–83 °C (from diethyl ether–hexanes, 1:2) (Found: C, 78.1, H, 8.7; N, 12.9. $C_{21}H_{27}N_3$ requires C, 78.5; H, 8.5; N, 13.1%); δ_H 0.79 (6 H, t, *J* 6.9, 2 Me), 1.25 (8 H, m, 2 CH_2CH_2), 2.63 (4 H, m, 2 CH_2), 6.63 (1 H, d, *J* 7.5, 7-H Bt), 7.08–7.38 (7 H, m) and 8.05 (1 H, d, *J* 8.3, 4-H Bt); δ_C 13.85 (Me), 22.76 (CH_2), 25.34 (CH_2), 36.55 (CH_2), 70.40 [N(1)C], 112.21 (C-7 Bt), 119.83 (C-4 Bt), 123.39 (C-5 Bt), 126.18, 126.39, 127.64 (C-6 Bt), 128.49, 132.21 (C-7a Bt), 142.87 and 146.82 (C-3a Bt).

2-(*Benzotriazol*-1-*yl*)-1,2,3-*triphenylpropane* **8b**. Yield 1.56 g, 100%, m.p. 168–169 °C (from diethyl ether–hexanes, 1:3) (Found: C, 82.9; H, 6.0; N, 10.6. $C_{27}H_{23}N_3$ requires C, 83.3; H, 6.0; N, 10.8%); δ_H 3.91 (4 H, s, CH_2), 6.53 (1 H, d, *J* 8.4, 7-H Bt), 6.57 (2 H, d, *J* 7.0, *o*-H Ph), 6.98–7.38 (14 H, m) and 8.05 (1 H, d, *J* 8.4, 4-H Bt); δ_C 43.72 (CH_2), 71.58 [N(1)C], 112.71 (C-7 Bt), 120.01 (C-4 Bt), 123.49 (C-5 Bt), 126.38, 126.90, 127.42, 127.78, 128.10, 128.39 (C-6 Bt), 130.74, 133.19 (C-7a Bt), 135.14, 140.92 and 146.75 (C-3a Bt).

1,2,3-*Triphenylpropane* **9**.—A mixture of compound **7a** (1.56 g, 4.00 mmol), $LiAlH_4$ (0.17 g, 4.40 mmol) and $AlCl_3$ (0.59 g, 4.40 mmol) in toluene was stirred under reflux for 40 min. After cooling, ice–water (40 cm^3) was added, followed by extraction with light petroleum (3 × 30 cm^3). The combined extracts were washed with NaOH (5 mol dm^{-3}; 20 cm^3) and water and dried ($MgSO_4$). Evaporation of the solvent yielded 1.07 g (98%) of the product, b.p. 162–165 °C/1 Torr (lit.,[20] 179–181 °C/2 Torr) (Found: M^+, 272.1567. $C_{21}H_{20}$ requires *M*, 272.1566); δ_C 42.50 (CH_2), 49.93 (CH), 125.83, 126.14, 127.92, 128.08, 128.11, 129.14, 140.49 and 144.27.

5-*Phenylnon*-4-*ene* **10a**.—Compound **8a** (1.33 g, 5.00 mmol) in glacial acetic acid (8 cm^3) was heated at 140 °C in a sealed tube for 13 h. Water (20 cm^3) was added, followed by extraction with diethyl ether (3 × 20 cm^3). The combined organic layers were washed with 10% NaOH (3 × 20 cm^3) and water (20 cm^3) and dried ($MgSO_4$). Evaporation of the solvent followed by distillation yielded 0.61 g (83%) of the product, b.p. 82–86 °C/0.8 Torr (lit.,[32] 117–121 °C/6 Torr); δ_H 0.80–0.90 (3.5 H, m, CH_2-CH_2Me, *Z*-isomer, and $CH_2CH_2CH_2Me$), 0.96 (2.5 H, t, *J* 7.3, CH_2CH_2Me, *E*-isomer), 1.23–1.38 (4.33 H, m, CH_2CH_2Me, *Z*-isomer, and $CH_2CH_2CH_2Me$), 1.47 (1.67 H, sextuplet, *J* 7.3, CH_2CH_2Me, *E*-isomer), 1.89 (0.33 H, dt, *J* 7.1 and 7.2, CH_2CH_2Me, *Z*-isomer), 2.17 (1.67 H, dt, *J* 7.2 and 7.3, CH_2CH_2Me, *E*-isomer), 2.32 (0.33 H, t, *J* 7.1, $CH_2CH_2CH_2Me$, *Z*-isomer), 2.49 (1.67 H, t, *J* 7.1, $CH_2CH_2CH_2Me$, *E*-isomer), 5.42 (0.17 H, t, *J* 7.2, CH=, *Z*-isomer), 5.64 (0.83 H, t, *J* 7.2, CH=, *E*-isomer), 7.10–7.40 (5 H, m, Ph).

1,2,3-*Triphenylpropene* **10b**.—Compound **8b** (1.95 g, 5.00 mmol) in glacial acetic acid (8 cm^3) was heated at 140 °C in a sealed tube for 16 h. Water (20 cm^3) was added, followed by extraction with diethyl ether (3 × 20 cm^3). The combined organic layers were washed with 10% NaOH (3 × 20 cm^3) and water (20 cm^3), and dried ($MgSO_4$). Evaporation of the solvent followed by distillation yielded 1.28 g (95%) of the oily product, b.p. 175–180 °C/0.4 Torr (lit.,[33] 168–170 °C/0.3 Torr) (Found: M^+, 270.1413. $C_{21}H_{18}$ requires *M*, 270.1409); δ_H 3.81 (0.4 H, s, CH_2, *Z*-isomer), 4.16 (1.6 H, s, CH_2, *E*-isomer), 6.43 (0.2 H, s, CH=, *Z*-isomer) and 6.90–7.53 (15.8 H, m).

1,2-*Di*(*benzotriazol*-1-*yl*)-1,2-*diphenylethane* **12a**.—To a solution of compound **4a** (0.84 g, 4.00 mmol) in THF (28 cm^3) LDA (lithium diisopropylamide) (1.5 mol dm^{-3} solution in cyclohexane; 2.94 cm^3, 4.40 mmol) was added dropwise with stirring at −78 °C. After 15 min, 1,2-dibromoethane (0.38 cm^3, 4.40 mmol) in THF (6 cm^3) was added dropwise at −78 °C. The mixture was allowed to warm to 20 °C over *ca.* 5 h, and the solvent was evaporated under reduced pressure. The crude product was treated with methanol (30 cm^3), and the resulting precipitate of the meso-diastereoisomer of **11a** was filtered off, washed with water (2 × 20 cm^3), methanol (2 × 10 cm^3) and diethyl ether (10 cm^3) and dried under reduced pressure, yield 0.32 g (38%), m.p. 280–281 °C [from DMF (dimethylformamide)] (Found: C, 74.6; H, 4.8; N, 20.2. $C_{26}H_{20}N_6$ requires C, 75.0; H, 4.8; N, 20.2%); δ_H(CD_3SOCD_3) 7.04–7.56 (10 H, m), 7.74 (2 H, s, 2 CH), 7.82–7.96 (6 H, m) and 8.38 (2 H, d, *J* 8.0, 2 × 4-H Bt). The racemic diastereoisomer was obtained by silica gel column chromatography of the evaporated filtrate after isolation of the meso-diastereoisomer (eluent: chloroform–hexanes, 1:4). The yield 0.46 g (55%), m.p. 226–227 °C (from benzene–hexanes, 1:1) (Found: C, 76.3; H, 5.0; N, 18.4. 2 $C_{26}H_{20}N_6$ × C_6H_6 requires C, 76.5; H, 5.1; N, 18.5%); δ_H 7.18–7.28 (8 H, m), 7.30 (2 H, s, 2 CH), 7.36–7.46 (6 H, m), 7.66 (2 H, d, *J* 8.4, 2 H-7 Bt) and 7.85 (2 H, d, *J* 8.3, 2 4-H Bt); δ_C 65.68 (2 CH), 109.54 (2 C-7 Bt), 119.68 (2 C-4 Bt), 124.17 (2 C-5 Bt), 127.66 (2 C-6 Bt), 128.07, 128.78, 128.85, 132.99 (2 C-7a Bt), 135.29 and 145.52 (2 C-4a Bt).

1,2-*Di*(*benzotriazol*-1-*yl*)-1,2-*di*(p-*tolyl*)*ethane* **12b**.—To a solution of compound **4b** (0.89 g, 4.00 mmol) in THF (28 cm^3), LDA (1.5 mol dm^{-3} solution in cyclohexane, 2.94 cm^3, 4.40 mmol) was added dropwise with stirring at −78 °C. After 15 min 1,2-dibromoethane (0.38 cm^3, 4.40 mmol) in THF (6 cm^3) was added dropwise at −78 °C. The mixture was allowed to warm to 20 °C over *ca.* 5 h, and the solvent was evaporated under reduced pressure. The crude product was treated with methanol (30 cm^3), and the resulting precipitate of the mixture of diastereoisomers **12b** was filtered off, washed with water (2 × 20 cm^3), methanol (2 × 10 cm^3) and diethyl ether (10 cm^3) and dried under reduced pressure. Total yield of the mixture of diastereoisomers 0.65 g (73%). The major diastereoisomer was obtained by washing the mixture of diastereoisomers with diethyl ether (5 × 20 cm^3): isolated yield 0.29 g (33%), m.p. 305–307 °C (from toluene) (Found: C, 75.6; H, 5.5. $C_{28}H_{24}N_6$ requires C, 75.7; H, 5.4%); δ_H 2.06 (6 H, s, 2 Me), 6.89 (4 H, d, *J* 8.5, 2 × 2-H C_6H_4), 7.12 (2 H, s, 2 CH), 7.24–7.35 (4 H, m), 7.42–7.58 (6 H, m) and 7.93 (2 H, d, *J* 8.3, 2 4-H Bt).

Benzil Dianil **16**.—To a solution of compound **4a** (0.84 g, 4.00 mmol) in THF (28 cm^3), LDA (1.5 mol dm^{-3} solution in cyclohexane, 2.94 cm^3, 4.40 mmol) was added dropwise with stirring at −78 °C. The reaction mixture was allowed to warm to 15 °C, and water (20 cm^3) was added, followed by extraction with diethyl ether (3 × 20 cm^3). The combined organic layers were washed with water (3 × 20 cm^3) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the residue subjected to silica column chromatography (eluent: $CHCl_3$–hexanes, 1:4) to yield 0.43 g (60%) of the product, m.p. 142–143 °C (from methanol) (lit.,[30] 140–145 °C) (Found: C, 86.4; H, 5.5; N, 7.7. $C_{26}H_{20}N_2$ requires C, 86.6; H, 5.6; N, 7.8%); δ_C 120.07, 124.87, 128.33, 128.37, 128.73, 131.09, 137.64, 149.31 and 163.88 (2 C=N).

Benzil Dianil **16** *and* 4-*Phenyl*-1,2,4-*benzotriazine* **15**.—To a solution of compound **4a** (0.84 g, 4.40 mmol) in THF (28 cm^3), LDA (1.5 mol dm^{-3} solution in cyclohexane, 2.94 cm^3, 4.40 mmol) was added dropwise with stirring at −78 °C. The reaction mixture was allowed to warm to 15 °C and cooled to −78 °C. A solution of tosyl azide (0.87 g, 4.40 mmol) in THF (5 cm^3) was added dropwise at −78 °C over *ca.* 30 min. The mixture was allowed to warm to 20 °C over *ca.* 3 h, and water (20 cm^3) was added, followed by extraction with diethyl ether (3 × 20 cm^3). The combined organic layers were washed with water (3 × 20 cm^3) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the residue was subjected to silica gel column chromatography (eluent: $CHCl_3$–hexanes, 1:4) to yield (i) 0.35 g, (49%) of compound **16** and (ii) compound **15** (0.08 g, 10%), m.p. 124–125 °C (from acetone) (lit.,[34] 124–126 °C); δ_C 128.76, 128.91, 129.12, 129.56, 130.12, 131.42, 135.44, 135.61, 141.06, 146.45 (C-8) and 159.83 (C-3); *m/z* (70 eV) 179 $[M - N_2]^+$.

1,2-*Di*(N-*methylanilino*)-1,2-*diphenylethene* **17a**.—To a solution of compound **4a** (0.84 g, 4.00 mmol) in THF (28 cm^3) LDA

(1.5 mol dm^{-3} solution in cyclohexane, 2.94 cm^3, 4.40 mmol) was added dropwise with stirring at −78 °C. The reaction mixture was allowed to warm to −15 °C and cooled to −78 °C. Methyl iodide (0.62 g, 4.40 mmol) in THF (3 cm^3) was added dropwise with stirring. The mixture was allowed to warm to 20 °C over *ca.* 3 h, and water (20 cm^3) was added followed by extraction with diethyl ether (3 × 20 cm^3). Combined organic layers were washed with water (3 × 20 cm^3) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure to yield 0.64 g, (80%) of the product, m.p. 171–173 °C (from acetone) (lit.,[30] 173–175.5 °C); δ_H 2.67 (6 H, s, 2 Me) and 6.70–7.24 (20 H, m); δ_C 36.75 (2 Me), 115.71, 118.34, 126.94, 127.94, 128.41, 130.58, 136.99, 138.47 and 148.84.

1,2-*Di*(N-*methylanilino*)-1,2-*di*(p-*tolyl*)*ethene* **17b**.—To a solution of compound **4b** (0.89 g, 4.00 mmol) in THF (28 cm^3), LDA (1.5 mol dm^{-3} solution in cyclohexane, 2.94 cm^3, 4.40 mmol) was added dropwise with stirring at −78 °C. The reaction mixture was allowed to warm to 15 °C and cooled to −78 °C. Methyl iodide (0.62 g, 4.40 mmol) in THF (3 cm^3) was added dropwise with stirring. The mixture was allowed to warm to 20 °C over *ca.* 3 h, and water (20 cm^3) was added followed by extraction with diethyl ether (3 × 20 cm^3). The combined organic layers were washed with water (3 × 20 cm^3) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the residue recrystallized from acetone to give 0.13 g (16%) of the product, m.p. 209–212 °C (from acetone) (Found: C, 85.9; H, 7.2; N, 6.6. $C_{30}H_{30}N_2$ requires C, 86.1; H, 7.2; N, 6.7%); δ_H 2.29 (6 H, s, 2 Me), 2.64 (6 H, s, 2 MeN) and 6.70–7.20 (18 H, m); δ_C 22.24 (2 Me), 37.65 (2 MeN), 116.55, 119.07, 129.38, 129.74, 131.35, 136.54, 137.58, 137.66 and 150.06.

X-Ray Crystal Structure Determinations.—Crystal data for **12a**. $C_{26}H_{20}N_6 \cdot 0.5C_6H_6$, FW = 455.5. Monoclinic, a = 10.191(4), b = 17.642(8), c = 13.665(5) Å, β = 95.25(3)0, V = 2447(2) $Å^3$ (by least-squares refinement on 24 accurately centred reflections with $2\theta > 13°$; λ = 0.7107 Å) at −100 °C. Space group $P2_1/n$ (alt $P2_1/c$, No. 14), Z = 4, D_x = 1.237 g cm^{-3}. Colourless block with dimensions 0.28 × 0.20 × 0.12 mm, μ(Mo-Kα) = 0.71 cm^{-1}, F(000) = 956.

Crystal data for **17a**. $C_{28}H_{26}N_2$. FW = 390.5. Monoclinic, a = 9.501(5), b = 21.571(7), c = 11.520(7) Å, β = 114.35(4), V = 2151(2) $Å^3$ (by least-squares refinement on 25 accurately centred reflections with $2\theta > 14°$, λ = 0.7107 Å) at −80 °C. Space group $P2_1/c$ (No. 14), Z = 4, D_x = 1.206 g cm^3. Yellow block with dimensions 0.52 × 0.26 × 0.16 mm, μ(Mo-Kα) = 0.65 cm^{-1}, F(000) = 832.

Data collection.[35] Nicolet R3m four-circle diffractometer, $\omega/2\theta$ scan mode ($1.5 \leq \theta \leq 27.5°$, $\pm h$, $+k$, $+l$), graphite-monochromated Mo-Kα radiation. For **12a** 5829 reflections measured at −100 °C, 5604 unique (merging R = 0.022), giving 2191 with $I > 3\sigma(I)$. For **17a** 5152 reflections measured at −80 °C, 4913 unique (merging R = 0.018), giving 2467 with $I > 3\sigma(I)$. No absorption correction or crystal decay in either case.

*Structure solutions and refinements.** For both structures direct methods gave all non-hydrogen atoms. Full-matrix least-squared refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with isotropic temperature factors. The function minimized were $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + 0.0006F_o]^{-1}$. For **12a** the final R and R_w are 0.049 and 0.053 with S = 1.16 for 316 parameters. For **17a** the final R and R_w are 0.044 and 0.049 with S = 1.15 for 271 parameters. Final difference map features all <0.22 e $Å^{-3}$. For programs and computers see ref. 36.

* *Supplementary data.* Full tables of atom coordinates, bond lengths and angles, anisotropic displacement parameters and calculated hydrogen atom coordinates for both structures have been deposited at the Cambridge Crystallographic Data Centre. For full details of the C.C.D.C. deposition scheme see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

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