5.37; N, 21.93. Found: C, 67.30; H, 5.38; N, 21.74. **8c** was also obtained (18%).

1-(*p*-Methoxyphenyl)-4-(2-imidazolinyl)-5-(*p*-chlorophenyl)-1,2,3-triazole (6dd) and 8d. **6dd** was obtained (8%) as a white solid, mp 183–184.5 °C: IR (KBr) 3320 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 230 (4.28), 246 nm (4.25); ^1H NMR (DMSO-d_6) δ 3.18 (s, 1, NH), 3.50 (s, 4, CH_2CH_2), 3.74 (s, 3, OCH_3), 6.96 (d, 2, J = 9.0), 7.25 (d, 2, J = 9.0), 7.35 (s, 4); MS 353 (26, M^+), 352 (82, $M^+ - 1$), 324 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{15}H_{16}ClN_5O$: C, 61.10; H, 4.56; N, 19.80. Found: C, 60.69; H, 4.62; N, 19.60. **8d** was also obtained (10%).

1,5-Bis(*p*-methoxyphenyl)-4-(2-tetrahydropyrimidinyl)-1,2,3-triazole (7ad) and 9a. **7ad** was obtained (45%) as white crystals, mp 199.5–200.5 °C: IR (KBr) 3350 cm^{-1}; UV (EtOH) λ_{max} (lg ϵ) 248 nm (4.14); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.25 (t, 4), 3.71 (s, 3, OCH_3), 3.74 (s, 3, OCH_3), 6.83 (s, 1, NH), 6.78 (d, 2, J = 9.0), 7.06 (d, 2, J = 9.0), 6.90 (d, 2, J = 9.0), 7.16 (d, 2, J = 9.0); MS 363 (24, M^+), 363 (72, $M^+ - 1$), 335 (42, $M^+ - N_2$), 334 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{20}H_{21}N_5O_2$: C, 66.10; H, 5.83; N, 19.27. Found: C, 66.12; H, 5.83; N, 19.39. **9a** was also obtained (31%).

1-(*p*-Methoxyphenyl)-4-(2-tetrahydropyrimidinyl)-5-(*p*-methylphenyl)-1,2,3-triazole (7bd) and 9b. **7bd** was obtained (30%) as white crystals, mp 193–194 °C: IR (KBr) 3350 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 235 nm (4.17); ^1H NMR (DMSO-d_6) δ 1.62 (quin, 2), 3.21 (t, 4), 2.24 (s, 3, CH_3), 3.71 (s, 3, OCH_3), 6.67 (s, 1, NH), 7.05 (s, 4), 6.88 (d, 2, J = 9.0), 7.11 (d, 2, J = 9.0); MS 347 (29, M^+), 346 (80, $M^+ - 1$), 319 (35, $M^+ - N_2$), 318 ($M^+ - 1 - N_2$). Anal. Calcd for $C_{20}H_{21}N_5O$: C, 69.14; H, 6.09; N, 20.16. Found: C, 69.44; H, 6.09; N, 20.12. **9b** was also obtained (23%).

1-(*p*-Methoxyphenyl)-4-(2-tetrahydropyrimidinyl)-5-phenyl-1,2,3-triazole (7cd) and 9c. **7cd** was obtained (31%) as white crystals, mp 178.5–179.5 °C: IR (KBr) 3370 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 (4.27), 242 nm (sh); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.23 (t, 4), 3.73 (s, 3, OCH_3), 6.63 (s, 1, NH), 6.88 (d, 2, J = 9.0), 7.13 (d, 2, J = 9.0), 7.21 (s, 5); MS 333 (32, M^+), 332 (93, $M^+ - 1$), 305 (32, $M^+ - N_2$), 304 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{19}N_5O$: C, 68.45; H, 5.74; N, 21.01. Found: C, 68.65; H, 5.84; N, 20.72. **9c** was also obtained (21%).

1-(*p*-Methoxyphenyl)-4-(2-tetrahydropyrimidinyl)-5-(*p*-chlorophenyl)-1,2,3-triazole (7dd) and 9d. **7dd** was obtained (35%) as white crystals, mp 205–206 °C: IR (KBr) 3348 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 (4.35), 248 nm (sh); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.23 (t, 4), 3.75 (s, 3, OCH_3), 6.75 (s, 1, NH), 6.92 (d, 2, J = 9.0 Hz), 7.17 (d, 2, J = 9.0 Hz), 7.26 (s, 4); MS 367 (27, M^+), 366 (69, $M^+ - 1$), 339 (34, $M^+ - N_2$), 338 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{18}ClN_5O$: C, 62.04; H, 4.93; N, 19.04. Found: C, 62.45; H, 5.16; N, 19.27. **9d** was also obtained (15%).

Preparation of 1-(*p*-Nitrophenyl)-4-(1-methyl-2-imidazolinyl)-5-phenyl-1,2,3-triazole (11). A mixture of 1-methyl-2-(benzoylmethylene)imidazoline (**10**) (253 mg, 1.25 mol) and **5a** (205 mg, 1.25 mol) in dried 1,4-dioxine (10 mL) was stirred at ambient temperature for 50 h. After partial removal of solvent, **11** (390 mg, 83%) was crystallized out as yellow crystals, mp 209.5–210.5 °C: IR (KBr) 1520, 1340 (NO_2), 1588, 1560, 1495 cm^{-1}; UV (EtOH) λ_{max} (lg ϵ) 223 (4.23), 264 nm (4.22); ^1H NMR (DMSO-d_6) δ 2.76 (s, 3, CH_3), 3.15–3.75 (m, 4, CH_2CH_2), 7.31 (s, 5), 7.60 (d, 2, J = 9.0), 8.25 (d, 2, J = 9.0); MS 348 (40, M^+), 347 (100, $M^+ - 1$), 319 (30, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{16}N_6O_2$: C, 62.06; H, 4.63; N, 24.13. Found: C, 62.62; H, 4.63; N, 24.00.

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Novel Dimroth Rearrangements of the Benzotriazole System: 4-Amino-1-(arylsulfonyl)benzotriazoles to 4-[(Arylsulfonyl)amino]benzotriazoles

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A variety of mono- and diarylsulfonyl-substituted 4-aminobenzotriazoles were prepared. Thermal rearrangements of 4-amino-1-(arylsulfonyl)benzotriazoles to 4-[(arylsulfonyl)amino]benzotriazoles were observed and confirmed by separation of the rearrangement products. Their structures were characterized by spectral methods and by X-ray crystallography. The rearrangement rates were studied by variable-temperature NMR experiments. Crossover experiments support an intramolecular mechanism involving a heterolytic benzotriazole ring cleavage to form a diazo intermediate followed by recyclization to the 4-amino group.

Molecular rearrangements constitute an important aspect of ring-transformation reactions of heterocyclic compounds.[1] It has been known for a long time that 1*H*-1,2,3-triazoles **1** can exist in thermal equilibria with diazo imines **2** which may recyclize to **3**. This constitutes a subsection of the general class of heterocyclic reactions now known as Dimroth rearrangements.[2-4] Several molecular rearrangements of 4- or 5-substituted 1,2,3-triazoles **1** involving intermediates of type **2** have previously been reported,[5] in which the substituent was amino (**1** ⇌ **3**, R^5 = NH_2),[6] hydrazino (**1** ⇌ **5**, R^5 = $NHNH_2$),[7] diazomethyl (**1** ⇌ **6**, R = CHN_2),[8] and iminomethyl (**1** ⇌ **4**, R^4 = CH=NR).[9] Solvent and substituent effects on these rear-

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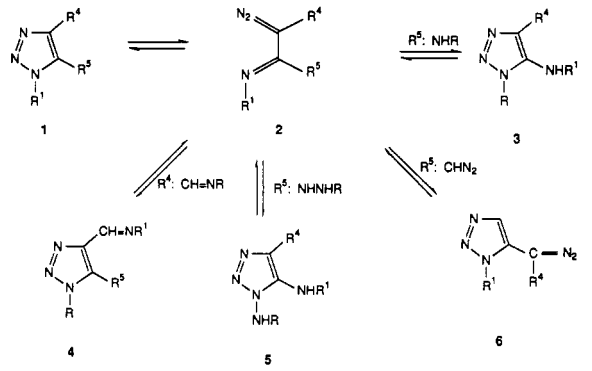
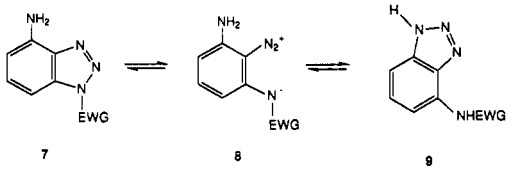
Scheme I



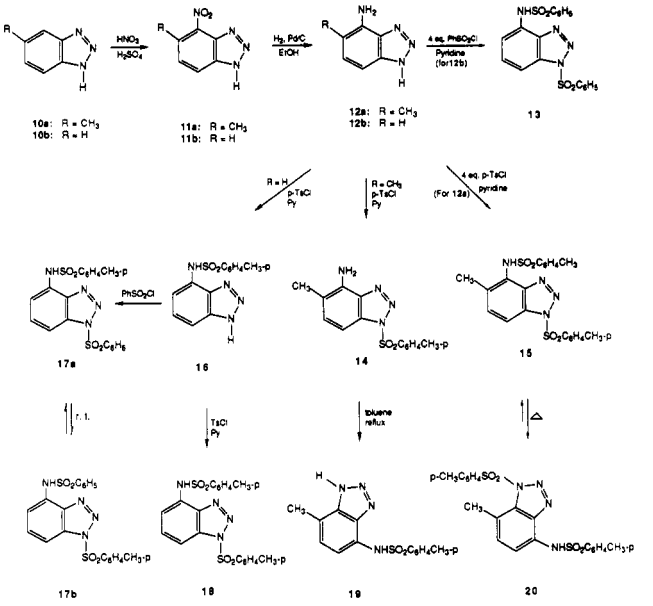
Scheme II



rangements have been studied.[10,11] Dimroth rearrangements also interconvert 5-mercapto-1,2,3-triazoles and 5-amino-1,2,3-thiadiazoles.[12] In addition to these examples for 1,2,3-triazoles, similar rearrangements are known for 1,2,4- and 1,3,4-thiadiazoles,[13] 1,2-benzisothiazoles,[14] and other five-membered heterocyclic ring systems.[2]

Although a variety of known Dimroth rearrangements involve 1*H*-1,2,3-triazoles, no similar rearrangements of 4-amino- or 4-imino-substituted 1*H*-benzotriazoles were known. Presumably, the benzotriazole ring is more stable and less susceptible toward ring opening than that of the 1*H*-1,2,3-triazoles. 1-[(Dialkylamino)methyl]-,[15] 1-[(α-alkylthio)alkyl]-,[16] 1-(alkoxymethyl)-,[17] and 1-(diarylmethyl)benzotriazoles[18] undergo reversible rearrangements into the corresponding 2-isomers; however, these interconversions proceed intermolecularly by a dissociation–recombination mechanism.[19] Usually, the benzotriazole ring is cleaved only under severe conditions to give, in most cases, products of nitrogen extrusion. Thus, photolysis of 1-phenylbenzotriazole in benzene gave a carbazole via a diradical intermediate.[20] Thermolysis of 1-phenylbenzotriazole at 360 °C also afforded carbazole, which was believed to form via the diazo intermediate; ring closure took place by an electrophilic ring substitution with nitrogen extrusion.[21] Flash-vacuum pyrolyses of 1-vinylbenzotriazoles yielded *N*-phenylketenimines with loss of nitrogen.[22] The photolyses and thermolyses of a number of benzotriazoles substituted in the 1-position with hetero-

Scheme III



aromatics and acyl groups, leading to the elimination of nitrogen followed by ring closure, have also been reported.[23,24]

In the course of our work utilizing benzotriazole as a synthetic auxiliary,[25] we have observed only rarely cleavage of the benzotriazole ring. Reactions of 1-imidoylbenzotriazole with Grignard reagents gave a variety of products in which the triazole ring opened.[26] Phenylenediamines were isolated as minor products during the reaction of Grignard reagents with 1-(1-alkoxyalkyl)- and 1-[1-(aryloxy)alkyl]benzotriazoles.[27] The triazole ring of carbanions, generated from 1-(diarylmethyl)benzotriazoles with *n*-butyllithium, opened with loss of nitrogen to yield the products formed by electrophilic attack at the ortho position of the phenyl ring.[28] Finally, we recently formed a new heterocyclic ring system, 4-(benzotriazol-1-yl)-6*H*-benzo[*c*]tetrazolo[1,5-*e*][1,2,5]triazepine, by a novel benzotriazole ring opening of 1,2-bis(benzotriazol-1-yl)-1,2-dichloroethane with sodium azide.[29]

Although no Dimroth rearrangements of 4-substituted 1*H*-benzotriazoles have previously been reported, ring-opening reactions of benzotriazoles leading to diazo intermediates are feasible. These could undergo rearrangements without the extrusion of nitrogen if the 4-substituent is an amino group. Moreover if the N-1 substituent is strongly electron withdrawing and weakens the N1–N2 bond, it is possible that the molecular rearrangement from structure **7** to structure **9** via intermediate **8** could take place under relatively mild conditions. We now report the first examples of thermal Dimroth rearrangements in the 4-aminobenzotriazole series. The isomers could be separated in some cases and were characterized by spectral techniques and by X-ray crystallographic analysis. The solution equilibria were monitored by var-

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iable-temperature NMR spectroscopy, from which the free energies of activation of the rearrangements were deduced. Cross-over experiments demonstrated that the rearrangements are intramolecular processes.

Results and Discussion

Preparation of Substrates. Sulfonylated benzotriazoles with amino substitution at the 4-position were prepared as shown in Scheme III. Nitration of 5-methylbenzotriazole (**10a**) gave 5-methyl-4-nitrobenzotriazole (**11a**) in 90% yield, and catalytic hydrogenation then afforded 4-amino-5-methylbenzotriazole (**12a**) in 68% yield. Compound **12a** reacted with an equimolar amount of *p*-toluenesulfonyl chloride in pyridine at room temperature to give 4-amino-5-methyl-1-(*p*-toluenesulfonyl)-benzotriazole (**14**) (44%) as the only isolated product. The bis-sulfonated derivative (**15**) was prepared in 91% yield by stirring compound **12a** with 4 equiv of *p*-toluenesulfonyl chloride in pyridine at 20 °C.

4-Aminobenzotriazole (**12b**) was prepared in a way similar to **12a**, but its reaction with 1 equiv of *p*-toluenesulfonyl chloride gave 4-[(*p*-toluenesulfonyl)amino]-benzotriazole (**16**). Further sulfonylation of compound **16** with *p*-toluenesulfonyl chloride or benzenesulfonyl chloride produced **18** and **17a** and/or its isomer **17b**, respectively. Bis-sulfonylation of 4-aminobenzotriazole with excess benzenesulfonyl chloride gave the expected compound **13**.

The sulfonylated benzotriazoles prepared and the synthetic intermediates were characterized by their elemental analyses and by their ^1H and ^{13}C NMR and IR spectra (see Experimental Section and discussion below). Significantly, the ^{13}C NMR spectra (run at 20 °C) of some of the benzotriazoles prepared here reflect their tautomeric equilibria as rapidly interconverting mixtures of 1*H*-, 2*H*-, and 3*H*-benzotriazoles, and coalescences occurred in dimethyl sulfoxide solution; therefore, the benzotriazole ring carbon atoms appeared as broad signals and the number of peaks was reduced (see Experimental Section). However, the substituents (CH_3 and arylsulfonyl groups) showed clear and sharp peaks. The ^1H NMR spectra of all compounds are clear and all signals could readily be assigned.

Rearrangement. When 4-amino-5-methyl-1-(*p*-toluenesulfonyl)benzotriazole (**14**) was refluxed in toluene for 3 h, complete rearrangement into 7-methyl-4-[(*p*-toluenesulfonyl)amino]benzotriazole (**19**) (97% isolated yield) was observed. Refluxing the same compound in benzene for 1.5 h, however, only produced a trace of **19**. All attempts to convert **19** back to **14** were unsuccessful, indicating that **19** was more stable. Furthermore, when 4-aminobenzotriazole (**12b**) was treated with 1 equiv of *p*-toluenesulfonyl chloride in pyridine, 4-[(*p*-toluenesulfonyl)amino]benzotriazole (**16**) was obtained. It is not yet known if the 1-sulfonyl-substituted compound was formed first and then rearranged to **16** during the reaction. The TLC of the crude reaction product and the NMR after the first recrystallization from ethanol both showed a mixture of compound **16** and the bis-sulfonated product **18**. The signals of the byproduct corresponded exactly with those of pure **18**. Any unchanged starting material would have been removed by the recrystallization since it is freely soluble in ethanol. Compound **16** was obtained pure after several further recrystallizations, but in only 44% isolated yield. Compound **16** was stable, and no rearrangement was observed in refluxing toluene for up to 5 h (100% recovered). The mixed bis-sulfonylated compound **17** existed in solution as an equilibrium mixture of **17a** and **17b**. The presence of the two isomers was clearly shown by two sets of signals in the ^1H and ^{13}C NMR spectra (e.g., two CH_3 singlets at 2.39 and 2.36 ppm in the ^1H spectrum and at 21.2 and 20.9 ppm in the ^{13}C spectrum). The equilibrium occurs even in the process of running preparative TLC; hence, compounds **17a** and **17b** could not be separated. The elemental analysis of the mixture agrees with the structure assigned.

The bis-tosylate **15** was relatively stable and its rearrangement slow, especially in nonpolar solvents. Its freshly prepared DMSO-d_6 solution at 20 °C showed only three methyl signals both in the ^1H NMR (2.39, 2.31 and 2.22 ppm) and ^{13}C (21.4, 21.2 and 17.8 ppm) NMR spectra. The aromatic signals were also consistent with the presence of only one compound. When the DMSO-d_6 solution was allowed to stand for 18 h at room temperature, an equilibrium was observed as three extra methyl signals appeared in the NMR spectra (2.36, 2.29, and 1.75 ppm in the ^1H spectrum) and the integral ratio of **15** to **20** was 3:5. The conversion of compound **15** into **20** was accelerated by elevating the temperature as both isomers were observed when the ^1H NMR spectrum of **15** in DMSO-d_6 was taken at 35 °C within 15 min of mixing. The ratio of **15** to **20** decreased as the temperature increased and **15** was converted completely into **20** at 75 °C within 1 h. Solvents played important roles in the rearrangement; no rearrangement of **15** to **20** was observed in chloroform (4 days at 20 °C or 4 h at 40 °C). On heating in toluene (100 °C), however, rearrangement proceeded slowly. This solvent effect supported the formation of a polar intermediate or transition state. The rearrangement product **20** was stable at room temperature and could be separated by TLC from the mixture generated by heating **15** in toluene at 100 °C for 2 h. Compound **20** was characterized by spectral methods and by elemental analysis. The equilibrium mixture of **15** and **20** was also produced by heating compound **20** in toluene at 100 °C although it appeared that the conversion in this direction was even slower than that from **15** to **20**. No rearrangement from **20** to **15** was observed over several days in DMSO-d_6 at room temperature based on the NMR result.

Characterization of Compounds 14–16, 19, and 20. To confirm that the Dimroth rearrangements did occur in the present system, it was essential to confirm the structures of compounds **14–16**, **19**, and **20**. The confirmation of structures **14** and **15** was crucial. We used NOE experiments, IR spectra before and after deuteriation of the amino groups, and X-ray crystallographic analysis to identify these structures conclusively.

Nuclear Overhauser Effect Experiments. In the ^1H NMR spectrum of compound **14** in DMSO-d_6, a broad two proton singlet at 6.27 ppm was assigned to the 4-NH_2 group. When this signal was irradiated, a 6% intensity enhancement of the 5-CH_3 signal at 2.20 ppm was observed; at the same time the exchange (6.5%) between the signals of NH_2 and H_2O (3.44 ppm) was also observed. This NOE difference supported the 4-amino-5-methyl-substituted structure **14**.

When the one-proton singlet at 10.5 ppm assigned to the $NHSO_2$ group of compound **19** was irradiated, NOE enhancements were found for the two-proton doublet of ortho protons of the tosyl group at 7.70 ppm (13%) and for the one-proton doublet of 5-H of the benzotriazole ring at 6.82 ppm (9.5%). This is in good agreement with the structure assigned.

Complete assignment of the proton resonances of compound **15** in $CDCl_3$ solution was achieved by a combination of spin decoupling and nuclear Overhauser effect observation. Irradiation of the 2.46 ppm CH_3 produced a 14.4% NOE of the 6-proton at 7.54 ppm; its AB partner at 7.84 ppm was identified by inspection. A much smaller NOE

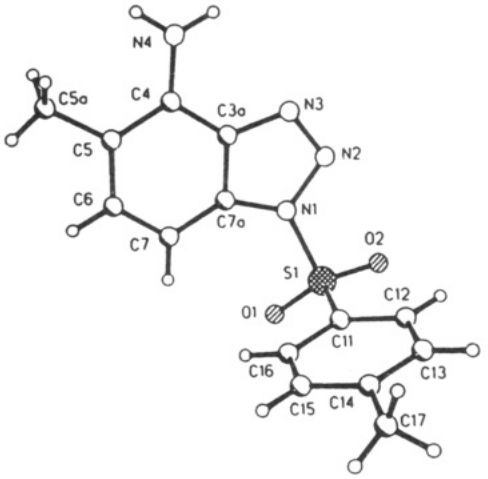

Figure 1. Perspective view and atom labeling of the crystal structure of 4-amino-5-methyl-1-(*p*-toluenesulfonyl)benzotriazole (**14**).

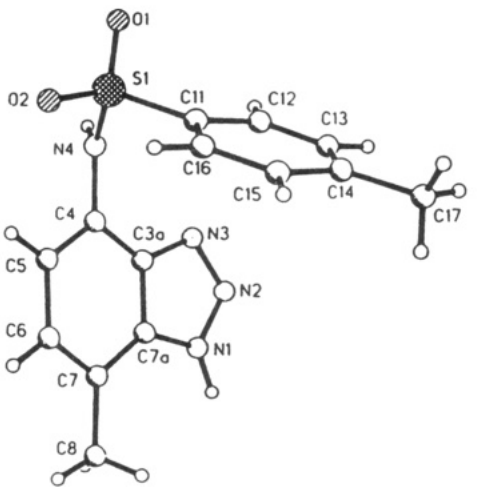

Figure 2. Perspective view and atom labeling of the crystal structure of 7-methyl-4-[(*p*-toluenesulfonyl)amino]benzotriazole (**19**).

(1.6%) was also seen to the tosylate ring protons at 7.45 ppm, assigning them to the protons next to SO_2 of the NHTs group. The remaining protons of this tosyl group are the 3,5-protons at 7.00 and the methyl at 2.27 ppm, confirmed by the sharpening of the peaks at 7.00 ppm as the CH_3 wsa irradiated (four-bond coupling between the CH_3 and the adjacent ring H) and a 14% NOE enhancement of the 7.45 ppm ring protons on irradiation of those at 7.00 ppm. The corresponding protons of the benzotriazole tosyl group appeared at 7.89, 7.31, and 2.40 ppm, confirmed by spin decoupling as before. The amide NH was seen at 6.96 ppm.

IR Spectral Method. Infrared spectra have previously been used to distinguish the amino (NH_2) and acylamino (RCONH) groups in heterocyclic chemistry.[30] Here, we have employed this method to characterize the different isomers. The primary amino (NH_2) group usually shows a doublet in the NH stretching region at 3500–3300 cm^{-1} and a band near 1600 cm^{-1} attributed to the NH_2 scissor motion,[31] for example, 3465, 3345 cm^{-1} and 1635 cm^{-1} for the tosyl derivative **14**. On the other hand, sulfonylamino ($-SO_2NH$) should show only one NH stretching band in the slightly lower region 3350–3250 cm^{-1}. 7-Methyl-4-[(*p*-toluenesulfonyl)amino]benzotriazole (**19**) shows the NHTs stretching band at 3316 cm^{-1} and the in-plane bending vibration at 1610 cm^{-1} and 4-[(p-toluenesulfonyl)amino]benzotriazole (**16**) at 3277 and 1610 cm^{-1}. When these compounds were dissolved in mixtures of DMSO and deuterium oxide and precipitated by the addition of excess deuterium oxide, the mobile hydrogens were replaced by deuterium. For the IR spectra of these deuterated compounds, only compound **14** showed a ND_2 doublet at 2590 (asym) and 2442 (sym) cm^{-1}. The band of 1635 cm^{-1} was removed. Compounds **19** and **16** showed ND bands at 2462 and 2438 cm^{-1}, respectively. A band at 3111 cm^{-1} in compound **19** shifted to 2277 cm^{-1} on deuteration and is assigned to ν N1-H. The differences between compound **14** and compounds **16** and **19** support the presence of an NH_2 group in **14** but not in the other two.

X-ray Crystal Analysis. The structures of 4-amino-5-methyl-1-(*p*-toluenesulfonyl)benzotriazole (**14**) and its thermal rearrangement product **19** were conclusively confirmed by X-ray crystallography as shown in Figures 1 and 2. The structure of 5-methyl-4-[(*p*-toluenesulfonyl)amino]-1-(*p*-toluenesulfonyl)benzotriazole (**15**) was also determined by X-ray as shown in Figure 3. The crystal data and X-ray experimental details for these three compounds are summarized in Table I.

Table I. Crystal Data and X-ray Experimental Details

	14	19	15
formula	$C_{14}H_{14}N_4O_2S$	$C_{14}H_{14}N_4O_2S$	$C_{21}H_{20}N_4O_4S_2$
molecular weight	302.4	302.4	456.5
crystal system	triclinic	monoclinic	triclinic
space group	*P*-1	$P2_1/c$	*P*-1
a (Å)	6.390 (3)	8.724 (5)	7.209 (2)
b (Å)	10.551 (7)	12.343 (8)	11.797 (3)
c (Å)	10.718 (6)	26.746 (14)	13.724 (4)
α (deg)	93.71 (5)	90	66.25 (2)
β (deg)	101.67 (4)	98.62 (4)	80.73 (2)
γ (deg)	104.52 (4)	90	84.09 (2)
V (Å^3)	680.0 (7)	2847 (3)	1053.5 (5)
D_c (g cm^{-3})	1.477	1.411	1.439
Z	2	8	2
F (000)	316	1264	476
μ (cm^{-1})	2.4	2.3	2.8
diffractometer	Nicolet R3m	Nicolet R3m	Nicolet R3m
radiation	Mo Kα	Mo Kα	Mo Kα
wavelength (Å)	0.71069	0.71069	0.71069
temperature (°C)	−100	−100	−100
crystal dimensions (mm)	0.48 × 0.43 × 0.30	0.52 × 0.34 × 0.20	0.58 × 0.39 × 0.22
scan mode	ω	ω	ω
2θ range (deg)	3–60	3–54	3–60
solution method	direct methods	direct methods	Patterson/Fourier
unique data	3943	7595	5821
observed data ($I > 3\sigma(I)$)	3297	2269	4645
no. of parameters	190	379	280
function refined	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weighting	$[\sigma^2(F_o) + gF_o^2]^{-1}$	$[\sigma^2(F_o) + gF_o^2]^{-1}$	$[\sigma^2(F_o) + gF_o^2]^{-1}$
g	0.000 10	0.000 02	0.000 05
residual features (e Å^{-3})	<0.40	<0.50	<0.52
R	0.042	0.067	0.039
wR	0.052	0.054	0.049

Variable-Temperature NMR Spectral Study. The equilibrium between 1-(benzenesulfonyl)-4-[(*p*-toluenesulfonyl)amino]benzotriazole (**17a**) and its isomer **17b**, which could not be separated, was studied by recording ^1H NMR spectra at various temperatures. The tempera-

(30) Boulton, A. J.; Katritzky, A. R. *Tetrahedron* **1961**, *12*, 51.
(31) Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr. *Introduction to Spectroscopy*; W. B. Saunders: Philadelphia, **1979**; pp 63–69.

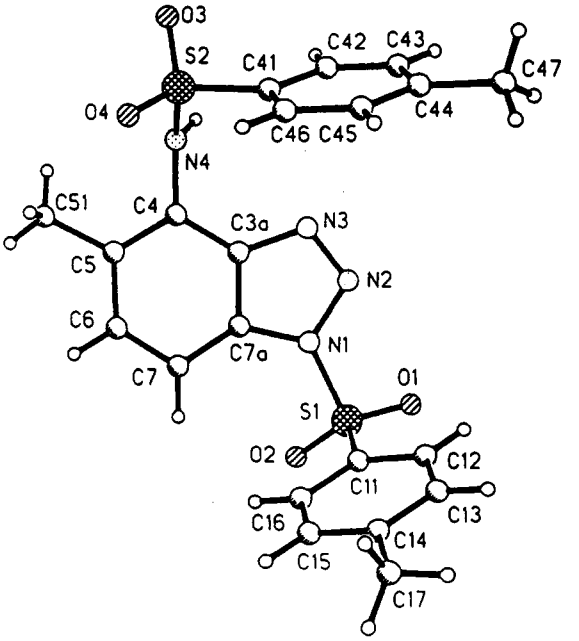

Figure 3. Perspective view and atom labeling of the crystal structure of 5-methyl-4-[(*p*-toluenesulfonyl)amino]-1-(*p*-toluenesulfonyl)benzotriazole (**15**).

ture at which the characteristic proton resonances of **17a** and **17b** coalesced was determined. Specifically, the signals of the sulfonylamino groups ($NHSO_2$) and of the methyl groups of the two isomers were monitored and the temperatures at which coalescence occurred visually estimated from their line shapes. The room-temperature ^1H NMR spectrum of the mixture in a mixed solvent (DMSO-d_6/$CDCl_3$) showed two NH singlets at 10.60 and 10.51 ppm and two CH_3 signals at 2.33 and 2.31 ppm, respectively. On warming, the NH peaks broadened and coalesced at about 65 °C. Similarly, the two methyl signals coalesced and became one peak at 70 °C. From the coalescence temperature and the separation of the NH signals, the approximate free energy of activation $\Delta G^{\ddagger}$ was calculated using the simplified eq 1[32] to be 20.8 kcal/mol, where T_c is in K and $\delta\nu$ is the chemical shift difference of the two separate peaks in the slow exchange region.

$$\Delta G^{\ddagger} = RT_c[22.96 + \ln (T_c/\delta\nu)] \quad (1)$$

Crossover Experiments. The most likely mechanism for the rearrangements observed is shown in Scheme I, as previously discussed. In bis-sulfonated compounds, the ring closure can occur in either direction. Although this seems to be the most reasonable mechanism, to exclude the possibility of an intermolecular process cross-over experiments were carried out. First, 4-[(benzenesulfonyl)amino]-1-(benzenesulfonyl)benzotriazole (**13**) and the bis(*p*-toluenesulfonyl)-substituted analogue **18** were mixed in DMSO-d_6 solution at room temperature. Both the ^1H and ^{13}C NMR spectra of the mixture represented the addition of the two separate spectra, e.g., two methyl signals at 2.40 and 2.33 ppm in the ^1H NMR and at 21.1 and 20.9 ppm in the ^{13}C NMR spectrum, revealing the presence of only two compounds since the rearrangements of both **13** and **18** are degenerate. No exchange of the arylsulfonyl groups between **13** and **18** indicated intramolecular rearrangements. Second, a mixture of compounds **13** and **15** was warmed in DMSO-d_6 to 70 °C. The rearrangement of the 5-methyl derivative **15** can be monitored, and the addition of **13** did not increase the number of the methyl signals beyond the six expected for the equilibrium between **15** and **20**. Once again, the spectra of the mixture were simple additions of the individual spectra. Therefore, the rearrangement is clearly shown to be an intramolecular process.

Conclusion

Strong electron-withdrawing substituents on N-1 of 4-aminobenzotriazoles make Dimroth rearrangements possible. The evidence is based on the separation and characterization of the products, NOE experiments, variable-temperature NMR studies, and X-ray crystal structure determinations. This is the first example of such a rearrangement in the benzotriazole system. Crossover experiments support an intramolecular mechanism.

Experimental Section

^1H and ^{13}C NMR spectra were taken at 300 and 75 MHz, respectively. Tetramethylsilane was used as the internal standard for the ^1H NMR spectra, and the central line of DMSO-d_6 (δ = 39.5) or $CDCl_3$ (δ = 77.0) was referenced in ^{13}C NMR spectra. As previously discussed, ^{13}C signals of some compounds prepared here (**11a**, **11b**, **12a**, **12b**, **14**, **16**, and **19**) are less than expected because of the tautomeric equilibria and coalescences. Crossover experiments were carried out by mixing equimolar solutions of both substrates and the spectra recorded.

5-Methyl-4-nitrobenzotriazole (11a). To 5-methylbenzotriazole (5 g, 37.5 mmol) in concentrated sulfuric acid (20 mL) was added a mixture of nitric acid (70%, 5 mL) and concentrated sulfuric acid (5 mL) at below 20 °C, and the resulting mixture was allowed to stand overnight. The solution was poured onto ice, and the resulting precipitate was collected by filtration, washed with water, and recrystallized from ethanol to give microcrystals (6.0 g, 90%): mp 254–255 °C (lit.[33] mp 255 °C); ^1H NMR (DMSO-d_6) δ 8.32 (d, J = 8.3 Hz, 1 H), 7.48 (d, J = 8.3 Hz, 1 H), 2.79 (s, 3 H, CH_3); ^{13}C NMR δ 144.4, 135.5, 132.7, 128.9, 124.3, 20.7.

4-Nitrobenzotriazole (11b). From a similar procedure, prisms (50%): mp 228–229 °C (lit.[34] mp 229 °C); ^1H NMR (DMSO-d_6) δ 8.47 (d, J = 8.0 Hz, 1 H), 8.42 (d, J = 8.0 Hz, 1 H), 7.58 (t, J = 8.0 Hz, 1 H); ^{13}C NMR δ 126.8, 126.7, 123.2, 122.8.

4-Amino-5-methylbenzotriazole (12a). 5-Methyl-4-nitrobenzotriazole (6.87 g, 38.6 mmol) in 95% ethanol (100 mL) was hydrogenated over 5% palladium/carbon (0.35 g) at room temperature and 60 psi for 48 h. The catalyst was filtered off and the solvent removed under reduced pressure to give crude product (5.6 g), which was purified by column chromatography (silica gel, diethyl ether) to afford prisms (3.85 g, 68%): mp 177–178 °C; ^1H NMR (DMSO-d_6) δ 7.10 (d, J = 8.3 Hz, 1 H), 6.89 (d, J = 8.3 Hz, 1 H), 5.59 (s, 2 H, NH_2), 2.23 (s, 3 H, CH_3); ^{13}C NMR δ 135.5, 130.4, 111.9, 98.3, 98.2. Anal. Calcd for $C_7H_8N_4$: C, 56.74; H, 5.44; N, 37.81. Found: C, 56.96; H, 5.47; N, 37.48.

4-Aminobenzotriazole (12b). 4-Nitrobenzotriazole (**11b**) (10 g, 61 mmol) in 95% ethanol was hydrogenated over 5% palladium/carbon (1 g) for 3 h at 20 °C and 60 psi. The catalyst was filtered off and the solvent removed under reduced pressure. The crude product was recrystallized from benzene to give (**12b**) (5.5 g, 67%): mp 148–149 °C; ^1H NMR (DMSO-d_6) δ 7.15 (t, J = 7.8 Hz, 1 H), 6.90 (d, J = 7.8 Hz, 1 H), 6.50 (d, J = 7.8 Hz, 1 H), 5.23 (brs, 2 H, NH_2); ^{13}C NMR δ 139.5, 128.5 (br), 105.0 (br), 98.0 (br). Anal. Calcd for $C_6H_6N_4$: C, 53.72; H, 4.51; N, 41.77. Found: C, 53.61; H, 4.44; N, 42.26.

4-Amino-5-methyl-1-(*p*-toluenesulfonyl)benzotriazole (14). 4-Amino-5-methylbenzotriazole (**12a**) (0.20 g, 1.3 mmol) was dissolved in pyridine (5 mL), and *p*-toluenesulfonyl chloride (0.28 g, 1.4 mmol) was added. After being stirred at 20 °C for 1 h, the mixture was diluted with water and the resulting precipitate collected. The solid was dissolved in ethanol and reprecipitated by dilution with water and finally purified by column chroma-

(32) Sandstrom, J. *Dynamic NMR Spectroscopy*; Adademic Press: New York, 1982; p 96.

(33) German Patent 2,031,254, 1971; *Chem. Abstr.* **1971**, *74*, 118358d.
(34) Fries, K.; Guterbock, H., Kuhn, H. *Ann.* **1934**, *511*, 213.

tography (silica, ethyl acetate) to give **14** as yellow prisms (0.18 g, 44%): mp 159–160 °C; ^{1}H NMR (DMSO-d_6) δ 7.95 (d, J = 8.2 Hz, 2 H), 7.44 (d, J = 8.2 Hz, 2 H), 7.34 (d, J = 8.2 Hz, 1 H), 7.06 (d, J = 8.2 Hz, 1 H), 6.27 (s, 2 H, NH_2), 2.34 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3); ^{13}C NMR δ 146.4, 138.7, 133.8, 130.3, 127.1, 115.0, 96.2, 21.1 16.3; HRMS m/z calcd 302.0837, found 302.0833. MS m/z 302 (M^+, 37.7), 195 (6), 139 (17.7), 119 (100), 92 (46). Anal. Calcd for $C_{14}H_{14}N_4O_2S$: C, 55.62; H, 4.67; N, 18.53. Found: C, 55.67; H, 4.59; N, 18.65.

7-Methyl-4-[(*p*-toluenesulfonyl)amino]benzotriazole (19). 4-Amino-5-methyl-1-(*p*-toluenesulfonyl)benzotriazole (**14**) (0.49 g, 1.6 mmol) was refluxed in toluene (5 mL) for 3 h. After being cooled the white solid was collected and dried (0.47 g, 97%): mp 179–180 °C; ^{1}H NMR (DMSO-d_6) δ 7.70 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 8.0 Hz, 2 H), 7.05 (d, J = 7.8 Hz, 1 H), 6.92 (d, J = 7.8 Hz, 1 H), 2.54 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3); ^{13}C NMR δ 143.2, 136.8, 129.5, 126.9, 20.9 (CH_3), 16.4 (CH_3); HRMS calcd 302.0837, found 302.0850. MS m/z 302 (M^+, 46.8), 237 (17.0), 147 (43.1), 119 (100), 92 (56.5). Anal. Calcd for $C_{14}H_{14}N_4O_2S$: C, 55.62; H, 4.67; N, 18.53. Found: C, 55.46; H, 4.63; N, 18.58.

4-[(*p*-Toluenesulfonyl)amino]benzotriazole (16). To 4-aminobenzotriazole (1 g, 7.5 mmol) in pyridine (25 mL) was added *p*-toluenesulfonyl chloride (1.42 g, 7.5 mmol) in one portion at 20 °C. The mixture was stirred for 1 h and poured into water. The resulting precipitate was collected and recrystallized from ethanol to give **16** as yellow prisms (0.95 g, 44%): mp 257–258 °C; ^{1}H NMR (DMSO-d_6) δ 7.74 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 7.9 Hz, 1 H), 7.33 (d, J = 8.4 Hz, 2 h), 7.30 (t, J = 7.9 Hz, 1 H), 7.05 (d, J = 7.9 Hz, 1 H), 2.32 (s, 3 H, CH_3); ^{13}C NMR δ 143.3, 136.9, 129.7, 129.6, 126.9, 126.2, 115.6, 109.9, 106.5, 21.2 (CH_3); MS m/z 288 (M^+, 18.7), 260 ($M^+ - N_2$, 7.8), 223 (21.3), 139 (18.7), 105 (100). Anal. Calcd for $C_{13}H_{12}N_4O_2S$: C, 54.16; H, 4.20; N, 19.43. Found: C, 54.19; H, 3.92; N, 19.68.

Mixture of 1-(Benzenesulfonyl)-4-[(*p*-toluenesulfonyl)amino]benzotriazole (17a) and 4-[(Benzenesulfonyl)amino]-1-(*p*-toluenesulfonyl)benzotriazole (17b). 4-[(*p*-Toluenesulfonyl)amino]benzotriazole (**16**) (0.40 g, 1.4 mmol) was dissolved in pyridine (5 mL). Benzenesulfonyl chloride (0.30 g, 1.7 mmol) added and the solution stirred at 20 °C for 1 h. The mixture was poured into water and extracted with diethyl ether. The ether solution was washed with dilute hydrochloric acid and water and dried over $MgSO_4$. Removal of the solvent gave the mixture of **17a** and **17b** (0.43 g, 73%): mp 66–68 °C; ^{1}H NMR (DMSO-d_6) δ 8.60 (br, 1 H, NH), 8.05 (d), 7.96 (d), 7.82 (d), 7.59–7.46 (m, 3 H), 7.42 (d), 7.34 (d), 7.20 (d), 2.39 (s, CH_3), 2.36 (s, CH_3); ^{13}C NMR δ 148.8, 146.3, 143.2, 139.2, 135.8, 135.0, 133.0, 132.4, 132.0, 131.0, 130.8, 129.9, 129.3, 129.1, 129.0, 128.5, 127.3, 127.2, 126.6, 126.5, 113.8, 113.7, 106.0, 105.8, 21.2 (CH_3), 20.9 (CH_3). Anal. Calcd for $C_{19}H_{16}N_4O_4S_2$: C, 53.26; H, 3.76; N, 13.08. Found: C, 53.26; H, 3.84; N, 13.36.

4-[(*p*-Toluenesulfonyl)amino]-1-(*p*-toluenesulfonyl)benzotriazole (18). Prepared from the reaction of compound **16** with *p*-toluenesulfonyl chloride as described above, 83%: mp 195–196 °C; ^{1}H NMR (DMSO-d_6) δ 8.61 (br, 1 H, NH), 7.93 (d, J = 8.4 Hz, 2 H), 7.81 (d, J = 8.4 Hz, 2 H), 7.67 (d, J = 8.1 Hz, 1 H), 7.51 (t, J = 8.1 Hz, 1 H), 7.40 (d, J = 8.1 Hz, 1 H), 7.35 (d, J = 8.4 Hz, 2 H), 7.22 (d, J = 8.4 Hz, 2 H), 2.39 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3); ^{13}C NMR δ 146.6, 143.5, 137.1, 136.3, 133.2, 132.0, 130.9, 130.0, 129.8, 129.2, 129.1, 127.4, 126.7, 126.6, 113.1, 105.9, 21.3 (CH_3), 21.0 (CH_3). Anal. Calcd for $C_{20}H_{18}N_4O_4S_2$: C, 54.29; H, 4.10; N, 12.66. Found: C, 54.59; H, 4.12; N, 12.82.

5-Methyl-4-[(*p*-toluenesulfonyl)amino]-1-(*p*-toluenesulfonyl)benzotriazole (15). Compound **15** was prepared from **12a** by following the above procedure except 4 equiv of *p*-toluenesulfonyl chloride was added: yield 33%; mp 163–164 °C; ^{1}H NMR (DMSO-d_6) δ 10.20 (br, 1 H, NH), 7.97 (d, J = 8.5 Hz, 2 H), 7.92 (d, J = 8.5 Hz, 1 H), 7.67 (d, J = 8.5 Hz, 1 H), 7.50 (d, J = 8.5 Hz, 2 H), 7.45 (d, J = 8.5 Hz, 2 H), 7.19 (d, J = 8.5 Hz, 2 H), 2.39 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3); ^{13}C NMR δ 147.6, 143.8, 143.3, 137.9, 135.1, 134.6, 132.9, 131.1, 130.3, 129.3, 127.8, 126.9, 126.2, 111.3, 21.4, 21.2, 17.8; MS m/z 456 (M^+, 5.6), 392 (14.4), 209 (65.1), 155 (47.1), 139 (62.1), 91 (100). Anal. Calcd for $C_{21}H_{20}N_4O_4S_2$: C, 55.25; H, 4.27; N, 12.17. Found: C, 54.87; H, 4.26; N, 12.10.

7-Methyl-4-[(*p*-toluenesulfonyl)amino]-1-(*p*-toluenesulfonyl)benzotriazole (20). Compound **15** was heated in toluene at 100 °C for 2 h. After cooling and removal of the solvent under reduced pressure, the mixture was separated by preparative TLC (silica, ethyl acetate): mp 233–235 °C; ^{1}H NMR (DMSO-d_6) δ 9.96 (s, 1 H, NH), 7.75 (d, J = 8.4 Hz, 1 H), 7.50 (d, J = 8.4 Hz, 2 H), 7.47 (d, J = 8.1 Hz, 2 H), 7.33 (d, J = 8.4 Hz, 2 H), 7.15 (d, J = 8.1 Hz, 2 H), 7.11 (d, J = 8.4 Hz, 1 H), 2.34 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3); ^{13}C NMR δ 144.8, 143.2, 142.2, 138.1, 137.6, 135.8, 133.4, 129.6, 128.3, 127.8, 126.7, 125.5, 115.8, 21.0, 20.8, 16.5. Anal. Calcd for $C_{21}H_{20}N_4O_4S_2$: C, 55.25; H, 4.42; N, 12.27. Found: C, 55.58; H, 4.19; N, 12.05.

4-[(Benzenesulfonyl)amino]-1-(benzenesulfonyl)benzotriazole (13). Compound **13** was prepared as described for **19**, 77%: mp 187–188 °C; ^{1}H NMR ($CDCl_3$) δ 11.0 (br, 1 H, NH), 8.05 (d, J = 7.5 Hz, 2 H), 7.93 (d, J = 7.2 Hz, 2 H), 7.72 (m, 2 H), 7.66–7.40 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 139.5, 137.5, 135.9, 135.2, 132.5, 132.0, 131.8, 129.9, 129.5, 128.5, 127.2, 126.6, 114.4, 106.1. Anal. Calcd for $C_{18}H_{14}N_4O_4S_2$: C, 52.16; H, 3.40; N, 13.52. Found: C, 52.02; H, 3.24; N, 13.60.

Preparation of Deuterated Samples for IR Spectra. Deuterium oxide was added to a solution of the benzotriazole in dimethyl sulfoxide (if a precipitate was formed, more dimethyl sulfoxide was added to dissolve it). The solution was stirred at room temperature for 1 h. Further deuterium oxide was added to precipitate the sample, which was collected and dried. The IR spectrum was then recorded as a Nujol mull.

Registry No. 10a, 136-85-6; **10b**, 95-14-7; **11a**, 31995-60-5; **11b**, 6299-39-4; **12a**, 137434-61-8; **12b**, 18076-61-4; **13**, 137434-63-0; **14**, 137434-64-1; **15**, 137434-65-2; **16**, 137434-66-3; **17a**, 137434-67-4; **17b**, 137434-62-9; **18**, 137434-68-5; **19**, 137434-69-6; **20**, 137434-70-9.

Supplementary Material Available: Tables of crystal data, X-ray experimental details, atom coordinates, anisotropic thermal parameters, and bond lengths and angles and views showing the conformation of three X-ray structures (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.