mentally, I and II are nitrated, for example, more readily than benzene, an observation in accord with the more nearly self-consistent calculations.

The bond orders of the N–N central bonds in the tetraazapentalene nuclei have the values $\rho_{NN} = 0.300$ (I), 0.285 (II), 0.300 (III), 0.297 (IV). The bond orders of the C–C central bonds in pentalene dianion and naphthalene are $\rho_{CC} = 0.531$ (PA), 0.518 (N), and the buildup of density in the central bond region is characteristic of normal aromatic structures. The appreciable bond orders of the tetraazapentalenes in this region further support the conclusion that these molecules are truly aromatic.

The ultraviolet spectra of I and II are complicated but are not unlike those expected for fully aromatic structures.[1a] In naphthalene, which contains ten π electrons, the three lowest observed singlet states correspond to states predicted by Pariser–Parr theory (employing all singly excited configurations)[13,14] which occur at 4.19 ($^1B_{3u}$), 4.48 ($^1B_{2u}$), and 5.92 ev ($^1B_{3u}$), and only transition to the latter two are allowed. The B_{2u} state is largely derived from the configuration V_{56}, obtained by promoting an electron from MO 5 to MO 6. The two B_{3u} states are obtained mostly from mixing of V_{57} and V_{46} which interact strongly because their energies are degenerate. Although $E(V_{56}) < E(V_{57}) = E(V_{46})$, the mixing depresses one of the resulting B_{3u} states so that it actually occurs below the B_{2u} state.

The isoelectronic pentalene dianion shows two strong absorptions in the ultraviolet region[15] which agree with the spectrum calculated by Pariser–Parr configuration interaction theory.[16] The three lowest singlets corresponding to those observed for naphthalene are predicted to occur at 4.57 ($^1B_{2u}$), 5.12 ($^1B_{3u}$), and 7.11 ev ($^1B_{3u}$), and here all three are allowed. The states of same symmetry are formed primarily from the same configurations as in naphthalene, but the nonalternant character of the molecular orbitals precludes the strong degenerate mixing of V_{46} and V_{57}. Thus, the B_{2u} state is the lowest, in accord with the observation that $E(V_{56}) < E(V_{57})$ or $E(V_{46})$. In pentalene dianion, the high-energy B_{3u} state occurs in the vacuum ultraviolet and has not yet been identified.

Three similar absorptions are expected to occur in the tetraazapentalenes Z and T. Inspection of Figure 2 shows that on going from pentalene dianion to Z, V_{56} decreases strongly in energy, V_{57} decreases only slightly, and V_{46} increases slightly. On going to T, V_{56} decreases less strongly than in Z, V_{57} decreases more strongly, and V_{46} decreases slightly. When two benzene rings are fused on Z and T to form I and II, the characteristic properties of the states in question are anticipated to be largely preserved.

Although the assignments for the spectra of I and II are yet unknown, it is reasonable that the three regions of absorption in them correlate with the three lowest energy configurations discussed above. From Table I in paper I we see that the two longest wavelength regions of I are indeed red shifted with respect to the aromatic hydrocarbon analog chrysene, and the highest energy absorption is blue shifted, as predicted. Also, in accord with expectation, the long-wavelength absorption of II is blue shifted with respect to that of I and occurs actually at about the same place as that in chrysene. The next two bands in II, however, are also blue shifted with respect to those in I. This crude picture is satisfying and is all we might have hoped for using such poor molecular orbitals as a basis and neglecting electron repulsion effects.

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(13) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

(14) H. E. Simmons, *ibid.*, **40**, 3554 (1964).

(15) T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).

(16) H. E. Simmons, unpublished results.

Aromatic Azapentalenes. V. 1,1′- and 1,2′-Bibenzotriazoles and Their Conversion to Dibenzotetraazapentalenes

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Received November 17, 1966

Abstract: The syntheses, physical properties, and structural assignments for 1,1′-bibenzotriazole (**4a**) and 1,2′-bibenzotriazole (**8**) are described. Both **4a** and **8** lose nitrogen on heating to give dibenzo-1,3a,4,6a-tetraazapentalene (**1**) and dibenzo-1,3a,6,6a-tetraazapentalene (**2**), respectively.

In earlier papers in this series,[1,2] the synthesis of dibenzo-1,3a,4,6a-tetraazapentalene (**1**) by thermal or photochemical decomposition of *o,o′*-diazidoazobenzene was described. This interesting heteroaromatic system has now been prepared by an alternative route, *i.e.*, through controlled thermal decomposition of 1,1′-bibenzotriazole (**4**). A similar thermolysis occurs with the isomeric 1,2′-bibenzotriazole (**8**) to form the corresponding dibenzo-1,3a,6,6a-tetraazapentalene (**2**).[2] This paper discusses the synthesis, proof of structure, and decomposition of the hexaaza compounds **4** and **8**.

1,1′-Bibenzotriazole. The hexaaza derivative **4** was prepared in goodyield from tetraazotized *o,o′*-diamino-

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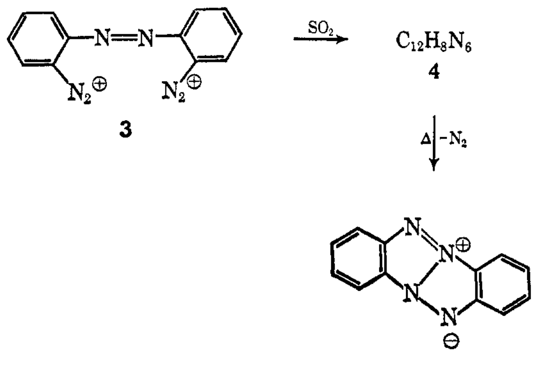
(1) R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.*, **84**, 2453 (1962).

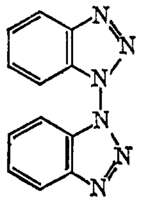
(2) R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *ibid.*, **89**, 2618 (1967).

azobenzene. When sulfur dioxide was passed rapidly through a cold aqueous solution of the *o,o'*-azobenzenebisdiazonium salt (**3**), the product **4** precipitated as a tan solid. Elemental analyses and molecular weight determinations on the purified colorless solid, mp 235° dec, are in accord with the empirical formula $C_{12}H_8N_6$.

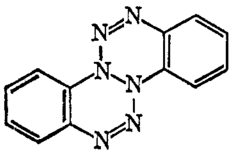


3 **4** **1**

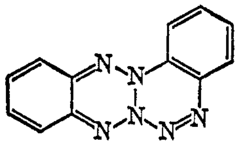
The synthetic route to **4** and the subsequent decomposition to **1** suggest four possible structures, **4a–d**, for the hexaaza product. These structures may form



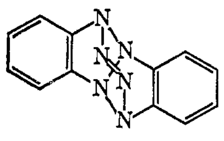
4a



4b



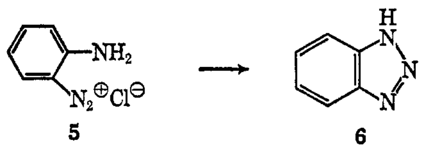
4c



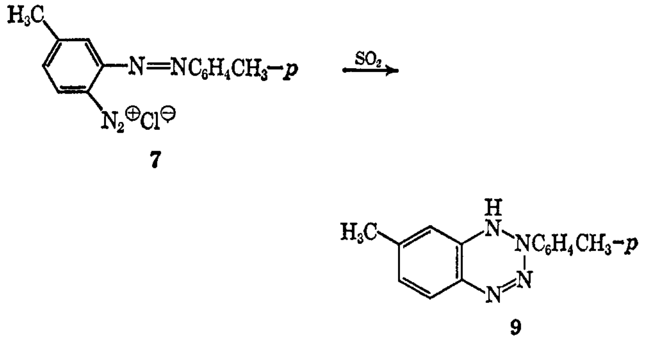
4d

by the addition of an electron to each diazonium group followed by addition of the resulting radicals to the azo group, either directly or with rearrangement of electrons.

Alternatively, **4a** and **b** may form *via* the intermediate hydrazo derivative by reaction of the diazonium groups with (a) their respective α-nitrogens (to give **4a**) or (b) their respective β-nitrogens (to yield **4b**). Intramolecular coupling of the first type occurs in the diazotization of *o*-phenylenediamine, where the intermediate *o*-aminobenzenediazonium ion (**5**) reacts with the amino substituent to yield 1H-benzotriazole (**6**).[3] On the other hand, Zincke and Lawson[4] observed that treatment of *o*-(*p*-tolylazo)-*p*-toluenediazonium chloride (**7**) with a reducing agent such as stannous chloride or sulfur dioxide produced a crystalline product which was assigned the benzotetraazine structure **9**.



5 **6**



7 **9**

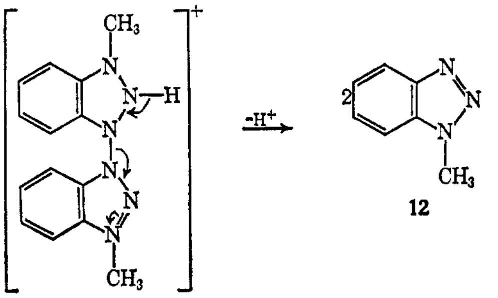
The ultraviolet spectrum of **4** shows two absorption maxima, at 252 mμ (ε 14,630) and 288 mμ (ε 7790). Thus a strong resemblance to the absorption spectrum of 1H-benzotriazole and 1-methylbenzotriazole is evident (Figure 1), providing a preference for the 1,1'-bibenzotriazole structure **4a**. Compounds **4b** and **c** which contain the aryl —N=N—N group in a six-membered ring would be expected to exhibit absorption at considerably longer wavelengths. For example, 3-phenyl-3,4-dihydro-1,2,3-benzotriazine exhibits an absorption maximum at 360 mμ.[5] Nuclear magnetic resonance (proton) spectroscopy was of little value for the structure proof, ill-defined spectra being obtained because of the low solubility of **4** in organic solvents.

Treatment of **4** with dimethyl sulfate gave successively a monoalkylation product **10** and a dialkylation product **11**. Methosulfates **10** and **11** are both water soluble and can be readily converted to the corresponding isolable iodides. However, the hydroxide of

$$4 \xrightarrow{(CH_3O)_2SO_2} \underset{\mathbf{10}}{C_{12}H_8N_6CH_3{}^+CH_3SO_4{}^-} \xrightarrow{(CH_3O)_2SO_2} \underset{\mathbf{11}}{C_{12}H_8N_6(CH_3)_2{}^{2+}2CH_3SO_4{}^-}$$

bismethosulfate **11** rapidly decomposed in water at room temperature to give 1 molar equiv of 1-methylbenzotriazole (**12**).[6] This provides a clear preference for the 1,1'-bibenzotriazole structure **4a**, in agreement with the ultraviolet spectral data. Thus, the formation of **12** may be represented by the sequence **4a** → **10** → **11** shown in Figure 2.

Further evidence for the bisbenzotriazole structure was obtained by the facile reductive cleavage of the bismethosulfate **11** by lithium aluminum hydride. When an ether solution of **11** was treated with excess lithium aluminum hydride at room temperature, an excellent yield (93%) of 1-methylbenzotriazole (**12**) (2 molar equiv) was obtained. Presumably the same kind of scission occurs here as in the hydroxide decomposition.



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(3) R. E. Damschroder and W. D. Peterson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 106.

(4) Th. Zincke and A. Th. Lawson, *Ber.*, **19**, 1452 (1886).

(5) P. Ramart-Lucas and J. Hoch, *Bull. Soc. Chim. France*, 447 (1949).

(6) 1-Methylbenzotriazole 2-N-oxide is assumed to be the other product of the hydroxide decomposition, but was not isolated.

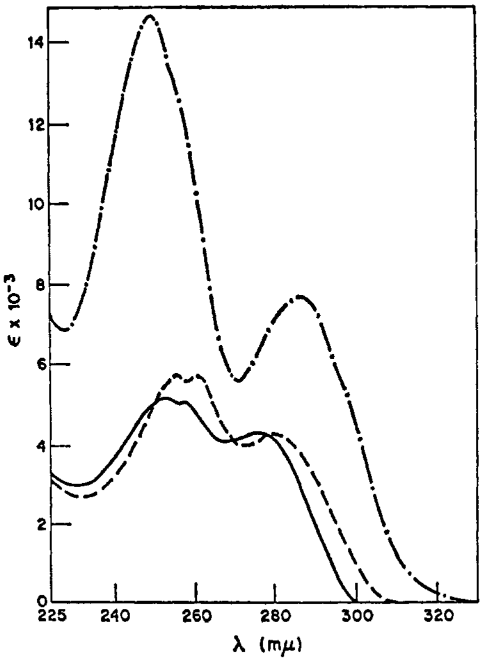

Figure 1. Ultraviolet spectra of 1H-benzotriazole, ———; 1-methyl-1H-benzotriazole, - - - -; and 1,1'-bibenzotriazole, —·—·—.

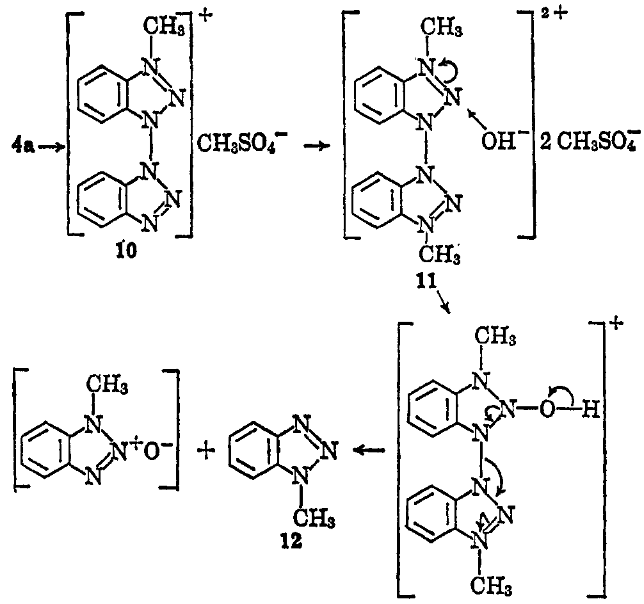

Figure 2.

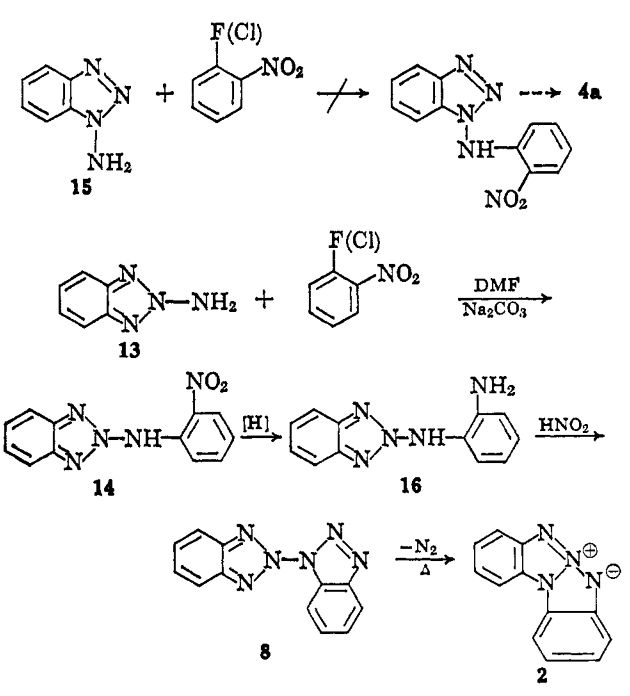

Figure 3.

The formation of more than 1 molar equiv of the benzotriazole derivative **12** strongly favors structure **4a**, since **4b–d** all would require extensive rearrangements.

The facile reduction of the bismethosulfate with lithium aluminum hydride is in sharp contrast to the stability of the unalkylated product **4** toward this reagent. The reactivity of **11** is undoubtedly associated with its positive charges which should facilitate hydride ion attack. Finally, the reduction cleavage of **4** itself was effected with aluminum amalgam in moist ether[7] to obtain somewhat greater than 1 molar equiv of 1H-benzotriazole (**6**), thus providing additional evidence in favor of 1,1'-bibenzotriazole (**4a**).

1,2'-Bibenzotriazole. In view of the interesting thermal transformation exhibited by 1,1'-bibenzotriazole (**4a**), the synthesis of the isomeric 1,2'-bibenzotriazole (**8**) was undertaken. A convenient route was provided by the intermediate 2-aminobenzotriazole.[8] The preparative route to **8** is summarized in Figure 3. Reaction of 2-aminobenzotriazole (**13**) with *o*-fluoro- or *o*-chloronitrobenzene in dimethylformamide in the presence of sodium carbonate gave 2-(*o*-nitrophenylamino)-2H-benzotriazole (**14**) in 85% yield. Under similar conditions, 1-aminobenzotriazole (**15**)[9] gave only tars. Hydrogenation of **14** to 2-(*o*-aminophenylamino)-2H-benzotriazole (**16**) was readily achieved in tetrahydrofuran with palladium on charcoal. Treatment of the amine **16** with nitrous acid gave a crystalline solid, mp 124°, to which we assign the structure 1,2'-bibenzotriazole (**8**). The preparation of 1-substituted 1H-benzotriazoles by diazotization of N-substituted *o*-phenylenediamines has ample precedent in the literature.[2,10] The ultraviolet spectrum (ethanol) of **8** showed λ_{max} 250 mμ (ε 8700), 282 mμ (ε 17,600), and 290 mμ (ε 16,700), consistent with the assigned structure.

Thermal Decomposition of the Bibenzotriazoles. Formation of Dibenzotetraazapentalenes. When a solution of 1,1'-bibenzotriazole in di-*n*-butyl phthalate was heated at 300°, 1 mole of nitrogen was evolved with concomitant deepening in color of the solution. The well-defined, yellow, crystalline product obtained, mp 240–241°, was identified as dibenzo-1,3a,4,6a-tetraazapentalene (**1**) by comparison with an authentic sample. 1,2'-Bibenzotriazole (**8**) underwent a similar transformation at 250° with formation of the isomeric dibenzo-1,3a,6,6a-tetraazapentalene (**2**).

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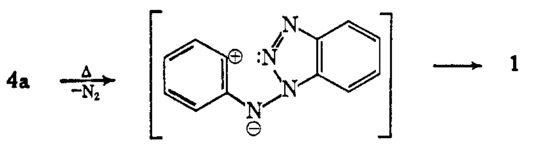
[7] We are indebted to Dr. C. S. Marvel for suggesting the use of this reagent.

[8] C. D. Campbell and C. W. Rees, *Chem. Commun.*, 192 (1965).

[9] R. Trave and G. Bianchetti, *Atti Accad. Nazl. Lincei, Rend., Classe Sci., Fis., Mat. Nat.*, **28**, 652 (1960).

[10] F. R. Benson and W. L. Sarell, *Chem. Rev.*, **46**, 1 (1950).

The mechanism for the tetraazapentalene formation in these thermolysis has not been studied. However, the reaction sequence may be represented as follows.



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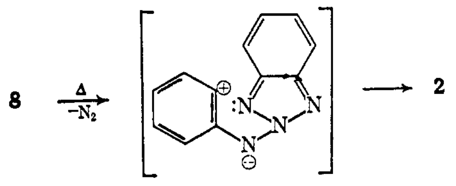

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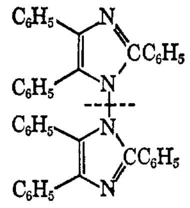
On heating, a molecule of azo nitrogen is eliminated from the 1H-benzotriazole moiety of each of the hexaaza derivatives with incipient or intermediate formation of the 1,3-dipolar intermediates, **17** and **18**, or their equivalents; subsequent bond formation between the ring carbon and the 2-N (in **17**) and 1-N (in **18**) yields the corresponding tetraazapentalenes **1** and **2**, respectively.

The thermolysis is reminiscent of the Graebe–Ullmann synthesis of carbazoles from 1-phenylbenzotriazoles, although the latter reaction involves the formation of a carbon–carbon bond rather than a carbon–nitrogen bond and also involves migration of a hydrogen atom.[11]

The thermal stability of the nitrogen–nitrogen bonds between each ring in the bibenzotriazoles **4a** and **8** is remarkably greater than those of the closely related lophine **19** and tetraphenylpyrrole dimer **20**, which are measurably dissociated into the corresponding free radicals at temperatures below 100°.[12]



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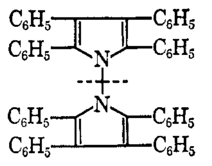

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Experimental Section[13]

1,1′-Bibenzotriazole (4a). To a mixture of 2.1 g (0.01 mole) of *o,o′*-diaminoazobenzene[14] in 25 ml of 12% hydrochloric acid was slowly added sodium nitrite (1.5 g, 0.022 mole) in 10 ml of water. The temperature was maintained at 0–5° during the addition and throughout the subsequent treatments. The clear, homogeneous diazotization mixture was stirred for an additional 30 min, then treated with sulfur dioxide. The latter was introduced in a moderately rapid stream with stirring. A solid began to separate almost immediately. After 20 min, the light tan precipitate (1.5 g, 63%) was collected by filtration and recrystallized from ethyl acetate, to obtain colorless needles, mp 233° dec. A second recrystallization from decahydronaphthalene gave **4a** as hairlike crystals, mp 235° dec.

Anal. Calcd for $C_{12}H_8N_6$: C, 61.0; H, 3.4; N, 35.6. Found: C, 60.8; H, 3.6; N, 35.6.

The ultraviolet spectrum (ethanol) shows λ_{max} 252 mμ (ϵ 14,600) and 288 mμ (ϵ 7800). The dipole moment is 5.16 D. (0.02 *M* in benzene at 25°).

2-(*o*-Nitrophenylamino)-2H-benzotriazole (14). A mixture of 34 g (0.25 mole) of 2-aminobenzotriazole (**13**), 35 g (0.25 mole) of *o*-fluoronitrobenzene,[15] 25.4 g (0.24 mole) of anhydrous sodium carbonate, and 120 ml of dimethylformamide was refluxed under nitrogen for 2 hr. The red-brown mixture was cooled and poured into 2.5 l. of water, precipitating a yellow solid. The latter was collected on a filter, washed with water, and recrystallized from 95% ethanol, giving 55 g (85%) of 2-(*o*-nitrophenylamino)-2H-benzotriazole, mp 144–145°.

Anal. Calcd for $C_{12}H_9N_5O_2$: C, 56.47; H, 3.55. Found: C, 56.53; H, 3.47.

2-(*o*-Aminophenylamino)-2H-benzotriazole (16). A mixture of 10.2 g (0.04 mole) of 2-(*o*-nitrophenylamino)-2H-benzotriazole, 0.3 g of 10% palladium on charcoal, and 75 ml of tetrahydrofuran was shaken at room temperature in a Parr apparatus under 40 psi hydrogen pressure. Hydrogen uptake was rapid, the theoretical amount being consumed in 10 min. The mixture was filtered, and the filtrate was evaporated nearly to dryness under nitrogen. The dark, partially crystalline residue was taken up in 95% ethanol, treated with charcoal, filtered, and diluted with water, giving tan leaflets (7 g, 78%), mp 100° dec. Recrystallization from ethanol–water gave colorless leaflets, mp 106° dec.

Anal. Calcd for $C_{12}H_{11}N_5$: C, 63.98; H, 4.92; N, 31.10. Found: C, 63.13; H, 5.16; N, 31.06.

The infrared spectrum of this product is consistent with the proposed structure **16**.

Because of the difficulties in obtaining this amine analytically pure, the slightly crude material was employed for conversion to 1,2′-bibenzotriazole.

1,2′-Bibenzotriazole (8). A solution of 6.0 g (0.0266 mole) of 2-(*o*-aminophenylamino)-2H-benzotriazole in 250 ml of 1 *N* hydrochloric acid was cooled to 0°, and a solution of 1.80 g (0.026 mole) of sodium nitrite in water was added dropwise with stirring. The gray precipitate was collected on a filter and dissolved in ether, and the solution was treated with charcoal and filtered. Evaporation of the solvent and subsequent crystallization of the residue from aqueous ethanol gave 4.0 g (63%) of pale tan crystals, mp 123.5–124.5°. The melt on cooling gave crystals which melted at 98°, formed a new solid phase at 102°, and remelted at 123.5–124.5°.

Anal. Calcd for $C_{12}H_8N_6$: C, 61.01; H, 3.41; N, 35.58; mol wt, 236. Found: C, 61.02; H, 3.74; N, 35.70; mol wt, 229.

The ultraviolet spectrum (ethanol) shows λ_{max} 290 mμ (sh) (ϵ 16,700), 282 mμ (ϵ 17,500), and 245 mμ (sh) (ϵ 8350).

The product on heating to 200° in air evolved a gas with concomitant formation of a higher melting solid, presumed to be dibenzo-1,3a,6,6a-tetraazapentalene (see below).

Reaction of Bibenzotriazoles with Lithium Aluminum Hydride. To a suspension of 1.50 g (0.04 mole) of lithium aluminum hydride in 100 ml of tetrahydrofuran was added a solution of 2.36 g (0.01 mole) of 1,2′-bibenzotriazole in 200 ml of tetrahydrofuran. The mixture was refluxed for 4 hr. After cooling, aqueous tetrahydrofuran was added to destroy unreacted hydride, and then the mixture was diluted with water and extracted with methylene chloride. The methylene chloride extracts were dried and evaporated, and the brown residue was treated with ether. The ether extract was filtered and evaporated, giving 1.3 g of brown crystals having an infrared spectrum nearly identical with that of benzotriazole. Recrystallization from water gave pure benzotriazole, identified by melting point and mixture melting point.

When 1,1′-bibenzotriazole was treated with lithium aluminum hydride as above, only starting material was recovered.

Reaction of 1,1′-Bibenzotriazole with Dimethyl Sulfate. a. Mono-N-alkylation. A mixture of 5.0 g (0.021 mole) of 1,1′-bibenzotriazole and 50 ml of purified dimethyl sulfate was stirred at 95° for 20 min. The unreacted starting material (1.0 g) was removed by filtration, and the filtrate was diluted to 300 ml with anhydrous ether. The colorless crystals which precipitated were washed with ether and air dried, weight 4.40 g (72% based on un-

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[11] C. Graebe and F. Ullmann, *Ann.*, **291**, 16 (1896).

[12] H. Zimmermann, H. Baumgartel, and E. Bakke, *Angew. Chem.*, **73**, 808 (1961).

[13] The ultraviolet spectra were obtained using a double-beam Model 14 Cary recording spectrophotometer. Dipole moments were determined by Mr. C. Wortz in benzene solution using a Dipol Meter Type DN-01 (Wissenschaftlich-Technische Werkstätten Weilheim, G.M.B.H., O.B., Germany).

[14] R. Willstätter and A. Pfannenstiel, *Ber.*, **38**, 2349 (1905).

[15] Dr. Charles Yembrick has shown that *o*-chloronitrobenzene may be substituted for *o*-fluoronitrobenzene if a reflux time of 4 hr is employed.

recovered starting material). Elemental analysis indicated that the product contained 18% of the di-N-alkylation product described below.

Anal. Calcd for 82% $C_{14}H_{14}N_6SO_4$ + 18% $C_{16}H_{20}N_6S_2O_8$: C, 45.13; H, 3.93; N, 22.10; S, 9.62. Found: C, 45.16; H, 3.88; N, 21.55; S, 9.64.

The monoalkylation product **10**, mp 180° dec, is very water soluble and is stable to light and air.

b. Di-N-alkylation. A mixture of 5.0 g (0.021 mole) of 1,1′-bibenzotriazole and 50 ml of purified dimethyl sulfate was stirred at 95–110° for 2 hr, followed by cooling to room temperature during 2.5 hr. The colorless crystals were collected on a filter, washed with ether, and dried over phosphorus pentoxide at room temperature. The product **6** (8.95 g, 86%) melted at 192–194° dec.

Anal. Calcd for $C_{16}H_{20}N_6S_2O_8$: C, 39.34; H, 4.13; N, 17.21; S, 13.13; mol wt, 163. Found: C, 38.96; H, 4.06; N, 17.51; S, 13.72; mol wt, 170, 179.

The dialkylation product **11** is very water soluble and is stable to light and air.

To a solution of 3.0 g of the above dialkylation product was added 17 ml of saturated aqueous sodium iodide solution. Red-orange crystals precipitated immediately, and the mixture was stored in the dark for 15 min. The crystals were then collected on a filter in the dark and washed with water. After drying, the diiodide weighed 1.70 g.

Anal. Calcd for $C_{14}H_{14}N_6I_2$: C, 32.33; H, 2.71; N, 16.16; I, 48.80. Found: C, 32.44; H, 2.72; N, 16.12; I, 47.45.

The diiodide turns brown on exposure to light and forms a dark oil on standing at room temperature for several weeks, even in the dark.

Decomposition of Dialkylation Product 11 with Base. To 20 ml of 1 *N* sodium hydroxide at room temperature was added 2.0 g (0.0041 mole) of the dialkylation product, giving a bright yellow mixture which rapidly changed to a nearly colorless mixture. The small amount of oil which formed slowly crystallized. The mixture was extracted with ether, and the ether extracts were dried and evaporated to give 0.55 g of nearly colorless crystals, mp 61.5–63.5°. Recrystallization from cyclohexane gave pure 1-methylbenzotriazole (**12**), mp 64.5–65.5°, identified by melting point and comparison of its infrared spectrum with that of an authentic sample.[16]

Reduction of 11 with Lithium Aluminum Hydride. A slurry of 1.0 g (0.026 mole) of lithium aluminum hydride in 125 ml of ether was stirred under nitrogen at room temperature while 3.0 g (0.006 mole) of the dialkylation product **11** was added. The light purple suspension which resulted was treated with an additional 0.65 g of lithium aluminum hydride during 6 hr, and the mixture was then allowed to stand overnight. Excess hydride was destroyed with ethyl acetate and water, then 80 ml of 10% sodium hydroxide was added, the solid was removed by filtration, and the filtrate was extracted three times with ether. The combined ether extracts were dried over sodium sulfate, and the solvent was removed, giving 1.58 g (97%) of light brown crystalline solid, mp 59–61°, the infrared spectrum of which was identical with that of 1-methylbenzotriazole. Recrystallization gave pure 1-methylbenzotriazole, mp 63–64°.

Reduction of 1,1′-Bibenzotriazole (4a). Aluminum amalgam was prepared by immersing 0.57 g (0.02 g-atom) of aluminum foil (0.001 in.) in 5% aqueous mercuric chloride at room temperature for 1.5 min. The foil was rapidly washed with water and added immediately to a suspension of 5.0 g (0.021 mole) of 1,1′-bibenzotriazole in 500 ml of moist ether. The mixture was refluxed for 3 hr, at which time all of the amalgam had been consumed. The ether layer was decanted and evaporated under a stream of nitrogen until nearly all of the unreacted starting material (1.50 g) had precipitated. The benzotriazole was removed by filtration, and the filtrate was evaporated further, giving 2.7 g of brown crystals, mp 82–89°, having an infrared spectrum nearly identical with that of benzotriazole. The yield of crude product based on unrecovered starting material was 77%. Recrystallization from benzene gave pure benzotriazole (55%), identified by melting point, mixture melting point, and comparison of its infrared spectrum with that of an authentic sample.

Thermolysis of 1,1′-Bibenzotriazole. A solution of 2.0 g (0.0085 mole) of 1,1′-bibenzotriazole in 25 ml of di-*n*-butyl phthalate was heated under nitrogen at 250° for 30 min. The dark mixture was cooled to room temperature, and the precipitate was collected on a filter, washed with pentane, and air dried. There was obtained 0.95 g (54%) of dibenzo-1,3a,4,6a-tetraazapentalene (**1**), mp and mmp 237–238° with an authentic sample.

Thermolysis of 1,2′-Bibenzotriazole. A solution of 0.50 g (0.0021 mole) of 1,2′-bibenzotriazole in 3.7 g of di-*n*-butyl phthalate was heated at 250° for 25 min, by which time nitrogen evolution had nearly ceased. The dark solution was cooled under nitrogen, 7 ml of petroleum ether was added, and the precipitated, feathery crystals were collected on a filter and dried. The product (0.30 g, mp 248°) was recrystallized from methylene chloride–petroleum ether, giving 0.11 g of nearly colorless crystals, mp 255°. The mixture melting point with an authentic sample of dibenzo-1,3a,6,6a-tetraazapentalene (**2**) was undepressed.

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(16) F. Krollpfeiffer, A. Rosenberg, and C. Mühlhausen, *Ann.*, **515**, 113 (1935).