Aromatic Azapentalenes. II. Reactions of Monobenzo- and Dibenzo-1,3a,4,6a-tetraazapentalenes[1]

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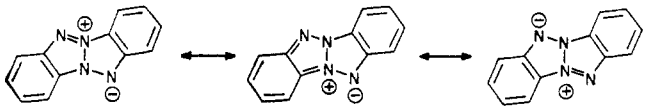
Abstract: The reactions of dibenzo-1,3a,4,6a-tetraazapentalene (I) with a variety of reagents are described. The directive influence of the tetraazapentalene nucleus on electrophilic substitution reactions at the benzene rings is discussed. Ring-opening reactions of I with peracetic acid, lithium aluminum hydride, and cuprous cyanide give 2-phenylbenzotriazole derivatives. Monobenzo-1,3a,4,6a-tetraazapentalenes have been prepared, and the physical and chemical properties of these compounds are described.

The nitrogen-containing analogs of pentalene, the azapentalenes, are represented by replacement of the ring carbon atoms (with any associated hydrogen atoms) by nitrogen atoms. Placement of the annular nitrogens at nonfused positions gives azapentalenes containing 8 π electrons. However, when both fused positions are occupied by nitrogen, the molecules possess electronic configurations similar to those of pentalene dianion or naphthalene. The preparation of dibenzo-1,3a,4,6a-tetraazapentalene (I) as well as the isomeric 1,3a,6,6a-tetraazapentalene was described previously.[2,3]

The heteroaromatic molecule I may be formally represented by a series of charge-separated structures Ia–c.

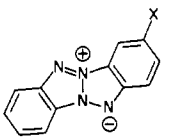


Ia Ib Ic

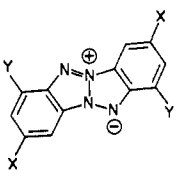
The chemical and physical properties of the dipolar tetraazapentalene might be expected to reflect a structure which lies between neutral naphthalene and pentalene dianion.[4] This paper describes some of the chemical and physical properties of I as well as those of monobenzo-1,3a,4,6a-tetraazapentalene.

Electrophilic Substitution. Dibenzo-1,3a,4,6a-tetraazapentalene (I) undergoes a number of facile electrophilic substitution reactions with and without disruption of the tetraazapentalene nucleus.

Treatment of I with chlorine or bromine in acetic acid or chloroform readily gave the dihalogenated derivatives IIIa,b in good yields. When I was treated with N-bromosuccinimide in acetonitrile, the monobromo



II a, X = Cl
b, X = Br
c, X = NO_2
d, X = NH_2



III a, X = Cl, Y = H
b, X = Br, Y = H
c, X = NO_2, Y = H
d, X = NH_2, Y = H
e, X, Y = NO_2
f, X = $SOCl_2$, Y = H

compound IIb was produced in 70% yield, together with a small quantity (5–10%) of dibromo derivative. Chromatography on alumina gave no evidence of additional monobromo isomers. Further bromination of this product with bromine in chloroform gave IIIb. A similar treatment of I with N-chlorosuccinimide in acetonitrile was less successful, yielding a mixture of monochloride IIa, dichloride IIIa, and some unreacted I.

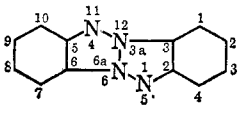
Nitration at 5° with 70% nitric acid gave a mixture of dinitro derivatives, from which the predominant isomer IIIc, mp 352°, was isolated. These nitrated products exhibit strong yellow-green fluorescence in solution. When I was treated with 90% nitric acid, the tetranitro derivative IIIe (mp 410° dec) was obtained in excellent yield. Surprisingly, the tetranitrated product was also formed when I was heated with 25% aqueous nitric acid at 60°. The latter is normally employed as an oxidizing rather than a nitrating medium. When I was treated at 0° with 25% aqueous nitric acid, a mononitro product formed. Evidence for only one mononitro isomer in the crude product was found.

Treatment of I with chlorosulfonic acid at 90° produced the bis(sulfonyl chloride) IIIf in 50% yield. This compound was relatively resistant to water but reacted with amines and ammonia to give the expected sulfonamides.

Stannous chloride reduction of the mono- and dinitrodibenzotetraazapentalenes gave incomplete conversions to the corresponding amines Id and IId, respectively, thus rendering difficult the purification of the latter products. However, catalytic hydrogenation in dimethylformamide with 10% palladium on carbon gave the desired amines which were more readily purified.

Position of Electrophilic Substitution. The halogenation of I occurs to a very large extent at the 2 (or 8)

(1) These compounds may be named 1,5-dehydrotriazolo[2,1-*a*]-benzotriazole and 5,11-dehydrobenzotriazolo[2,1-*a*]benzotriazole, respectively. The tetraazapentalene nomenclature is employed in this and subsequent papers to emphasize the role of the annular nitrogens of the central rings in providing the unusual properties of this novel system. The following numbering system has been adopted in this paper.

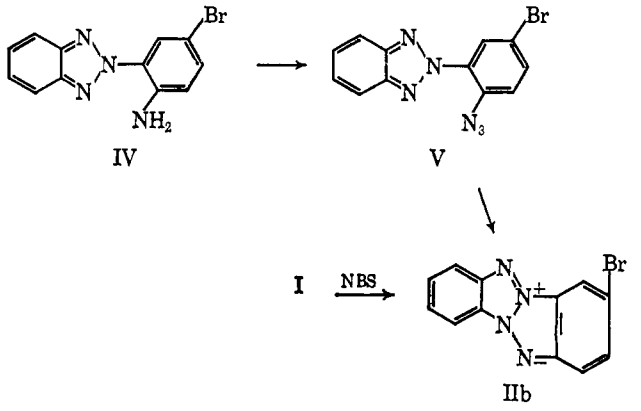


(2) R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.*, **84**, 2453 (1962).

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

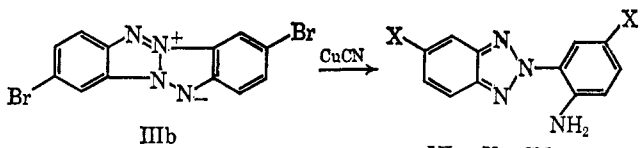
(4) (a) T. J. Katz and M. Rosenberger, *ibid.*, **84**, 865 (1962); T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964); (b) D. Peters, *J. Chem. Soc.*, 1274 (1960).

position(s) in the benzene rings, *i.e.*, *para* to the nonfused nitrogens. The position of the bromine atom in IIb was established through conversion of 2-(5′-bromo-2′-azidophenyl)-2H-benzotriazole (V) to the corresponding tetraazapentalene derivative which was identical with IIb. The location of the two bromo groups at the 2 and 8 positions in IIIb was established by con-



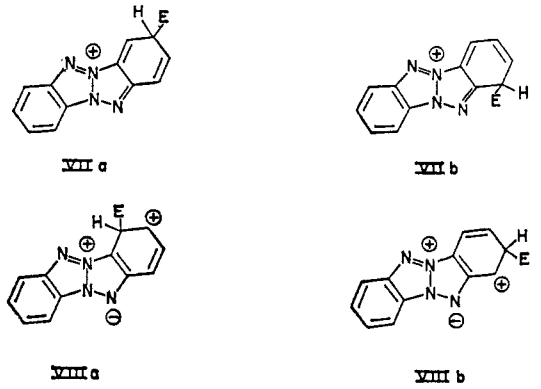
IV V IIb

version of the latter with cuprous cyanide to 2-(2′-aminophenyl)-5,5′-dicyano-2H-benzotriazole (VIa) and



IIIb VIa, X = CN; b, X = $CONH_2$

thence to the diamide VIb, which was identical with a sample prepared by an independent route. This reaction is discussed later. If the quasiquinoid intermediates VIIa and VIIb are accepted as models for the



VIIIa VIIIb

transition states during electrophilic attack, these transition states should be more stable than those for substitution at the 1,3 (7,9) positions (VIIIa,b). In the latter case, only limited charge delocalization is possible. Tetrasubstitution of I would similarly be expected to occur at the 2, 4, 8, and 10 positions. It is unlikely that the substitution reactions would be complicated by protonation of the ring nitrogens in view of their weakly basic character and the mild conditions employed (*e.g.*, 25% aqueous nitric acid).

The preferential substitutions at the 2, 4, 8, and 10 positions are also in accord with an approximate charge distribution calculated by molecular orbital methods.[5]

(5) Y. T. Chia and H. E. Simmons, *J. Am. Chem. Soc.*, **89**, 2638 (1967).

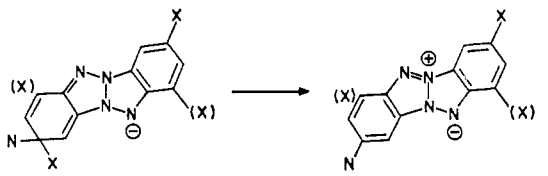
The apparent absence of isomers in the monobromination and -nitration is surprising since the calculated charge densities at C-2 and C-4 are close, and the localization energies associated with attack at either position might be expected to be comparable.

Tetracyanoethylene (TCNE), a weak electrophile which is capable of undergoing substitution reactions with reactive aromatic systems,[6] such as dimethylaniline, phenol, etc., did not give the tetracyanoethyl or tricyanovinyl derivative of I. Rather, an acetonitrile solution containing I and TCNE gave a deep color associated with formation of a π complex (see below).

Nucleophilic Displacement Reactions on Substituted Tetraazapentalenes. When a solution of tetranitrodibenzotetraazapentalene (IIIe) in dimethylformamide was treated with azide ion, a diazidodinitro derivative was produced. Milder conditions yielded the 2- (or 4-) monoazidotrinitro derivative.

The dinitrodibenzotetraazapentalene (IIIc) also was attacked by azide ion; however, the reaction proceeded more slowly.

As in the case of electrophilic attack, nucleophilic substitution might be expected to occur with relative ease at the 2,4 or 8,10 positions in tetraazapentalenes. Attack at these positions probably involves anionic intermediates which may serve as models for the rate-determining transition state. One important contributing resonance structure for such anions may be formulated as IXa. Corresponding stabilization of the transition state for substitution at the 1,3 or 7,9 positions is not possible.



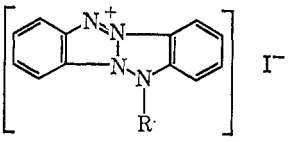
IXa IXb

Reaction with *n*-Butyllithium. Compound I undergoes a metalation reaction with *n*-butyllithium. Thus, when I was treated with *n*-butyllithium, followed by methyl iodide, a bright yellow crystalline product was obtained which analyzed correctly for the monomethyl derivative despite a broad melting point range. The strong resemblance of the infrared and ultraviolet spectra of the methyl derivative to those of the parent compound indicated little alteration in the electronic system, *i.e.*, the methyl group is attached to the benzene ring rather than to a nitrogen. When the crude product was chromatographed on nonalkaline Woelm alumina, a sharp-melting (200–201°) solid, characterized as the monomethyl derivative X, was isolated from the early eluates. The position of substitution has not yet been proved. However, the 4 (10) position (*i.e.*, "*ortho*" to nonfused N) should be favored by the ability of the metal to coordinate with an electron pair on the nitrogen while the hydrogen in the adjacent position is removed by attack from the protophilic butyl anion.[7]

(6) (a) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and G. F. Mower, *ibid.*, **80**, 2783 (1958); (b) J. R. Roland and B. C. McKusick, *ibid.*, **83**, 1652 (1961).

(7) H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 261 (1954).

Reactions at the Nitrogen Atoms. When propylene was passed into a solution of I in concentrated sulfuric acid under the normal Friedel–Crafts conditions, little, if any, C-alkylated product was obtained; rather, a high yield of N-isopropyltetraazapentalenium hydrogen sulfate formed. The latter was isolated as the iodide XIa by neutralization of the reaction mixture and treatment with sodium iodide.



XIa, R = *i*-C_3H_7
b, R = CH_3

The N-methyl derivative XIb was prepared by prolonged treatment of I with methyl iodide, and more readily with methyl sulfate at 150°, followed by treatment of the resulting water-soluble methosulfate with aqueous sodium iodide.

The cationic derivatives are light-sensitive, crystalline solids. The yellow iodide XIb, when heated at reduced pressure, reverted to methyl iodide and I. The ultraviolet spectra of I, XIa, and XIb are shown in Table I.

Table I. Ultraviolet Absorption Maxima for Dibenzotetraazapentalene I and Its N-alkylated Derivatives XIa,b

I		XIa		XIb	
λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
402	38,300	378	19,700	377	20,000
382	23,300	362	19,200	361	19,900
364	7,740	323	10,100	323	10,400
323	4,110				
308	2,850				
255	63,300	241	32,900	239	35,000

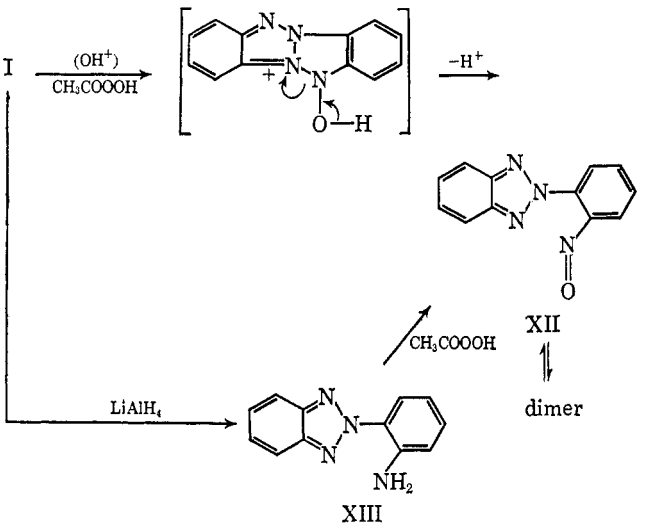
The ultraviolet spectrum of the N-isopropyl cation XIa is almost identical with that of the N-methyl derivative XIb. The spectra of XIa and XIb are equally shifted toward shorter wavelengths with respect to the corresponding peaks in the spectrum of I.

Complex Formation. Dibenzo-1,3a,4,6a-tetraazapentalene functions as a moderately weak π base in the presence of strong π acids such as tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane (TCNQ).[8] The latter appears to form a more stable complex with I than does tetracyanoethylene. Treatment of TCNQ with compound I in warm acetonitrile gave dark green crystals of the 1:1 π complex. The complex is diamagnetic and exhibits a resistivity of 4.6×10^8 ohm cm. The solid gives green solutions when cold; however, the color is discharged on heating, indicating thermal dissociation. The complex is also dissociated in chloroform by differential solubility of its two components; the insoluble TCNQ separates, leaving the soluble compound I behind. Compound I thus appears to be only a moderately strong π base, which is not surprising in view of the presence of the four electronegative ring nitrogen atoms.

Silver salts and salts of copper(I) also react with compound I to form 2:1 complexes. The silver nitrate complex was unaffected by recrystallization from dimethylformamide, while the cuprous cyanide adduct was broken into its components on warming in acetonitrile.

Reactions with Ring Opening. Although an acetone solution of I is stable to potassium permanganate, the molecule is readily attacked by peracetic acid under relatively mild conditions with cleavage of a N–N bond. When a chloroform solution of I was treated with peracetic acid, an oxidative cleavage occurred with the formation of 2-(*o*-nitrosophenyl)-2H-benzotriazole (XII). This cream-colored solid, mp 185–185.5°, dissolves in organic solvents to yield green solutions, characteristic of nitroso compounds. The physical and spectral data suggest that the nitroso compound probably exists as the dimer in the solid state.

The structure of the product was substantiated by an independent synthesis through peracetic acid oxidation of 2-(*o*-aminophenyl)-2H-benzotriazole (XIII).[3b]



XIII

A nonfused nitrogen with its relatively high electron density would be a favorable site of attack for the electrophilic peracid. The accompanying electron shift leads directly to the corresponding nitrosophenylbenzotriazole XII.

Similarly, lithium aluminum hydride converts dibenzo-1,3a,4,6a-tetraazapentalene to 2-(*o*-aminophenyl)-2H-benzotriazole (XIII).[3b]

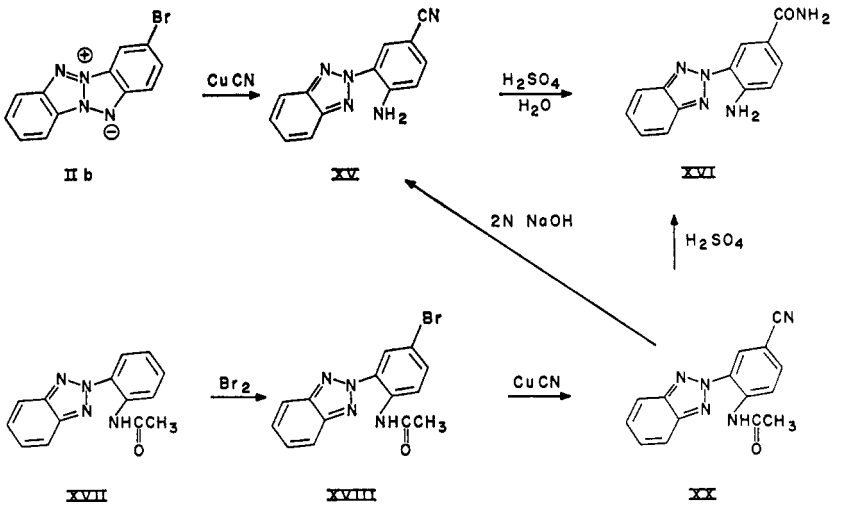
When the tetraaza derivative I was hydrogenated in acetic acid at 125° with 5% palladium on carbon, a colorless solid, mp 121–122°, which was identified as 2-(*o*-acetamidophenyl)-2H-4,5,6,7-tetrahydrobenzotriazole (XIV), was isolated. The identical substance was obtained from the catalytic hydrogenation[9] of XIII followed by acetylation.

An attempt to replace the halogen atom in the monobromodibenzotetraazapentalene IIb with a nitrile group by reaction with cuprous cyanide in refluxing N-methylpyrrolidone[10] resulted in N–N cleavage to a cyano-2-(*o*-aminophenyl)-2H-benzotriazole (XV) in 60% yield. XV was converted to the corresponding

(8) (a) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958); (b) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *ibid.*, **84**, 3374 (1962).

(9) K. Fries, W. Franke, and W. Burns [*Ann.* **511**, 241 (1934)] reported that hydrogenation of 2-phenyl-2H-benzotriazole with Pd–$BaSO_4$ in acetic acid gave reduction of the fused six-membered ring, leaving the 2-aryl group intact.

(10) M. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961).



IIb XV XVI

XVII XVIII XX

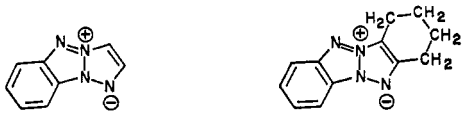
carboxamido derivative XVI by hydrolysis with sulfuric acid.

Identification of XV and XVI as 5′-cyano- and 5′-carboxamido-2′-aminophenyl-2H-benzotriazoles, respectively, was established through independent synthesis. 2-(*o*-Acetamidophenyl)-2H-benzotriazole (XVII) was brominated in acetic acid to obtain the 5′-bromo derivative XVIII. The position of the bromo substituent *para* to the acetamido group was confirmed by examination of the proton nmr spectrum. Replacement of the halogen by cyano with cuprous cyanide followed by hydrolysis with dilute alkali or concentrated sulfuric acid gave the same cyano and carboxamido derivatives, XV and XVI, respectively, as did the ring cleavage described above.

Identity of derivatives from both routes confirms: (a) that the preferred position for halogenation (and presumably nitration) in dibenzo-1,3a,4,6a-tetraazapentalene is at the 2 (or 8) position, *i.e.*, *para* to a nonfused nitrogen; (b) that the ring-opening reaction proceeds *via* cleavage of the N–N bond in which the nonfused nitrogen is attached to the negatively substituted benzene ring.

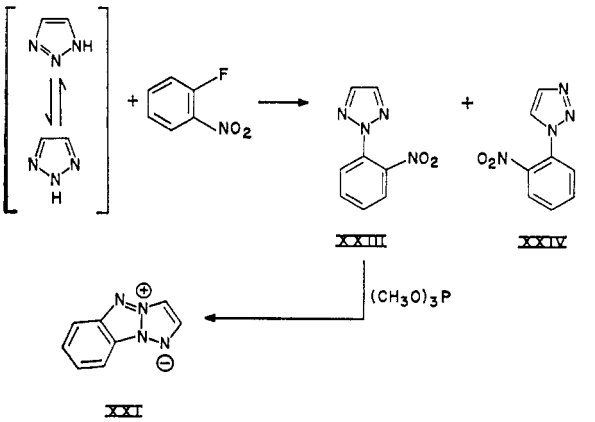
In a similar manner, treatment of the dibromide IIIb with cuprous cyanide produced the corresponding 5,5′-dicyano-2-(2′-aminophenyl)-2H-benzotriazole (VIa), while the mononitrotetraazapentalene IIc yielded the 2-(2′-amino-5′-nitrophenyl)-2H-benzotriazole (XIX). The unsubstituted pentalene I also underwent cleavage, though at an appreciably slower rate, to form compound XIII. This ring-opening reaction did not occur with sodium cyanide.

Monobenzo-1,3a,4,6a-tetraazapentalenes. It was of interest to determine the physical and chemical consequences of removing one of the benzo moieties from the central hetero system. Two routes were found which gave 2,3-benzo-1,3a,4,6a-tetraazapentalene (XXI) and the 5,6-tetramethylene-2,3-benzo derivative XXII, respectively.



XXI XXII

The monobenzotetraazapentalene XXI was prepared by deoxycyclization of 2-(*o*-nitrophenyl)-2H-triazole (XXIII) with trimethyl phosphite.[11] Compound XXIII was prepared by treatment of 1,2,3-triazole with *o*-fluoronitrobenzene.



XXIII XXIV XXI

The resulting mixture of 1- and 2-arylated triazoles could be separated by distillation. The 1 isomer XXIV was identified by comparison with an authentic sample prepared by the addition of acetylene to *o*-nitrophenyl azide.[11]

Purification of the monobenzotetraazapentalene by vacuum distillation and recrystallization from ethanol gave colorless crystals, mp 108.8–109.7°, whose analysis was in agreement with the structure XXI ($C_8H_6N_4$). The compound possessed a distinct quinoline-like odor.

A similar deoxygenative cyclization with *o*-nitrophenyl-1H-triazole (XXIV) gave the isomeric 2,3-benzo-1,3a,6,6a-tetraazapentalene.[11]

5,6-Tetramethylene-2,3-benzo-1,3a,4,6a-tetraazapentalene (XXII) was prepared by conversion of 2-(*o*-aminophenyl)-2H-tetrahydrobenzotriazole (XXV) to the corresponding azide XXVI followed by thermal decomposition, in a manner similar to that employed in the preparation of I.[3] From the concentrated reaction mixture was obtained the tetraazapentalene XXII as an almost colorless solid, mp 131.5–133°.

A comparison of the ultraviolet absorption spectra of the two monobenzotetraazapentalenes in Table II reveals their similarity.

The nonfluorescent XXI and XXII exhibit a pronounced hypsochromic shift in the ultraviolet spectra,

(11) J. C. Kauer and R. A. Carboni, *J. Am. Chem. Soc.*, **89**, 2633 (1967).

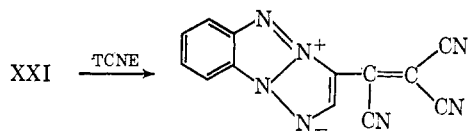
Table II. Ultraviolet Absorption Spectra of Monobenzotetraazapentalenes[a] XXI and XXII

XXI		XXII	
λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
343	21,800	351	28,200
278	3,040	278	2,850
236	27,700	242	25,900

[a] Measured in ethyl alcohol.

compared to the dibenzo analog I. The long-wavelength region is without the prominent fine structure which characterizes compound I and its benzo–naphtho analogs.[3]

Both of the benzotetraazapentalenes XXI and XXII reacted with tetracyanoethylene (TCNE) in tetrahydrofuran solution to form a deep blue complex. In the case of XXI, however, the solution liberated hydrogen cyanide slowly, and the blue color was replaced with a deep reddish purple. These transformations were much more rapid in N,N-dimethylformamide. The deeply colored tricyanovinyl derivative XXVII precipitated on dilution of the solution with water.



XXVII

The monobenzotetraazapentalene reacted much more rapidly with methyl iodide than did the dibenzo derivative I. The resulting stable methiodide XXVIII exhibited an ultraviolet spectrum in water solution very similar to that of the pentalene XXI in hydrochloric acid, suggesting that the positions of methylation and alkylation are the same.

Experimental Section

Monobromodibenzotetraazapentalene (IIb). a. From Bromination of I. A solution of 20.8 g (0.10 mole) of dibenzo-1,3a,4,6a-tetraazapentalene (I) in 2 l. of refluxing acetonitrile was stirred vigorously while 17.8 g (0.10 mole) of N-bromosuccinimide in 250 ml of acetonitrile was added dropwise over a period of 20 min. The clear yellow solution was refluxed for 2.5 hr, during which time a yellow solid (dibromo derivative) precipitated. The latter was removed from the hot mixture by filtration. The filtrate was concentrated to two-thirds of its original volume, then filtered while hot to remove a small quantity of solid. The acetonitrile solution was cooled to 5° to give 20 g (70%) of product, mp 196–198°. Successive recrystallizations from benzene and hexane gave an analytical sample, mp 201.0–202.5°.

Anal. Calcd for $C_{12}H_7N_4Br$: C, 50.19; H, 2.46; N, 19.51; Br, 27.83. Found: C, 50.26; H, 2.47; N, 19.39; Br, 27.66.

b. From Thermolysis of 2-(5′-Bromo-2′-azidophenyl)-2H-benzotriazole (V). A solution of 3.4 g of V in 30 ml of *o*-dichlorobenzene was heated at 180° for 1 hr, during which time nitrogen evolved and the solution turned yellow-brown. The solution was concentrated to one-third volume and cooled. The yellow crystalline solid (2.4 g) was collected by filtration, washed with fresh solvent, and dried, mp 205–206°. The infrared spectrum of this material was identical with that of the product from method a.

Dibromodibenzo-1,3a,4,6a-tetraazapentalene (IIIb). a. A warm, stirred mixture of I (1.0 g, 0.005 mole) and 85 ml of glacial acetic acid (50°) was treated with 2 g (0.0125 mole) of bromine in acetic acid. A bright yellow precipitate formed almost immediately. The mixture was heated at 70° for 15 min, cooled to 50°, and filtered. The first crop of crystals (1.4 g) was recrystallized from *o*-dichlorobenzene to obtain bright yellow crystals, mp 295–297°.

Anal. Calcd for $C_{12}H_6Br_2N_4$: C, 39.38; H, 1.65; N, 15.31; Br, 43.67. Found: C, 39.15; H, 1.60; N, 15.15; Br, 43.20.

The ultraviolet spectrum (in chloroform) exhibited the characteristic three areas of absorption, the strongest peaks in each group being 424 mμ (ε 52,000), 314 (3660), and 268 (75,760).

b. Bromination of IIb. A solution of 2.87 g (0.01 mole) of IIb in chloroform was treated with 1.6 g (0.01 mole) of bromine in chloroform, giving an immediate yellow product (3.2 g) which exhibited the same infrared spectrum and melting point as the dibromo derivative above.

Dichlorodibenzo-1,3a,4,6a-tetraazapentalene (IIIa). Compound I (1.0 g, 0.005 mole) was added to a stirred solution of 0.8 g (0.11 mole) of chlorine in 34 ml of glacial acetic acid. The mixture was gradually heated to reflux, and approximately half of the solvent was removed by distillation. The cooled concentrate was diluted with three volumes of water, and the insoluble precipitate was collected by filtration (1.0 g). Two recrystallizations of the dried solid from *o*-dichlorobenzene gave yellow, fanlike crystals, mp 303–304°.

Anal. Calcd for $C_{12}H_6N_4Cl_2$: C, 52.01; H, 2.19; Cl, 25.59. Found: C, 51.85; H, 2.48; Cl, 25.65.

Nitration of Dibenzo-1,3a,4,6a-tetraazapentalene. Mononitration (IIc). To 700 ml of cold (10°) 25% nitric acid was added with stirring 50 g of I. The yellow suspension was stirred vigorously while warming to room temperature during 1.5 hr. After standing overnight at 25°, an orange solid was collected by filtration, washed with water, and dried. The crude mononitro derivative (11 g, 91%) was purified by chloroform extraction, mp 301–303°.

Anal. Calcd for $C_{12}H_7N_5O_2$: C, 56.91; H, 2.79; N, 27.66. Found: C, 57.21; H, 3.00; N, 27.92.

Dinitration (IIIc). Compound I (1.0 g) was added in small portions to 15 ml of concentrated nitric acid at 5° with stirring. The mixture was stirred for an additional 30 min, then poured into ice-water. A quantitative yield of the yellow-orange dinitro compound, mp 340° dec, was obtained. *Anal.* Calcd for $C_{12}H_6N_6O_4$: C, 48.33; H, 2.03; N, 28.18. Found: C, 48.21; H, 2.25; N, 28.08.

Tetranitration (IIIe). To a stirred solution of 1 g of I in concentrated H_2SO_4 was added an excess (20 ml) of fuming red nitric acid with slight cooling. After 15 min, the mixture was heated to 60° and maintained at this temperature for an additional 15 min. The orange mixture was cooled somewhat and poured into five volumes of ice–water. The orange tetranitro derivative was collected by filtration (1.55 g). Recrystallization from dimethylformamide yielded an orange-red solid, mp 410° dec, which contained one solvent molecule of crystallization.

Anal. Calcd for $C_{16}H_{11}N_9O_9$: C, 39.05; H, 2.40; N, 27.33. Found: C, 39.47; H, 1.65; N, 27.82.

Dilute solutions of each of the nitro compounds in organic solvents such as acetone, tetrahydrofuran, or dimethylformamide exhibited a strong greenish fluorescence.

Monoaminodibenzo-1,3a,4,6a-tetraazapentalene (IId). A slurry of 10 g of the nitro compound IIc and 10% palladium-on-carbon catalyst (0.5 g) in 150 ml of N,N-dimethylformamide was hydrogenated at 30–40 psi of hydrogen for 1 hr. Most of the hydrogen was absorbed during the first 10 min. The yellow-green slurry was heated to boiling and filtered under nitrogen. On cooling, a crop (5.4 g) of coppery crystals separated. An additional 2.3 g of product was obtained from the concentrated filtrate. The crude product was purified by continuous extraction with chloroform. An analytical sample was prepared by sublimation at 250° (1 mm). The light yellow needles darkened in air at 240° and melted slowly when placed in a bath at 318°.

Anal. Calcd for $C_{12}H_9N_5$: C, 64.56; H, 4.07; N, 31.38. Found: C, 64.35; H, 3.89; N, 31.13.

Acetamide derivative, recrystallized from acetonitrile, had mp 334°, λ_{max}^{EtOH} 420 mμ (ε 42,800), 397 (24,700), 378 (8650), 324 (2100), 311 (4200), and 264 (55,600).

Anal. Calcd for $C_{14}H_{11}ON_5$: C, 63.39; H, 4.18; N, 26.40. Found: C, 63.78; H, 4.45; N, 26.37.

Benzamide derivative, yellow needles from acetonitrile, had mp 278–280°.

Anal. Calcd for $C_{19}H_{13}ON_5$: C, 69.73; H, 4.01; N, 21.40. Found: C, 69.97; H, 4.17; N, 21.03.

Diaminodibenzo-1,3a,4,6a-tetraazapentalene (IIId). The dinitro derivative (5.0 g, IIIc) was hydrogenated as described above. The solid (2.8 g) which separated from the dimethylformamide solution was purified by successive extractions with 20 ml of hot N,N-dimethylformamide and four 25-ml portions of dimethyl sulfoxide. Dilution of the combined extracts with methanol gave 1.6 g (40%) of the diamino derivative. An additional 1.1 g of crude product was recovered from the original reaction solution by dilu-

tion with water. An analytical sample was prepared by recrystallization from dimethyl sulfoxide. The maroon needles melted with decomposition at *ca.* 265°.

Anal. Calcd for $C_{12}H_{10}N_6$: C, 60.49; H, 4.24; N, 35.28. Found: C, 60.24; H, 4.24; N, 35.00.

Dibenzamide derivative, maroon crystals, had mp 380° dec.

Anal. Calcd for $C_{26}H_{18}O_2N_6$: C, 69.94; H, 4.08; N, 18.82. Found: C, 69.57; H, 3.96; N, 18.92.

Dibenzo-1,3a,4,6a-tetraazapentalene-2′,8′-disulfonyl Chloride (IIIe). A solution of 25 g of dibenzo-1,3a,4,6a-tetraazapentalene in 250 ml of chlorosulfonic acid was stirred, and the temperature was raised to 90° over a period of 3 hr. The solution was heated for 1 hr at 90°. It was then cautiously poured onto ice (behind shields in a fume hood). The solid was separated by filtration and was thoroughly washed with water and then air-dried. The crude yellowish solid weighed 49 g. A 36-g portion was extracted with 400 ml of boiling ethyl acetate. After cooling, the undissolved solid disulfonyl chloride (13.8 g) was separated by filtration. The filtrate was evaporated, and the residue was extracted with 400 ml of ethyl acetate at room temperature. The undissolved solid disulfonyl chloride (3.9 g) was combined with the 13.8-g fraction and recrystallized from methylene chloride–hexane to obtain golden yellow platelets melting at 268–269.5° dec; λ_{max} 426 mμ (ε 45,700), 350 (2140), 333 (2350), 283 (54,600), and 238 (2690).

Anal. Calcd for $C_{12}H_6N_4S_2O_4Cl_2$: C, 35.58; H, 1.49; N, 13.83; Cl, 17.50. Found: C, 36.06; H, 1.58; N, 13.64; Cl, 17.05.

By reprocessing the residues, an over-all yield of 51% of this disulfonyl chloride could be obtained. The disulfonyl chloride was very resistant to hydrolysis in neutral solution (*e.g.*, boiling aqueous acetone) but reacted with ammonia and amines to form sulfonamides.

N,N,N′,N′-Tetramethyldibenzo-1,3a,4,6a-tetraazapentalenedisulfonamide, from dimethylamine and IIIe in methylene chloride, gave fluorescent yellow crystals, mp 318–320°, when recrystallized from methylene chloride–hexane.

Anal. Calcd for $C_{16}H_{18}N_6O_4S_2$: C, 45.50; H, 4.30; N, 19.90. Found: C, 45.45; H, 4.40; N, 19.60.

Diazidodinitrodibenzo-1,3a,4,6a-tetraazapentalene. To a hot, stirred solution (135°) of tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (IIIe, 10 g) in 400 ml of dimethylformamide was added 10 g of lithium azide in 80 ml of dimethylformamide. The mixture deepened in color. The reaction mixture was kept at 80–85° for 1 hr, then cooled in an ice bath. The yellow-orange crystals which separated were collected by filtration and washed with ethyl alcohol, then ether. The yield was 8.4 g. A sample melted with vigorous decomposition when placed in a bath at 200°. *Anal.* Calcd for $C_{12}H_4N_{12}O_4$: C, 37.90; H, 1.06; N, 44.21. Found: C, 37.95; H, 1.06; N, 44.00.

The infrared absorption of the compound exhibited the characteristic azide band at 4.75 μ and the nitro bands in the 6.5–7.5-μ region.

2-(*o*-Nitrosophenyl)-2H-benzotriazole (XII). a. From I and Peracetic Acid. A mixture of 8.3 g (0.04 mole) of the tetraaza compound I in 120 ml of chloroform and 20 ml of 40% peracetic acid in 16 ml of glacial acetic acid was heated on a steam bath for 1.5 hr. The mixture was cooled and poured into a cold solution containing 50 g of sodium hydroxide. The organic layer was separated and evaporated to dryness. The solid residue was recrystallized from chloroform to yield crystals melting at 191–192° dec. The total yield was 7.2 g (75%). The infrared spectrum of the solid showed a strong band at 7.87 μ characteristic of nitroso dimers. The ultraviolet spectrum in ethanol showed a weak maximum at 740 mμ (ε 45) as well as strong absorption at 284 mμ (ε 18,500) and 227 mμ (ε 22,600).

b. From 2-(*o*-Aminophenyl)-2H-benzotriazole (XIII) and Peracetic Acid. 2-(*o*-Aminophenyl)-2,1,3-benzotriazole (XIII) (8.3 g, 0.04 mole) in 100 ml of chloroform was treated with 12 ml of 40% peracetic acid in a manner similar to that described above. There was obtained a total of 7.3 g of pale yellow product, mp 185–186° dec, whose infrared spectrum was identical with that of the nitroso product XII obtained from the tetraazapentalene I.

Anal. Calcd for $C_{12}H_8N_4O$: C, 64.28; H, 3.60; N, 24.99; mol wt (monomer), 224. Found: C, 63.96; H, 3.72; N, 24.56; mol wt (in ethylene chloride), 229.

Complex Formation with Dibenzotetraazapentalene (I). a. With Silver Nitrate. To a solution of 1.0 g of I in 75 ml of warm tetrahydrofuran was added a solution of silver nitrate (2 g) in acetonitrile. A yellow solid formed immediately. The mixture was stirred for 3 hr, filtered, and washed with fresh acetonitrile and chloroform (1.7 g). Recrystallization from dimethylformamide yielded a crop of yellow crystals, mp >300°.

Anal. Calcd for $[C_{12}H_8N_4 \cdot 2AgNO_3]$: C, 26.30; H, 1.47; N, 15.34. Found: C, 26.66; H, 1.44; N, 15.62.

b. With Tetracyanoquinodimethane (TCNQ). A solution of 0.4 g (0.02 mole) of TCNQ in hot acetonitrile (25 ml) was mixed with 0.41 g (0.02 mole) of the tetraazapentalene I in 25 ml of hot acetonitrile. The resulting yellow-green solution was heated at reflux for 5 min and allowed to cool slowly. A crop of dark green crystals (0.52 g) separated. *Anal.* Calcd for $C_{24}H_{12}N_8$ (1:1 complex): C, 69.89; H, 2.94; N, 27.17. Found: C, 69.90; H, 3.51; N, 27.80.

The complex is diamagnetic and exhibits a resistivity of 4.6×10^8 ohm cm. The product is decomposed to starting materials by differential solubility (in chloroform).

c. With Cuprous Cyanide. Compound I (2.08 g, 0.01 mole) and cuprous cyanide (0.89 g, 0.005 mole—as $[CuCN]_2$) were each dissolved in 25 ml of warm N-methylpyrrolidone, mixed, and heated on a steam bath for 30 min. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was triturated in benzene, collected by filtration, and then dried. The light yellow-green solid (1.72 g, 89% yield) melted at 277–278° dec.

Anal. Calcd for $C_{14}H_8N_6Cu_2$ (1:1 complex): C, 43.42; H, 2.09; N, 21.70. Found: C, 41.14; H, 2.22; N, 20.88.

The infrared spectrum showed an absorption band at 4.65 μ (CuCN) and all the bands of I except that at 8.0 μ.

Reaction with *n*-Butyllithium. Compound I (6.5 g, 0.025 mole) in 250 ml of benzene was treated with a hexane solution of *n*-butyllithium (0.06 mole) at room temperature with stirring for 1 hr. The mixture was refluxed for 2 hr and treated with 0.07 mole of methyl iodide. After an additional hour of heating, the mixture was cooled and treated with water. The dried benzene layer was evaporated to dryness to yield a yellow solid residue (5.4 g). Portions of the product were recrystallized from various solvents including ethanol, benzene, and cyclohexane. The bright yellow crystals analyzed correctly for a monomethyl derivative X despite a broad melting point range, suggesting an isomeric mixture.

Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.25; H, 4.54; N, 25.21. Found: C, 70.26; H, 4.91; N, 24.99.

The infrared and ultraviolet spectra of the methyl derivative are very similar to those of the parent compound, indicating that the electronic system has been little altered, *i.e.*, the methyl group is attached to the benzene ring rather than to a nitrogen. The solid was chromatographed on nonalkaline Woelm alumina with benzene, benzene–methylene chloride, and finally ethyl acetate. A small quantity of sharp-melting (200–201°) product (X) was isolated from the initial eluates; λ_{max} 405 mμ (ε 44,400), 385 (24,400) 367 (7810), 324 (4620) sh 313 (2640), 310 (2975), 303 (2264), 296 (2240), and 259 (60,825).

N-Alkylations of I. a. Dibenzo-1-isopropyl-1,3a,4,6a-tetraazapentalenium Iodide (XIa). A solution of I (10 g, 0.048 mole) in 50 ml of concentrated sulfuric acid was stirred while propylene was passed in during a 20-min period. The reaction mixture was cooled with an ice bath during this period, and the reaction flask was provided with a Dry Ice–acetone condenser to prevent loss of propylene. The mixture was allowed to come to room temperature slowly, and the mixture was poured onto 800 g of ice. After a small amount of waxy material was removed by filtration, the pH of the mixture was adjusted to 8 with sodium carbonate, and the clear yellow solution was allowed to stand at room temperature for 3 days. Excess saturated aqueous sodium iodide solution was added, giving an immediate bright-yellow precipitate. The latter was collected by filtration, washed with water, and dried *in vacuo* at room temperature. The product XIa (16 g, 88%) melted with decomposition at 140° after recrystallization from methylene chloride. *Anal.* Calcd for $C_{15}H_{15}N_4I$: C, 47.63; H, 4.00; N, 14.81; I, 33.55. Found: C, 47.92; H, 4.16; N, 14.93; I, 34.22.

b. Dibenzo-1-methyl-1,3a,4,6a-tetraazapentalenium Iodide (XIb). A mixture of 5 g (0.0024 mole) of I and 200 ml of methyl iodide was heated at reflux for 1 week. The orange crystals (2 g, 24%) which separated were collected by filtration and air dried, mp 191° dec (to blue melt).

Anal. Calcd for $C_{13}H_{11}N_4I$: C, 44.59; H, 3.17; N, 16.00; I, 36.24. Found: C, 45.00; H, 3.53; N, 15.60; I, 36.01.

c. Dibenzo-1-methyl-1,3a,4,6a-tetraazapentalenium Methosulfate. A mixture of 15 g (0.072 mole) of I and 140 ml of freshly distilled dimethyl sulfate was heated at 150° for 45 min, cooled, and treated with 1 l. of ether containing 80 ml of methylene chloride. The ether solution was separated by decantation, and the insoluble oil was further extracted with a mixture comprising 400 ml of

methylene chloride and 400 ml of acetone, whereupon the oil changed to a light-tan solid (18.3 g). The latter was recrystallized from a methanol–acetone–ether mixture, yielding nearly colorless crystals of the methosulfate, mp 199° dec.

Anal. Calcd for $C_{14}H_{14}N_4O_4S$: N, 16.76; S, 9.59. Found: N, 16.51; S, 9.71.

2-(*o*-Aminophenyl)-2H-4,5,6,7-tetrahydrobenzotriazole (XXV). A solution of 1.3 g of 2-(*o*-aminophenyl)-2H-benzotriazole (XIII) in 25 ml of acetic acid was hydrogenated at 40 psi using 100 mg of 10% palladium-on-charcoal catalyst. The solution was filtered, and solvent was removed under vacuum. An ethereal solution of the residue was washed with dilute sodium carbonate solution. Evaporation of the organic layer yielded colorless crystals of the tetrahydro derivative (XXV) (85% yield) which, after recrystallization from petroleum ether, melted at 78–80°; λ_{max}^{EtOH} 320 mμ (ε 7200), 269 (9610), and 238 (20,500).

Anal. Calcd for $C_{12}H_{14}N_4$: C, 67.26; H, 6.59; N, 26.15. Found: C, 67.43; H, 6.51; N, 26.06.

N-Acetyl derivative XIV, mp 121–122°, was identical with the product formed when the tetraazapentalene I was hydrogenated in acetic acid at 125° with 5% palladium-on-carbon and a hydrogen pressure of 1000 psi.

2-(*o*-Azidophenyl)-5,6,7,8-tetrahydrobenzotriazole (XXVI). Compound XXV (10.3 g, 0.05 mole) in 40 ml of concentrated hydrochloric acid and 50 ml of water was diazotized at 5° with a solution of sodium nitrite (3.7 g, 0.05 mole) which was added dropwise. The mixture was stirred for an additional 90 min and filtered to remove a small amount of undissolved solid. The cold, stirred filtrate was treated dropwise with an aqueous solution of sodium azide (3.3 g, 0.05 mole). A gummy solid separated, and nitrogen was evolved. The reaction mixture was stirred rapidly at 5° for 90 min, during which time the product was transformed to a grainy, light yellow solid (6.3 g). The azide melted at 48.5–49.6° after recrystallization from pentane.

Anal. Calcd for $C_{12}H_{12}N_6$: C, 59.98; H, 5.03; N, 34.98. Found: C, 60.49; H, 4.96; N, 35.27.

5,6-Tetramethylene-2,3-benzo-1,3a,4,6a-tetraazapentalene (XXII). A solution of 10.3 g of crude azide XXVI in 200 ml of decalin was heated at reflux for 1 hr, during which time 1 mole of nitrogen was evolved. Most of the decalin was removed by distillation at atmospheric pressure. On cooling, the concentrated solution set to a brownish yellow crystalline mass. The solid was collected by filtration and recrystallized from hexane. A crop of yellow nonfluorescent crystals (mp 131.5–133°, 4.35 g) was obtained. An additional 0.9 g of product was isolated from the concentrated mother liquor; λ_{max}^{EtOH} 351 mμ (ε 28,200), 278 (2850), and 242 (25,900).

Anal. Calcd for $C_{12}H_{12}N_4$: C, 67.90; H, 5.70; N, 26.40. Found: C, 68.32; H, 5.94; N, 26.25.

2-(*o*-Nitrophenyl)-2H-triazole (XXIII). A mixture of 6.9 g of 1,2,3-triazole, 14.1 g of *o*-fluoronitrobenzene, and 10.6 g of sodium carbonate (anhydrous) in 45 ml of N,N-dimethylformamide was heated to reflux for 65 hr. The product was poured onto ice and extracted with ether. The ether extract was dried with magnesium sulfate, and solvent was removed under reduced pressure. The residue was distilled (oil bath) through a Vigreux column to yield 11.6 g (62%) of 2-(*o*-nitrophenyl)-2H-triazole, bp 97–99° (40 μ). The pot residue was nearly pure 1-(*o*-nitrophenyl)-1H-triazole (XXIV, 20%) which was also prepared by the reaction of acetylene with *o*-nitrophenyl azide.[11] The 2H-triazole XXIII was recrystallized from pentane–benzene (5:3) at −20° to obtain colorless crystals, mp 27.0–27.5°.

Anal. Calcd for $C_8H_6N_4O_2$: C, 50.53; H, 3.18; N, 29.47. Found: C, 50.87; H, 3.30; N, 29.66.

2,3-Benzo-1,3a,4,6a-tetraazapentalene (XXI). A solution of 10.5 g (0.05 mole) of 2-(*o*-nitrophenyl)-2H-triazole (XXIII) and 25 g of triethyl phosphite in 25 ml of xylene was heated for 6 hr in an oil bath maintained at 150°. The product was vacuum distilled, and 6.81 g of crude 2,3-benzo-1,3a,4,6a-tetraazapentalene (XXI) was collected at 100° (50 μ). The distillate solidified and was recrystallized from ethanol to yield 5.5 g (70%) of colorless crystals which melted at 107–108°. A sample recrystallized three times from ethanol melted at 108.8–109.7°; ν_{max} (KBr) 3150 m, 3110 m, 1515, 1472 m, 1460, 1370 vs, 1349, 1270, 1210, 1168, 1097, 995 m, 920 vs, 890 m, 792 m, 746 vs, 731 vs, 703 m, and 688 vs cm^{-1}; $\lambda_{max}^{10\%\ HCl_{aq}}$ 311 mμ (ε 14000), 267 (5450), 238 (9390), and 222 (14970).

Anal. Calcd for $C_8H_6N_4$: C, 60.75; H, 3.82; N, 35.42. Found: C, 60.67; H, 4.22; N, 35.19.

6-(α,β,β-Tricyanovinyl)-2,3-benzo-1,3a,4,6a-tetraazapentalene (XXVII). A solution of 0.84 g of XXI (0.0053 mole) in 5 ml of N,N-dimethylformamide (DMF) was treated with a solution of 0.70 g of tetracyanoethylene in 10 ml of DMF. The initial green color of the solution gradually turned to deep red. The solution was warmed on the steam bath for 30 min and was poured over 100 g of ice. The solid product was separated by filtration, water washed, and dried under a nitrogen stream (0.85 g). The deep maroon crystals of tricyanovinyl derivative XXVI melted at 264–265.5° after recrystallization (with some difficulty) from a mixture of 125 ml of benzene and 100 ml of hexane; λ_{max}^{EtOH} 505 mμ (ε 27,500), 383 (6300), 322 (12,100), 308 (9750), and 231 (16,620).

Anal. Calcd for $C_{13}H_5N_7$: C, 60.23; H, 1.94. Found: C, 61.00; H, 2.06.

N-Methyl-2,3-benzo-1,3a,4,6a-tetraazapentalenium Iodide (XXVIII). A solution of 0.30 g of 2,3-benzo-1,3a,4,6a-tetraazapentalene in 10 ml of methyl iodide was sealed in a glass tube and heated at 100° for 20 hr. The tube was cooled and opened, and the solid product was separated by filtration and washed with carbon tetrachloride. The yellow, crystalline, water-soluble product XXVIII melted at 193.6–194° dec; $\lambda_{max}^{H_2O}$ 318 mμ (ε 14,850), 268 (4560), and 225 (33,300).

Anal. Calcd for $C_9H_9N_4I$: C, 36.02; H, 3.02; N, 18.68. Found: C, 36.04; H, 3.02; N, 18.90.

Reactions of Dibenzotetraazapentalene Derivatives with Cuprous Cyanide. a. 2-(2′-Amino-5′-nitrophenyl)-2H-benzotriazole (XIX) from IIc. A mixture of IIc (5.0 g, 0.02 mole), 1.8 g (0.02 mole) of cuprous cyanide, and 20 ml of N-methylpyrrolidone was heated under reflux for 2 hr and poured into a mixture of 10 ml of ethylenediamine and 50 ml of water. The solid was collected by filtration, washed with water, then methanol, and finally dried (6.4 g). The solid was continuously extracted with benzene in a Soxhlet apparatus for 12 hr. From the evaporated benzene extract there was obtained 2.3 g (46%) of XIX. An analytical sample, purified by benzene recrystallization and sublimation, melted at 251–253°; λ_{max}^{EtOH} 350 mμ (ε 20,900), 295 (19,100), and 235 (16,600).

Anal. Calcd for $C_{12}H_9N_5O_2$: C, 56.47; H, 3.55; N, 27.44: Found: C, 55.61; H, 3.58; N, 27.26.

b. 2-(2′-Amino-5′-cyanophenyl)-2H-benzotriazole (XV) from IIb. A mixture of 2.87 g (0.01 mole) of IIb, 1.6 g (0.009 mole) of cuprous cyanide, and 20 ml of N-methylpyrrolidone was heated at reflux for 4 hr and poured into a dilute hydrochloric acid solution containing 5 g of ferric chloride. The mixture was warmed on a steam bath for 15 min and then cooled, and the solid was collected by filtration. The pasty solid was triturated with methanol and extracted with hot benzene. From the latter, 1.5 g (63% yield) of solid, whose infrared spectrum was consistent with the structure for XV, was isolated. Two benzene recrystallizations yielded crystalline XV, mp 232–234°; λ_{max}^{EtOH} 362 mμ (ε 13,500), 300 (12,700), 276 (36,100), and 233 (28,300).

Anal. Calcd for $C_{13}H_9N_5$: C, 66.37; H, 3.86; N, 29.77. Found: C, 66.78; H, 3.91; N, 30.39.

Compound XV was prepared by an independent route by refluxing a mixture of 2-(2′-acetamido-5′-bromophenyl)-2H-benzotriazole (2.5 g) (XVIII) (see below) with cuprous cyanide (1 g) in 20 ml of N-methylpyrrolidone. The reaction mixture was poured into an ethylenediamine–water mixture (10:100, v/v). The solid (1.42 g) was collected by filtration and recrystallized from methanol, mp 210–213°.

Hydrolysis of the 2-(2′-acetamido-5′-cyanophenyl)-2H-benzotriazole (XX) with 1 equiv of sodium hydroxide (2 *N* solution) gave the amine XV, which was identical with the product obtained from IIb.

c. 2-(2′-Amino-5′-carboxamidophenyl)-2H-benzotriazole (XVI). A mixture of XV or XX with sulfuric acid was heated at 100° for 30 min, then poured onto ice; mp 282–284.5° from aqueous ethanol.

Anal. Calcd for $C_{13}H_{11}ON_5$: C, 61.65; H, 4.38; N, 27.66. Found: C, 61.85; H, 4.20; N, 27.60.

d. 2-(2′-Aminophenyl)-5′,5- (or 4-) -dicyano-2H-benzotriazole (VIa) from IIIb. A mixture of IIIb (3.7 g, 0.01 mole), 2.7 g (0.03 mole) of cuprous cyanide, and 20 ml of N-methylpyrrolidone was heated at reflux for 2 hr, then poured into a mixture of 50 g of ethylenediamine and 300 ml of water. The solid was collected on a filter, washed thoroughly with water, then extracted repeatedly with hot benzene. Evaporation yielded 1.2 g (45%) of product. Two recrystallizations from toluene–hexane yielded a yellow crystalline solid VIa, mp 244–246°; λ_{max}^{EtOH} 381 mμ (ε 13,600), 280 (29,900), and 247 (28,100).

Anal. Calcd for $C_{14}H_8N_6$: C, 64.61; H, 3.09; N, 32.29. Found: C, 64.64; H, 3.00; N, 31.95.

2-(2′-Acetamido-5′-bromophenyl)-2H-benzotriazole (XVIII). To a stirred solution of 84 g (0.357 mole) of 2-(*o*-acetamidophenyl)-2H-

benzotriazole (XVII) in 1.2 l. of glacial acetic acid containing 2 molar equiv of fused sodium acetate was added 112 g (0.70 mole) of bromine. The mixture was stirred at 50° for 3 hr, cooled, and diluted with water. Crude XVIII was obtained in 90% yield. Two recrystallizations from methanol yielded a colorless product, mp 179.5–180°; λ_{max}^{EtOH} 320 (sh) mμ (ε 11,100), 299 (16,450), 265 (17,800), 257 (sh) (16,200), and 299 (29,000).

Anal. Calcd for $C_{14}H_{11}BrN_4O$: C, 50.78; H, 3.35; N, 16.92: Found: C, 50.64; H, 3.39; N, 17.21.

The proton nmr spectrum is in accord with structure XVIII.

Aromatic Azapentalenes. III. 1,3a,6,6a-Tetraazapentalenes

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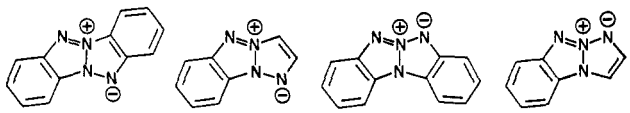
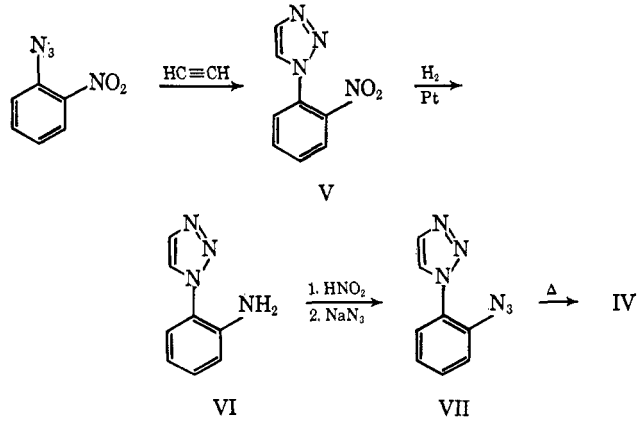
Abstract: Syntheses of mono- and dibenzo-1,3a,6,6a-tetraazapentalene derivatives are described. A new ring-closure reaction leading to these as well as to the isomeric 1,3a,4,6a-tetraazapentalenes is based on the trialkyl phosphite deoxygenation of *o*-nitrophenyltriazole derivatives.

Previous papers in this series have described the preparation of several new aromatic azapentalene ring systems: dibenzo-1,3a,4,6a-tetraazapentalene (I),[1-3] 2,3-benzo-1,3a,4,6a-tetraazapentalene (II),[3] and dibenzo-1,3a,6,6a-tetraazapentalene (III).[2] This paper discusses the preparation and chemical properties of mono- and dibenzo-1,3a,6,6a-tetraazapentalenes and their derivatives.



I II III IV

Synthetic Routes to 1,3a,6,6a-Tetraazapentalenes. The synthesis of III by the pyrolysis of 1-(*o*-azidophenyl)-1H-benzotriazole has been previously reported.[2] Pyrolysis of 1-(*o*-azidophenyl)-1H-triazole in a similar fashion led to the monobenzo-1,3a,6,6a-tetraazapentalene IV in 44% yield. The cyclization is probably effected by interaction of the 2p electrons of the center nitrogen of the triazole ring with the developing nitrene during pyrolysis. The precursory nitrophenyltriazole V was prepared *via* reaction of *o*-azidonitrobenzene with acetylene. Catalytic reduction of V gave the corresponding amine VI, which was converted to azide VII by diazotization and treatment with azide ion.



Benzo-1,3a,6,6a-tetraazapentalene (IV) is a colorless, nearly odorless solid with a dipole moment of 4.73 D. at 25° in benzene. Like the dibenzo derivative III, IV exhibits three main regions of absorption in the ultraviolet (Table I).

Table I. Ultraviolet Absorption Maxima for 1,3a,6,6a-Tetraazapentalenes

III		IV		II		XVII	
λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
356	39,800	335	16,100	343	21,800	343	16,400
343	32,500	326	15,200			335	16,600
280	8,250	293	4,110	278	3,040	299	4,080
271	5,900	285	3,760			290	3,440
234	35,000	232	28,600	236	27,700	236	29,800

The ultraviolet absorption peaks of the isomeric benzo-1,3a,4,6a-tetraazapentalene II are included in the table for comparison.[3] It will be noted that the long-wavelength absorption of II is more intense and is hypsochromically shifted with respect to the corresponding absorption in IV. A similar effect has been noted in the dibenzo analogs I and III. The origins of these differences will be discussed in a subsequent communication.[4]

Several alternative procedures for generating these tetraazapentalenes directly from the more accessible nitro compounds were examined. An unsuccessful attempt was made to effect a deoxygenative ring closure of 1-(*o*-nitrophenyl)-1H-benzotriazole (VIII) to III by pyrolysis with ferric oxalate.[5,6] However, deoxygena-

(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).
(3) R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, *ibid.*, **89**, 2626 (1967).
(4) Y. T. Chia and H. E. Simmons, *ibid.*, **89**, 2638 (1967).
(5) H. C. Waterman and D. L. Vivian, *J. Org. Chem.*, **14**, 289 (1949).
(6) R. A. Abramovitch and K. A. H. Adams, *Can. J. Chem.*, **39**, 2516 (1961). These authors reported the successful ring closure of 2-(*o*-nitrophenyl)pyridine to pyrido[1,2-*b*]indazole.