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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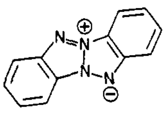
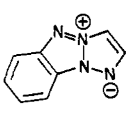
Received November 17, 1966

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.

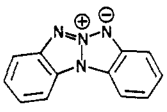
Previous papers in this series have described the preparation of several new aromatic azapentalene ring systems: dibenzo-1,3a,4,6a-tetraazapentalene (I),[1-3] 2,3-benzo-1,3a,4,6a-tetraazapentalene (II),[3] and dibenzo-1,3a,6,6a-tetraazapentalene (III).[2] This paper discusses the preparation and chemical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



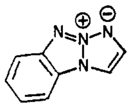
I



II

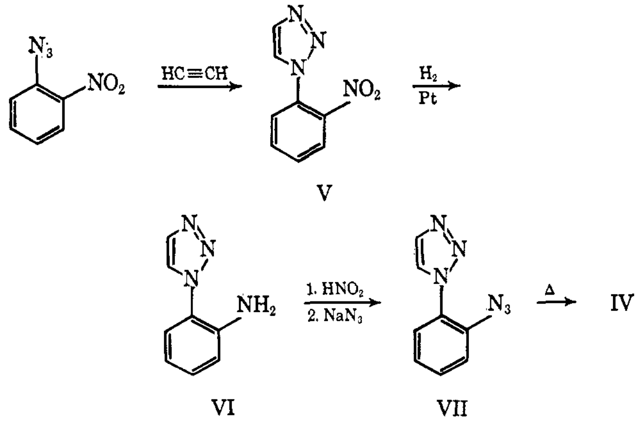


III



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-

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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).

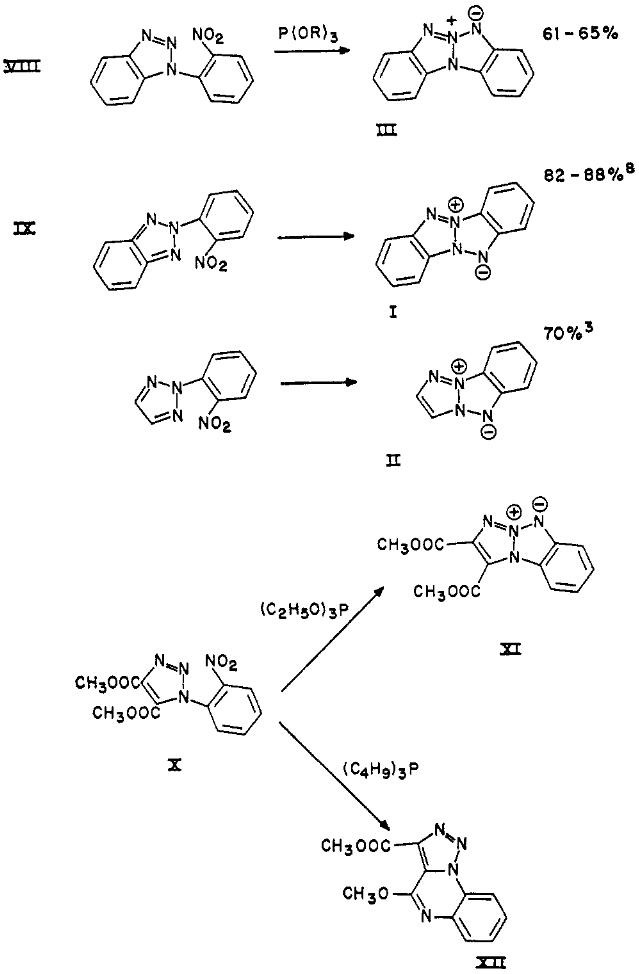
(3) R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, *ibid.*, **89**, 2626 (1967).

(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).

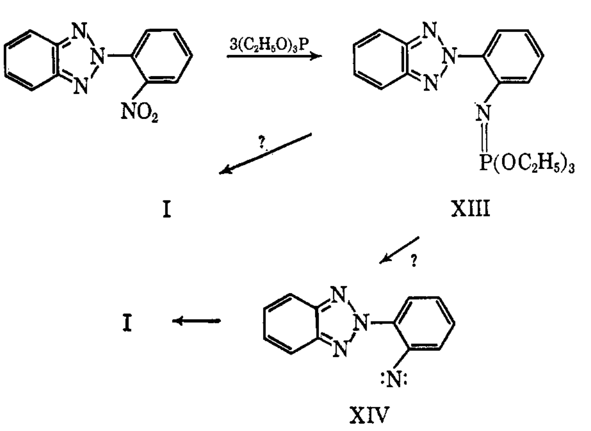
(6) R. A. Abramovitch and K. A. H. Adams, *Can. J. Chem.*, **39**, 2516 (1961). These authors reported the successful ring closure of 2-(*o*-nitrophenyl)pyridine to pyrido[1,2-*b*]indazole.

tive cyclization of this triazole with phosphites and phosphines proceeded smoothly.[7] When VIII was heated with excess triethyl phosphite in xylene, tetraazapentalene III was isolated from the cooled solution in good yield and high purity. The by-products appeared to be very soluble in aromatic hydrocarbon solvents, facilitating the isolation of III. The *o*-nitrophenyltriazoles IX and X likewise gave the corresponding tetraazapentalenes in fair to good yields.



This reaction is importantly affected by the nature of the phosphorus compound. For instance, the reaction of VIII or IX with tributylphosphine is more rapid than with the less nucleophilic triethyl phosphite. The yields and product purities are much higher with the latter reagent, however. When the phosphine was employed with the ester X, attack at both the carbonyl oxygen atom and the nitro group occurred. The resulting product has been tentatively assigned the triazoloquinoxaline structure XII.

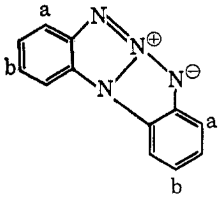
Several intermediates are possible for these reactions. A univalent nitrogen species XIV may form by removal of oxygen atoms from the nitro groups. A prior formation of phosphinimine (*e.g.*, XIII) with subsequent elimination of triethyl phosphite may likewise lead to the nitrene XIV. Finally, intramolecular displacement of the phosphite group in XIII by a triazole nitrogen may lead directly to the azapentalene.



The last two sequences were shown to be highly unlikely when the phosphinimine XIII (prepared from the corresponding azide and triethyl phosphite) failed to yield I on pyrolysis in refluxing xylene.

Chemical Properties. The chemical reactivity of the dibenzotetraazapentalene III (*e.g.*, in electrophilic substitution reactions) parallels closely that reported for the isomeric 1,3a,4,6a system I.[3]

Mononitration occurred in 25% nitric acid at room temperature. Dinitro and tetranitro derivatives formed at 0–5° in 70 and 90% nitric acid, respectively. Treatment of III with chlorine or chlorosulfonic acid yielded the corresponding dichloro and bis(chlorosulfonyl) derivatives, respectively. Although the positions of substitution in these electrophilic reactions have not been rigorously proved, charge density and localization energy considerations similar to those employed for the 1,3a,4,6a isomer I[2,4] favor positions a and b as sites for attack.



The tri- and tetranitro derivatives of I and III gave positive Janovski reactions,[9] while the mono- and dinitro derivatives did not. Two nitro groups of the tetranitro derivative were readily replaced by azide ion, in a manner similar to that of the 1,3a,4,6a system, to yield the corresponding dinitro diazide.

III reacted slowly with methyl iodide at 100° to yield an unstable adduct which could be isolated in an impure state. On the other hand, treatment of a solution of III in concentrated sulfuric acid with propylene led smoothly to an N-isopropyl methosulfate derivative, which was converted to the iodide for characterization.

Catalytic hydrogenation of III (palladium catalyst at 125°) resulted in a rupture of the pentalene moiety with

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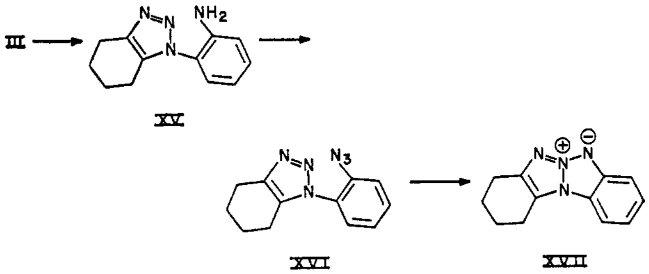
(7) The generation of nitrene-like intermediates in the phosphite deoxygenation of nitro compounds has been discovered independently in other laboratories: (a) J. I. G. Cadogan and M. Cameron-Wood, *Proc. Chem. Soc.*, 361 (1962); (b) J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 4831 (1965); (c) B. M. Lynch and Y-Y. Hung, *J. Heterocyclic Chem.*, **2**, 218 (1965); (d) R. J. Sundberg, *Tetrahedron Letters*, 477 (1966).

(8) Studies in these and in other laboratories[7b] indicate that I can be obtained in good yield by the reaction of *o,o'*-dinitroazobenzene with trialkyl phosphites. The nitrophenyltriazole IX may be an intermediate in this reaction.

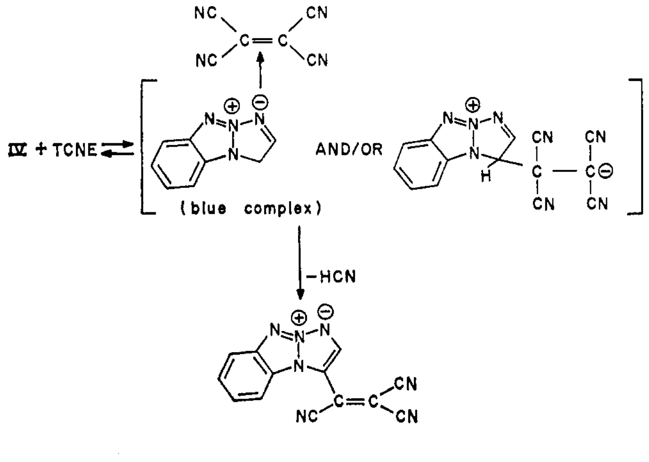
(9) Aromatic systems with two or more *meta*-positioned nitro groups generally react at the doubly activated position (*ortho* to one nitro group, *para* to the other) with alkaline acetone to form an intensely colored ion. See, for instance, R. Foster and R. K. Mackie, *Tetrahedron*, **18**, 1131 (1962); **19**, 691 (1963).

subsequent hydrogenation of the benzo ring. The resulting 1-(*o*-aminophenyl)-4,5,6,7-tetrahydro-1H-benzotriazole (XV) was then reconverted in the usual manner (*via* the azide XVI) to a new tetraazapentalene derivative XVII. Compound XVII exhibits an ultraviolet spectrum very similar to that of the monobenzo derivative IV (see Table I).



The unsubstituted monobenzopentalene IV exhibits distinctly greater reactivity toward electrophiles than does its dibenzo analog. Nitration leads rapidly to a dinitro derivative which, under slightly more vigorous conditions, is converted to a trinitro compound. The trinitro derivative gives a positive Janovski reaction while the dinitro does not.[9] This suggests that the first two nitro groups enter the tetraazapentalene ring and the benzo ring, respectively. More vigorous conditions result in the introduction of a second nitro group in the benzo ring. Nmr studies have verified these conclusions. Unlike its dibenzo analog, IV reacts readily with methyl iodide to form a stable N-methyl derivative. The ultraviolet spectrum of the latter in water is very similar to that of the benzotetraazapentalene IV in hydrochloric acid, indicating that the sites of protonation and methylation are the same. Insoluble metal complexes were formed with a wide variety of heavy metal salts.

In contrast to the dibenzo derivatives I and III, the monobenzotetraazapentalene IV reacts readily with the weak electrophile tetracyanoethylene (TCNE) in N,N-dimethylformamide (DMF). A deep blue complex forms initially in concentrated solution, followed by evolution of hydrogen cyanide and the development of the purple color of the tricyanovinyl derivative XVIII.[10] The loss of hydrogen cyanide is much slower in tetrahydrofuran solution, and the blue color of the complex persists for many hours in solution. The following reaction sequence is suggested.



Electrophilic attack by tetracyanoethylene on IV undoubtedly occurs at the pentalene ring rather than on the benzo substituent. This conclusion is supported by the nonoccurrence of a similar reaction with either of the dibenzo analogs I and III or with the substituted monobenzotetraazapentalene XVII. The latter compound forms a similar (isolable) blue complex; however, lack of an available position on the pentalene ring precludes the subsequent collapse of the complex to the corresponding tricyanovinyl derivative.

Experimental Section

All melting points are corrected. Nmr spectra were obtained with a Varian A-60 spectrometer. Saturated deuteriochloroform solutions with tetramethylsilane as an internal standard were used unless otherwise noted. Peak center positions are reported as $\tau = 10 - \delta_H$ ppm; number of protons (by integration) is given in parentheses.

Infrared spectra were determined in potassium bromide wafers with a Perkin-Elmer 21 spectrophotometer unless otherwise noted. Peak positions are reported in wavenumbers; m and w indicate medium and weak intensities, respectively. Ultraviolet spectra were determined in ethanol. Dipole moments were determined in benzene solution at 25°.

***o*-Azidonitrobenzene.** The following modification of the procedure of Noelting and Michel[11] was used.

A solution of 48.4 g of *o*-nitroaniline in 500 ml of hot 19% hydrochloric acid was poured while stirring onto 500 g of ice contained in a 4-l. beaker immersed in a methanol–ice bath. The resulting slurry was diazotized by the slow addition of an aqueous solution of 26 g of sodium nitrite while the temperature was maintained at 0–5°. The solution was stirred for 1 hr at this temperature, ice was added, and the solution was filtered quickly and returned to the 4-l. beaker. A solution of 24.5 g of sodium azide in 75 ml of water was added dropwise at 0–7°. A layer of ether on the solution minimized frothing. The solution was stirred for 2 hr, and ether was added to dissolve the solid. The ether layer was separated, washed with water, and dried over magnesium sulfate. Solvent was removed under reduced pressure to a final volume of 150 ml, and a total of 100 ml of warm pentane was added slowly to the warm ether solution with stirring. A total of 53 g (98%) of *o*-azidonitrobenzene (mp 51–52°) was obtained in two crops.

1-(*o*-Nitrophenyl)-1H-triazole (V). A solution of 50 g of *o*-azidonitrobenzene in 300 ml of acetone in a 1-l. autoclave was heated with acetylene gas under a pressure of *ca.* 10 atm at 50° for 6 hr, at 60° for 6 hr, and at 70° for 6 hr. The autoclave was cooled and vented between cycles to remove accumulated nitrogen. Solvent was removed under reduced pressure, and the product was crystallized from a mixture of 150 ml of benzene and 50 ml of hexane to yield 34 g (59%) of V in two crops. The major by-product was benzofuroxan, which can optionally be distilled from the crude reaction mixture (oil bath at 135° (1 mm)). A portion of V recrystallized from benzene–hexane melted at 94.3–95.1°; λ 290 (sh) mμ (ϵ 1650) and 223 (sh) (13,800); ν_{max} 3180 w, 3130 w, 1620 m, 1595 m, 1535, 1517 m, 1458 w, 1360, 1327, 1308, 1234, 1202 w, 1130 w, 1105 w, 1086 m, 1045, 1026, 988 m, 958 w, 948 m, 885 m, 854, 795, 784, 748, 714 m, 704 m, and 698 m cm^{-1}.

Anal. Calcd for $C_8H_6N_4O$: C, 50.53; H, 3.18. Found: C, 50.61; H, 3.18.

1-(*o*-Aminophenyl)-1H-triazole (VI). A solution of 25 g of V in 150 ml of *n*-propyl alcohol was hydrogenated at 40 psig with 0.2 g of platinum oxide. The product was flash distilled (oil bath; bp 135° (0.2 mm)) to yield 18.4 g (87%) of VI, mp 38.7–39.3°, ν_{max} (neat) 3420, 3310, 3200 m, 3120 m, 1620, 1512, 1478 m, 1460, 1430 w, 1320, 1272 m, 1225, 1195 m, 1158 m, 1120 w, 1090 m, 1040, 1025, 980, 788 m, 750, 718, and 670 m cm^{-1}.

Anal. Calcd for $C_8H_8N_4$: C, 59.98; H, 5.03; N, 34.98. Found: C, 59.96; H, 5.21; N, 35.25.

1-(*o*-Azidophenyl)-1H-triazole (VII). A solution of 37.3 g of VI in 250 ml of concentrated hydrochloric acid was poured onto 750 g of ice contained in a 2-l. beaker cooled to −30° with a Dry Ice–

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(10) Reactive benzene derivatives such as phenols, N,N-dimethylaniline, etc., are reported to form tricyanovinyl derivatives under similar conditions. See, for instance, J. R. Roland and B. C. McKusick, *J. Am. Chem. Soc.*, **83**, 1652 (1961).

(11) E. Noelting and O. Michel, *Ber.*, **26**, 86 (1893).

carbon tetrachloride–chloroform bath. A solution of 18 g of sodium nitrite in 50 ml of water was added dropwise at −20 to −22°. The solution was stirred for 2 hr, and a solution of 18 g of sodium azide in 50 ml of water was added dropwise at −20 to −22°. Ether was added to minimize frothing. After being stirred for 3 hr, the solution was warmed to room temperature, neutralized with sodium hydroxide solution, and extracted with ether. The ether layer was dried over magnesium sulfate, and solvent was removed under vacuum to a volume of 300 ml. Hexane (250 ml) was added, and 22.2 g (51%) of white crystals of VII was collected. A portion recrystallized from ether melted at 70.3–71.2°; λ 335 (sh) mμ (ϵ 82), λ_{max} 254 mμ (ϵ 12,100), λ 235 (sh) mμ (ϵ 11,700); ν_{max} 3120, 2250, 2220, 1600 m, 1510 m, 1480 m, 1470 m, 1318, 1270 w, 1236, 1195 m, 1160 m, 1133 w, 1108 m, 1090 m, 1042, 1032 m, 986 m, 955 w, 945 w, 810, 758, 735 w, 710 m, and 700 m cm^{-1}.

Anal. Calcd for $C_8H_6N_6$: C, 51.61; H, 3.25; N, 45.15. Found: C, 51.91; H, 3.40; N, 44.88.

Benzo-1,3a,6,6a-tetraazapentalene (IV). A solution of 25.4 g (0.136 mole) of the azide VII in 75 ml of *o*-dichlorobenzene was heated in an oil bath at 175–200°. When gas evolution (0.14 mole total) had ceased, the solvent was removed under reduced pressure (2.0 mm) at 80° in a rotary film evaporator. The residue in methylene chloride was eluted continuously through a column of 400 ml of Woelm neutral alumina. (A heavy-liquid continuous extraction apparatus can be conveniently adapted for this purpose.) Solvent was distilled from the eluate to yield 11.24 g of IV. Recrystallization from ethanol yielded 9.45 g (44%) in two crops, mp 121.6–122.2°, λ_{max} (concentrated hydrochloric acid) 311 mμ (ϵ 14,100), 267 (5450), 238 (9390), and 222 (14,970) (see Table I for ethanol solvent); ν_{max} 3150 m, 1620 m, 1582 w, 1512 m, 1478, 1440 w, 1375, 1340, 1330 m, 1305 m, 1280 m, 1196 w, 1186 w, 1157, 1137, 1110 w, 1080 m, 1007, 983 w, 978 m, 863 m, 810, 747, 734, 727, and 700 m cm^{-1}.

Anal. Calcd for $C_8H_6N_4$: C, 60.75; H, 3.82; N, 35.43. Found: C, 60.97; H, 3.38; N, 35.71, 35.76.

This compound could also be prepared in 36% yield by heating to reflux overnight a solution of 1.14 g of V and 4.0 g of trimethyl phosphite in 10 ml of xylene.

Silver nitrate complex was formed in 89% yield from acetonitrile solutions of IV and silver nitrate; white crystals, mp 200° dec.

Anal. Calcd for $C_8H_6N_4 \cdot AgNO_3$: C, 29.29; H, 1.84; N, 21.35. Found: C, 29.29, 29.19; H, 2.45, 2.10; N, 21.44.

Cupric chloride complex was prepared in 95% yield by the addition of 1.0 g of cupric chloride dihydrate to a solution of 0.50 g of IV in 50 ml of warm ethanol; blue–black crystals, mp 179–182°.

Anal. Calcd for $C_{12}H_8N_4 \cdot CuCl_2$: C, 32.84; H, 2.07; N, 19.15; Cu, 21.72. Found: C, 33.73; H, 2.14; N, 19.16; Cu, 21.04.

Mercuric chloride complex was formed in 27% yield from 0.6 g of mercuric chloride and a solution of 0.2 g of IV in 5 ml of ethanol; white crystals, mp 170–172°.

Anal. Calcd for $C_8H_6N_4HgCl_2$: C, 22.36; H, 1.41; N, 13.04. Found: C, 22.63; H, 1.84; N, 13.18.

Manganese chloride complex was prepared in 20% yield from 1.97 g of manganese chloride tetrahydrate and 1.58 g of IV in 150 ml of warm ethanol; yellow, water-sensitive crystals, mp 310–315°.

Anal. Calcd for $C_8H_6N_4MnCl_2$: C, 33.83; H, 2.13; Mn, 19.34. Found: C, 33.98; H, 2.26; Mn, 19.25.

Dimethyl 1-(*o*-Nitrophenyl)-1H-triazole-4,5-dicarboxylate (X). A solution of 41 g of *o*-azidonitrobenzene and 40 g of dimethyl acetylenedicarboxylate in 25 ml of chloroform was held at 30° for 15 days. The crystalline adduct (35.7 g) was separated by filtration and washed with 1:3 chloroform–hexane. The combined filtrates and washings were warmed to 70° for 2 hr, and volatile products were removed under reduced pressure (100° (0.5 mm)). The residue was recrystallized from 80% methanol to yield an additional 23.8 g of adduct. A portion recrystallized successively from methanol–water and from benzene–hexane melted at 87.5–88°; ν_{max} 1730, 1610 m, 1590 w, 1535, 1505 m, 1452 m, 1440 m, 1378 m, 1348, 1305, 1258, 1220, 1208, 1168 w, 1107, 1080 w, 1008, 962 m, 937 m, 853, 830 m, 810 m, 788, 748, 728 w, and 695 m cm^{-1}.

Anal. Calcd for $C_{12}H_{10}N_4O_6$: C, 47.06; H, 3.29; N, 18.30. Found: C, 47.20; H, 3.44; N, 18.36.

Dimethyl 4,5-Benzo-1,3a,6,6a-tetraazapentalene-2,3-dicarboxylate (XI). Under nitrogen a solution of 7.0 g of triethyl phosphite in 50 ml of toluene was added over 24 hr to a refluxing solution of 6.12 g of X in 100 ml of toluene. The solution was heated to reflux for 6 hr, and solvent and volatile products were removed under reduced pressure. The resulting oil crystallized partially. The white crystals (1.35 g) were dried on a clay plate, and after successive recrystallization from methanol and benzene–hexane melted at 127.0–128.4°; λ_{max} 353 mμ (ϵ 14,400), 284 (9650), 250 (18,900), and 223 (16,200); ν_{max} 4140 w, 4100 w, 3960 w, 1740, 1705, 1570 w, 1522, 1480 m, 1445 m, 1430 m, 1395 m, 1382, 1345, 1344, 1315 w, 1295, 1238, 1212 m, 1195 m, 1160 m, 1122 m, 1048 m, 1030 w, 985 w, 970, 892 w, 862, 808, 756, and 714 m cm^{-1}.

Anal. Calcd for $C_{12}H_{10}N_4O_4$: C, 52.85; H, 3.68; N, 20.43. Found: C, 52.86; H, 3.76; N, 20.50.

Methyl 4-Methoxy-*v*-triazolo[3,4-*a*]quinoxaline-3-carboxylate (XII). A solution of 8.46 g of tributylphosphine in 50 ml of benzene was added slowly over 50 hr to a refluxing solution of 6.12 g of V in 50 ml of toluene. The resulting gray crystals (1.97 g) were dried on a clay plate and washed with pentane. After two recrystallizations from methanol the white crystalline product melted at 193.8–195.0°; λ_{max} 331 mμ (ϵ 11,420), 317 (13,400), 305 (8250), 291 (7500), 280 (7530), 265 (8520), 249 (13,900), and 222 (24,000); ν_{max} 3100 w, 2950 w, 1635, 1578, 1552, 1490 m, 1480 m, 1455, 1385, 1335, 1320 m, 1283 w, 1265, 1247, 1230 m, 1210, 1186, 1137 m, 1095, 1007, 970, 900 m, 793 m, 769, 764, 735 m, 720 w, 713 m, and 688 w cm^{-1}; nmr τ 1.9–2.4 (4), multiplet, 5.65 (3), and 5.83 (3).

Anal. Calcd for $C_{12}H_{10}N_4O_3$: C, 55.81; H, 3.90; N, 21.70. Found: C, 55.85; H, 4.02; N, 21.55.

Dinitrobenzo-1,3a,6,6a-tetraazapentalene. Compound IV (2.0 g) was added in small portions to 100 ml of 70% nitric acid at 0–5° with stirring. The solution was stirred for 15 min at 0° and was then allowed to warm to room temperature. The resulting orange crystals (1.95 g) of dinitro derivative were separated by filtration, and after recrystallization from 400 ml of acetone melted at 277.5–280°; λ_{max} 420 mμ (ϵ 20,900), 348 (6130), 338 (6130), 312 (11,900), 278 (sh) (8300), 270 (9380), and 250 (11,900).

Anal. Calcd for $C_8H_4N_6O_4$: C, 38.72; H, 1.62; N, 33.87. Found: C, 38.74; H, 1.83; N, 34.09.

Trinitrobenzo-1,3a,6,6a-tetraazapentalene. Compound IV (5.7 g) was added in small portions to 75 ml of 95% (yellow fuming) nitric acid at 0–5° with stirring. The solution was warmed to room temperature, poured onto ice, and filtered. The olive-colored product weighed 7.50 g. After successive recrystallizations from acetone and 1:1 acetone–ethanol, it melted at 305–306.5° dec; λ_{max} 434 mμ (ϵ 27,900), 335 (5300), and 294 (16,400); nmr (1:1 CD_3SOCD_3–CH_3COCH_3) τ 0.43 (1), doublet (J = 2.1 cps), 0.60 (1), 0.82 (1), doublet (J = 2.1 cps).

Anal. Calcd for $C_8H_9N_7O_6$: C, 32.77; H, 1.03; N, 33.45. Found: C, 32.62; H, 1.12; N, 33.51.

Tricyanovinylbenzo-1,3a,6,6a-tetraazapentalene (XVIII). A solution of 0.84 g of IV in 10 ml of dimethylformamide (DMF) was treated with a solution of 0.70 g of tetracyanoethylene in 10 ml of DMF. The initial greenish blue color of the complex gradually changed to purple. The solution was warmed on the steam bath for 30 min and was then poured onto 200 ml of crushed ice and stirred for 15 min. The precipitated purple crystals (0.85 g) were filtered and washed with water. A portion after recrystallization from benzene–hexane melted at 236–237.4°; λ_{max} (acetonitrile) 534 mμ (ϵ 24,700), 333 (6470), 310 (6310), 278 (4730), and 225 (19,050); ν_{max} 3120 w, 2210, 1565 w, 1522, 1493, 1440, 1432, 1413 m, 1360, 1313, 1270, 1207, 1170, 1152, 890 w, 863 w, 808, 782 m, 757, 748 m, 737 m, 694 m, and 668 w cm^{-1}.

Anal. Calcd for $C_{13}H_5N_7$: C, 60.23; H, 1.94; N, 37.83. Found: C, 60.01; H, 2.23; N, 37.62.

1(6)-Methylbenzo-1,3a,6,6a-tetraazapentalenium Iodide. A mixture of 0.30 g of IV and 10 ml of methyl iodide was sealed in a glass tube and heated for 20 hr at 100°. The yellow crystalline product (0.46 g) was separated by filtration and washed with carbon tetrachloride, mp 193.6–194° dec. The product was very soluble in water, slightly soluble in acetonitrile; λ_{max} (H_2O) 309 mμ (ϵ 12,600), 222 (38,100); λ_{max} (ethanol) 318 mμ (ϵ 14,300), 268 (4610), 245 (sh) (8340), and 225 (31,500); nmr (D_2O) τ 1.02 (1), doublet (J = 2 cps), 1.43 (1), doublet (J = 2 cps), 1.70 (1), multiplet, 2.13 (3), multiplet, and 5.70 (3); ν_{max} 3070, 3020 m, 1620 m, 1530, 1490 w, 1472 w, 1450, 1430, 1380, 1340 m, 1315 m, 1185, 1162 m, 1135, 1012 m, 935 m, 880 w, 860 w, 840, 788 m, 757 vs, and 700 cm^{-1}.

Anal. Calcd for $C_9H_9N_4I$: C, 36.02; H, 3.02; N, 18.68. Found: C, 36.04, 36.27; H, 3.02, 3.17; N, 18.90.

Dibenzo-1,3a,4,6a-tetraazapentalene (I)[2,8] was isolated in 82–88% yield by treating IX[2] with 3.1–4.1 moles of triethyl or tri-*n*-butyl phosphite for 17 hr in refluxing xylene. When the solution had cooled, nearly pure I crystallized. When IX was heated for 3 hr in refluxing xylene with 3.0 moles of tri-*n*-butylphosphine, I was isolated in 75% yield.

Dibenzo-1,3a,6,6a-tetraazapentalene (III)[2] was isolated in 61–65% yield when VIII was heated for 20 hr in refluxing xylene with 3.2–

3.5 moles of triethyl phosphite. When triphenyl phosphite (neat) was substituted, only 17% of III was isolated after 96 hr at 100°.

Silver nitrate complex was prepared in 100% yield by mixing a solution of 11 g of III in 700 ml of warm tetrahydrofuran with a solution of 20 g of silver nitrate in 100 ml of acetonitrile; white crystals, mp 282.5–283.5°.

Anal. Calcd for $C_{12}H_8N_4 \cdot AgNO_3$: C, 38.12; H, 2.13; N, 18.53. Found: C, 38.23, 38.47; H, 2.57, 2.45; N, 18.40.

Cupric chloride complex was formed in 87% yield by treating a solution of 0.42 g of III in 150 ml of warm ethanol with 50 g of cupric chloride dihydrate; bronze crystals, mp 281–284° dec.

Anal. Calcd for $C_{12}H_8N_4 \cdot CuCl_2$: C, 42.06; H, 2.36; N, 16.35; Cu, 18.54. Found: C, 43.10; H, 2.69; N, 16.47; Cu, 17.62.

Triethyl N-[*o*-(Benzo-2H-triazol-2-yl)phenyl]phosphorimidate (XIII). A solution of 16.6 g of triethyl phosphite in 50 ml of benzene was added dropwise to a solution of 20.8 g of 2-(*o*-azidophenyl)-2H-benzotriazole[2] in 200 ml of benzene. When nitrogen evolution had ceased, unreacted phosphite and solvent were removed under reduced pressure. The oily residue (32 g) was crystallized from hexane at 5°, mp 28.7–31°; λ_{max} 284 mμ (ϵ 11,420) and 237 (16,500); ν_{max} (neat) 3060 w, 2980 m, 2900 w, 1602, 1570 w, 1508 m, 1475; 1443 m, 1382, 1360 m, 1340 m, 1292 m, 1263 w, 1215 m, 1170 m, 1164 m, 1132 m, 1112 m, 1025, 968, 828 w, 790 m, 748, and 705 m cm^{-1}.

Anal. Calcd for $C_{18}H_{23}N_4O_3P$: C, 57.76; H, 6.26; N, 14.97. Found: C, 57.81, 57.90; H, 5.98, 6.31; N, 15.09.

Although this compound decomposed slowly when heated at 150°, the infrared spectrum of the product provided no evidence for the presence of III.

Nitrodibenzo-1,3a,6,6a-tetraazapentalene. A solution of 5.0 g of III in 200 ml of methylene chloride was stirred vigorously with 70 ml of 25% nitric acid for 7 days. The organic layer was separated and dried with magnesium sulfate. Solvent was removed, and the residue was crystallized from 2.5 l. of boiling 95% ethanol to yield 1.23 g of golden yellow platelets. After two recrystallizations from chloroform the mononitro derivative melted at 285–286°; λ_{max} 410 mμ (ϵ 24,800), 313 (11,700), 275 (8930), and 230 (30,700).

Anal. Calcd for $C_{12}H_7N_5O_2$: C, 56.90; H, 2.79; N, 27.66. Found: C, 57.15; H, 2.85; N, 27.91.

Dinitrodibenzo-1,3a,6,6a-tetraazapentalene. Five grams of III was added in small portions to 100 ml of concentrated (70%) nitric acid at 0–5°. A vigorous reaction occurred, and 6.4 g of crude dinitro dervative separated. A portion recrystallized from acetone melted at 400–403° dec; λ_{max} 424 mμ (ϵ 36,700), 330 (12,600), 274 (14,300), and 237 (32,400).

Anal. Calcd for $C_{12}H_6N_6O_4$: C, 48.33; H, 2.03; N, 28.18. Found: C, 48.06; H, 2.01; N, 28.36.

Tetranitro-1,3a,6,6a-tetraazapentalene was prepared by the cautious addition of III or its mono- or dinitro derivatives (described above) to ice-cold yellow fuming (95%) nitric acid. The solution] was warmed briefly and poured onto ice. The resulting tetranitro derivative was recrystallized from boiling acetone, mp 400° dec; λ_{max} 450 mμ (ϵ 54,400), 375 (3240), 308 (17,180), 260 (sh) (ϵ 12,980), and 207 (39,200); ν_{max} 3070 m, 1630 m, 1595 m, 1535, 1452 m, 1410, 1375, 1325, 1258, 1190 m, 1165 m, 1116, 1073 m, 948 m, 869 m, 832 m, 773, 718 m, 740, 728, and 690 cm^{-1}

Anal. Calcd for $C_{12}H_4N_8O_8$: C, 37.12; H, 1.04; N, 28.86. Found: C, 36.81; H, 1.46; N, 28.66.

Dibenzo-1,3a,6,6a-tetraazapentalenebis(sulfonyl chloride). One-half gram of III was dissolved cautiously in 10 ml of chlorosulfonic acid, and the temperature of the solution was slowly raised to 90°. After 30 min at this temperature the solution was cooled and was poured *cautiously* onto ice. The solid product was separated by filtration, washed thoroughly with water, and air dried. After two recrystallizations from acetic acid–carbon tetrachloride, the pale yellow crystals melted at 263–265° dec.

Anal. Calcd for $C_{12}H_6N_4S_2O_4Cl_2$: C, 35.58; N, 13,83; S, 15.83. Found: C, 35.62; N, 13.53; S, 15.29.

1-Isopropyldibenzo-1,3a,6,6a-tetraazapentalenium Iodide. A stream of propylene was passed for 20 min through a solution of 4.3 g of III in 25 ml of concentrated sulfuric acid at 0°. The solution was allowed to warm to room temperature, and the gas stream was continued for 20 min. The cloudy solution was poured onto 400 g of ice. After standing overnight, the solution was neutralized with sodium bicarbonate and then allowed to stand for 2 weeks. It was then filtered, and a solution of 15 g of sodium iodide in 50 ml of water was added. The whitish precipitate (4.2 g) was separated by filtration. A portion recrystallized from methylene chloride–hexane melted at 174° dec; λ_{max} 276 mμ (ϵ 5480), 338 (22,900), and 348 (sh) (ϵ 21,000); nmr (CD_3SOCD_3) τ 0.9–2.4 (8), multiplet, 4.20 (1), septet ($J = 6.5$), and 8.17 (6), doublet.

Anal. Calcd for $C_{15}H_{15}N_4I$: C, 47.63; H, 4.00; N, 14.81. Found: C, 47.50; H, 3.99; N, 14.54.

1-(*o*-Aminophenyl)-4,5,6,7-tetrahydro-1H-benzotriazole (XV). A solution of 45 g of III in 650 ml of ethanol was hydrogenated at 125° and 1000 psi with 3 g of 5% palladium-on-carbon catalyst. The resulting solution was filtered, and solvent was removed under reduced pressure. The residual oil was crystallized from a mixture of 85 ml of benzene and 150 ml of hexane to yield 14.1 g (30%) of XV in two crops. A portion recrystallized from benzene–hexane melted at 115.5–116.2°; λ_{max} 299 mμ (ϵ 3470) and 231 (15,000); λ_{max} 3460, 3380, 3210 m, 2970, 2950, 2850 w, 1635, 1585 m, 1512, 1475 m, 1462 m, 1450 m, 1382 m, 1315, m, 1292 m, 1270 w, 1250 m, 1240 w, 1218, 1158 m, 1136 m, 1088, 1035 w, 1004, 963 m, 934, 848 m, 767, 721 w, and 703 w cm^{-1}.

Anal. Calcd for $C_{12}H_{14}N_4$: C, 67.26; H, 6.58; N, 26.16. Found: C, 67.49; H, 6.91; N, 26.25.

1-(*o*-Azidophenyl)-4,5,6,7-tetrahydro-1H-benzotriazole (XVI). A solution of 13.9 g of XV in 250 ml of 22% hydrochloric acid was poured onto 150 g of ice and was diazotized at −20 to −25° with a solution of 4.8 g of sodium nitrite in 30 ml of water. The mixture was stirred for 1 hr at −25°, and a solution of 5.0 g of sodium azide in water was added slowly at −20 to −25°. Ether was added to suppress foaming. The resulting solution was allowed to warm slowly to room temperature. It was made alkaline with potassium hydroxide, and the precipitated solid (11.7 g, 75%) was recrystallized from benzene–hexane; mp 105–106.5°; λ_{max} 248 mμ (ϵ 12,300).

Anal. Calcd for $C_{12}H_{12}N_6$: C, 59.98; H, 5.03; N, 34.98. Found: C, 60.53; H, 5.27; N, 35.72.

4,5-Tetramethylene-2,3-benzo-1,3a,6,6a-tetraazapentalene (XVII). A solution of 8.0 g of XVI in 50 ml of *o*-dichlorobenzene was added slowly to 40 ml of *o*-dichlorobenzene in a flask immersed in an oil bath maintained at 180°. After 1 hr nitrogen evolution had ceased. Solvent was removed under reduced pressure (70° (0.3 mm)), and the residue was dissolved in methylene chloride and eluted continuously with methylene chloride through a column of Woelm neutral alumina.

The eluate was evaporated under reduced pressure, and the resulting nearly white crystals (3.75 g, 53%) were recrystallized from ethanol and from methanol to yield shiny colorless leaflets melting at 176.5–177.5°. A second crystalline modification could also be isolated (see Table I for ultraviolet absorptions); ν_{max} 3060, 2940, 2850 w, 1615, 1582, 1510, 1480, 1445, 1432 m, 1405 m, 1372, 1335 m, 1245 m, 1230, 1208 m, 1128, 1080 m, 1020, 995, 970, 922, 893, 872, 837, 818, m, 744, 731, 732, and 693 m cm^{-1}.

Anal. Calcd for $C_{12}H_{12}N_4$: C, 67.90; H, 5.70; N, 26.40. Found: C, 68.07; H, 5,71; N, 26.17, 26.41, 26.42.

This compound, like III, formed a blue complex with tetracyanoethylene, but did not react further in DMF solution, and so did not yield a tricyanovinyl analog of XVIII.