The mass spectrum of **4** determined on a CEC 21-130A instrument at 70 ev showed a parent peak at *m/e* 106, a base peak at 78, and other intense peaks at 91, 39, and 105.

3-N,N-Dimethyltricyclo[3.3.0.0^{2,6}]octylamino Oxide (34). To a 50-ml flask was added **32** (0.718 g, 4.75 mmoles), methanol (2 ml), and hydrogen peroxide (30%, 2 ml), and the reaction mixture was let stand at room temperature for 2 days. A small amount of platinum black was added to destroy any remaining hydrogen peroxide. The solvent was removed under reduced pressure, leaving a white solid (0.86 g). The amine oxide was recrystallized from tetrahydrofuran to yield crystalline **34** (0.76 g, 95%), mp 104–106°, no dec.

Pyrolysis of Amine Oxide 34. Pyrolysis of the amine oxide **34** was accomplished by heating in a round-bottomed flask equipped with a capillary nitrogen inlet and connected through a short column to two traps in series, cooled in Dry Ice. The nitrogen pressure was reduced to 10 mm, and most of the amine oxide decomposition took place between 180 and 210°. An nmr spectrum of the crude volatile products showed that only about 5% was the hoped for tricyclooctene **4**, while the rest seemed to be aromatic.

Aromatic Azapentalenes. I. Dibenzo-1,3a,4,6a-tetraazapentalene and Dibenzo-1,3a,6,6a-tetraazapentalene.[1] New Heteroaromatic Systems

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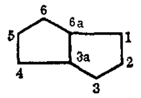
Abstract: The new heteroaromatic compounds, dibenzo-1,3a,6,6a-tetraazapentalene (III) and -1,3a,4,6a-tetraazapentalene (II), have been prepared in good yield by the thermal and photochemical decompositions of the *o*-azido phenyl derivatives of 1H- and 2H-benzotriazoles, respectively. The physical and spectral properties of these unusually stable pentalene analogs are described, as well as their structure determination. The mode of formation of the tetraazapentalene and the role of the annular nitrogen atoms in providing a $4n + 2$ π electron system are discussed.

In recent years, there has been great interest in formulating and demonstrating aromatic character for a variety of carbocyclic and heterocyclic systems.[2] Aromatic stability has been demonstrated in cyclopropenium, cyclopentadienide, benzene, tropylium, and cyclononatetraenide, as well as in nonalternant and hetero systems, such as ferrocene, tropolone, and azulene.[3] All of these compounds contain 2, 6, 10, etc., π electrons and illustrate an extension of Hückel's argument that cyclic molecules having $4n + 2$ π electrons possess closed shells of electrons and large delocalization energies.[4]

The hydrocarbon pentalene, an 8 π electron system, has never been synthesized despite repeated efforts.[5] Condensed pentalenes have been prepared and found to possess no special stability; for example, dibenzopentalene is reported to exhibit olefinic properties around the central pentalene nucleus, which undergoes polymerization, addition of bromine, etc.[5b]

The azapentalenes are of special interest since their properties are governed to a striking extent by the orientation of the hetero atoms. Thus, azapentalenes



I

with pyridine-type nitrogens at the nonfused positions (*e.g.*, 1–6 of compound I) in either or both rings contain 8 π electrons and are expected to be nonaromatic.

Paul and Weise found that both 2,3-benzo-1-azapentalene and 5,6-benzo-1-azapentalene are brown, unstable materials which could not be isolated pure.[6]

Kato and Ohta[8] were unsuccessful in an attempt to prepare the 8 π electron dibenzo-1,4-diazapentalene from diindole. Treibs[9] reported the preparation of this derivative through dehydrogenation of diindole; however, this work was recently reported[10] to be erroneous.

The preparation of the highly stable, heteroaromatic compound, dibenzo-1,3a,4,6a-tetraazapentalene (II), was described earlier.[11a] Recently, we have synthe-

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[1] These compounds may be named as 5,11-dehydro-5H,11H-benzotriazolo[2,1-*a*]- and 5,7-dehydro-5H,7H-benzotriazolo[1,2-*a*]-benzotriazole, respectively. The trivial name of azapentalenes is employed in this and subsequent papers in order to call attention to the central rings, to which these systems owe so much of their properties.

[2] Excellent reviews of these topics have appeared recently. See, for instance: (a) "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959; (b) M. E. Vol'pin, *Russ. Chem. Rev.*, **29**, 129 (1960).

[3] Leading references to recent works appear in E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 1941 (1965).

[4] E. Hückel, *Z. Physik.*, **70**, 204 (1931).

[5] (a) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936); (b) C. T. Blood and R. P. Linstead, *ibid.*, 2255, 2263 (1952); C. C. Chuen and S. W. Fenten, *J. Org. Chem.*, 23, 1538 (1958); (c) J. D. Roberts and W. F. Gorham, *J. Am. Chem. Soc.*, **74**, 2278 (1952); (d) M. Gates and S. P. Malchick, *ibid.*, **79**, 5546 (1957).

[6] H. Paul and A. Weise, *Tetrahedron Letters*, 163 (1963). These authors dispute an earlier report of the synthesis of 2,3-benzo-1-azapentalene.[7]

[7] W. Treibs, *Naturwissenschaften*, **46**, 170 (1959).

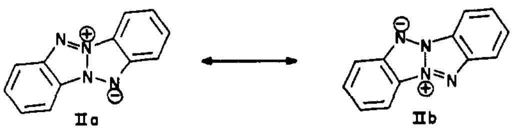
[8] H. Kato and M. Ohta, *Bull. Chem. Soc. Japan*, **34**, 357 (1961).

[9] W. Treibs, *Naturwissenschaften*, **48**, 130 (1961).

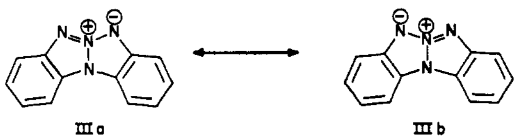
[10] H. Paul and A. Weise, *Z. Chem.*, **4**, 147 (1964).

[11] (a) R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.*, **84**, 2453 (1962). Since this report, several other examples of aromatic azapentalenes have appeared; *e.g.*, (b) T. W. G. Solomons and F. W. Fowler, *Chem. Ind.* (London), 1462 (1963); (c) T. W. G. Solomons, F. W. Fow-

sized a new tetraazapentalene system, dibenzo-1,3a,6,6a-tetraazapentalene (III), which exhibits aromatic properties very similar to II. Unlike azapentalenes which do not contain bridgehead nitrogen atoms, these tetraazapentalenes can only be represented as hybrids of a number of charge-separated forms, *e.g.*, IIa,b and IIIa,b. The four nitrogen atoms, two of which occupy the bridgehead positions, contribute six electrons to the π system, and the parent structures may be considered in terms of their relationship with the isoelectronic naphthalene and the carbocyclic analog, pentalene dianion.[12] Other examples of aromatic azapentalenes with nitrogens at the bridgehead have recently been described.[11b-f]



IIa IIb



IIIa IIIb

This paper presents the synthesis, structure, and properties of II and III as well as a discussion of their relationship to each other.

Results and Discussion

Dibenzo-1,3a,4,6a-tetraazapentalene (II) is a yellow, crystalline solid, mp 237–238°, which exhibits yellowish green fluorescence when viewed under ultraviolet light. It is only weakly basic, being insoluble in dilute mineral acids, but dissolves in concentrated sulfuric acid; however, II precipitates when the pale yellow acid solution is diluted with water. The crystalline methiodide is formed very slowly on prolonged heating with methyl iodide, a reaction which is readily reversible at higher temperatures. Compound II has no detectable dipole moment in benzene solution.

The isomeric dibenzo-1,3a,6,6a-tetraazapentalene (III) is a colorless solid, mp 255°, which does not exhibit visible fluorescence in solution. Although this isomer is also weakly basic, it appears to be slightly more soluble than II in mineral acids and does not form a methiodide readily. Compound III has a dipole moment in benzene of 4.36 D.

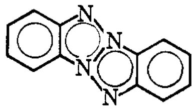
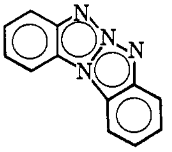
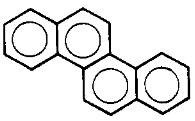
Both heteroaromatic systems are little affected by heating in solvents below 300° and can be sublimed unchanged at atmospheric pressure. Both are also recovered unchanged after treatment with warm alkali or with sulfuric acid.

Precision heat of combustion and heat of sublimation measurements for these isomeric dibenzotetraazapentalenes show that the heat of formation of III is 11 kcal/mole greater than that of II.[13]

The dibenzotetraazapentalenes exhibit an interesting variety of chemical reactions which reflect the dual pyrrole–pyridine nature of the annular nitrogen atoms. Thus, electrophilic substitution reactions were observed on both benzenoid and heterocyclic rings. These reactions and others of the tetraazapentalenes are described in separate papers.

The ultraviolet spectra of the two dibenzotetraazapentalenes show many of the characteristic similarities and differences that have been noted[14] between aromatic heterocyclics and their carbocyclic analogs. Both II and III exhibit three main regions of absorption in the ultraviolet spectrum. In this respect, they resemble the annularly condensed tetracyclic hydrocarbons, *e.g.*, the benzophenanthrenes, such as chrysene. Principal absorptions of II and III are given in Table I with those of chrysene. The major regions of absorption are separated in the table, those in each group clearly forming a vibrational subsystem.

Table I. Absorption Maxima of the Two Dibenzotetraazapentalenes and Chrysene[a] in Ethanol

					
λ_{max}, mμ	ϵ	λ_{max}, mμ	ϵ	λ_{max}, mμ	ϵ
402	38,300	356	39,700	360	630
382	23,300	343	32,300	352	360
364	7,740			343	630
323	4,110	280	8,250	320	14,200
				306	13,500
308	2,850	271	5,900	295	12,100
				281	12,100
255	63,300	234	25,000	268	
				257	
				241	
				220	

[a] W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* (London)' **A152,** 299 (1935).

The long-wavelength absorptions of the tetraazapentalenes are about 50 times more intense than the α band of chrysene. Similar comparisons have been noted by Badger and his co-workers[14] for many aromatic azahydrocarbon–hydrocarbon combinations. It is noteworthy that the absorptions of 1,3a,4,6a-tetraazapentalene (II) show an appreciable shift to longer wavelengths compared to the 1,3a,6,6a isomer (III) or chrysene, particularly in the long-wavelength region. The spectrum of III also contains less fine structure than that of II.

A. **Dibenzo-1,3a,4,6a-tetraazapentalene (II).** This compound is prepared in excellent yield by the thermal or photochemical decomposition of *o,o'*-diazidoazobenzene (IV) (see Chart I). The yellow diazide IV, mp 116–117° dec, is formed in greater than 90% yield on treatment of tetraazotized *o,o'*-diaminoazobenzene (V) with 2 equiv of sodium azide. When a solution of IV in a high-boiling solvent, such as decahydronaphtha-

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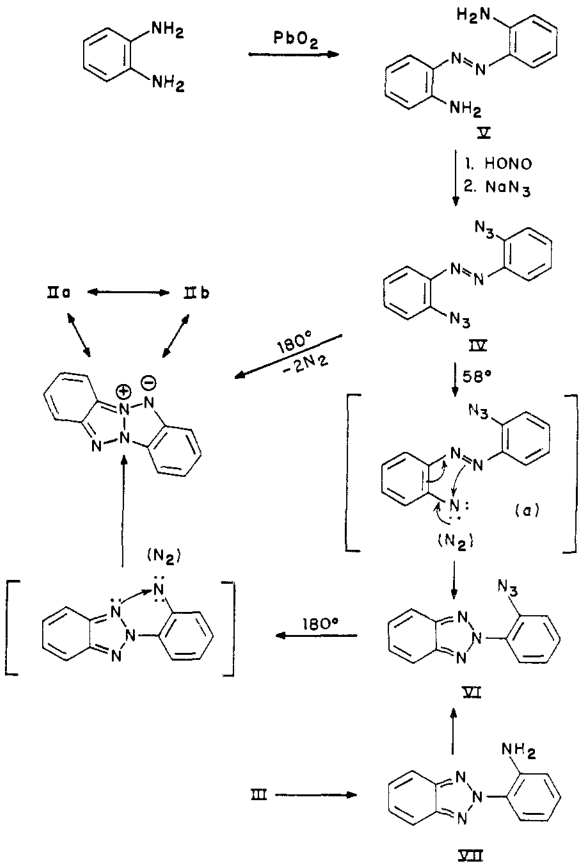
ler, and J. Calderazzo, *J. Am. Chem. Soc.*, **87**, 528 (1965); (d) R. Pfleger, E. Garthe, and K. Rauer, *Ber.*, **96**, 1827 (1963) (this paper reports several compounds which had been previously characterized[11e] as tetraazacyclooctatetraenes); (e) R. Pfleger and H.-G. Hahn, *Ber.*, **90**, 2411 (1957): (f) S. Trofimenko. *J. Am. Chem. Soc.*, **87**, 4393 (1965); **88,** 5588 (1966); (g) T. W. G. Solomons and C. F. Voight, *J. Am. Chem. Soc.*, **87**, 5256 (1965); **88**, 1992 (1966).

(12) (a) T. J. Katz and M. Rosenberger, *ibid.*. **84**, 865 (1962); (b) T. J. Katz. M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

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

(14) G. M. Badger, R. S. Pearce, and R. Pettit, *J. Chem. Soc.*, 3199 (1951).

Chart I



lene or *o*-dichlorobenzene, is heated at 180°, 2 moles of nitrogen is smoothly evolved. From the cooled, concentrated mixture, long, yellow needles of II are precipitated.

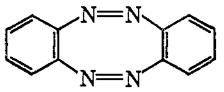
It was found, however, that the nitrogen was liberated in two distinct stages, 1 mole at the surprisingly low temperature of 58° and the second mole at approximately 170°. Thus, when *o,o'*-diazidoazobenzene was heated in refluxing acetone or benzene for 2 hr, the orange-red color characteristic of the azo derivative disappeared. The crystalline product which was isolated in good yield still contained an azido group. The solid, mp 77–78°, was identified as 2-(*o*-azidophenyl)-2H-benzotriazole (VI).

The infrared spectrum of this material was quite similar to those of a number of 2-arylbenzotriazoles. An absorption was noted at approximately 10.3 μ in each of the 2(aryl)-2H-benzotriazoles prepared in this study. The spectrum of VI also contained characteristically strong peaks at 4.75 μ for the azido function. The structure of VI was confirmed by an independent synthesis in which *o,o'*-diaminoazobenzene was oxidized with cupric sulfate[15] in pyridine to form 2-(*o*-aminophenyl)-2H-benzotriazole (VII), mp 97–98°. Diazotization of VII followed by treatment with sodium azide gave a product, mp 77–78°, which was identical with VI.

When 2-(*o*-azidophenyl)-2H-benzotriazole was dissolved in decahydronaphthalene and heated to 160–170°, another mole of nitrogen was evolved and II was obtained in nearly quantitative yield. These transformations were also obtained when benzene solutions of either the diazidoazobenzene or 2-(*o*-azidophenyl)-2H-benzotriazole were exposed to sunlight for several days.

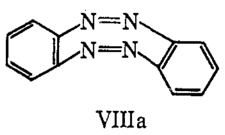
The formation of 1,3a,4,6a-tetraazapentalene II and its intermediate products may be represented by the reaction scheme shown in Chart I. The azidophenylbenzotriazole VI may form by a concerted reaction involving rupture of the N–N$_2$ bond of the first azide in IV by light or heat with concomitant cyclization or by formation, at least incipiently, of the neutral, electron-deficient species (a). To be specific, this chemistry will be discussed in terms of nitrene intermediates, although no compelling evidence for this interpretation is yet in hand. A cyclization can then be effected by the transfer of electrons from the neighboring, electron-rich, azo link to the developing univalent nitrogen to form 2-(*o*-azidophenyl)-2H-benzotriazole (VI). In a similar manner, the decomposition of the second azide group may be accompanied by interaction between the electrons of N-1 or N-3 and the electrophilic nitrogen of the decomposing azide. The higher temperature required for the second cyclization may reflect the decreased availability of electrons on the triazole nitrogens.

The planar tetraazapentalene structure of II has been conclusively established by X-ray,[16] and all chemical evidence supports this conclusion. It is important to note that the dibenzotetraazapentalene II is a valence isomer of dibenzo-1,2,5,6-tetraazacyclooctatetraene (VIII), a structure that might have been anticipated to be capable of existence. This molecule could form on decomposition of the azide VI by rupture of the N–N bond of the triazole followed by formation of a new bond between the azido nitrogen and the 1- or 3-nitrogen of the triazole. Compounds claimed to be derivatives of the simple tetraazacyclooctatetraene ring system have been described as high-melting, fluorescent solids of high thermal stability.[11e,17] Some of these derivatives were shown recently to be simple tetraazapentalene systems.[11d,18]

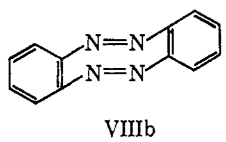


VIII

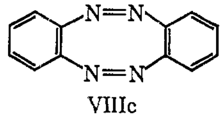
Of the three possible conformers of the tetraazacyclooctatetraene VIIIa–c, only *trans*-VIIIb and the planar VIIIc structures are possible in view of the observed zero dipole moment of the molecule. The proton nmr spectrum of II in deuteriochloroform revealed a complex ABCD pattern containing at least 15



VIIIa



VIIIb



VIIIc

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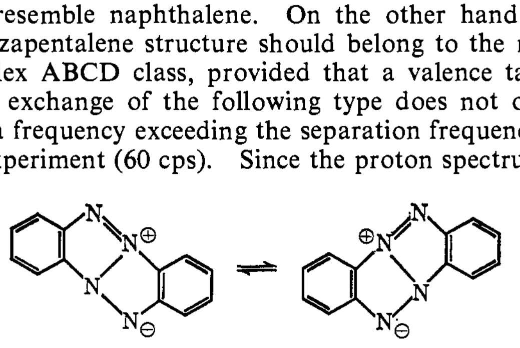
[15] E. Hoggarth in "Chemistry of Carbon Compounds," Vol. IVa, E. H. Rodd, Ed., Elsevier Publishing Co., Amsterdam, 1957, p 450.

[16] (a) M. B. Laing and K. N. Trueblood, in preparation; (b) M. E. Burke, R. A. Sparks, and K. N. Trueblood, *Acta Cryst.*, **16**, A64 (1963).

[17] R. Metze, *Angew. Chem.*, **68**, 580 (1956).

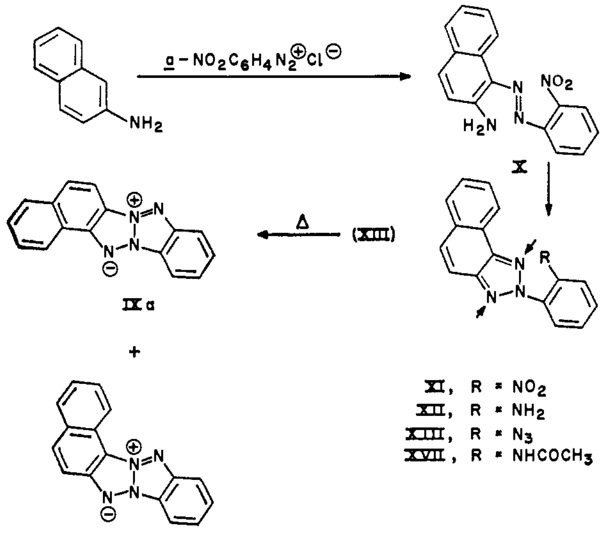
[18] M. Brufani, W. Fedeli, G. Giacomello and A. Vaciago, *Chem. Ber.*, **96**, 1840 (1963).

lines, each of which possessed fine structure. The spectrum showed no tendency to change to a symmetrical A_2B_2 pattern at higher temperatures (up to 225°). The tetraazacyclooctatetraene structures VIIIb and VIIIc would be expected to have an A_2B_2 spectrum and thus resemble naphthalene. On the other hand, the tetraazapentalene structure should belong to the more complex ABCD class, provided that a valence tautomeric exchange of the following type does not occur with a frequency exceeding the separation frequency of the experiment (60 cps). Since the proton spectrum is invariant over a wide temperature range, we conclude that the product is best represented by structure II and, furthermore, that no exchange as represented by the valence tautomerism occurs.



In order to obtain further evidence for the tetraazapentalene structure and its possible valence tautomerism, an analogous compound was prepared in which one of the benzene rings is replaced by a naphthalene nucleus with fusion at the α,β position.

The synthesis of the naphtho–benzo compound was achieved in a manner similar to that employed for the preparation of II. 1-(*o*-Nitrophenylazo)-2-naphthylamine (X) was obtained by the reaction of 2-naphthylamine and *o*-nitrophenyldiazonium chloride in dilute acid.[19] This was converted *via* cupric sulfate–ammonia oxidation to 2-(*o*-nitrophenyl)-2H-naphtho[1,2-*d*]triazole (XI) in 83% yield. Reaction of the aminoazo derivative X with thionyl chloride at 80° also gave a 70% yield of naphthotriazole XI. Reduction to the corresponding aminophenylnaphthotriazole XII was accomplished with iron powder and acetic acid (70% yield) and with alcoholic sodium sulfide (91% yield). Diazotization, followed by aqueous sodium azide treatment, yielded 2-(*o*-azidophenyl)-2H-naphtho[1,2-*d*]triazole (XIII) in 95% yield.



XI, R = NO_2
XII, R = NH_2
XIII, R = N_3
XVII, R = $NHCOCH_3$

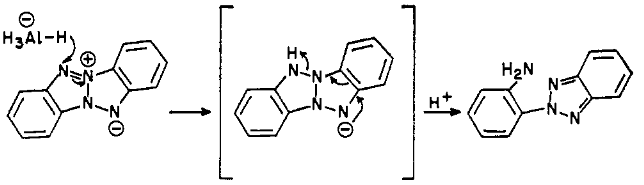
The developing nitrene intermediate derived from XIII by loss of nitrogen could now close at either of the naphthotriazole nitrogen atoms marked by arrows to give IXa and IXb. If the tetraazapentalene formulation of the nucleus is correct and if there is a large barrier for the valence tautomeric exchange, then we would expect to observe the formation of *two nonsuperimposable* isomers IXa and IXb. Formation of the naphthobenzotetracyclooctatetraene should give rise to but *one* isolable product.

Thermal decomposition of the azidophenylnaphthotriazole in *o*-dichlorobenzene or decahydronaphthalene at 170–180° proceeded smoothly with evolution of 1 mole of nitrogen to yield a yellow, crystalline product, mp 190–200°. The solid exhibited yellow-green fluorescence under ultraviolet light, similar to that of dibenzotetraazapentalene II. Chemical analyses corresponded well for $C_{16}H_{10}N_4$ despite the wide melting-point range. This suggested a mixture of at least two products of identical empirical formula. Chromatographic separation employing mixed solvents yielded two sharp-melting products, mp 212–213 (faster moving) and 243–245° (slower moving), in addition to an intermediate fraction composed of the two unseparated components. Each of the isomers analyzed correctly, and their infrared spectra showed strong similarities. A 1:1 composite of the pure isomers accounts for all of the peaks observed in the spectrum of the original, wide-melting solid.

These results clearly support the tetraazapentalene structure in preference to the tetraazacyclooctatetraene structure. Furthermore, no evidence for the interconversion of IXa and IXb could be obtained, since both are stable at their melting points.

It was of interest to determine which of the structures IXa and IXb was associated with the higher and the lower melting isomers, respectively. One method for accomplishing this was suggested by the action of lithium aluminum hydride on the tetraazapentalene nucleus.

When a solution of the dibenzotetraazapentalene II in tetrahydrofuran was treated with an excess of lithium aluminum hydride at 60°, cleavage of a N–N bond occurred with the formation, after hydrolysis, of 2-(*o*-aminophenyl)-2H-benzotriazole (VII). It is possible to rationalize this reductive ring cleavage by attack of a hydride ion at N-1 according to the scheme shown, followed by hydrolysis to yield the benzotriazole derivative VII.



Li⊕

VII

Similar treatment of each of the isomeric naphthobenzotetraazapentalenes IXa and IXb might, therefore, be expected to give different mixtures of triazoles XII and XIV, and XII and XV, respectively, as shown in Chart II. Identification of either mixture of products should determine the configuration of both isomers.

Samples of each pure isomer were treated with excess lithium aluminum hydride in tetrahydrofuran at

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(19) R. Meldola and F. Hughes, *J. Chem. Soc.*, 59, 372 (1891).

Chart II

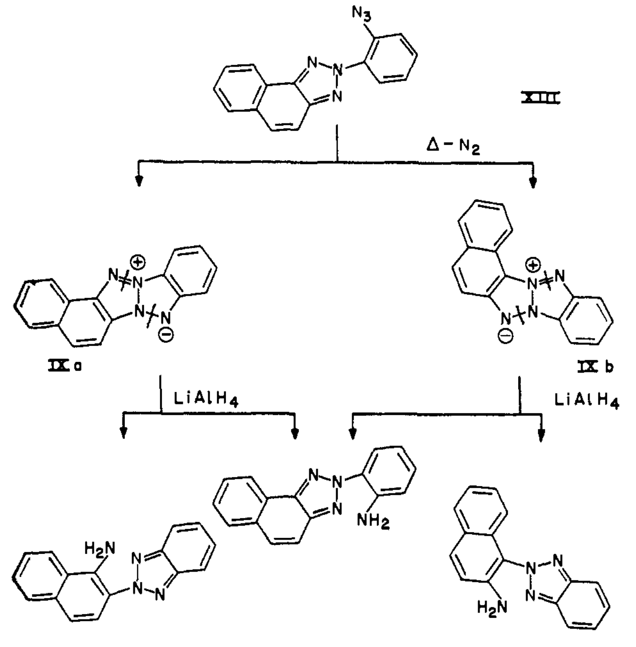
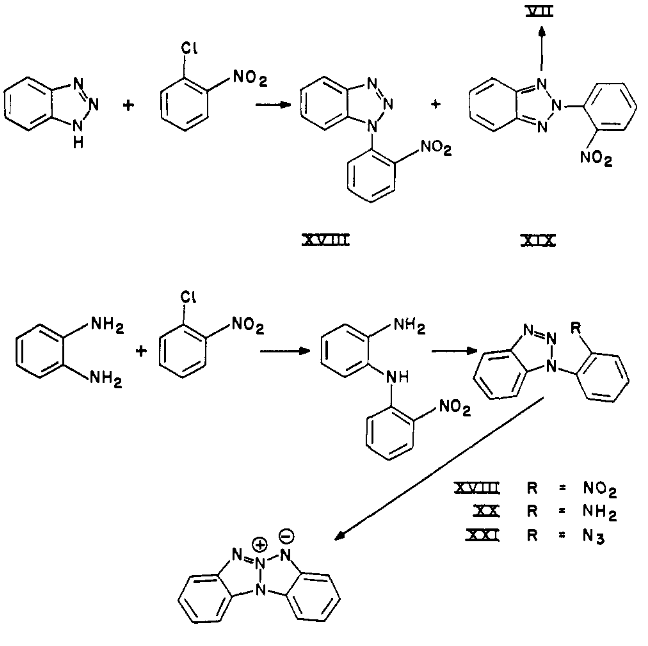


Chart III

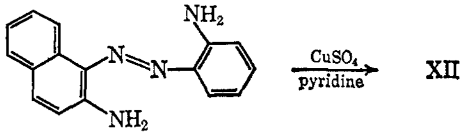


60–70° for several hours. The excess hydride was destroyed, and the reaction products were isolated in each case. Infrared spectra of the product mixtures were compared with authentic composites of XII and XV which were prepared by independent syntheses.

As expected, the similarities in spectra for the two reaction mixtures presented some difficulties. This was augmented by the formation in each case of the common product, 2-(*o*-aminophenyl)-2H-naphtho[1,2-*d*]-triazole (XII), as the major component. However, the very close similarity between a 3:1 synthetic mixture of XII and XV and the products from the low-melting isomer indicated that the latter possessed structure IXb. The infrared spectrum of the higher melting isomer's reduction products, though exhibiting many similarities to the synthetic mixture, nevertheless showed several variations including significant differences in the 10.6–11.2 μ region.

Attempted chromatographic separation of the reduction products of IXb led to the isolation of the more abundant naphthotriazole XII; however, the β-aminonaphthylbenzotriazole XV was not isolated in the pure state.

The preferential cleavage of IXa and b to give XII as the major component is not unexpected in view of its formation as the sole product from the oxidative cyclization of the diaminoazo derivative XVI with copper sulfate–pyridine.



XVI

B. Dibenzo-1,3a,6,6a-tetraazapentalene (III). This compound was prepared by the thermal decomposition of 1-(*o*-azidophenyl)-1H-benzotriazole (XXI) in a manner analogous to that employed for the preparation of II from VI (see Chart III). The isomeric tetraazapentalene (III) is a colorless, crystalline solid whose physical and chemical properties closely resemble those of II. It differs from II in its spectral properties and in having an appreciable dipole moment (4.36 D in benzene at 25°). The large dipole moment is in accord with the formulation of III as a mesoionic structure with unsymmetrically distributed charge.

The 1-(*o*-azidophenyl)-1H-benzotriazole (XXI) was prepared from the corresponding amine XX which, in turn, was obtained from the nitrophenylbenzotriazole XVIII. This latter compound was prepared originally by the reaction of *o*-chloronitrobenzene with benzotriazole, as described by Vystrcil, *et al.*,[20] We found, however, that this procedure leads to a mixture of 1H- and 2H-*o*-nitrophenylbenzotriazoles (XVIII and XIX) in yields of 39 and 16%, respectively. The two isomers (XVIII and XIX) were separated by column chromatography. The structure of isomer XIX was verified by catalytic reduction to 2-(*o*-aminophenyl)-2H-benzotriazole (VII). A more satisfactory synthesis of XVIII was achieved by diazotization of *o*-amino-*o*′-nitrodiphenylamine, in turn conveniently available from *o*-phenylenediamine by a modification of the procedure of Kehrmann and Steiner.[21]

Structure of Tetraazapentalenes. The electronic structure and spectra of the tetraazapentalenes will be discussed in more detail in a later paper.[13] Perhaps the most striking aspect of II and III is their pronounced aromatic character as revealed in their thermodynamic stability, chemical reactivity, and electronic spectra. Closely related to their stability is the question of valence isomerization with a tetraazacyclooctatetraene, as illustrated for the unsubstituted nucleus where the asterisks label the course of isomerization.

The azapentalenes Z and Z′ are clearly equivalent when unlabeled and could be interconverted by ring opening to C_1 and/or C_2. Experimentally, this does not occur for the dibenzo derivatives and means that a large energy barrier separates Z and C_1 or C_2. Since

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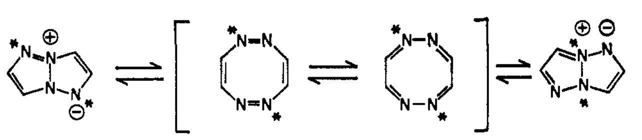
(20) B. Starkova, A. Vystrcil, and L. Starka, *Collection Czech. Chem. Commun.*, **22**, 1019 (1957).

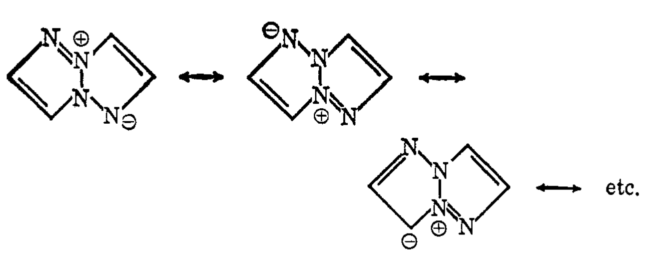
(21) F. Kehrmann and G. Steiner, *Ber.*, **34**, 3089 (1901).



Z C_1 C_2 Z'

all attempts in this laboratory and elsewhere[11d,e] to prepare tetraazacyclooctatetraenes have given tetraazapentalenes instead, it seems very likely that the latter structure is the more thermodynamically stable. In fact, the evidence thus far suggests that a tetraazacyclooctatetraene would go over exothermically and spontaneously to the corresponding tetraazapentalene.

In Z two nitrogens are pyridine-like and two pyrrole-like, so that the system contains 10 π electrons. In molecular orbital language, the aromaticity of Z results from a closed decet of π electrons in a cyclic molecule which obeys Hückel's $4n + 2$ rule. Alternatively, in valence-bond language, a high resonance energy is expected based on the observation that 12 *nonexcited* structures in the Pauling sense can be written along with a very large number of mono- and higher excited structures. The resonance should be particularly important, since many of the nonexcited structures, such as



are of comparable energy. The fact that only charge-separated structures can be written for the tetraazapentalenes seems to be intimately related to large resonance energies and aromaticity. In fact, calculations suggest that 10 π electron azapentalenes which can be written without forced charge separation are less stable than corresponding isomers which require charge-separated structures.[13]

The relative stabilities of the 8 π electron cyclooctatetraene structures and 10 π electron pentalene structures can be deduced by considering the delocalization energy of planar cyclooctatetraene and of pentalene dianion. Hückel theory predicts delocalization energies of 1.66β and 2.46β, respectively, where β is the usual resonance integral for an ethylenic double bond. Even with the assumption of a fictitious planar cyclooctatetraene whose degenerate ground state has been neglected, the stabilization energy per π electron is larger in the 10 π system (0.25β/electron) than in the 8 π system (0.21β/electron).

Precisely the same relative stability is found in the nitrogen analogs. Hückel calculations were carried out for Z, C_1, and C_2 employing reasonable parameters,[13,22] and it could be shown that delocalization is even more important in stabilizing the tetraazapentalenes than the carbon analog. It was also shown that the chemical reaction C_1 (or C_2) $\rightarrow$ Z is expected to be exothermic by a substantial degree, although accurate predictions cannot be made.

Explicit calculations also reveal that the molecular orbitals of the 1,3a,4,6a- and 1,3a,6,6a-tetraazapentalene systems are remarkably similar, and we conclude that the precise location of the nitrogen atoms in charge-separated tetraazapentalenes has only a minor effect on stability. These conclusions and those given above serve to support the view that tetraazapentalenes must be considered truly aromatic molecules.

Experimental Section[23]

***o,o′*-Diaminoazobenzene** (V). To a stirred mixture of 45 g (0.5 mole) of *o*-phenylenediamine and 2 l. of benzene was added 239 g (1.0 mole) of lead dioxide. After 1 hr the mixture was brought to reflux and maintained thus for 3 hr. The insoluble lead salts were removed by filtration and the deep orange filtrate was cooled. Concentrated hydrochloric acid (150 ml) was added to the latter with stirring, and the solid which precipitated was collected by filtration. The solid, suspended in cold water (300–400 ml), was treated with sodium hydroxide solution to a pH of approximately 9. The alkaline mixture was extracted with methylene chloride, and the extract was dried over magnesium sulfate, then evaporated to dryness. Recrystallization of the residue from benzene gave two crops of orange crystals, mp 133–134° (lit.[24] 133–134°). The yield was 20 g.

***o,o′*-Diazidoazobenzene** (IV). A solution of 7 g (0.1 mole) of sodium nitrite in 40 ml of water was added dropwise to a stirred mixture of 8.6 g (0.04 mole) of *o,o′*-diaminoazobenzene, 60 ml of concentrated hydrochloric acid, and 80 ml of water at 0–2°. The temperature was maintained below 10° during the addition. Stirring was continued for an additional hour after the nitrite addition. Sodium azide (6.5 g, 0.1 mole) in 40 ml of water was slowly added to the diazonium solution at 5° with continued stirring. Nitrogen evolved, and the yellow diazide precipitated during the addition. The mixture was stirred for an additional 2 hr, then filtered to obtain the diazidoazobenzene (9.8 g, 93% yield), mp 110–111° dec.

Anal. Calcd for $C_{12}H_8N_8$: C, 54.54; H, 3.05; N, 42.41. Found: C, 54.75; H, 3.31; N, 42.37.

2-(*o*-Aminophenyl)-2H-benzotriazole (VII). *o,o′*-Diaminoazobenzene (4.4 g, 0.02 mole) was dissolved in 50 ml of pyridine and treated with 12.8 g (0.08 mole) of copper sulfate added in portions with stirring. After 30 min at room temperature, the reaction mixture was heated at reflux for 2 hr, cooled, and poured into 4–5 volumes of cold water with stirring. The dark solid which separated was collected by filtration and washed with water. Two recrystallizations from ethanol and one from hexane with concomitant treatment with activated carbon yielded well-defined, yellow crystals of VII, mp 97–98°; yield, 65%.

Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.55; H, 4.79; N, 26.65. Found: C, 68.55; H, 4.98; N, 26.56.

The infrared spectrum contains a peak at 10.3 μ, which was found in all 2-aryl-2H-benzotriazoles examined in this investigation. The ultraviolet spectrum in ethyl alcohol exhibits absorption maxima at 357 mμ (ϵ 9700), 296 (12,000), 268 (6400), and 229 (20,000).

2-(*o*-Azidophenyl)-2H-benzotriazole (VI). A solution of *o,o′*-diazidoazobenzene (5 g) in acetone or benzene was heated at reflux for 2 hr. One mole of nitrogen evolved, and the orange color was discharged. The solvent was removed by distillation, and the crystalline residue was recrystallized from petroleum ether or aqueous acetone (70% yield). The light yellow needles melted at 78–79°.

Anal. Calcd for $C_{12}H_8N_6$: C, 61.01; H, 3.41; N, 35.58. Found: C, 61.04; H, 3.65; N, 35.94.

When a benzene solution of the diazidoazobenzene was exposed to sunlight for 3 days, a crystalline product was isolated, mp 76–77°, whose infrared spectrum was identical with that of the product

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[22] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 135.

[23] All melting points are corrected. Nmr spectra were obtained with Varian HR-60 and A-60 spectrometers. Saturated deuteriochloroform solutions with tetramethylsilane as an internal standard were used unless otherwise noted. Infrared spectra in potassium bromide wafers were determined with a Perkin-Elmer 21 spectrometer. Ultraviolet spectra were determined in ethanol. Dipole moments were determined by Mr. C. Wortz in benzene solution at 25° using a Type DM-01 Dipolmeter (Wissenschaftlich-Technische Werkstätten Weilheim O.B., Germany).

[24] R. Willstätter and A. Pfannenstiel, *Ber.*, **38**, 2348 (1905).

described above. The presence of an azido group was clearly indicated by the strong absorption at 4.75 μ in the infrared spectrum; a band at 10.3 μ is associated with the 2H-triazole structure.

Dibenzo-1,3a,4,6a-tetraazapentalene (II). (A) From *o,o'*-Diazidoazobenzene (IV). The diazide (8.2 g, 0.031 mole) in 700 ml of decalin was gradually heated to 175° with stirring. Nitrogen evolution occurred at approximately 60° with discharge of the orange azo color. At 170°, nitrogen was again evolved. The temperature was maintained at 175–185° for 2–3 hr, and the solution was concentrated to approximately 100 ml. The dibenzotetraazapentalene II separated as long, yellow needles (6.0 g, 93% yield) which melted at 237–238°; ν_{max} 3070, 1615, 1580 (w), 1490, 1435, 1390, 1330, 1253, 1248, 1237, 1004, 997, 943, 937, 838 (w), 832 (w), 812, 747, and 731 cm^{-1}.

Anal. Calcd for $C_{12}H_8N_4$: C, 69.22; H, 3.87; N, 26.91; mol wt, 208. Found: C, 69.06; H, 3.99; N, 26.92; mol wt, 221.

(B) From 2-(*o*-Azidophenyl)-2H-benzotriazole (VI). The benzotriazole derivative VI in decalin was heated at 175–185° for 2–3 hr in the manner described above. Compound II was obtained in 95% yield.

When a benzene solution of VI was exposed to sunlight for 10 days, a yellow, crystalline product precipitated, mp 236–237°, whose infrared spectrum was identical with that of II from the thermal method.

Lithium Aluminum Hydride Reduction of Dibenzo-1,3a,4,6a-tetraazapentalene (II). A solution of 2.0 g of II in 200 ml of tetrahydrofuran was added slowly to a suspension of 5 g of lithium aluminum hydride in 75 ml of tetrahydrofuran. The mixture was stirred at 25° for 1 hr and was heated at reflux for 4 hr. The cooled mixture was carefully poured into cold water, and the organic products were extracted with methylene chloride. Evaporation of the solvent yielded 2-(*o*-aminophenyl)-2H-benzotriazole (VII), identical in chemical and spectral properties with the material described above.

1-(*o*-Nitrophenylazo)-2-naphthylamine (X). Compound X was prepared by the method of Meldola and Hughes[19] by diazotizing reprecipitated *o*-nitroaniline (27.6 g, 0.2 mole) with 13.0 g (0.2 mole) of sodium nitrite, filtering, and adding the diazonium solution to a cold, stirred solution of 2-naphthylamine (25 g, 0.18 mole) in dilute hydrochloric acid. The mixture was stirred for 1 hr and filtered to collect the dark solid (yield, 48 g). Recrystallization from acetic acid yielded lustrous, bronze-like crystals, mp 202–202.7° (lit.[19] 198°).

2-(*o*-Nitrophenyl)-2H-naphtho[1,2-*d*]triazole (XI). Method I. A mixture of 7.5 g of azo derivative X in 75 ml of pyridine and 20 g of anhydrous $CuSO_4$ was refluxed with rapid stirring for 4 hr. The cooled reaction mixture was poured into four volumes of water and filtered to obtain a reddish solid (7.2 g). Recrystallization from 225 ml of ethanol yielded a crop of yellowish crystals (5.5 g). An additional 0.75 g was obtained on dilution of the mother liquor with water (total yield 83%). The product melted at 121–122°.

Method II. To a mixture of the azo compound X (5 g) in 50 ml of benzene was added 3.0 g of thionyl chloride. The mixture was heated at reflux with stirring for 18 hr. The brown-yellow mixture was evaporated to dryness, and the solid residue was recrystallized from 100 ml of ethanol to yield 3.5 g (70%) of pale yellow solid. An additional alcohol recrystallization yielded almost colorless, transparent plates, mp 121.8–122.2°. The infrared and ultraviolet spectra of this product were identical with the product obtained in method I.

Anal. Calcd for $C_{16}H_{10}N_4O_2$: C, 66.20; H, 3.48; N, 19.30. Found: C, 66.03; H, 3.33; N, 19.58.

1-(*o*-Aminophenylazo)-2-naphthylamine (XVI). An attempt to form the 2-(2'-amino-1'-naphthyl)-2,1,3-benzotriazole (XV) by reductive cyclization of 1-(*o*-nitrophenylazo)-2-naphthylamine (X) gave, instead, the diaminoazo derivative XVI by simple reduction.

To a warm, stirred mixture of 7 g (0.024 mole) of X in 210 ml of ethanol was added a solution of 24 g (0.1 mole) of sodium sulfide nonahydrate. The mixture was heated at reflux for 3 hr. An additional 12 g of the sodium sulfide was added after the first hour. The cooled mixture was filtered to collect the reddish crystals (3.5 g). Dilution of the filtrate with 500 ml of water yielded an additional 2 g of product (total yield 87%). A sharp melting point was not achieved despite several recrystallizations from various solvents. However, the structure of the product was ascertained by spectra and by chemical reactions described below.

2-(*o*-Aminophenyl)-2H-naphtho[1,2-*d*]triazole (XII). The amino derivative XII was prepared by treating the corresponding nitro compound XI with iron powder in acetic acid (yield, 70%) and by reduction with sodium sulfide (yield 91%). After recrystallization from ethanol, XII melted at 126–127°.

Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.82; H, 4.64; N, 21.53. Found: C, 74.09; H, 4.65; N, 21.72.

Compound XII shows a marked blue fluorescence when viewed under ultraviolet illumination, both in solution and in the solid state. The N-acetyl derivative XVII was prepared in 86% yield by heating with acetic anhydride. After recrystallization from ethanol, the melting point was 159.2–160.6°.

Anal. Calcd for $C_{18}H_{14}N_4O$: C, 71.50; H, 4.67; N, 18.53. Found: C, 71.29; H, 5.27; N, 18.35.

2-(*o*-Azidophenyl)-2H-naphtho[1,2-*d*]triazole (XIII). The 2-(*o*-aminophenyl)-2H-naphtho[1,2-*d*]triazole (XII) (13 g, 0.05 mole) was diazotized with a solution of 4.5 g (0.065 mole) of sodium nitrite in 30 ml of water. The mixture was stirred for 1 hr, during which a yellow solid separated. An aqueous solution of 4.5 g (0.07 mole) of sodium azide was added dropwise at 5° with continued stirring. No immediate evolution of gas was apparent. However, after 10 min gas evolution became quite evident with accompanying foam formation. After 1.5 hr, the bright yellow color was discharged. The cream-colored, solid azide was collected by filtration and recrystallized from 600 ml of ethanol, mp 124.2–124.8° dec, yield, 13.6 g (95%).

Anal. Calcd for $C_{16}H_{10}N_6$: C, 67.12; H, 3.52; N, 29.36. Found: C, 67.42; H, 3.72; N, 29.14.

α,β-Naphthobenzotetraazapentalenes (IXa,b). The azido compound XIII (5.8 g, 0.02 mole) was heated in 200 ml of decalin at 180° for 2 hr with stirring. The color deepened to a brownish yellow during this period. The hot solution was treated with activated carbon, filtered, and allowed to cool slowly. A total of 3.4 g (65%) of IXa,b was obtained in two crops, mp 192–220°.

Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.70. Found: C, 74.14; H, 4.08; N, 22.13.

This mixture was subjected to chromatography through neutral Woelm alumina, using chloroform and eventually chloroform–methylene chloride as the developing solvents. The faster moving fraction was predominantly the lower melting isomer IXb, the intermediate fractions were mixtures, and the later fractions contained primarily the high-melting isomer IXa. Recrystallization of the lower and higher melting fractions gave yellow crystals, mp 211.5–212.5 and 244.5–245°, respectively.

Anal. Found (lower melting isomer): C, 73.90; H, 4.14; (higher melting isomer) C, 74.26; H, 4.03.

Comparison of the infrared spectra of the two isomers showed several differences in the fingerprint region. However, all of the peaks encountered in the spectrum of the original isomer mixture are accounted for by the spectra of the pure isomers.

Lithium Aluminum Hydride Reduction of the Low-Melting Isomer (IXb). A mixture of 0.300 g of the low-melting naphthobenzotetraazapentalene isomer in 25 ml of tetrahydrofuran was treated with a filtered solution of lithium aluminum hydride (excess) in tetrahydrofuran. The mixture was stirred at 25° for 30 min, at reflux for 1 hr, then overnight at room temperature (in a second run, the reaction mixture was refluxed for 5 hr with similar results). The now deeply colored mixture was treated with ethyl acetate, then with water to destroy excess hydride. The mixture was made acid with hydrochloric acid, poured into water, then again made alkaline. The mixture was extracted twice with ether and the latter dried over sodium sulfate, then evaporated to dryness, yielding an oily residue. Comparison of the infrared spectrum of this product with that of a 3:1 synthetic mixture of XII and XV showed that they were almost identical.

Chromatographic separations on Woelm neutral alumina employing ether, ether–methylene chloride, methylene chloride, and methylene chloride–ethyl acetate yielded 2-(*o*-acetamidophenyl)-2H-naphtho[1,2-*d*]triazole (XVII) as a crystalline solid which was identical with an authentic sample. Attempts to isolate the expected minor component XV were not successful.

Note! Acetylation of the amine apparently occurred during chromatographic development with ethyl acetate. In one run, a fast-moving component was isolated from a methylene chloride–ethyl acetate fraction and appeared to have a nonamidic N–H group. This material, which may have been the product of incomplete reduction, did not appear to be either of the expected products.

Lithium Aluminum Hydride Reduction of the High-Melting Isomer IXA. This reduction was carried out as described for the low-melting isomer (above). The oily residue isolated from this reaction showed some significant differences from the authentic composite in infrared spectrum.

1-(*o*-Nitrophenyl)-1H-benzotriazole (XVIII). (A) From Benzotriazole. In this modification of the procedure of Vystrcil, *et al.*,[20] a mixture of 119.1 g of 1H-benzotriazole, 125 g of powered sodium acetate, and 0.5 g of cupric acetate was placed in a 500-ml three-necked flask immersed in an oil bath held at 220–230°. The flask was equipped with a magnetic stirrer and a short distilling column. Over a period of 40 hr, 27 ml of acetic acid was collected, The black product was subjected to steam distillation to remove excess *o*-chloronitrobenzene. The viscous, black residue was rinsed with water and extracted with a mixture of benzene and methylene chloride. The extract was filtered and dried over magnesium sulfate. Most of the methylene chloride was removed under reduced pressure, and the benzene solution remaining was eluted with benzene through 900 g of chromatographic grade silicic acid contained in a 125-mm diameter, sintered-glass funnel. After a forerun containing *o*-chloronitrobenzene, a fraction containing 37.5 g (16%) of 2-(*o*-nitrophenyl)-2H-benzotriazole (XIX) was collected (*ca.* 1500 ml of benzene was required; see below). The column was then eluted with 5 l. of methylene chloride; this yielded 95 g (39%) of 1-*o*-nitrophenyl-1H-benzotriazole (XVIII), mp 118.9–120° (lit. mp 115°,[11] 118°[25]).

(B) **From *o*-Amino-*o*′-nitrodiphenylamine.** A mixture of 250 g of *o*-phenylenediamine, 500 g of *o*-chloronitrobenzene, and 2 l. of absolute alcohol was mechanically stirred and heated to reflux on a steam bath for 3 days. The mixture was then subjected to steam distilltion, and the nonvolatile residue was extracted with a total of 4 l. of chloroform. The extract was filtered, water washed, and dried over magnesium sulfate. Solvent was removed under reduced pressure, and the residue was recrystallized from about 1800 ml of alcohol to yield 305 g (58%) of *o*-amino-*o*′-nitrodiphenylamine in two crops, mp 106–107° (lit.[21] mp 103°).

A hot solution of 236 g of this product in 240 ml of acetic acid, 1 l. of water, and 1 l. of alcohol was poured onto 1500 g of crushed ice, and a solution of 100 g of sodium nitrite in 200 ml of water was added all at once while stirring. The mixture was stirred overnight and filtered. The solid was separated by filtration, washed with water, suction dried, and recrystallized to yield 223 g (90%) of 1-(*o*-nitrophenyl)-1H-benzotriazole, whose infrared spectrum was identical with that of the product obtained by method A.

2-(*o*-Nitrophenyl)-2H-benzotriazole (XIX). The crude chromatographic product described above was eluted with methylene chloride through a column of Woelm neutral alumina and recrystallized from ethanol to yield white crystals melting at 132.8–133.8°; λ_{max} 302 mμ (ϵ 14,710), 290 (13,830), and 223 (25,000).

Anal. Calcd for $C_{12}H_8N_4O_2$: C, 60.00; H, 3.36; N, 23.33. Found: C, 59.70; H, 3.46; N, 23.03.

Structure XIX was verified by reduction to the corresponding amine using hot, aqueous, ethanolic sodium sulfide solution. The amine (mp 93.5–94°) was identical (mixture melting point, infrared spectrum) with the 2-(*o*-aminophenyl)-2H-benzotriazole (VII) described above.

1-(*o*-Aminophenyl)-1H-benzotriazole (XX). A solution of 25.7 g of XVIII in 400 ml of ethanol was hydrogenated at 3 atm using 0.2 g of platinum oxide catalyst. The solution was filtered and evaporated to dryness to yield a tan solid, which was recrystallized from 180 ml of 95% alcohol to yield 16 g of 1-(*o*-aminophenyl)-1H-benzotriazole. A second crop of 2.9 g was obtained by evaporation of the solvent to a final volume of 50 ml. A portion recrystallized from ethanol melted at 132–132.4°; λ_{max} 287 mμ (ϵ 5780) and 242 (15,700); ν_{max} 3410, 3320, 3200, 1622, 1570, 1465, 1452, 1314, 1290, 1268, 1243, 1182, 1160, 1122, 1080, 1040, 948, 853, 785, 762, and 692 cm^{-1}.

Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.55; H, 4.79; N, 26.61. Found: C, 68.64; H, 4.85; N, 26.75, 26.95.

1-(*o*-Azidophenyl)-1H-benzotriazole (XXI). A solution of 11.6 g of XX in 40 ml of hydrochloric acid was placed in a beaker equipped with a stirrer and immersed in an ice bath, and 60 g of crushed ice was added, followed by the dropwise addition of a solution of 3.9 g of sodium nitrite in 25 ml of water at 0–3°. After addition was complete, the solution was filtered into an ice-cooled flask, and a solution of 3.8 g of sodium azide in 25 ml of water was added dropwise while the reaction temperature was maintained at 0–5°. (Some ether was added to suppress foaming.) The reaction mixture was stirred overnight, and the solid product was collected by suction filtration and water washed. The crude 1-(*o*-azidophenyl)-1H-benzotriazole weighed 12.4 g (99%) and was used in the next step without further purification. A portion recrystallized from hexane melted at 84.6–85°; λ_{max} 254 mμ (ϵ 18,600), 235 (14,300), and 285 (sh) (680).

Anal. Calcd for $C_{12}H_8N_6$: C, 61.01; H, 3.42; N, 35.58. Found: C, 61.52; H, 3.66; N, 36.07.

Dibenzo-1,3a,6,6a-tetraazapentalene (III). A solution of 12.4 g of XXI in 30 ml of *o*-dichlorobenzene was added dropwise to 20 ml of refluxing *o*-dichlorobenzene heated with an oil bath. The solution was heated at reflux for 3 hr after addition was complete. Activated charcoal was added, and the mixture was filtered hot. On cooling, it deposited 8.13 g (74%) of crude III as grayish white needles. The product was purified by continuous elution with methylene chloride through a bed of Woelm neutral activated alumina. A heavy-solvent liquid–liquid extractor was found to be convenient for this purification. A layer of *ca.* 30 g of alumina was placed on top of a layer of glass wool in the bottom of the apparatus. The crude azapentalene was placed on top of the alumina and was slowly eluted through the alumina by the condensed vapors of refluxing methylene chloride. A portion of the product recrystallized from ethanol melted at 254.8–255.2°.

Anal. Calcd for $C_{12}H_8N_4$: C, 69.22; H, 3.88; N, 26.91. Found: C, 69.30; H, 3.88; N, 26.97; dipole moment: 4.36 D (0.002 *M* in benzene at 25°).

Three crystalline forms of the product could be obtained which differed somewhat in infrared spectrum. These were converted to the same form by melting and cooling; ν_{max} 3070, 1515, 1490, 1460, 1450, 1430, 1390, 1325, 1310 (w), 1290, 1253, 1155, 1148, 1121 (w), 1090 (w), 1030, 1005 (w), 963, 930, 898 (w), 870 (w), 842 (w), 745, 730, and 724 (sh) cm^{-1}.

Acknowledgments. We are very grateful to Professor J. D. Roberts, whose advice was of vital importance to us in the early stages of this work, and to Dr. D. S. Thatcher for assistance and helpful discussions.

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(25) D. Dal Monte, A. Mangini, R. Passerini, and C. Zauli, *Gazz. Chim. Ital.*, 88, 977 (1958).