# Cyclo-octa[*def*]carbazole, a New Paratropic Ring System

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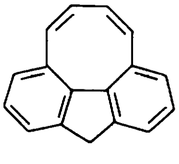
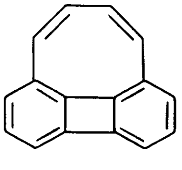
Products of the photolyses of the naphthylbenzotriazoles (**3**) include the red cyclo-octa[*def*]carbazoles (**4**), a new ring system formed by an unusual cyclisation onto the naphthalene 8a-position; from its $^1$H n.m.r. spectrum and chemical reactivity, (**4**) is considered to have antiaromatic paratropic character, associated with the 16π-electron periphery (**12**), comparable to the isoelectronic fluorenyl anion derived from (**1**).

There has recently been much interest in the paratropic antiaromatic character of planar cyclo-octatetraenes embedded in polycyclic structures such as cyclo-octa[*def*]fluorene (**1**), a red oil,[1] cyclo-octa[*def*]biphenylene (**2**), a red solid,[2] and the related bis-cyclo-octa biphenylene, a transient blue-black solid which is only moderately stable in dilute solution at −30 °C.[3] The dark red fluorenyl anion derived from (**1**), which can be considered to have a fully conjugated 16π periphery, exhibits enhanced paratropic character relative to (**1**).[1] We now describe the formation and properties of the first heterocyclic system of this kind, cyclo-octa[*def*]carbazole (**4**).

Irradiation of 1-(2-methylnaphth-1-yl)benzotriazole (**3b**) in acetonitrile at 254 nm gave 6a-methylbenzo[*a*]carbazole and an indenoquinoline derived from it by aza-di-π-methane rearrangement,[4] together with a deep red compound (30%), m.p. 69—72 °C, isomeric with the other products and now shown to be 1-methylcyclo-octa[*def*]carbazole (**4b**).† In the $^1$H n.m.r. spectrum of this compound all the protons except the *N*-H resonated upfield of δ 7.1, in marked contrast with the starting material (**3b**). The methyl group was still present and decoupling experiments showed that the remaining protons were in groups of 2, 3, and 4, all isolated from each other, with the last group resonating at significantly higher field than the other two. The $^{13}$C n.m.r. spectrum showed only one carbon (Me group) to be sp$^3$ hybridised, the rest being sp$^2$. Nuclear Overhauser enhancement (n.O.e.) experiments indicated that the *N*-H proton is adjacent to the methyl group and to one proton of the 3-proton group, and that the methyl group is also adjacent to one proton of the 2-proton group. If each group of protons is separated by a ring junction one arrives at the molecular periphery of structure (**4b**), which is finally constructed by inserting the two remaining sp$^2$ carbon atoms. Crystals of (**4b**) were too disordered for direct *X*-ray diffraction analysis, but the structure was confirmed by crystal structure determination[5] of the Diels–Alder adduct (**5a**) formed quantitatively from (**4b**) and 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) in dichloromethane at 0 °C.



(**1**)



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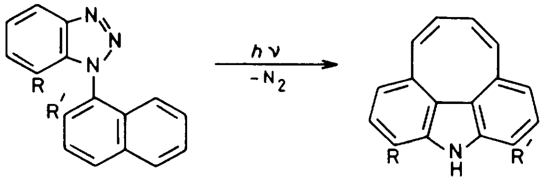


(**3**) (**4**)

**a**; R = R′ = H

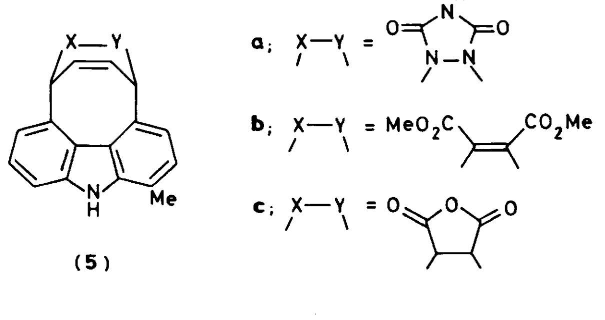
**b**; R = H, R′ = Me

**c**; R = R′ = Me

Formation of the new ring system (**4**) by photolysis of benzotriazole (**3**) presents an interesting mechanistic problem, one solution of which is shown in Scheme 1. The initially formed triplet diradical (**6**) could give a singlet species, *e.g.* imidoyl carbene (**7**);[6] cyclisation of this to the naphthalene 2-position yields the 4a*H*-carbazole derivative discussed before[4] whilst cyclisation to the 8a-position gives (**8**), an alternative 4a*H*-carbazole ring system. The stable product isolated could then be formed by (thermal) [1,5] and [1,9] vinyl and hydrogen shifts. Alternatively, conversion of intermediate (**9**) into (**10**) could be a further photochemical process, proceeding by way of a di-π-methane rearrangement. Intramolecular attack at the naphthalene ring junction, the key step proposed here, is very rare (as it is intermolecularly) and only one, distantly related, example could be found. Structure (**11**), formed by cycloaddition of the nitrene derived from 1-(2-azidobenzyl)naphthalene to the 1–8a naphthalene bond, was proposed as the precursor of a minor product of thermolysis of the azide.[7]

In view of the novelty of the cyclo-octa[*def*]carbazole structure and of the mechanism of its formation, we sought other examples of the rearrangement, particularly that leading to the parent compound (**4a**). It seemed likely that photolysis of the unmethylated benzotriazole (**3a**) would simply give benzo[*a*]carbazole, as does its thermolysis.[8] Irradiation of 1-(naphth-1-yl)benzotriazole (**3a**) in acetonitrile at 254 nm proved to be lower yielding than that of (**3b**), though the main product was indeed the photolabile benzo[*a*]carbazole; nevertheless a small amount (5%) of the unsubstituted cyclo-octa[*def*]carbazole (**4a**) was formed, and isolated by chromatography on silver nitrate-impregnated silica gel as a red solid, m.p. 131—134 °C.

From the relative yields of the two cyclo-octacarbazoles (**4a**)



(**5**)

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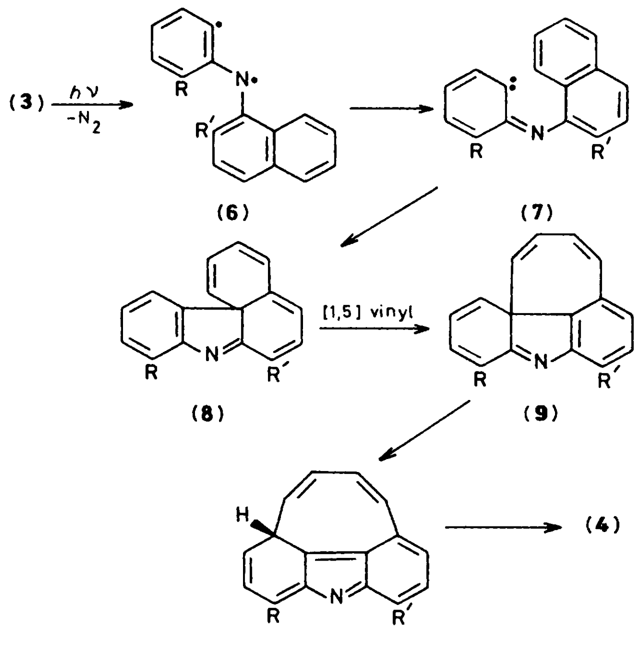
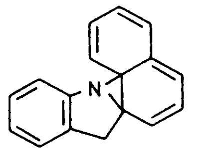
† Representative spectroscopic data for compound (**4b**): $\nu_{max.}$ (CCl$_4$) 3470 cm$^{-1}$; long wavelength $\lambda_{max.}$ (EtOH) 418 nm (log ε 3.52); $\delta_H$ (250 MHz, CDCl$_3$) 2.34 (3H, s), 5.24—5.39 (2H, m, H-5, H-6), 5.76—5.87 (2H, m, H-4, H-7), 6.48 (1H, d, *J* 7.4 Hz, H-3), 6.57 (1H, dd, *J* 6.6 Hz, 1.4 Hz, H-8), 6.82 (1H, d, *J* 7.4 Hz, H-2), 7.01 (1H, t, *J* 6.6 Hz, H-9), 7.05 (1H, dd, *J* 6.6 Hz, 1.4 Hz, H-10), and 7.84 (1H, br., N-*H*); $\delta_C$ (62.9 MHz, CDCl$_3$) 16.5, 113.0, 120.2, 121.2, 122.1, 124.4, 125.5, 126.6, 127.2, 128.0, 128.3, 130.9, 133.1, 133.2, 133.6, 139.5, and 139.9.



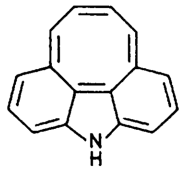
**Scheme 1**

and (**4b**) it appears that the steric effect of the 2-methyl group in benzotriazole (**3b**) favours closure of the intermediate singlet species to the 8a-position. Therefore decomposition of the dimethyl naphthylbenzotriazole (**3c**) was studied in the hope of providing a reasonable yield of a symmetrical derivative (**4c**) of the cyclo-octacarbazole system, together with general support for the proposed rearrangement mechanism. 7-Methyl-1-(2-methylnaphth-1-yl)benzotriazole (**3c**), m.p. 150.5—152 °C, was prepared by cycloaddition of 3-methylbenzyne to 1-azido-2-methylnaphthalene, $\nu_{max.}$ 2102 cm$^{-1}$, and separation from the accompanying regioisomer. Photolysis of (**3c**) again gave stable products arising from collapse of the intermediate to the naphthalene 2-position[4] together with the desired 1,10-dimethylcyclo-octa[*def*]carbazole (**4c**) (20%) as red crystals, m.p. 164—165.5 °C.

Comparison of chemical shifts in the $^1$H n.m.r. spectra indicates that the cyclo-octacarbazole ring system (**4**) exhibits a degree of paratropicity similar to the isoelectronic cyclo-octafluorenyl anion derived from (**1**);[1] this is associated with the conjugated 16$\pi$ peripheral structure (**12**). The high chemical reactivity of compounds (**4**), and particularly their anions, also accords with this general antiaromatic character. Deprotonation of the *N*-H to form what would be a peripherally conjugated 16$\pi$ anion led to total destruction of the molecule, even under mild experimental conditions. Attempted *N*-alkylation and acylation reactions were equally unsuccessful. Additionally, compound (**4b**) was immediately destroyed by treatment with triphenylmethyl fluoroborate or 3-chloroperbenzoic acid in dichloromethane at 0 °C. However the strained butadiene portion of the molecule proved reactive towards addition and cycloaddition. Thus compound (**4b**) gave high yields of colourless Diels–Alder adducts with dimethyl acetylenedicarboxylate, (**5b**) (m.p. 227—228.5 °C); maleic anhydride, (**5c**), (*endo* adduct only, m.p. 251—252 °C); and PTAD, (**5a**) (m.p. 273—275 °C); catalytic hydrogenation gave the tetrahydro derivative, m.p. 95.5—97 °C, and di-iron nonacarbonyl gave the $\eta^4$-dienetricarbonyl-iron complex, m.p. 175—177 °C (decomp.). Interestingly, the chemical shifts of the carbazole ring protons in all these adducts were seen to move downfield by 0.3—0.6 p.p.m. relative to (**4b**) itself, thus supporting the extended 16$\pi$ peripheral structure (**12**) of the cyclo-octacarbazole system.



(**11**)



(**12**)

We thank the S.E.R.C. for financial support, Dr. D. J. Williams for the *X*-ray structure determination, and Dr. D. Neuhaus for help with the n.m.r. spectroscopy.

*Received, 26th February 1985; Com. 266*

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