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

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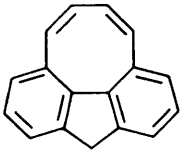
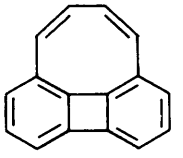
Photolysis of the 1-(1-naphthyl)benzotriazoles (**5a,b,g,h**) was found to give the deep red cyclo-octa[*def*]carbazoles (**6a,b,g,h**), a new heterocyclic ring system formed by an unusual cyclisation onto the naphthalene ring junction (Scheme 1). The ^{1}H n.m.r. spectra and high chemical reactivity of these cyclo-octacarbazoles (**6**) are consistent with antiaromatic paratropic character, associated with the 16π-electron periphery (**25**), comparable with the isoelectronic fluorenyl anion (**4**). The strained butadiene portion of the cyclo-octacarbazoles (**6**) is reactive towards addition and cycloaddition reactions, forming a tricarbonyliron complex (**27**) and Diels–Alder adducts (**28**). Naphthylbenzotriazoles (**5c,d,e**) with lone pair bearing substituents (MeO, Cl, Br) adjacent to the triazole ring do not give cyclo-octacarbazoles, but only products derived by cyclisation onto the naphthalene 2-position. On similar photolysis the quinolinyltriazoles (**39**) give the stable ylides (**40**) and the acridinylbenzotriazole (**45**) gives the quinoacridine (**46**). Mechanisms are proposed for all of these reactions.

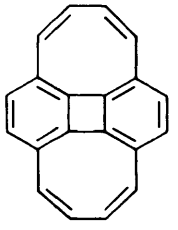
Recent interest in the properties of compounds which contain one or more planar [4n] π-electron components embedded in a polycarbocyclic framework has led to the preparation of cyclo-octa[*def*]fluorene (**1**), a red oil,[1] cyclo-octa[*def*]biphenylene (**2**), a red solid,[2] and dicyclo-octa[*def,jkl*]biphenylene (**3**), a transient blue-black solid showing only moderate stability in solution at −30 °C.[3] The olefinic proton resonances in the n.m.r. spectra of compounds (**1**)—(**3**) show a pronounced upfield shift when compared with model non-planar cyclo-octatetraene derivatives, indicating that a significant paramagnetic ring current is associated with the planar cyclo-octatetraene portion of these compounds.[4] The dark red fluorenyl anion obtained on deprotonation of (**1**) exhibits enhanced paratropic character relative to (**1**) itself; this is attributed to a substantial contribution from structure (**4**), with a 16π periphery perturbed by the ethylene bridge.[1]



(**1**)



(**2**)



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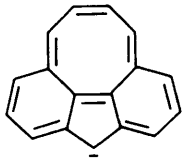
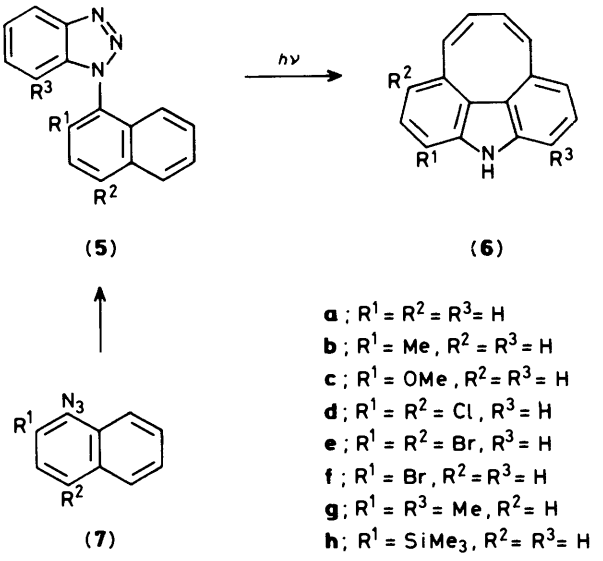


(**4**)

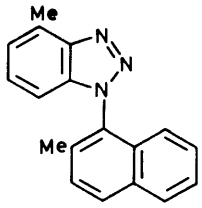
We now report full details of an unusual photochemical preparation of the first heterocyclic derivatives of (**4**), cyclo-octa[*def*]carbazole (**6**), from 1-(1-naphthyl)benzotriazoles (**5**).[5] The properties of the new ring system are also described.

Results and Discussion

Preparation of the Triazoles.—Benzotriazoles (**5a**—**f**) were prepared by cycloaddition of the appropriate 1-azidonaphthalene (**7a**—**f**) to benzyne.[6] Cycloaddition of 1-azido-2-methylnaphthalene (**7b**) to 3-methylbenzyne gave triazole (**5g**) which was separated from the accompanying regioisomer (**8**). Naphthotriazole (**9**) was similarly prepared from (**7b**) by cycloaddition to 2,3-dihydronaphthalene. The triazole (**5h**) was prepared from the bromo derivatives (**5f**) by lithiation and reaction with chlorotrimethylsilane.



The azides (**7d**—**f**) were prepared by the method of Dyall *et al.* for the preparation of 1-azidonaphthalene (**7a**),[7] involving protic diazotisation of the appropriate naphthylamine with aqueous sodium nitrite, followed by treatment with sodium azide. For the azide (**7b**), diazotisation was best achieved by treatment of the amine hydrochloride with pentyl nitrate in a mixture of ethanol and acetic acid. The azide (**7c**) was formed in extremely low yield after diazotisation by either of these methods, presumably because of diazo coupling between the diazonium salt and unchanged amine. However, addition of pentyl nitrite to a two-phase system consisting of 2-methoxy-1-naphthylamine and acetic acid in ether and of aqueous sodium azide gave a high yield of azide (**7c**); presumably as the diazonium salt was formed it passed into the aqueous phase where it reacted with the azide ion to give the organic azide which returned to the organic layer.



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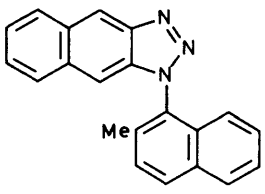

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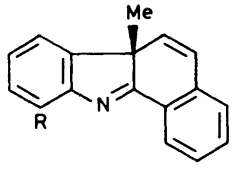

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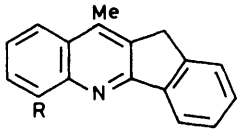
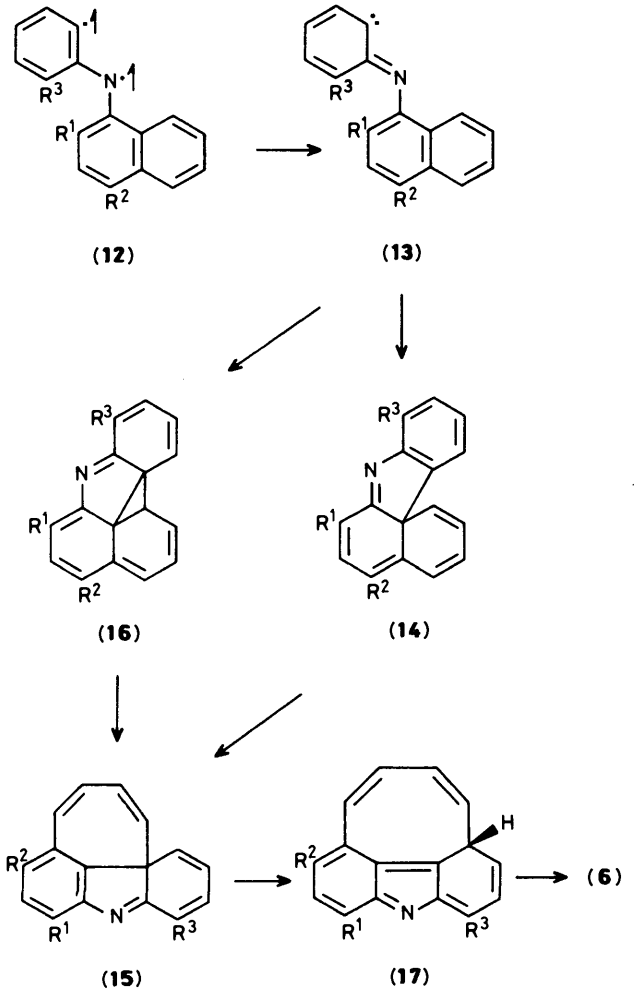


(11)

a; R = H
b; R = Me

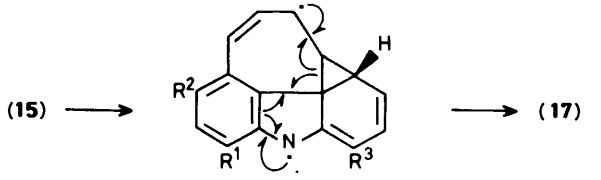
Formation of the Cyclo-octacarbazoles.—Irradiation of the triazole (**5b**) in acetonitrile at 254 nm gave 1-methylcyclo-octa[*def*]carbazole (**6b**) as a deep red solid, m.p. 69—72 °C in 30% yield, together with 6a-methyl-6a*H*-benzo[*a*]carbazole (**10a**) (24%) and the indenoquinoline (**11a**) (32%), arising by a further photochemical (aza-di-π-methane) rearrangement of (**10a**).[8] Similar irradiation of the triazole (**5g**) afforded the symmetrical 1,10-dimethylcyclo-octacarbazole (**6g**) as deep red crystals, m.p. 164—165.5 °C, in 20% yield, together with the 6a*H*-benzo[*a*]carbazole (**10b**) (25%) and the indenoquinoline (**11b**) (42%).[8]

The mechanism of the ring expansion observed in the formation of the cyclo-octacarbazoles (**6b,g**) poses an interesting problem, possible solutions to which are outlined in Scheme 1. The initially formed triplet diradical (**12**)[9] could give rise to a singlet species, the imidoyl carbene (**13**); cyclisation of this to the naphthalene 2-position leads to the 6a*H*-benzocarbazoles (**10a,b**). Similar cyclisation of the carbene (**13**) to the naphthalene 8a-position would give the 4a*H*-carbazole (**14**) which could rearrange by a (thermal) [1,5]vinyl shift to the alternative 4a*H*-carbazole (**15**). This intermediate could also arise by cycloaddition of the carbene to the naphthalene 8–8a bond followed by ring opening of the resulting norcaradiene (**16**). A further (thermal) [1,9]vinyl shift in (**15**) would give (**17**) which then leads to the isolated product (**6**) by hydrogen migration. A similar mechanism has been proposed for the transformation of the presumed intermediate (**18**), obtained on photolysis or thermolysis of 3-diazo-2,5-diphenylpyrrole in benzene, to the cyclo-octapyrrole (**19**).[10] Conversion of the 4a*H*-carbazole intermediate (**15**) into (**17**) could also be a further photochemical process, proceeding by way of a di-π-methane rearrangement (Scheme 2).



(12) (13) (16) (14) (15) (17) (6)

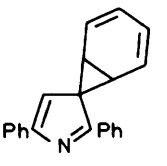
Scheme 1.



Scheme 2.

Intramolecular attack at the naphthalene ring junction, the key step proposed here, appears to be extremely rare, as it is intermolecularly. The only previous case of which we are aware is in the proposed formation of intermediate (**20**) by addition of the nitrene derived from 1-(2-azidobenzyl)naphthalene to the 8–8a bond, to account for the isolation of a small amount of the ring-opened benzazepine from thermolysis of the azide.[11]

In view of the novelty of the cyclo-octa[*def*]carbazole structure and of the mechanism of its formation, we sought



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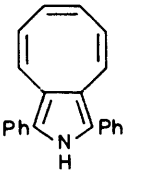

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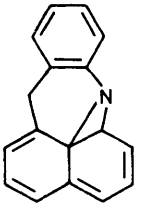

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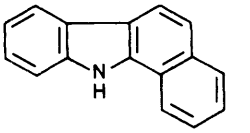
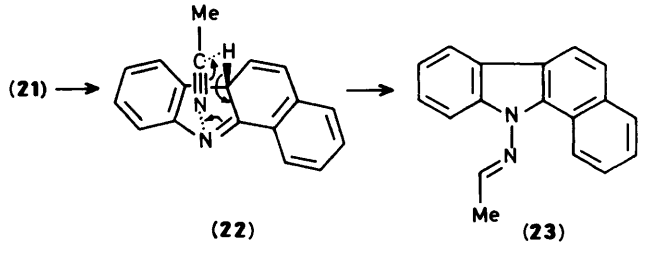


(21)

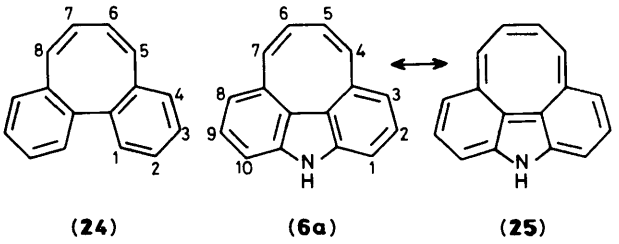
other examples of this rearrangement, particularly that leading to the parent compound (**6a**). It seemed likely that photolysis of the unmethylated benzotriazole (**5a**) would simply give benzo[*a*]carbazole (**21**), as it does on thermolysis.[12] However, irradiation of (**5a**) in acetonitrile at 254 nm did give some cyclo-octa[*def*]carbazole (**6a**), isolated by chromatography on silver nitrate–impregnated silica gel as a red solid, m.p. 131—134 °C, though in low yield (5%). The benzocarbazole (**21**) was also obtained (10%) together with another, unstable, product (20%) from which it could not be separated. The 220 MHz ^{1}H n.m.r. spectrum of the mixture showed, *inter alia*, a three proton doublet at δ 2.04 coupled to a one proton quartet at δ 6.39 (*J* 8 Hz) suggesting that on photolysis the solvent (acetonitrile) had become incorporated into this product, as a $CH_3CH{=}N{-}$ unit. A separate experiment showed that this unstable compound is a further product of the irradiation of the benzocarbazole (**21**) in acetonitrile. Furthermore it is converted back into the benzocarbazole on hydrogenolysis. These observations strongly suggest the *N*-iminocarbazole structure (**23**), which could be formed by photoexcitation of (**21**) to the 6a*H*-tautomer (**22**) followed by an ene-type reaction with acetonitrile, as shown in Scheme 3. Unfortunately we were unable to *N*-aminate benzocarbazole (**21**), in an attempted independent synthesis of (**23**).

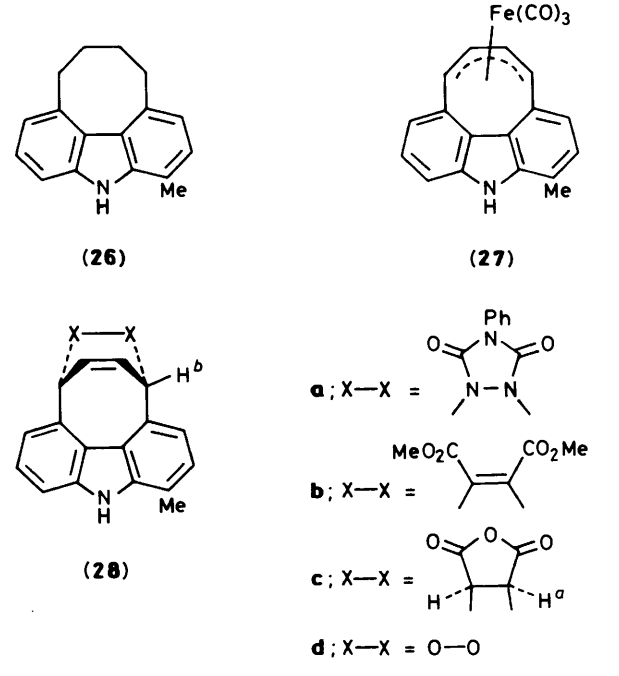


Scheme 3.

The increase in yield of cyclo-octacarbazole on moving from photolysis of 1-(1-naphthyl)benzotriazole (**5a**) to the 2-methyl-naphthyl derivative (**5b**) suggests that the steric effect of the naphthyl 2-substituent plays a significant role in directing attack of the intermediate carbene to the naphthalene 8a-position. Thus photolysis of the more bulky 2-trimethylsilyl derivative (**5h**) might give an even higher yield of ring expanded product. Indeed, irradiation of (**5h**) gave 47% of 1-trimethylsilyl-cyclo-octa[*def*]carbazole (**6h**), and no products were isolated from cyclisation onto the naphthalene 2-position.

Properties of the Cyclo-octacarbazoles.—The cyclo-octa-[*def*]carbazoles (**6a,b,g**) were obtained as deep red solids, and (**6h**) as a deep red gum. The 220 MHz ^{1}H n.m.r. spectrum of (**6a**) in $CDCl_3$ showed the N–H resonance as a broad singlet at δ 7.9, a four proton multiplet at δ 6.99—7.06 (1-, 2-, 9-, and 10-H), a two proton multiplet at δ 6.57 (3- and 8-H), a two proton multiplet at δ 5.73 (4- and 7-H), and a two proton multiplet at δ 5.35 (5- and 6-H). Comparison of the chemical shifts of the olefinic protons with those of the non-planar reference compounds, dibenzo[*a,c*]cyclo-octatetraene (**24**) [δ 6.82 (5- and 8-H), and δ 6.32 (6- and 7-H)],[1] and the cyclo-octa[c]pyrrole (**19**) (δ 5.79—6.36),[10] reveals a significant upfield shift indicative[4] of a paratropic ring current associated with the flattened cyclo-octatetraene ring of (**6a**). An *X*-ray crystal structure determination of the more highly crystalline dimethyl-cyclo-octacarbazole (**6g**) showed the eight-membered ring to deviate only slightly from planarity.[13] Comparison of the chemical shift values of the carbazole protons in the n.m.r. spectrum of (**6a**) with those of carbazole itself [δ 7.49 (1- and 8-H), δ 7.37 (2- and 7-H), and δ 7.16 (3- and 6-H)][14] also reveals an upfield shift, indicating that the 16π-peripheral structure (**25**) makes a significant contribution to the structure of the cyclo-octacarbazole ring system. However, it has been stressed that peripheral circuit structures such as (**25**) only make a contribution to the overall structure of a polycyclic molecule, and all possible 'circuit currents' within the molecule must be taken into account.[15] Comparison of the chemical shifts for the olefinic protons of (**6a**) with those for cyclo-octa[*def*]fluorene (**1**) [δ 5.90 (4- and 7-H) and δ 5.68 (5- and 6-H)][1] and the derived anion [δ 5.42 (4- and 7-H) and δ 4.96 (5- and 6-H)][1] suggests that the paratropicity of (**6a**) lies somewhere between the two. However, the upfield shift observed for the protons of the cyclo-octafluorenyl anion results not only from the paratropic effect associated with the 16π-conjugated peripheral anion (**4**) but also from the inductive shielding effect of the negative charge. Thus it seems likely that the cyclo-octacarbazole system provides, to a first approximation, a good measure of the paratropicity of the isoelectronic anion (**4**) which is independent of the shielding effect of the negative charge.

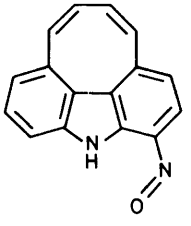




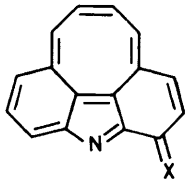
The chemical properties of the cyclo-octacarbazole ring system were investigated using the readily accessible 1-methyl derivative (**6b**). This was thermally and photochemically stable but the strained butadiene portion of the molecule was reactive towards addition and cycloaddition reactions. Thus catalytic hydrogenation gave the tetrahydro derivative (**26**) and nona-carbonyldi-iron gave the tricarbonyliron complex (**27**), though attempted epoxidation with 1 equivalent of 3-chloroperbenzoic acid at 0 °C caused immediate destruction of the ring system. Treatment of (**6b**) with dienophiles led to high yields of colourless 1:1-adducts; thus 1-phenyltriazoline-2,5-dione gave

(**28a**), dimethyl acetylenedicarboxylate gave (**28b**) and maleic anhydride gave (**28c**), the 220 MHz proton n.m.r. spectrum of which showed no coupling of H^a to the bridgehead proton H^b indicating that the *endo*-adduct had been formed exclusively. Singlet oxygen gave a somewhat lower yield of the unstable peroxide (**28d**). The structure of the cycloadduct (**28a**) was confirmed by *X*-ray crystallographic analysis.[13] The chemical shifts of the carbazole ring protons in the n.m.r. spectra of the adducts (**26**)—(**28**) were observed to move downfield relative to (**6b**) by 0.3—0.6 p.p.m., thus supporting a contribution from the extended 16π-peripheral structure (**25**) to the overall structure of the ring system (**6**). As is to be expected, however, the chemical reactivity of the cyclo-octacarbazoles is better rationalised in terms of the lower energy diene-fused carbazole structure (**6**).

Attempted *N*-deprotonation of (**6b**) to form what would be a peripherally conjugated 16π-anion failed, instantaneous decomposition occurring on treatment with base. Similarly, hydride abstraction from nitrogen to form an aromatic peripheral 14π-nitrenium ion also failed, treatment with triphenylmethyl tetrafluoroborate at 0 °C again resulting in rapid decomposition. Attempted *N*-alkylation and acylation reactions were equally unsuccessful, and thus the electronic effects of different *N*-substituents on the stability of the ring system could not be assessed. We also investigated deprotonation of the tricarbonyliron complex (**27**) since we expected to be able to regenerate the uncomplexed cyclo-octacarbazole after substitution on nitrogen; however all attempts to deprotonate (**27**) failed, undeuteriated complex being recovered in high yield on quenching with deuterium oxide; attempted deprotonation of the phenyltriazolinedione complex (**28a**) was also unsuccessful.



(**29**)

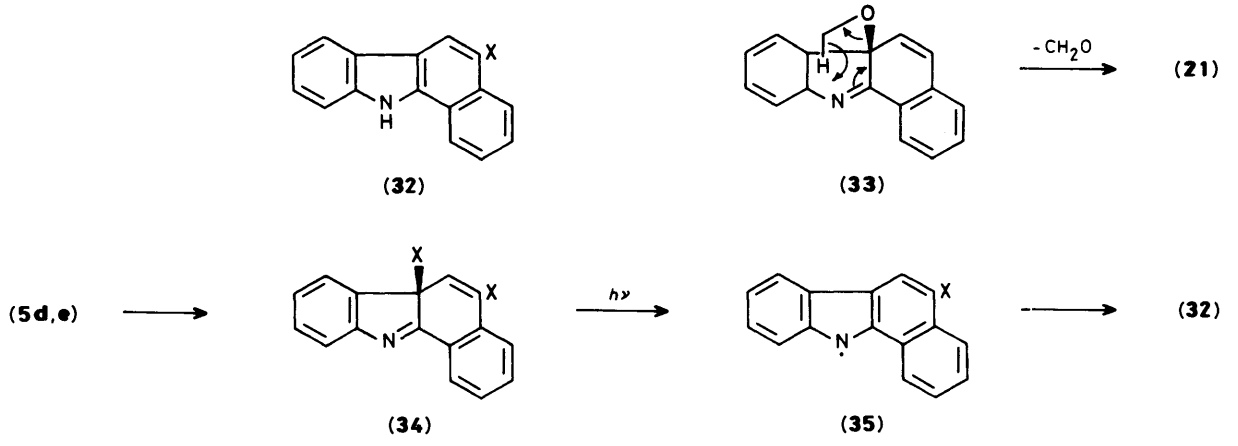


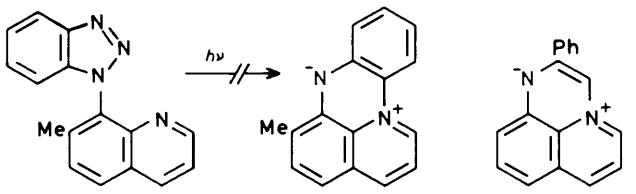
(**30**) X = NOH
(**31**) X = O

Electrophilic substitution reactions of 1-trimethylsilylcyclo-octacarbazole (**6h**) were briefly investigated. We were particularly attracted to nitrosation since the 1-nitroso compound (**29**) could also exist as the tautomer (**30**), the oxime of the peripheral 14π, potentially aromatic, ketone (**31**). However, attempted nitrosation of (**6h**) using either pentyl nitrite or sodium nitrite in the presence of trifluoroacetic acid[16] resulted in rapid decomposition of the ring system, and it was shown by ^1H n.m.r. spectrometery that the cyclo-octacarbazole (**6h**) is extremely acid sensitive, being completely destroyed in a few minutes. Protodesilylation under non-acidic conditions was also unsuccessful.

Attempted Preparation of 1-*Heteroatom-substituted Cyclo-octa*[def]*carbazoles.*—From the results already described it appears that formation of the cyclo-octacarbazole ring system on photolysis of 1-(1-naphthyl)benzotriazoles is favoured by a substituent at the naphthalene 2-position. The formation of cyclo-octa[*def*]carbazole (**6a**) itself in low yield from the unsubstituted benzotriazole (**5a**) also suggested that photolysis of any 2-substituted 1-(1-naphthyl)benzotriazole should give a low yield at least of the corresponding cyclo-octacarbazole. We therefore photolysed 1-(2-methoxy-1-naphthyl)benzotriazole (**5c**) hoping that the resulting 1-methoxycyclo-octacarbazole (**6c**) would be a useful intermediate in the synthesis of the peripheral 14π-ketone (**31**). We were surprised to find that photolysis of (**5c**) gave benzo[*a*]carbazole (**21**) as the sole isolable product (64%) and none of the cyclo-octacarbazole (**6c**). Similarly, irradiation of the 2,4-dihalogeno derivatives (**5d**) and (**5e**) failed to give any of the cyclo-octacarbazoles (**6d**) and (**6e**), 5-halogenobenzo[*a*]carbazoles (**32**; X = Cl) (31%) and (**32**; X = Br) (22%) being the only products arising from extrusion of nitrogen from the triazoles. An inseparable mixture of 1-(2- and 4-halogenonaphthyl)benzotriazoles, arising from homolysis of the carbon–halogen bonds and hydrogen abstraction from the solvent, was also obtained in each case [10% from (**5d**) and 30% from (**5e**)]. The benzocarbazoles (**21**), (**32**; X = Cl), and (**32**; X = Br) obtained from (**5c**), (**5d**), and (**5e**) respectively clearly arise from attack of the carbene at the naphthalene 2-position, and are presumably formed by loss of the 6a-substituent from the intermediate 6a*H*-substituted benzo[*a*]carbazole. Thus, photolysis of (**5c**) would give the 6a-methoxy-6a*H*-benzocarbazole (**33**) which can aromatise directly by elimination of formaldehyde in a retro-ene reaction, as shown. Similarly, photolysis of the dihalogeno compounds would give the 5,6a-dihalogenobenzo[*a*]carbazole (**34**) which, on further (photolytic)homolysis of the C(6a)–halogen bond gives the aromatic radical (**35**) which can afford the observed product by hydrogen abstraction from the solvent, acetonitrile.

This apparently exclusive attack of the carbene at the naphthalene 2-position in the photolysis of benzotriazoles (**5c**—**e**) could be explained by an attractive interaction between the electron deficient carbene and a lone pair of electrons on the 2-substituent, the carbenic centre thus being held in a conformation which would favour collapse onto the C-2 of the



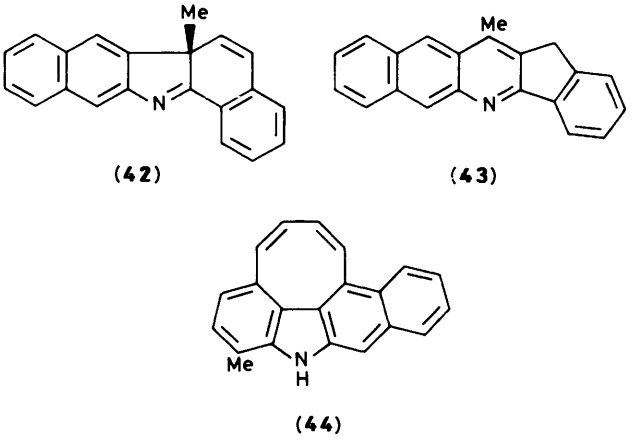


(36) (37) (38)

naphthalene ring. A similar, but irreversible, collapse of this type of carbene onto a nitrogen lone pair has been used in the preparation of five-membered heterocyclic compounds such as benzimidazoles by photolysis of the appropriate benzotriazoles.[17] We therefore considered photolysis of the quinolinyltriazole (**36**) to be of considerable interest since a similar attraction between the carbene and the quinoline nitrogen atom could strongly favour ultimate collapse of the carbene onto the quinoline 8a-position.

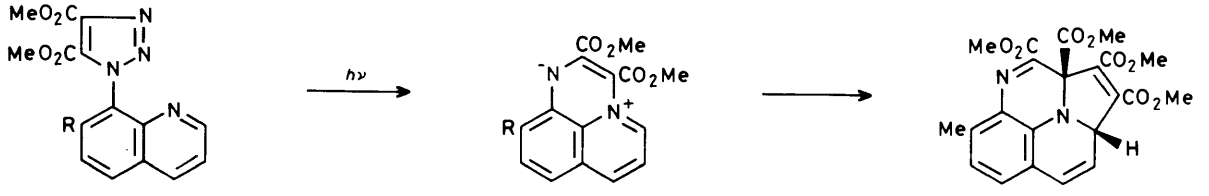
The triazole (**36**) was prepared by cycloaddition of 8-azido-7-methylquinoline to benzyne. However, on photolysis of (**36**) no simple products could be isolated from the intractable tar produced. At least no heterocyclic analogues of compounds (**10a**) and (**11a**), arising from carbene attack at the quinoline 7-position, were observed and hence further evidence for the intermediacy of the ylide (**37**) in this photolysis was sought. Kanemasa and co-workers have reported the generation of the related, unstable ylide (**38**) and its trapping by 1,3-dipolar cycloaddition to dimethyl acetylenedicarboxylate.[18] Photolysis of the triazole (**36**) in the presence of this acetylene did not furnish a cycloadduct and again an intractable tar was produced. We did find, however, that photolysis of the diesters (**39a**) and (**39b**), obtained from dimethyl acetylenedicarboxylate and 8-azidoquinoline and 8-azido-7-methylquinoline respectively, gave very high yields of the stable, isolable deep red ylides (**40a**) and (**40b**), obtained in each case as the sole product. The much increased stability of these compounds over the ylides (**37**) and (**38**) presumably results from delocalisation of the negative charge, as found with ylides generally. Dipolar cycloaddition of the ylide (**40b**) to dimethyl acetylenedicarboxylate gave the almost colouress adduct (**41**) in 41% yield.

Attempted Benzannelation of Cyclo-octa[def]*carbazole.*—The effect of benzannelation on the stability and reactivity of the cyclo-octacarbazoles could provide further insight into the electronic structure of the ring system. Photolysis of the naphthotriazole (**9**) gave 6a-methyl-6a*H*-dibenzo[*a*,*h*]carbazole (**42**) in 23% yield, though none of the di-π-methane photorearrangement product (**43**) was observed, presumably because this reactive, linearly fused benzoquinoline would not survive the reaction conditions. The expected benzo-fused cyclo-octacarbazole (**44**) was also not isolated; this too could result from a destabilising effect of the fusion of an orthoquinonoid ring to the [*b*]-face of the carbazole ring, again underlining the predominant contribution of electronic structure (**6**) over structure (**25**). Finally, we investigated the photolysis of the



(42) (43) (44)

readily available acridinylbenzotriazole (**45**) since collapse of the intermediate carbene to either ring junction position, followed by the rearrangement of Scheme 1, should give exclusively a stable benzo[*a*]-fused azacyclo-octacarbazole. This photolysis did indeed give one product in high yield. However, this was a pale yellow, very polar compound which, in addition to an N–H signal, showed only aromatic protons in the n.m.r. spectrum. Further n.m.r. studies, including n.O.e.



(39) (40) (41)

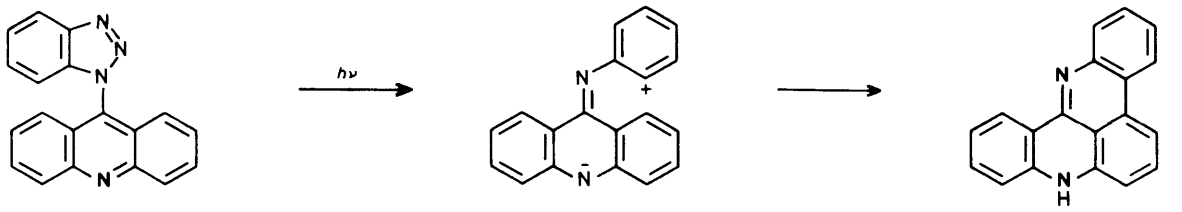
a; R = H
b; R = Me

The formation of ylides (**40a,b**) to the exclusion of other products on photolysis of the triazoles (**39a,b**) (particularly the former where a significant amount of product arising from carbene cyclisation onto the unsubstituted quinoline 7-position was to be expected) illustrates how effectively a carbene can be intercepted by a neighbouring heteroatom lone pair. This is considered to provide support for our explanation for the failure of benzotriazoles (**5c—e**) to give any products derived from attack of the intermediate carbene at the naphthalene 8a-position on photolysis.

difference and 2D spectra, led unambiguously to the structure (**46**).[19] Thus the intermediate carbene has not undergone the electrocyclisation reaction observed before (Scheme 1), but has attacked the, unconjugated acridine 1- (or 8-) position. This could be an intramolecular electrophilic attack favoured by the dipolar form (**47**) of the carbene.

Experimental

For general points see reference 20.



(45) (47) (46)

1-*Azido*-2,4-*dichloronaphthalene* (**7d**).—A slurry of 1-amino-2,4-dichloronaphthalene (860 mg, 4.1 mmol) in 6M-hydrochloric acid (4—5 ml) was diazotised at 0—5 °C by treatment with a solution of sodium nitrite (520 mg, 7.5 mmol) in water (2 ml) over 1.5 h. The resultant solution was then treated with a solution of sodium azide (520 mg, 8 mmol) and sodium acetate (4.10 g, 50 mmol) in water (35 ml) in one portion, and was then allowed to stand for 16 h at 4 °C. The mixture was extracted with ether (2 × 10 ml), and the combined ether extracts were washed with saturated aqueous sodium hydrogen carbonate (3 × 30 ml), water (10 ml), and brine (10 ml), and then dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave the *azide* as a pale brown solid (888 mg, 91%), m.p. 67—69 °C. An analytical sample was obtained by chromatography on silica gel, m.p. 70—71 °C (Found: C, 50.7; H, 2.2; Cl, 30.2; N, 17.5. $C_{10}H_5Cl_2N_3$ requires C, 50.5; H, 2.1; Cl, 29.8; N, 17.7%); $\nu_{max.}$(Nujol) 2 130 cm^{-1}; δ (90 MHz, $CDCl_3$) 7.38 (1 H, s), 7.43—7.58 (2 H, m), and 8.00—8.17 (2 H, m); *m/z* 239 (M^+ + 2), 237 (M^+), 213, 211, 209, 176, and 174 (base).

Similarly prepared were the following. 1-*Azido*-2,4-*dibromonaphthalene* (**7e**) (85% based on recovered starting material), m.p. 66.5—68 °C (Found: C, 36.9; H, 1.5; Br, 48.9; N, 12.7. $C_{10}H_5Br_2N_3$ requires C, 36.7; H, 1.5; Br, 48.9; N, 12.85%); $\nu_{max.}$(Nujol) 2 139 cm^{-1}; δ (90 MHz, $CDCl_3$) 7.50—7.70 (2 H, m), 7.81 (H s), and 8.03—8.25 (2 H, m); *m/z* 329 (M^+ + 4), 327 (M^+ + 2), 325 (M^+) 303, 301, 299, 297, 220, 218 (base), and 139.

1-Azido-2-bromonaphthalene (**7f**) (58%) as an oil; $\nu_{max.}$(neat) 3 134 cm^{-1}. This material darkened rapidly on isolation, and was used immediately without further purification.

8-*Azidoquinoline* as a gum (26%) (Found: M^+, 170.0590. $C_9H_6N_4$ requires 170.0592); δ (250 MHz, $CDCl_3$) 7.33 (H dd, *J* 7, 1 Hz), 7.38—7.48 (2 H, m), 7.54 (1 H, dd, *J* 8, 1 Hz), 8.10 (1 H, dd, *J* 8, 1 Hz), and 8.88 (1 H, dd, *J* 4, 1 Hz); *m/z* 170 (M^+), 144, 142 (base), 115, 88, and 73.

8-*Azido*-7-*methylquinoline* (57%), m.p. 53—54 °C (Found: C, 65.2; H, 4.3; N, 30.4. $C_{10}H_8N_4$ requires C, 65.2; H, 4.3; N, 30.4%); $\nu_{max.}$(Nujol) 2 119 cm^{-1}; δ (250 MHz, $CDCl_3$) 2.46 (3 H, s), 7.31 (1 H, d, *J* 8 Hz), 7.38 (1 H, dd, *J* 8, 4 Hz), 7.47 (1 H, d, *J* 8 Hz), 8.10 (1 H, dd, *J* 8, 1 Hz), and 8.86 (1 H, dd, *J* 4, 1 Hz); *m/z* 184 (M^+), 156, 155, 130, 129, and 102.

1-*Azido*-2-*methylnaphthalene* (**7b**).—A stirred slurry of 2-methyl-1-naphthylammonium chloride (1.00 g, 5.2 mmol) in a mixture of ethanol (15 ml) and acetic acid (5 ml) was diazotised at 0—5 °C by treatment with a solution of isopentyl nitrite (0.74 ml, 5.5 mmol) in ethanol (3 ml) over 5 min. The mixture was stirred for a further 2 h before the addition of a solution of sodium azide (720 mg, 11 mmol) in water (15 ml). The mixture was stirred at 0—5 °C for 16 h, then water (50 ml) was added, and the mixture extracted with ether (2 × 20 ml). The combined ether extracts were extracted with saturated aqueous sodium hydrogen carbonate (5 × 15 ml), water (2 × 10 ml), and brine (10 ml), and then dried ($MgSO_4$). Removal of the solvent under reduced pressure gave a red oil which was chromatographed on silica gel to give the *azide* as a pale yellow oil (510 mg, 54%) (Found: C, 72.05; H, 5.0; N, 23.0. $C_{11}H_9N_3$ requires C, 72.1; H, 4.95; N, 22.9%); $\nu_{max.}$(neat) 2 102 cm^{-1}; δ (90 MHz, $CDCl_3$) 2.43 (3 H, s), 7.07 (1 H, d, *J* 8 Hz), 7.18—7.70 (4 H, m), and 8.03 (1 H, m); *m/z* 183 (M^+), 155, 154 (base), 140, 128, and 127.

1-*Azido*-2-*methoxynaphthalene* (**7c**).—A stirred two-phase mixture comprising solutions of 1-amino-2-methoxynaphthalene (1.00 g, 5.8 mmol) in ether (20 ml) and of sodium azide (1.3 g, 20 mmol) and acetic acid (5 ml) in water (20 ml) was treated at 0—5 °C with isopentyl nitrite (0.9 ml, 6.5 mmol), and stirring was continued at this temperature for 20 h; then the ether layer was separated, washed with saturated aqueous sodium hydrogen carbonate (5 × 10 ml), water (10 ml), and brine (10 ml), and then dried ($MgSO_4$). Evaporation of the solvent left a pale yellow solid, which was chromatographed on silica gel to give the *azide* (790 mg, 69%), m.p. 72—74 °C (Found: C, 66.3; H, 4.55; N, 21.1. $C_{11}H_9N_3O$ requires C, 66.2; H, 4.5; N, 21.1%); $\nu_{max.}$(Nujol) 2 112 cm^{-1}; δ 3.91 (3 H, s), 7.00—7.70 (5 H, m), and 8.01 (1 H, m): *m/z* 199 (M^+), 171, 170, 156, 143, 128 (base), and 101.

1-(1-*Naphthyl*)*benzotriazole* (**5a**).—A stirred solution of 1-azidonaphthalene (**7a**) (8.45 g, 50 mmol) and isopentyl nitrite (13.5 ml, 100 mmol) in dichloromethane (400 ml) was heated under reflux and treated with a solution of anthranilic acid (13.7 g, 100 mmol) in acetone (100 ml) over 2 h. Heating was continued for a further 1 h, after which the mixture was cooled and evaporated under reduced pressure to leave a brown oil. Chromatography of this on silica gel afforded the triazole as a white crystalline solid (9.15 g, 75%), m.p. 114—115 °C (lit.,[12] 114 °C).

Similarly prepared were the following. 1-(2-Methyl-1-naphthyl)benzotriazole (**5b**) (60%), m.p. 135—136 °C (lit.,[8] 135—137 °C).

1-(2-*Methoxy*-1-*naphthyl*)*benzotriazole* (**5c**) (57%), m.p. 187.5—189 °C (Found: C, 73.95; H, 4.8; N, 15.35. $C_{17}H_{13}N_3O$ requires C, 74.2; H, 4.8; N, 15.3%); $\nu_{max.}$(Nujol) 1 629, 1 595, 1 510, 1 490, 1 476, 1 272, 1 149, 1 065, 810, 770, 752, and 749 cm^{-1}; δ (90 MHz, $CDCl_3$) 3.80 (3 H, s), 6.90—7.50 (7 H, m), and 7.70—8.20 (3 H, m); *m/z* 275 (M^+) 247, 246, 232 (base), 217 and 216.

1-(2,4-*Dichloro*-1-*naphthyl*)*benzotriazole* (**5d**) (69%), m.p. 145—145.5 °C (Found: C, 61.2; H, 2.9; Cl, 22.6; N, 13.4. $C_{16}H_9Cl_2N_3$ requires C, 61.2; H, 2.75; Cl, 22.5; N, 13.4%); $\nu_{max.}$(Nujol) 1 611, 1 580, 1 490, 1 280, 1 201, 1 148, 1 040, 973, 870, 860, 783, 768, 760, and 750 cm^{-1}; δ (90 MHz, $CDCl_3$) 6.97—7.30 (2 H, m), 7.32—7.78 (4 H, m), 7.79 (1 H, s), and 8.10—8.39 (2 H, m); *m/z* 317 (M^+ + 4), 315 (M^+ + 2), 313 (M^+), 289, 287, 285, 252, 250 (base), 214, 160, 125, 107, and 28.

1-(2,4-*Dibromo*-1-*naphthyl*)*benzotriazole* (**5e**) (64%), m.p. 156—157 °C (Found: C, 48.0; H, 2.2; Br, 39.2; N, 10.2. $C_{16}H_9Br_2N_3$ requires C, 47.7; H, 2.25; Br, 39.65; N, 10.4%); $\nu_{max.}$(Nujol) 1 610, 1 578, 1 375, 1 280, 1 053, 1 045, 868, 832, 784, 769, 758, 745 cm^{-1}; δ (250 MHz, $CDCl_3$) 6.97 (1 H, d, *J* 8 Hz), 7.17 (1 H, m), 7.44—7.56 (3 H, m), 7.69 (1 H, m), 8.20 (1 H, s), 8.25 (1 H, m), and 8.36 (1 H, d, *J* 8 Hz); *m/z* 405 (M^+ + 4), 403 (M^+ + 2), 401 (M^+), 377, 376, 375, 374, 373, 372, 296, 294 (base), 214, 125, 100, and 83.

1-(2-*Bromo*-1-*naphthyl*)*benzotriazole* (**5f**).—A slurry of benzenediazonium-2-carboxylate prepared from anthranilic acid (10 mmol) in a solution of 1-azido-2-bromonaphthalene (**7f**) (417 mg, 1.68 mmol) in 1,2-dichloroethane (40 ml) was heated to reflux for 40 min, and then cooled. Evaporation of the solvent and chromatography afforded the *triazole* as crystals (408 mg, 75%), m.p. 128.5—130 °C (Found: C, 59.5; H, 3.0; Br, 24.5; N, 12.9. $C_{16}H_{10}BrN_3$ requires C, 59.3; H, 3.1; Br, 24.65; N, 13.0%); δ (250 MHz, $CDCl_3$) 6.98 (1 H, m), 7.15—7.21 (1 H, m), 7.40—7.55 (3 H, m), 7.59 (1 H, ddd, *J* 8, and 7, 1 Hz), 7.85 (1 H, d, *J* 9 Hz), 7.98 (1 H, dd, *J* 8, 1 Hz), 7.99 (1 H, d, *J* 9 Hz), and 8.21—8.28 (1 H, m); *m/z* 325 (M^+ + 2), 323 (M^+), 297, 296, 295, 294, 216 (base), 126 and 107.

Similarly prepared was 1-(7-*methylquinolin*-8-*yl*)*benzotriazole* (**36**) (80%), m.p. 182—183 °C (Found: C, 73.85; H, 4.5; N, 21.3. $C_{16}H_{12}N_4$ requires C, 73.8; H, 4.65; N, 21.5%); δ (250 MHz, $CDCl_3$) 2.26 (3 H, s), 7.10 (1 H, m), 7.38—7.47 (3 H, m), 7.63 (1 H, d, *J* 8 Hz), 7.99 (1 H, d, *J* 8 Hz), 8.18—8.28 (2 H, m), and 8.75 (1 H, dd, *J* 4, 2 Hz); *m/z* 260 (M^+), 232, 231 (base), 141, 115, and 69.

Dimethyl 1-(*Quinolin*-8-*yl*)*triazole*-4,5-*dicarboxylate* (**39a**).—An intimate mixture of 8-azidoquinoline (200 mg, 1.2 mmol) and dimethyl acetylenedicarboxylate (250 μl, 2 mmol) was stirred in the dark for 16 h. Trituration with ether–pentane (1:3) (5 ml) gave a precipitate which was collected and recrystallised from chloroform–hexane to give the *triazole* as crystals (350 mg, 95%), m.p. 167—168 °C (Found: C, 57.7; H, 3.8; N, 17.9. $C_{15}H_{12}N_4O_4$ requires C, 57.7; H, 3.9; N, 17.9%); δ (250 MHz, $CDCl_3$) 3.63 (3 H, s), 4.02 (3 H, s), 7.50 (1 H, dd, *J* 8, 4 Hz), 7.73 (1 H, dd, *J* 8, 7 Hz), 8.03 (1 H, dd, *J* 8, 1 Hz), 8.10 (1 H, dd, *J* 8, 1 Hz), 8.27 (1 H, dd, *J* 9, 2 Hz), and 8.81 (1 H, dd, *J* 4, 2 Hz); *m/z* 312 (M^+), 284 (base), 253, 225, 195, 181, 168, 128, and 121.

Similarly prepared was *dimethyl* 1-(7-*methylquinolin*-8-*yl*)-*triazole*-4,5-*dicarboxylate* (**39b**) (91%), m.p. 145—146 °C (Found: C, 59.15; H, 4.3; N, 17.2. $C_{16}H_{14}N_4O_4$ requires C, 58.9; H, 4.25; N, 17.1%); $\nu_{max.}$(Nujol) 1 737, 1 731, 1 625, 1 594, 1 290, 1 250, 1 231, and 1 211 cm^{-1}; δ (250 MHz, $CDCl_3$) 2.40 (3 H, s), 3.63 (3 H, s), 4.05 (3 H, s), 7.41 (1 H, dd, *J* 8, 4 Hz), 7.58 (1 H, d, *J* 9 Hz), 7.94 (1 H, d, *J* 9 Hz), 8.20 (1 H, dd, *J* 8, 2 Hz), and 8.76 (1 H, dd, *J* 4, 2 Hz); *m/z* 326 (M^+), 298 (base), 267, 239, 209, 180, 168, and 142.

7-*Methyl*-1-(2-*methyl*-1-*naphthyl*)*benzotriazole* (**5g**).—A solution of 1-azido-2-methylnaphthalene (**7b**) (1.65 g, 9 mmol) and pentyl nitrite (1.90 ml, 14 mmol) in dichloromethane (80 ml) was heated under reflux and a solution of 3-methylanthranilic acid (2.00 g, 13 mmol) in acetone (20 ml) was added over 1.5 h. Heating was continued for a further 2 h; the dark solution was then cooled and evaporated. The residue was partitioned between ether (70 ml) and sodium hydroxide solution (2M, 50 ml). The ether layer was separated, washed with sodium hydroxide solution (2M, 50 ml), water (2 × 50 ml), and dried ($MgSO_4$). Evaporation of the solvent and chromatography gave (i) a mixture of isomers [predominantly 4-methyl-1-(2-methyl-1-naphthyl)benzotriazole (**8**)] (740 mg), and (ii) 7-*methyl*-1-(2-*methyl*-1-*naphthyl*)*benzotriazole* (**5g**) (520 mg, 1.9 mmol, 21%), m.p. 150—152 °C (EtOH–H_2O) (Found: C, 79.05; H, 5.5; N, 15.1. $C_{18}H_{15}N_3$ requires C, 79.1; H, 5.5; N, 15.35%); $\nu_{max.}$ 1 622, 1 602, 1 591, 1 521, 1 512, 1 247, 1 232, 1 219, 1 189, 1 111, 1 068, 1 050, 972, 912, 880, 820, 794, 786, 759, and 692 cm^{-1}; δ 1.79 (3 H, s), 2.11 (3 H, s), 6.84 (1 H, d, *J* 8 Hz), 7.13—7.54 (6 H, m), 7.92 (1 H, d, *J* 8 Hz), 8.00 (1 H, d, *J* 9 Hz), and 8.07 (1 H, d, 8 Hz); *m/z* 273 (M^+), 245, 244, 230 (base), 139, 122, and 115.

1-(2-*Methyl*-1-*naphthyl*)*naphtho*[4,5-b]*triazole* (**9**).—A solution of 1-azido-2-methylnaphthalene (500 mg, 2.7 mmol) and pentyl nitrite (0.4 ml, 3 mmol) in dimethoxyethane (20 ml) was heated to reflux and a solution of 3-amino-2-naphthoic acid (500 mg, 2.7 mmol) in dimethoxyethane (10 ml) was added over 30 min. The mixture was heated for a further 1 h after which it was cooled and evaporated under reduced pressure. The residual gum was partitioned between ether (20 ml) and sodium hydroxide solution (2M; 20 ml). The ether layer was separated, washed with aqueous sodium hydroxide (2M; 2 × 10 ml) and water (20 ml), and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure and chromatography of the residue afforded the *triazole* (**9**) as a pale yellow gum (176 mg, 21%) (Found: M^+, 309.1274. $C_{21}H_{15}N_3$ requires 309.1266); $\nu_{max.}$(Nujol) 1 412, 1 389, 1 366, 858, 812, and 780 cm^{-1}; δ (250 MHz, $CDCl_3$) 2.16 (3 H, s), 6.93 (1 H, dd, *J* 8, 1 Hz), 7.33 (1 H, m), 7.42—7.63 (5 H, m), 7.80 (1 H, m), 7.96 (1 H, d, *J* 9 Hz), 8.04 (1 H, d, *J* 9 Hz), 8.13 (1 H, m), and 8.80 (1 H, s); *m/z* 309 (M^+), 280, 266, 142, and 115.

1-(2-*Trimethylsilyl*-1-*naphthyl*)*benzotriazole* (**5h**).—A stirred solution of 1-(2-bromo-1-naphthyl)benzotriazole (**5f**) (276 mg, 0.85 mmol) in tetrahydrofuran (9 ml) was cooled to −70 °C, and a solution of t-butyl-lithium (1.8M; 690 μl, 1.25 mmol) was added dropwise. The red solution was stirred at −70 °C for 45 min after which freshly distilled chlorotrimethylsilane (220 μl, 1.7 mmol) was added. The temperature was maintained at −70 °C for 6 h and then allowed slowly to attain room temperature. The mixture was partitioned between ether (30 ml) and water (30 ml). The ether layer was separated and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure and chromatography of the residue gave the *triazole* (188 mg, 69%), m.p. 93.5—95 °C (Found: C, 72.0; H, 6.1; N, 13.3. $C_{19}H_{19}N_3Si$ requires C, 71.9; H, 6.0; N, 13.2%); $\nu_{max.}$(Nujol) 1 610, 1 590, 1 270, 1 248, 1 062, 872, 839, 818, 760, and 748 cm^{-1}; δ (250 MHz, $CDCl_3$) −0.01 (9 H, s), 6.61 (1 H, dd, *J* 8, 1 Hz), 7.04—7.12 (1 H, m), 7.29 (1 H, ddd, *J* 9, 8, 1 Hz), 7.38—7.47 (2 H, m), 7.50 (1 H, ddd, *J* 9, 8, 1 Hz), 7.79 (1 H, d, *J* 8 Hz), 7.93 (1 H, d, *J* 8 Hz), 8.06 (1 H, d, *J* 8 Hz), and 8.16—8.24 (1 H, m); *m/z* 317 (M^+), 289, 274, 91, 85, 83 (base), and 73.

Photolysis of 1-(2-*Methyl*-1-*naphthyl*)*benzotriazole* (**5b**).—A solution of the benzotriazole (**5b**) (253 mg, 0.95 mmol) in acetonitrile (180 ml) was irradiated at 254 nm for 10 h. Evaporation of the solvent under reduced pressure and chromatography of the residue on silica gel gave (i) 1-*methyl-cyclo-octa*[def]*carbazole* (**6b**) (52 mg, 24%; 30% based on consumed material) as a red gum, which solidified with time, m.p. 69—72 °C (from light petroleum) (Found: C, 88.5; H, 5.6; N, 6.1. $C_{17}H_{13}N$ requires C, 88.3; H, 5.7; N, 6.1%); $\nu_{max.}$(CCl_4) 3 470, 3 035, 3 010, 2 910, 2 870, 1 600, 1 590, 1 415, 1 400, 1 380, 1 370, 1 310, 1 155, and 1 030 cm^{-1}; $\lambda_{max.}$(cyclohexane) 212 (log ε 4.46), 242sh (4.61), 245sh (4.66), 247 (4.69), 267 (4.26), 274 (4.31), 282 (4.24), 332sh (3.68), 339 (3.79), 356 (3.79), 382sh (3.56), 394 (3.65), 408sh (3.53), and 418 nm (3.52); δ_H([$^2H_8$]-THF) 2.36 (3 H, s, Me), 5.17 (1 H, m, 5 H), 5.22 (1 H, m, 6-H), 5.62 (1 H, m, 4-H), 5.67 (1 H, m, 7-H), 6.40 (1 H, d, *J* 7.5 Hz, 3-H), 6.48 (1 H, d, *J* 7 Hz, 8-H), 6.75 (1 H, dd, *J* 7.5, 1 Hz, 2-H), 6.94 (1 H, t, 7.5 Hz, 9-H), 7.07 (1 H, dd, *J* 7.5, 1 Hz, 10-H), and 10.17 (1 H, br s, NH); δ_C($CDCl_3$) (quaternary) 120.2, 121.2, 122.1, 130.9, 133.2, 139.5, and 139.9; (non-quaternary) 16.5, 113.0, 124.4, 125.5, 126.6, 127.2, 128.0, 128.3, 133.1, and 133.6; *m/z* 231 (M^+; base), and 205. *Picrate*; dark brown needles, m.p. 175—177 °C (decomp.) (from ethanol) (Found: C, 60.2; H, 3.6; N, 12.15. $C_{23}H_{16}N_4O_7$ requires C, 60.0; H, 3.5; N, 12.2%).

(ii) A green gum (157 mg) which n.m.r. analysis indicated to consist of starting benzotriazole (**5b**) (24%), the 6a*H*-benzo[*a*]-carbazole (**10a**) (19%; 24% based on consumed starting material), and the indenoquinoline (**11a**) (23%; 31% based on consumed starting material). The two products were identified by comparison with independently prepared materials.[8]

Photolysis of 7-*Methyl*-1-(2-*methyl*-1-*naphthyl*)*benzotriazole* (**5g**).—Similar irradiation of a solution of benzotriazole (**5g**) (100 mg) in acetonitrile (100 ml) for 20 h and chromatography gave (i) 6,10-dimethylindeno[1,2-*b*]quinoline (**11b**) (34 mg, 37%; 42% based on consumed starting material);[8] (ii) 1,10-*dimethylcyclo-octa*[def]*carbazole* (**6g**) (16 mg, 18%; 20% based on consumed starting material), m.p. 164—165.5 °C (Found: C, 87.9; H, 6.0; N, 5.4. $C_{18}H_{15}N$ requires C, 88.1; H, 6.2; N, 5.7%); $\nu_{max.}$(Nujol) 3 479, 1 620, 1 597, 1 580, 1 572, 1 420, 1 391, 1 377, 1 320, 1 292, 1 260, 1 248, 1 238, 1 167, 1 041, 1 011, 860, 830, 815, 716, and 710 cm^{-1}; δ (250 MHz, $CDCl_3$) 2.41 (6 H, s, br, $w_{\frac{1}{2}}$ 2 Hz), 5.23—5.36 (2 H, m), 5.63—5.78 (2 H, m), 6.51 (2 H, d, *J* 7 Hz), 6.84 (2 H, dd, *J* 7, 1 Hz), and 7.69 (1 H, br); *m/z* 245 (M^+, base) and 219; (iii) 6a,10-dimethyl-6a*H*-benzo[*a*]carbazole (**10b**) (20 mg, 22%; 25% based on consumed starting material);[8] and (iv) starting benzotriazole (**5g**) (11 mg, 11% recovery).

Photolysis of 1-(1-*Naphthyl*)*benzotriazole* (**5a**).—Similar irradiation of a solution of benzotriazole (**5a**) (257 mg) in acetonitrile (180 ml) for 20 h and chromatography on silver nitrate-impregnated silica gel gave (i) *cyclo-octa*[def]*carbazole* (**6a**) (11 mg, 5%), m.p. 131—134 °C (Found: M^+, 217.0887. $C_{16}H_{11}N$ requires 217.0891); $\nu_{max.}$($CHCl_3$) 3 470, 1 632, 1 615, 1 610, 1 599, 1 587, 1 313, and 1 149 cm^{-1}; $\nu_{max.}$(Nujol) 3 443, 3 400, 1 620, 1 612, 1 602, 1 585, 1 422, 1 318, 1 199, 1 158, 1 150, 1 040, 795, 789, 721, and 700 cm^{-1}; δ (250 MHz, $CDCl_3$) 5.35 (2 H, m), 5.73 (2 H, m), 6.57 (2 H, m), 7.02 (4 H, m), and 7.91 (1 H, br); *m/z* 217 (M^+, base) and 191; and (ii) an inseparable mixture (76 mg) which appeared from the ^1H n.m.r. spectrum to consist of benzo[*a*]carbazole (**21**) (10%) and another component tentatively identified as *N*-ethylideneiminobenzo[*a*]carbazole (**23**) (20%) (see Discussion).

Photolysis of 1-(2-*Trimethylsilyl*-1-*naphthyl*)*benzotriazole* (**5h**).—Similar irradiation of a solution of benzotraizole (**5h**) (160 mg) in acetonitrile (180 ml) for 10 h and chromatography gave 1-*trimethylsilylcyclo-octa*[def]*carbazole* (**6h**) (68 mg, 47%) as a red oil (Found: M^+, 289.1283. $C_{19}H_{19}NSi$ requires 289.1287); $\nu_{max.}$(neat) 3 460, 1 620, 1 602, 1 430, 1 369, 1 311, 1 250, 1 042, 1 021, 872, 859, 849, 806, 780, 755, 740, 715, and 701 cm^{-1}; δ (250 MHz, $CDCl_3$) 0.41 (9 H, s), 5.32—5.46 (2 H, m), 5.69—5.83 (2 H, m), 6.55—6.63 (2 H, m), 7.00—7.11 (2 H, m), 7.16 (1 H, d, *J* 7 Hz), and 7.90 (1 H, br); *m/z* 289 (M^+, base) 273 and 272.

The carbazole (**6h**) (5 mg) in deuteriochloroform (0.5 ml) was treated with trifluoroacetic acid (0.2 ml) and the ^1H n.m.r. spectrum was monitored in the region δ 8—4 at 30 s intervals. The carbazole (**6h**) had decomposed completely in 6 min.

Photolysis of 1-(2-*Methoxy*-1-*naphthyl*)*benzotriazole* (**5c**).—Similar irradiation of a solution of benzotriazole (**5c**) (250 mg) in acetonitrile (180 ml) at 254 nm for 10 h and chromatography gave (i) benz[*a*]carbazole (**21**) (51 mg, 26%; 64% based on consumed starting material), m.p. 221—223 °C (lit.,[12] 225 °C); and (ii) starting triazole (**5c**) (150 mg, 60% recovery).

Photolysis of 1-(2,4-*Dichloro*-1-*naphthyl*)*benzotriazole* (**5d**).—Similar irradiation of a solution of benzotriazole (**5d**) (250 mg) in acetonitrile (180 ml) for 10 h and chromatography gave (i) 5-*chlorobenz*[a]*carbazole* (62 mg, 31%), m.p. 131—133 °C (EtOH–H_2O) (Found: C, 76.3; H, 3.9; Cl, 13.8; N, 5.6. $C_{16}H_{10}ClN$ requires C, 76.35; H, 4.0; Cl, 14.1; N, 5.6%); $\nu_{max.}$($CHCl_3$) 3 467, 1 460, 1 360, 1 270, 949, 908, and 870 cm^{-1}; δ (250 MHz, $CDCl_3$) 7.31 (1 H, dd, *J* 7, 7 Hz), 7.4 (1 H, dd, *J* 7, 7 Hz), 7.54—7.69 (3 H, m), 8.07 (1 H, d, *J* 8 Hz), 8.13 (1 H, m), 8.23 (1 H, s), 8.43 (1 H, m), and 8.77 (1 H, broad); *m/z* 253 (M^+ + 2), 251 (M^+, base), 216, 189, 126, 108, and 95; and (ii) a mixture (22 mg, 10%) which appeared by n.m.r. and m.s. analysis to consist of 1-(2-chloro-1-naphthyl)benzotriazole and 1-(4-dichloro-1-naphthyl)benzotriazole.

Photolysis of 1-(2,4-*Dibromo*-1-*naphthyl*)*benzotriazole* (**5e**).—Similar irradiation of a solution of benzotriazole (**5e**) (250 mg) in acetonitrile (180 ml) for 10 h and chromatography gave (i) 5-*bromobenz*[a]*carbazole* (28 mg, 15%; 22% based on consumed starting material), m.p. 128.5—130 °C (EtOH–H_2O) (Found: C, 65.2; H, 3.3; N, 4.6. $C_{16}H_{10}BrN$ requires C, 64.9; H, 3.4; N, 4.7%); $\nu_{max.}$($CHCl_3$) 3 470, 1 460, 1 358, 1 269, and 900 cm^{-1}; δ (250 MHz, $CDCl_3$) 7.31 (1 H, m), 7.46 (1 H, m), 7.55—7.70 (3 H, m), 8.03—8.15 (2 H, m), 8.40 (1 H, m), 8.44 (1 H, s), and 8.79 (1 H, br); *m/z* 297 (M^+ + 2), 295 (M^+, base), 216, 189, 148, 147, 108, and 95; (ii) starting benzotriazole (**5e**) (64 mg, 26%); and (iii) a mixture (46 mg, 23%; 30% based on consumed starting material) which appeared by n.m.r. and m.s. analysis to consist of 1-(2-bromo-1-naphthyl)benzotriazole and 1-(4-bromo-1-naphthyl)benzotriazole.

Photolysis of 1-(7-*Methylquinolin*-8-*yl*)*benzotriazole* (**36**).—Similar irradiation of a solution of benzotriazole (**36**) (25 mg) in acetonitrile (180 ml) for 10 h gave an intractable tar. A repetition of this irradiation, but in the presence of a large excess of dimethyl acetylenedicarboxylate (10 ml), also gave only an intractable tar.

Photolysis of 1-(2-*Methyl*-1-*naphthyl*)*naphtho*[4,5-b]*triazole* (**9**).—Similar irradiation of a solution of naphthotriazole (**9**) (150 mg) in acetonitrile (150 ml) for 15 h and chromatography gave (i) an unidentified yellow solid (5 mg); (ii) starting naphthotriazole (**9**) (12 mg, 8% recovery) and (iii) 6a-*methyl*-6aH-*dibenzo*[a,h]*carbazole* (**42**) as a pale yellow gum (28 mg, 23%) which solidified with time, m.p. 125—127 °C (Found: C, 89.5; H, 5.5; N, 4.7. $C_{21}H_{15}N$ requires C, 89.65; H, 5.4; N, 5.0%); $\nu_{max.}$(Nujol) 1 562, 1 548, 881, 789, 772, 760, 748, 740, and 725 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.50 (3 H, s), 6.51 (1 H, d, *J* 10-Hz), 6.64 (1 H, d, *J* 10 Hz), 7.27 (1 H, m), 7.38—7.52 (4 H, m), 7.83 (1 H, s), 7.84—7.94 (2 H, m), 8.06 (1 H, s), and 8.09 (1 H, m); *m/z* 281 (M^+), 266 (base), 155, 133, 127, and 119.

Photolysis of 1-(*Acrydin*-9-*yl*)*benzotriazole* (**45**).—Similar irradiation of a solution of the benzotriazole (**45**)[6] (200 mg) in acetonitrile (180 ml) for 10 h and chromatography gave (i) unchanged triazole (**45**) (82 mg, 41% recovery) and (ii) 8*H*-quinolino[4,3,2-*gh*]phenanthridine (**46**) (70 mg, 39%; 66% based on consumed starting triazole) as a pale yellow solid, m.p. > 280 °C (Found: C, 84.8; H, 4.5; N, 10.3. $C_{19}H_{12}N_2$ requires C, 85.05; H, 4.5; N, 10.4%); δ (250 MHz, [$^2H_6$]-DMSO) 7.08—7.17 (2 H, m), 7.22 (1 H, d, *J* 8 Hz), 7.38—7.54 (2 H, m), 7.60 (1 H, m), 7.70 (1 H, t, *J* 8, Hz), 7.83 (1 H, dd, *J* 8, 1 Hz), 7.94 (1 H, d, *J* 8 Hz), 8.42 (1 H, dd, *J* 8, 1 Hz), 8.56 (1 H, dd, *J* 8, 1 Hz), and 10.94 (1 H, s); *m/z* 268 (M^+, base) and 134 (M^+).

Photolysis of Dimethyl 1-(*Quinolin*-8-*yl*)*triazole*-4,5-*dicarboxylate* (**39a**).—A solution of triazole (**39a**) (150 mg) in acetonitrile (150 ml) was photolysed at 254 nm for 10 h. Evaporation of the solvent left a gum which was dissolved in ether (30 ml) and washed with cold dilute (0.2M) hydrochloric acid (3 × 10 ml). The combined aqueous layers were extracted with ether (10 ml) and the combined ether layers were dried ($MgSO_4$) and evaporated to leave a gum, which was chromatographed to give unchanged triazole (**39a**) (104 mg, 70% recovery). The aqueous layer was made alkaline (1M sodium hydroxide) and extracted with ether (2 × 15 ml); the combined ether extracts were dried (Na_2SO_4) and evaporated to leave the *ylide* (**40a**) as a purple-red solid of undefined m.p. (33 mg, 24%; 80% based on consumed triazole) (Found: M^+, 284.0802. $C_{15}H_{12}N_2O_4$ requires 284.0797); $\nu_{max.}$(Nujol) 1 730,

1 670, 1 601, 1 575, 1 290, 830, 807, 780, 770, and 759 cm^{-1}; δ (250 MHz, $CDCl_3$) 3.73 (3 H, s), 3.90 (3 H, s), 6.87 (1 H, dd, *J* 8, 1 Hz), 6.92—7.03 (2 H, m), 7.26 (1 H, t, *J* 8 Hz), 7.49 (1 H, d, *J* 8 Hz), and 9.51 (1 H, dd, *J* 6, 1 Hz); *m/z* 284 (M^+, base), 253, 225, 195, 181, 168, 144, and 140.

Photolysis of Dimethyl 1-(7-*Methylquinolin*-8-*yl*)*triazole*-4,5-*dicarboxylate* (**39b**).—Similarly, photolysis of a solution of the triazole (**39b**) (187 mg) in acetonitrile (180 ml) at 254 nm for 10 h gave the *ylide* (**40b**) (85 mg, 50%; 74% based on consumed starting material) as a red gum (Found: M^+, 298.0961. $C_{16}H_{14}N_2O_4$ requires 298.0954); $\nu_{max.}$(Nujol) 1 739, 1 722, 1 663, 1 658, 1 645, 1 490, 1 435, 1 409, 1 356, 1 290, 1 272, 1 240, 1 212, 1 188, 1 170, 1 130, 1 108, 913, 821, 781, and 750 cm^{-1}; δ (250 MHz, $CDCl_3$), 2.26 (3 H, s), 7.32 (3 H, s), 3.89 (3 H, s), 6.83 (1 H, d, *J* 8 Hz), 6.87 (1 H, dd, *J* 9, 6 Hz), 7.21 (1 H, d, *J* 8 Hz), 7.37 (1 H, d, *J* 9 Hz), and 9.49 (1 H, d, *J* 6 Hz); *m/z* 298 (M^+, base), 267, 239, 209, 180, and 154.

Treatment of a solution of the ylide (**40b**) (10 mg) in methanol (1 ml) with dimethyl acetylenedicarboxylate (50 mg) for 16 h, and evaporation of the solvent gave a gum. Chromatography afforded the *adduct* (**41**) as a pale yellow solid (6 mg, 41%), m.p. 167—169 °C (Found: M^+, 440.1215. $C_{22}H_{20}N_2O_8$ requires 440.1220); δ (250 MHz, $CDCl_3$) 2.46 (3 H, s), 3.77 (3 H, s), 3.79 (3 H, s), 3.80 (3 H, s), 3.89 (3 H, s), 5.16 (1 H, dd, *J* 5 and 2 Hz), 5.94 (1 H, dd, *J* 10 and 5 Hz), 6.39 (1 H, dd, *J* 10, 2 Hz), 6.62 (1 H, d, *J* 7 Hz), and 6.78 (1 H, d, *J* 7 Hz).

Attempted Photolysis of 1-*Methylcyclo-octa*[def]*carbazole* (**6b**).—A solution of 1-methylcyclo-octa[*def*]carbazole (**6b**) (16 mg) in acetonitrile (30 ml) was irradiated at 254 nm for 10 h. Evaporation of the solvent under reduced pressure and chromatography gave starting material (15 mg, 94%).

Similarly, irradiation of the carbazole (**6b**) at 350 nm for 10 h gave unchanged (**6b**) (99%).

Attempted Thermolysis of 1-*Methylcyclo-octa*[def]*carbazole* (**6b**).—A solution of (**6b**) (16 mg) in toluene (3 ml) was heated to reflux for 72 h. Evaporation of the solvent under reduced pressure and chromatography of the residue gave unchanged (**6b**) (15 mg, 94%).

Flash vacuum pyrolysis of (**6b**) (14 mg) at 720 °C and 2×10^{-2} Torr gave unchanged (**6b**) (13 mg, 92%).

Hydrogenation of 1-*Methylcyclo-octa*[def]*carbazole* (**6b**).—A solution of the carbazole (**6b**) (25.2 mg, 0.11 mmol) in methanol (2 ml) was stirred under a hydrogen atmosphere in the presence of a 10% palladium on charcoal catalyst (5 mg) for 16 h. The catalyst was removed by filtration through Celite and the filtrate was evaporated under reduced pressure to leave a yellow gum, which solidified with time. Chromatography gave 1-*methyl*-4,5,6,7-*tetrahydrocyclo-octa*[def]*carbazole* (**26**) as crystals (23.7 mg, 92%), m.p. 95.5—97 °C (ethanol–water) (Found: C, 86.75; H, 7.2; N, 5.9. $C_{17}H_{17}N$ requires C, 86.8; H, 7.3; N, 5.95%); $\nu_{max.}$(Nujol) 3 410, 1 602, 1 580, 1 570, 1 511, 1 490, 1 388, 1 316, 810, 781, 762, 736, and 730 cm^{-1}; δ (250 MHz, $CDCl_3$) 2.09 (4 H, m), 2.52 (3 H, br s, $w_{\frac{1}{2}}$ 2 Hz), 3.15—3.40 (4 H, m), 6.88 (1 H, d, *J* 8 Hz), 6.96 (1 H, m), 7.09 (1 H, dd, *J* 8, 1 Hz), 7.24—7.29 (2 H, m), and 7.99 (1 H, br); *m/z* 235 (M^+, base), 220, 207, 206, 205, 204, 194, 193, 192, 191, and 28.

Tricarbonyl-1-*methylcyclo-octa*[def]*carbazoleiron* (**27**).—A stirred mixture of the carbazole (**6b**) (23.1 mg, 0.1 mmol), 4-methoxybenzylideneacetone (1.0 mg, 6 μmol) and nonacarbonyldi-iron (250 mg, 0.7 mmol) in benzene was heated to reflux under a nitrogen atmosphere for 16 h. The brown mixture was then cooled, evaporated under reduced pressure and the residue triturated with ether (5 ml) and filtered through Celite. Evaporation of the filtrate under reduced pressure and chromatography of the residue afforded the *complex* (**27**) as a pale yellow solid (27.2 mg, 74%), m.p. 175—177 °C (decomp.) (Found: C, 64.8; H, 3.4; N, 3.7. $C_{20}H_{13}NO_3Fe$ requires C, 64.7; H, 3.5; N, 3.8%); $\nu_{max.}$(Nujol) 3 462, 2 039, 1 965, 1 951, 800, and 730 cm^{-1}; δ (250 MHz, $CDCl_3$) 2.49 (3 H, s), 4.60 (2 H, m), 5.39 (2 H, m), 7.11 (1 H, d, *J* 7 Hz), 7.21 (1 H, d, *J* 7 Hz), 7.23—7.33 (3 H, m), and 8.10 (1 H, br); *m/z* 371 (M^+), 343, 315, 287, 247, 231 (base), and 217.

Cycloaddition Reactions of 1-*Methylcyclo-octa*[def]*carbazole* (**6b**).—(i) *With* 4-*phenyl*-1,2,4-*triazole*-3,5-*dione*. A solution of the carbazole (**6b**) (11.6 mg, 0.05 mmol) and 4-phenyl-1,2,4-triazole-3,5-dione (8.8 mg, 0.05 mmol) in dichloromethane (0.5 ml) was stirred at room temperature for 16 h and then evaporated under reduced pressure to leave a pale yellow solid. Recrystallisation from nitromethane gave the colourless *adduct* (**28a**) (17.8 mg, 87%), m.p. 273—275 °C (Found: C, 73.6; H, 4.3; N, 13.75. $C_{25}H_{18}N_4O_2$ requires C, 73.9; H, 4.5; N, 13.8%); δ($CDCl_3$) 2.43 (3 H, s), 5.97 (2 H, m), 6.26 (2 H, m), 7.05—7.48 (10 H, m), and 8.81 (1 H, br s); *m/z* 407, 406 (M^+), 245, 244, 231, 230, 218 (base), and 217.

(ii) *With dimethyl acetylenedicarboxylate*. A solution of the carbazole (**6b**) (23.1 mg, 0.1 mmol) and dimethyl acetylenedicarboxylate (25 μl, *ca.* 0.2 mmol) in toluene (1 ml) was heated to reflux for 40 h and then cooled. Evaporation of the solvent under reduced pressure and chromatography of the residue gave unchanged starting material (7.4 mg, 32%), and the *adduct* (**28b**) as crystals (20.4 g mg, 55%; 81% based on consumed starting material), m.p. 227—228.5 °C (Found: C, 74.0; H, 5.1; N, 3.75. $C_{23}H_{19}NO_4$ requires C, 73.8; H, 5.0; N, 3.9%); $\nu_{max.}$ 3 330, 1 720, 1 715, 1 670, 1 638, 1 607, 1 321, 1 269, 1 068, 829, 810, 796, 770, 738, 721, 688, and 680 cm^{-1}; δ (250 MHz, $CDCl_3$) 2.46 (3 H, s), 3.68 (6 H, s), 4.52—5.61 (2 H, m), 6.02—6.12 (2 H, m), 7.05—7.16 (3 H, m), 7.24—7.32 (2 H, m), and 8.22 (1 H, broad); *m/z* 373 (M^+), 342, 314, 313, 282, 255, 231, and 83 (base).

(iii) *With maleic anhydride*. A solution of the carbazole (**6b**) (23 mg, 0.1 mmol) and maleic anhydride (20 mg, 0.2 mmol) in toluene (1 ml) was heated to reflux for 24 h and then cooled to room temperature. The mixture was kept at this temperature for a further 36 h and then evaporated under reduced pressure. Chromatography of the residue gave the endo *adduct* (**28c**) (31.2 mg, 95%) as crystals, m.p. 251—252 °C (Found: C, 76.5; H, 4.5; N, 4.2. $C_{21}H_{15}NO_3$ requires C, 76.6; H, 4.6; N, 4.3%); $\nu_{max.}$(Nujol) 3 404, 1 850, 1 770, 1 609, 1 321, 1 065, 937, 792, 770, 740, and 720 cm^{-1}; δ (250 MHz, $CDCl_3$) 2.58 (3 H, s), 3.70 (2 H, s), 4.25 (2 H, m), 6.15 (2 H, m), 7.12 (1 H, d, *J* 7 Hz), 7.19 (1 H, dd, *J*, 7, 2 Hz), 7.21 (1 H, dd, *J* 7, 1 Hz), 7.38 (1 H, dd, *J* 8, 6 Hz), and 7.46 (1 H, dd, *J* 8, 2 Hz); *m/z* 329 (M^+, base), 257, 256, 242, 241, 231, 44, and 28.

(iv) *With singlet oxygen*. Air was bubbled through a solution of (**6b**) (29.3 mg, 0.13 mmol) in methanol (10 ml) containing Rose Bengal adsorbed on Dowex ion exchange resin and the mixture was irradiated with a medium-pressure mercury lamp for 8 h. The sensitiser was filtered off and the filtrate was evaporated to leave a brown solid. Chromatography gave starting material (7.1 mg, 24%) and the *adduct* (**28d**) (10.5 mg, 31%; 41% based on recovered starting material) (Found: M^+, 263.0938. $C_{17}H_{13}NO_2$ requires 263.0946); δ (250 MHz, $CDCl_3$) 2.58 (3 H, s), 5.67—5.78 (2 H, m), 6.21—6.33 (2 H, m), 7.09 (1 H, d, *J* 7 Hz), 7.15 (1 H, dd, *J* 7, 1 Hz), 7.22 (1 H, dd, *J* 7, 1 Hz), 7.39 (1 H, dd, *J* 7, 6 Hz), 7.50 (1 H, dd, *J* 6, 1 Hz), and 8.21 (1 H, br); *m/z* 263 (M^+), 234, 231, 218 (base), 204, and 191.

Photolysis of Benzo[a]*carbazole*.—A solution of benzo-[*a*]carbazole (**32**; X = H) (200 mg) in acetonitrile (170 ml) was irradiated at 254 nm for 13 h. Evaporation of the solvent under reduced pressure and chromatography of the residue gave a

mixture (116 mg) which, from the evidence of ^{1}H n.m.r. analysis, was shown to consist predominantly of benzo[*a*]carbazole (*ca.* 70%) together with another component identical to that produced in the photolysis of benzotriazole (**5a**) above and tentatively identified as *N*-ethylideneaminobenzo[*a*]carbazole (**23**) (*ca.* 30%).

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