An Unusual Photoproduct of *o*-Azidobiphenyl with Tetracyanoethylene; Trapped 2-Azacycloheptatrienylidene

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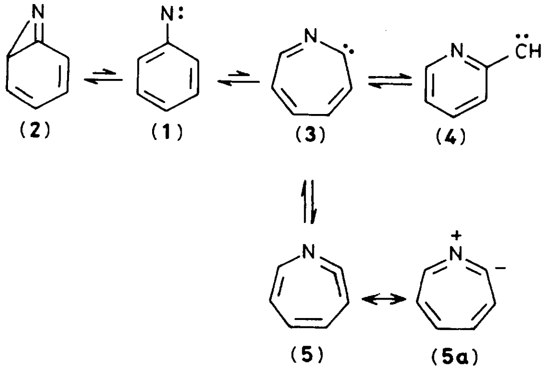
A photoproduct of *o*-azidobiphenyl in acetonitrile in the presence of tetracyanoethylene (TCNE), analysed by *X*-ray crystallography and high-resolution n.m.r. spectroscopy, was shown to have the spiro structure corresponding to the nucleophilic addition of 2-azacyclohepta-2,4,6-trienylidene to TCNE.

Singlet phenylnitrene (**1**) is believed to be in equilibrium with the benzazirine (**2**); the latter is the valence isomer which is attacked by a nucleophilic solvent to give a 2-substituted-3*H*-azepine.[1] It has also been suggested that on pyrolysis in the gas phase, (**1**) rearranges to 2-azacycloheptatrienylidene (**3**) and 2-pyridylcarbene (**4**),[2] although these two intermediates are theoretically[3] and thermochemically[4] less stable than (**1**). An i.r. study of the matrix-isolated photoproduct of (**1**) indicates the azacycloheptatetraene structure (**5**).[5]

When phenyl or *o*-alkylphenyl azide is photolysed at 254 nm in acetonitrile in the presence of tetracyanoethylene, TCNE, a product which shows a characteristic ^{1}H n.m.r. signal at δ 8.2—8.5 is obtained. This product cannot be isolated because of its instability and difficulty of separation from other products. In the case of *o*-azidobiphenyl, however, the corresponding compound (**7**) is isolated in 35% yield; carbazole (**6**) is also obtained in 43% yield. We report here the structure and reactions of (**7**) which appears to be the first example of 2-azacycloheptatrienylidene (**3**) externally trapped with an electrophilic olefin.



The adduct (**7**) crystallized as pale yellow needles, m.p. *ca.* 175 °C (decomp.) (from CH_2Cl_2–n-hexane), and an *X*-ray crystal structure determination indicated that it had the structure shown in Figure 1.† The unusual 2*H*-azepine ring in (**7**) assumes a near boat form. The inversion of the ring in solution is slow on the n.m.r. time scale since all the four cyano carbon atoms are inequivalent in the ^{13}C n.m.r. spectrum.‡ Just as cycloheptatrienylidene is trapped by electrophilic olefins to give spiro[2.6]nona-4,6,8-trienes,[6] (**7**) is considered formally to be obtained from 2-aza-7-phenylcycloheptatrienylidene trapped by TCNE. Alternatively, the formation of (**7**) could occur *via* an electrophilic reaction of TCNE with azacycloheptatetraene which has a canonical structure (**5a**).[5]

The strained structure of (**7**) led us to examine its thermolysis in diglyme at 132 °C. Compound (**7**) was consumed completely in 3.5 h, with the formation of (**6**) (18%)

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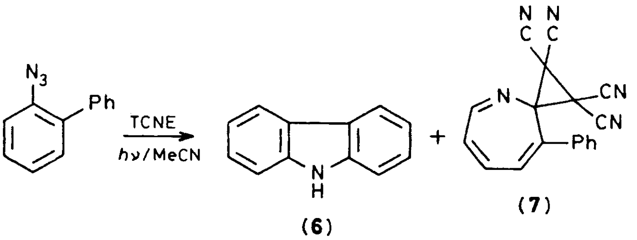
† *Crystal data:* $C_{18}H_9N_5$; M = 295.30, monoclinic, $P2_1/a$, Z = 4, a = 19.964(2), b = 8.421(1), c = 9.126(1) Å; β = 92.35(1)°; U = 1533.0(3) Å^3; D_c = 1.29 g cm^{-3}; μ(Mo-K_α) = 0.880 cm^{-1}. A total of 2166 independent reflections with $F_o > 3\sigma(F_o)$ were collected on a Rigaku AFC-5 diffractometer with monochromatized Mo-K_α radiation. The structure was solved by direct methods (MULTAN 78) and refined by the block-diagonal least-square technique. The final R and R_w values were 0.047 and 0.044, respectively. All the calculations were carried out on a HITAC M-200H computer with crystallographic computation program systems, MULTAN and UNICS III, filed at the Computer Center of the Institute for Molecular Science.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ ^{1}H N.m.r. (399.7 MHz), ^{13}C n.m.r. (100.4 MHz), and mass spectral data are consistent with structures (**7**) and (**8**).



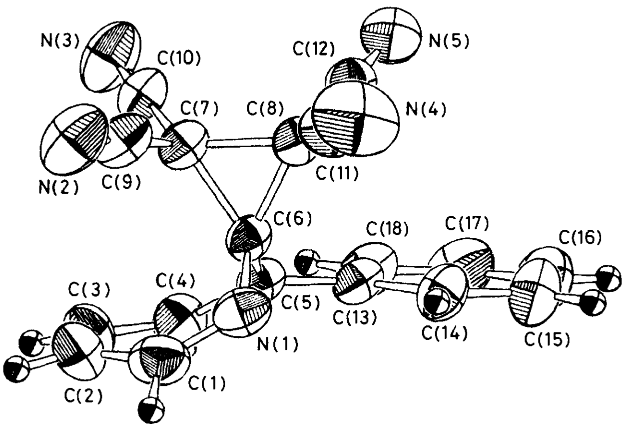
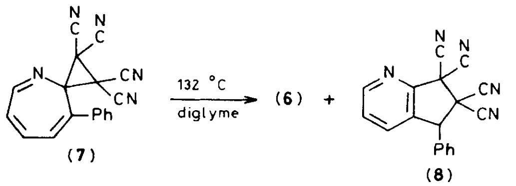
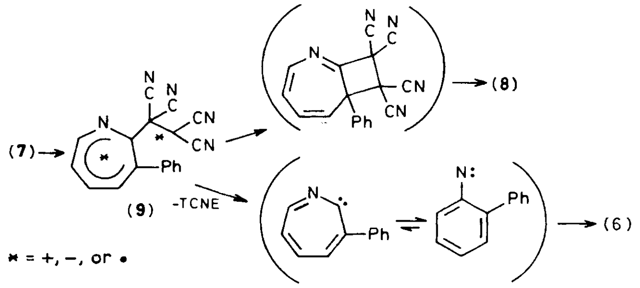


Figure 1. Molecular structure of (**7**). Carbon and nitrogen atoms are shown as 50% probability surfaces and hydrogen atoms are displayed as arbitrary spheres.

and (**8**) [29%, colourless needles, m.p. 157—158 °C (from CH_2Cl_2–n-hexane)].‡ A similar ring transformation was reported by Jones and his co-workers for cycloheptatriene derivatives.[6] Carbazole (**6**) is thought to be obtained from 2-aza-7-phenylcycloheptatrienylidene [formed by the elimination of TCNE from (**7**) or (**9**)] followed by isomerization to 2-nitrenobiphenyl, the lower energy isomer.





It is interesting that (**7**), which can be regarded as the product of the trapping of 2-azacycloheptatrienylidene (**3**) and/or heptatetraene (**5**) by TCNE, is a source of a phenylnitrene.

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