Photochemical Benzylation of 1,4-Dicyanonaphthalene; *X*-Ray Crystal Structure of 6,11-Dicyano-5,11-methano-5,6,11,12-tetrahydrodibenzo-[*a*,*e*]cyclo-octene

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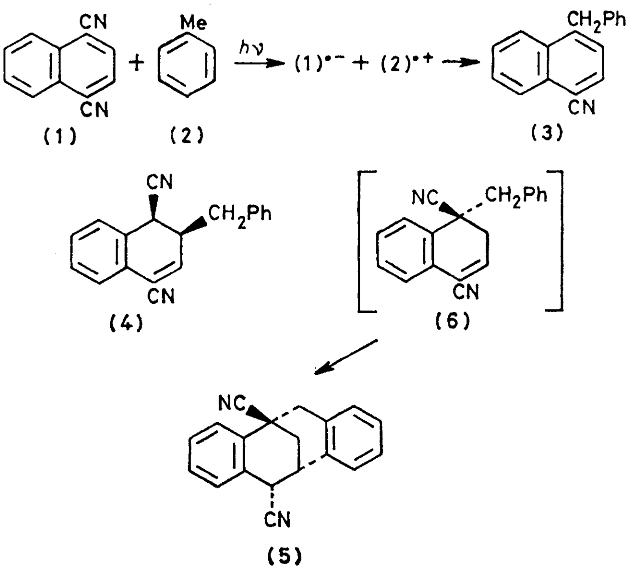
Summary The irradiation of 1,4-dicyanonaphthalene in the presence of toluene in acetonitrile gives adducts bearing the benzyl group in positions 1 and 2 of the naphthalene nucleus; two of the isolated products arise from rearomatisation or from a further photoreaction, and the structure of one of the products has been determined by *X*-ray crystallography.

AROMATIC nitriles and esters have been shown to sensitize, through electron transfer, the photochemical reactions of phenyl-substituted alkenes,[1] β-phenylethyl ethers,[2] diphenyloxirans,[3] and diphenylcyclopropanes.[4] However, no such reaction has been reported with simple arenes, although the fact that these are known to form exciplexes with aromatic nitriles[5] suggests that the electron-transfer step could take place. However, irradiation of the preformed ground-state complex between tetracyanobenzene and toluene was found to lead to a reaction.[6]

We now report that a photochemical reaction also occurs in a system which does not form a ground-state complex, offering a further example of photoreaction *via* radical ions. In fact, on excitation of 1,4-dicyanonaphthalene (**1**) in cyclohexane solutions containing toluene (**2**) the known exciplex emission[5] is observed, but no chemical change takes place even on prolonged irradiation. When the irradiation is carried out in acetonitrile, however, the exciplex emission is much reduced, but a chemical reaction as well as the quenching of the fluorescence of (**1**) are observed. At complete conversion three products (**3**)—(**5**) are isolated in yields of 12, 7, and 23% respectively.



Scheme

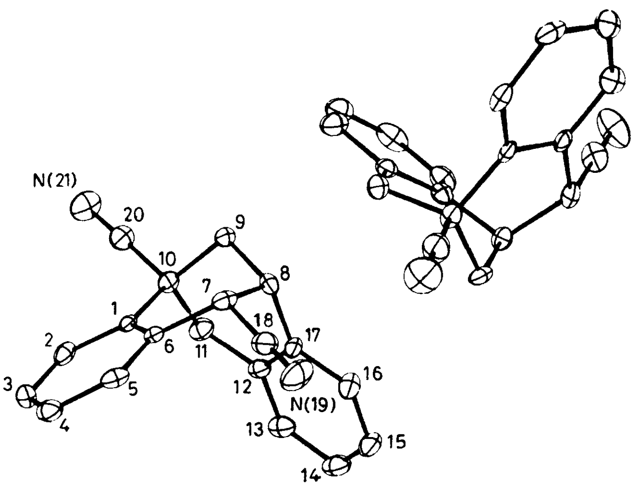


Figure. *X*-Ray structure of compound (**5**) showing the two independent molecules in the asymmetric unit.

Product (**3**)‡ is 1-cyano-4-benzylnaphthalene, while the structure of product (**4**) was inferred from its spectroscopic properties [λ_{max} (ethanol) 280 (log ϵ 3·93), 274 (3·95), 269 (3·92), and 228·5 (4·23) nm; δ ($CDCl_3$) 6·6 (1H, d, J 3 Hz) and 3·95 (1H, d, J 4·5 Hz), the small coupling constant showing the *cis*-arrangement of the vicinal cyano and benzyl groups]. Finally, the structure of the tetracyclic derivative (**5**) was determined by single-crystal *X*-ray analysis.§ Apparently (**5**) is the product of a further photoreaction of a non-isolated adduct (**6**).

The available evidence [quenching of the fluorescence of (**1**) by (**2**), occurrence of the reaction in polar media] suggests that the formation of the products (**3**)—(**5**) occurs *via* the radical ions (**1**)$^{\cdot-}$ and (**2**)$^{\cdot+}$ formed by the interaction of singlet excited (**1**) with (**2**). It appears likely that a proton is then transferred from (**2**)$^{\cdot+}$ to (**1**)$^{\cdot-}$ and that the two radicals¶ thus formed couple to give adducts in both positions 1 and 2 of the naphthalene ring. A photochemical phenylation of alkenes bearing electron-withdrawing substituents, analogous to the presumed formation of (**5**) from (**6**) has previously been reported, although in that case a proton source was needed.[7] HCN elimination leading to the rearomatized product has also previously been suggested to explain the benzylation of tetracyanobenzene.[6]

The mechanism proposed here (Scheme) has some analogy with that postulated for the photochemical reaction of 1-cyanonaphthalene with methoxyphenylacetic acids,[8] but in the present case different products are formed. Also, the present results bear some analogy to those recently communicated for the related (**1**) and alkene systems.[9]

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‡ All new products give satisfactory analytical data.

§ *Crystal data:* monoclinic, space group $P2_1/c$; a = 16·158(2), b = 17·803(3), c = 10·186(2) Å; β = 91·1(2)°; Z = 8. 2659 independent reflections up to θ = 20° were collected with a Philips PW 1100 4-circle diffractometer (Mo-K_α radiation, λ = 0·7107 Å, ω scan technique). Intensities were corrected for Lorentz and polarisation factors but not for absorption. The structure was solved by direct methods (MULTAN 78; P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq, and M. M. Woolfson, 'MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from *X*-ray diffraction Data,' Universities of York and Louvain, 1978) and refined with full-matrix least-squares calculations [only reflections with $I > 3\sigma(I)$ were regarded as observed]. Positional parameters for H atoms were calculated on the basis of geometrical considerations; they were inserted but not allowed to vary in the anisotropic refinement. The final R index was 4·8% for the observed reflections (R_{all} = 11·8%). Scattering factors were those listed in the International Tables for *X*-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974, pp. 99—101). Atomic co-ordinates 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.

¶ Traces of 1,2-diphenylethane are indeed obtained, which is probably some indication of the presence of benzyl radicals.

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