

## Interaction between photoexcited naphthalenenitriles and dienes: addition and sensitization

Angelo Albini and Elisa Fasani

Dipartimento di Chimica Organica, Università, I-27100 Pavia, Italy

**Abstract** - Various adducts are formed when 1- or 2-naphthalenenitrile or 1,4-naphthalenedinitrile are irradiated in the presence of dienes (1,3-cyclohexadiene, 2,3-dimethyl-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene). When electron transfer from the diene to the singlet excited naphthalene derivative is largely endothermic, 4+4 addition predominates, whereas when electron transfer becomes easier, 2+2 addition is the main process, although with a lower quantum yield than in the previous case. With the hexadiene addition onto the cyano group takes likewise place. Besides the naphthalene-diene adducts, 2+2 and 4+2 diene dimers are formed, and their distribution depends on the sensitizing nitrile and on the solvent polarity. The mechanistic implications of these reactions are discussed with reference to the excited state energy and redox characteristics of these compounds.

### INTRODUCTION

The reaction between photoexcited aromatics and alkenes has been the subject of numerous investigations (see, e.g., ref 1-12) and leads either to cycloaddition, probably via an exciplex, or to electron transfer and following radical ion chemistry (Fig. 1).

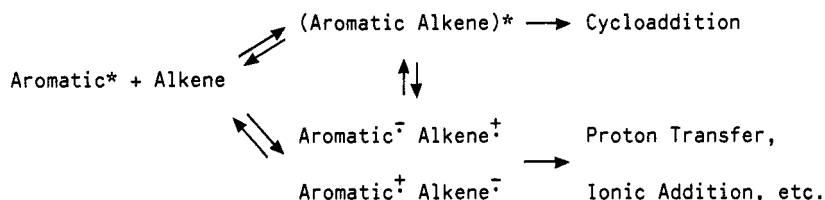


Fig. 1

The feasibility of the charge transfer pathway can be determined on the basis of the Weller equation (ref. 13). Furthermore, increasing the solvent polarity has often a dramatic effect on product distribution, since the radical ions are stabilized by solvation. With naphthalenes, as an example, 2+2 photoaddition in apolar solvents leads to cyclobutanaphthalenes (ref. 14-29). In polar solvents radical ions are formed and react. Typically, the radical cation of alkenes undergoes proton transfer from the allylic position (ref. 6), addition of nucleophiles (ref. 30) cycloaddition, (ref. 29, 31-2) (Fig. 2).

The photochemical reaction of naphthalene derivatives in the presence of dienes has been less thoroughly investigated, but both cycloaddition and ionic processes have been documented in selected cases (ref. 33-5).

The present paper describes the photochemical reaction of 1- and 2-naphthalenecarbonitriles (1-NN and 2-NN) as well as of 1,4-naphthalenedicarbonitrile (NDN) with representative dienes both in apolar and in polar solvents.

The reaction leads both to naphthalene-diene adducts and to diene dimers.

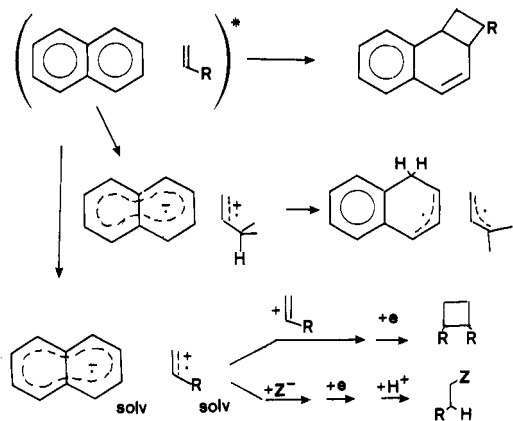


Fig. 2. Photochemical reaction of naphthalene with alkenes.

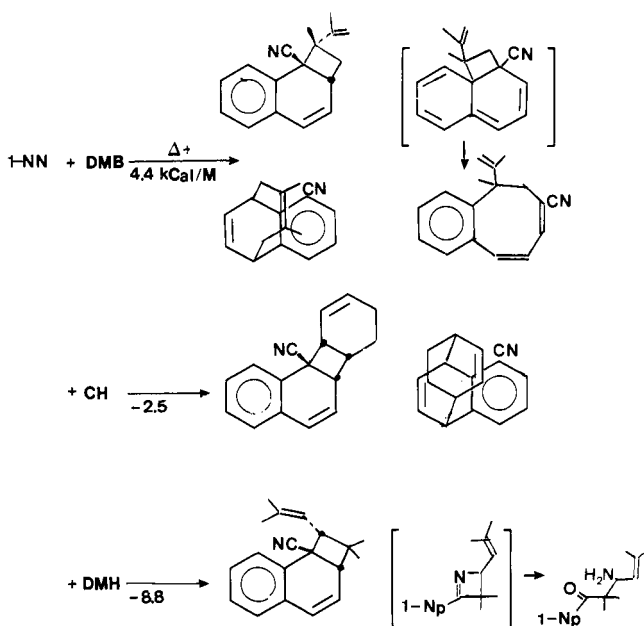


Fig. 3. Photochemical reaction of 1-naphthalene-carbonitrile with dienes.

#### NAPHTHALENE-DIENE ADDUCTS

Adducts of different structure are obtained in the different cases.

Thus, the reaction of 1-NN with 2,3-dimethyl-1,3-butadiene (DMB) follows three main pathways, viz. 2+2 addition onto the 1,2 naphthalene bond; 2+2 addition onto the 1,8a bond (in this case an electrocyclic rearrangement ensues and leads to the isolated benzocyclooctatriene); 4+4 addition onto the unsubstituted naphthalene ring (Fig. 3).

With 1,3-cyclohexadiene (CH) 2+2 addition onto the 1,2 bond and 4+4 addition are observed. With 2,5-dimethyl-2,4-hexadiene (DMH) 2+2 addition onto the naphthalene ring is accompanied by addition onto the cyano group to yield a naphthylazetine. The latter product undergoes hydrolysis during chromatographic work up and a β-aminoketone is obtained (Fig. 3).

With 2-NN and DMB the only process is 4+4 addition, involving in this case both naphthalene rings. CH yields both a 2+2 adduct on the substituted and a 4+4 adduct on the unsubstituted ring, and DMH gives a 2+2 adduct and the adduct onto the cyano group (Fig. 4).

With NDN, DMB yields a 2+2 adduct onto position 1 and 8a (and again an electrocyclic rearrangement leads to the isolated benzocyclooctatriene) and a 4+4 adduct. With the other dienes, no adduct is formed (Fig. 5).

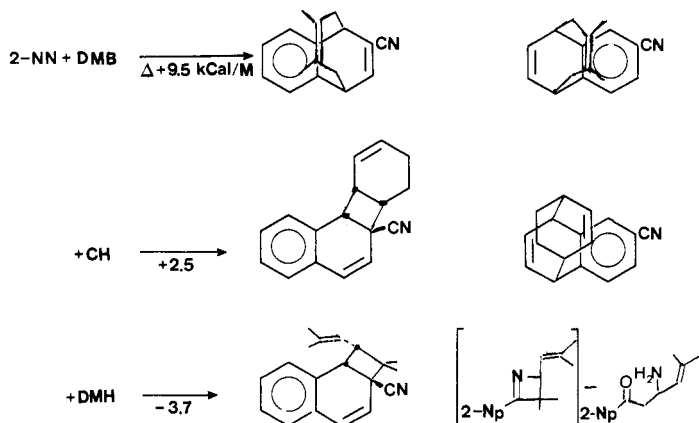


Fig. 4. Photochemical reaction of 2-naphthalenecarbonitrile with dienes

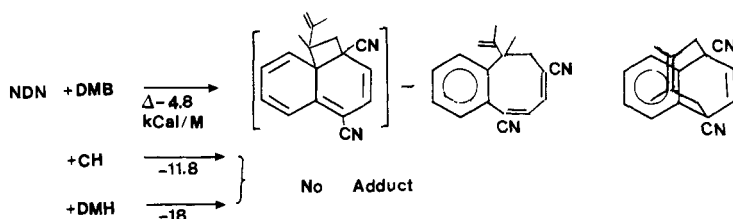


Fig. 5. Photochemical reaction of 1,4-naphthalenedicarbonitrile with dienes.

All of these reactions involve the singlet excited state of the nitriles. We have no evidence suggesting other rearrangements of the adducts during irradiation or work up, and the above mentioned reactions (2+2 addition onto the 1,2 or 1,8a position, 4+4 addition, addition onto the cyano group) are taken as primary processes. The selectivity observed can be rationalized with references to the charge transfer characteristics of the various naphthalene-diene pairs. In Fig. 3-5 the quantity  $\Delta = E(\text{ox}) - E(\text{red}) - E(\text{ex})$ , (respectively, oxidation potential of the diene, reduction potential of the naphthalene, excitation energy of the naphthalene), is indicated for each reaction.

This quantity corresponds to the  $\Delta G$  for electron transfer in the excited state, apart from the ion separation term, which depends on solvent polarity and ion distance (ref. 13).

One can see that in the 2-NN - DMB case, with  $\Delta = 9.5 \text{ kcal/M}$ , only 4+4 cycloaddition takes place, just as it happens with unsubstituted naphthalene and dienes, with an even lower value (ref. 33). This mode of reaction is favoured by a good energy and sign matching between naphthalene and diene FMOs, and thus by a favourable LUMO-LUMO and HOMO-HOMO interaction (note a). Lowering the energy of naphthalene MOs with respect to the diene ones disfavours this interaction, and indeed as the electron transfer process becomes easier the importance of 4+4 addition drops and 2+2 addition predominates. However, cycloaddition through a charge transfer complex is less efficient, and limiting quantum yield is lower ( $\leq 0.1$ ) than in the previous case. For large negative  $\Delta$  values no adducts are formed any more (see Fig. 5).

On the other hand, steric factors have a role in these reactions, as shown by the regio- and stereo selectivity in the formation of the ring adducts and by the formation of adducts onto the cyano group only with DMH (a *s-trans* diene).

Several of these reaction (e.g. 1-NN or 2-NN + DMB) are not substantially influenced by solvent polarity. In other cases the products mixture obtained in polar solvents is more complicated. The results reported in Fig. 3-5 refers to apolar media (cyclohexane or benzene).

## DIENE DIMERS

Besides naphthalene-diene adducts, diene dimers are obtained in these experiments via photosensitization by the aromatics. The product distribution depends on the nitrile used and on the solvent polarity.

As an example, with CH four dimers are obtained, viz. 4+2 endo and exo as well as 2+2 endo and exo derivatives (Fig. 6).

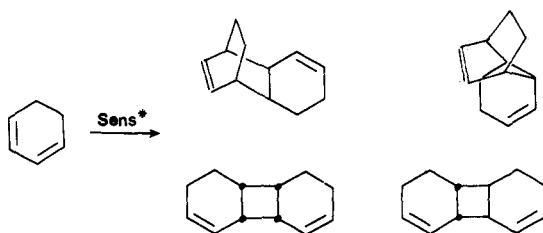


Fig. 6 Photosensitized dimerization of cyclohexadiene in the presence of naphthalene nitriles.

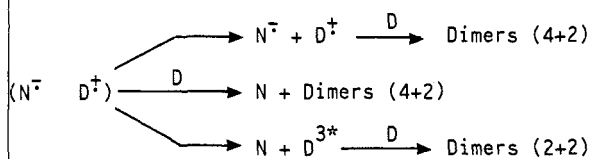


Fig. 7. Pathways for the sensitized diene isomerization

4+2 Dimers are the almost exclusive products in polar solvents, such as acetonitrile. This reaction involves the alkene radical cation (compare ref. 37) or the strongly polarized naphthalene (N) - diene (D) exciplex (compared ref. 35). In apolar solvents the quantum yield for dimerization is lower and 2+2 addition is much more important since the exciplex or the radical ion pair (ref. 38) undergoes intersystem crossing to the low lying diene triplet (compare ref. 39) (Fig. 7).

Note a. For a discussion of the correlation diagram of this and related photoaddition reactions, compare ref. 36 and therein reported references.

This triplet pathway is less important with NDN, since the radical ion pair has a lower energy than with the mononitrile.

Solvent polarity and diene concentration have a different effect in the various cases.

### CONCLUSION

The degree of charge transfer in the interaction between photoexcited naphthalenenitriles and dienes determines the course of the photochemical reaction.

### Acknowledgement

We thank Ministero Pubblica Istruzione, Rome, for partial funding of this research.

### REFERENCES

1. J.J. Mc Cullough, Chem.Rev. **87**, 811 (1987).
2. R.A. Caldwell and D. Creed, Acc. Chem. Res. **13**, 45 (1980).
3. F.D. Lewis, Acc. Chem. Res. **12**, 152 (1979).
4. N.C. Yang, R.L. Yates, J. Masnovi, D.M. Shold and W.E. Chiang, Pure Appl. Chem. **51**, 173 (1979).
5. N.C. Yang, J. Masnovi, W.L. Chiang, T. Wang, H. Shon and D.D.H. Yang, Tetrahedron **37**, 3285 (1981).
6. D.R. Arnold, P.C. Wong, A.J. Maroulis and T.S. Cameron, Pure Appl. Chem. **52**, 2609 (1980).
7. A. Albin and A. Sulpizio, Aromatics, in M.A. Fox and M. Chanon (eds.), Photoinduced Electron Transfer, Elsevier, Amsterdam, in press.
8. F.D. Lewis, Carbon-Carbon Multiple Bonds, in ref. 6.
9. S. Farid and S.L. Mattes, Organic Photochem. **6**, 233 (1983)
10. J. Mattay, Tetrahedron **41**, 2393 and 2405 (1985).
11. R.S. Davidson, in R. Forster (ed.), Molecular Association, vol. 1, Academic Press, New York, 1975, p. 216.
12. D. Bryce-Smith and A. Gilbert, Tetrahedron **33**, 2459 (1977).
13. D. Rehms and A. Weller, Isr. J. Chem. **8**, 259 (1970).
14. D. Bryce-Smith, A. Gilbert and B.H. Orgar J.Chem. Soc., Chem. Commun. 593 (1966).
15. Y. Inowe, K. Nishida, K. Ishibe, T. Hakushi and N.J. Turro, Chem.Lett., 171 (1982).
16. R.M. Bowman, T.R. Chamberlain, C.W. Huang and J.J. Mc Cullough, J.Am.Chem.Soc. **96**, 692 (1974).
17. H.D. Scharf, H. Leismann, W. Erb, H.W. Gaidetska and J. Aretz, Pure Appl. Chem. **41**, 581 (1975).
18. A. Kashoulis, A. Gilbert and G. Ellis-Davies, Tetrahedron Lett., 2905 (1984).
19. C. Pac, K. Mizuno, T. Sugioka and H. Sakurai, Chem. Lett. 187, (1973).
20. K. Mizuno, C. Pac and H. Sakurai, J.Chem.Soc., Chem.Commun., 748 (1974).
21. C. Pac, T. Sugioka, K. Mizuno and H. Sakurai, Bull.Chem.Soc. Jpn. **46**, 238 (1973).
22. C. Pac, T. Sugioka and H. Sakurai, Chem. Lett., 39 (1972).
23. T. Sugioka, C. Pac and H. Sakurai, Chem. Lett., 791 (1972).
24. T.R. Chamberlain and J.J. Mc Cullough, Can. J. Chem., **51**, 2578 (1973).
25. K. Mizuno, C. Pac and H. Sakurai, J. Chem.Soc. Perkin 1, 2221 (1975).
26. J.J. Mc Cullough, R.C. Miller and W.S. Wu, Can.J.Chem., **55**, 2910 (1977).
27. J.J. Mc Cullough, W.K. Mac Innis, C.J.L. Lock and R. Faggiani, J.Am.Chem.Soc., **104**, 4644 (1982).
28. N.C. Young, B.Kim., W. Chiang and T. Hamada, J.Chem.Soc., Chem.Commun., 729 (1976).
29. T. Majima, C. Pac, A. Nakasone and H. Sakurai, J.Am.Chem.Soc., **103**, 4499 (1981).
30. A.J. Maroulis, Y. Shigemitsu and D.R. Arnold, J.Am.Chem.Soc., **100**, 535 (1978).
31. R.A. Neunteufel and D.R. Arnold, J.Am.Chem.Soc., **95**, 4080 (1973).
32. S.L. Mattes and S. Farid, J.Am.Chem.Soc., **108**, 7356 (1986).
33. N.C. Yang, L. Libman and M. Savitzky, J.Am.Chem.Soc., **94**, 9226 and 9228 (1972).
34. J. Mattay, J. Gersdorf and J. Martes, J.Chem.Soc., Chem.Commun. 1088 (1985).
35. G.C. Calhoun and C.B. Schuster, J.Am.Chem.Soc., **108**, 8021 (1986).
36. R.A. Caldwell, J.Am.Chem.Soc., **102**, 4004 (1980).
37. D.J. Bellville, D.D. Wirth and N.L. Bauld, J.Am.Chem.Soc., **103**, 718 (1981).
38. A. Weller, Z. Phys. Chem., **133**, 93 (1982).
39. D. Valentine, N.J. Turro and G.S. Hammond, J.Am.Chem.Soc., **86**, 5202 (1964).