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PHOTOCHEMICAL REACTION OF 1- AND 2-NAPHTHALENECARBONITRILE WITH SOME METHYLBENZENES

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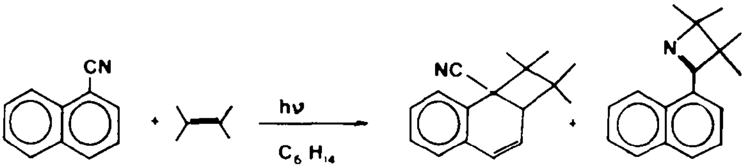
Abstract—1- and 2-Naphthalenecarbonitriles (1- and 2-NN) photochemically react with 1,2,4,5,-tetramethylbenzene (**4**) (but not with lower homologues). The products are 1,1'-(1,2-ethanediyl)bis-(2,4,5-trimethylbenzene) (**5**) and 3-hydroxy-1-naphthalenecarbonitrile with 1-NN and **5** and 1,2-dihydro-2-naphthalenecarbonitrile with 2-NN. The reaction involves electron transfer to the NN singlet excited state followed by proton transfer. 4-Methylbenzyl-(1-cyano-4-naphthyl)methyl ether (**9**) and the corresponding trimethylbenzylderivative **10**, which contain donor and acceptor chromophores linked together, were prepared and found to show enhanced excimer emission but no photochemical reactivity, 1- and 2-NN react with 1-methoxy-4-methylbenzene (but not with the 3-isomer) analogously as with **4**, but in this case small amounts of benzylated 1,2-dihydro-1-naphthalenecarbonitriles and 1,4-dihydro-2-naphthalenecarbonitriles are also formed. The mechanism is discussed in comparison with the corresponding reaction of 1,4-naphthalenecarbonitrile.

The formation of exciplexes between excited aromatic molecules and alkenes and the related photochemical reactions have been the subject of extensive investigation.[1] In particular, the photochemical reaction between naphthalenecarbonitriles and alkenes has been recently considered in detail both by Arnold[2] and McCullough[3] (for photophysical studies on the same systems see Ref. 4). Two types of reaction seem to emerge, *viz* exciplex mediated 2 + 2 cycloaddition at the C=C double bond in 1,2 or in some cases at the C ≡ N triple bond, which predominates with poorer electron acceptors, e.g. mono-nitriles, and in apolar solvents, (eqn 1),[5] and electron transfer followed by proton transfer and radical coupling, which predominates with stronger electron acceptors, e.g. dinitriles, and in polar solvents, which favour the cleavage of the exciplex into radical ions of opposite sign (eqn 2).[2]

We have been concerned for some time in the photoreaction of naphthalenecarbonitriles with methylbenzenes.[6] Toluene is less easily oxidized than, e.g. 2,3-dimethylbutene, and quenches the fluorescence of 1,4-naphthalenedicarbonitrile (NDN) at a lower rate. There is no photochemical reaction in apolar solvents, but in acetonitrile three products are formed (eqn 3). This reaction has been shown to involve water mediated proton transfer within the exciplex and in cage coupling of the radicals to stereospecifically yield products **2** and **3**. Escaped benzylic radicals couple to bibenzyl or are trapped by NDN to yield the substitution product **1**. This reaction is of interest both from the mechanistic point of view, i.e. for the comparison of the exciplex vs radical ions reactivity, or as an experimental indication of the acidity of the toluene radical cation, which has been recently studied from the theoretical point of view,[7] outside the metal catyzed chemistry, as well as from



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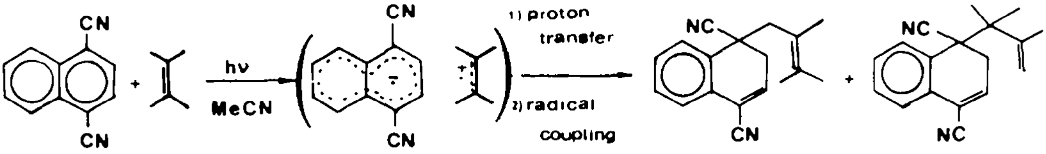

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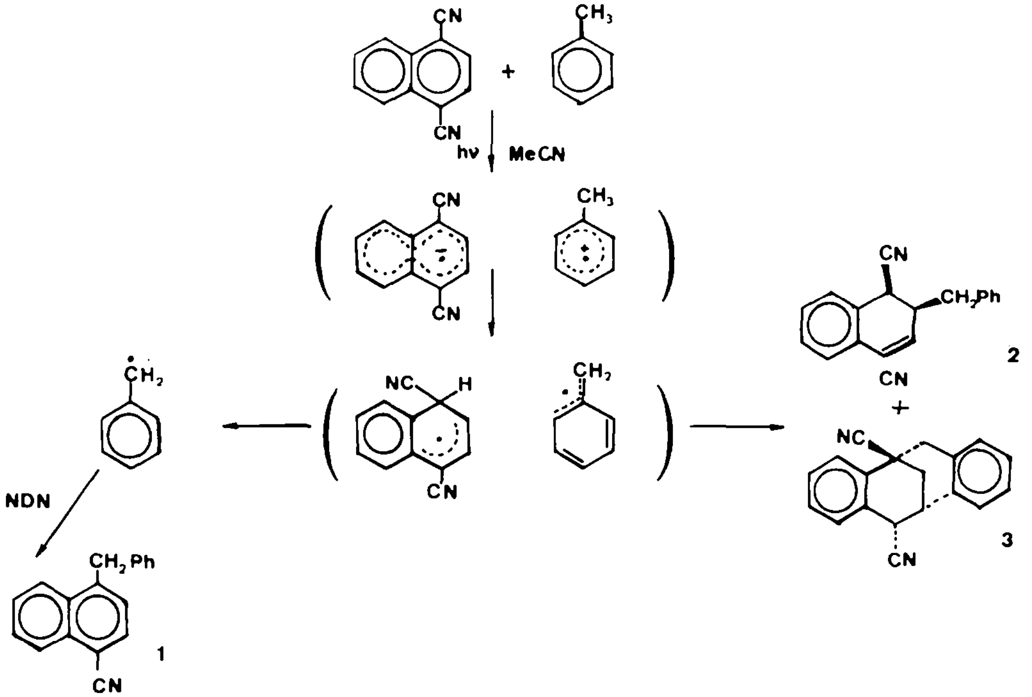

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the synthetic point of view (three chiral centers are specifically formed in product **3**, two in product **2**).

Therefore we decided to investigate the extension of this reaction to the corresponding mononitriles, and presently refer about the reaction of 1-naphthalenecarbonitrile (1-NN) and 2-naphthalenecarbonitrile (2-NN) with some methylbenzenes under irradiation, as well as about the photochemical properties of some bichromophoric molecules containing both donor and acceptor moieties.

RESULTS AND DISCUSSION

Photochemical reaction of the naphthalenecarbonitriles with methylbenzenes

Toluene, 1,4-dimethylbenzene and 1,3,5-trimethylbenzene practically do not quench the fluorescence of either 1-NN or 2-NN and one has to proceed further in substitution to 1,2,4,5-tetramethylbenzene (**4**), which strongly quenches the fluorescence of 1-NN and, to a lesser degree, also that of 2-NN. In the system 1-NN-**4** exciplex emission is conspicuous in apolar solvents and detectable, although weak in more polar ones. With 2-NN only an enhancement in the tail of the monomer emission can be attributed to the exciplex.

The free energy change for the electron transfer process

$$1\text{-NN}^* + \mathbf{4} \rightarrow 1\text{-NN}^{\cdot-} + \mathbf{4}^{\cdot+} \qquad (4)$$

can be calculated from the Weller equation[8]

$$\Delta G = E(D/D^{\cdot+}) - E(A/A^{\cdot-}) - (e^2/\epsilon\alpha) - E_{00} \qquad (5)$$

and the available literature data,† and results to be slightly negative in polar solvents (-0.3 kCal M^{-1}). The degree of charge transfer character of the excited complex can be evaluated by recording the shift of the exciplex emission band as a function of the solvent polarity. According to Weller *et al.*,[11] the shift of the emission maximum is proportional to the exciplex dipole moment μ as shown in the following equation

$$\bar{\nu}_{CT}^{max} = \text{constant} - 2\mu^2(f - f'/2)hc\sigma^3 \qquad (6)$$

where the solvent characteristics are expressed by means of the parameters $f = (\epsilon - 1)/(2\epsilon + 1)$ and $f' = (n^2 - 1)/(2n^2 + 1)$.

The data for the system 1-NN – **4** are reported in Fig. 1, showing a behaviour similar to that exhibited by typical charge transfer exciplexes, i.e. the shift of the emission maximum is irregular due to the specific interaction with each solvent, but a definite trend with $f - f'/2$ is obtained. A rough evaluation of the exciplex dipole moment μ would be 10 D, assuming that the cavity radius σ has a value of 5Å. This value of μ is the same as that observed e.g. for the anthracene-diethylamine exciplex.[11]

To the efficient complexation corresponds only a limited chemical reactivity. A slow photochemical reaction between 1-NN and **4** takes place in acetonitrile, with $\Phi_r < 0.01$ in conditions in which 80% of the 1-NN singlet excited state is quenched. The products obtained after chromatographic separation are 1,1′-(1,2-ethanediyl)bis-(2,4,5-trimethylbenzene) (**5**, 90% yield calculated on the converted 1-NN) and 3-hydroxy-1-naphthalenecarbonitrile (**6**, 18%). The latter compound probably arises from the rearomatization during the work up of the corresponding dihydro derivative (eqn 7), in turn formed from the

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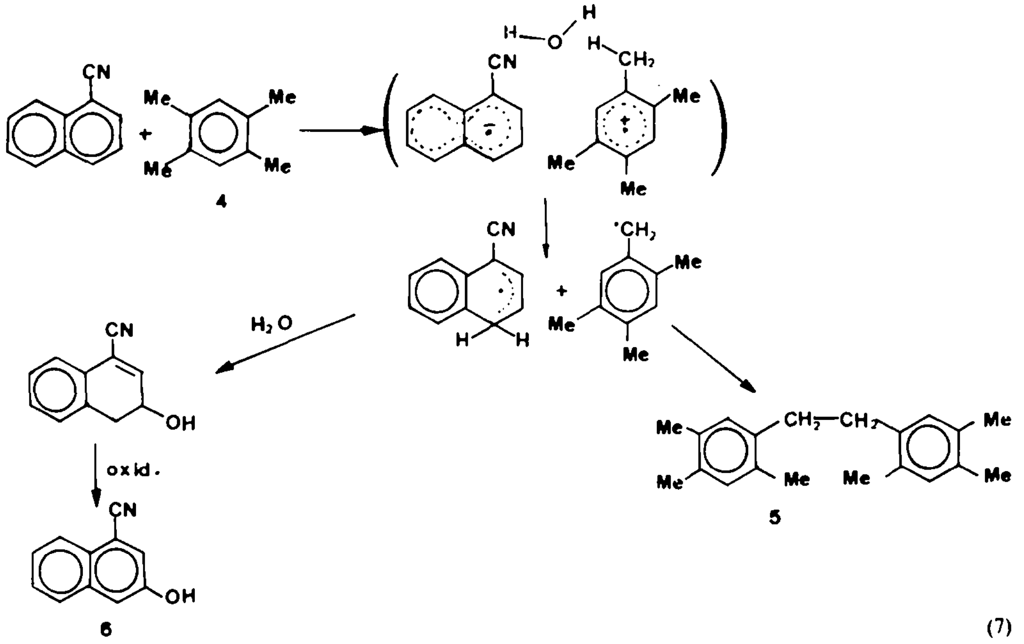
†See Refs. 9 and 10 for the parameters of 1-NN and **4** respectively.



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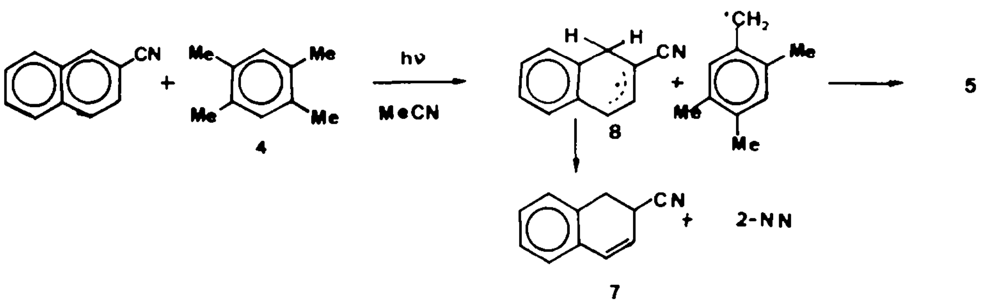

(8)

reaction of the initially produced naphthalenyl radical and water present in the solvent.†

Thus products arising through radicalic pathways are formed in this case, but no adducts between 1-NN and **4** are obtained. This result can be compared with the reaction beween NDN and **4** in the same conditions. Charge transfer to the excited nitrile takes place in both cases, as shown by the fluorescence quenching, and is followed by proton transfer to form a couple of radicals. However, while with NDN in cage coupling leads to the adducts, in the present case the radicals diffuse apart, as shown by the formation of the bibenzyl **5**. Apparently, proton transfer is promoted also in this case by the small amount of water present, as shown by the formation of the hydroxynaphthalene **6**. The sequence electron exchange-proton exchange for the formation of benzylic radicals is confirmed by the suppression of the reaction to the bibenzyl **5** in the presence of 0.01M trifluoroacetic acid, which would protonate the 1-NN radical anion (see Ref. 6*a*).

The irradiation of the isomeric 2-NN in the presence of **4** in acetonitrile neatly occurs with over all hydrogen transfer taking place *via* successive electron and proton transfer. The products obtained are the bibenzyl **5** (85% of the reacted 2-NN) and 1,2-dihydro-2-naphthalenecarbonitrile (**7**; 46%), the latter reasonably arising from the disproportionation of the initially formed naphthalene radical **8** (see Ref. 2). Again the addition of 0.01M trifluoroacetic acid quenches the formation of product **5**.

Thus, although the naphthalene mononitriles are similar to NDN in their ability to abstract hydrogen via a charge transfer mechanism from the methylbenzenes which are sufficiently good donors in order to quench their singlet excited states, this does not leads to in cage formation of the adducts, nor are escaped benzylic radicals trapped by 1-NN or 2-NN,

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†This corresponds to the reaction of an allylic radical with water, and finds precedent in the reaction of benzylic radicals with water (see e.g. C. Giordano, A. Belli, A. Citterio and F. Minisci. *J. Org. Chem.* **44**, 2314 (1979). Another possibility to rationalize the formation of product **6** is that it arises from the reaction of traces of oxygen present in solution, even after argon flushing, with the radical.

Table 1. Quenching of the fluorescence of naphthalenecarbonitriles by methylbenzenes.[a]

	$k_q \times \tau$, M^{-1}	
Quencher	1-NN	2-NN
Toluene	<2	<2
1,3,5-Trimethylbenzene	4.5	<2
1,2,4,5-Tetramethylbenzene	126.5	12
1-Methoxy-4-methylbenzene	162	155
1-Methoxy-3-methylbenzene	98	32.5

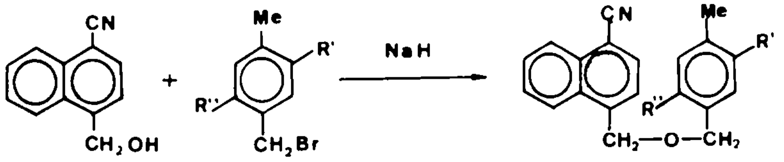
a. In acetonitrile, degassed solutions.

and the only pathway open remain homo coupling of the benzylic radicals to bibenzyl. In order to better understand the different behaviour of mono and dinitriles, further experiments were carried out following two approaches. First, donor and acceptor were linked together in a bichromophoric molecule. Hydrogen transfer and hetero radical coupling could be expected to occur more efficiently in the intra than in the intermolecular case. On the other hand, the reaction of the mononitriles with methylbenzenes substituted with electron donating groups was investigated, in order to test the effect of a larger difference in redox properties.

Reactions of donor-acceptor bichromophoric compounds

The bichromophoric compounds **9** and **10** containing both naphthalenecarbonitrile and polymethylbenzene moieties linked by a three atoms chain were prepared from 4-hydroxymethyl-1-naphthalenecarbonitrile and the appropriate benzyl bromide following a strategy recently used by McCullough[3] to prepare the analogue naphthalenecarbonitrile–alkene bichromophoric compounds.

As expected, the excited naphthalene chromophore strongly interacts with the benzene moiety. Thus, even in compound **9**, which contains a chromophore corresponding to 1,4-dimethylbenzene, not able itself to intermolecularly quench the fluorescence of 1-NN, the fluorescence quantum yield is much reduced in comparison with that of 1-NN ($\Phi_f = 0.21$ in cyclohexane, compare with the data in Table 2). In addition to the monomer fluorescence, the spectrum of compound **9** shows a long wavelength tail attri-



(9)

9 R', R'' =H

10 R', R'' =Me

Table 2. Parameters of the exciplex fluorescence

Fluorophor	Quencher	Solvent	λ^{ex}_{max}, nm	Φ_F^{mon}	Φ_F^{ex}
1-NN	**4**	Cyclohexane	362		.47^a
		Acetonitrile	410		.10^a
1-NN	**11**	Cyclohexane	394		.26^a
		Acetonitrile	450		.01^a
9		Cyclohexane		.075^b	.01^c
		Acetonitrile		.085^b	.01^c
10		Cyclohexane	374	.025^b	.03^c
		Acetonitrile	413	.014^b	.10^c

a. Quantum yield of the exciplex fluorescence, estrapolated at total monomer quenching

b. Quantum yield of the part of the fluorescence spectrum attributable at the monomer emission

c. Quantum yield of the part of the fluorescence spectrum attributable at the excimer emission.

butable to the exciplex emission, and a well defined exciplex band is apparent in the spectrum of compound **10**. By superimposing the spectrum of 1-NN the emission spectrum of the bichromophoric compounds can be divided into the monomer and the exciplex part, and the quantum yield for the two phenomena can be evaluated. In the case of compound **10**, exciplex emission predominates over the monomer and, contrary to the general finding in intermolecular exciplexes, is increased in polar solvents.

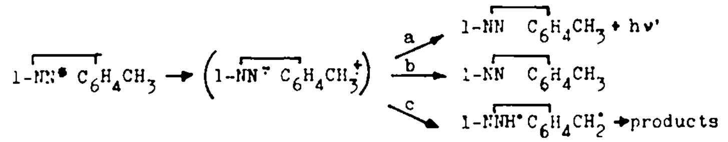
However, no chemical consequence comes from the complexation. Thus, both compound **9** and **10** show very little photochemical reactivity ($\Phi_r < 0.01$). Some fragmentation appears to occur, but we were unable to isolate any product arising from the reaction between the two chromophores. This result contrasts with that found in the case of the 1-NN alkene bichromophoric derivatives, which react much more efficiently than in the intermolecular case, giving 2 + 2 addition.[3] Thus, in the present case linking together the two chromophores facilitates excited state complexation, but, among the possible exciplex decay pathways, exciplex emission and back electron transfer (paths a, b in eqn 10) are largely favoured by the proximity of the two aromatic rings with respect to proton transfer from the benzylic position (path c). On the other side, the different behaviour of the 1-NN-alkene and the 1-NN-methylbenzene bichromophoric compounds is not completely unexpected in view of the fact that in the former case the exciplex minimum is conveniently situated along the pathway which leads to addition, while in the latter case holding the two aromatic rings parallel one to another, while certainly favouring exciplex emission (for analogies see e.g. Ref. 12) and back electron transfer, maintains a conformation not suited for intramolecular proton transfer.

Reactions with methylbenzenes

1-Methoxy-4-methylbenzene (**11**) and 1-methoxy-3-methylbenzene (**12**) quench the fluorescence of both 1-NN and 2-NN, as it is expected for these good electron donors. In the system 1-NN-**11** the exciplex emission is apparent and undergoes a regular shift to the red with increasing solvent polarity (Fig. 1), proving again the high charge transfer character of the complex. In the system 2-NN-**11** the exciplex emission, although less well resolved from the monomer emission in apolar solvents, becomes progressively disentangled at higher polarity, allowing the conclusion that also 2-NN gives polar exciplexes, at least with methoxybenzenes.

However, also with these derivatives the photochemical reactivity remains very slow. In comparison with the reaction with the tetramethylbenzene the product distribution is richer, Thus, from the reaction of 1-NN with **11** in acetonitrile in addition to 1,1'-(1,2-ethanediyl)bis-(4-methoxybenzene) (**13**) (50% yield calculated on the converted 1-NN), a complex mixture of several products each in a yield of a few percent or less is formed. Repeated chromatography and final distillation allow to obtain three products in the pure state. These were shown by analysis and spectroscopical methods (see Experimental) to be all benzylated 1,2-dihydro-1-naphthalenes, namely the *cis* 2-(4-methoxybenzyl) derivative (**14**), the corresponding *trans* isomer (**15**), distinguished from the former for the different coupling constants of the proton in position 2, as well as the 1,2-bis-(4-methoxybenzyl) derivative **16**. (eqn 11).

The photochemical reaction of 2-NN with **11** yielded again addition products, although only as a minor pathway. Thus, the main products are the bibenzyl **13** and reduction products from 2-NN, viz. 1,2-dihydro-2-naphthalenecarbonitrile (**7**; 38%) and 1,2,3,4,-tetrahydro-2-naphthalenecarbonitrile (**17**; 5%), the latter arising from further photochemical reduction of the former, but from the mixture of minor products three compounds analysing as adducts were isolated, On the basis of the spectroscopic properties (Experimental), these compounds were assigned the structure of 1-(4-methoxybenzyl)-1,4-dihydro-2-naphthalenecarbonitrile (**18**),



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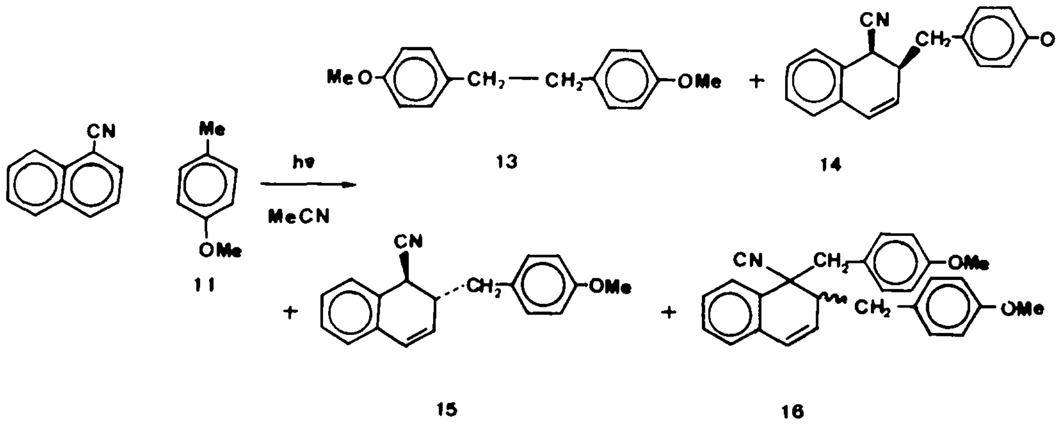

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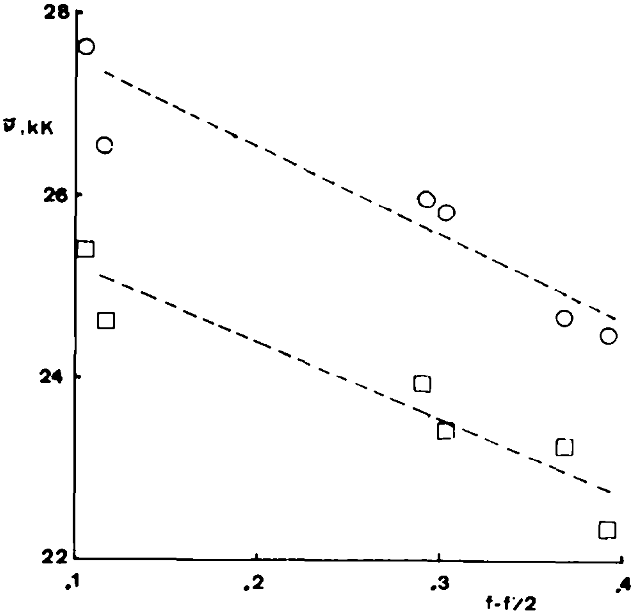
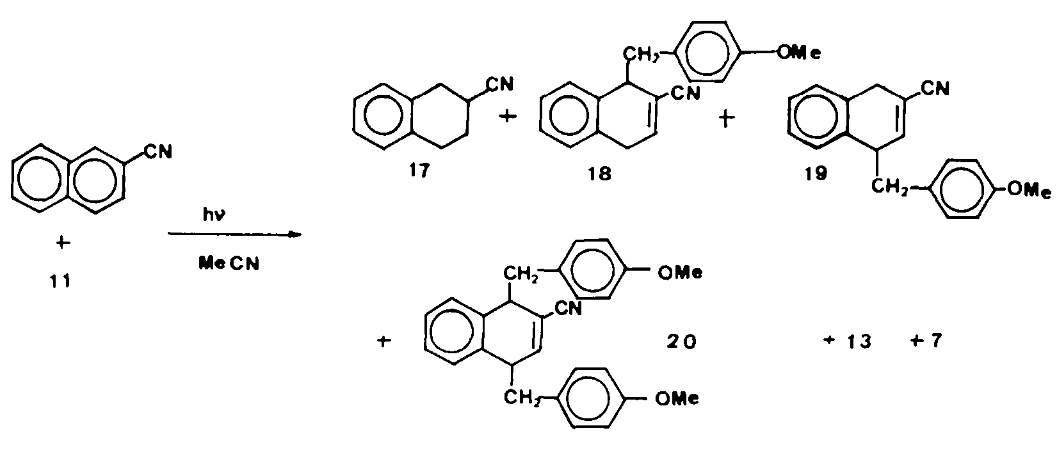


Fig. 1. Plot of the exciplex emissium maximum *vs* the solvent parameter f − f′/2 (see text): ○, system 1-NN-1,2,4,5,-tetramethylbenzene; □, system 1-NN-1-methoxy-4-methylbenzene. Solvents: cyclohexane, benzene, ethyl acetate, 1,2-dimethoxyethane, acetone, acetonitrile.

the corresponding 4-(4-methoxybenzyl) derivative (**19**) and the 1,4-bis(4-methoxybenzyl) derivative (**20**). However, we were unable to unambiguously distinguish which of the two mono benzyl derivatives corresponds to each formula, as well as the stereochemistry of the bis benzyl derivative **20**. Further products are certainly present, i.e. benzylated 1,2-dihydro-2-naphthalenecarbonitrile, but sufficient amounts of reasonably pure samples were not obtained. (eqn 12).

The photochemical reaction of both 1-NN and 2-NN with the isomeric methoxymethylbenzene **12** is almost negligible. Only from 2-NN some of the 1,2-dihydroderivative **7** was formed after prolonged irradiation, showing that hydrogen abstraction takes place as usually, although on a much reduced scale. On the other hand 1-methoxy-3-methylbenzene shows little reactivity also with NDN, and we have attributed it to a lesser tendency of the benzylic radical cation to deprotonate.

Comparison with the reaction of NDN is again instructive. Thus, although with 1-methoxy-4-methylbenzene benzylated products are obtained also from the mono naphthalenecarbonitrile, the



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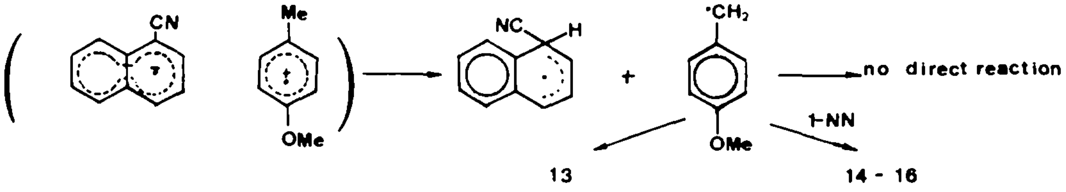

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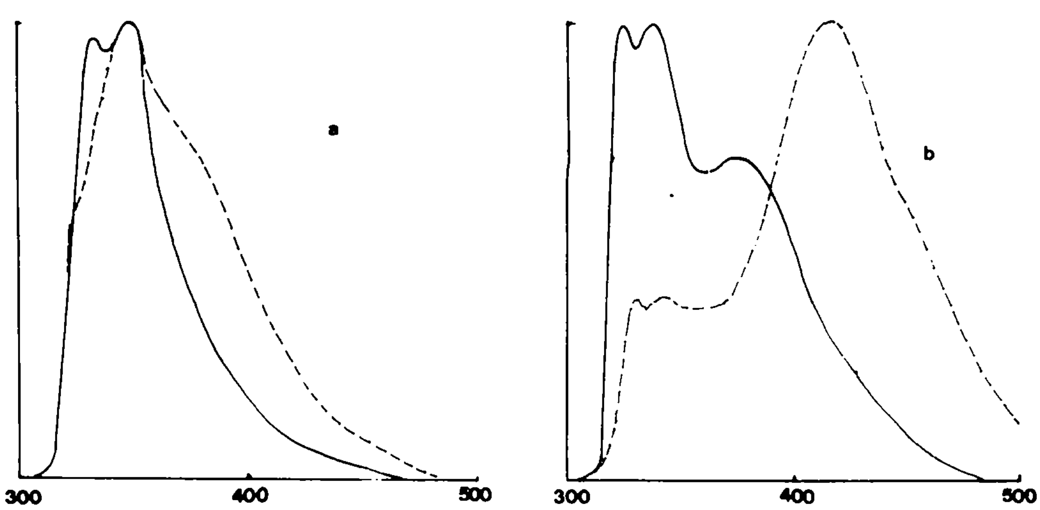

Fig. 2. Emission spectrum of the bichromophoric compounds **9** (Fig. a) and **10** (Fig. b), normalized to the emission maximum: —, in cyclohexane; - - - - -, in acetonitrile.

reaction clearly differs from that of NDN in that the adducts are formed only in tiny amounts (and with low quantum yield) and not stereospecifically. This supports the idea that the mechanism is different. In the NDN reaction the two radicals are held together by the interaction of the aromatic rings, so that they react in the same conformation in which are formed, the latter being in turn determined by the exciplex conformation, whereas in the present case the non stereospecificity in the adducts formation shows that the radicals fall apart before they react, and in a following step benzylic radicals are trapped by 1-NN or 2-NN.

CONCLUSIONS

These findings show that the stereospecific photochemical addition of methylbenzenes to NDN cannot be extended to mono naphthalenecarbonitriles. Of the three consecutive steps of this reaction the first, i.e. single quenching with formation of a charge transfer exciplex takes place efficiently in favourable cases, and the second, i.e. proton transfer within the exciplex is also observed, although with a lower probability (Φ_{hm}, *ca.* 0.1 in the NDN reaction, Φ_{hm} lower than 0.01 in the present case). However the third step, in cage reaction of the initially formed radicals is too slow with the mononitriles. This is an intrinsic difference due to a better interaction between the radicals in the NDN case, and cannot be offset by improving the entropic factor, as in the bichromophoric compounds **9** and **10**. The second cyano group is apparently playing a key role in this step. Thus other reactions compete successfully with in cage coupling, and the only chemical products obtained arise from out of cage radical reactions, It is also possible that reactions competing with the proton transfer, viz. exciplex emission and back electron transfer occur to a higher rate with mononitriles. As for the first possibility, it is noteworthy that exciplex emission is observed with 1-NN and methylbenzenes also in strongly polar solvents, while this is not the case for NDN.

EXPERIMENTAL

1- and 2-Naphthalenecarbonitrile as well as the methylbenzenes **4**, **11**, **12** were commercial materials and were recrystallized or distilled prior to use. Spectrograde solvents were used as received. UV spectra were measured on a Cary 210 spectrophotometer, IR spectra (nujol mull or KBr dispersion when solids, neat when liquids) on a Perkin-Elmer 197 spectrophotometer, NMR spectra on a Brucker 80 instrument ($CDCl_3$ soln, TMS as internal standard), mass spectra on a Dupont 291 spectrometer, elemental analysis on a Carlo Erba instrument.

Photochemical reactions with the naphthalenecarbonitriles. A soln containing 1.53 g (10 mmol) of either 1- or 2-naphthalenecarbonitrile and 100 mmol of the appropriate methylbenzene in 1L acetonitrile was degassed by boiling and flushing with Argon and irradiated in an immersion well apparatus by means of a Pyrex-filtered 500 W Helios Italquarz mercury arc. The irradiation was continued until sufficient conversion (30–50%) was determined by TLC and UV (7-20 h). The solvent was evaporated and the residue chromatographed on a silica gel column eluting first with cyclohexane in order to collect the unreacted methylbenzene and the bibenzyl formed, then with cyclohexane–ethyl acetate mixtures. The products obtained in the various fractions were finally purified by recrystallization or bulb to bulb distillation (Büchi Kugelrohr apparatus). Experiments with different methylbenzene concentration were carried out on a smaller scale and did not give appreciably different results.

Reaction between 1-*naphthalenecarbonitrile and* 1,2,4,5-*tetramethylbenzene* (**4**). The products obtained are **5** and **6**,[13] identical to known compounds. Several other products which we did not succeed in purifying are present in small yield. However, spectra of chromatographic fractions were not suggestive of the presence of adducts between 1-NN and 4.

Reaction between 2-*naphthalenecarbonitrile and* 1,2,4,5-*tetramethylbenzene* (**4**). The products isolated are the bibenzyl **5** and 1,2-dihydro-2-naphthalenecarbonitrile, NMR δ 5.85 dd (J = 11, 4.5), 6.6 dd (J = 11, 2), 3.5 m (1H), 3.1 m (2H) , already obtained by photoreduction of 2-NN in the presence of electron donors.[14]

Reaction between 1-*naphthalenecarbonitrile and* 1-*methoxy-4-methylbenzene.* (**11**). In addition to the known **13**, a large array of minor products are formed. From different chromatographic fractions three pure compounds were obtained as viscous oils, two analysing for a 1:1 adduct and one for a 1:2 adduct. UV and NMR spectra clearly showed the presence of the 1,2-dihydronaphthalene chromophore and thus the products were assigned as follows. *cis* **14**, NMR δ 6.5 dd (J = 11, 1.5), 5.85 dd (J = 11, 2), 3.95 d (4), 2.85 (AA′). (Found: C, 82.59, H, 6.41; N, 5.05. Calc. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22, N, 5.09%). The *trans* isomer **15**, NMR δ 6.5 dd (J = 13, 2), 5.9 dd (13, 5), 4.3d (6.5), 2.75 (AA′). (Found: C, 83.12; H, 6.18; N, 4.85%). Compound, **16**, NMR δ 5.85 dd (J = 12, 2), 2.8 (two superimposing AA′ systems). (Found: C, 81.71; H, 6.69; N, 3.66. Calc. for $C_{27}H_{27}NO_2$; C, 81.99, H, 6.97; N, 3.54%).

Reaction between 2-NN and 1-methoxy-4-methylbenzene (**11**). In addition to the bibenzyl **13** and compounds **7** and **17**, the latter identical to the compound obtained by cycloaddition from xylene and acrylonitrile,[15] small amounts of 2-NN-**11** adducts were obtained from different chromatographic fractions as viscous oils. Two of them analyze for 1:1 adducts and one for a 1:2 adduct. There are no separated olefinic signals as it would be expected for 1,2-dihydro-2-naphthalene-carbonitriles and the UV spectra show less conjugation than in the case of **7**. Thus, these products are 1,4-dihydro derivatives, the absorption of the proton in 3 being hidden under the aromatic signal, which extends up to 6.5 δ. The structure of **18** and **19** are assigned with reasonable confidence to the two 1:1 adducts, without specific attribution. NMR δ 3 m (5 H) for the first eluted, δ 3.15 m (3 H), 2.9 m (2 H) for the second. (Found: C, 83.01; H, 6.32; N, 4.83. Calc. for $C_{19}H_{17}NO$; O, 82.88; H, 6.22; N, 5.09% for the first and C, 83.09; H, 6.30; N, 4.79 for the latter). As for the 1:2 adduct, this is **20**, NMR δ 2.9 m (6 H). (Found: C, 82.21; H, 7.05, N, 3.42. Calc for $C_{27}H_{27}NO_2$; C, 81.99; H, 6.97; N, 3.54%). The NMR spectrum of a further fraction, obtained in trace amounts shows the signal expected from a benzylated 1,2-dihydro-2-naphthalenecarbonitrile.

4-*Methylbenzyl*-(1-*cyano*-4-*naphthyl*)*methyl ether* (**9**). A soln of 0.50 g (27 mmol) 4-hydroxymethyl - 1 - naphthalenecarbonitrile[3] in 20 mL anhyd THF was treated with 0.095 g (35 mmol) 80% sodium hydride under N_2-stream. The mixture was stirred and refluxed for 30 min and then treated with 1.11 g (60 mmol) 4-methylbenzyl bromide in 20 mL THF. After further 3 hr refluxing the mixture was cooled and 20 mL water were added dropwise. The aqueous layer was extracted with diethyl ether and then with benzene, and the reunited organic fraction was dried over $MgSO_4$ and evaporated. Chromatography of the residue on a silica gel column eluting with cyclohexane yielded, after some unreacted starting materials, a colourless solid which was recrystallized from cyclohexane to yield 0.345 g (45% yield) of product **9**, m.p. 59–60°, NMR δ 5.1 s (2 H), 4.7 s (2 H), 2.4 s (3 H), IR 2220 cm^{-1}. (Found: C, 83.55; H, 5.90; N, 4.68. Calc. for $C_{20}H_{17}NO$: C, 83.69; H, 5.96; N, 4.88%). In the same way starting from 2,4,5-trimethylbenzyl bromide 0.43 g (48%) of 2,4,5-*trimethylbenzyl*-(1-*cyano*-4-*naphthyl*)-*methyl ether* (**10**) were obtained, m.p. 108–109°, NMR δ 5.05 s (2 H), 4.65 s (2 H), 2.25 s (3 H), 2.2 s (6 H), IR 2220 cm^{-1}. (Found: C, 83.53; H, 6.59; N, 4.21. Calc. for $C_{22}H_{21}NO$; C, 83.77; H, 6.71; N, 4.44%).

Photochemistry of bichromophoric compounds **9** *and* **10**. A soln of 0.3 g of either **9** or **10** in 300 mL acetonitrile was degassed by boiling and bubbling with Argon and irradiated by means of a 150 W Helios Italquarz medium pressure mercury arch through Pyrex. After 15 hr of irradiation TLC showed only moderate conversion. Evaporation and chromatography on silica gel of the residue yielded 70% unreacted starting material. Several products were present in tiny amounts. NMR spectra of some fractions were indicative of fragmentation rather than internal addition.

Quantitative measurements. Photochemical quantum yields were measured at 313 nm by means of a collimated Osram 200 W high pressure mercury arc and an interference filter ($\Delta\lambda_{\frac{1}{2}}$ 9 nm) (radiating flux *ca* 10^{-7} Einstein/min on a 3 cm^2 surface), Potassium ferrioxalate was used as actinometer.

Fluorescence spectra and quantum yields were measured by means of an Aminco Bowman MPF fluorescence spectrophotometer, taking 1-naphthalenecarbonitrile as a standard ($\Phi_a = 0.21$ in cyclohexane[4b]).

For both photochemical and photophysical measurements the solutions were degassed by four freeze-degasse-thaw cycles.

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