Photochemical Reaction between Acenaphthene and Arenecarbonitriles

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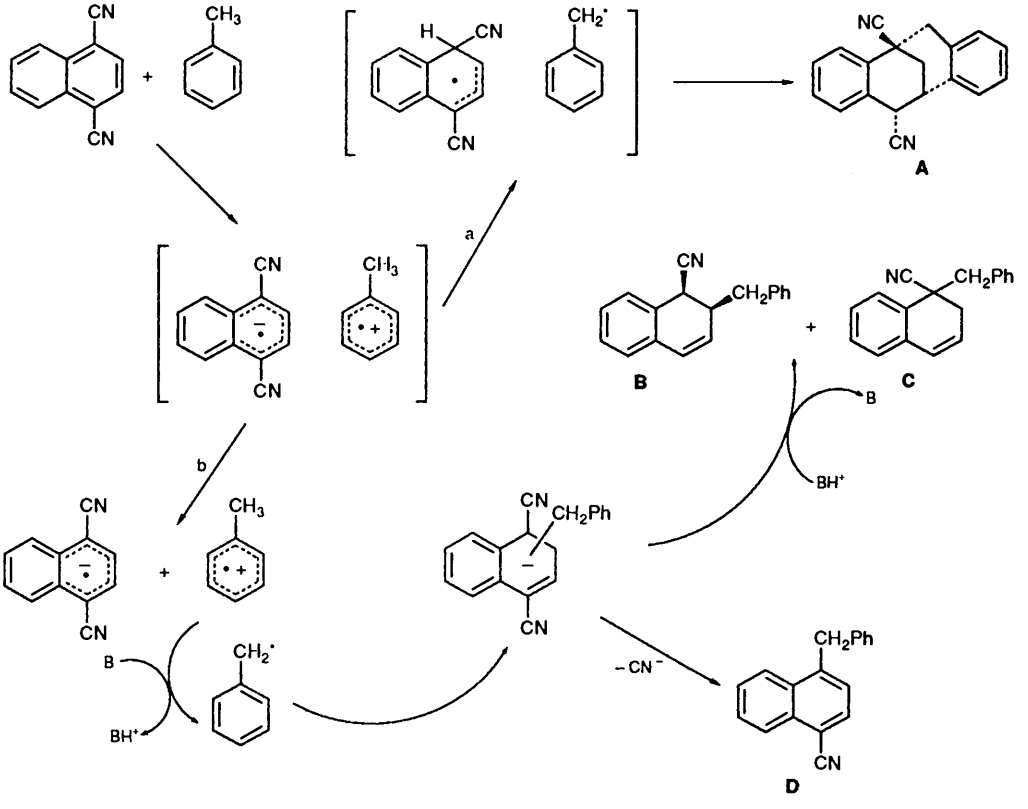
Various aromatic nitriles have been irradiated in acetonitrile in the presence of acenaphthene. The observed reactions involve electron-transfer quenching of the singlet excited state of the nitriles, and lead to replacement of a cyano group with an acenaphthenyl when starting from 1,4-dicyanobenzene and 1,2,4,5-tetracyanobenzene [here, also irradiating the ground-state electron-donor–acceptor (EDA) complex]. With 9,10-dicyanoanthracene (DCA) only biacenaphthenyls and reduced DCA are formed. With 1,4-dicyanonaphthalene the reaction is more complex, and both substitution of a cyano group and addition to yield 1- or 2-(acenaphthen-1-yl)-1,2-dihydro derivatives are obtained; furthermore, a product resulting from both reaction at the benzylic position and cycloaddition onto the 2a,3 bond of acenaphthene is isolated, and shown to be formed independently from the above adducts.

Alkyl aromatics are often used as donors in photochemically initiated electron-transfer reactions with acceptors.[1,2] Fragmentation of a bond (whether C–H,[2–6] C–C,[5–11] or C–Heteroatom[6,12–15]) β to the aromatic ring to yield a benzyl radical is usually the main chemical consequence (in competition with back-electron-transfer), and a typical example is reported in Scheme 1 [reaction between dicyanonaphthalene (DCN) and toluene leading to products **A**–**D**].[4] The substrates actually used are benzene derivatives, *e.g.* toluene and other alkylbenzenes.[3–6] Among the few alkylaromatics containing a different nucleus which have been tested, there are 1-methylnaphthalene and 9-methylanthracene;[3] the former has been found to react photochemically with benzonitrile, the latter with none of the arenenitriles used although the free-energy change for electron transfer from the methylarene to the excited

Table 1 Products from the irradiation of aromatic nitriles in the presence of acenaphthene in acetonitrile

Nitrile	Irradiation conditions	Products (% yield)
DCB	*a*	**1** (45)
TCB	*a*	**2** (90), **3** (1.5)[d]
TCB	*b*	**2** (90)
DCN	*c*	**4** (10), **5** (5.5), **6** (5.5), **7** (8.5), **8** (7.5), **9** (9)
DCA	*c*	1,1′-Biacenaphthenyl

[a] High-pressure mercury arc, through quartz. [b] Phosphor-coated lamps, emission centred at 405 nm. [c] High-pressure mercury arc, through Pyrex. [d] A small amount of acenaphthenequinone was also isolated.



Scheme 1

acceptor was negative in several cases. However, this is not sufficient, since even when the radical cation is formed efficiently its deprotonation may be too slow to compete with back-electron-transfer, and to allow the formation of a sizeable amount of arylmethyl radicals, the key intermediates of the following reactions.[3]

We now report the photochemical reactions of a particular alkylaromatic derivative, acenaphthene (AN), in the presence of various aromatic nitriles and comment on the bearing that these results have on the mechanism of this class of reaction.

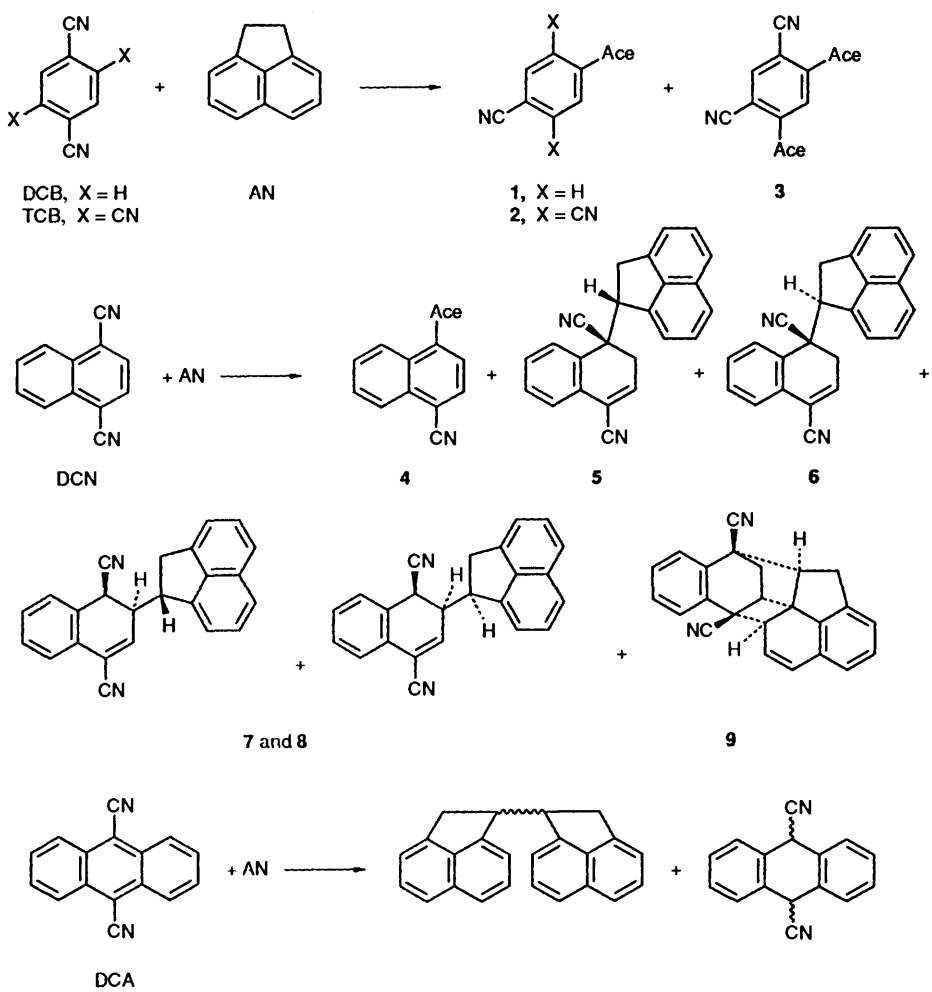
Results

Owing to the similarity of their electronic spectra, when a mixture of acenaphthene (AN) and 1,4-dicyanobenzene (DCB) in acetonitrile was irradiated with a high-pressure mercury arc through quartz both molecules absorbed the light. Under the conditions given in Table 1 absorption by AN prevailed by ~3:1. A slow photoreaction ensued, and led to a single photoproduct, identified as compound **1**, resulting from the substitution of a cyano group, from its analytic and spectroscopic properties. Experiments with different concentrations of the starting materials, and thus different distribution of the absorbed light, gave analogous results. On the other hand, irradiation in benzene or dichloromethane for up to 20 h caused no detectable consumption of the starting materials or formation of new products (Table 1, Scheme 2).

Mixing of AN and 1,2,4,5-tetracyanobenzene (TCB) in acetonitrile, dichloromethane or benzene generated a yellow colour indicative of a ground-state complex (λ_{max} 448 nm in MeCN). Irradiation either at 320 nm (both AN and TCB absorb, see the Experimental section), 366 nm (TCB and the complex absorb) or at 405 nm (only the complex absorbs) led to the same chemical consequence, *viz.* the main product arose again from the substitution of the acenaphthenyl radical for a cyano group (compound **2**). Minor products were a dialkylated derivative, the 4,6-disubstituted 1,3-dinitrile **3** (structure assignment on the basis of the asymmetric ^{1}H NMR aromatic signal, see the Experimental section) and a little acenaphthenequinone. Likewise irradiation in dichloromethane gave product **2**, though more slowly.

Irradiation of AN and 1,4-dicyanonaphthalene (DCN) in acetonitrile with Pyrex-filtered light (absorbed only by the latter substrate) led to a complex mixture from which several fractions were isolated. One of the products arose again from substitution of a cyano group (structure **4**). The remaining products were all adducts of the two reagents, as shown by mass spectrometry and elemental analysis. Of these, two were characterized by showing two independent ABX systems in their ^{1}H NMR spectra (at δ ~2.9 and 6.3 and at ~3.5 and 4.25, respectively, for the fast eluting isomer, and at δ ~2.7 and 6.7 and at ~3.5 and 4.5, respectively, for the slow one). Thus, they were recognized as the diastereoisomeric 1-acenaphthenyl-1,4-dicyano-1,2-dihydronaphthalenes. Stereochemical assignment on the basis of the available spectroscopic evidence did not seem possible. However, secondary photochemical reaction (see below) did give useful information and structures **5** and **6** (the *RR*/*SS* and the *RS*/*SR* diastereoisomers, respectively) were assigned to these compounds in order of elution.

Another fraction, which we could not separate, was shown by



Scheme 2 Ace = acenaphthen-1-yl

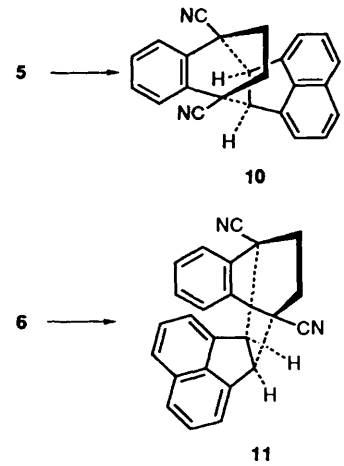
NMR spectroscopy to be a mixture of two adducts in a ~55:45 ratio. However, the ^{1}H NMR spectrum was sufficiently resolved to allow their recognition as diastereoisomeric 2-(1-acenaphthyl)-1,4-dicyano-1,2-dihydronaphthalenes (see details in the Experimental section). Four diastereoisomers are theoretically possible in this case, but the number of possibilities can be reduced since the relative configuration of two chiral centres could be recognized. Indeed, the coupling constants for the protons in positions 1 and 2 in the naphthalene ring were almost identical (6 and 6.5 Hz) and fitted with the values we had previously observed in a series of *cis*-2-alkyl-1,4-dicyano-1,2-dihydronaphthalenes,[4–6] whereas a much smaller value had been observed in the *trans* derivatives.[6] Therefore, it was assumed that the acenaphthenyl and the 1-cyano groups were *cis* also in these compounds (structures **7** and **8**), and the diastereoisomerism arose from the configuration of the newly formed carbon–carbon bond (notice, *inter alia*, the difference in the H–H coupling constants across that bond, indicative of different preferential conformations).

Finally, a further product, again an adduct, contained seven aliphatic protons, six of which appearing as two unconnected ABX or ABC systems. The seventh aliphatic proton was coupled to two coupled olefinic protons, and the remaining signals were for a three-proton and a four-proton aromatic system. This fitted well with a structure where a 1-acenaphthenyl radical was linked to the 1-(1,4-dicyano-1,2-dihydronaphthenyl) radical (the mass spectrum showed that the skeleton of both starting materials was conserved) but required also that the double bond in the 3,4-position of the naphthalene and the one in the 2a,3-position of the acenaphthene ring both be saturated. The obvious way to explain this was to postulate the presence of a cyclobutane ring. The ^{13}C NMR spectrum fully confirmed the above structure, showing, besides two methylenes and three methines, three aliphatic quaternary carbons as well as appropriate olefinic and aromatic signals (see details in the Experimental section). Hence a four-membered and a five-membered ring connected the two addends. Of the four possible regioisomers for such a structure (involving formation of a single bond from position 1 of the naphthalene to either position 1 or position 2 of the acenaphthene; a four-membered ring involving either the 2,2a or the 8,8a acenaphthene bond) only one was reasonable (see structure **9**) and with the stereochemistry shown, while the other ones were too strained, as judged from an inspection of molecular models.

Isolation of this cage compound raised the problem of its origin, either as a primary or as a secondary photoproduct.

This compound might reasonably result from intramolecular 2 + 2 cycloaddition of the above mentioned 1-alkyl-1,2-dihydronaphthalenes (**5** or **6**), and indeed there is precedent for a related process[16] (see the Discussion section). Therefore, the photochemistry of these compounds was examined. They were indeed found to be photolabile, and direct irradiation converted each compound into a single product isomeric with the starting material. Neither of these, however, corresponded to compound **9**. In both of these compounds the 3,4-double bond in the dihydronaphthalene moiety was absent, the naphthalene ring in the acenaphthene group was intact, and the general appearance of the ^{1}H NMR spectrum was quite symmetric with an AA'BB' system and a two-proton singlet in the aliphatic region. Thus, a new carbon–carbon bond had been formed between position 4 of the dihydronaphthalene and position 2 of the acenaphthenyl moieties, and the structures of the products were **10** (the *exo* isomer, recognized from the more deshielded aliphatic resonances since here the protons experience the effect of the aromatic rings) and **11** (the *endo* isomer) (Scheme 3). Products **10** and **11** were present in trace amounts in the DCN–AN photolysate.

An unexpected result of this experiment was that it afforded



Scheme 3

evidence for the identification of the stereochemistry of products **5** and **6** as proposed above (see Scheme 2). Indeed, the *exo* photoproduct **10** can arise only from structure **5**, and **11** from **6**, and since the photoisomerization was completely stereospecific, no doubt was left about the original stereochemistry.

The photochemistry of compounds **5** and **6** in the presence of DCN (which absorbed the light) and in the presence of an excess of AN was also investigated. The compounds were decomposed under these conditions too, and the reactions were rather complex. However, in no case was compound **9** formed and as a consequence compound **9** was recognized as a primary photoproduct from DCN and AN.

As for the solvent effect in the DCN–AN system, irradiation of these two molecules in apolar dichloromethane or benzene (20 h) caused virtually no reaction.

Finally, irradiation of AN and 9,10-dicyanoanthracene (DCA, light absorbed by the nitrile) followed, as in the previous cases, by chromatography, led to substantial recovery of DCA (though in the photolysate it appeared to have been largely consumed as judged by TLC) and separation of the two diastereoisomeric biacenaphthenyls. Further products were present only in trace amounts.

Discussion

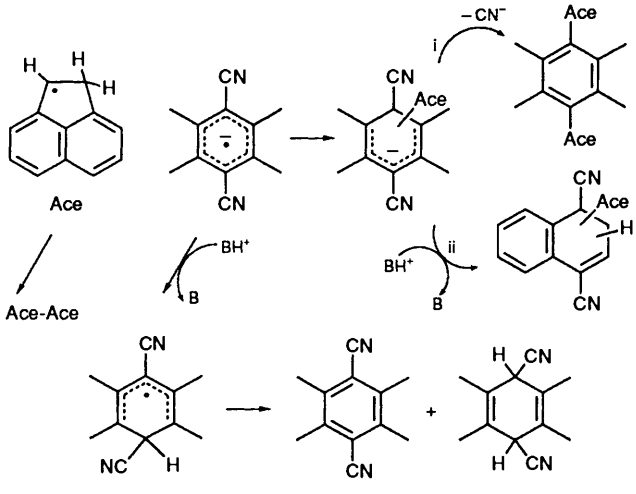
The formation of the observed products can be rationalized through a sequence involving electron transfer, deprotonation of the acenaphthene radical cation, carbon–carbon bond formation, and finally reprotonation or anion loss. As for the first step, all of the present reactions clearly involve a charge-transfer interaction in the singlet excited state; fluorescence measurements showed quenching of both DCN and DCA singlet excited states by AN, (K_{sv} 175 and 210 dm^3 mol^{-1}, respectively) and the calculated free-energy change for electron transfer to the excited nitriles is negative in all cases (relevant data for calculations were taken from ref. 17*a*). On the other hand, association in the ground state is negligible, as expected with these relatively weak acceptors [E_{red} −0.89 and −1.28 V *vs.* saturated calomel electrode (SCE) for DCA and DCN, respectively].[17a] Only with the better acceptor TCB (E_{red} −0.7 eV)[17a] was a ground-state EDA complex detected (λ_{max} 448 nm in acetonitrile; compare TCB–durene, λ_{max} 400 nm, K 0.3 dm^3 mol^{-1} and TCB–pyrene, λ_{max} 495 nm, K 12.4 dm^3 mol^{-1} in chloroform.[17b] The selective irradiation experiments performed with the last system in every case caused the same chemical reaction. Thus, the interesting point is that the same excited complex is reached starting from excited nitrile and ground-state AN, excited AN and ground-state nitrile, or a ground-state nitrile AN complex (Scheme 4).

$$TCB^{1*} + AN \longrightarrow (TCB\cdots AN)^*$$
$$\uparrow \qquad\qquad \uparrow$$
$$TCB + AN \longrightarrow (TCB\cdots AN)$$

Scheme 4

For the following steps of the process, a polar medium such as acetonitrile is required, the reaction proceeding only sluggishly or not at all in apolar solvents (except, again, in the case of the preformed EDA complex AN–TCB).

The solvated radical cation of acenaphthene undergoes deprotonation from the benzylic position, a process which has ample precedent,[1–6] the solvent acting as proton acceptor, and the benzyl radical adds to the nitrile radical anion. In this way an anion is formed, and the subsequent reaction depends on the structure of the starting nitrile; when benzene nitriles are used, the carbanion undergoes elimination of cyanide anion (path i in Scheme 5), thus regenerating aromaticity. This results in formal substitution of an alkyl for a cyano group, the usually observed reaction with benzenenitriles.[18–22]



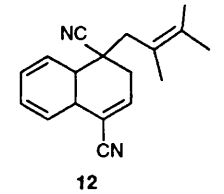
Scheme 5

With DCA both subsitution to yield an alkylcyanoanthracene and addition to yield an alkyldicyanodihydro derivative have been previously observed.[12,23–25] However, in the present case the stability of both the acenaphthenyl radical and DCA radical anion due to extensive delocalization and their large steric hindrance change the course of the reaction. Hence the acenaphthenyl radicals undergo coupling to the dimers, while $DCA^{-\bullet}$ is probably protonated, and the dicyanoanthracenyl radicals diproportionate to DCA and $DCAH_2$ (see Scheme 5), the latter being reoxidized to the former during work-up. This explains the fact that DCA, not present in the raw photolysate, is recovered from the column chromatography eluates.

As for DCN, adducts (dihydroaromatics) are the main products in the present as well as in the previous cases,[4–6] as one might expect since the loss of aromaticity is less than with benzene derivatives and steric hindrance less than with anthracenes. Therefore adducts of types **B** and **C** (see Scheme 1) are formed besides the product resulting from cyano substitution (type **D**). The stability and bulk of the acenaphthenyl radical have an important effect, however, since no analogue of compound **A**, the main product with toluene (indeed, likewise not formed from diphenylmethane)[6] is obtained, and the products are rather the two possible alkyl-1,2-dihydro derivatives. Notice, however, that in the 2-alkyl derivatives the stereoselectivity observed with both toluene and the alkylbenzenes is conserved and the groups are in a *cis* arrangement in this case also. This can be rationalized by assuming that products of type **B** arise from radical–radical anions recombination, and protonation of the resulting anion is the last step (see Scheme 1) and occurs from the least hindered side.[4]

The present results from the irradiation of DCN and acenaphthene and the previous results with other benzylic donors[4–6] show a common trend. With relatively less stable radical cations (those from alkylbenzenes) proton transfer within the initially formed radical ion pair (finally to yield products **A**, path a in Scheme 1) is important, and the neutral radicals thus formed couple stereospecifically in the cage (see Scheme 1) while more stabilized radical cations (*e.g.*, those of diphenylmethanes,[6] *p*-methoxytoluene[4] and, here, acenaphthene) diffuse and deprotonate as the free species (path b and not path a in Scheme 1). The neutral benzylic radicals then combine with the nitrile radical anion as mentioned above.

The secondary photochemical reaction of adducts **5** and **6** offers some unexpected features. No 2 + 2 cycloaddition takes place, though such a process had been previously observed with alkenyl (but not with benzyl) derivatives of related structure, *e.g.*, compound **13** from **12**.[16] On the other hand benzyl derivatives of type **C** are photostable. In the present case, intramolecular hydrogen abstraction from the very reactive acenaphthenyl methylene predominates. Radical reactivity of the triplet state of compounds **5** and **6**, probably localized on the α-cyanostyrene moiety, is not unreasonable, at least to the extent of allowing an intramolecular abstraction from a good hydrogen-donating site to yield one of the two diradicals **14** and from these are derived the observed products.



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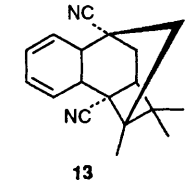

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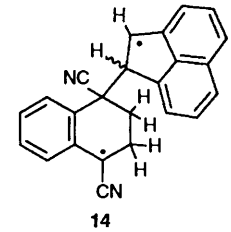

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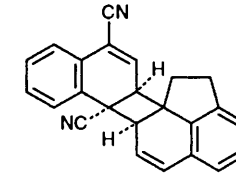

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Formation of product **9**, in contrast, is difficult to reconcile with the general mechanism as depicted in Scheme 1. A path we postulate is that 2 + 2 cycloaddition precedes hydrogen transfer, and the first photochemical step involves the 2a,3-acenaphthene double bond to yield product **15**, while the second photochemical reaction is a triplet-radical abstraction, similar to that observed in the **5** ⟶ **10** or **6** ⟶ **11** conversion. However, we have no evidence for the intermediacy of adduct **15**.

This study supports and enriches the scope of the proposed mechanism for the formation and the reactivity of benzyl radicals in the arene nitrile–alkylaromatic systems, adding to the class of very stable benzyl radicals, and showing the relation between ground and excited state change-transfer complexes. Furthermore, if our hypothesis concerning the origin of compound **9** is correct, in the DCN–AN system the point is reached where the electron-transfer–proton-transfer process and the cycloaddition (*via* exciplex) process compete. AN certainly would appear to be a favoured partner for both types of reaction.

Experimental

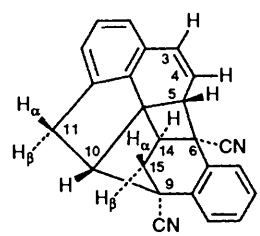
AN was recrystallized from ethanol (**CAUTION**: impurities in commercial samples, probably arising from oxidation, quench the photoreaction). The nitriles were prepared according to literature procedures and were purified by alumina chromatography and recrystallization. Silica gel Merck 60 HR was used for column chromatography. ^1H and ^{13}C NMR spectra were measured on a Bruker 300 instrument with Me_4Si as internal standard (all coupling constants are in Hz). IR and UV spectra were measured on a Perkin-Elmer 187 and a Cary 19 instrument, respectively. Elemental analysis was performed on a Carlo Erba microanalyser. Mass spectra were obtained on a Finnigan MAT 8222 instrument (mass spectra of all new compounds gave evidence both for the molecular weight and for the conservation of the skeleton of the addends).

Irradiation of DCB and AN.—AN (450 mg, 2.9 mmol) and DCB (170 mg, 1.33 mmol) were dissolved in MeCN (100 cm^3), and the solution was refluxed and cooled under an argon stream, and irradiated by means of a high-pressure mercury arc (Philips HPK 125W) in a quartz well at 17 °C, while being stirred under a slow stream of argon. After 11 h the solution was evaporated and the residue was chromatographed on a silica gel column and eluted with cyclohexane–ethyl acetate mixtures (from 95:5 to 50:50). Besides unchanged AN, the separation gave: unchanged DCB (80 mg) and 4-(*acenaphthen-1-yl*)*benzonitrile* **1** (80 mg, 45% on consumed DCB) as crystals, m.p. 107–110 °C (from EtOH) (Found: C, 89.4; H, 5.0; N, 5.4. $C_{19}H_{13}N$ requires C, 89.38; H, 5.13; N, 5.49%); δ_H 3.3 (dd, J_{vic} 4, J_{gem} 19) and 4.0 (dd, J_{vic} 9) (acenaphthyl CH_2), 4.95 (dd, acenaphthyl CH) and 7.0–7.8 (10 H, m, ArH); ν_{max}/cm^{-1} 2210.

Irradiation of TCB and AN.—Analogous irradiation of TCB (120 mg, 0.65 mmol) and AN (400 mg, 2.6 mmol) for 12 h, followed by work-up as above, gave unchanged TCB (20 mg); 5-(*acenaphthen-1-yl*)*benzene-1,2,4-tricarbonitrile* **2** (198 mg, 90%) as crystals, m.p. 175–178 °C (from EtOH) (Found: C, 82.5; H, 3.65; N, 13.5. $C_{21}H_{11}N_3$ requires C, 82.61; H, 3.63; N, 13.76%); δ_H 3.25 (dd, J_{vic} 4, J_{gem} 19) and 4.25 (dd, J_{vic} 9) (acenaphthyl CH_2), 5.45 (dd, acenaphthyl CH) and 7.0–7.6 (6 H, m), 7.8 (1 H, s) and 8.1 (1 H, s) (ArH); ν_{max}/cm^{-1} 2210 acenaphthoquinone (~2 mg); 4,6-*di*(*acenaphthen-1-yl*)*benzene-1,3-dicarbonitrile* **3** (5 mg, 1.5%) as crystals, m.p. 168–170 °C (from EtOH) (Found: C, 88.6; H, 4.75; N, 6.35. $C_{32}H_{20}N_2$ requires C, 88.86; H, 4.66; N, 6.48%); δ_H 3.2 (2 H, two almost superposed dd, J_{vic} 4, J_{gem} 19), 4.0 (1 H, dd, J_{vic} 9) and 4.05 (1 H, dd, J_{vic} 9) (acenaphthyl CH_2), 5.2 (2 H, two almost superposed dd, acenaphthyl CH), and 7.75 (12 H, m), 7.75 (s) and 8.05 (s) (ArH).

Selective Irradiations in the TCB–AN Systems.—Irradiation at selected wavelengths were performed on samples (50 cm^3) (concentrations as above) contained in quartz tubes. These were degassed, serum capped, and externally irradiated by means of an Applied Photophysic multilamp apparatus fitted with three pairs of phosphor-coated lamps, with the emission centred at 320, 365 or 405 nm respectively.

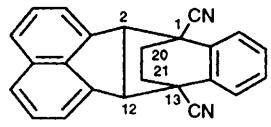
Irradiation of DCN and AN.—Irradiation of DCN (150 mg, 0.84 mmol) and AN (450 mg, 2.9 mmol) was carried out as above, for 2 h, except that a Pyrex cooling well was used. Analogous work-up gave unchanged DCN (30 mg); 4-(1-*acenaphthenyl*)*naphthalene-1-carbonitrile* **4** (26 mg, 10%) as crystals, m.p. 189–190 °C (from EtOH) (Found: C, 90.4; H, 4.9; N, 4.55. $C_{23}H_{15}N$ requires C, 90.46; H, 4.95; H, 4.59%); ν_{max}/cm^{-1} 2210; δ_H 3.4 dd (1 H, *J* 5 and 18), 4.15 (1 H, *J* 9 and 18) and 5.65 (1 H, dd); (1R,αR/1S,αS)-1-(1-*acenaphthenyl*)-1,2-*dihydronaphthalene*-1,4-*dicarbonitrile* (faster eluting diastereoisomer) **5** (15 mg, 5.5%) as crystals, m.p. 178–179 °C (Found: C, 86.6; H, 4.9; N, 8.2. $C_{24}H_{16}N_2$ requires C, 86.72; H, 4.85; N, 8.43%); δ_H 2.9 (2 H, m, AB part of an ABX system, 2-H), 3.55 (2 H, AB part of an ABX system, acenaphthyl CH_2), 4.25 (t, *J* 5, acenaphthyl CH), 6.35 (*J* 5, 3-H) and 6.75–8.0 (10 H, m, ArH); ν_{max}/cm^{-1} 2220; (1R,αS/1S,αR)-1-(1-*acenaphthenyl*)-1,2-*dihydronaphthalene*-1,4-*dicarbonitrile* (slower eluting diastereoisomer) **6** (15 mg, 5.5%) as crystals, m.p. 169–171 °C (from EtOH) (Found: C, 86.5; H, 4.9; N, 8.2%); δ_H 2.7 (2 H, m, AB part of an ABX system, X at δ 6.7), 3.3 dd (J_{vic} 4, J_{gem} 18) and 3.6 (dd, J_{vic} 7) (acenaphthyl CH_2), 4.5 (dd, acenaphthyl CH), 6.7 (t, *J* 5, 3-H) and 6.8–7.8 (10 H, m, ArH); ν_{max}/cm^{-1} 2220; 2-(1-*acenaphthenyl*)-1,2-*dihydronaphthalene*-1,4-*dicarbonitrile* [mixture of the (1R,2S,αR/1S,2R,αS)- and the (1R,2S,αS/1S,2R,αR)-diastereoisomers] **7** and **8** (45 mg, 16%) as crystals, m.p. 158–160 °C (Found: C, 86.5; H, 4.9; H, 8.2%); δ_H(major isomer, 55%) 3.2 (dd, J_{vic} 3.5, J_{gem} 17) and 3.6 (dd, J_{vic} 8, J_{gem} 17) (acenaphthyl CH_2), 4.25 (dd, acenaphthyl CH), 3.35 (dt, $J_{1,2}$ 6.5, $J_{2,3}$ 3.5, $J_{2\text{-acenaphthyl}}$ 3.5, 2-H), 4.4 (d, 1-H), 6.55 (d, 3-H) and 7.2–7.8 (10 H, m, ArH); (minor isomer, 45%) 3.15 (dt, $J_{1,2}$ 6, $J_{2,3}$ 4, $J_{2\text{-acenaphthyl}}$ 6, 2-H), 3.55 (dd, J_{vic} 3, J_{gem} 17), 3.8 (J_{vic} 8, J_{gem} 17) (acenaphthyl CH_2), 4.15 (d, 1-H), 4.15 (dd, acenaphthyl CH), 7.1 (d, 3-H) and 7.2–7.8 (10 H, m, ArH); ν_{max}/cm^{-1} 2220; *heptacyclo*[13.6.1.0^{1,12}.0^{2,11}.0^{4,21}.0^{5,10}.0^{19,22}]*docosa-5,7,9,13,15,17,19(22)-heptaene*-4,11-*dicarbonitrile* **9** (25 mg, 9%) as crystals, m.p. 202–205 °C (from EtOH) (Found: C, 86.7; H, 4.9; N, 8.10%); δ_H 2.1 (d, $J_{3\alpha,3\beta}$ 17, 3α-H), 2.65 (dd, $J_{2,3\beta}$ 5, 3β-H), 3.0 (dd, $J_{12,14}$ 2, $J_{12,13}$ 3, 12-H), 3.15 (dd, $J_{20\alpha,21}$ 7, $J_{20\alpha,20\beta}$ 15) and 3.35 (dd, $J_{20\beta,21}$ 7) (20-H_2), 3.25 (dd, 21-H), 3.9 (d, 2-H), 6.2 (dd, $J_{13,14}$ 10, 13-H), 6.75 (dd, 14-H), 7.0 (d, *J* 7), 7.1 (d, *J* 7), 7.25 (t, *J* 7), (16-, 17- and 18-H), and 7.4–7.55 (2 H, m), 7.6–7.7 (1 H, m) and 7.8–7.9 (1 H, m) (6-, 7-, 8- and 9-H); δ_C 36.45t, 37.05t, 44.0s, 48.5s, 50.95d, 52.35d, 56.45s, 61.05d, 119.05s (CN), 120.25s (CN), 123.85d, 124.65d, 125.5d, 126.5d, 127.85d, 128.7d, 128.8d, 129.05s, 129.7d, 132.7s, 136.8s, 136.9s and 138.55s.



Irradiation of DCA and AN.—Irradiation of DCA (170 mg, 0.75 mmol) and AN (850 mg, 5.52 mmol) in MeCN (600 cm^3) for 2 h under the same conditions as above, and similar work-up, gave unchanged AN, unchanged DCA (160 mg), and the stereoisomeric 1,1′-biacenaphthenyls (26 mg each). In the NMR spectrum of the last compounds the ABX systems were at δ 3.0, 3.65, and 4.45 for the fast eluting and δ 2.9, 3.25 and 4.4 for the slower eluting isomer. Their physical properties were identical with the literature data.

Irradiation of Product **5**.—An aliquot (20 mg) of this compound in MeCN (20 cm^3) in a quartz tube was purged with argon and irradiated by means of an external high-pressure mercury arc. After 2 h the compound was cleanly converted into a new product, which was recrystallized from EtOH to yield *hexacyclo*[11,6.2.1^{3,7}.0^{2,12}.0^{11,22}.0^{14,19}]*docosa*-3,5,7,9,11-(22),14,16,18-*octaene*-1,13-*dicarbonitrile* (*exo-isomer*) **10**, m.p. 230–232 °C (decomp.) (Found C, 86.9; H, 4.7; N, 8.6%); δ_H 2.15 (2 H, m) and 2.6 (2 H, m) (AA′BB′ system, 20- and 21-H_2), 4.4 (2 H, s, 2- and 12-H), and 7.05 (2 H, m), 7.25 (2 H, m), 7.45 (2 H, m), 7.55 (2 H, m) and 7.75 (2 H, m) (ArH); ν_{max}/cm^{-1}

2220. This product was also obtained, in trace amounts, from the irradiation of DCN and AN.



Irradiation of Product **6**.—An aliquot (20 mg) of this compound in MeCN (20 cm^3) was irradiated as above to yield product **11**, *endo*-isomer of **10**, m.p. 235–239 °C (from EtOH, decomp.) (Found: C, 86.95; H, 4.85; H, 8.35%); δ_H 1.6 (2 H, m) and 1.8 (2 H, m) (AA'BB' system, 20- and 21-H_2), 4.1 (2 H, s, 2- and 12-H), and 7.55 (2 H, m), 7.65 (2 H, m), 7.78 (2 H, m), 7.82 (2 H, m) and 7.92 (2 H, m) (ArH); ν_{max}/cm^{-1} 2220. This product was also obtained, in trace amounts, from the irradiation of DCN and AN.

Fluorescence Quenching.—The quenching of the fluorescence of DCN and DCA by AN was determined by using vacuum-degassed, 1 cm optical path couvettes. Fluorescence intensity was measured by means of an Aminco-Bowman MPF spectrofluorimeter. Linear Stern–Volmer plots were obtained in every case.

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References

1 A. Albini and A. Sulpizio in *Photoinduced Electron Transfer*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, vol. C, 88.
2 F. D. Lewis, *Acc. Chem. Res.*, 1986, **19**, 401.
3 F. D. Lewis and J. R. Petisce, *Tetrahedron*, 1986, **42**, 6207.
4 A. Albini, E. Fasani and A. Sulpizio, *J. Am. Chem. Soc.*, 1984, **106**, 3562.
5 A. Albini, E. Fasani and M. Mella, *J. Am. Chem. Soc.*, 1986, **108**, 4119.
6 A. Sulpizio, A. Albini, N. d'Alessando, E. Fasani and S. Pietra, *J. Am. Chem. Soc.*, 1989, **111**, 5773.
7 D. R. Arnold and A. Maroulis, *J. Am. Chem. Soc.*, 1976, **98**, 5931.
8 D. R. Arnold and R. Popielarz, *J. Am. Chem. Soc.*, 1990, **112**, 3068.
9 J. Libman, *J. Am. Chem. Soc.*, 1975, **97**, 4139.
10 A. Albini and M. Mella, *Tetrahedron*, 1986, **42**, 6219.
11 H. F. Davis, P. K. Das, L. W. Reichel and G. W. Griffin, *J. Am. Chem. Soc.*, 1984, **106**, 6968.
12 D. F. Eaton, *J. Am. Chem. Soc.*, 1981, **103**, 7235.
13 K. Mizuno, M. Ikeda and Y. Otsuji, *Tetrahedron Lett.*, 1985, **26**, 461.
14 K. Mizuno, K. Terasaka, M. Yasueda and Y. Otsuji, *Chem. Lett.*, 1988, 145.
15 J. Y. Lan and G. B. Schuster, *J. Am. Chem. Soc.*, 1985, **107**, 6710.
16 D. R. Arnold, P. C. Wong, A. J. Maroulis and T. S. Cameron, *Pure Appl. Chem.*, 1980, **52**, 2609.
17 (*a*) *Handbook of Organic Photochemistry*, ed. J. C. Scaiano, CRC Press, Boca Raton, 1989; (*b*) A. S. Bailey, B. R. Henn and J. M. Langdon, *Tetrahedron*, 1963, **19**, 161.
18 A. Yoshino, M. Ohashi and T. Yonezawa, *Chem. Commun.*, 1971, 97.
19 M. Ohashi and N. Nakayama, *Chem. Lett.*, 1967, 1143.
20 M. Ohashi, S. Suwa, U. Osawa and K. Tsujimoto, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2219.
21 K. Tsujimoto, K. Miyake and M. Ohashi, *J. Chem. Soc., Chem. Commun.*, 1976, 386.
22 M. Ohashi and K. Miyake, *Chem. Lett.*, 1977, 615.
23 E. Hasegawa, M. A. Brumfield and P. S. Mariano, *J. Org. Chem.*, 1988, **53**, 5435.
24 M. Ohashi, H. Kudo and S. Yamada, *J. Am. Chem. Soc.*, 1979, **101**, 2201.
25 J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, W. P. Todd and S. L. Mattes, *J. Am. Chem. Soc.*, 1989, **111**, 8973.

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