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The Photochemical Reactions of 9,10-Anthracenedicarbonitrile and 1,4-Naphthalenedicarbonitrile in Acetonitrile in the Presence of Bases

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Abstract. Irradiation of 9,10-anthracenedicarbonitrile(DCA) in MeCN-MeOH or MeCN-H_2O containing hydroxides or methoxides leads to 9-methylimino-10-anthracenecarbonitrile (isolated, but easily hydrolyzed to the corresponding amine). Minor products are polycyanated amines and 9-hydroxy-10-anthracenecarbonitrile. Irradiation in neat MeOH causes decyanation. In both cases the first step is reduction to $DCA^{-\cdot}$, which persists for hours under these conditions. Evidence for the mechanism leading from the radical anion to the observed products is supplied. The key steps are protonation to yield the radical $DCAH^{\cdot}$ and addition of the latter to acetonitrile, or to better nucleophiles when these are present. 1,4-Naphthalenedicarbonitrile is similarly transformed to the 4-amino-1-carbonitrile.

The recent literature shows the variety of useful chemical reactions one can obtain via radical cations formed by electron transfer photosensitization (PET).[1,2] This involves electron transfer from a donor to a photoexcited sensitizer (eq.1) and requires that the radical cation undergoes a fast process (eq.2, e.g. addition, rearrangement, fragmentation) in competition with back electron transfer (eq.3).

$$\mathrm{Sens}^{*} + \mathrm{D} \rightarrow \mathrm{Sens}^{-\cdot} + \mathrm{D}^{+\cdot} \qquad (1)$$

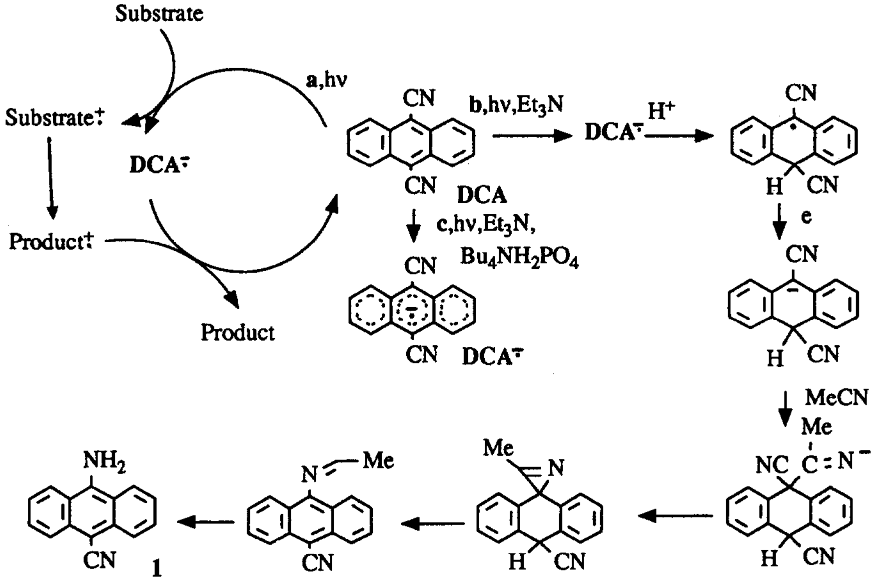
$$\mathrm{D}^{+\cdot} \rightarrow \mathrm{Products} \qquad (2)$$

$$\mathrm{Sens}^{-\cdot} + \mathrm{D}^{+\cdot} \rightarrow \mathrm{Sens} + \mathrm{D} \qquad (3)$$

In order that preparatively useful reactions via the radical cation take place, it is obviously desirable that neither the excited sensitizer nor the corresponding radical anion suffer a significant decomposition under the experimental conditions. Quinones (sensitizing through their triplet state)[3,4] and, even better, aromatic nitriles (through the singlet)[5-9] meet this requirement, at least when they are used in an inert (and polar, in order to facilitate charge separation, eq.1) solvent. Indeed, the single most largely used system involves 9,10-anthracenedicarbonitrile (DCA) as the sensitizer and acetonitrile as the solvent. As as example, DCA efficiently sensitizes the PET dimerization and oxygenation of arylalkenes[6-8] (the general scheme for a PET sensitized reaction is shown in Scheme 1, path a). This material (easily synthetized and also commercially available) is a popular sensitizer for photophysical and photochemical studies in view of its convenient absorption and strong oxidizing properties in the excited state ($E_{red}(S_o) = -0.89$ V vs SCE, $E_{red}(S_1) = 1.97$).

However, there are some disturbing reports about its photostability under electron transfer conditions. Thus, Ohashi et al reported that DCA is converted to 10-amino-9-anthracenecarbonitrile (1) by irradiation in acetonitrile in the presence of triethylamine, and further established that the amino nitrogen originates from the solvent and that a protic agent is required for the reaction to occur. The mechanism these Authors propose is depicted in Scheme 1, path b;[10] although it might seem unusual, this bears, as they remarked, some analogy with that invoked for the photoreactions of some nitroaromatics.[11] The formation of amine 1 was observed also by Mariano (with both amines and α-silylamines as the donors).[12] On the other hand, Whitten et al reported[13] that slightly changing the conditions (i.e. adding an "inert" salt, tetrabutylammonium dihydrogenphosphate) resulted in the formation of the radical anion $\mathrm{DCA}^{-\cdot}$ as an indefinitely stable species (Scheme 1, path c) through a slow but clean reaction with no attending conversion to 1.

In view of the above mentioned large use of the DCA/MeCN combination in photoelectron transfer reactions, it appeared worthwhile to ascertain the scope and the mechanism of any reaction occurring in this and related systems and to explore whether a single mechanism could account for the different observations reported.



Scheme 1.

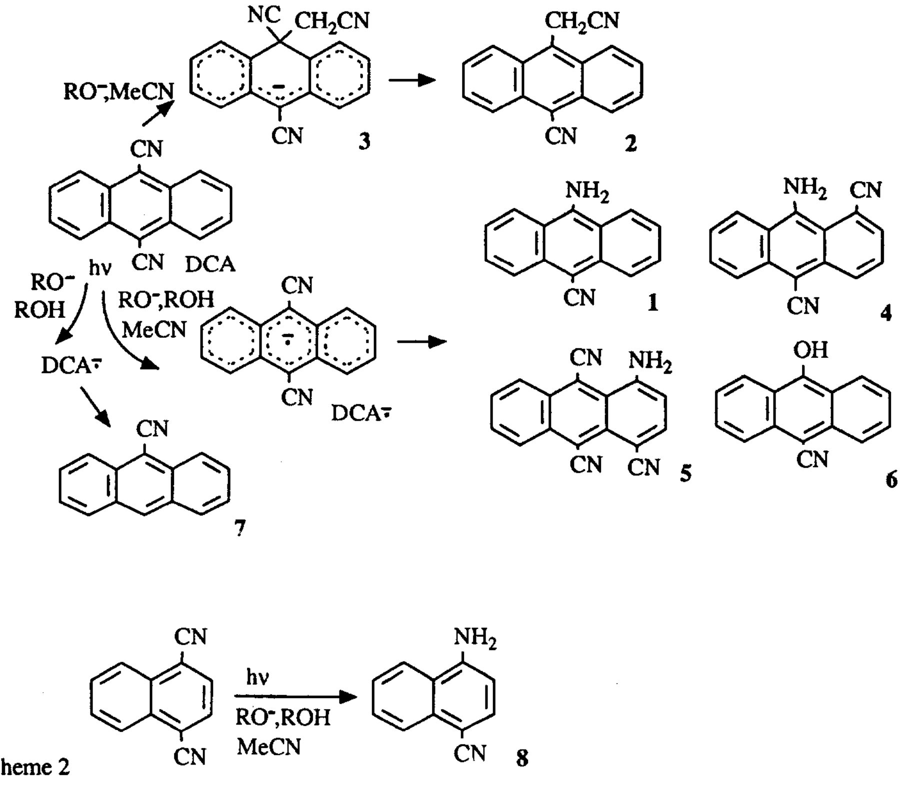
RESULTS

Scope of the reaction. In the studies mentioned above, the amine 1 had been obtained in aqueous-organic solution containing a donor (amine/MeCN/H_2O), presumably via the DCA radical anion,[10] while the latter species had been generated and remained stable when a phosphate had been added to the solution, a fact rationalized as due to the stabilizing effect by the counterion.[13] We noticed that the ΔG for electron transfer from the hydroxide ion to DCA^{1*} is calculated to be negative by the Weller equation.[14,15] This suggested to explore the photochemical behaviour of DCA in the presence of mineral bases, which could both act as donors

Table 1. Isolated products from the irradiation of 9,10-anthracenedicarbonitrile (DCA) and 1,4-naphthalenedicarbonitrile (DCN) in the presence of bases.

Substrate(M)	Solvent	Base(M)	Irradiation time (h)	Products (% Yield)
DCA,5×10^{-4}	MeCN,1M MeOH	MeONa,1.5×10^{-2}	2.5[a]	DCA(16), 1(60), 2(8), 4(12), 5(2), 7(tr)
DCA,5×10^{-4}	MeCN,0.5M H_2O	Bu_4NOH,5×10^{-4}	8	DCA(10), 1(30), 2(10), 4(15), 5(5), 6(5), 7(tr)
DCA,5×10^{-4}	MeCN,1.4M H_2O	Bu_4NOH,1.5×10^{-2}	15	DCA(40), 1(18), 2(tr), 4(12), 5(10), 6(10), 7(tr)
DCA,8×10^{-5}	MeOH	MeONa,9×10^{-3}	30	DCA(15), 7(82)
DCN,5×10^{-3}	MeCN,0.2M MeOH	MeONa,1.2×10^{-2}	15	DCN(30),8(40)
DCN,5×10^{-3}	MeCN,1M H_2O	Bu_4NOH,5×10^{-3}	20	DCN(35),8(35)

a. when the reaction is similarly carried out in the presence of 10^{-3}M Bu_4NCN, the yield of products **4** and **5** is increased to 15 and 6% respectively.



Scheme 2

and afford the counterion, and to look for conditions in which the conversion DCA - DCA$^{-\cdot}$ - **1** could be demonstrated in a single experiment.

However, addition of bases such as sodium methoxide or tetrabutylammonium hydroxide to an acetonitrile solution of DCA caused a thermal reaction to occur. Thus, a violet colour developed (see Figure

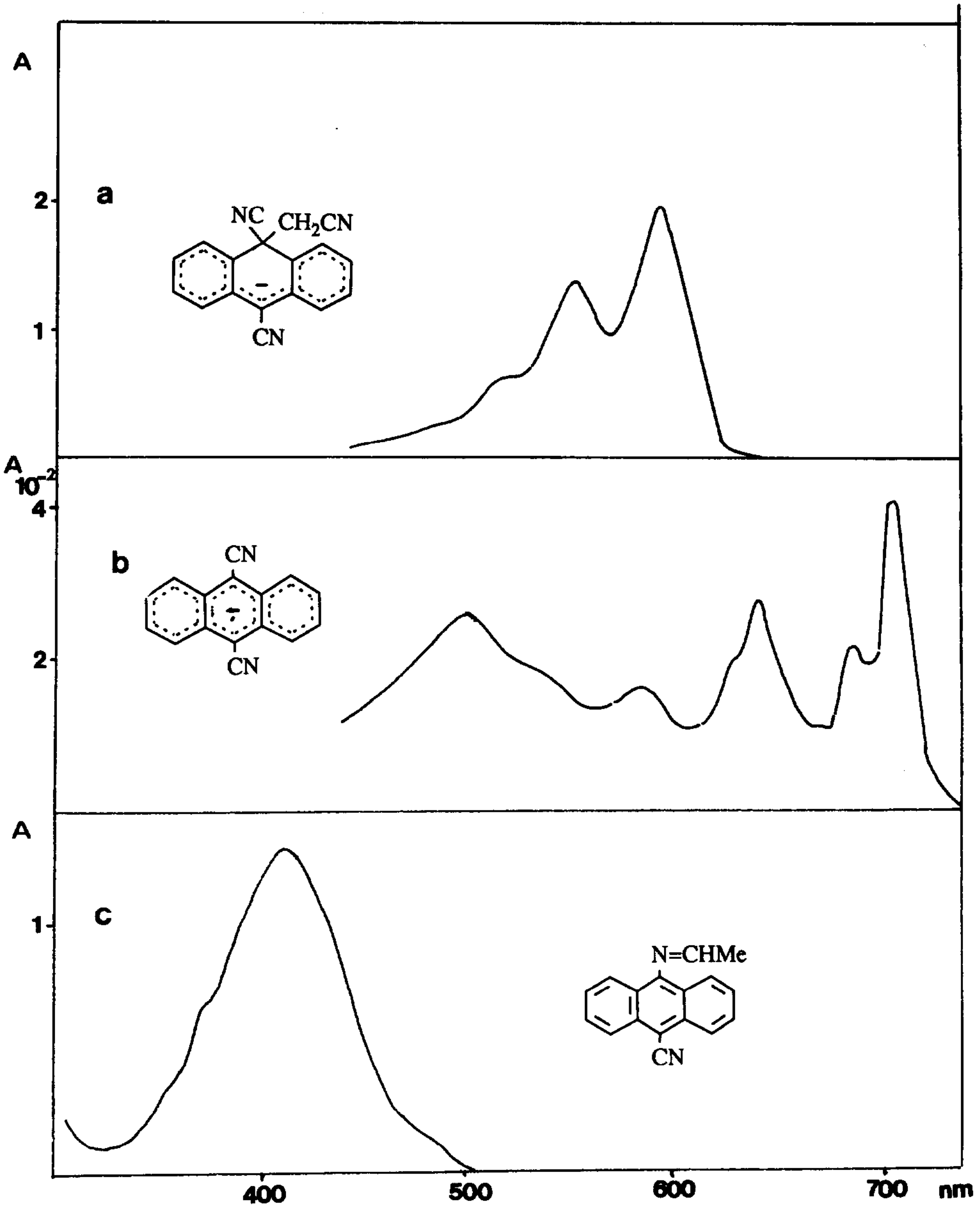


Fig.1 a. Spectrum of a solution obtained by adding 200 μL of 0.56M solution of NaOMe in MeOH to 20 mL of a 1.5x10^{-4}M solution of DCA in MeCN, as measured 1h after mixing. b. Spectrum of a degassed 2.5x10^{4}M solution of DCA in MeCN 1M in MeOH and 7x10^{-3}M in NaOMe after 20 min of irradiation. c. Spectrum of a 10^{-4}M solution of the imine 9 in MeCN.

1a) that was discharged in hours while the substrate was converted to a single product. This was identified as the anthracenylacetonitrile **2** (see Experimental Section, tautomerism was evidenced by the easy exchange of the α proton), thereby indicating that the colored intermediate was the Meisenheimer anion **3** (Scheme 2). Decreasing the amount of the base slowed down the thermal reaction, although this was still occurring measurably at $5x10^{-3}$M. However, increasing the amount of the corresponding acid (methanol or water) up to 1 M virtually suppressed the thermal reaction.

Irradiation of deaerated base containing MeCN-MeOH or MeCN-H_2O solutions of DCA followed by neutralization with NH_4Cl and silica gel chromatography led to the isolation of various products (Scheme 2, Table 1). Apart from the dinitrile **2**, when present, these included the above mentioned amine **1**, under most conditions the main product, as well as several colored products. The most abundant among these minor products were isolated and recognized from their analytical and spectroscopic properties as two further amines, viz 10-amino-1,9-anthracenedicarbonitrile (**4**) and 4-amino-1,9,10-anthracenetricarbonitrile (**5**) (see Experimental). A further product, 10-hydroxyanthracene-9-carbonitrile (**6**) was obtained from the irradiations in MeCN-H_2O. Furthermore, a small amount of 9-anthracenecarbonitrile (**7**) was generally found in traces, while DCA was cleanly decyanated to compound **7** by irradiation in methanol containing sodium methoxide. Repetition of the reaction under Ohashi's conditions (MeCN-H_2O-Et_3N) showed that minor products including the amines **4** and **5** were formed along with **1** also in that case.

Having thus ascertained that the amine **1** is obtained from DCA by irradiation in base containing MeCN, we explored the scope of the reaction. Indeed, irradiation of 1,4-naphthalenedicarbonitrile (DCN) in MeCN-MeOH containing sodium methoxide gave 4-amino-1-naphthalenecarbonitrile (**8**) as the only isolated product. In this case, the range of useful base and methanol concentrations was larger, and no thermal reaction took place under the conditions explored. However, no significant reaction took place by irradiation of either 1-naphthalenecarbonitrile or 9-anthracenecarbonitrile under comparable conditions.

Intermediates in the formation of the amine. As seen above, irradiation of DCA in the presence of bases within certain limits of concentration leads to the amine **1** in good yield. Examination of the reaction in more detail revealed several interesting features. First, an intense blue color developed during the preparative experiments above (Figure 1b). This was more conveniently studied by irradiation of dilute DCA solutions under the same conditions and direct spectroscopic examination of the solution. The spectrum observed was identic to that measured by Gould et al in flash photolysis experiments in the presence of biphenyl[16] and by Whitten et al in steady state irradiations in the $Bu_4N^+H_2PO_4^-/Et_3N$/MeCN system.[13] Identification as the radical anion $DCA^{-\cdot}$ was further confirmed by the fact that readmitting oxygen caused the immediate conversion to DCA (while anion **3** was stable under this conditions). Using the reported[16] molar absorption of $DCA^{-\cdot}$ it was calculated that this reoxidation was quantitative.

In the absence of oxygen the blue absorption faded in hours and was substituted by a new absorption centered at 410 nm (Figure 1c). HPLC analysis after that the bleaching was complete revealed the presence of one main product and a couple of minor components, but of only a tiny amount of the amine **1**, although the concentration of the last compounds grew slowly when the solution was left at room temperature. However, when the solution was stirred with silica gel, the amines **1**, **4** and **5** were formed. A quantitative measurement showed that under this condition more than 90% of $DCA^{-\cdot}$ was converted to the amines (mainly **1**), with practically no reoxidation to DCA (Table 2). While unstable to silica gel the amine precursor could be purified by fluorisil chromatography, and even by silica chromatography provided that separation was sufficiently fast.

Examination of a >95% pure sample obtained in this way (a light yellow solid) showed the same molecular peak (244m/z) reported by Ohashi for an "unstable intermediate" obtained in his reaction (and indeed by repeating his experiment we obtained an identical sample). The formula proposed by Ohashi (the imine **9**) was confirmed by elemental analysis, and although at first the NMR spectra seemed in contrast since the methyl and CH=N signal were not apparent, further examination showed that this was due to a line broadening occurring at room temperature, and spectra at -30°C clearly showed the two imine configurations (see Experimental). The stability of this material depended on conditions. It was immediately hydrolyzed to the amine **1** by silica gel as well as by several nucleophiles, e.g. secondary amines, while it was quite stable in acetonitrile solution both under the conditions where it was formed, viz in the presence of mineral bases, and after neutralization. The conversion to equimolecular amounts of the amine **1** and acetaldehyde could be conveniently followed by NMR when **9** was dissolved in acetone (probably again by ionic catalysis due to impurities).

Table 2. Formation of the DCA radical anion and the amine 1 by irradiation of 2.47 10^{-4} M solutions of DCA in MeCN-MeOH in the presence of NaOMe.

[NaOMe]	Irradiation time	[DCA][a]	[DCA$^{-\cdot}$][b]	[1][c]
$8.7x10^{-3}$	30 sec	$6.8x10^{-5}$	$6.1x10^{-5}$	$5.8x10^{-5}$
$5.2x10^{-3}$	30 sec	$5.0x10^{-5}$	$4.9x10^{-5}$	$4.6x10^{-5}$
$5.2x10^{-3}$	5 min	$5.0x10^{-5}$	$4.9x10^{-5}$	4.7x10-5
$2.6x10^{-3}$	30 sec	$2.4x10^{-5}$	$2.3x10^{-5}$	2.2x10-5
$2.6x10^{-3}$	5 min	$4.1x10^{-5}$	$4.2x10^{-5}$	$3.9x10^{-5}$

a. Moles of DCA consumed; measured by HPLC after 20 h; the same value is obtained before and after the stirring with silica gel (see Experimental Section). b. Spectrophotometrically measured using the ε value reported in ref.16 (8500 M^{-1} at 704.5 nm). c. Measured by HPLC after 20 h and stirring with silica gel.

Irradiation of DCA in basic methanol also led to the same blue intermediate, likewise long-lived in deoxygenated solutions. In this case it was quantitatively converted on standing to the mononitrile **7**.

In view of this difference, it was explored which MeCN-MeOH ratios led to the conversion of DCA to either **1** or **7**. As Table 3 shows the two products were formed in equal molar ratio in 1:9 MeCN-MeOH (in volume), with a regular variation above and below. It will also be noticed that the rate of conversion of DCA dropped regularly when the MeOH content was increased.

Origin of the minor products. All the experiments reported above were performed with carefully purified acetonitrile. Thus formation of the polycyanoamines **4** and **5** reasonably involved some reaction with cyanide formed during the reaction, rather than initially present. Indeed, when the reaction was carried out in the presence of 10^{-3}M Bu_4NCN the yield of products **4** and **5** increased somewhat (Table 1). However, when the cyanide was added to the photolyzed MeOH-MeOH-MeO^- solution containing the imine **9** no further reaction was observed either thermally or photochemically. Likewise the amine **1** underwent no reaction in the presence of Bu_4NCN.

Table 3. Influence of the solvent nature on the formation of 10-amino-9-anthracenecarbonitrile (1) and 9-anthracenecarbonitrile (7) by irradiation in the presence of 9×10^{-3}M MeONa.[a]

MeCN/MeOH ratio (vol)	[MeCN]	[MeOH]	Irradiation time, h	Consumed DCA, M	Products		Ratio
					[1]	[7]	1/7
25:3	17	3	2.5	2.25×10^{-4}	2.1×10^{-4}	8×10^{-6}	26
2:1	12.7	8.2	3.5	1.3×10^{-4}	1.0×10^{-4}	1.3×10^{-5}	8
1:2	6.3	16.5	4	9.4×10^{-5}	5.9×10^{-5}	2.0×10^{-5}	3
1:9	2.5	21.4	4	3.4×10^{-5}	1.4×10^{-5}	1.5×10^{-5}	1
5:95	1.3	23	6	4.6×10^{-5}	1.9×10^{-5}	2.2×10^{-5}	0.9

a Determined by HPLC.

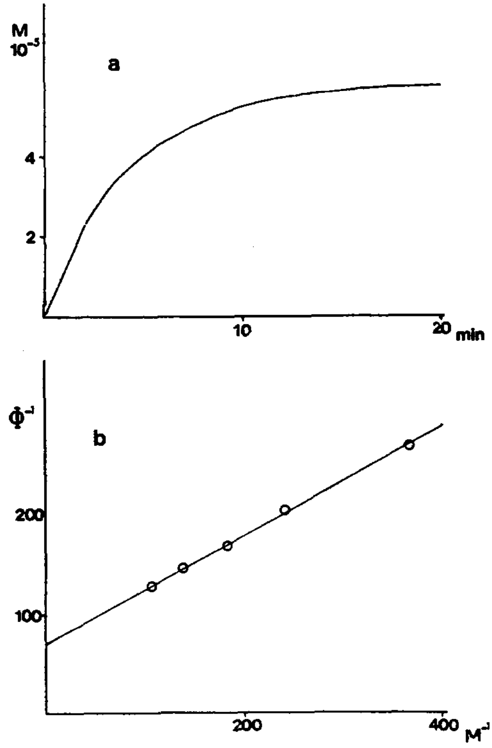


Fig.2. a. Formation of $DCA^{-\cdot}$ (as measured by the absorption at 705 nm) by irradiation of a 2.5×10^{-4}M solution of DCA in MeCN 3M in MeOH and 1.35×10^{-2}M in NaOMe as a function of the irradiation time (min). b. Double reciprocal plot for the quantum yield of $DCA^{-\cdot}$ formation (as measured during the linear part of the photoreaction in MeCN 3M in MeOH) vs the concentration of NaOMe.

Kinetic measurements. Various steps of the reaction were subjected to kinetic studies. In order to characterize the primary photoprocess the Stern-Volmer constants for the quenching of the DCA and DCN fluorescence by Bu_4NOH and MeONa in mixed solvents were obtained (Table 4). On the contrary, the emission of 1-naphthalenecarbonitrile and 9-anthracenecarbonitrile was not quenched under these conditions.

Table 4. Steady state parameters for the photoreactions.[a]

Substrate	Solvent	K_{sv},M^{-1}	K',M^{-1}	Φ_{lim}(-DCA)	Φ_{lim}($DCA^{-\cdot}$)	Φ_{lim}(Products)
DCA	MeCN, 1M MeOH	154	167	$2.2x10^{-2}$	$2x10^{-2}$	(1), $1.9x10^{-2}$
DCA	MeCN, 3M MeOH	126	128	$1.5x10^{-2}$	$1.4x10^{-2}$	(1), $1.3x10^{-2}$
DCA	MeOH	89	101	$2x10^{-3}$	$2x10^{-3}$	(7), $1.9x10^{-3}$
DCN	MeCN, 0.8M MeOH	109				

a. Determined as in Table 2 (see Experimental). K' is the intercept/slope ratio from Fig.2b.

Table 5. Pseudo-first order rate constants observed for the bleaching of the blue colour formed by irradiation of DCA in the presence of NaOMe.

[MeONa]	Solvent			
	MeCN,0.2M MeOH	MeCN,1M MeOH	MeCN,3M MeOH	MeOH
	k_{obs}, min^{-1}			
$9x10^{-3}$			$1.3x10^{-2}$	$5.5x10^{-2}$
$4.3x10^{-3}$		$5.7x10^{-3}$	$3x10^{-2}$	
$2.5x10^{-3}$	$9.2x10^{-3}$	$9.9x10^{-3}$		

The quantum yield of formation of $DCA^{-\cdot}$ under the same conditions was likewise measured. It was noticed that the photoreaction proceeded linearly with the absorbed dose only at low conversion, while later a plateau was reached (Fig.2a). The initial quantum yield evaluated from the linear part of the plot was then plotted against the base concentration in Fig.2b. The limiting quantum yield and the intercept vs slope ratio K' thus obtained are reported in Table 4.

The disappearance of $DCA^{-\cdot}$ in various MeCN-MeOH mixtures as well as in neat MeOH (to give **9** or respectively **7**) was then monitored. In every case a clean first order conversion was followed. The observed rate constants are reported in Table 5.

DISCUSSION

The present investigation shows that the substitutive amination of DCA previously reported to occur in amine containing MeCN actually takes place also under different conditions, notably in the presence of alkoxides or hydroxides, and that it follows a more complex course leading also to the polycyanoamines **4** and

5 and the phenol **6**. The same amination has been found to occur also with DCN. Furthermore, the formation of the radical anion under the same conditions has been evidenced, and its conversion to the Schiff base **9** and hence to the amine **1** has been demonstrated and followed step by step in a single experiment. The relation of this amination with the decyanation occurring in basic methanol has been explored. In the following the various steps of this complex reactions are discussed.

Photoinduced electron transfer. As shown in Table 4, the hydroxide and methoxide anions quench the fluorescence of DCA and DCN. The electron transfer to the excited state of these nitriles is exergonic.[14] The reaction has been thoroughly investigated for DCA. In this case, an accompanying phenomenon is the thermal reaction leading to the Meisenheimer anion **3** and to the dinitrile **2** from it. This is obviously due to the formation of the acetonitrile carbanion. Therefore, addition of ROH up to ca 1 M is sufficient to depress the concentration of the carbanion in the equilibrium

$$RO^- + MeCN \rightleftharpoons ROH + {}^-CH_2CN$$

to the degree that no thermal reaction takes place on the time scale of the photochemical experiment.

By irradiation of DCA, the reduction to the radical anion is directly evidenced through the conspicuous absorption of the latter species, and the study of the dependence of the quantum yield of reduction vs donor concentration proves that the process originates from DCA^{1*}. On the contrary, with 9-anthracenecarbonitrile or 1-naphthalenecarbonitrile neither fluorescence quenching[14] nor photoreduction are observed.

The minimum scheme accounting for the photochemical electron transfer is the following one (in RO^-, R is Me or H)

$$DCA^{1*} + RO^- \rightarrow [DCA^{-\cdot}\, RO^{\cdot}] \qquad (4)$$

$$[DCA^{-\cdot}\, RO^{\cdot}] \rightarrow DCA^{-\cdot} + RO^{\cdot} \qquad (5)$$

$$[DCA^{-\cdot}\, RO^{\cdot}] \rightarrow DCA + RO^- \qquad (6)$$

$$RO^{\cdot} \rightarrow \text{Products} \qquad (7)$$

$$DCA^{-\cdot} + RO^{\cdot} \rightarrow DCA + RO^- \qquad (8)$$

Some quantitative data about the competition between these processes are available. Thus, the limiting quantum yield for the formation of the radical anion is ca 2% in MeCN-MeOH, showing that back electron transfer (before ions separation, see below) is the main limiting factor.

$$\Phi_{lim}(DCA^{-\cdot}) = k_5/(k_5+k_6) = 0.02 \qquad (9)$$

The radical $RO^{\cdot}$ is rapidly consumed and this allows that $DCA^{-\cdot}$ is accumulated. An estimate of this phenomenon can be obtained as follows. As it can be noticed from Fig.2a the formation of the latter species by irradiation of dilute solution with a constant light flux reaches a plateau after some minutes. On this time scale the chemical reaction of $DCA^{-\cdot}$ discussed below is still unsignificant, nor is there a serious inner filter effect. Thus, the reaching of an equilibrium must be due to the reoxidation of $DCA^{-\cdot}$; under these conditions back electron transfer (eq.8) balances the forward process (eq.4,5).

$$k_8[DCA^{-\cdot}][RO^{\cdot}] = \delta[DCA^{-\cdot}]/\delta t = \Phi_{lim}(DCA^{-\cdot}) \times I_{abs} = \Phi_{lim}(RO^{\cdot}) \times I_{abs} \qquad (10)$$

We assume that the strongly exergonic electron transfer between the two radical species $DCA^{-\cdot}$ and $RO^{\cdot}$ is faster than their addition, and that it occurs at the diffusion controlled rate ($k_8 \approx k_{diff}$). Thus, under our conditions with an absorbed flux of ca 1.6×10^{-5} Einstein $L^{-1}sec^{-1}$ ca $3x10^{-7}$ moles of $DCA^{-\cdot}$ and an equivalent amount of $RO^{\cdot}$ radicals are generated per sec. On the other hand, the steady state concentration of the alkoxy radicals evaluated from eq.10 is $3x10^{-11}$, consistent with the idea that these species are consumed by some fast reaction (reasonably hydrogen abstraction from methanol).

Obviously the limit in the attainable steady state concentration of $DCA^{-\cdot}$ does not preclude a near to quantitative conversion of the substrate in preparative irradiations, since in that case the experiment is prolonged for many hours and there is time for the irreversible reaction of the radical anion (see below).

Persistence of the radical anion and chemical reaction. The lifetime of $DCA^{-\cdot}$ and the efficiency of its chemical reaction depends on conditions. An essentially identical product distribution (with the imine 9 predominating) is obtained by irradiation of DCA both in the presence of amines and in the presence of mineral bases, but in the former case the radical anion does not accumulate (its steady state concentration under comparable conditions is at least 20 times lower). We assume that the reaction involves in both cases the same intermediates, $DCA^{-\cdot}$ and $DCAH^{\cdot}$ (vide infra), but they attain different steady state concentrations. In turn, this depends on the *radical cation* reactivity. Thus, while in the former case reaction of the radical $RO^{\cdot}$ formed from RO^{-} (eq.7, see above) competes successfully with back electron transfer and thus $DCA^{-\cdot}$ accumulates, in the latter one deprotonation (eq.13) is the only path alternative to back electron transfer (eq.12) available for the amine radical cation. Thus the mechanism of this step need to be considered.

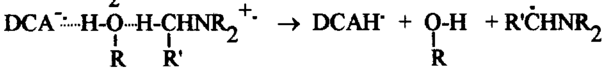
The proton could be transferred to $DCA^{-\cdot}$, but this is an inefficient process, since aromatic radical anions are known to be very poor nucleophiles.[17,18] As it will be discussed in more detail below, equilibrium with a protic agent (ROH, H_2O, eq.14) is shifted to the left. With RO^{-} and OH^{-} as the donors protonation of $DCA^{-\cdot}$ occurs only according to eq.14, and this species reaches a high concentration. In the case of the amine radical cations, proton transfer involves ionic fragmentation of a C-H bond in the α-position (eq.13)[18,19]. This is a slow but irreversible reaction (and indeed Mariano obtained the alkylation of DCA by α-amino radicals formed through this path),[12] though again the poor nucleophilicity of the radical anion make this an inefficient process in comparison with back electron transfer (eq.12). However, it is likely that it can be significantly accelerated in the presence of protic and nucleophilic agents such as water and alcohol (eq.15).

$$DCA^{1*} + R_2NCH_2R' \rightarrow DCA^{-\cdot} + R_2NCH_2R'^{+\cdot} \qquad (11)$$

$$DCA^{-\cdot} + R_2NCH_2R'^{+\cdot} \rightarrow DCA + R_2NCH_2R' \qquad (12)$$

$$DCA^{-\cdot} + R_2NCH_2R'^{+\cdot} \rightarrow DCAH^{\cdot} + R_2N\dot{C}HR' \qquad (13)$$

$$DCA^{-\cdot} + H_2O \rightarrow DCAH^{\cdot} + OH^{-} \qquad (14)$$



$$DCA^{-\cdot}\cdots H\text{-}\underset{\substack{|\\R}}{O}\cdots H\text{-}\underset{\substack{|\\R'}}{C}HNR_2{}^{+\cdot} \rightarrow DCAH^{\cdot} + \underset{\substack{|\\R}}{O}\text{-}H + R'\dot{C}HNR_2 \qquad (15)$$

We suggest that the increase in the rate of substitutive amination obtained by Ohashi with amines through the addition of protic cosolvents is due to the fact that the last mechanism (and not, as originally proposed, direct protonation of $DCA^{-\cdot}$ by the cosolvent, eq.15 rather than 14) competes with back electron transfer better than unassisted proton transfer (eq.13). Obviously, in this way the radical anion does not accumulate, since it undergoes fast protonation to the anthracenyl radical $DCAH^{\cdot}$, from which starts the sequence leading to the final product (see below). An analogous mechanism could be operative in the amination in the presence of α-silylamines observed by Mariano, where the electrofugal group is the silyl cation rather than the proton. Conversely, the persistence of the radical anion observed by Whitten in the presence of $Et_3N/Bu_4NH_2PO_4$[13] is due to the fact that in the strongly polar medium separation and solvation of the radical ions is more extensive. Thus, under this condition the amine radical cation undergoes deprotonation, oxidation (e.g. by DCA) and hydrolysis as the free species (the products are acetaldehyde and diethylamine) with no proton transfer to $DCA^{-\cdot}$

$$R_2NCH_2R'^{+\cdot} + H_2PO_4^{-}(\text{or Solv}) \rightarrow R_2N\dot{C}HR' + H_3PO_4(\text{or SolvH}^{+}) \qquad (16)$$

$$R_2N\dot{C}HR' \xrightarrow{-e} R_2N\overset{+}{C}HR' \qquad (17)$$

$$R_2N\overset{+}{C}HR' + H_2O \rightarrow R_2NH + R'CHO + H^+ \qquad (18)$$

Thus, the radical cation is consumed and this prevents back electron transfer; as a consequence, $DCA^{-\cdot}$ is observed as a persisting species, while no amination takes place, since the required protonation is too slow under these conditions.[20] Whether stabilization of the radical anion by the counterion is *per se* a determining factor is not sure.

The third case is that of a chemically inert radical cation, such as biphenyl. There back electron transfer is the only path, $DCA^{-\cdot}$ is observed only as a transient,[16] and there is no irreversible chemistry.

Chemical reaction of the radical anion. As reported in the results section, the radical anion $DCA^{-\cdot}$ is slowly converted in MeCN-MeOH solution to a single main product, the imine **9**, easily hydrolysed to the amine **1**. Some minor peaks with retention time similar to that of **9** are detected by HPLC, and reasonably two of them are the analogous Schiff bases of the amines **4** and **5**, since these minor components are generated together with **1** when the bleached solution is stirred with silica gel. The conversion of $DCA^{-\cdot}$ to these products is practically quantitative, with almost negligible reoxidation to DCA and good material balance of the isolated products. On the other hand, $DCA^{-\cdot}$, similarly generated in basic MeOH is quantitatively decyanated to **7**, and this reaction predominates in MeCN-MeOH mixtures with >90% methanol content.

These data unambiguously establish the intermediacy of $DCA^{-\cdot}$ both in the substitutive amination and in the decyanation. $DCA^{-\cdot}$ can be regarded as a free radical anion in solution, since the absorption spectrum in MeOH or in MeCN (both in presence and in the absence of the counter ion) are almost superimposable see Figure 1 and ref.16). Furthermore, the data in Table 5 show that the rate of bleaching of the radical anion depend on the proticity of the medium, increasing at higher methanol content and at lower MeO^-/MeOH ratio (the range of concentration explored is limited due to the requirement of avoid competition by the thermal reaction of DCA). The effect is not large: e.g. about one order of magnitude between 1M (i.e.4%) MeOH, where almost only the imine **9** is formed, and neat MeOH, where only decyanation to **7** takes place.

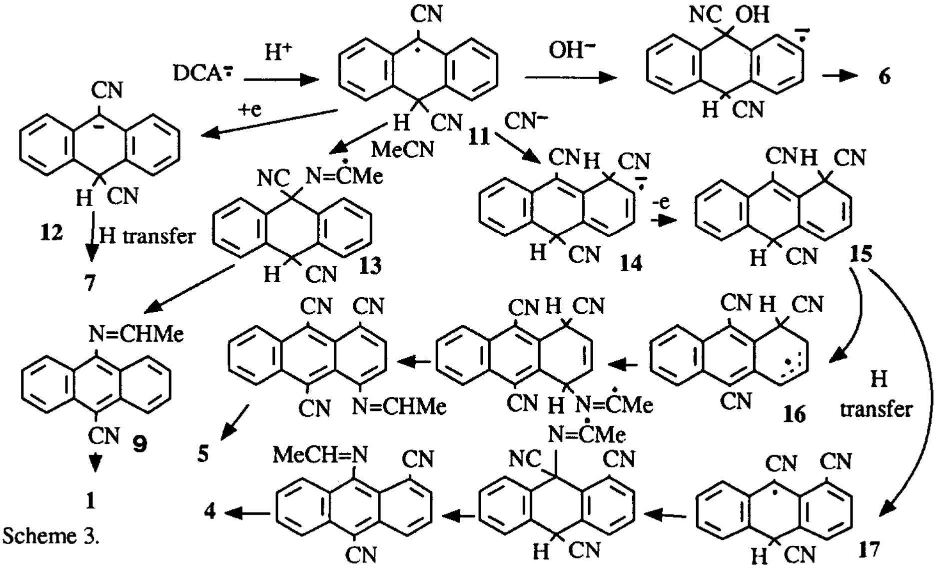
Thus, protonation is the first step in both reactions. The equilibrium 14 is largely to the left, but the small amount of anthracenyl radical (**11**) present in protic media react further to the final products.

As for the decyanation, it is fully reasonable that, as found in previous cases,[21] it follows the familiar path of the "photo-Birch" reduction[22] with secondary electron transfer to the radical (reasonably again by the hydroxide or methoxide anions) and either cyanide loss directly from the anion **12** or protonation and base-induced dehydrocyanation (Scheme 3). It is known that the photochemical reduction of aromatics is quite different from the alkali metal-induced (Birch) reduction in the sense that the reducing agent is not as abundant, and therefore the radical formed in the first step often undergoes competing reactions, such as dimerization, disproportionation and coupling with the radical originating from the donor.[22] The decyanation of DCA in MeO^-/MeOH occurs quite cleanly. Apparently, the medium offers the right reducing and protonating properties, and on the other hand the bulky radical **11** does not dimerize, and the RO$^\cdot$ radical reacts too fast with the solvent for allowing a bimolecular reaction with **11** to occur.

However, the situation is different in the presence of ≥5% acetonitrile, where solvent addition is the main path. Rationalizing the path leading from DCAH$^\cdot$ to the imine **9** is not trivial. As reported in the introduction, Ohashi's original proposal is that the carbanion **12** is involved also in this case and adds to MeCN, with ensuing rearrangement and base-induced ring-opening of the three-membered ring (Scheme 1b). This is not unreasonable, though some features are not fully convincing. As an example, it is not easy to see while the structurally analogous carbanion **3** does not add to MeCN under the same conditions, and in general there is little support in the literature for a similar carbanion addition to MeCN. Furthermore this mechanism does not easily account for the polycyanoamines formed as minor products, including product **5** which is aminated at an unsubstituted position, and for which the Ohashi's mechanism can not be operative (as mentioned above, these products do not originate from secondary reactions).

A plausible, if admittedly unsupported, alternative is presented in Scheme 3, and is suggested by the formation of the anthracenol **6** as one of the minor products in MeCN-H_2O-OH^-. This is reminiscent of the $S_{RN}1$ type benzyl susbstitution observed e.g. in *p*-nitrocumylderivatives,[23] where the key step is addition of a nucleophile onto the benzyl radical. Radical **11** is expected to have a similar reactivity, since it likewise is an electron-withdrawing-substituted benzyl radical. The difference is, that addition of a nucleophile to the *p*-nitrocumyl radical is favoured the stabilization of the charge in the resulting radical anion by the nitro group; in the present case, the driving force is elimination of a cyanide anion regenerating the neutral radical. Thus, **6** could be formed by such an addition in the very polar aqueous-organic medium and following rearomatization through cyanide loss and H transfer (more exactly, under these conditions the interaction between **11** and OH^- leads to competition between electron transfer and addition).

On the same line of thought, however, acetonitrile itself could act as a nucleophile and combine with radical **11** to yield the new radical **13**. In turn, this species undergoes reduction, inter- or intramolecular hydrogen transfer and rearomatization through cyanide loss at the anion stage (or deydrocyanation of the dihydroanthracene) to yield **9**. In the initial stage of the reaction the poor nucleophile MeCN has no competitors, but as the conversion proceeds, the good nucleophile CN^- is set free. Its addition to radical **11** in position 10 of course is a degenerate process, but if the addition involves the unsubstituted ring, then radical anion **14** is formed and the neutral compound **15** from it. Such species would function as a good hydrogen donor toward the other (radical) species present, and the new radicals **16** and **17** thus formed would evolve to the observed polycyanated amines **4** and **5** through a the same sequence seen above for amine **1**.



Scheme 3.

N-addition to acetonitrile has been considered for alkyl radicals in the gas phase,[24] and radical **11** may be sufficiently nucleophilic for undergoing such a process (particularly since there are no other easy pathways available). At this stage, we will not further speculate on this proposal. We notice, however, that the role of three-electron interaction has been discussed recently,[25] and that the above mentioned *p*-nitrocumyl substitution with neutral nucleophiles such as amines supplies some analogy. At any rate, Scheme 3 accounts for all products observed through an unitary mechanism.

Conclusions. The observations presented above show several useful aspects. On one hand, this work confirms that aromatic nitriles, in particular DCN and DCA are potent and "robust" electron transfer photosensitizers in view of the chemical stability of their singlet excited state and radical anion. Indeed, they can be used to produce hydroxyl radicals as an alternative to the established method of heterogeneous photosensitization with inorganic materials.

On the other hand, in order that they act as "true sensitizers" it is required that back electron transfer from the products radical cation closes the sensitization circle (path a, Scheme 1). If this is not the case, the sensitizer is consumed, and this includes, besides the known alkylation by radicals, reactions with commonly used solvents such as acetonitrile and methanol.

As for the last reactions, it has been demonstrated that in a single experiment it is possible to photoreduce DCA to the radical anion and to monitor the further reaction (initiated by protonation) to the imine **9** (which has been isolated and shown to be the precursor of the previously obtained amine **1**) or to the monocyano derivative **7** respectively. The dependence on experimental parameters of the radical anion persistence and the chemical reaction efficiency have been rationalized, with the identification of the radical cation reactivity as the key factor for the persistence of the radical anion. The substitutive amination has been extended to DCN, which is likewise reduced by hydroxy or methoxy anions. Finally, a mechanism has been proposed which reconciles this peculiar reaction with a known general class of radical reactions.

EXPERIMENTAL SECTION

General. ^1H and ^{13}C NMR spectra are reported in ppm relative to Me_4Si. Column chromatography separations employed Merk type 60 (230-400 mesh) silica gel. DCA and DCN were prepared from the corresponding dibromides and purified by alumina chromatography (eluting with cyclohexane-benzene mixtures) and recrystallization. All photochemical reactions were performed by using Ar-purged solutions in an immersion well apparatus with a 125-W medium-pressure mercury lamp and Pyrex glass filter. Acetonitrile for the photoreactions was passed through a column of activated alumina and directly percolated in the previously dried photochemical reactor.

Photoreaction of DCA in MeCN-MeOH in the presence of MeONa. A solution of DCA (114mg,0.5mmol) in 966 mL MeCN dehydrated as above was heated to the boiling point and then allowed to cool under an argon stream. Freshly prepared NaOMe obtained by dissolving 345 mg (15 mg-at) of Na in 33.9 mL (1mol) MeOH was added while continuing the argon purging. A weak violet color developed after some minutes. After 5 min of irradiation the solution took a deep blue color that was conserved until the end (4h). An identical solution kept in the dark remained violet-colored and analysis after 4 h showed no significant reaction of the substrate.

The irradiated solution was evaporated, the residue stirred with 0.5 L dichloromethane and satd aq

NH_4Cl until pH7 was reached (ca 50 mL). The organic layer was dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel eluting with cyclohexane-EtOAc mixtures to give 18 mg(16%) of DCA, 65.5 mg (60%) of 10-amino-9-anthracenecarbonitrile **1** (identical with a sample prepared under the conditions of ref.10), 10 mg(8%) of 10-cyano-9-anthraceneacetonitrile (**2**)(mp 235-38°C dec), 14.5 mg (12%) of 9-amino-1,10-anthracenedicarbonitrile (**4**) (mp>340°C), 3 mg (2%) of product **5** (see below), and ca 1 mg 9-anthracenecarbonitrile (**7**).

2: ^{1}H NMR (DMSO) δ 5.15(s,2 H, CH_2), 7.9(m,4 H,arom), 8.38 (d,J=8.5 Hz, 2 H, arom $H_{1,8}$), 8.62(d,J=8.5 Hz, 2 H, arom $H_{4,5}$); ^{13}C NMR (DMSO) δ 16.3(CH_2), 105.9 and 116.6 (CN), 118.4, 125.25, 125.3, 127.9, 128.6, 129.6, 130.9, 132.2 (arom); IR (KBr) 2248,2217 cm^{-1}. MS m/z 242. Anal.Calcd for$C_{17}H_{10}N_2$: C,84.27; H,4.16; N, 11.56. Found: C, 84.2; H,4.1; N,11.5.

4: ^{1}H NMR (DMSO) δ 7.55 (dd,J=9 and1 Hz, 1H, H_3), 7.6(t,J=9Hz,1H,H_6), 7.9(t,J=9Hz,1H,H_7), 8.22(d,J=9Hz,1H,H_8), 8.33 (dd,J=9 and 1Hz,1H,H_2), 8.42 (exch,2H,NH_2), 8.63(d,J=9Hz,1H,H_5), 8.9(dd,J=1 and 9 Hz, 1H,H_4); ^{13}C NMR (DMSO) δ 117.8 and 117.85 (CN), 84.5, 106.0, 115.5, 116.3, 121.5, 124.2, 124.3, 124.5, 130.3, 130.5, 131.2, 136.1, 140.7, 150.4; IR(KBr)3384, 3278, 2222, 2195, 1654 cm^{-1}. MS m/z 243. Anal.Calcd for $C_{16}H_9N_3$: C,78.99;H,3.73;N,17.28. Found:C,79.8;H,3.65;N,17.15.

Photoreaction of DCA in MeCN-H_2O in the presence of *n*-Bu_4NOH. A solution of DCA (114mg, 0.5mmol) in 992 mL MeCN was heated to the boiling point and then allowed to cool in an argon stream. 8 ml of a 1.6% aq solution of *n*-Bu_4OH (0.5 mmol) were added while continuing the argon purging. After 8h the solution was concentrated to 10 mL under reduced pressure, 200 mL CH_2Cl_2 were added and the organic layer was washed with satd aq NH_4Cl until neutral and then with water, dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel eluting with cyclohexane-ethyl acetate mixtures to give 11.5mg(10%) of DCA, 33mg (30%) of **1**, 12 mg (10%) of **2**, 18 mg (15%) of **4**, 6.5 mg(5%) of 4-amino-1,9,10-anthracenetricarbonitrile (**5**)(mp>350°C), 5.5 mg(5%) of 10-hydroxy-9-anthracenecarbonitrile (**6**)(mp292-5°C, lit.[26], 294-5°C), 1 mg of **7**.

5: ^{1}H NMR (DMSO) δ 7.54(d,J=9.5Hz,1H,H_3), 7.92(t,J=7Hz,1H) and 8.02(t,J=7,1H) ($H_{6,7}$), 8.37(d,J=7Hz) and 8.39(d,J=7Hz) ($H_{5,8}$) 8.4 (d,J=9.5,1H,H_2); ^{13}C NMR (DMSO) δ 115.4, 115.5, 115.8(CN), 102.7, 112.4, 124.0, 124.7, 125.9, 126.9, 127.2, 128.0, 128.8, 131.4, 131.8, 134.7, 156.9; IR(KBr) 3342, 3150, 2220, 2216, 1647, 1612 cm^{-1}; MS 268 m/z. Anal. Calcd:C,76.10;H,3.01;N,20.88. Found:C,75.8;H,2.95;N,20.6.

6: ^{1}H NMR (CD_3COCD_3) δ 2.95(exch,1H,OH), 7.63(dt,J=9 and1Hz, 2H), 7.82(dt, J=9 and1Hz,2H), 8.30(d,J=9Hz,2H), 8.61(d,J=9Hz,2H)(arom); ^{13}C NMR (CD_3COCD_3) δ 117.6(CN), 95.6; 119.7; 123.4, 125.0, 125.2, 129.8, 134.8, 155.1.

Photoreaction of DCN in MeCN-MeOH in the presence of MeONa. A solution of DCN (270mg,1.5mmol) in 300 mL MeCN was heated to the boiling point and then allowed to cool under an argon stream. Freshly prepared NaOMe obtained by dissolving 83 mg (3.6mg-at) Na in 2 mL MeOH was added while maintaining the argon purging. The solution was irradiated for 12h, then evaporated under vacuum, the residue taken up with 200 mL CH_2Cl_2 and 10 mL satd aq NH_4Cl, the organic layer dryed over $MgSO_4$ and evaporated, and the residue chromatographed on silica gel eluting with cyclohexane-ethyl acetate mixtures to give 81mg(30%) DCN and 102mg(40%) 4-amino-1-naphthalenecarbonitrile (**8**)(mp174°C).

8: ^{1}H NMR ($CDCl_3$) δ 4.7(exch,2H,NH_2), 6.72(d,J=7.5Hz,1H,H_3), 7.55(t,J=8Hz,1H) and 7.67(t,J=8Hz,1H)($H_{6,7}$), 7.72(d,J=7.5Hz,1H,H_2), 7.82(d,J=8Hz,1H,H_8), 8.18(d,J=8Hz,1H,H_5); IR(KBr)

3380, 3330, 3215, 2215, 1660, 1565 cm^{-1}. Anal.calcd.for $C_{11}H_8N_2$:C,78.55;H,4.79; N,16.66. Found:C,78.55;H,4.85;N,16.6.

Thermal reaction of DCA in MeCN-MeOH in the presence of NaOMe. To a solution of 25 mg (0.11 mmol) of DCA in 200 mL of MeCN dehydrated as above freshly prepared NaOMe obtained by dissolving 25.5mg(1.1 mg-at) Na in 2 mL MeOH was added; the solution was purged with argon and left 16 h at rT. The colour was initially yellow, then deeply violet. Evaporation, treatment of the residue with 50 mL CH_2Cl_2 and 10 mL satd aq NH_4Cl, drying and evaporation of the organic layer and chromatography on silica gel of the residue eluting with cyclohexane-ethyl acetate gave 2.5 mg (10%) of DCA and 18.5 mg (70%) of 2. None of the other products obtained from the photochemical reactions above was present.

Photoreaction of DCA in MeCN-MeOH in the presence of MeONa. Isolation of compound 9. To a solution of 4.5 mg (0.02mmol)DCA in 70 mL of MeCN dehydrated as above freshly prepared NaOMe obtained by dissolving 11.5 mg(0.5mg-at)Na in 2.5mL MeOH was added. This solution, equally distributed in four serum-capped tubes, was purged with argon and irradiated by means of six external phosphor-coated 15-W lamps (center of emission, 350 nm) for 2½h. The base was eliminated by passing the solution through a 5g fluorisil column, and the residue was chromatographed on silica gel eluting with cyclohexane-ethyl acetate 8:2 mixture to give 3 mg(60%) of *N*-ethylydene-10-amino-9-anthracenecarbonitrile (9)(mp140-44°C).

9: ^{1}H NMR (CD_3COCD_3 at -30°C) (Z,78% of the isomeric mixture) δ 2.6(d,J=5Hz,3H,Me),7.67(dd, J=7 and 9Hz,2H), 7.92(dd,J=7 and 9 Hz, 2H), 8.14(d,J=9,2H), 8.36(d,J=9Hz,2H)(arom), 8.17(q,J=5Hz,-CH=); (*E*) δ 1.75(d,J=5Hz,3H,Me), 7.69(dd,J=7 and 9Hz,2H), 7.93(dd,J=7 and 9Hz,2H), 8.07(d,J=9Hz,2H), 8.38(d,J=9Hz,2H)(arom), 8.62(q,J=5Hz,1H,-CH=) (after 24h 9 had completely disappeared and had been substituted by the absorption of 1 and CH_3CHO, δ 2.12(d,J=3Hz,3H), 9.72(q,J=3Hz,1H)); ^{13}C NMR (DMSO) δ 117.3(CN), 123.5, 123.7, 125.0, 125.3, 126.0, 129.0, 129.7, 130.5(arom);(CD_3COCD_3,rT, only arom CH given) (*Z*) δ 124.7, 125.0, 125.8, 129.5; (*E*) δ 123.3, 123.4, 129.2, 129.5; IR(KBr) 2209, 1661, 1554, 1438, 1270 cm^{-1}; MS m/z 244. Anal.calcd for $C_{11}H_8N_2$:C,83.58; H,4.95;N,11.47. Found: C,83.6;H,5.0;N,11.4.

Quantum yield measurements. Measurements were made on 2.6×10^{-4}M solutions of DCA in MeCN dehydrated as above, after the addition of the appropriate amount of NaOMe in MeOH. 3 mL aliquots in 1 cm optical path couvettes were degassed by four freeze-degas-thaw cycles and irradiated on a optical bench fitted with a high-pressure 200-W mercury arc and a wide-band filter transmitting at 340-390 nm. The light-intensity was measured by ferrioxalate actinometry (absorbed flux under ca 3×10^{-6} Einstein min^{-1} in the 3 mL volume). The radical anion formed was monitored through the reported absorbance (ε at 704.8 nm is 8400 M^{-1}cm^{-2}).[16] The DCA consumed and products formed were measured by HPLC (μ-Bondapack-C18 column, eluant MeCN-H_2O 6:4 mixture) either directly or after adding 1 drop water, 30 mg silica gel, evaporating the solvent and eluting the silica with CH_2Cl_2. The thermal bleaching of the blue absorption was spectrophotometrically monitored at 20°C.

Fluorescence quenching. Fluorescence measurements were made with an Aminco-Bowman MPF spectrofluorimeter. Solution were made from freshly prepared stock solutions of NaOMe or Bu_4NOH. Degassing was effected as above.

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