methylcyclohexanone, 2816-57-1; 2-bromo-2,6-dimethylcyclohexanone, 55234-03-2; 6-chloro-2,6-dimethyl-2-cyclohexen-1-one, 89529-60-2; 2,6-dimethyl-6-(phenylethynyl)-2-cyclohexen-1-one, 83188-15-2; 2,6-dimethyl-6-[(phenylthio)ethynyl]-2-cyclohexen-1-one, 83188-18-5; 6-ethynyl-2,6-dimethyl-2-cyclohexen-1-one, 83188-16-3; 2,6-dimethyl-6-vinyl-2-cyclohexen-1-one, 83188-17-4; 2-methyl-1-tetralone, 1590-08-5; 2-(chloroethynyl)-2-methyl-1-tetralone, 83188-19-6; 2-ethynyl-2-methyl-1-tetralone, 83188-20-9; 2-methyl-2-vinyl-1-tetralone, 83188-35-6; 2,2,6-trimethylcyclohexanone, 2408-37-9; 2-(chloroethynyl)-2,6,6-trimethylcyclohexanone, 83188-21-0; 2,6,6-trimethyl-2-(phenylethynyl)cyclohexanone, 83188-22-1; 2,6,6-trimethyl-2-vinylcyclohexanone, 78828-56-5; methyl cyclohexanecarboxylate, 4030-82-4; methyl 1-(chloroethynyl)cyclohexanecarboxylate, 83188-24-3; methyl 1-(phenylethynyl)cyclohexanecarboxylate, 83188-25-4; methyl 1-[(phenylthio)ethynyl]cyclohexanecarboxylate, 83188-29-8; methyl 1-ethynylcyclohexanecarboxylate, 83188-26-5; methyl 1-vinylcyclohexanecarboxylate, 83188-27-6; 2,6-dimethylphenol, 576-26-1.

Supplementary Material Available: Calculation of the isotope effect by using the method of Melander and Saunders, ^{13}C NMR data in tabular form, and tables of crystallographic data (10 pages). Ordering information is given on any current masthead page.

On the Mechanism of the Photochemical Reaction between 1,4-Naphthalenedicarbonitrile and Methylbenzenes

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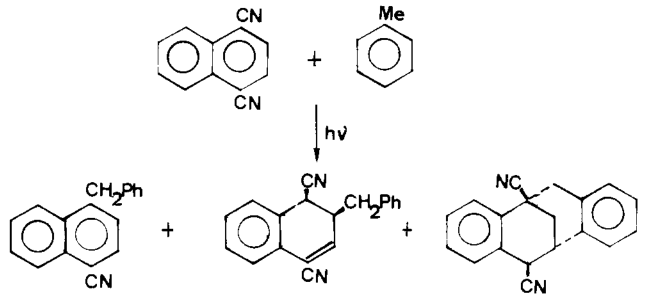
Abstract: On the basis of the correlation between fluorescence quenching and reaction quantum yield and of deuteration studies, it is shown that the photochemical reaction between 1,4-naphthalenedicarbonitrile (NDN) and methylbenzenes involves (i) water-mediated proton transfer within the charge-transfer exciplex, (ii) in-cage reaction of the two radicals to form 2-benzyl-1,2-dihydro-1,4-naphthalenedicarbonitrile (**2**) and 6,11-dicyano-5,11-methano-5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**3**), the formation of the latter product requiring a further water-mediated hydrogen transfer, and (iii) escape of the benzylic radical, which is trapped by NDN, to give 4-benzyl-1-naphthalenecarbonitrile (**1**), a product formed also when benzylic radicals are generated from other sources.

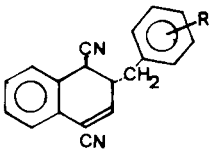
Aromatic molecules in their excited states differ from their ground-state counterpart mainly in their tendency to form complexes with other molecules containing n or π electrons.[1] This is a relevant change in the chemical properties, and the formation of an excited complex is, in some cases, revealed by the appearance of a new emission or by a chemical reaction. The latter possibility is of great interest because of the regio- and stereoselectivity often observed in the reaction, which can be attributed to the existence of preferred conformation in the excited complex. However, establishing a correlation between the photophysics of the exciplex and the chemical pathway to the products is usually not straightforward.

A large number of theoretical[2] and experimental[3-7] studies have been devoted to the photochemical reaction between aromatic molecules and alkenes or polyenes, to the elucidation of the role of exciplexes, and to the exploitation of the synthetic potential,[8] whereas mechanistic knowledge about photochemical reaction between aromatics is limited, being mainly confined to the 4 + 4 photodimerization of anthracenes and derivatives.[9]

Scheme I



We recently reported a new reaction with methyl aromatics. Thus, 1,4-naphthalenedicarbonitrile (NDN) and toluene photochemically react in polar media to yield products **1**–**3** (Scheme I), whereas in apolar solvents exciplex emission but no photochemical reaction is observed.[10] With 1,3,5-trimethyl- and 1,2,4,5-tetramethylbenzene the reaction is similar except that minor amounts of the stereoisomers **4** and **5** are formed.



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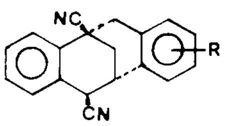

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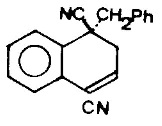

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The reaction is of interest in its stereochemical control, particularly in regard to the formation of the tetracyclic compound **3**, which appears to be a primary photoproduct (e.g., it does not arise from further photoreaction from **6**).[10] Different mechanistic pathways can be considered. Does the reaction proceed via hydrogen abstraction and direct coupling of the radicals or by

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[1] (a) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970. (b) Stevens, B. *Adv. Photochem.* **1971**, *8*, 161. (c) Gordon, M.; Ware, W. R. "The Exciplex"; Academic Press: New York, 1975.

[2] Houk, K. N. *Pure Appl. Chem.* **1982**, *54*,

[3] Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609.

[4] Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45.

[5] Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80.

[6] Yang, N. C.; Yates, R. L.; Masnovi, J.; Shold, D. M.; Chiang, W. *Pure Appl. Chem.* **1979**, *51*, 173.

[7] Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1977**, *33*, 2459.

[8] Morrison, H. *Acc. Chem. Res.* **1979**, *12*, 383. (b) Wender, P. A.; Howbert, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 688.

[9] (a) Bowen, E. J. *Adv. Photochem.* **1963**, *1*, 23. (b) Saltiel, J.; Townsend, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 6140.

[10] Albini, A.; Fasani, E.; Oberti, R. *Tetrahedron* **1982**, *38*, 1027.

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Table I. Quenching of the NDN Fluorescence by Methylbenzenes and Parameters of the Photochemical Reaction

methylbenzenes	$k_3\tau$,[a] M^{-1}	k_3,[b] $M^{-1}\ s^{-1}$	k_3/k_2,[c] M^{-1}	$E(D/D^+)$,[d] V	ΔG, kcal M^{-1}	Φ_r,[e]
$C_6H_5CH_3$ (**7**)	19	0.19×10^{10}	18.5	1.98	−4.1	0.07
1,3,5-$C_6H_3(CH_3)_3$ (**8**)	111	1.10×10^{10}	100	1.80	−8.3	0.03
1,2,4,5-$C_6H_2(CH_3)_4$ (**9**)	164	1.63×10^{10}	152	1.67	−12.5	0.045
$C_6D_5CD_3$ (**10**)	18	0.18×10^{10}	18			0.018

[a] From the fluorescence quenching (Figure 1 and eq 8). [b] Taking τ_S = 10.0 ns from: Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931. [c] Intercept divided by slope of plots in Figure 2. [d] Vs. SCE from: Pisch, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124. Eberson, L.; Nyberg, K. *J. Am. Chem. Soc.* **1966**, *88*, 1686. [e] Limiting quantum yield at infinite methylbenzene concentration by irradiation at 313 nm.

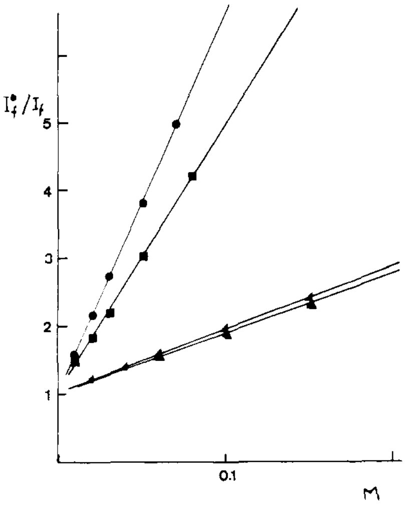

Figure 1. Stern–Volmer plot for the fluorescence quenching of the NDN fluorescence by the methylbenzenes **7** (◇), **8** (■), **9** (●), and **10** (▲).

electron transfer followed by proton donation from the acidic toluene radical cation to give the corresponding radical? Does the entire process take place in a tight complex or are separated, solvent-stabilized radicals or radical ions involved?

A preliminary hypothesis was formulated on the basis of the preparative results alone,[10] but a more extensive and quantitative investigation was obviously required.

Results and Discussion

The occurrence of the reaction only in polar media and the fluorescence quenching point to the involvement of the singlet state of NDN in an electron-transfer process. Thus a subject to investigate is the relationship between fluorescence and reaction quantum yields. A further obvious point is the effect of deuteration, as a benzylic C–H bond is at some stage broken. Finally as benzylic radicals are suspected to participate in the reaction, a comparison with the reaction of NDN with radicals generated from some other source is useful.

Dependence on the Methylbenzene Concentration. Linear Stern–Volmer plots are obtained for the quenching of NDN fluorescence in acetonitrile by toluene (**7**), 1,3,5-trimethylbenzene (**8**), and 1,2,4,5-tetramethylbenzene (**9**) with virtually no exciplex emission or modification of the absorption spectrum or curvature of the plot up to 0.05 M (Figure 1). The rate constants for the quenching are large and, in the case of the polymethylebenzenes **8** and **9**, close to the diffusion-controlled limit. This is expected as the electron-transfer process from the NDN singlet state to the methylbenzenes, as calculated form eq 1,[11] is increasingly

$$\Delta G = E(D/D^+) - E(A/A^-) - (e^2/\epsilon\alpha) - E_{00} \qquad (1)$$

negative for the compounds **7**, **8**, and **9** due to the decreasing ionization potential of these compounds (see Table I). On the contrary, the electron transfer from the methylbenzenes to the NDN triplet state is endothermic. The quenching of the NDN singlet is assumed to be virtually irreversible.

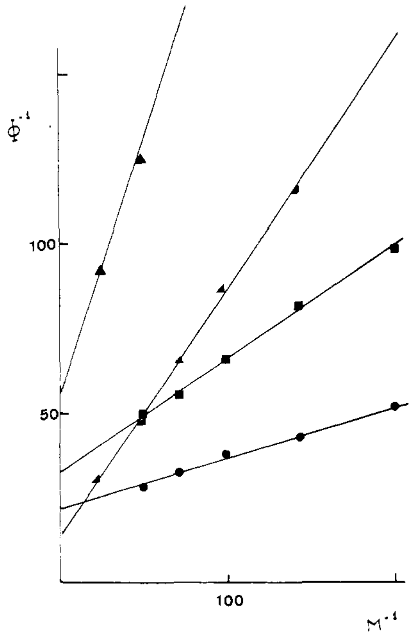

Figure 2. Inverse plot for the quantum yield of the photochemical reaction of NDN in the presence of the methylbenzenes **7** (◇), **8** (■), **9** (●), and **10** (▲).

The reaction quantum yield is also strongly dependent on the methylbenzene concentration. With toluene a limiting quantum yield of 0.07 is observed. If the NDN singlet is the reactive state, the following minimal kinetic scheme is valid:

$$NDN^{1*} \rightarrow NDN \qquad (2)$$

$$NDN^{1*} + PhMe \rightarrow (NDN\cdots PhMe)^* \qquad (3)$$

$$(NDN\cdots PhMe)^* \rightarrow NDN + PhMe \qquad (4)$$

$$(NDN\cdots PhMe)^* \rightarrow \text{products} \qquad (5)$$

Thus

$$\Phi_{react} = \frac{k_3k_5[PhMe]}{(k_4 + k_5)(k_2 + k_3[PhMe])} \qquad (6)$$

or in the inverse form

$$\Phi_{react}^{-1} = \frac{k_4}{k_4 + k_5}\left(1 + \frac{k_2}{k_3[PhMe]}\right) \qquad (7)$$

The inverse plot in Figure 2 shows that eq 7 is followed. From the linear plot the quantity k_3/k_2 can be obtained as the ratio intercept/slope. The value obtained (18.5 mol^{-1}) does not differ significantly from the value obtained from the fluorescence quenching,

$$I^\circ_{fluor}/I_{fluor} = (k_3/k_2)[PhMe] \qquad (8)$$

thus supporting the involvement of the excited singlet, or rather

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[11] (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Weller, A. *Nobel Symp.* **1967**, *No. 5*, 413. (c) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834.

Table II. Results from the Photochemical Reactions[a]

reagents	products (yields)		
$C_6H_5CH_3$, H_2O 0.05%	**1** (38)	**2** (32)	**3** (17.5)
$C_6H_5CH_3$, H_2O 0.18%	**1** (30)	**2** (18)	**3** (40)
$C_6H_5CH_3$, H_2O 0.3%	**1** (32)	**2** (17)	**3** (38), **4** (2)
$C_6H_5CH_3$, D_2O 0.3%	**1** (30)	**2″** (23)	**3″** (25), **4″** (6)
$C_6D_5CD_3$, H_2O 0.18%	**1′** (24)	**2′** (13)	**3′** (40)
$(C_6H_5CH_2N)_2$	**1** (10)		
$(C_6H_5CH_2)_2CO$	**1** (18)		

[a] Percent yield on the reacted NDN, in acetonitrile (NDN 0.02 M, methylbenzenes 0.3 M). See Experimental for irradiation conditions. Separated experiments showed that a variation of the water content from 0.05% to 0.3% brings about a variation in the reaction quantum yield of about 10%.

of an excited complex derived from it, in the chemical reaction and allowing the evaluation of the partition factor k_4/k_5 between unproductive decay and reaction of the complex as 13. The intervention of a complex following the NDN singlet in the chemical pathway is further supported by the complete reaction quenching by oxygen, which has only a limited effect on the NDN singlet lifetime ($I_{\text{fluor}}(\text{aerated})/I_{\text{fluor}}(\text{degassed}) = 0.67$).

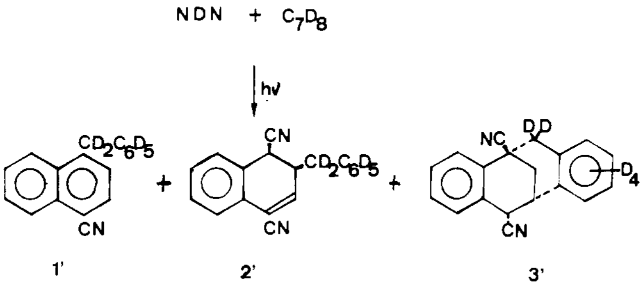
This scheme can also be satisfactorily applied in the case of the reaction between NDN and the methylbenzenes **8** and **9**. Here again there is a correspondence between the data of the fluorescence quenching and the reaction quantum yield, in the sense that the ratio k_2/k_3 evaluated from eq 9 and 7 is always within 10% (see Table I).

Deuteration Studies. The above analysis establishes the role of an excited complex formed between singlet excited NDN and the methylbenzenes. A study with deuterated molecules can then offer more information about the mechanism of the chemical reaction in two ways. First, the effect on the overall efficiency of the reaction is related to the type if intermediate in which a carbon–hydrogen bond is broken. Second, the deuteration pattern in the products must also be informative. Thus, product **2** arises from the formal addition of the methylbenzene (a benzylic radical and an hydrogen atom) across a double bond in the naphthalene ring, and it has to be checked whether the source of the hydrogen atom is indeed the methyl group. Also, in the case of product **3** two hydrogen atoms are transferred to the naphthalene ring, seemingly one from the methyl group and one from the benzene ring, and this has also to be checked. Experiments with octadeuteriotoluene should clarify the mechanism of formation of both products, **2** and **3**.

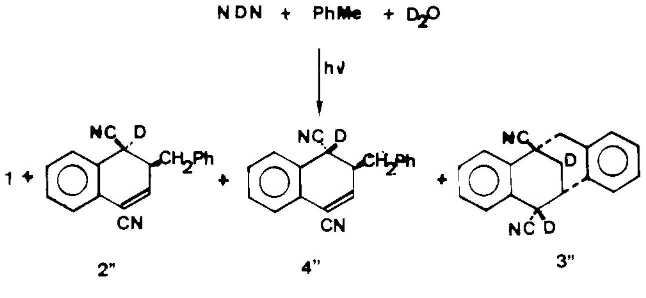
As for the first point, a deuterium effect in the reaction quantum yield is apparent. $C_6D_5CD_3$ (**10**) quenches the fluorescence of NDN with virtually the same efficiency as undeuterated toluene, and again the dependence of the reaction quantum yield on the quencher concentration is well fitted by eq 7 giving the expected k_2/k_3 value, but the limiting quantum yield is now much smaller, 0.018, that is $k_4/k_5 = 55$. Thus although C_7D_8 quenches the excited singlet of NDN just as well as C_7H_8, the chemical evolution that occurs after the excited complex is formed is affected by the strength of the benzylic C–H or C–D bond.

Moreover, important information is obtained from the deuteration pattern in the products. Thus, the reaction between NDN and **10** yields **1′**, **2′**, and **3′**. Apparently compounds **2** and **3** are not the products of direct addition of toluene to NDN, as one atom of hydrogen in the case of **2** and two in the case of **3** come from some other source.

Scheme II



Scheme III



Water is suspected to be the source of these hydrogen atoms because of the hygroscopy of the acetonitrile that was used as a solvent. Even using freshly dried acetonitrile, water could be transported in the reaction mixture by the argon used for deoxygenation. Therefore, no experiment was made in the absolute exclusion of water.

In a series of experiments using acetonitrile with known water contents between 0.05 and 0.3% (see Table II) the quantum yield showed a limited enhancement, and the product distribution underwent some change, the yield of products **1** and **2** decreasing while the yield of product **3** increased. Furthermore a certain amount of product **4**, the stereoisomer of compound **2**, is found. The effect of water is due to a reaction with the exciplex and not with the singlet excited state of NDN, as shown by the absence of measurable effect on the NDN fluorescence in the presence of small amounts of water (Table III, Schemes II and III).

The mode of the reaction with water was definitely checked by using acetonitrile containing small amounts of D_2O. In this case beside undeuterated **1**, compounds **2″**, deuterated in the position α to the cyano group, and **3″**, bearing one deuterium at the methylene bridge and one α to the cyano group, are obtained, as well as minor amount of product **4″**, the stereoisomer of **2″**.

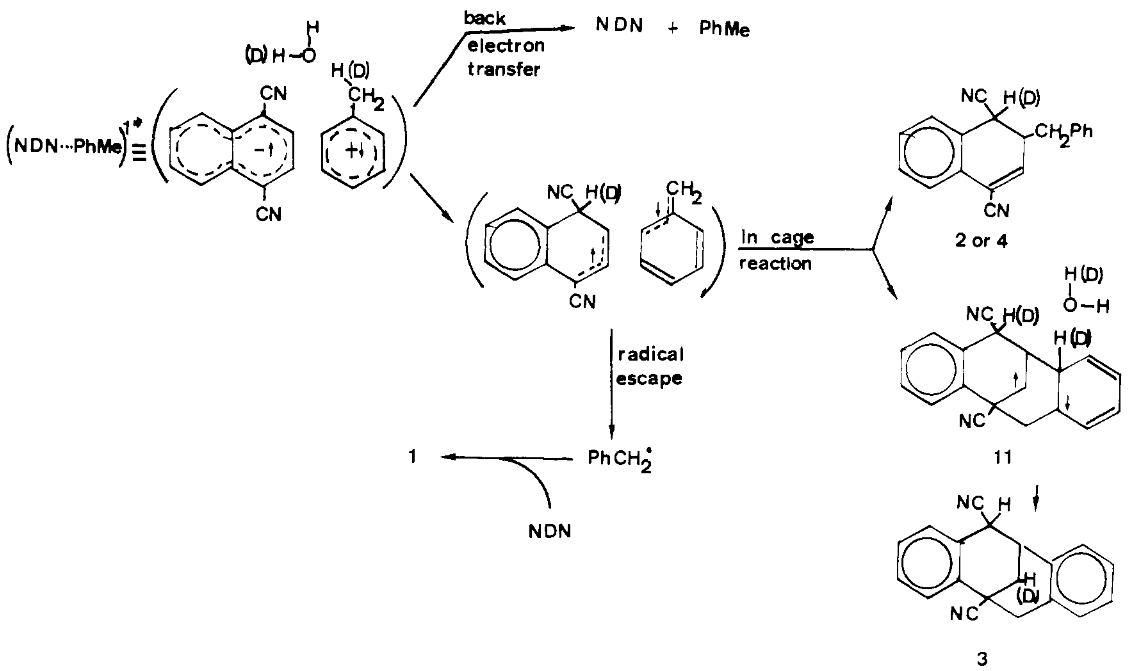
Reaction with Benzylic Radicals. In this case we wanted to check the possible role of "free" benzylic radicals in similar conditions as those in the reaction previously discussed. Therefore, we avoided introducing the heterogeneous reactions that would be required to form benzylic radicals by the oxidation of toluene by inorganic oxidizers, and, instead, we investigated the photochemical decomposition in acetonitrile in the presence of NDN of compounds known to generate benzylic radicals, such as azodibenzyl and dibenzyl ketone. (This experiment is complicated by the contemporary excitation of NDN, but the advantage of

Table III. Relevant Spectroscopic Data for the Deuterated Products[a]

	^1H NMR					
compds	benzylic CH_2	olefinic CH[b]	CHCN	bridged CH_2	bridgehead CH	molecular ion
1′						250
2′		6.8d (J = 3)	3.95			277
3′			4.5	2.6	3.7	276
2″	3.05	6.8d (J = 3)				271
3″	3.45			2.6 (1 H)	3.7	272
4″	2.95	6.7d (J = 4.5)				271

[a] To be compared with the data for the undeuterated products in ref 10. IR and UV spectra are also in accord. [b] J in Hz.

Scheme IV



operating under the same conditions as in the reaction under study is of the major importance at least for obtaining negative evidence.) In these conditions bibenzyl is of course the main product, but a low amount of compound **1** indeed was obtained. Other NDN deriving products could be present in the complex mixture of minor products, but we found no trace of compounds **2** and **3**. Thus NDN functions even at low concentrations as a trap for benzylic radicals, but the only reaction is the substitution of one cyano group. Therefore compounds **2** and **3** are not formed by reaction of benzylic radicals with NDN, while it is possible that **1** arises from this pathway.

Conclusive Remarks

A photochemical reaction between aromatic nitriles and methylbenzenes has been already reported by Ohashi.[12] In that case, a benzyl group substitutes a cyano group in 1,2,4,5-tetracyanobenzene. Mechanistic investigations showed that a ground-state complex preexists and that it is excitation in the specific absorption band of this complex that causes the reaction. The excited charge-transfer complex is emissive and its role has been proven by quenching with acids. Furthermore the reaction occurs both in polar and apolar solvents.[12]

In the present case there is no evidence for a preformed ground-state complex, and the solvent polarity has a profound effect in that exciplex emission and no photochemical reaction is observed in apolar media, while the exciplex emission is completely quenched in the strongly polar medium where the reaction takes place. More importantly, both cyano group substitution and formal addition of the methylbenzene to NDN are observed in the present case, the latter process occurring stereospecifically. Thus the mechanism of the two reactions is different at least in part (Scheme IV).

The reaction clearly proceeds from the singlet excited state of NDN, as shown by the correspondence between the results from fluorescence quenching and reaction quantum yield. The mere quenching by methylbenzenes with formation of an exciplex is not sufficient, as in that case the main decay pathway for the exciplex is emission. A polar medium is required in order to facilitate charge transfer from the methylbenzene to NDN. However, the hypothesis that the reaction requires total electron transfer, separation of the radical ions of opposite sign, and detachment of a proton from the "free" toluene radical cation to form a benzyl radical that then reacts cannot be reconciled with the previously discussed evidence, and particularly with the stereospecificity of the reaction, the role of water, the deuteration pattern in the products, and the lack of correspondence with true radical reactions.

Considering the sequential steps of the reaction, we begin by the initial electron and proton transfer. The kinetic situation exactly parallels that found by Wagner[13] in the photochemical reaction between α,α,α-trifluoroacetophenone and methylbenzenes in that deuteration does not affect the first step, i.e., electron transfer, but depresses the yield of proton transfer in comparison to the decay from the exciplex to ground-state reactants (a reduction to one-third is observed in both cases[13]). This similarity is not obvious as charge transfer from toluene to the localized n orbital of a ketone in a triplet state produces spin-parallel radical ions probably capable of better solvent stabilization, whereas in the present case a singlet complex is formed from a π donor and a π acceptor and thus differs in both spin factor and electron delocalization. Apparently the closeness of the two partners enhances both the rate of back electron transfer and proton transfer, which remain of comparable size (however, see below) although the former process, which corresponds to the energy wasting process of eq 4, remains by far predominant. Although only a limited number of quantum yield measurements are available in the literature,[14] this appears to be the rule with photochemical reactions of aromatics proceeding through electron transfer in the singlet excited state and is due to the closeness of the two spin-paired radical ions. Furthermore, direct proton transfer is inefficient, and the process measured here requires the presence of a base, such as water, which is capable of effectively mediate the proton transfer before back electron transfer takes place. A water content of 0.05% is sufficient to catalyze this reaction, and only a limited enhancement is observed at higher water content. Notice, however, that the yield of product **3**, which requires a further water-mediated step (vide infra), clearly grows in going to a water content of 0.3%, while the yield of products **1** and **2** drops correspondingly (see Table II).

The concurrence between back electron transfer and water-mediated proton transfer is also influenced by steric factors. Thus,

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[12] (a) Yoshino, A.; Ohashi, M.; Yonezawa, T. *Chem. Commun.* **1971**, 9. (b) Yoshino, A.; Yamasaki, K.; Yonezawa, T.; Ohashi, M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 735. (c) Ohashi, M.; Nakayama, N. *Chem. Lett.* **1976**, 1143.

[13] (a) Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669. (b) Wagner, P. J.; Lam, H. M. H. *Ibid.* **1980**, *102*, 167.

[14] Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535.

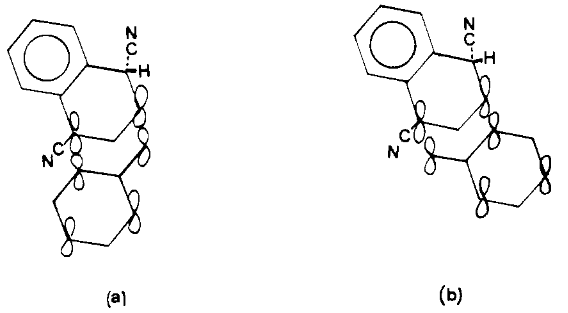

Figure 3. Schematic representation of the conformation of the two radicals that lead (a) to product **2** and (b) product **3** (see Scheme IV).

the ratio k_4/k_5 is larger with 1,3,5-trimethylbenzene (**8**) than with 1,2,4,5-tetramethylbenzene (**9**), probably because the methyl group in 3 makes the attainment of the correct conformation in the exciplex less favored in the former case.

As for the following steps, products **1** can be formed by benzylic radicals escaping from the solvent cage and being trapped by NDN with substitution of a cyano group. This product is reminescient of the substitution of a cyano group by ketyl radicals observed in the case of some heterocyclic nitriles.[15] Escaped benzyl radicals also couple to bibenzyl, but the process is inefficient. The bibenzyl formed correspond only to ca. 5% of the reacted NDN in the case of toluene and is obtained in traces with the other methylbenzenes.

On the contrary the deuteration pattern shows that the other products arise from in-cage reaction. A high rate for recombination of the spin-paired radicals before they fall apart and are stabilized by the solvent is expected and explains the stereoselectivity of the reaction (Figure 3).

The formation of compound **2** is straightforward, whereas product **3** is best explained as involving (possibly concerted) 3 + 3 cycloaddition. Although there is little precedent for this "ortho" reactivity of the benzylic radical, the high stereoselectivity observed fits with the idea of the two radicals remaining parallel and maximizing the interaction between frontier orbitals. Formation of product **3** requires a further interaction with water in order to intramolecularly transfer a proton in the diradical (or zwitterionic) intermediate **11**.

We think that the present mechanistic discussion is also relevant from the synthetic point of view, as it shows the role of bases in developing the potential acidity of toluene in charge-transfer exciplexes and thus it describes a method to induce carbon–carbon bond generation in exciplexes, taking advantage of the stereoselectivity implicit in the geometric requirements of the complex.

Experimental Section

1,4-Naphthalenedicarbonitrile was prepared and purified as previously described.[16] Methylbenzenes, dibenzylketone, and azodibenzyl were purified by distillation or crystallization. Spectrograde acetonitrile was used as received or after dehydration by boiling over CaH_2.

Preparative Reactions of NDN with Methylbenzenes. Seventy milliliters of an acetonitrile solution containing 250 mg (1.4 mM) of NDN and 21 mM of the appropriate methylbenzene was flushed with purified argon and irradiated with a Pyrex-filtered 150-W medium-pressure mercury lamp at 17 °C until NDN was almost completely converted (TLC). After evaporation of the solvent, the photolysate was chromatographed on silica gel eluting with cyclohexane in order to eliminate the residual methylbenzenes and then with cyclohexane–ethyl acetate mixtures. In some cases repeated chromatography was required in order to achieve a satisfactory separation.

The products were then purified by crystallization from cyclohexane (product **1**), benzene–cyclohexane (products **2** and **4**), and toluene (product **3**). Small amounts of 1,2-diphenylethane were also obtained. The water content in the reaction medium was determined by means of the Karl Fischer test.

Photochemical Decomposition of Azodibenzyl and Dibenzyl Ketone in the Presence of NDN. Seventy milliliters of an acetonitrile solution containing 250 mg (1.4 mM) of NDN and 25 mM of either dibenzyl ketone or azodibenzyl were flushed with purified Argon and irradiated through quartz with a 20-W low-pressure mercury arc at 17 °C until substantial conversion of NDN. Work up as above afforded, besides a large amount of 1,2-diphenylethane, low yields of compound **1** (see Table II). Compounds **2** and **3** were not present.

Characterization of the Photoproducts. UV spectra were recorded in ethanol with a Perkin-Elmer 200 spectrophotometer; IR spectra were recorded in Nujol mull or in KBr pellets by means of a Perkin-Elmer 197 spectrophotometer. PMR spectra were recorded in CCl_4 (products **1**) or $CDCl_3$ (the other products) by means of a Brucker 80 instrument with tetramethylsilane as internal standard. Mass spectra were measured by means of a Du Pont 292 instrument. The relevant data are reported in Table III. See also ref 10 for the non-deuterated products.

Quantitative Measurements. Fluorescence spectra were measured by means of a Aminco-Bowman MPF spectrophotometer. Fluorescence intensities and photochemical quantum yields were measured in 1-cm optical path cells after deoxygeneration by means of four freeze–degas–thaw cycles. The photochemical reaction was effected with 313-nm radiation (intensity ca. 10^{-7} Einstein min^{-1} cm^{-2}) obtained from a focalized high-pressure mercury arc by means of an interference filter ($\Delta\lambda_{1/2}$ = 5 nm).

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Registry No. 1, 78075-59-9; **1′**, 89773-49-9; **2**, 83242-06-2; **2′**, 89773-51-3; **2″**, 89773-50-2; **3**, 89826-73-3; **3′**, 89773-54-6; **3″**, 89773-52-4; **4**, 83242-09-5; **4″**, 89773-53-5; PhMe, 108-88-3; $PhCD_3$, 1124-18-1; $(PhCH_2N)_2$, 3395-76-4; $(PhCH_2)_2CO$, 102-04-5; NDN, 3029-30-9; H_2O, 7732-18-5.

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