Model 8460A MRR R band spectrophotometer. Scan rates of 10 and 1 MHz/sec with time constants of 0.3–1 sec were usually used. Longer time constants were avoided because of spectral distortion at these sweep rates. Frequency measurements were based on the average of the position of peak maximum in forward and reverse scans. Frequency accuracy depended on the width of the bands and varied from 1 to 20 MHz. To maximize the signal, a sample pressure of 100 μ (if possible) and a Stark voltage of 1800 V were used. Higher pressures were avoided because of danger of arcing in the cell. All liquid samples were injected using the direct inlet port to minimize the effect of volatile trace impurities.

Room temperature nmr measurements were made on a Varian A-60 nmr spectrometer using CCl_4 as a solvent and cyclohexane as internal reference. With the exception of isotopic modifications and methyl ionones, all compounds were obtained from the usual commercial sources. A 50–50 mol % mixture of VI and VII (Irone Alpha) and VIII were obtained from Givaudan Corp. α,α,α-Trideuterio-p-anisaldehyde was prepared in a Williamson synthesis[37] by a reaction in heavy water of the sodium salt of p-hydroxybenzaldehyde with perdeuteriodimethyl sulfate (Aldrich). All materials were purified, if necessary, and assayed using vapor phase chromatography (vpc) on a Carbowax 20M column at 160°. Isotopic and isomeric purity and identity were checked using nmr. In cases where in spectrometer isomerization was feared, the material was injected into the spectrometer, recovered, and analyzed by vpc.

(37) H. Gilman, Ed., "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 50.

Medium Effects and Quantum Yields in the Photoaddition of Naphthalene and Acrylonitrile.[1] Chemical Evidence on an Exciplex Structure

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Abstract: The photoaddition of naphthalene and acrylonitrile at 313 nm and in hydroxylic solvents to afford endo-7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (1), the endo-8-isomer, and 1- and 2-naphthylpropionitrile (3 and 4) is investigated. The reactive state is naphthalene S_1 which is determined by kinetically relating quantum yields and fluorescence quenching dependences on acrylonitrile concentration. The fluorescence quenching is proposed to occur by charge-transfer exciplex formation. Good Stern–Volmer plots are obtained for quenching in acetonitrile and tert-butyl alcohol, and the rate constant for the latter is 14×10^7 M^{-1} sec^{-1}. Fluorescence of indene and anthracene is also quenched, the rate for indene being diffusion controlled. The dilution plot of reciprocal quantum yield against reciprocal acrylonitrile concentration is linear if 2,3-dimethylbuta-1,3-diene is added to prevent triplet-sensitized decomposition of 1. It is proposed that the exciplex responsible for fluorescence quenching has a polar structure, and the substituted products 3 and 4 arise from protonation of the exciplex. The evidence is that (i) the fraction of substitution increases with medium polarity and (ii) reaction in deuteroxylated solvents gives 3 and 4 labeled in the methyl groups. It is believed that indene reacts similarly and some results for the latter are presented. The exciplex structure is discussed. A correlation exists between the energetics of electron transfer and exciplex behavior for some reactions of naphthalene and benzene derivatives and acrylonitrile. This correlation may be of useful predictive value.

Formation of excimers[3] or exciplexes[4] by reaction with ground-state molecules is an important mode of deactivation of numerous excited states. The rapid chemical reactions which give rise to exciplexes have been extensively studied, mainly by fluorescence quenching measurements, and a number of reviews have been published.[3,5–8]

There is convincing evidence that charge- and electron-transfer processes are important in the formation and decay of many exciplex species. For example, rates of quenching are known to depend on the donor-acceptor properties of the quenchee and quencher,[9] and good correlations of quenching rates with ionization potentials,[10–15] and with oxidation and reduction

(1) For preliminary reports of this work see (a) R. M. Bowman and J. J. McCullough, *Chem. Commun.*, 948 (1970); (b) R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Amer. Chem. Soc.*, **92**, 4106 (1970).

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(3) Th. Forster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969).

(4) M. S. Walker, T. W. Bednar, and R. Lumry, *J. Chem. Phys.*, **45**, 3455 (1966).

(5) B. Stevens, *Advan. Photochem.*, **8**, 161 (1971).

(6) (a) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968); (b) *Progr. React. Kinet.*, **1**, 187 (1961).

(7) L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 260 (1969).

(8) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

(9) S. Ander, H. Blume, G. Heinrich, and D. Schulte-Frohlinde, *Chem. Commun.*, 745 (1968); D. Schulte-Frohlinde and R. Pfefferkorn, *Ber. Bunsenges. Phys. Chem.*, **72**, 330 (1968).

(10) H. S. Samant and A. J. Yarwood, *Can. J. Chem.*, **49**, 2053 (1971).

(11) B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).

(12) T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971).

(13) (a) J. B. Guttenplan and S. G. Cohen, *Tetrahedron Lett.*, 2163 (1972); (b) *J. Amer. Chem. Soc.*, **94**, 4040 (1972); (c) S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968).

(14) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

(15) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972).

potentials,[8,13] have been demonstrated for gas-phase[10] and solution reactions.[8,11-15]

Of particular importance to the present work is the effect of medium polarity on the fate of exciplexes in solution. Mataga[16,17] and Weller[18-20] have studied the effects of medium polarity on exciplex luminescence in arene-amine systems. The exciplex luminescence (fluorescence) is quenched in more polar media,[16,18-20] with electron transfer, to form ions becoming dominant in very polar media.[8,16-20] The ions formed by electron transfer have been observed directly in certain cases.[21] However, two different mechanisms have been advanced to explain the increased quenching of exciplex fluorescence, as medium polarity is increased.[16,18] Apparently exciplexes, solvated ion pairs, and free ions may all be formed, as a result of "charge-transfer" quenching.

In this and a subsequent paper,[22] we will consider the role which these various species play in the photochemistry of donor–acceptor pairs in polar media. We have studied two systems: (a) naphthalene (and indene) and acrylonitrile, in which the potential donor, naphthalene (indene), is excited; and (b) naphthonitriles and tetramethylethylene, in which the acceptor, the naphthonitrile, is the excited species. In this paper, we describe our results on the mechanism of the naphthalene and indene additions with acrylonitrile and propose an interpretation which may be generally applicable.
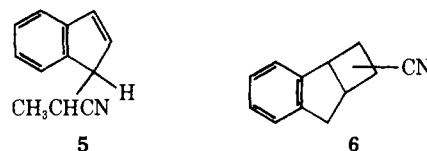
Results

We have reported the structures of the products of irradiation of naphthalene and indene with acrylonitrile, in alcohol solution.[23-25] The products of the naphthalene reaction are 1:1 adducts and include the cyclobutanes 1 and 2 (ratio 13:1) together with the substituted

1 2 3 and 4
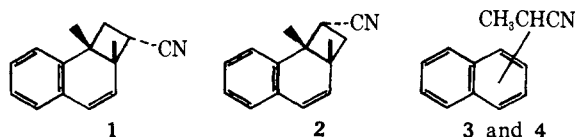
naphthalenes, 3 and 4. The ratio cyclobutanes: substituted naphthalenes is variable and depends on the alcohol used as solvent.

The indene–acrylonitrile photoaddition also gives 1:1 adducts, formally analogous to the naphthalene products, and includes the substituted indene 5 and a mixture of cyclobutanes, 6.[23,25]

(16) T. Okada, H. Matsui, H. Oohari, H. Matsumoto, and N. Mataga, *J. Chem. Phys.*, **49**, 4717 (1968), and references cited therein.

(17) Y. Taniguchi and N. Mataga, *Chem. Phys. Lett.*, **13**, 596 (1972).

(18) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **63**, 791 (1963).

(19) H. Knibbe, K. Rollig, F. P. Schafer, and A. Weller, *J. Chem. Phys.*, **47**, 184 (1967).

(20) H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967).

(21) (a) R. H. Grellman, A. R. Watkins, and A. Weller, *J. Lumin.*, 1/2, 678 (1970); (b) M. Koizumi and H. Yamashita, *Z. Phys. Chem. (Frankfurt am Main)*, **57**, 103 (1968); H. Yamashita, H. Kokubun, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **41**, 2312 (1968); J. K. Roy and D. G. Whitten, *J. Amer. Chem. Soc.*, **94**, 7162 (1972).

(22) J. J. McCullough and W. S. Wu, in preparation.

(23) J. J. McCullough and C. W. Huang, *Can. J. Chem.*, **47**, 757 (1969).

(24) R. M. Bowman, C. Calvo, J. J. McCullough, R. C. Miller, and I. Singh, *Can. J. Chem.*, **51**, 1060 (1973).

(25) R. M. Bowman, J. J. McCullough, and J. S. Swenton, *Can. J. Chem.*, **47**, 4503 (1969).

5 6

This work to be described here is part of a quantitative study, whose objective was to elucidate the mechanism of formation of the adducts 1–6 and to determine the factors which control the ratio of products. Most of the results were obtained for the naphthalene reaction, but we will extend our conclusions to include indene, as far as available data allows.

The mechanistic problem was approached in a number of ways, which included solvent effect studies, fluorescence quenching and quantum yield measurements, and isotope labeling experiments.

Fluorescence Quenching. It was found that the fluorescence emissions of naphthalene, indene, and anthracene were quenched by acrylonitrile, and the Stern–Volmer plots for naphthalene, 1,1-dimethylindene,[26] and anthracene are shown in Figures 1 and 2. It is clear from these linear plots that the fluorescent state (S_1) of these hydrocarbons is being quenched in a bimolecular process by acrylonitrile, in accord with the well-known equation

$$I_0/I = \Phi_0/\Phi = 1 + k_q\tau[A] \tag{1}$$

I and I_0 are the quenched and unquenched fluorescence intensities, and Φ and Φ_0 are the corresponding quantum yields of fluorescence. The fluorescence lifetime is τ, and k_q is the quenching rate constant; [A] is the acrylonitrile concentration. The lifetimes for naphthalene and anthracene fluorescence have been measured in a variety of solvents, including methanol, ethanol, and acetonitrile, and the lifetime of 1,1-dimethylindene was measured in our laboratory. Therefore, the quenching rate constants, k_q, can be calculated. The lifetimes, slopes, and values of k_q are given in Table I.

Clearly, acrylonitrile quenches the singlet S_1 of the three hydrocarbons, and the rate for 1,1-dimethylindene is close to the diffusion limit (k_{diff} for ethanol = 8.5×10^9 M^{-1} sec^{-1}).[27] This immediately suggests that, since the intersystem crossing rates of aromatic hydrocarbons are generally low,[28] the additions to acrylonitrile are probably from the lowest singlet-excited states, S_1. This conclusion receives support from the fact that triplet sensitization of the indene reaction affords cyclobutanes only,[23,25] and no addition occurs when naphthalene is sensitized.[23] However, to definitely assign the excited-state multiplicity, the quantum yield for formation of products 1–4 was measured as a function of acrylonitrile concentration. The multiplicity of the addition was determined by relating quantum yields and fluorescence quenching as described in the following section.

Naphthalene–Acrylonitrile. Quantum Yields and Multiplicity. Quenching of the fluorescence of indene, naphthalene, or anthracene by acrylonitrile cannot be

(26) 1,1-Dimethylindene was used in the fluorescence study, since it is easier to purify than indene.

(27) P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **91**, 3085 (1969).

(28) Typical values for k_{ic} are: benzene, 8.6×10^6 sec^{-1}; naphthalene, 1–4×10^6; anthracene, 110×10^6 sec^{-1}; see J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, London, 1970, p 286.
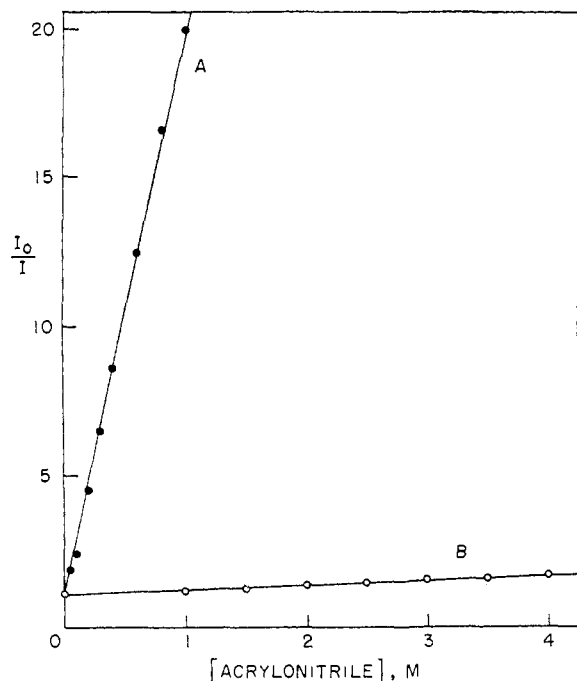
Figure 1. Stern–Volmer plots for the fluorescence quenching of 1,1-dimethylindene (A) and anthracene (B) by acrylonitrile in ethanol.

Figure 2. Stern–Volmer plots for fluorescence quenching of naphthalene by acrylonitrile in *tert*-butyl alcohol (A) and acetonitrile (B).

Table I. Fluorescence Quenching of 1,1-Dimethylindene, Naphthalene, and Anthracene by Acrylonitrile

Fluorescer	Solvent[a]	Lifetime (τ), nsec	Slope, M^{-1}	$k_q \times 10^{-9}$, M^{-1} sec^{-1}
1,1-Dimethylindene	Ethanol	4.1[b]	19.90	4.85
Naphthalene	*tert*-Butyl alcohol	94[c]	2.18	0.023
Naphthalene	Acetonitrile	104[d]	0.77	0.0074
Anthracene	Ethanol	5.5[e]	0.43	0.078

[a] Solutions were deoxygenated by purging with argon. Spectra were measured at room temperature. [b] This lifetime was measured by Mr. M. McClory using the biacetyl quenching method. Details will be published elsewhere. [c] This is the average of several literature values for methanol and ethanol: naphthalene fluorescence lifetimes used were (1) for ethanol, 105 nsec, B. Stevens and M. Thomaz, *Chem. Phys. Lett.*, 1, 549 (1968); (2) for methanol, 91 nsec, G. N. Taylor and G. S. Hammond, *J. Amer. Chem. Soc.*, 94, 3684 (1972); and (3) for methanol, 85 nsec, P. Lentz, H. Blume, and D. Schulte-Frohlinde, *Ber. Bunsenges. Phys. Chem.*, 74, 484 (1970). [d] Naphthalene fluorescence lifetimes used were for acetonitrile, 118 nsec, N. Mataga, M. Tomura, and H. Nishimura, *Mol. Phys.*, 9, 367 (1965), and 90 nsec from G. N. Taylor and G. S. Hammond, ref 2 in footnote c. [e] This value, 5.5 nsec, for anthracene fluorescence in ethanol and other alcohols has been reported by several workers: (1) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, London, 1970, p 127, and references cited; (2) D. O. Cowan and W. W. Schmiegel, *J. Amer. Chem. Soc.*, 94, 6779 (1972).

due to energy transfer. Acrylonitrile has a weak absorption band at 215.5 nm, log ϵ 1.69, corresponding to an energy of 133 kcal/mol, which is considerably higher than $'\Delta E_{0,0}$ of naphthalene[8] (91 kcal), anthracene[29] (76 kcal), or indene[30] (95 kcal). Therefore, the quenching of these singlets must be by chemical interaction, such as complexing or electron transfer.

If it is assumed that naphthalene S_1 is the photo-

(29) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 73, 834 (1969).
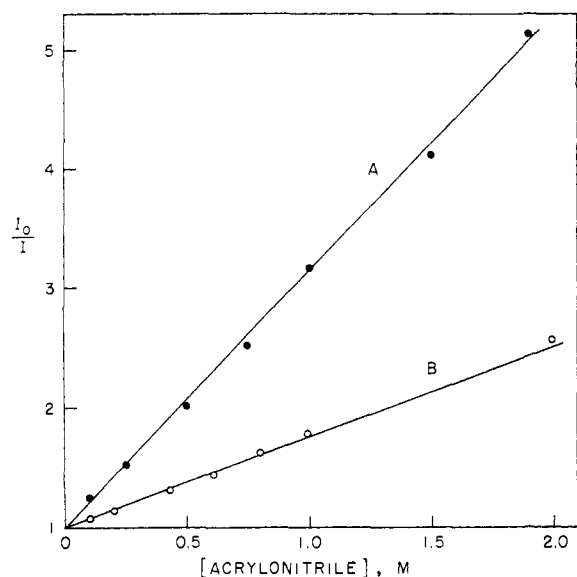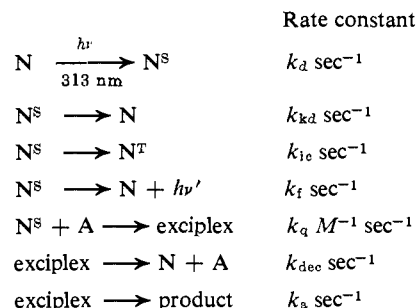
(30) Measured in our laboratory by Mr. M. McClory.

chemically active state and quenching occurs by complex formation, Scheme I may be used to derive a

Scheme I

	Rate constant
$N \xrightarrow[313\ nm]{h\nu} N^S$	k_d sec^{-1}
$N^S \longrightarrow N$	k_{kd} sec^{-1}
$N^S \longrightarrow N^T$	k_{ic} sec^{-1}
$N^S \longrightarrow N + h\nu'$	k_f sec^{-1}
$N^S + A \longrightarrow$ exciplex	k_q M^{-1} sec^{-1}
exciplex $\longrightarrow N + A$	k_{dec} sec^{-1}
exciplex $\longrightarrow$ product	k_a sec^{-1}

relationship between fluorescence, photoaddition quantum yields, and acrylonitrile concentration, using the usual steady-state assumption for naphthalene singlets.

N and A are ground-state naphthalene and acrylonitrile, N^S and N^T are naphthalene S_1 and T_1 states, respectively, and exciplex is the excited complex, presumed to be an intermediate in the photoaddition.[31] The steady-state treatment gives eq 2. Equation 3

$$\Phi_f^{-1} = 1 + \frac{k_{ic} + k_d}{k_f} + \frac{k_q[A]}{k_f} \tag{2}$$

$$\Phi_a^{-1} = \frac{k_a + k_{dec}}{k_a}\left(1 + \frac{k_f + k_{ic} + k_d}{k_q[A]}\right) \tag{3}$$

relates Φ_a and [A]. If Scheme I is correct, the product of the intercepts of (2) and (3) should equal the product of the slopes. To make this comparison, quantum yields for total adduct formation (1–4) were measured as a function of acrylonitrile concentration, and the results are shown in Table II and Figure 3. In early experiments (measurements 7–10 in Table II, plot A in Figure 3), a considerable deviation from the expected linear relationship between Φ_a^{-1} and [A]$^{-1}$ was ob-

(31) Our earlier scheme[1a] involved parallel processes leading to quenching and reaction, respectively, rather than an exciplex. The two are *kinetically* indistinguishable.

Table II. Quantum Yields of Adduct Formation in Photoreaction of Naphthalene and Acrylonitrile

Measurement[a]	Acrylonitrile concn, M	DMBD[b] concn, M	Light, mEinstein	Total products, mg	Quantum yield, Φ, mmol/mEinstein	Acrylonitrile concn^{-1}, M^{-1}	Φ^{-1}, mEinstein/ mmol
1	2.00	0.01	0.0994	6.08	0.34	0.50	2.94
2	0.67	0.01	0.1729	7.41	0.24	1.49	4.17
3	0.40	0.01	0.2538	7.80	0.17	2.50	5.88
4	0.30	0.01	0.2534	6.79	0.15	3.33	6.67
5	0.25	0.01	0.2971	6.87	0.13	4.00	7.69
6	0.20	0.01	0.3019	6.00	0.11	5.00	9.09
7	1.00	0	0.0762	3.63	0.26	1.00	3.80
8	0.67	0	0.0888	3.02	0.19	1.49	5.26
9	0.40	0	0.1036	1.80	0.096	2.50	10.4
10[c]	0.22	0	0.1752	18.23	0.057	4.54	17.4

[a] Solvent was *tert*-butyl alcohol, at 27°. Naphthalene was 0.02 M in 1–6 and 0.0075 M in 7–10. [b] 2,3-Dimethylbuta-1,3-diene to suppress triplet decomposition of the cyclobutanes. [c] This measurement was not performed with the monochromator but with an apparatus employing a 500-W super-pressure mercury lamp and solution filters; it will be described fully elsewhere.
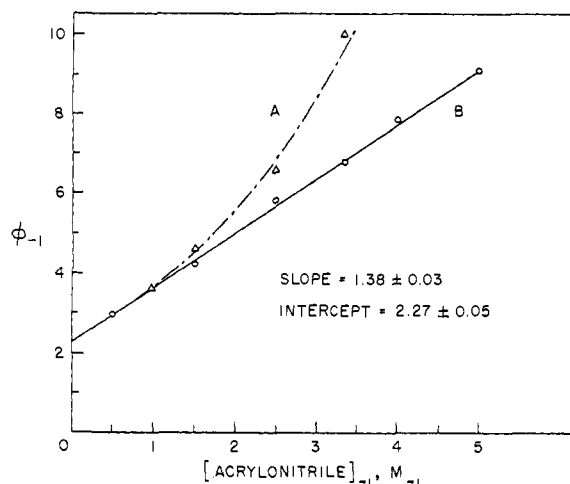

Figure 3. Dilution plots for quantum yields of naphthalene-acrylonitrile addition. In A no quencher was used; in B 0.1 M 2,3-dimethylbuta-1,3-diene was added to quench decomposition of 1. Solvent was *tert*-butyl alcohol.

served, and the deviation became very large at low acrylonitrile concentrations. This deviation was due to triplet-sensitized decomposition of 1, since this cyclobutane decomposed rapidly when sensitized with benzophenone or naphthalene,[32] to give naphthalene;[34] see Chart I.

Chart I
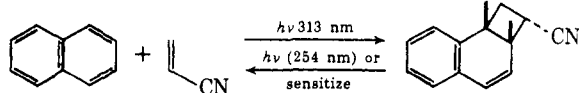
Clearly, the decomposition of 1 would cause the measured quantum yield to be less than the true yield, the difference between them depending on the acrylonitrile concentration and the light intensity.

(32) Benzophenone and naphthalene have T_1 energies of 68.5 and 60.9 kcal, respectively.[33] It was found that fluorenone (T_1 = 53.3)[33] did not sensitize the fragmentation of 1, which indicates a T_1 energy of 55–60 kcal/mol for 1. We found that 1,1-dimethylindene has a T_1 energy of 60 kcal/mol, from phosphorescence emission.

(33) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(34) Adduct 1 decomposes when irradiated at 253.7 nm.[23] This "photofragmentation" of the 2,3-benzobicyclo[4.2.0]octa-2,4-diene ring system appears to be general and has also been observed for substituted derivatives.[35]

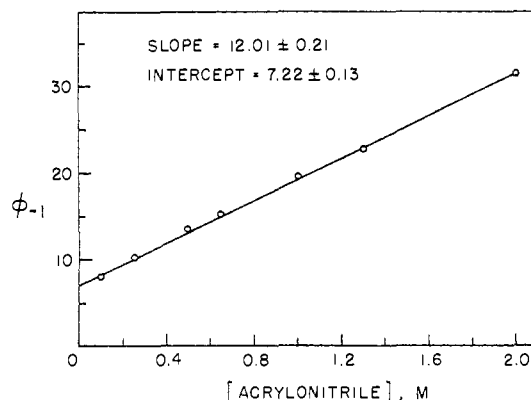(35) T. R. Chamberlain and J. J. McCullough, *Can. J. Chem.*, **51**, 2578 (1973).

Figure 4. Stern–Volmer plot for naphthalene fluorescence quenching by acrylonitrile in *tert*-butyl alcohol in the presence of 0.1 M 2,3-dimethylbuta-1,3-diene.

Fortunately, it was possible to prevent the decomposition of 1 almost completely by the addition of 0.1 M 2,3-dimethylbuta-1,3-diene. This diene quenches naphthalene singlet inefficiently[7] and should have the triplet (T_1) energy of a *transoid* diene.[36] In control experiments, where 1 was sensitized with naphthalene, it was found that 0.1 M of the diene prevented decomposition of 1, without causing side reactions. Plot B in Figure 3 shows the linear relationship which is obtained for Φ_a^{-1} vs. [A]$^{-1}$, when 0.1 M diene is added in the quantum yield determinations.

Although 2,3-dimethylbuta-1,3-diene does not quench naphthalene S_1 efficiently,[7] the lifetime of the latter is however, shortened in 0.1 M diene.[37] For this reason, the Stern–Volmer plot for quenching of naphthalene fluorescence by acrylonitrile was determined with 0.1 M diene in the naphthalene solutions. The data are shown in Table III and the plot in Figure 4.

It can be seen that, as predicted by eq 2 and 3, the products of the slopes and of the intercepts of the linear relationship in Figures 3 (plot B) and 4 are equal, verifying that naphthalene S_1 is the photoreactive state and corroborating Scheme 1.

(36) This is taken to be 60 kcal/mol. For an account of triplet energies of 1,3-dienes, see A. A. Lamola and N. J. Turro, "Technique of Organic Chemistry, XIV," P. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, pp 99–103.

(37) A linear Stern–Volmer plot is obtained for quenching of naphthalene fluorescence by 2,3-dimethyl-1,3-butadiene in *tert*-butyl alcohol. A slope of 2.89 M^{-1} gives k_q = 0.03 × 10^{-9} M^{-1} sec^{-1}. This is close to k_q for hexane (ref 7) and gives I_0/I (0.1 M diene) = 0.78, in close agreement with the measured factor of 0.77.

Table III. Data Used in Stern–Volmer Plot[a] Shown in Figure 4

Measure-ment	Acryloni-trile, M	I_0/I[b]	Φ_f[c]	$1/\Phi_f$
1	2.0	4.56	0.032	31.3
2	1.3	3.34	0.044	22.7
3	1.0	2.88	0.051	19.6
4	0.65	2.21	0.066	15.2
5	0.50	1.97	0.074	13.5
6	0.25	1.48	0.098	10.2
7	0.10	1.18	0.124	8.1
8	0	1.00	(Φ_f^0) 0.146	6.8

[a] Naphthalene was 0.002 M, and 0.1 M 2,3-dimethylbuta-1,3-diene was present; solvent was *tert*-butyl alcohol. Solutions were deoxygenated by purging with argon. [b] Ratio of unquenched (I_0) to quenched (I) fluorescence intensities. [c] Quantum yield of fluorescence (Φ_f) was obtained taking the quantum yield of naphthalene fluorescence, in the absence of quenchers, as 0.19. In 0.1 M 2,3-dimethylbuta-1,2-diene, the intensity of fluorescence is reduced by a factor of 0.77, therefore $\Phi_f^0 = 0.146$.

Medium Effects. It was noted in preparative scale irradiations of naphthalene and acrylonitrile in various alcohols that the ratios of products varied with the alcohol used as solvent. We performed a quantitative study of the effect of some solvents on this reaction.

Table IV shows the ratio of cyclobutane to sub-

**Table IV.** Solvent Dependence of Naphthalene–Acrylonitrile Addition

Solvent	Fraction ($\%$)[a,b] of substituted naphtha-lenes (3 + 4)	Quantum yield (all adducts)	Dielectric constant[c] (pK_a)[d]	Z value[f]
HCO2H	95		58.5 (3.77)[d]	90[g]
CH3CO2H	8.8	0.16	6.15 (4.76)[d]	79.2
CF3CH2OH	53.8	0.28	(12.37)[e]	86.3[h]
CH2ClCH2OH	43.2	0.24	25.8 (14.31)[e]	
CH3OH	29.4	0.26	32.63 (15.5)[e]	83.6
CH3CH2OH	7.8	0.28	24.3 (15.9)[e]	79.6
(CH2)2CHOH	1	0.32	18.3 (18.0)	76.3
(CH3)3COH	Small (<1)	0.27	10.9 (19.0)	71.3
CH2OHCH2OH	40		37.7 (15.4)[e]	85.1
CH3CN	0	Small	29.5	71.3
Dioxane	0	Small	2.21	

[a] Assay was by vpc analysis on 5 ft × 1/8 in. of 4% QF-1 on Diato-port at 190°. [b] The balance consisted of the cyclobutanes (1 and 2), which were stable in all of these solvents. The acrylonitrile was 1 M and 0.1 M 2,3-dimethyl-1,3-butadiene was added to prevent decomposition of 1, in all runs except formic acid. [c] *Nat. Bur. Stand.* (*U. S.*) *Circ.*, No. 514 (1951). [d] J. D. Roberts and M. Casserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964, p 510. [e] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 82, 795 (1960). [f] See ref 38, p 301. [g] Estimated from the Y value. [h] Taken as equal to the value for 2,2,3,3-tetrafluoropropanol-1 (ref 38, p 301).

stituted naphthalene type products, in various solvents. The quantum yields of product formation are also shown, and some properties of the solvents, *e.g.*, dielectric constant, acidity, and Z values,[38] are included. Quite clearly, the higher fraction of substituted naphthalenes in the addition is associated with the more polar solvents, taking the dielectric constant or the Z value as a measure of solvent polarity.

(38) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, pp 293–315.

A further significant result was the finding that if methanol-*O-d* or deuterium acetate (CH3CO2D) were used as solvents, the substituted naphthalenes, **3** and **4**,
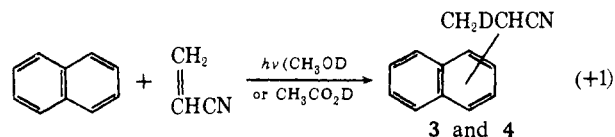
contained one deuterium atom, in the methyl groups. The deuterium content was determined by nmr and mass spectrometry. The simultaneously formed cyclobutane **1** contained deuterium in natural abundance only.

Indene–Acrylonitrile. Since the direct irradiation of indene and acrylonitrile[23] gives products (**5** and **6**) formally analogous to those from the naphthalene reaction, medium effects on the indene addition were also studied. The results are shown in Table V. These

Table V. Ratio of Substitution Products to Cycloadducts Indene–Acrylonitrile Addition

Solvent	Fraction ($\%$) of substituted indenes[a,b]	Relative reac-tion rate[c]
CH3CO2H	80	1.0
CH3OH	78	1.0
CH3CH2OH	80	1.2
(CH3)2CHOH	82	1.2
(CH3)3COH	78	1.1
CH3CN	76	1.2
Cyclohexane	83	0.70
Dioxane	81	1.0

[a] Fraction and relative rates were measured by vpc analysis on a 5 ft × 1/8 in. column of SE-30 at 180°, using benzophenone as internal standard. [b] This figure represents the total content of 1- and 3-substituted indenes (see ref 23). [c] Irradiations were taken to 4–6% conversion.

results contrast with those in Table IV in that there appears to be no significant solvent effect on the products' ratio in the indene reaction.

Further, it was shown when 1,1,3-trideuterioindene is used in the addition that the methyl group in product **5** is labeled with deuterium. Thus, the proton necessary to form the methyl group of **5** comes from indene and not from the solvent.

Discussion

Photoadditions of arenes and their noncarbonyl derivatives have been known for a long time,[39] yet the mechanisms of most of these additions have not been investigated. This contrasts with the recent considerable research activity on mechanisms of photoadditions of other organic molecules, *e.g.*, of enones[40] and dienes.[7,41] Consequently, while photoaddition behavior of enones and dienes is, in general, predictable, this is not true for the arenes and their derivatives. Indeed, it is often difficult to say, *a priori*, whether *any* reaction will occur in a given case! Therefore, following our discovery of the interesting photoadditions of indene and naphthalene to acrylonitrile (photoreac-

(39) A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968, pp 97–99 and 109–117.
(40) P. de Mayo, *Accounts Chem. Res.*, 4, 41 (1971).
(41) (a) R. Srinivasan, *Advan. Photochem.*, 4, 113 (1966); (b) G. J. Fonken, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 197.

tions of naphthalene are still relatively scarce),[42] we proceeded to investigate these reactions quantitatively. The aim of the present work was to determine the intermediates involved, including the excited-state multiplicity in the above reactions, and to find out which properties of the reactants can be used to predict reactivity and structures of products.

The question of multiplicity was fully discussed above, in the Results section, and there is no doubt that these additions involve the singlet-excited states (S_1) of the indene and naphthalene, respectively. This is consistent with the relatively low intersystem crossing rates of arenes in general,[28] and singlet additions are commonly found among the reactions of aromatic compounds.[43]

It is now well known that singlet-excited states of most aromatic compounds have a propensity to form excimers[3] and exciplexes[4] with many ground-state molecules, and these complexes have been invoked as intermediates in some photoaddition processes.[44] We have already noted that the quenching of naphthalene and indene fluorescence by acrylonitrile must involve chemical interaction, such as exciplex formation. Therefore, some kind of exciplex of naphthalene (indene) and acrylonitrile was considered as an intermediate in the additions. The deuterium labeling experiment in the naphthalene reaction provided good support for this hypothesis. In this experiment, use of CH_3OD or CH_3CO_2D led to substituted products 3 and 4, having deuterium in the methyl groups.

The deuterium label from the ionizable OD group of the solvents is incorporated in the acrylonitrile chain of the products, 3 and 4, at the position corresponding to the β carbon of acrylonitrile. No known ground-state ionic process can account for the transfer of a proton (deuteron) from these solvents to acrylonitrile,[45] the double bond of which is a very poor proton acceptor.[47] It is also most unlikely that the proton from solvent is incorporated by protonation of some excited state of acrylonitrile (CH_2=CHCN* in Scheme II) either vibrationally or electronically excited. Such a mechanism would require that the carbonium ion (CH_2DC^+-

(42) For a list of naphthalene additions see D. R. Arnold, L. B. Gillis, and E. B. Whipple, *Chem. Commun.*, 918 (1969).

(43) For example, anthracene dimerization, discussed in E. J. Bowen *Advan. Photochem.*, 1, 36 (1963), and in Th. Forster, ref 3; dimerization of stilbenes, H. Ulrich, D. V. Rao, F. A. Stuber, and A. A. R. Sayigh, *J. Org. Chem.*, 35, 1121 (1970); dimerization of 1,2-diphenyl-cyclobutene, C. D. DeBoer and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 90, 803 (1968); addition of fluorenone and ketenimines, L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, 91, 897 (1969); addition of tetramethylethylene and stilbene, O. L. Chapman and R. D. Lura, *ibid.*, 92, 6352 (1970).

(44) (a) For numerous references, see W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, 93, 5502 (1971), ref 37 and 38; (b) R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, 36, 102 (1971).

(45) The relative strengths of the O–H (O–D) bond *vs.* a C–H bond (110.6 kcal and 98.7 kcal/mol, respectively) preclude homolytic transfer of hydrogen (ref 46).
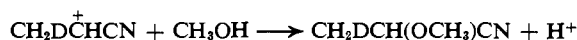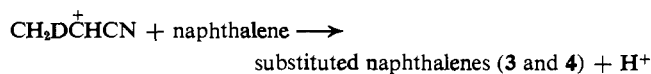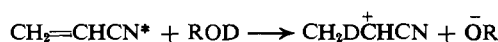
(46) Bond energies from J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965, p 77.

(47) Protonation leading to hydration of ethylenes and styrenes is slow under more strongly acidic conditions than our reactions (ref 48). The well-known electron-withdrawing effect of the nitrile function (ref 49) should preclude protonation at the β carbon of ground-state acrylonitrile.

(48) (a) W. M. Schubert and J. R. Keefe, *J. Amer. Chem. Soc.*, 93, 539 (1971); (b) A. J. Kresge, Y. Chiang, P. H. Fitzgerald, R. S. Mc-Donald, and G. H. Schmid, *ibid.*, 93, 4907 (1971).

(49) The σ+ values of methyl and nitrile groups are −0.31 and 0.66, respectively (from ref 38, p 49).

Scheme II

$$CH_2=CHCN^* + ROD \longrightarrow CH_2D\overset{+}{C}HCN + \overset{-}{O}R$$

$$CH_2D\overset{+}{C}HCN + naphthalene \longrightarrow$$
$$substituted\ naphthalenes\ (3\ and\ 4) + H^+$$

$$CH_2D\overset{+}{C}HCN + CH_3OH \longrightarrow CH_2DCH(OCH_3)CN + H^+$$

HCN) react with 0.01 *M* naphthalene at a rate exceeding the diffusion-controlled rate. This follows if the rate of collapse of the secondary carbonium ion with methanol[50] is 10^9 sec^{-1} and the diffusion-controlled rate constant[51] is 15×10^9 M^{-1} sec^{-1}. Since 2-methoxypropronitrile was not found in the reaction products, the intervention of a free carbonium ion seems unlikely. The methoxy–nitrile is stable under irradiation and is easy to detect by vpc. Further, it was found that acrylonitrile, recovered from the irradiations in CH_3OD or CH_3CO_2D, contained only natural abundance deuterium. This eliminates a second pathway by which the secondary carbonium ion could react by deprotonation to give acrylonitrile.

$$CH_2DC^+HCN \longrightarrow CHD=CHCN + H^+$$
$$not\ observed$$
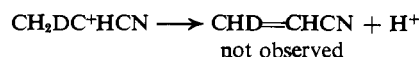
We noted above that the cyclobutane adduct 1 formed in the deuterated solvents also contained only natural abundance deuterium, as did the naphthalene recovered from these reactions. This is consistent with the rather inefficient photochemical hydrogen exchange of naphthalene in strongly acidic solutions.[52]

The following mechanism (Scheme III) is consistent

Scheme III
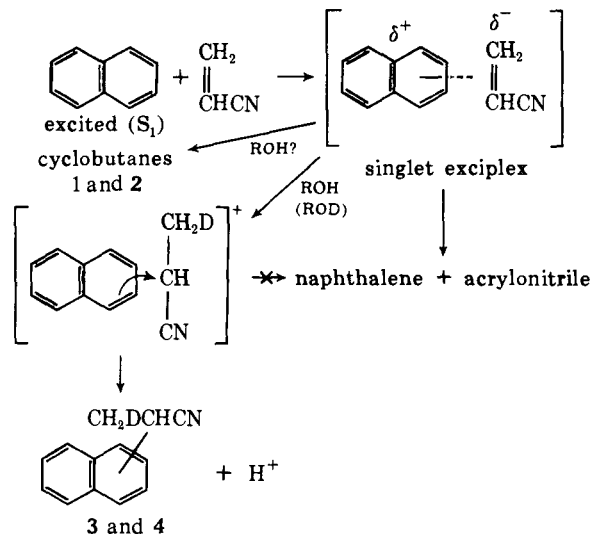
with the above product structures and pathway of deuterium in the labeling experiments. In this mechanism, the exciplex of the naphthalene S_1 state and acrylonitrile is the key intermediate, and its nature is discussed more fully below; for the moment we will assume that it is a polar, charge-transfer excited com-

(50) S. Winstein, *Quart Rev., Chem. Soc.*, 23, 141 (1969), gives an estimate of the rate of collapse of a secondary carbonium ion in aqueous acetone as 10^9 sec^{-1}.

(51) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, 90, 2232 (1968).

(52) The quantum yield of exchange (hydrogen/tritium) for naphthalene is 4.9×10^{-2} in a acetic acid–sulfuric acid mixture with $H_0 = -2.18$: M. G. Kuzmin, V. L. Ivanov, and Yu. Yu. Kulis, *Khim. Vys. Energ.*, 2, 228 (1968).
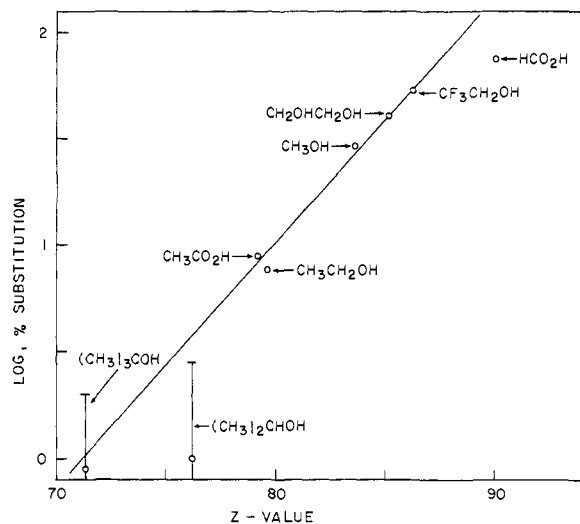
Figure 5. Dependence of the fraction of substitution on the solvent polarity in naphthalene–acrylonitrile addition.
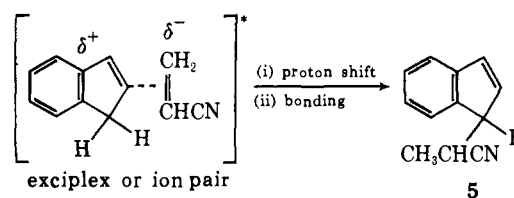
Scheme IV

plex, which is sufficiently long lived to react with the solvent. The exciplex is protonated at the β carbon of the acrylonitrile chain to afford the charged intermediate of Scheme III. The latter affords **3** and **4** on proton loss. Notably, the recovered acrylonitrile from these labeling experiments contained only natural abundance deuterium, showing that the protonation step is essentially irreversible. The second fate of the exciplex species is collapse to the cyclobutanes, **1** and **2**, and it appears that a protic solvent is necessary for formation of these products (Table III, in particular the result in acetonitrile). Finally, the exciplex does dissociate to a significant extent giving ground-state reactants, and the fraction of exciplexes decaying may be obtained from the intercept in Figure 3 and is 0.56 in *tert*-butyl alcohol. This decay must occur before the proton of the solvent is incorporated, to account for the absence of deuterium from recovered acrylonitrile in the labeling experiments.

We propose that the substituted indene **5** is formed by a similar mechanism to that outlined above for naphthalene. The steps are capture of indene S_1 by the acrylonitrile (forming an exciplex), proton transfer from the indene to acrylonitrile, and subsequent collapse to give **5**. The quenching experiments with 1,1-dimethylindene and acrylonitrile show that k_q (Table I) is near the diffusion limit, and it is unlikely that significant intersystem crossing occurs at the acrylonitrile concentrations used in our experiments.

In this addition, the proton required for the methyl group of **5** is provided by the indene (as shown by deuterium labeling) and not by the protic solvent, as in the naphthalene reaction. This means that protonation in the indene case is intramolecular (within the exciplex) and occurs because indene has a relatively acidic proton which naphthalene lacks. The pathway for formation of **5** is outlined in Scheme IV.

Medium Effects and the Exciplex Structure. The effects of changing the solvent polarity on quantum yield and products' distribution in the naphthalene addition are shown in Table IV and Figure 5. A clear trend is evident in the relationship between the fraction of substituted products (**3** and **4**) and the solvent polarity, while the total quantum yield is essentially inde-
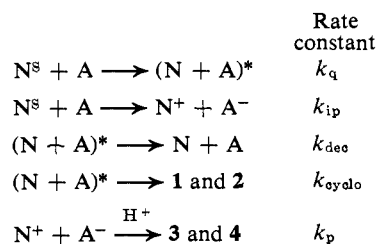
pendent of solvent, at least for the hydroxylic solutions. Of the various available solvent parameters, the Z value [38] gives the best correlation with ratios of products. Neither acidity nor dielectric constant give such a correlation, since acetic acid and ethanol (which have quite different dielectric and dissociation constants) cause about the same amount of substitution. These two solvents do have similar Z values, however. Figure 5 shows a correlation of log (fraction of substitution) with Z value, and it can be seen that a reasonable linear relationship exists, for those solvents in which the ratio substitution/cycloaddition can be measured accurately.

Since the Z value is a measure of the solvent's ability to facilitate charge separation,[38] the relationship in Figure 5 strongly suggests that *a species which is highly polar in character is involved in formation of the substituted naphthalenes.* In view of the work of Weller[8,18-20] and of Mataga[16] on solvent quenching of exciplex fluorescence, it is possible to speculate on the manner in which the solvent alters the polarity of the naphthalene–acrylonitrile complex. We note in passing that no exciplex emission could be observed in our experiments, in any solvent studied, at room temperature. The scheme which Weller proposed involves electron transfer in the more polar media, to give a solvated ion pair, which is nonfluorescent. The solvent dependence in the naphthalene–acrylonitrile case can indeed be explained by an intermediate ion pair, and the processes are listed in Scheme V.

Scheme V

	Rate constant
$N^s + A \longrightarrow (N + A)^*$	k_q
$N^s + A \longrightarrow N^+ + A^-$	k_{ip}
$(N + A)^* \longrightarrow N + A$	k_{dec}
$(N + A)^* \longrightarrow 1 \text{ and } 2$	k_{cyclo}
$N^+ + A^- \xrightarrow{H^+} 3 \text{ and } 4$	k_p

Clearly, if k_{ip} increases with solvent polarity while k_{cyclo} remains constant, then the ratio of $3 + 4$–1 will vary as shown in Table IV and Figure 5. One difficulty with this mechanism, however, lies in explaining that the total quantum yield (cycloaddition plus substitution) is essentially independent of solvent (Table IV). It is possible, however, that k_{ip} increases with solvent polarity while k_{cyclo} decreases, but k_{dec} is insensitive to solvent.

A scheme based on Mataga's interpretation of solvent effects can also account for the present results, but we cannot detail the kinetic scheme at present, and further kinetic work is needed. It does appear, however, that ion-pair formation in the polar media is quite possible on energetic grounds, as is shown in the following section.

Energetics of Electron Transfer. There are reports

in which quenching rates are correlated with excitation energy and oxidation and reduction potentials of donor and acceptor in the reaction[8,11-13]

$$D^* + A \longrightarrow \text{quenching } via \text{ exciplex}$$

This suggests that the types of products formed in additions of donor–acceptor pairs might be related to these energies. Table VI shows the singlet-excitation

Table VI. Excitation and Oxidation Energies of Aromatic Reactants

Compd	$'\Delta E_{o,o}$, kcal/mol	$-E(D/D^+)$, kcal/mol	$-'\Delta E_{o,o} - E(D/D^+)$ kcal/mol
Indene	97.8[a]	36.7[b,e]	−61.1
Naphthalene	91.1[c]	36.9[c]	−54.2
Anthracene	75.7[d]	26.3[d]	−49.4
Phenanthrene	82.8[a]	35.3[e]	−47.5
Benzene	108.0[a]	53.1[e]	−54.9
Anisole	101.5[a]	40.6[c]	−60.9
1-Methoxynaphthalene	85.6[a]	31.8[b]	−53.8
2-Methoxynaphthalene	85.4[c]	32.8[c]	−52.6

[a] Measured from fluorescence and absorption spectra. [b] N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968). [c] From ref 8. [d] D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969). [e] L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, **37**, 916 (1972).

energies ($'\Delta E_{o,o}$) and the oxidation potentials of a number of simple aromatic compounds which are known to react with acrylonitrile. The last column in Table VI gives the difference between the excitation and oxidation potentials. Since the reduction potentials of a few α,β-unsaturated nitriles are known,[53] the potential for acrylonitrile can be estimated as 52.4 kcal/mol. Comparison of this figure with the last column of Table VI is most interesting. In solvents of similar polarity to acetonitrile, in which the electrochemical data were determined, electron transfer from the aromatic S_1 to acrylonitrile is strongly exothermic in case of indene and anisole. It is endothermic in the cases of anthracene and phenanthrene and isoenergetic in the remaining cases, which include naphthalene and its methoxy derivatives and benzene.

Apparently, a correlation exists between the electron-transfer energies and amount of substitution. For example, indene and anisole[54] give a lot of substitution on irradiation with acrylonitrile, and electron transfer in these cases is certainly exothermic and should, incidentally, be diffusion controlled[6a] (see Table I). Anthracene and phenanthrene[55] react with acrylonitrile, but no substitution products are formed, and electron transfer here is endothermic. The remaining cases[54] (except benzene) have been studied in polar solvents, and varying amounts of substitution are observed.

This correlation is consistent with the proposal that substitution is dependent on the rate of ion-pair formation, which is enhanced by exothermic electron

transfer and by more polar solvents. It is possible that the reactions of indene, naphthalene, and anisole occur, at least partly, *via* ion pairs in polar solvents.

One result which this picture does not seem to explain is that in Table V, which shows that the substitution–cycloaddition ratio for the indene reaction is independent of solvent. However, we note that this reaction involves an *intramolecular* hydrogen shift (*i.e.*, within the exciplex), which may in fact occur as a hydrogen-atom transfer.[8,13] Cohen[13c] was the first to suggest such a mechanism, to explain the rapid rate of photoreduction of ketones by amines. Also, the indene–acrylonitrile electron-transfer process is quite exothermic and this may enable an ion pair or polar exciplex to form in the nonpolar solvents.

A further apparent anomaly is the effect of acetonitrile solvent on the naphthalene–acrylonitrile addition. Not only is formation of the substituted naphthalenes inhibited, but the cyclobutane adducts form inefficiently, if at all. Apparently, the exciplex requires some specific kind of solvation to collapse to product, which only the hydroxylic solvents can provide.[56] We also note that k_q for quenching of naphthalene fluorescence by acrylonitrile is lower in acetonitrile than *tert*-butyl alcohol (Table I), although the two have similar Z values. This also suggests that solvent–exciplex interactions are present, such as hydrogen bonding to the alcohol.

Finally, we point out that the principles described in this paper are applicable not only to donor–acceptor interaction when the excited partner is the donor but also when it is the acceptor. For example, the reductions which occur on irradiation of naphthalene and amines[57] and 2-naphthonitrile and tetramethylethylene[58] are consistent with electron transfer from the amine or olefin to the excited naphthalene derivative, which is calculated to be exothermic. The prediction of Nasielski,[59] that photoinduced electron transfer should appear in a wide range of substrates, is now corroborated by our results.

Experimental Section

Materials. All solvents were reagent grade and were distilled before use. Acrylonitrile was Eastman Practical Grade and was purified by the method of Bevington and Eaves.[60] It was distilled and stored in the refrigerator and was distilled again, bp 75–76°, from hydroquinone and under nitrogen immediately before use. Naphthalene (Fisher Reagent) was crystallized from ethanol and had mp 78.5–80°. 2,3-Dimethylbuta-1,3-diene (Aldrich Chemical Co.) was distilled, bp 78–80°, under nitrogen, before use. 2,2,2-Trifluoroethanol was from Aldrich and was distilled, bp 74–75°. Deuteriomethanol (CH_3OD) was prepared as described by Streitwieser and coworkers.[61] Deuterium acetate was prepared by the hydrolysis of acetic anhydride with D_2O. The D_2O was specified at 99% and was from Columbia Organic Chemicals, Inc. *p*-Terphenyl used as internal standard in the vpc measurements was from Aldrich and had mp 212–213° from ethanol. 2-Methoxypropio-

(53) H. O. House, L. E. Huber, and M. J. Umen, *J. Amer. Chem. Soc.*, **94**, 8471 (1972).

(54) Anisole reacts with acrylonitrile on irradiation in ethanol to give 2-(*p*-methoxyphenyl)propionitrile in 50% yield: T. R. Chamberlain and J. J. McCullough, unpublished results. 1-Methoxynaphthalene also gives considerable substitution on irradiation with acrylonitrile in ethanol; 2-methoxynaphthalene gives a few per cent substitution: ref 35 and unpublished results of S. Olynyk and J. J. McCullough.

(55) T. Miryamoto, T. Mori, and Y. Odaira, *Chem. Commun.*, 1598 (1970).

(56) It is possible that solvation of the naphthalene–acrylonitrile exciplex by acetonitrile or alcohol could inhibit or facilitate collapse of the exciplex to product. Exciplexes apparently can form complexes with small dipolar molecules such as acetonitrile: E. A. Chandross and J. T. Thomas, *Chem. Phys. Lett.*, **9**, 397 (1971).

(57) J. A. Barltrop and R. J. Owers, *Chem. Commun.*, 1462 (1970).

(58) J. J. McCullough and W. S. Wu, *Chem. Commun.*, 1136 (1972).

(59) J. Nasielski, A. Kirsch-Demesmaeker, P. Kirsch, and R. Nasielski-Hinkens, *Chem. Commun.*, 302 (1970).

(60) J. C. Bevington and D. Eaves, *Trans. Faraday Soc.*, **55**, 1777 (1959).

(61) A. Streitwieser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

nitrile was prepared as described by Adams, *et al.*,[62] and had bp 112–116.5° (lit.[62] 112.5–116.5°). 1,1-Dimethylindene[63] and 1,1,3-trideuterioindene[64] were prepared by the literature methods.

Quantum Yield Measurements. The irradiations were performed using a Bausch and Lomb Model 33-86-01 high-intensity monochromator, fitted with an achromatic condenser lens, and coupled to an Osram HBO 200W super-pressure lamp. The uv–vis grating was used, and entrance and exit slit widths were set to give a band pass of 15 nm at 313 nm. The parallel beam from the monochromator was split by a quartz plate, $2 \times 2 \times \frac{1}{8}$ in., fixed at 45° to the beam. About 10% of the beam was reflected into cell A which always contained actinometer. The transmitted beam was incident on cell B, which contained actinometer in runs 1 and 3, and naphthalene–acrylonitrile solution in run 2. In run 2, cell C was placed behind cell B, to measure the light transmitted by the naphthalene solution, which was about 4% of the incident light. Cells A and B were 5.0 cm long and had a volume of 26 ml; cell C was 2.5 cm in length and contained 13 ml. The cells were jacketed to allow water at 27° to be circulated. The cells were of Suprasil quartz and made by the Hellma Co., Gmbh, Germany. Light intensities were measured by ferrioxalate actinometry.[65] All solutions (actinometer and naphthalene–acrylonitrile) were purged with argon for 20 min prior to and during irradiations. Thus, for a quantum yield measurement, the ratio of reflected–transmitted beam was determined in runs 1 and 3. Light incident on the naphthalene–acrylonitrile solution was calculated from run 2, using the ratio from runs 1 and 3.

The products formed in run 2 were assayed by vpc analysis at 190° on a Varian Aerograph Model 204-B gas chromatograph, with flame-ionization detectors, on a 5 ft $\times$ $\frac{1}{8}$ in. column of 4% QF-1 on Diatoport S, 60–80 mesh (F and M Scientific Corp.). Helium at 40 ml/min was used as carrier gas. The irradiated naphthalene solutions were evaporated, *p*-terphenyl (internal standard) was added, and the mixture was dissolved in ethyl acetate for vpc analysis. The vpc response factors for adducts *vs.* *p*-terphenyl were determined by calibrating with standard solutions, and the calibration was repeated periodically. Peak areas were measured by a Varian electronic integrator. The reproducibility of this method was better than ±3%. Retention times are given in ref 24, except *p*-terphenyl which had a retention time of 5.5 min.

The same optical bench and analytical procedure were used in measuring solvent effects, and the quantum yield and ratio of products were measured for each solvent.

Fluorescence Measurements. Fluorescence intensities for naphthalene were measured on an Aminco-Bowman spectrofluorimeter, with irradiation at 303 nm and monitoring at 339 nm in the naphthalene experiments. Fluorescence cells fitted with a standard taper joint and a stopcock were used, and solutions were deaerated by purging with argon. In a quenching experiment each value of intensity with quencher (I) was checked against the unquenched intensity (I_0) by using two cells, one with and one without quencher.

Fluorescence of 1,1-dimethylindene was excited at 279 nm and monitored at 330 nm.

Deuterium-Labeling Experiments. Acrylonitrile (2 g; 0.0377 mol) and naphthalene (0.1 g; 0.00078 mol) in deuterium acetate (70 ml) (under nitrogen at 30°) were irradiated through Corex with the Hanovia 450W lamp for 90 min. The mixtures from five such reactions were evaporated and combined, and the mixture was separated by column chromatography as described previously[23] to obtain 3-deuterio-2-(1-naphthyl)- and -(2-naphthyl)propionitriles, 3 and 4, and *endo*-7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (1). The products were subjected to nuclear magnetic resonance and mass spectral analysis.

To analyze the deuterium content in the recovered acrylonitrile, the distillate (which contained mainly deuterium acetate and unreacted acrylonitrile) was treated with 5 ml of freshly distilled cyclopentadiene, and the mixture was allowed to stand for 3 hr and was evaporated. The residue which contained a mixture of 4-*endo*- and -*exo*-cyanobicyclo[2.2.1]hep-2-ene was dissolved in ether and washed with bicarbonate solution. The ether layer was dried and evaporated. The residue was then purified by vpc on 5 ft $\times$ $\frac{3}{8}$ in. 10% SE-30 on Chromosorb W, 170°. The mass spectrum of the mixture of adducts showed a $(M + 1)^+$ peak with a relative intensity of 10.4% relative to the molecular ion peak (M^+). A blank obtained from the same procedure (excluding the photolysis) showed a $(M + 1)^+$ peak with relative intensity of 9.9%. This showed that no more than 0.5% of the recovered acrylonitrile had deuterium incorporated.

Solvent Effect on the Indene–Acrylonitrile Photoaddition. Indene (0.2 g; 0.0017 mol) and acrylonitrile (2 g; 0.0377 mol) in various solvents (70 ml) were irradiated through Vycor for 1 hr. The solutions were contained in 1-in. diameter quartz tubes, which were irradiated simultaneously with the Hanovia 450W lamp. On termination of the irradiation (at about 6% conversion), benzophenone was added as internal standard, and the ratio of cycloaddition:substitution and approximate was determined by analysis on 5 ft $\times$ $\frac{1}{8}$ in. of 5% SE 30 on 60–80 Chromosorb W at 180°. The results are given in Table V.

Search for 2-Methoxypropionitrile in the Irradiation of Naphthalene and Acrylonitrile. Naphthalene (0.1 g) and acrylonitrile (2.0 g) in methanol (70 ml) were irradiated through Pyrex for 30 min, as described in the previous experiment. The solution was examined by vpc on 5 ft $\times$ $\frac{1}{8}$ in. of 5% SE 30 on Chromosorb W at 70° for 2-methoxypropionitrile. None of the latter, which had a retention time of 2 min, was detected. By irradiation of a similar solution to which 2-methoxypropionitrile had been added, it was shown that the ether was stable under the reaction conditions.

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