The results are summarized in Table III. 9-Cyanophenanthrene was adsorbed at 24 (36 mg/g of silica gel) and 50% (76 mg/g of silica gel) coverage on degassed dried (200 °C; 0.3 mmHg) silica gel. It is believed that dimerization did not proceed from microcrystals because (a) the dimerization in the crystals was very inefficient both at +10 and +70 °C, (b) crystals could not be observed by microscope (×128), (c) crystals in contact with silica gel gradually disappeared, and (d) the lifetimes (air) of the nitrile in the crystal (τ_1, 29 ns; τ_2, 25 ns) were longer than in the adsorbed state (24% coverage; τ_1, 4.8 ns; τ_2, 17 ns). Dimerization was induced by irradiation with a 150-W xenon lamp through a Corning 0-52 filter. The tube containing the nitrile was rotated for 7 h. Disappearance of the starting material was monitored by the UV absorption in a cyclohexane–silica gel slurry by comparison with a nonirradiated blank. The dimer was thermally unstable at GC injection temperature (250 °C) but is stable at 80 °C.

Emission Spectra and Decay Kinetics of Adsorbed Pyrene on Dry Silica Gel. A cyclohexane solution (ca. 15 mL) containing a suitable amount of pyrene and the quencher was adsorbed on activated silica gel by simply evaporating the solvent slowly. The sample was transferred into a Suprasil cell with 2-mm optical path length. Then the system was degassed (10^{-5} mmHg) at room temperature or 60 °C for ~40 min. The weight loss of pyrene is negligible under these conditions, although a small amount (ca. 2×10^{-6} mol) of 2-chloro- or 2-bromonaphthalene is lost when heated. The degassed cell was sealed off. Emission spectra were recorded on a Perkin-Elmer MPF-4 emission spectrophotometer with a cell holder specially designed to hold the cell at a ca. 45° angle to the incident excitation light beam. The emission from the front surface of the cell was monitored with a slit width of the monochromator of 0.75 nm. For the comparison of emission intensity, the mean value of at least three measurements on the same sample were used. Emission decay profiles were measured with a PRA 3000 single photon lifetime apparatus with excitation and emission monochromators (slit width 8 nm). Deconvolution was performed with PRA software which employs iterative least-squares deconvolution. A similar procedure was used for the decay kinetics of anthracene and 9-cyanophenanthrene.

Full (100%) monolayer surface coverages correspond to 97, 28, and 152 mg/g of silica gel for pyrene, anthracene, and 9-cyanophenanthrene.

Intergranular Transfer of 2-Bromonaphthalene and Pyrene. Equal amounts (ca. 500 mg) of silica gel were coated with pyrene (7×10^{-7} mol/g) and 2-bromonaphthalene (1.4×10^{-4} mol/g) and placed in the branches A and B, respectively, of the apparatus shown in Figure 9. After evacuation for 2 h (~10^{-5} mmHg) the system was sealed from the vacuum line. The "pyrene" sample was then carefully introduced into the sample cell avoiding contamination by the "bromonaphthalene" sample. The pyrene mean lifetime was 290 ns. After standing for 1 day the samples were mixed and shaken vigorously for 5 min. The lifetime of the pyrene was 142 ns reduced to 140 ns after 30 min of shaking. A similar experiment carried out under nitrogen (200 mmHg) gave the same results.

Intergranular Transfer of Acenaphthalene and Pyrene. Silica gel (35–70 mesh, Merck) was divided into coarse and fine fractions using a 50-mesh sieve. Acenaphthylene (ca. 12 mg) was adsorbed onto 500 mg of either coarse or fine silica gel by evaporation of a cyclohexane solution. The silica gel was then mixed with an equal amount of uncoated silica gel of opposite grain size and shaken for 5 or 30 min. The mixed powder was again separated into coarse and fine. The error in the separation was <15%. Each portion of the separation silica was extracted with methylene dichloride and the acenaphthylene estimated spectroscopically. The same procedure was used with pyrene; the results are given in Table V.

Acknowledgment. One of us (P. de M.) thanks the Ontario Ministry of the Environment and donors of the Petroleum Fund administered by the American Chemical Society for partial support of this work. We thank Dr. A. C. Weedon and Mr. G. S. K. Wong for useful discussions.

Registry No. 1, 208-96-8; **2**, 15065-28-8; **3**, 14620-98-5; 4, 83-32-9; **5**, 2510-55-6; pyrene, 129-00-0; 2-bromonaphthalene, 580-13-2; anthracene, 120-12-7.

Naphthonitrile–Alkene Exciplexes. Comparison of Bimolecular and Bichromophoric Cases: Effects of Linking on Fluorescence and Photochemistry

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Abstract: The fluorescence quenching and photochemistry of 2-methyl-, 4-methyl-, and 6-methyl-1-naphthonitrile with tetramethylethylene have been studied in nonpolar solvents. Stern–Volmer constants (benzene solvent) are 10.1, 15.7, and 7.2 M^{-1}, respectively, showing that quenching is insensitive to the position of the methyl group. Exciplex emission was observed in each case, and exciplex lifetimes were measured by single photon counting techniques. The methylnaphthonitriles react with tetramethylethylene to give 1-cyano-7,7,8,8-tetramethyl-2,3-benzobicyclo[4.2.0]-2,4-octadiene derivatives, and limiting quantum yields were measured. In the case of 4-methyl-1-naphthonitrile, quenching with biacetyl showed that the exciplex is an intermediate in the cycloaddition reaction and no triplets are formed in the exciplex decay. Rates of exciplex collapse to cyclobutane products were derived. The bichromophoric molecules **1**, **2**, and **3**, in which the chromophores are linked by a three-atom chain, were synthesized. All three show strong quenching of the monomer (naphthonitrile) fluorescence, and weak exciplex emission. Compounds **1**, **2**, and **3** also react on irradiation, giving internal cycloaddition products. The structures of the latter were determined, and the structure work is described. Comparison of quantum yields for internal cycloaddition with limiting quantum yields for the bimolecular cases shows that the three-atom chain greatly facilitates collapse of the exciplexes to products in these systems. Exciplex formation and decay are discussed in terms of current theory. The structure of one photoproduct, 7-cyano-5,6,6-trimethyl-8,9-benzo-3-oxatricyclo[5.4.0.$0^{1,5}$]-8,10-undecadiene (**10**), was determined by X-ray diffraction, and the structure is described.

Exciplex formation was proposed some time ago by Hammond and co-workers[2] to account for the quenching of fluorescence of aromatic compounds by dienes.[2] The observation of exciplex fluorescence from 1-naphthonitrile and electron-rich alkenes by Taylor[3] showed that exciplexes are indeed formed in fluorescence quenching by ethylene derivatives. A kinetic analysis of the 1-naphthonitrile–olefin system has been carried out.[4,5] Exciplex formation was found to be reversible, and rate constants for the

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[1] (a) Department of Chemistry; (b) Institute of Materials Research.

[2] (a) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, 16, 125 (1968); (b) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Am. Chem. Soc.*, 94, 3679 (1972); (c) G. N. Taylor and G. S. Hammond, *ibid.*, 94, 3684; 94, 3687 (1972).

[3] G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

[4] W. R. Ware, D. Watt, and J. D. Holmes, *J. Am. Chem. Soc.*, 96, 7853 (1974).

[5] (a) D. V. O'Connor and W. R. Ware, *J. Am. Chem. Soc.*, **98**, 4706 (1976); (b) *ibid.*, **101**, 121 (1979).

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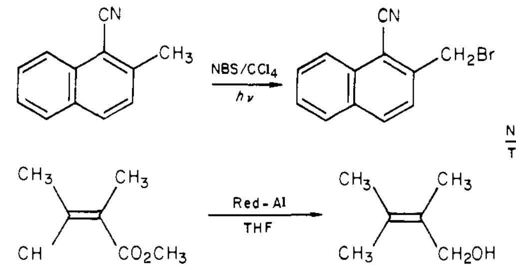
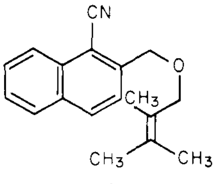
Scheme I



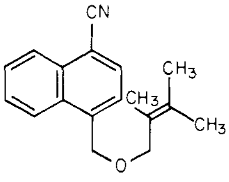
different processes were determined.[4,5]

Fluorescent exciplexes were shown to be intermediates in the (2 + 2) cycloaddition reaction between aromatic singlets and the ethylene derivatives.[6,7] Thus, the exciplexes are of interest in physical organic chemistry.

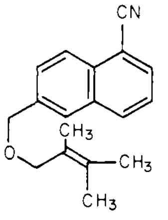
We have been interested in mechanistic[8,9] and preparative[10] aspects of singlet (2 + 2) photoadditions for some time. In the present paper we report studies of geometric factors in the formation and photochemical reactions of 1-naphthonitrile–tetramethylethylene (TME) exciplexes.[11] Our initial aim was to use the bichromophoric molecules **1–3**, in which the three-atom chain is attached at different positions of the naphthonitrile ring, to study the effect of linking on exciplex formation and photochemistry.



1



2

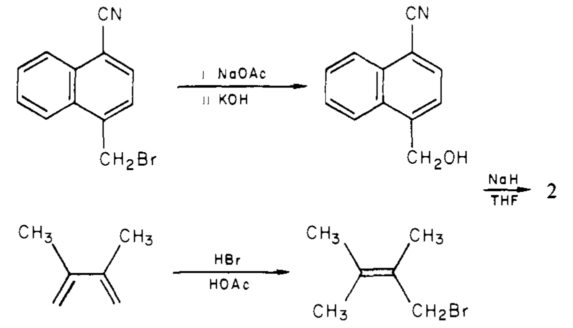


3

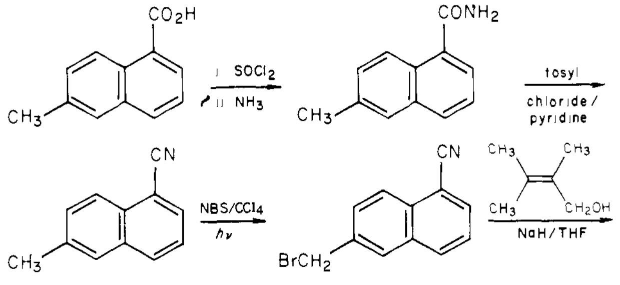
However, the linking in **1–3** introduces an alkyl substituent at different ring positions, and the effect of alkyl substitution on the factors we wanted to study was not known. Therefore, we also investigated the fluorescence and photochemistry of 2-methyl-, 4-methyl-, and 6-methyl-1-naphthonitrile with TME, for comparison. The results from the methylnaphthonitriles are interesting in their own right, and are described along with those of the bichromophoric molecules.

The results are discussed in terms of current theory and are of interest from the viewpoints of mechanism and photokinetics. We note, however, that photoreactions of bichromophoric molecules are being used in the synthesis of various ring systems,[12] including natural products.[13] Thus, factors controlling these photoreactions are clearly of practical importance.

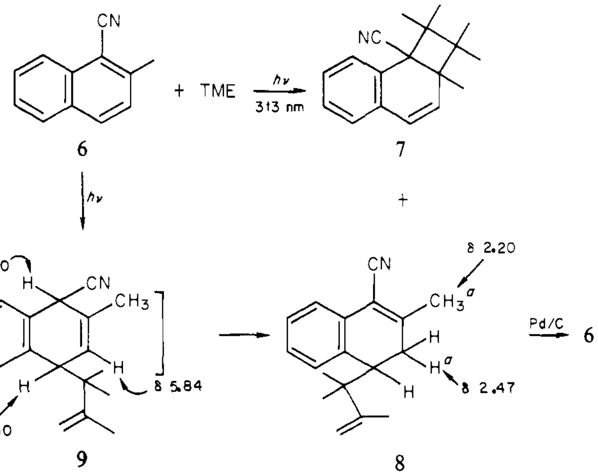
Scheme II



Scheme III



Scheme IV



[a] Protons readily exchanged by base.

Results

A. Syntheses. Preparation of Bichromophoric Molecules. We initially tried to link the naphthonitrile and olefinic chromophores with a three-atom alkane chain, but because of synthetic problems decided to use the ether linkage[14] (structures **1–3**). The required compounds were obtained by the Williamson ether synthesis, but preparation of **1** and **2** was not straightforward.

Synthesis of 2,3-dimethyl-2-butenyl(1-cyano-2-naphthyl)methyl ether (**1**) is shown in Scheme I. The alternate way of making the ether linkage (from 1-cyano-2-naphthalenemethanol and 1-bromo-2,3-dimethyl-2-butene) was unsuccessful, since attempted preparation of 1-cyano-2-naphthalenemethanol gave only the lactone of the corresponding naphthoic acid.[15]

The latter approach, with 1-cyano-4-naphthalenemethanol and 1-bromo-2,3-dimethyl-2-butene, was used to obtain 2,3-dimethyl-2-butenyl (1-cyano-4-naphthyl)methyl ether (**2**), as shown in Scheme II. The route corresponding to Scheme I was un-

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[6] R. A. Caldwell and D. Creed, *Acc. Chem. Res.*, **13**, 45 (1980), and references therein.

[7] F. D. Lewis, *Acc. Chem. Res.*, **12**, 152 (1979), and references therein.

[8] R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Am. Chem. Soc.*, **96**, 692 (1974).

[9] (a) J. J. McCullough, R. C. Miller, D. Fung, and W. S. Wu, *J. Am. Chem. Soc.*, **97**, 5942 (1975); (b) J. J. McCullough, R. C. Miller, and W. S. Wu, *Can. J. Chem.*, **55**, 2909 (1977).

[10] (a) T. R. Chamberlain and J. J. McCullough, *Can. J. Chem.*, **51**, 2578 (1973); (b) I. A. Akhtar and J. J. McCullough, *J. Org. Chem.*, **46**, 1447 (1981).

[11] For a preliminary report, see J. J. McCullough, W. K. MacInnis, C. J. L. Lock, and R. Faggiani, *J. Am. Chem. Soc.*, **102**, 7780 (1980).

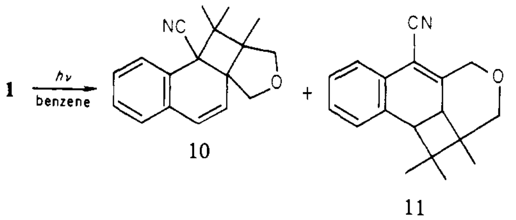
[12] Some examples: (a) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 703 (1970); (b) J. A. Ors and R. Srinivasan, *ibid.*, **100**, 315 (1978); *J. Chem. Soc., Chem. Commun.*, 400 (1979); (c) H. Morrison, *Acc. Chem. Res.*, **12**, 383 (1979); (d) R. G. Salomon, D. J. Coughlin, and E. M. Easler, *J. Am. Chem. Soc.*, **101**, 3961 (1979); (e) K. Maruyama and T. Ishitoku, *Chem. Lett.*, 359 (1980); (f) C. Kaneko, T. Naito, and M. Somei, *J. Chem. Soc., Chem. Commun.*, 804 (1979); (g) A. Padwa and M. Pulwer, *J. Am. Chem. Soc.*, **102**, 6386 (1980).

[13] See, for example: (a) longifolene: W. Oppolzer and T. Godel, *J. Am. Chem. Soc.*, **100**, 2583 (1978); (b) cedrene: M. Fetizon, S. Lazare, C. Pascard, and T. Prange, *J. Chem. Soc., Perkin Trans. 1*, 1407 (1979); (c) α-cedrene: P. A. Wender and J. J. Howbert, *J. Am. Chem. Soc.*, **103**, 688 (1981); (d) isocomene: M. C. Pirrung, *ibid.*, **103**, 82 (1981).

[14] Bis(arylmethyl) ethers have been used to study intramolecular photochemistry: H. Bouas-Laurent, A. Castellan, and J.-P. Desvergne, *Pure Appl. Chem.*, **52**, 2633 (1980), and references therein.

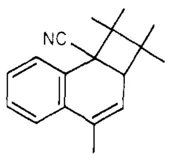
[15] Compare the case of (1-cyano-2-naphthyl)methanethiol: G. W. Stacy, A. J. Papa, F. W. Villaescusa, and S. C. Ray, *J. Org. Chem.*, **29**, 607 (1964).

Scheme V



successful, the major product being an insoluble stilbene derivative, apparently formed from 4-(bromomethyl)-1-naphthonitrile. The third bichromophoric molecule, 2,3-dimethyl-2-butenyl(1-cyano-6-naphthyl)methyl ether (3), was prepared as shown in Scheme III; 6-methylnaphthalene-1-carboxylic acid[16] was converted to the nitrile, which was brominated and the benzylic bromide was used in the Williamson synthesis.

B. Photochemical Reactions. Structures of Products. Irradiation of **4-methyl-1-naphthonitrile or 6-methyl-1-naphthonitrile** with TME in benzene or ethyl acetate (313-nm light or Pyrex filter) gives the cyclobutane adducts **4** and **5**, respectively. No



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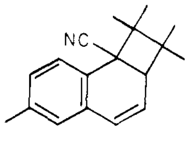

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other products were observed, and the structures were determined from analytical and spectral data, given in the Experimental Section. The regiochemistry of addition has precedent in many reactions of naphthalene and ethylene derivatives,[9,10] including that of 1-naphthonitrile and TME.[9]

Irradiation of **2-methyl-1-naphthonitrile (6)** and TME in benzene gave rise to a more complex reaction, shown in Scheme IV. With light of wavelength >300 nm, short irradiation times, and normal reaction conditions (ambient temperature, solvent evaporation at ~50 °C), the products isolated are **7** and **8**. These are formed in equal amounts and can be separated by preparative VPC. Cyclobutane **7** is an oil whose structure was readily assigned from spectral data (MS, NMR, and IR; see Experimental Section).

Photoproduct **8** can be obtained in quantity by irradition with a Corex filter. Under these conditions, cyclobutane **7** is cleaved to **6** and TME, and since **8** is stable to irradiation, it is the eventual product. It is isolated in 30% yield by column chromatography and has a melting point of 101–102 °C. The structure was assigned as follows. Attempted dehydrogenation with Pd/C resulted in loss of the side chain to give 2-methyl-1-naphthonitrile. The ^{1}H NMR spectrum showed resonances at δ 0.78 and 0.97 (s, 3 H each, *gem*-dimethyl group), 1.80 (dd, J = 1.2 and 0.75 Hz, 3 H, side chain allylic CH_3), 2.20 (s, 3 H, ring CH_3), 2.47 (m, 2 H, ring methylene), 2.93 (dd, J = 6.0 and 2.4 Hz, 1 H, ring methine), 4.80 and 4.90 (m, 1 H each, vinylic CH_2), 7.1–7.5 (m, 4 H, aromatics). Ring methyl and methylene protons (resonances at δ 2.20 and 2.47; see Scheme IV) were rapidly exchanged with methoxide in CH_3OD. The IR spectrum showed an intense band (CN) at 2220 cm^{-1}. The structure 1-(2,3-dimethyl-1-buten-3-yl)-3-methyl-4-cyano-1,2-dihydronaphthalene (**8**) is assigned.

However, **8** was shown not to be a primary product, but is formed from an intermediate. The reaction was run at 0 °C, aliquots were evaporated in the cold, and IR and NMR spectra were run immediately. The IR spectrum showed a band (CN) at 2242 cm^{-1}, and NMR resonances of **8** were not observed. Resonances of equal intensity appeared at δ 3.50 and 5.84, which are assigned to the ring methine and vinylic protons as indicated in **9**, Scheme IV. The side-chain vinylic protons appeared at δ 4.81 and 4.60 (cf. **8** above). The latter showed a definite shoulder (δ ~4.50), which is assigned to the methine proton α to the nitrile. These chemical shifts are in reasonable agreement with other 1,4-dihydronaphthalenes.[17] Isomerization of **9**[18] to **8** is also reasonable.

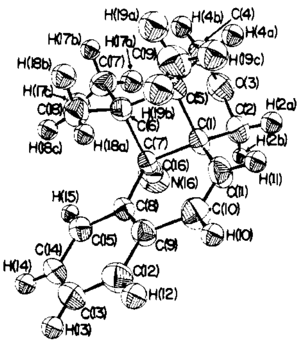
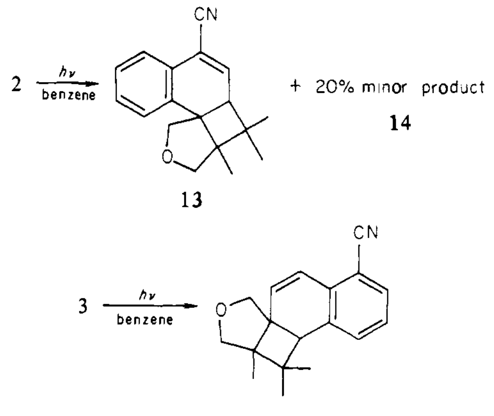


Figure 1. The molecule 7-cyano-5,6,6-trimethyl-8,9-benzo-3-oxatricyclo[5.4.0.0^{1,5}]-8,10-undecadiene (**10**, $C_{18}H_{19}NO$), showing the atom numbering.

Scheme VI



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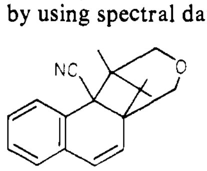
Photochemistry of Bichromophoric Molecules. Irradiation of compound **1** in benzene resulted in the rapid formation of two products, **10** and **11**, by intramolecular cyclization. The products are shown in Scheme V. The initial ratio (**10**:**11**) was 20:1 (determined by VPC), but at longer irradiation times **11** was the major product. The compounds were readily separated by column chromatography.

It was not possible to distinguish between the furan (**10**) and pyran (**12**) derivatives by using spectral data, and the structure



12

of **10** was determined by single-crystal X-ray diffraction. The structure is shown in Figure 1, and details are given in the Experimental Section. The structure is described in detail below. Formation of **10** is consistent with the "rule of five",[19] and although

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[16] C. C. Price, E. C. Chapin, A. Goldman, E. Krebs, and H. M. Shafer, *J. Am. Chem. Soc.*, **63**, 1857 (1941).

[17] See, for example: (a) N. L. Holy, H. P. Vail, A. Nejad, S. Huang, J. L. Marshall, O. Saracoglu, and C. R. McDaniel, Jr., *J. Org. Chem.*, **45**, 4271 (1980); (b) P. W. Rabideau, *Acc. Chem. Res.*, **11**, 141 (1978), and references therein.

[18] (a) Formation of 9 is formally an eight-electron ene-type reaction (photochemically allowed), but nonconcerted mechanisms are possible. The process has been observed before: D. Bryce-Smith, B. E. Foulger, A. Gilbert, and P. J. Twitchett, *J. Chem. Soc. D*, 794 (1971). (b) Isomerization of 9 to 8 occurs at ~50 °C or even at 25 °C on standing in condensed media and is probably base-catalyzed under these conditions. It occurs very rapidly on addition of methoxide. The isomerization on VPC probably occurs on injection and not in the column.

[19] R. Srinivasan and K. L. Carlough, *J. Am. Chem. Soc.*, **89** 4932 (1967); R. S. Lui and G. S. Hammond, *Ibid.*, **89**, 4936 (1967).

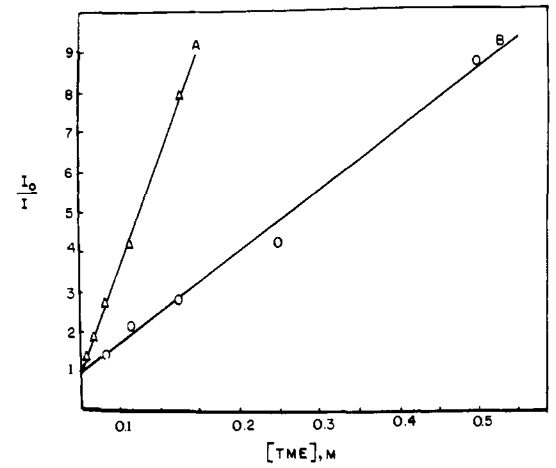

Figure 2. Stern-Volmer plots for quenching of 4-methyl-1-naphthonitrile fluorescence by tetramethylethylene in ethyl acetate (A) and benzene (B).

12 was not observed, it could be present as a minor product.

Structure **11** was assigned from its spectra: IR 2217 cm^{-1} (conjugated CN); ^{1}H NMR (FT, 80 MHz, CDCl$_3$) δ 7.0 (m, 4 H, aromatics), 3.95 (d, J = 9.8 Hz, 1 H, benzylic methine), 3.74 (2 H, AB quartet, J = 10.0 Hz, allylic CH$_2$), 3.15 (2 H, AB quartet, J = 5.0 Hz, CH$_2$), 2.95 (d, 1 H, J = 9.8 Hz, allylic methine), 0, 0.59, and 1.10, (s, 3 H each, methyls).

Preparative irradiation of bichromophoric compound **2** gave a yellow solution, and VPC analysis showed two products in the ratio 5:1. The major product, isolated by column chromatography, was assigned structure **13** (Scheme VI) from its spectra.

Important features included the following: IR 2220 cm^{-1} (conjugated CN); ^{1}H NMR (FT, 80 MHz, CDCl$_3$) δ 0.81, 0.97, and 1.15 (s, 3 H each, methyls), 2.98 (d, J = 5.6 Hz, 1 H, ring methine), 6.54 (d, J = 5.6 Hz, 1 H, vinyl). The methylene groups gave two AB quartets, with the high-field branches overlapping (multiplet at δ 3.47) and the low-field branches at δ 4.30 and 3.96 (J = 10.0 and 9.3 Hz, respectively). The aromatics gave three multiplets between δ 6.9 and 7.6, total area, 4 H. The regiochemistry of **13** (i.e., furan rather than pyran ring) is assigned by analogy with **10**.[20]

The minor product of this reaction was not characterized. On chromatography, intractable material containing oxygen was isolated, indicating that the compound had reacted with air. Attempts to detect the compound by NMR (of the reaction mixture) were unsuccessful. The compound may not be a primary product, since on photolysis to low conversion it was not detected, e.g., in quantum yield measurements.

The product of irradiation of **3** proved the most difficult to characterize. Although a single product was formed (VPC analysis), it was an oil and was only obtained 90% pure. The photoreaction was difficult to scale up, since the product absorbed light at high conversions and reverted to **3**. The following spectral data were obtained: IR 2219 cm^{-1} (conjugated CN); ^{1}H NMR (FT, 80 MHz) δ 0.93, 1.25, and 1.32 (s, 3 H each, methyls), 6.00 and 7.07 (d, J = 10.0 Hz, 1 H each, vinylic, 7.2-7.7 (m, 3 H, aromatics). The methylene groups gave two AB quartets, downfield branches at δ 4.47 and 3.98, J = 9.5 Hz, and high-field branches giving a multiplet at δ 3.45, combined with the benzylic methine. The structure **15** is assigned, but more work is needed on this product.

Quantum Yield Measurements. Quantum yields for cycloaddition ($\Phi_{\lim}{}^{A}$) were measured for the three methylnaphthonitriles and TME, at limiting TME concentration. In the case of 4-methyl-1-naphthonitrile, the effect of varying the TME concentration on addition quantum yield was also investigated. The latter will be considered first.

Table I. Fluorescence Quenching Data for 1-Naphthonitriles and Tetramethylethylene

fluorescer	solvent[a]	lifetime[e] (τ), ns	K_{SV},[c] M^{-1}	$K_{SV}/\tau^{f} \times 10^{-9}$
1-naphthonitrile (1-NN)	benzene	9.8[d]	41.7	4.26
	ethyl acetate	11.8[e]		
2-methyl-1-naphthonitrile	benzene	11.1	10.1	0.91
	ethyl acetate	11.6	48.4	4.17
4-methyl-1-naphthonitrile	benzene	9.2[g]	15.7	1.71
	ethyl acetate	10.0	53.0	5.30
6-methyl-1-naphthonitrile	benzene	11.1	9.0	0.81
	ethyl acetate	9.8	37.4	3.82

[a] Solutions deoxygenated by purging with argon (K_{SV}) or by freeze-pump-thaw (τ measurements). [b] Single photon counting technique. [c] Average of several runs, individual runs were within ±6%. [d] R. C. Miller, Ph.D. Thesis, McMaster University, 1978. [e] From ref 5b. [f] All measurements made at 22 °C. [g] Lifetime was the same at 3 × 10^{-4} and 6 × 10^{-5} M.

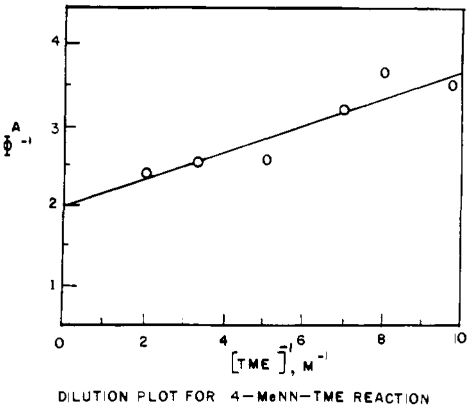

Figure 3. Dilution plot for addition of 4-methyl-1-naphthonitrile and tetramethylethylene in benzene. Naphthonitrile was 10^{-3} M.

The quantum yield for addition (Φ^{A}) is related to TME concentration by eq 1, if only one quenchable excited state is involved

$$\Phi^{A^{-1}} = \Phi_{\lim}{}^{A-1}(1 + K_{SV}{}^{-1}[\mathrm{TME}]^{-1}) \qquad (1)$$

in the reaction. K_{SV} is the slope of the Stern-Volmer quenching of the excited state by TME and is given by the well-known eq 2. $\Phi_0{}^{F}$ and Φ^{F} are fluorescence quantum yields of naphthonitrile,

$$\Phi_0{}^{F}/\Phi^{F} = 1 + K_{SV}[\mathrm{TME}] \qquad (2)$$

unquenched and quenched, respectively. Stern-Volmer plots for quenching of 4-methyl-1-naphthonitrile fluorescence by TME in benzene and ethyl acetate are shown in Figure 2.

Similar plots were obtaied for the other naphthonitriles, and the slopes (K_{SV}) of these plots are given in Table I. The value of K_{SV} is related to the fluorescence lifetime (τ) of the naphthonitrile, and these lifetimes are also given.

The K_{SV}/τ values are significant and are also included in Table I; they will be used later in the discussion of kinetics.

The plot of $\Phi^{A^{-1}}$ vs. [TME]$^{-1}$ (dilution plot) for 4-methyl-1-naphthonitrile-TME addition is shown in Figure 3. The plot is linear, as expected from eq 1. Also, K_{SV} from this plot is 11.6 M^{-1}, which is in fair agreement with the value in Table I (15.7 M^{-1}). The plot in Figure 3 was only obtained after considerable effort. In early measurements, naphthonitrile concentration was 0.02 M, and curved dilution plots were obtained; cf. ref 8. Addition of 0.01 M of 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide,[22] an

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[20] Since the ^{1}H NMR spectra of **10**, **13**, and **15** show quite different chemical shifts for the protons of each CH$_2$ group, we considered using these chemical shifts to distinguish between five- and six-membered ether rings. However, these protons are too far from the benzene ring (from models and X-ray structure of **10**) for ring-current effects to be significant. We thank Dr. M. J. McGlinchey for discussion of this point.

[21] The naphthonitrile lifetimes in benzene are shorter than would have been expected from the trend observed by Ware (ref 5b).

[22] E. F. Ullman and P. Singh, *J. Am. Chem. Soc.*, 94, 5077 (1972).

Table II. Limiting Quantum Yields and Exciplex Lifetimes for Naphthonitrile–TME Exciplexes

exciplex	solvent	emission max, nm	$\Phi_{\mathrm{lim}}{}^{\mathrm{A}}$ [a]	$\Phi_{\mathrm{lim}}{}^{\mathrm{F}}$ [a]	τ_{lim}, ns[a]
1-NN–TME[b]	hexane	372		0.05	3.75 (3.31)[c]
	benzene	403	0.14	0.094	10.4
	dimethoxyethane	435		0.05	12.6
2-Me-1-NN–TME	benzene	391	0.02	0.17	13.8
	ethyl acetate	424			15.0
4-Me-1-NN–TME	benzene	392	0.51	0.08	6.2
	ethyl acetate	424	0.19		11.2
6-Me-1-NN–TME	benzene	392	0.28	0.12	9.8
	ethyl acetate	424			12.5
1-NN-DMCP[b,d]	hexane	382		0.058	5.01 (5.75)[a]
	benzene	408		0.13	16.2

[a] Measured at 22 °C and at a TME concentration that quenched 96% of naphthonitrile fluorescence; realistic errors are Φ^{A}, ±15%; Φ^{F}, ±20%; τ, ±5%. [b] Data from R. C. Miller, Ph.D. Thesis, McMaster University, 1978. [c] Data of Ware et al.[4a] [d] 1,2-Dimethylcyclopentene.

effective triplet quencher, gave linear dilution plots, with derived $K_{\mathrm{SV}} = 10.1\ \mathrm{M}^{-1}$. This indicates that triplet decomposition of cyclobutane product **4** was a problem. It was noted also that 0.02 M naphthonitrile gives a high absorbance at 313 nm, and this could lead to local depletion of naphthonitrile and buildup of product **4**. Thus, the quantum yields were measured at 10^{-3} M naphthonitrile, which gave the plot in Figure 3, without triplet quencher. The values used in this plot are probably very close to the true quantum yields for the reaction.

Note that $\Phi_{\mathrm{lim}}{}^{\mathrm{A}}$ can be obtained from the intercept of Figure 3. For the other naphthonitriles, complete dilution plots were not obtained, but $\Phi_{\mathrm{lim}}{}^{\mathrm{A}}$ was determined from a single quantum yield at TME concentration sufficient to quench >95% of the naphthonitrile fluorescence. This quantum yield is a fair approximation to $\Phi_{\mathrm{lim}}{}^{\mathrm{A}}$ (see below), and values obtained are given in Table II.

Exciplex Fluorescence. Limiting Lifetimes and Quantum Yields. All these naphthonitriles show red-shifted exciplex fluorescence on quenching with TME. The emission is at shorter wavelength than that of the 1-naphthonitrile–TME exciplex[3-5] (Table II), showing that the exciplex is destabilized by methyl substitution.

Quantum yields of exciplex fluorescence were measured at TME concentrations that quenched >95% of monomer (naphthonitrile) fluorescence. These quantum yields ($\Phi_{\mathrm{lim}}{}^{\mathrm{F}}$) represent the limiting quantum yields for exciplex fluorescence. They are used in the derivation of rate constants for exciplex decay and are given in Table II.

Fluorescence lifetimes for the exciplexes were also measured at high TME concentration. The decays were all single exponential, and it can readily be shown that the lifetime $(\tau_{\mathrm{lim}}) = (k_{\mathrm{a}} + k_{\mathrm{d}}' + k_{\mathrm{f}}')^{-1}$, where $k_{\mathrm{a}}, k_{\mathrm{d}}'$, and k_{f}' are the rate constants of cycloaddition, radiationless decay, and fluorescence, respectively, from the exciplex (see Appendix 1).

Mechanism of Cycloaddition. The Exciplex as Intermediate. Exciplexes have long been considered as intermediates in photochemical reactions.[8,9a,23] However, much of the evidence was indirect, since in many cases the exciplex did not emit.[8,23] Caldwell used chemical quenchers to show that exciplex fluorescence and cycloaddition from 9-cyanophenanthrene–styrene derivatives were quenched to the same extent.[6] This meant that the fluorescent exciplex, or a species in equilibrium with it, was an intermediate in the cycloaddition. Lewis carried out a similar experiment with 1-naphthonitrile and 1,2-dimethylcyclopentene.[24] Because of the rapid reversibility of 1-naphthonitrile–TME exciplex formation at ambient temperatures,[4,5] a meaningful experiment depended on selective quenching of the exciplex, but not the naphthonitrile, fluorescence. Several quenchers were investigated, such as fumaronitrile, but none proved to be completely satisfactory. We therefore decided to work in the low-temperature region,[5] where exciplex formation is irreversible, and at limiting TME concentration (96% quenching of naphthonitrile singlet by TME). Under these conditions, the classical quencher biacetyl should effectively intercept the exciplex. Biacetyl is well-known to quench many triplets[25] and singlets[26] by collisional energy transfer, although it has apparently not been used to quench exciplexes.[27]

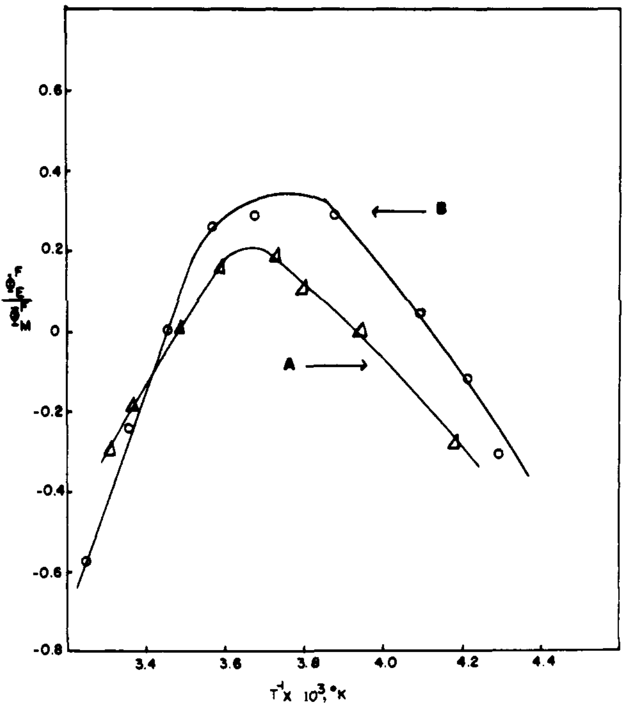

Figure 4. Temperature dependence of exciplex:monomer fluorescence ratio in ethyl acetate: (A) 4-Me-1-NN-TME; (B) 2-Me-1-NN-TME.

The temperature range of irreversible complexing for the 4-methyl- and 2-methyl-1-naphthonitrile–TME exciplexes in ethyl acetate was determined from plots of $\ln(\Phi_{\mathrm{E}}{}^{\mathrm{F}}/\Phi_{\mathrm{NN}}{}^{\mathrm{F}})$ vs. $1/T$, which are shown in Figure 4. These plots are often used in kinetic analyses,[28] and the curves in Figure 4 are typical. For 4-methyl-1-NN, the irreversible range is below −5 °C, while the +5 °C exciplex formation is in the "fast equilibrium" range (see Appendix 2).

The quenching experiments were carried out with 4-methyl-1-naphthonitrile, 1 M TME in ethyl acetate, at −14.5 °C. Biacetyl concentration was 4.3×10^{-3} M. The exciplex fluorescence was

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(23) P. P. Wells and H. Morrison, *J. Am. Chem. Soc.*, **97**, 154 (1975), and references therein; see also bibliography in ref 6–8.

(24) F. D. Lewis and B. Holman, III, *J. Phys. Chem.*, **84**, 2328 (1980).

(25) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960); **16** 958 (1962).

(26) (a) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, 39, 377 (1963); (b) J. T. Dubois and M. Cox, *ibid.*, **39**, 2536 (1963).

(27) Energy transfer should be diffusion controlled (singlet energies from fluorescence maxima are 67 and 62 kcal/mol for exciplex and biacetyl, respectively).

(28) (a) F. Meers, M. Van der Auweraer, and F. C. De Schryver, *J. Am. Chem. Soc.*, **102**, 4017 (1980); (b) M. Van der Auweraer, A. Gilbert, and F. C. De Schryver, *ibid.*, **102** 4007 (1980); (c) K. A. Zachariasse, W. Kuhnle, and A. Weller, *Chem. Phys. Lett.*, **59**, 375 (1978); (d) R. J. McDonald and B. K. Selinger, *Mol. Photochem.*, **3**, 99 (1971).

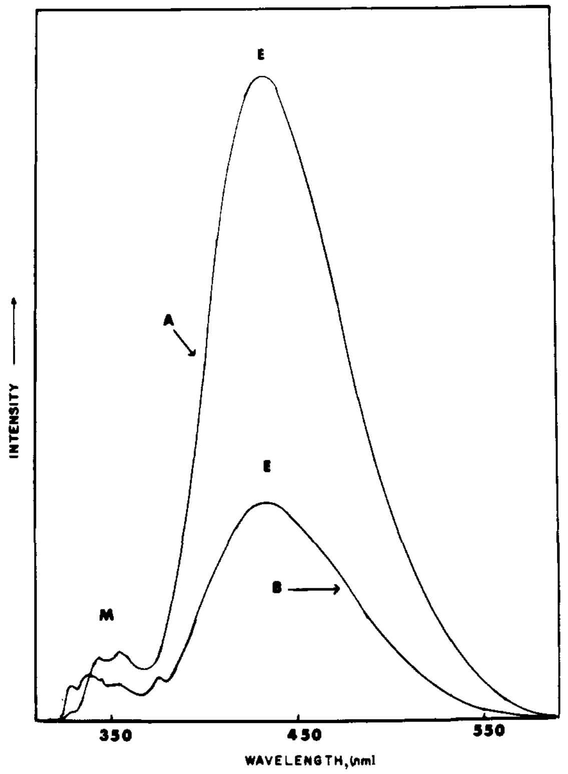

Figure 5. Quenching of 4-methyl-1-naphthonitrile–TME exciplex with biacetyl in ethyl acetate at −14.5 °C. Exciplex fluorescence (E) and residual monomer fluorescence (M) are visible. (A) Unquenched; (B) quenched by 4.3 × 10^{-3} M biacetyl. TME was 1 M,

quenched by a factor of 3 (see Figure 5). The ratio of quantum yields for cycloaddition (formation of **4**) under identical conditions, with and without biacetyl, was determined. The reaction was quenched by a factor of 2 by the biacetyl, and we conclude that the exciplex is an intermediate in the formation of **4**.

Quenching of the exciplex by biacetyl is close to diffusion controlled. The diffusion rate constant can be calculated from the Debye equation and the viscosity of ethyl acetate and compared with that obtained from quenching of exciplex fluorescence. The latter is 2.3 × 10^{10} M^{-1} s^{-1} (using an estimated lifetime of 20 ns at −15 °C), and the calculated $k_{diff} = 1.24 \times 10^{10}$ M^{-1} s^{-1}.

Since the exciplex lifetimes were measured at high (0.5–2.0 M) TME concentration, it was important to determine if the *exciplex* was quenched by TME, i.e., whether the following process was significant:

$$\underset{\text{exciplex}}{(\text{NN-TME})^*} + \text{TME} \rightarrow \text{NN} + 2\text{TME}$$

Thus, the exciplex lifetimes were measured for 2-methyl-1-naphthonitrile at 2.0 and 3.0 M TME in deoxygenated benzene, where the high olefin concentration should not change the solvent polarity. The lifetimes were 14.1 and 13.6 ns, respectively, showing that the above process is not important at the TME concentrations used.

Finally, to interpret the quantum yields (see Discussion) it was necessary to know if triplets were produced on decay of the exciplexes. This was done by using biacetyl phosphorescence as a triplet monitor. In a control experiment, 2-methyl-1-naphthonitrile (2.0 × 10^{-4} M in benzene) was found to sensitize biacetyl (1 × 10^{-4} M) phosphorescence (monitored at 520 nm).[26a] At this acceptor concentration, ~1% of naphthonitrile singlets were quenched. In the presence of 2.0 M TME, however, no phosphorescence at 520 nm could be detected. Again, quenching of the singlet exciplex was insignificant (see lifetimes in Tables I and II). Similarly, no phosphorescence was detected from a solution containing bichromophoric compound **1** (2.2 × 10^{-4} M in benzene) and biacetyl (1 × 10^{-4} M).

Fluorescence of the Bichromophoric Molecules. Fluorescence spectra of the three bichromophoric molecules, **1–3**, are shown in Figure 6. All three spectra show exciplex fluorescence, resembling the bimolecular complexes. The unsaturated chain quenches the monomer fluorescence (λ_{max} 340 nm) by a factor of 20. Thus, the spectra in Figure 6 are of low intensity.[29] The monomer fluorescence is also strongly quenched in benzene, but the exciplex emission is not well-resolved.

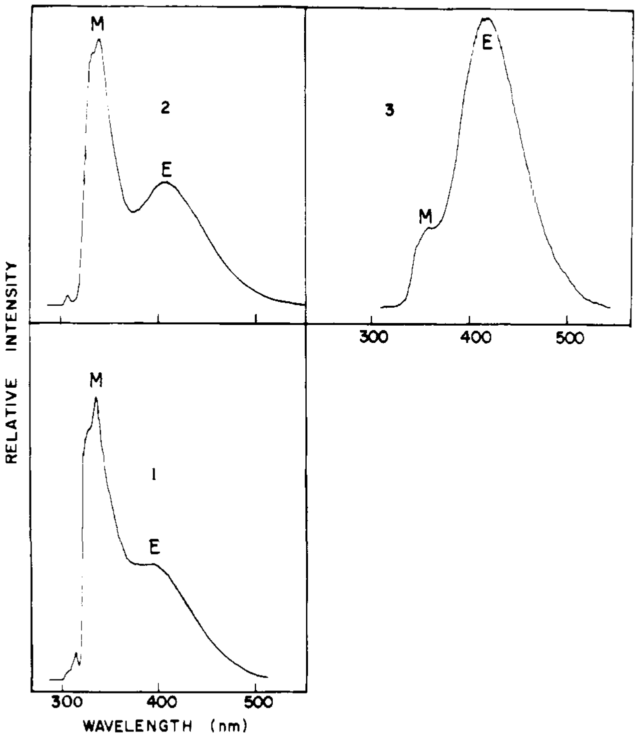

Figure 6. Fluorescence spectra of **1**, **2**, and **3** in ethyl acetate at 10^{-4} M monomer (M). Exciplex emission is visible with the latter at 418 (**1**), 428 (**2**), and 420 (**3**) nm.

Quantum yields in benzene for intramolecular addition are **1**, 0.69; **2**, 0.44; and **3**, 0.54 (formation of **10**, **13**, and **15**, respectively). Thus in the bichromophoric cases, cycloaddition is an important exciplex-decay pathway.

Discussion

Formation of cyclobutanes **4** and **5** was expected from previous experience with photoadditions of naphthonitriles[9] and other substituted naphthalenes.[9,10] Also, the limiting quantum yields for these additions are high, in the range 0.2–0.5 (Table II). Photoaddition of 2-methylnaphthonitrile (**6**) and TME differed in being less efficient ($\Phi_{lim}{}^{A} = 0.02$) and in the simultaneous formation of different products (Scheme IV). Formation of cyclobutane (**7**) is remarkable in that four quaternary centers are formed at once,[30] and the inefficiency is not surprising. Product **9** is interesting,[18] and may be formed in a concerted reaction, via electron transfer or by hydrogen abstraction from the TME.[31]

The intramolecular reactions of compounds **1–3** form an interesting comparison with the bimolecular cases. Reaction of **1** giving **10** involves addition of the TME chromophore mainly to the 1,2 bond of the naphthonitrile, as with 2-methylnaphthonitrile and TME. However, the quantum yield is much higher for the former (0.68 vs. 0.02). Also, intramolecular addition of **2** and **3**, where addition to the naphthonitrile 1,2 bond is restricted by the chain, gives **13** and **15**, respectively, with reasonable quantum yields (0.44 and 0.54). These products involve addition at the naphthonitrile 3,4 and 5,6 bonds, processes that are not observed in the bimolecular reactions.

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(29) (a) E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, 9, 393 (1971). (b) R. S. Davidson and K. R. Tretheway, *J. Chem. Soc., Chem. Commun.*, 827 (1976).

(30) TME dimerizes slowly on direct irradiation: D. R. Arnold and V. Y. Abraitys, *J. Chem. Soc., Chem. Commun.*, 1053 (1967).

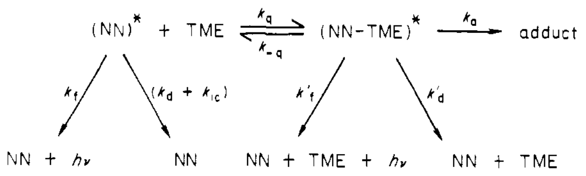
(31) This process has recently been observed by Lewis and co-workers: F. D. Lewis, personal communication.

Table III. Rate Constants for 1-Naphthonitrile-TME Exciplexes

naphthonitrile	solvent	k_q/k_{-q}, M^{-1}	$10^7k_f'$, s^{-1}	$10^7k_d'$, s^{-1}	$10^7k_a'$, s^{-1}
1-NN	hexane	4.80 (4.50)[a]	1.3[b,c]		
	benzene	44.2	0.90[b]		
	dimethoxyethane		0.40[b]		
2-Me-1-NN	benzene	12.6	1.2	5.9	0.15
	ethyl acetate	62.3			
4-Me-1-NN	benzene	10.6	1.3	6.7	8.2
	ethyl acetate	59.0			1.7
6-Me-1-NN	benzene	7.93	1.2	6.2	2.8
	ethyl acetate	48.0			

[a] Values at 25 °C from ref 5a. [b] From R. C. Miller, Ph.D. Thesis, McMaster University, 1978. [c] Temperatures in 22-24 °C range.

Scheme VII



It had been shown previously that linking with a saturated chain could facilitate excimer fluorescence[32,33] and intramolecular reactions.[12,34,35] Since exciplexes are apparently intermediate in these reactions (see Results), the chain could affect the addition reaction at two points: (a) in exciplex formation and/or (b) in exciplex collapse to product. In the remainder of the discussion we will consider the effect of linking and of methyl substitution on these two steps in the reaction.

Exciplex Formation. The studies of Ware and co-workers[4,5] have shown that for nonpolar and medium-polarity solvents, the processes summarized in Scheme VII are sufficient to describe the photokinetics of 1-naphthonitrile (NN) and TME. Our results are in agreement. In the case of methylnaphthonitriles, exciplex formation is also rapidly reversible above +5 °C; the exciplex does not decay to triplet naphthonitrile, and the exciplex is apparently an intermediate in the cycloaddition. Also, quenching of the exciplex by TME is unimportant in the 1-3 M TME range.

All the decay rate constants for 2-methyl- and 4-methyl-1-naphthonitrile-TME systems in benzene were derived by using steady-state data and lifetimes. Eq 1-5 were also used.

$$\Phi_0^F/\Phi^F = 1 + K_{SV}[\text{TME}] \qquad (2)$$

where

$$K_{SV} = \frac{k_q(k_f' + k_d' + k_a)\tau_0}{k_{-q} + k_f' + k_d' + k_a}$$

$$\Phi_{\text{lim}}^F = \frac{k_f'}{k_f' + k_d' + k_a} = k_f'\tau_{\text{lim}} \qquad (3)$$

$$\Phi_{\text{lim}}^A = \frac{k_a}{k_f' + k_d' + k_a} = k_a\tau_{\text{lim}} \qquad (4)$$

$$\Phi_0^F = \frac{k_f}{k_f + k_d} = k_f\tau \qquad (5)$$

$\Phi_E^F\Phi_M^F$ is the ratio of exciplex:NN fluorescence quantum yields. Also, Φ_{lim}^F and Φ_{lim}^A were determined from the intercepts of dilution plots (see eq 1). Note that $(k_f' + k_d' + k_a)$ is the single exponential decay constant for exciplex fluorescence at infinite [TME]. In practice, τ_{lim} was measured at >95% monomer quenching, so rate constants derived with eq 3 and 4 are approximate. However, τ_{lim} for hexane is close to the value determined in the complete kinetic analysis of the 1-NN-TME exciplex[4a] (see Table II). The exciplex-decay rate constants are given in Table III. Rate constants for exciplex formation (k_q and k_{-q}) could not be determined from the present data. The ratio k_q/k_{-q}, which approximates to an equilibrium constant in this temperature range (20-25 °C), was determined from the Stern-Volmer eq 2, the monomer and exciplex lifetimes were used. These ratios are also given in Table III.

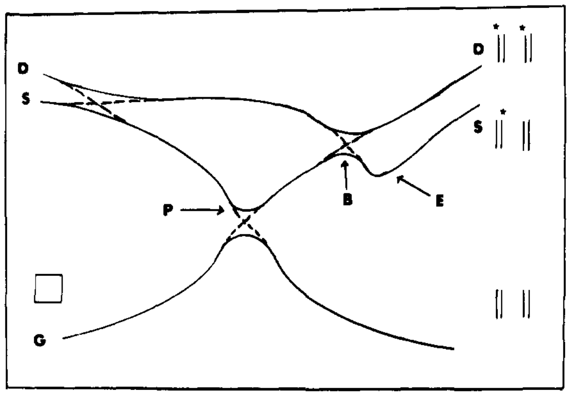


Figure 7. Energy vs. reaction coordinate for the 2 + 2 cycloaddition, showing the ground state (G), singly excited singlet (S), and double excited state (D). The fluorescent exciplex is at (E), and the pericyclic minimum is at P (from ref 41).

The ratios k_q/k_{-q} are apparently good measures of exciplex stability, since they parallel the wavelength shift in exciplex fluorescence (Table II) and show the expected trend on methyl substitution or change in solvent.[36] Note that the position of methyl substitution is unimportant, indicating there is little steric interference with exciplex formation.[37]

The fluorescence spectra of **1**, **2**, and **3** in ethyl acetate are shown in Figure 6. The monomer emission is approximately 95% quenched by the unsaturated side chain. Therefore, although the internal exciplexes are formed efficiently, their emission is weak[29] (except for **3**, where exciplex fluorescence intensity is similar to the bimolecular exciplexes). These spectra show that formation of the fluorescent exciplex does not require bonding of the TME unit at a specific ring position of the naphthonitrile, which is consistent with the absence of a steric effect on methyl substitution.[38]

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(32) For references to early work see: (a) F. C. De Schryver, N. Boens, J. Huybrechts, J. Daemen, and M. De Brackeleire, *Pure Appl. Chem.*, **49**, 237 (1977); (b) F. C. De Schryver, N. Boens, and J. Pat, *Adv. Photochem.*, **10**, 359 (1977).

(33) (a) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 3586 (1970); (b) K. A. Zachariasse, W. Kühnle, and A. Weller, *Chem. Phys. Lett.*, **59**, 375 (1978); (c) K. Zackariasse and W. Kühnle, *Z. Phys. Chem. (Wiesbaden)*, **101**, 267 (1976), and discussion therein.

(34) (a) E. A. Chandross and A. H. Schiebel, *J. Am. Chem. Soc.*, **95**, 611 (1973); (b) G. Kaupp and I. Zimmerman, *Angew. Chem., Int. Ed. Eng.*, **15**, 441 (1976); (c) A. Castellan, J.-P. Desvergne, and H. Bouas-Laurent, *Nouv. J. Chim.*, **3**, 231 (1979).

(35) Note that linking does not always increase reaction efficiency: W. R. Bergmark, G. Jones, II, T. E. Reinhardt, and A. M. Halpern, *J. Am. Chem. Soc.*, **100**, 6665 (1978).

(36) F. D. Lewis and C. E. Hoyle, *J. Am. Chem. Soc.*, **99**, 3779 (1977), and references therein.

(37) Steric effects on fluorescence quenching have not been extensively investigated: (a) P. M. Froehlich and H. A. Morrison, *J. Am. Chem. Soc.*, **96**, 332 (1974); (b) M. Irie, T. Yorozu, and K. Hayashi, *ibid.*, **100**, 2237 (1978).

Table IV. Selected Interatomic Distances and Angles

		Distance, Å			
C(1)-C(2)	1.521 (4)	C(2)-O(3)	1.427 (3)	O(3)-C(4)	1.425 (4)
C(4)-C(5)	1.529 (4)	C(5)-C(1)	1.586 (3)	C(5)-C(6)	1.575 (4)
C(6)-C(7)	1.592 (3)	C(7)-C(1)	1.581 (3)	C(7)-C(8)	1.524 (3)
C(8)-C(9)	1.394 (3)	C(9)-C(10)	1.457 (4)	C(10)-C(11)	1.317 (4)
C(11)-C(1)	1.479 (3)	C(9)-C(12)	1.390 (4)	C(12)-C(13)	1.377 (5)
C(13)-C(14)	1.371 (4)	C(14)-C(15)	1.386 (4)	C(15)-C(8)	1.389 (4)
C(5)-C(19)	1.521 (4)	C(6)-C(17)	1.533 (3)	C(6)-C(18)	1.520 (4)
C(7)-C(16)	1.465 (3)	C(16)-N(16)	1.141 (3)	C(2)-H(2a)	0.98 (3)
C(2)-H(2b)	1.01 (3)	C(4)-H(4a)	1.01 (3)	C(4)-H(4b)	1.01 (2)
C(10)-H(10)	0.97 (2)	C(11)-H(11)	0.97 (3)	C(12)-H(12)	0.99 (3)
C(13)-H(13)	0.96 (3)	C(14)-H(14)	0.99 (3)	C(15)-H(15)	0.99 (2)
C(17)-H(17a)	1.04 (3)	C(17)-H(17b)	1.00 (3)	C(17)-H(17c)	1.00 (3)
C(18)-H(18a)	0.99 (2)	C(18)-H(18b)	0.97 (3)	C(18)-H(18c)	0.97 (3)
C(19)-H(19a)	0.99 (3)	C(19)-H(19b)	1.03 (3)	C(19)-H(19c)	0.99 (4)
		Angle, deg			
C(5)-C(1)-C(2)	103.3 (2)	C(5)-C(1)-C(7)	90.2 (2)	C(5)-C(1)-C(11)	117.4 (2)
C(2)-C(1)-C(7)	115.2 (2)	C(2)-C(1)-C(11)	113.8 (2)	C(7)-C(1)-C(11)	114.5 (2)
C(1)-C(2)-O(3)	105.7 (2)	C(1)-C(2)-H(2a)	112 (2)	C(1)-C(2)-H(2b)	113 (1)
O(3)-C(2)-H(2a)	110 (1)	O(3)-C(2)-H(2b)	107 (1)	H(2a)-C(2)-H(2b)	109 (2)
C(2)-O(3)-C(4)	104.7 (2)	O(3)-C(4)-C(5)	106.5 (2)	O(3)-C(4)-H(4a)	109 (1)
O(3)-C(4)-H(4b)	111 (1)	C(5)-C(4)-H(4a)	111 (1)	C(5)-C(4)-H(4b)	114 (2)
H(4a)-C(4)-H(4b)	107 (2)	C(4)-C(5)-C(1)	102.2 (2)	C(4)-C(5)-C(6)	115.6 (2)
C(4)-C(5)-C(19)	111.1 (3)	C(1)-C(5)-C(6)	90.1 (2)	C(1)-C(5)-C(19)	118.2 (2)
C(6)-C(5)-C(19)	117.5 (2)	C(5)-C(6)-C(7)	90.2 (2)	C(5)-C(6)-C(17)	115.5 (2)
C(5)-C(6)-C(18)	114.2 (2)	C(7)-C(6)-C(17)	114.3 (2)	C(7)-C(6)-C(18)	113.1 (2)
C(17)-C(6)-C(18)	108.8 (2)	C(6)-C(7)-C(8)	116.0 (2)	C(6)-C(7)-C(1)	89.6 (2)
C(6)-C(7)-C(16)	113.1 (2)	C(8)-C(7)-C(1)	116.8 (2)	C(8)-C(7)-C(16)	107.8 (2)
C(1)-C(7)-C(16)	112.8 (2)	C(7)-C(8)-C(9)	120.4 (3)	C(7)-C(8)-C(15)	120.3 (2)
C(9)-C(8)-C(15)	119.3 (2)	C(8)-C(9)-C(10)	120.3 (2)	C(8)-C(9)-C(12)	118.9 (3)
C(10)-C(9)-C(12)	120.8 (2)	C(9)-C(10)-C(11)	123.1 (2)	C(9)-C(10)-H(10)	117 (2)
C(11)-C(10)-H(10)	120 (2)	C(10)-C(11)-C(1)	124.5 (3)	C(10)-C(11)-H(11)	118 (1)
C(1)-C(11)-H(11)	148 (1)	C(9)-C(12)-C(13)	121.5 (3)	C(9)-C(12)-H(12)	116 (2)
C(13)-C(12)-H(12)	123 (2)	C(12)-C(13)-C(14)	119.5 (3)	C(12)-C(13)-H(13)	121 (1)
C(14)-C(13)-H(13)	119 (1)	C(13)-C(14)-C(15)	120.2 (3)	C(13)-C(14)-H(14)	120 (1)
C(15)-C(14)-H(14)	120 (1)	C(14)-C(15)-C(8)	120.6 (3)	C(14)-C(15)-H(15)	121 (2)
C(8)-C(15)-H(15)	118 (2)	C(7)-C(16)-N(16)	178.4 (3)	C(6)-C(17)-H(17a)	112 (2)
C(6)-C(17)-H(17b)	111 (2)	C(6)-C(17)-H(17c)	110 (2)	H(17a)-C(17)-H(17b)	110 (2)
H(17a)-C(17)-H(17c)	109 (3)	H(17b)-C(17)-H(17c)	105 (3)	C(6)-C(18)-H(18a)	111 (2)
C(6)-C(18)-H(18b)	113 (2)	C(6)-C(18)-H(18c)	110 (1)	H(18a)-C(18)-H(18b)	109 (2)
H(18a)-C(18)-H(18c)	105 (2)	H(18b)-C(18)-H(18c)	108 (2)	C(5)-C(19)-H(19a)	112 (2)
C(5)-C(19)-H(19b)	111 (2)	C(5)-C(19)-H(19c)	110 (2)	H(19a)-C(19)-H(19b)	110 (2)
H(19a)-C(19)-H(19c)	109 (3)	H(19b)-C(19)-H(19c)	105 (2)		

Exciplex Decay Processes. The first-order rate constants for exciplex decay are given in Table III, and the processes involved are given in Scheme I. The radiative rate constants (k_f') are independent of methyl substitution of the naphthonitrile[39] but decrease with increasing solvent polarity.[36] Reactivity in photoadditions has recently been discussed theoretically.[40,41] The rate constants of greatest chemical interest are k_a and k_d', and these can be interpreted by using the Michl model.[41] The energy profiles shown in Figure 7 are derived from calculations, but recent experimental work is consistent with the model.[6,7,36,39] In the reaction profile for cycloaddition, the fluorescent exciplex (E), which is polar, is formed initially. There is an energy barrier (B) that the system must cross to reach the pericyclic minimum (P), and after crossing to the ground-state surface at (P), either collapse to product or dissociation to reactants can occur. The transition state (B) and minimum (P) are less polar than the exciplex.

The results in Table III are consistent with this picture. Rate constant k_a is smaller in ethyl acetate than in benzene for the 4-methylnaphthonitrile–TME exciplex. Comparison of k_a and k_d' for 4-methyl- and 2-methylnaphthonitrile systems is interesting. The sum ($k_a + k_d'$) is 14.9×10^7 and 6.05×10^7 s^{-1}, respectively. The ratios k_a/k_d' are 1.22 and 0.025, respectively. Thus, the *o*-methyl group has little effect on the activation energy (B) or on exciplex formation (see above), but it retards the formation of addition product from the minimum (P).

Although individual rate constants for the intramolecular exciplexes were not determined, some comments can be made, based on products formed and quantum yields. Linking with the three-atom chain significantly favors collapse of the exciplex to the cyclobutane product. With **2** and **3**, intramolecular addition occurs at ring positions not observed in the bimolecular cases, giving **13** and **15** with quite high quantum yields (0.44 and 0.54, respectively). Presumably pericyclic minima are involved that are not reached in the bimolecular reactions. In the case of **1**, the pericyclic minimum can have a geometry similar to the bimolecular reaction (giving **7**), yet the quantum yield for **1** (0.68) is much higher than for adduct **7** ($\Phi_{\lim} = 0.02$). The way in which the linking chain influences exciplex decay is an interesting problem that should be studied further.

Description of Structural Photoproduct 10. The structure of the tricyclic ring system of **10** showed some interesting features, which are described. The molecule is illustrated in Figure 1 and bond distances and angles are given in Table IV. Bond lengths within the naphthalenic portion of the molecular agree well with those found previously by us in a similar structure.[42] In particular,

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[38] R. A. Caldwell has pointed out (*J. Am. Chem. Soc.*, **100**, 2905 (1978)) that entropies of exciplex formation are in the −13 to −20-eu range, which does not suggest a particularly ordered structure. One should be cautious in generalizing from entropy data. Entropies of exciplex formation (e.g., B. Stevens, *Adv. Photochem.*, **8**, 188 (1971)) are often in the above range, but entropies of ground-state complex formation are often less negative (R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, 1969, pp 191, 210). Also, entropies of formation of 1-NN-dimethylcyclopentene exciplex are as low as −23.0 eu.[5a]

[39] Compare the exciplexes formed by substituted 9-cyanophenanthrenes: R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, **100**, 2905 (1978).

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

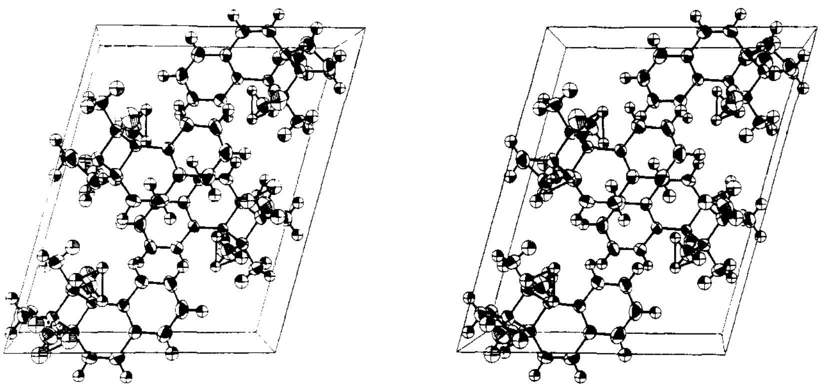

Figure 8. Packing of the molecules in the unit cell. *a* and μ^* are parallel to the bottom and side of the page, respectively, and the view is down *b*.

the bond lengths in the benzene ring agree well with those obtained for benzene.[43] The olefinic bond, C(10)–C(11), is shorter than in ethylene (1.317 (4) vs. 1.332 (2) Å[44]) and is apparently not conjugated with the benzene ring as shown by the C(9)–C(10) single bond (1.457 (4) Å) and the non-zero C(8)C(9)C(10)C(11) torsional angle of 2.5 (2)° (Table V). The cyclobutane ring is planar (Table IV), as is commonly found in fused ring systems,[45] and thus differs from the structurally similar compound we examined previously, where the dihedral fold angle was 21°.[42] This may be caused by the additional steric constraints of the fused tetrahydrofuran ring in the present compound. One feature of the present structure, also observed by Bowman et al.,[42] is that the bond lengths in the cyclobutane ring are significantly longer (1.575 (4) to 1.592 (3) Å) than the average value of 1.551 (3) Å for organic fused cyclobutanes calculated by Cotton and Frenz.[45] Values as large have been observed previously, but generally involve large errors; more accurate structures have smaller values. The large bond lengths suggest greater strain than usual in the cyclobutane ring.

Tetrahydrofuran (THF) is a very flexible molecule and can exist in a number of conformations. Here, however, the steric requirements imposed by the planar cyclobutane ring force the four-carbon fragment of the THF ring to be planar (torsion angle 1.0 (2)°) and thus the O atom is bent out of this plane (C(1)C(2)C(4)C(4)–C(2)O(3)C(4), dihedral angle 40.6 (2)°). A similar conformation has been observed previously (dihedral angles 40[46] and 39°[47]). The C–O bond lengths within the tetrahydrofuran fragment are almost identical with the values in gaseous THF (1.427 (3), 1.425 (4) Å vs. 1.428 Å[48]). There are differences in the C–C distances, however, since the long C(1)–C(5) distance (1.586 (3) Å) results in shorter C(4)–C(5) (1.529 (4) Å) and C(1)–C(2) (1.521 (4) Å) distances compared to 1.536 Å in gaseous THF. The average (1.545 Å) is close to and larger than the value for THF, as would be expected.[49]

The packing of the molecules in the crystal is shown in Figure 8. The molecules form columnar stacks at $x = {}^1/_2, y = 0$ and $x = {}^1/_2, y = {}^1/_2$, the naphthalenic section of one molecular partially overlapping similar sections of centrosymmetrically related molecules above and below along the *b* direction. The overlap is not sufficient enough, however, to give substantial π–π interactions between molecules. The naphthalenic planes of the adjacent stacks along *c* are canted with respect to each other, the dihedral angle being 136.4 (2)° (Table IV). Interactions between the stacks in the *a* and *c* direction are van der Waals.

Table V. Best Planes and Dihedral and Torsional Angles

plane	distance of atoms from plane, Å
1, C(8)C(9)C(12)C(13)C(14)C(15)	C(8) 0.017(3); C(9) −0.005 (3); C(12) −0.010 (3); C(13) 0.014; C(14) 0.000 (3); C(15) −0.013 (3)
2, C(5)C(1)C(6)C(7)	C(5) 0.006 (3); C(6) −0.005 (3); C(7) 0.004 (2); C(1) −0.006 (3)
3, C(2)C(1)C(5)C(4)	C(2) −0.004 (3); C(1) 0.005 (3); C(5) −0.005 (3); C(4) 0.004 (3)
4, C(2)C(4)O(3)	
5, C(1)C(7)C(8)C(9)C(10)C(11)	C(1) 0.013 (3); C(7) 0.009 (2); C(8) −0.035 (3); C(9) 0.028 (3); C(10) 0.004 (3); C(11) −0.029 (3)

Dihedral Angles, deg

plane 1–plane 5 3.6 (2); plane 5–plane 2 117.7 (2); plane 2–plane 3 63.8 (2); plane 3–plane 4 40.6 (2); plane 1–plane 1′ = (2)
(1′ is related to 1 by 2_1)

Torsional Angles, deg

C(1)C(7)C(8)C(9)	4.8 (3)	C(1)C(2)O(3)C(4)	41.1 (2)
C(7)C(8)C(9)C(10)	−6.2 (3)	C(2)O(3)C(4)C(5)	−41.1 (2)
C(8)C(9)C(10)C(11)	2.5 (2)	O(3)C(4)C(5)C(1)	23.7 (2)
C(9)C(10)C(11)C(1)	2.9 (2)	C(4)C(5)C(1)C(2)	1.0 (2)
C(10)C(11)C(1)C(7)	−3.9 (2)	C(5)C(1)C(2)O(3)	−25.2 (2)
C(11)C(1)C(7)C(8)	0.0 (2)		
		C(1)C(5)C(6)C(7)	−0.9 (2)
		C(5)C(6)C(7)C(1)	0.9 (2)
		C(6)C(7)C(1)C(5)	−0.9 (2)
		C(7)C(1)C(5)C(6)	0.9 (2)

Experimental Section

Materials. All solvents were reagent grade and were distilled before use. Benzene was carefully fractionated to remove water. Tetrahydrofuran was freshly distilled from sodium and benzophenone before use.

Tetramethylethylene was obtained either from Aldrich (Gold Label 99+% grade) or from the Fairfield Chemical Co. It was distilled through a short Vigreux column prior to use; bp 73 °C. For quantiative work, tetramethylethylene was chromatographed on basic alumina (I.C.N. Pharmaceuticals, activity 1) immediately before use.

1-Bromo-2-methylnaphthalene, 1-bromo-4-methylnaphthalene, *N*-methylpyrrolidinone, 2-furoic acid, 2,3-dimethyl-1,3-butadiene, and ethyl 2-bromopropionate were obtained from Aldrich.

CH_3OD was prepared by the method of Streitwieser and co-workers.[51] Dimethyl carbonate was obtained from BDH Ltd.

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Photochemical and Analytical Methods. All irradiations were done under argon (Canadian Liquid Air, certified grade) in either a Srinivasan–Griffin photochemical reactor (Rayonet) with RPR 3000-Å type lamps or with a Hanovia Type L 450-W mercury vapor lamp in a quartz water-cooled immersion well.

Column chromatography was performed on silica gel (Baker Analyzed Reagent grade, 60–200 mesh), Fisher grade 923 (100–200 mesh), or Macherey, Nagel and Co. (MN Kiesel gel G). The chromatographic technique of Still and co-workers[52] required the use of Merck silica gel 60 (30–230 mesh). All columns were dry-packed and were 6 in. long. The diameter of the column depended upon the weight of the material to be chromatographed.

Analytical vapor-phase chromatography (VPC) was performed on a Varian-Aerograph series 200 or a Tracor 560 dual column instrument with flame-ionization detectors. The column used on the Varian instrument was 5 ft × $^1/_8$ in. of 5% SE-30 on 60/80 Chromosorb W. The Tracor instrument was used with (a) 6 ft × $^1/_4$ in. column of 3% OV-1 on Chromosorb WHP or (b) 4 × $^1/_4$ in. column of 3% OV-1 on Chromosorb WHP. The flow rate of the carrier gas (helium) was 45–55 mL/min. Integration of VPC peak areas was carried out by using a Varian Aerograph Model 485 electronic digital integrator.

Preparative VPC was performed on an Aerograph Model 200 dual column instrument with thermal conductivity detectors. A helium flow rate of ca. 50 mL/min was used with 7 ft × $^1/_4$ in. of 15% SE-30 on Chromosorb W.

For high-pressure liquid chromatography, a system with a single 2000-psi pump was used. The detection system was a fixed wavlength (254 nm) ultraviolet monitor. "Reverse-phase" chromatography was used with 95% methanol/water on a Whatman Magnum-90DS-2 9.0 × 500 mm column with 10-μm packing and a guard column.

The nuclear magnetic resonance (NMR) spectra were obtained with a Varian EM-390 or a Bruker WH-90 FT spectrometer. Chemical shifts (δ) are reported as ppm downfield from tetramethylsilane as internal standard. Mass spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer with spectral grade chloroform as solvent. Ultraviolet spectra were run on a Cary 14 spectrophotometer.

Fluorescence spectra were taken on an Aminco Bowman spectrofluorimeter utilizing a Hanovia 200-W mercury–xenon lamp. Melting points were measured on a Kofler hot stage and are reported uncorrected. Microanalyses were determined by Galbraith Laboratories, Inc.

2-Methyl-1-naphthonitrile. 1-Bromo-2-methylnaphthalene (38.4 g, 0.174 mol) and cuprous cyanide (18.6 g, 0.209 mol) were added to 90 mL of *N*-methylpyrrolidinone. The solution was stirred and refluxed under nitrogen for 3 h, cooled slightly, and carefully poured into 400 mL of benzene and 200 mL of 20% aqueous sodium cyanide. The resulting mixture was filtered through Celite, and the aqueous layer was washed with 100 mL of benzene. The combined benzene extracts were washed with 200 mL of 10% aqueous sodium cyanide and 200 mL of water, dried (Na_2SO_4), and concentrated to give a dark brown solid. Chromatography on Baker 60-200 mesh silica gel (9 × 9 cm) with ether as eluent gave 1900 mL, which was concentrated to give a light brown solid. Recrystallization from 60–110 °C petroleum ether with charcoal treatment yielded white needles: 16.2 g (55%); mp 87–88 °C (lit.[53] 87–88 °C); NMR ($CDCl_3$) δ 2.68 (m, 6 H); IR ($CHCl_3$) 2220 cm^{-1} (CN).

4-Methyl-1-naphthonitrile. 4-Methyl-1-naphthonitrile was prepared similarly from 1-bromo-4-methylnaphthalene (7.3 g, 0.033 mol) and cuprous cyanide (5.4 g, 0.06 mol). Recrystallization from 60–110 °C petroleum ether yielded 2.55 g (46%) of white needles: mp 53–54 °C (lit.[54] 53–54 °C); NMR ($CDCl_3$) δ 2.73 (s, 3 H), 7.2–8.3 (m, 6 H); IR ($CHCl_3$) 2220 cm^{-1} (CN).

6-Methyl-1-naphthamide. 6-Methyl-1-naphthoic acid[16] (13 g, 0.07 mol) was stirred and refluxed in 52 mL of thionyl chloride for 5 h. The thionyl chloride was distilled, and the remaining liquid was cooled in ice. Concentrated NH_4OH (200 mL) was added, and the mixture was warmed to room temperature. After 40 min, the resulting brown solid was collected and washed with 200 mL of water. Initial purification by vacuum sublimation at 170 °C gave 7.7 g of a pale yellow solid. Recrystallization from 40 mL of benzene and 200 mL of absolute ethanol gave white needles: 4.75 g (37%); mp 212–214 °C; NMR (acetone-d_6) δ 2.47 (s, 3 H), 2.76 (br s, 2 H), 7.3–7.9 (m, 5 H), 8.12 (b d, 1 H); IR (KBr disk) 3380, 3180, 1648, 1618 cm^{-1}; mass spectrum, *m/e* 185 (M^+). Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.60. Found: C, 77.81; H, 6.13; N, 7.39.

6-Methyl-1-naphthonitrile. Tosyl chloride (4.7 g, 0.025 mol) was added portionwise to a mixture of 6-methyl-1-naphthamide (4.5 g, 0.024 mol) and dry pyridine (10 mL). The mixture was stirred and gently refluxed for 24 h and cooled, and 50 mL of H_2O was added. The aqueous mixtue was extracted with ether (2 × 50 mL). The combined ether extracts were washed with 10% aqueous HCl (2 × 50 mL) and saturated $NaHCO_3$ (2 × 50 mL), dried (Na_2SO_4), and concentrated to give 3.9 g of crude nitrile. Recrystallization from 60–110 °C petroleum ether gave colorless needles: mp 67.5–68.0 °C, 2.8 g (69%); NMR ($CDCl_3$) δ 2.52 (3 H), 7.3–8,2 (m, 6 H); IR ($CHCl_3$) 2220 cm^{-1} (CN); mass spectrum, *m/e* 167 (M^+). Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.38; H, 5.48; N, 8.24.

Photoaddition of 2-Methyl-1-naphthonitrile and Tetramethylene in Benzene. A. Irradiation in the Rayonet Reactor. 2-Methyl-1-naphthonitrile (0.585 g, 3.5 mmol) and tetramethylethylene (6.318 g, 0.075 mol) in benzene (50 mL) were degassed by three freeze–pump–thaw cycles and sealed in Pyrex. The sample was irradiated for 68 h with ten RPR-3000 lamps. Analysis on 5 ft × $^1/_4$ in. 5% SE-30 Chromosorb W at 180 °C showed three peaks with retention times of 9.0, 14.0, and 15.0 min, corresponding to **7**, **9**, and **8**, respectively. Upon standing, the peak corresponding to **9** disappeared, with a concomitant increase in the peak corresponding to **8**. In this run, approximately 70% of 2-methyl-1-naphthonitrile was unreacted. Adducts **7** and **8** were isolated from the mixture by preparative VPC on 7 ft × $^1/_4$ in. 15% SE-30 on Chromosorb W at 177 °C. The compound with the lowest retention time was an oil, which declined to crystallize. Analytical VPC showed one peak corresponding to the photoproduct **7**. It also showed a parent ion of *m/e* 251.1674, corresponding to $C_{18}H_{21}N$. On the basis of its NMR and IR spectra, the adduct was assigned the structure 6,7,7,8,8-pentamethyl-2,3-benzobicyclo[4.2.0]-2,4-octadiene (**7**): ^1H NMR ($CDCl_3$) δ 0.79, 0.96, 1.20, 1.30 (S, 3 H each, CH_3 group), 5.71 and 6.29 (d, J = 10.2 Hz, 1 H each, vinylics), 7.00–7.22 (m, 4 H, aromatics); IR ($CHCl_3$) 2225 cm^{-1} (CN).

1-(2′,3′-Dimethyl-1-buten-3-yl)-3-methyl-4-cyano-1,2-dihydronaphthalene (**8**) was isolated as an oil. Trituration (30–60 °C petroleum ether) gave colorless crystals: mp 101–102 °C; mass spectrum, *m/e* 251 (M^+). Anal. Calcd for $C_{18}H_{21}N$: C, 86.02; H, 8.42; N, 5.57. Found: C, 85.86; H, 8.31; N, 5.77.

B. Irradiation through Corex. 2-Methyl-1-naphthonitrile (1.01 g, 0.006 mol) and tetramethylethylene (8.0 g, 0.095 mol) in benzene (400 mL) were irradiated under a blanket of argon with a Hanovia 450-W lamp through Corex for 15.5 h. The benzene was removed, and analysis of the residue on 5 ft × $^1/_8$ in. 5% SE-30 on Chromosorb W at 180 °C showed one major peak corresponding to **8**. In this run, approximately 25% of the 2-methyl-1-naphthonitrile was unreacted. Trituration of the residue with 30–60 °C petroleum ether at 0 °C gave a solid. Recrystallization from 60–110 °C petroleum ether gave 0.341 g of colorless needles; mp 101–102 °C. The mother liquor was chromatographed on a 3 × 58 cm column of silica gel (Fisher grade 923, 100–200 mesh). Elution was with 20% 30–60 °C petroleum ether in CCl_4, and 25-mL portions were collected. Fractions 9 and 10 contained **8**. Fractions 11–17 contained **8** and 2-methyl-1-naphthonitrile. The solid from fractions 9 and 10 was recrystallized from 60–110 °C petroleum ether to give 0.111 g; mp 101–102 °C. The total yield of **8** was 0.452 g (30%).

Structural Evidence for 1-(2,3-Dimethyl-1-buten-3-yl)-3-methyl-4-cyano-1,4-dihydronaphthalene (9). 2-Methyl-1-naphthonitrile (0.996 g, 6 mmol) and tetramethylethylene (8.02 g, 0.095 mol) in benzene (400 mL) were irradiated under argon with a Hanovia 450-W lamp (Corex filter) for 23 h. A 10-mL aliquot was removed and the benzene evaporated. The NMR and IR spectra were taken immediately. The NMR spectrum ($CDCl_3$) indicated that **8** was not present in appreciable quantity. Multiplets of equal area were detected at δ 3.50 and 5.80. The IR ($CHCl_3$) showed a band at 2242 cm^{-1}. After the spectra were obtained, VPC analysis of the product mixture on 6 ft × $^1/_4$ in. of 3% OV1 on Chromosorb WHP at 180 °C showed peaks due to **9** (70%) and **8** (21%). All glassware used in this experiment was acid washed and dried.

Deuterium Exchange of 1-(2,3-Dimethyl-1-buten-3-yl)-3-methyl-4-cyano-1,2-dihydronaphthalene (8). Methanol-*d* (10 mL) 0.1 g sodium, and **8** (0.096 g) were stirred under reflux for 17 h. The methanol was removed, and 5 mL D_2O was added. The aqueous fraction was extracted with ether (2 × 10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated to give a yellow oil: NMR ($CDCl_3$) δ 0.78 and 0.97 (s, 3 H each), 1.80 (b s, 3 H), 2.93 (s, 1 H), 4.80 and 4.90 (m, 1 H each), 7.1–7.5 (m, 4 H); see also Scheme IV.

Dehydrogenation of 1-(2,3-Dimethyl-1-buten-3-yl)-3-methyl-4-cyano-1,2-dihydronaphthalene (8). A mixture of **8** (0.17 g) and 0.15 g of 10% palladium on charcoal in 15 mL of *p*-xylene was refluxed for 6 days. The catalyst was filtered, and the solution was concentrated to give an oil. VPC analysis on 6 ft × $^1/_4$ in. of 3% OV-1 on Chromosorb WHP at 180 °C indicated that 90% of **8** had reacted. Two major products were observed. The first had a retention time of 144 s, which was identical with that of authentic 2-methyl-1-naphthonitrile. The second product

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[54] H. G. Rule, *J. Chem. Soc.*, 1816 (1950).

had a retention time of 319 s. The ratio of the products was 2:1. Crystals formed on standing, and recrystallization from 60–110 °C petroleum ether gave white needles of 2-methyl-1-naphthonitrile, mp 85.5–86.0 °C (lit.[53] 87–88 °C). The NMR was identical with that of an authentic sample. The compound with longer retention time was not isolated.

Photoaddition of 4-Methyl-1-naphthonitrile and Tetramethylethylene in Benzene. A solution of 4-methyl-1-naphthonitrile (0.589 g, 3.5 mmol) and teramethylethylene (6.342 g, 0.075 mol) in benzene (50 mL) was degassed by three freeze–pump–thaw cycles and was sealed in Pyrex. The sample was irradiated for 42 h with 10 RPR-3000 lamps. Analysis on 5 ft × $^1/_8$ in. of 5% SE-30 on Chromosorb W at 165 °C showed one major peak of retention time 8.3 min. In this run, approximately 30% of 4-methyl-1-naphthonitrile was unreacted. The benzene was evaporated, leaving a yellow solid. Recrystallization from 30–60 °C petroleum ether gave white needles of 4 (74 mg), mp 93–94 °C. The mother liquor was concentrated and chromatographed on 1 × 51 cm of Kieselgel G silica gel with 20% ether in CCl_4; 30 mL fractions were collected. Fractions 1–35 contained the cyclobutane **4**. Fractions 36–45 contained 4-methyl-1-naphthonitrile. The former fractions were concentrated, and the solid was recrystallized twice from 30–60 °C petroleum ether to give white needles of 1-cyano-4,7,7,8,8-pentamethyl-2,3-benzobicyclo[4.2.0]-2,4-octadiene (**4**): 0.141 g; mp 93–94 °C, mass spectrum, *m/e* 251 (M^+); ^1H NMR ($CDCl_3$) δ 0.77, 0.90 (s, 3 H each, CH_3), 1.30 (s, 6 H, CH_3), 2.03 (dd, J = 1.2 and 1.8 Hz, 3 H, allylic CH_3, 3.27 (dd, J = 4.8 and 1.2 Hz, 1 H, allylic methine), 5.57 (dd, J = 4.8 and 1.8 Hz, 1 H, vinylic), 7.23 (m, 4 H, aromatics). Irradiation at δ 2.03 gave two doublets at δ 3.27 and 5.57, J = 4.8 Hz; IR ($CHCl_3$) 2221 cm^{-1} (CN). Anal. Calcd for $C_{18}H_{21}N$: C, 86.02; H, 8.42; N, 5.57. Found: C, 86.00; H, 8.44; N, 5.46.

Photoaddition of 6-Methyl-1-naphthonitrile and Tetramethylethylene in Benzene. A solution of 6-methyl-1-naphthonitrile (0.522 g, 3.1 mmol) and tetramethylethylene (4.00 g, 0.046 mol) in benzene (50 mL) was irradiated through Pyrex under argon with 14 RPR-3000 lamps for 6 h. Analysis on 4 ft × 4 mm of 3% OV-1 on Chromosorb WHP at 190 °C showed two product peaks of retention time 6.1 and 10.0 min, in the ratio 9:1, respectively. In this run, approximately 70% of the naphthonitrile was unreacted. The benzene was evaporated, and the residue was chromatographed by using the chromatography technique of Still and co-workers.[55] A 50-mm diameter column of silica gel was used with 10% ethyl acetate in 30–60 °C petroleum eter as eluent; 50-mL fractions were collected. Fractions 6–8 contained the major adduct. Fractions 9–13 contained 6-methyl-1-naphthonitrile. Concentration of fractions 6–8 gave an oil (0.18 g). Upon standing at 0 °C, the oil solidified. Recrystallization from 60–110 °C petroleum ether gave 1-cyano-7,7,8,8-tetramethyl-2,3-(4-methylbenzo)bicyclo[4.2.0]-2,4-octadiene (**5**): 0.051 g; mp 79–80 °C; ^1H NMR ($CDCl_3$) δ 0.77, 0.90, 1.27, 1.30, 2.26 (s, 3 H each, H_3), 3.09 (dd, J = 4.8 and 1.8 Hz, 1 H, allylic methene), 5.67 (dd, J = 10.2 and 4.8 Hz, 1 H, vinylic), 6.27 (dd, J = 10.2 and 1.8 Hz, 1 H, vinylic), 6.80–7.00 (m, 3 H, aromatics); IR ($CHCl_3$) 2221 cm^{-1} (CN); mass spectrum *m/e*, 251 (M^+). Anal. Calcd for $C_{18}H_{21}N$: C, 86.02; H, 8.42; N, 5.57. Found: C, 86.15; H, 8.49; N, 5.60.

The product with retention time 10.0 min was not isolated. When the reaction is taken to low conversion, little of this compound is detected. It is speculated that this substance is an azetine.

Photoadditions in Ethyl Acetate. Irradiation of 4-methyl- or 6-methyl-1-naphthonitrile with TME as above with ethyl acetate as solvent gave cyclobutanes 4 and **5**, respectively. Similar irradiation of 2-methyl-1-naphthonitrile with TME gave several products formed in a slow reaction. These products were not investigated.

Synthesis of Bichromophoric Molecules. 2-Bromomethyl-1-naphthonitrile was synthesized according to the method of Stacy and co-workers.[15] *N*-Bromosuccinimide (17.21 g, 0.097 mol) and 2-methyl-1-naphthonitrile (16.15 g, 0.097 mol) were added to 100 mL of CCl_4, and the solution was continuously irradiated with a 1000-W tungsten lamp. The mixture was stirred and refluxed for 3 h. The warm mixture was filtered and the filtrate concentrated to give a yellow solid. Two recrystallizations from CCl_4 yielded 15.73 g of light yellow needles, mp 99.5–101.5 °C (lit.[15] 101–102.5 °C). NMR, however, indicated that the crystals were a mixture of 81% 2-bromomethyl-1-naphthonitrile and 19% 2-methyl-1-naphthonitrile.

A sample (2.0 g) of the mixture was chromatographed on Baker analyzed 60–200 mesh silica gel (29 × 3.5 cm), with 5% ether in hexane as eluent; 6-mL 6Ml fractions were collected. Fractions 65–130 yielded upon concentration 1.2 g of 2-bromomethyl-1-naphthonitrile. Recrystallization from CCl_4 gave 0.95 g of white needles: mp 110–110.5 °C; NMR ($CDCl_3$) δ 4.80 (s, 2 H), 7.5–8.3 (m, 6 H); IR ($CHCl_3$) 2220 cm^{-1} (CN stretch). The mass spectrum showed parent ions of *m/e* 245 and 247. Anal. Calcd for $C_{12}H_8BrN$: C, 58.56; H, 3.28; N, 5.69; Br 32.47. Found: C, 58.40; H, 3.18; N, 5.60; Br, 32.30.

The mixture was also purified by the chromatographic technique used above.[55] A 50-mm diameter column was used with 20% ethyl acetate in 30–60 °C petroleum ether as the eluent; 50-mL fractions were collected. A sample (10.0 g) of the mixture was chromatographed in 1.0 g portions. The fractions were assayed by VPC (6 ft × $^1/_4$ in. of 3% OV-1 on 80/100 Chromosorb WHP at 190 °C). The appropriate fractions were collected and concentrated to give a white solid that, upon two recrystallizations from CCl_4, gave 2-(bromomethyl)-1-naphthonitrile (3.1 g), mp 110–110.5 °C.

Ethyl 2,3-Dimethyl-2-butenoate. The title compound was synthesized according to the method of Huston and Goerner.[56]

Ethyl 3-hydroxy-2,3-dimethylbutanoate was first prepared by a Reformatsky reaction. Thirty mesh zinc (45 g) was cleaned and dried by the method of Fieser and Johnson.[57] Initially, 4.8 g of acetone, 3.4 g of ethyl 2-bromopropionate, and 1.5 mL of BuLi (2 M in hexane) in 15 mL of benzene were added to the zinc. The mixture was heated to reflux, and a solution of ethyl 2-bromopropionate (90 g) and acetone (43 g) in 125 mL of benzene was added dropwise over a period of 30 min. After the mixture was refluxed and stirred for 2 h, it was cooled and poured, with vigorous stirring, into 500 mL of ice-cold 10% sulfuric acid, and when hydrolysis was complete, the benzene layer was separated and the aqueous layer was washed with 50 mL of benzene. The combined benzene extracts were washed with saturated Na_2CO_3 (50 mL) and water (50 mL) and dried (Na_2SO_4). The benzene solution was distilled until the distillate became clear. Then 57 g of phosphorus pentoxide was added to the benzene solution, and the mixture was refluxed for 4 h. After cooling, the benzene layer was decanted, and the black solid was washed with 100 mL benzene. The benzene was removed by fractional distillation through a Dewar-jacketed column packed with glass helices. The residue was fractionated in a spinning-band still. The yield of ethyl 2,3-dimethyl-2-butenoate (bp 93–94 °C (59 mm)) was 15.1 g (21%): NMR ($CDCl_3$) δ 1.33 (t, J = 7.0 Hz, 3 H), 1.87 (br s, 6 H), 2.07 (br s, 3 H), 4.33 (q, J = 7.0 Hz, 2 H).

Earlier fractions contained ethyl 2,3-dimethyl-3-butenoate, which was isomerized as follows: 12 g of crude ethyl 2,3-dimethyl-3-butenoate was stirred with 1 mL of benzyltrimethylammonium hydroxide (40% in methanol) at room temperature under nitrogen for 40 h. The solution was then added to 10 mL of 10% aqueous HCl. The mixture was extracted with ether (2 × 20 mL), and the organic extracts were dried (Na_2SO_4). Distillation on a spinning-band still yielded 7.4 g of ethyl 2,3-dimethyl-2-butenoate. The total yield was 22.5 g (31%).

2,3-Dimethyl-2-buten-1-ol. A solution of 25 mL of Red-Al (Aldrich, 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene) in 250 mL of THF was added under argon over a period of 1.5 h to a stirred ice-cooled solution of 2,3-dimethyl-2-butenoate (10 g, 0.065 mol) in 50 mL of THF. The solution was then stirred with cooling for 4 h, at which time 75 mL of 5% aqueous NaOH was added. The mixture was stirred until the white precipitate dissolved, and the aqueous layer was extracted with ether (2 × 100 mL). The organic fractions were dried (Na_2SO_4), and the ether and THF were removed by fractional distillation through a Dewar-jacketed column containing glass helices. The residue was transferred to a spinning-band still, and distillation yielded 6.12 g (87% yield) of 2,3-dimethyl-2-buten-1-ol (bp 82–83 °C (59 mm)); NMR ($CDCl_3$) δ 1.67 (br s, 9 H), 2.37 (s, 1 H), 4.03 (s, 2 H). This alcohol has also been synthesized by the reduction of α,β,β-trimethylacrylic acid with lithium aluminum hydride.[58]

2,3-Dimethyl-2-butenyl (1-Cyano-2-naphthyl)methyl Ether (1). 2,3-Dimethyl-2-buten-1-ol (0.872 g, 8.7 mmol) in 30 mL of THF was added dropwise to sodium hydride (50% dispersion in oil, 0.469 g, 9.8 mmol) that had previously been washed with 20 mL of THF. The reaction was carried out under an atmosphere of oxygen. The mixture was stirred and refluxed for 2 h, at which time 2-(bromomethyl)-1-naphthonitrile (1.063 g, 4.3 mmol) in 30 mL of THF was added dropwise. After the mixture was stirred and refluxed for 4 h, it was cooled and 25 mL of water was added. The aqueous layer was extracted with ether (3 × 25 mL). The organic fractions were dried (Na_2SO_4), concentrated, and chromatographed on Baker 60–200 mesh silica gel (31 × 3.5 cm) with 5% ether in hexane as eluent. Fractions (7 mL each) were collected, and concentration of fractions 38–74 yielded 0.70 g of an oil that solidified upon cooling. Recrystallization from 60–110 °C petroleum ether gave white needles of 2,3-dimethyl-2-butenyl (1-cyano-2-naphthyl)methyl ether (**1**, 0.307 g, 27% yield): mp 55–56 °C; NMR ($CDCl_3$) δ 1.65 (br s, 6 H), 4.03 (s, 2 H), 4.73 (s, 2 H), 7.4–8.2 (m, 6 H); IR ($CHCl_3$) 2220 cm^{-1} (CN); mass spectrum, *m/e* 265 (M^+). Anal. Calcd for $C_{18}H_{19}NO$: C,

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81.47; H, 7.22; N, 5.28. Found: C, 81.39; H, 7.23; N, 5.28.

Further attempts to synthesize **1** by using the same conditions as described above gave lower yields. As a result, the following procedure was adopted. Yields were variable.

2,3-Dimethyl-2-buten-1-ol (0.310 g, 3.1 mmol) and 2-(bromomethyl)-1-naphthonitrile (0.502 g, 2.0 mmol) in 15 mL of THF was added slowly under an atmosphere of argon to a more rapidly stirred mixture of NaH (80% dispersion in oil, 0.116 g, 3.9 mmol) in 10 mL of THF. The NaH was previously washed with 5 mL of THF. The mixture was stirred and refluxed under argon for 8 h. After cooling, 25 mL of water was added, and the aqueous extract was washed with ether (3 × 25 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. This procedure was repeated 3 more times, and the resulting 1.92 g of oil was divided into two equal batches that were individually chromatographed as before.[55] A 50-mm diameter column was used. The eluent was 5% ethyl acetate in 30–60 °C petroleum ether. In one run, fractions 19–30 were collected, and in the second run on the same column, fractions 9–20 were collected. These fractions were combined and concentrated to give 0.772 g of crude **1**. Recrystallization from absolute ethanol gave 0.513 g (24% yield) of pure 2,3-dimethyl-2-butenyl (1-cyano-2-naphthyl)methyl ether, mp 55–56 °C.

4-(Bromomethyl)-1-naphthonitrile. This compound was synthesized according to the method of Stacy and co-workers.[15] 4-Methyl-1-naphthonitrile (4 g, 0.024 mol) and *N*-bromosuccinimide (4.3 g, 0.024 mol) were added to 30 mL of CCl_4, and the solution was irradiated continuously with a 1000-W tungsten lamp. The mixture was stirred and refluxed for 4 h. The warm solution was filtered, and the filtrate concentrated to give a yellow solid. Two crystallizations from CCl_4 gave 4.0 g of slightly yellow crystals, mp 135–137 °C (lit.[15] 135.5 °C). The NMR spectrum of the crystals indicated that they were composed of 88% 4-(bromomethyl)-1-naphthonitrile and 12% 4-methyl-1-naphthonitrile.

A sample (2.0 g) of the mixture was chromatographed on Baker 60–200 mesh silica gel (30 × 3.5 cm) with 5% ether in hexane as eluent; 7-mL fractions were collected. After fraction 70, the eluent was changed to ether. The ether eluent (550 mL) was collected and concentrated to give 1.6 g of a yellow solid. Recrystallization from CCl_4 gave 1.3 g of colorless needles: mp 135–136 °C; NMR ($CDCl_3$) δ 4.92 (s, 2 H), 7.5–8.4 (m, 6 H); IR ($CHCl_3$) 2219 cm^{-1} (CN); mass spectrum, m/e 245 and 247 (M^+). Anal. Calcd for $C_{12}H_8BrN$: C, 58.56; H, 3.28; N, 5.69; Br, 32.47. Found: C, 58.37; H, 3.48; N, 5.75; Br, 32.31.

1-Cyano-4-(hydroxymethyl)naphthalene. Crude 4-(bromomethyl)-1-naphthonitrile (3.0 g, 0.012 mol, 135–137 °C) and 6.6 g of potassium acetate were added to 32 mL of glacial acetic acid. The solution was stirred and refluxed for 5 h. It was then poured into 100 mL of water. The solid that formed was collected and washed with water. The crude 1-cyano-4-(acetoxymethyl)naphthalene with 0.9 g KOH was added to 24 mL of 17% aqueous ethanol. The mixture was stirred and refluxed for 3 h. Upon cooling, a yellow solid separated and was collected, washed with water, and chromatographed on Baker 60–200 mesh silica gel (29 × 3.5 cm) with 50% ether in hexane as eluent; 7-mL fractions were collected, and after fraction 75, the column was washed with 400 mL of ether. Fractions 70–75 were combined with the ether fraction and were concentrated to give 1.3 g of crude alcohol. Recrystallization from ethanol gave 1.1 g (49% yield) of 1-cyano-4-(hydroxymethyl)naphthalene as pale yellow needles, mp 118–119 °C. An analytical sample was prepared by treatment with charcoal: mp 118–119 °C; NMR ($CDCl_3$) δ 2.17 (t, *J* = 6.0 Hz, 1 H), 5.12 (d, *J* = 6.0 Hz, 2 H), 7.5–8.3 (m, 6 H); IR ($CHCl_3$) 3610, 3450, 2220 cm^{-2} (CN); mass spectrum, *m/e* 183 (M^+). Anal. Calcd for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.56. Found: C, 78.79; H, 5.20; N, 7.59.

1-Bromo-2,3-dimethyl-2-butene. 2,3-Dimethyl-1,3-butadiene (5.0 g, 0.038 mol) was added to 13.2 mL of HBr (45% w/v) in glacial acetic acid, with ice cooling. After standing for 2 days in the cold, the solution was poured into 60 mL of cold water. The green liquid was separated, dried ($CaCl_2$), and distilled to give 4.2 g (43% yield) of 1-bromo-2,3-dimethyl-2-butene as a pale yellow liquid (bp 68–72 °C (44 mm)); NMR ($CDCl_3$) 1.79 (br s, 9 H), 4.07 (s, 2 H). 1-Bromo-2,3-dimethyl-2-butene has also been prepared by heating 2,4-dibromo-2,3-dimethylbutane in pyridine.[59] The above method resembles the 1,4 addition of HBr and isoprene.[60]

2,3-Dimethyl-2-butenyl (1-Cyano-4-naphthyl)methyl Ether (2). 1-Cyano-4-(hydroxymethyl)naphthalene (0.50 g, 2.7 mmol) in 20 mL of THF was added dropwise to sodium hydride (50% dispersion in oil, 0.146 g, 3.0 mmol) that had been washed with 25 mL of THF. The reaction was run under an atmosphere of argon. The mixture was stirred and refluxed for 1 h, after which 1-bromo-2,3-dimethyl-2-butene (1.0 g, 6.2 mmol) in 20 mL of THF was added. The solution was then stirred and refluxed for 3 h. After cooling, 20 mL of water was added, and the aqueous fraction was extracted with ether (3 × 30 mL). The organic extracts were dried (Na_2SO_4), concentrated, and chromatographed on Baker 60–200 mesh silica gel (30 × 3.5 cm) with 10% ether in hexane as eluent; 7-mL Fractions were collected, and concentration of fractions 50–75 gave 0.4 g of an oil that solidified upon cooling. Recrystallization from 30–60 °C petroleum ether gave 0.31 g (43% yield) of 2,3-dimethyl-2-butenyl (1-cyano-4-naphthyl)methyl ether (**2**) as white crystals: mp 43–44 °C; NMR ($CHCl_3$) δ 1.70 (s, 9 H), 4.07 (s, 2 H), 4.85 (s, 2 H), 7.4–8.3 (m, 6 H); IR ($CHCl_3$) 2221 cm^{-1} (CN); mass spectrum, *m/e* 265 (M^+). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.53; H, 7.23; N, 5.16.

6-(Bromomethyl)-1-naphthonitrile. 6-Methyl-1-naphthonitrile (1.50 g, 9.0 mmol) and *N*-bromosuccinimide (1.62 g, 9.1 mmol) were added to 15 mL of CCl_4. The solution was continuously irradiated with a 1000-W tungsten lamp and was stirred and refluxed for 3 h. The warm solution was filtered and the filtrate concentrated to give a yellow solid. Recrystallization from CCl_4 gave 1.0 g; mp 106–114 °C. A second recrystallization from CCl_4 gave 0.45 g (20%) of 6-(bromomethyl)-1-naphthonitrile as white needles: mp 114–115 °C, NMR ($CDCl_3$) δ 4.63 (s, 2 H), 7.4–8.3 (m, 6 H); IR ($CHCl_3$) 2221 cm^{-1} (CN); mass spectrum, *m/e* 245 and 247 (M^+). Anal. Calcd for $C_{12}H_8BrN$: C, 58.56; H, 3.28; N, 5.69. Found: C, 58.56; H, 3.24; N, 5.72.

2,3-Dimethyl-2-butenyl (1-Cyano-6-naphthyl)methyl Ether (3). 2,3-Dimethyl-2-buten-1-ol (0.370 g, 3.70 mmol) in 15 mL of THF was added dropwise to sodium hydride (50% dispersion in oil, 0.200 g, 4.2 mmol) that had been previously washed with 15 mL of THF. The reaction was carried out under an atmosphere of argon. The mixture was stirred and refluxed for 1.5 h, at which time 6-(bromomethyl)-1-naphthonitrile (0.459 g, 1.9 mmol) in 15 mL of THF was added. After stirring and refluxing for 3 h, the mixture was cooled and 30 mL of water was added. The aqueous fraction was extracted with ether (3 × 20 mL). The organic fractions were dried (Na_2SO_4), concentrated, and chromatographed on Baker 60–120 mesh silica gel (31 × 3.5 cm) with 10% ether:hexane as eluent; 7-mL fractions were collected, and concentration of fractions 60–185 gave 0.42 g of colorless oil that solidified upon cooling; mp 68–71 °C. Two recrystallizations from 60–110 °C petroleum ether gave 0.194 g (39%) of 2,3-dimethyl-2-butenyl (1-cyano-6-naphthyl)methyl ether (**3**) as white needles: mp 73–74 °C; NMR ($CDCl_3$) δ 1.63 (s, 9 H), 4.03 (s, 2 H), 4.45 (s, 2 H), 7.3–8.3 (m, 6 H); IR ($CHCl_3$) 2220 cm^{-1} (CN); mass spectrum, *m/e* 265 (M^+). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.51; H, 7.30; N, 5.13.

Photochemistry of Bichromophoric Molecules. Photoreaction of 2,3-Dimethyl-2-butenyl (1-Cyano-2-naphthyl)methyl Ether (1) in Benzene. A solution of 2,3-dimethyl-2-butenyl (1-cyano-2-naphthyl)methyl ether 0.398, 1.5 mmol) in benzene (50 mL) was purged with argon and irradiated through Pyrex with 14 RPR-3000 lamps. The progress of the reaction was monitored by VPC (6 ft × $^1/_4$ in. of 3% OV-1 on Chromosorb WHP at 200 °C). After 45 min, two products with retention times of 7.1 and 9.6 min were formed in a ratio of 1:15, respectively. The starting material **1** had a retention time of 12.6 min and represented 59% of the mixture. The irradiation was terminated after 7 h. Compound **1** (17%) was still present, and the ratio of the major product (retention time 9.6 min) to the minor product (7.1 min) was 3:1. The mixture was chromatographed by using the usual technique.[55] A 35-mm diameter column was used with 10% ethyl acetate in 30–60 °C petroleum ether as eluent; 25-mL fractions (25 mL each) were collected, and the fractions were assayed by VPC (6 ft × $^1/_4$ in. of 3% OV-1 on Chromosorb WHP at 200 °C). Fractions 2–9 (0.109 g) contained **1** and the minor photoproduct **11**. Fractions 10–18 (0.077 g) were enriched in **11**, with **10** as a minor component. Fractions 19–23 (0.053 g) contained the major photoproduct **10**, with **11** as an impurity. Fractions 24–36 (0.12 g) were comprised of the major photoadduct **10**. The recovery from the column was 90%. Concentration of fractions 24–36 gave crystals, mp 130–140 °C. Two recrystallizations from 60–110 °C petroleum ether gave 7-cyano-5,6,6-trimethyl-8,9-benzo-3-oxatricyclo[5.4.0.0^{1,5}]-8,10-undecadiene (**10**) as white needles (0.038 g, 10%) mp 141.5–142.5 °C; IR ($CHCl_3$) 2225 cm^{-1} (CN); mass spectrum, *m/e* 265 (M^+). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.23. Found: C, 81.66; H, 7.30; N, 5.16.

^{1}H NMR: methyl groups at δ 0.73, 1.03, 1.37 (s, 3 H each). Two AB quartets (δ 3.30, 4.43 *J* = 10.2 Hz, 2 H; and δ 3.36, 4.28, *J* = 10.2 Hz, 2 H) were attributed to the methylene groups. The vinylic protons showed as an AB quartet (δ 5.40, 6.36, *J* = 10.0 Hz, 2 H). The protons of the aromatic ring resonated at δ 7.0–7.3.

Fractions 10–18 were concentrated and chromatographed on a 25-mm diameter column with 20% ethyl acetate in 30–60 °C petroleum ether

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Table VI

compd	$C_{18}H_{19}NO$
M_r	265.35
cryst size, mm	cylinder, $r = 0.115$, $l = 0.33$
systematic absences	0k0, $k = 2n + 1$; h01, $l = 2n + 1$
space group	$P2_1/c$
unit cell parameters	$a = 12.089$ (3) Å; $c = 15.152$ (3) Å; $b = 8.163$ (2) Å; $\beta = 105.27$ (2)°
V, Å^3	1442.5 (6)
Z	4
ρ_{calcd}, g cm^{-3}	1.222
ρ_{obsd}, g cm^{-3}	1.20 (1)
linear abs coeff, cm^{-1}	0.81
max 2θ, quadrant	55°, $h, k, \pm l$
std reflcns (esd, %)	306 (1.95); 423 (1.96)
temp, °C	22 °C
no. of independent reflcns	3457
no. with $I > 3\sigma(I)$	1387
$3\sigma(I) > 1 > \sigma(I)$	1386[a]
$I < \sigma(I)$, rejected	684[a]
final R_1[b], R_2[b]	0.064, 0.060
final shift/error, max (ave)	0.12 (0.02)
final difference map:	
highest peak (e/Å^3); location	0.12; 0.80, 0.25, 0.05
lowest valley (e/Å^3); location	0.14; 0.50, 0.30, 0.15
g secondary extinction)	3.41×10^{-7}
weighting	$w = (\sigma^2 + (0.03F_O)^2)^{-1}$
error in an obsn of unit wt	1.081

[a] Most unobserved values occurred for $2\theta > 35°$. [b] $R_1 = \Sigma||F_O| - |F_c||/\Sigma|F_O|$; $R_2 = \{\Sigma w(|F_O| - |F_c|)^2/\Sigma wF_O{}^2\}^{1/2}$.

as eluent; 7-mL fractions were collected, and concentration of fractions 9–13 gave 35.6 mg, mp 90–105 °C. Two recrystallizations from absolute ethanol gave 6-cyano-1,10,10-trimethyl-7,8-benzo-3-oxatricyclo-[5.3.1.1^{5,9}]-5,7-decadiene (**11**) as white needles (3.8 mg): mp 119–120 °C; IR ($CHCl_3$) 2217 cm^{-1} (CN); mass spectrum, *m/e* 265 (M^+). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.23. Found: C, 81.35; H, 7.34; N, 5.20. The ^1H NMR spectrum is given in the text.

Collection of the X-ray Data of 10. A parallelpiped crystal, homogeneous under the polarizing microscope, was ground into a cylinder and used for X-ray studies. Precession photographs showed that the crystal was monoclinic. Unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range $20° < 2\theta < 31°$ recorded on a Syntex P2$_1$ diffractometer with graphite-monochromated Mo Kα_1 radiation (λ 0.70926 Å). Crystal data and other numbers related to data collection are summarized in Table VI. Densities were obtained by flotation in an aqueous zinc bromide solution. Intensity data were also recorded on the Syntex P2$_1$ diffractometer with a coupled θ(crystal)–2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[61,62] Corrections were made for Lorentz polarization effects, but not absorption. This will make a maximum error in F of <1.5%.

Solution of the Structure. The phase problem was solved by direct methods using 50 reflections with $|E| > 1.20$ and 12 sets of starting phases. A subsequent E map with the most reliable phases yielded the carbon, oxygen, and nitrogen atoms. A series of full-matrix least-squares refinements followed by three-dimensional difference syntheses revealed all the atoms, In subsequent refinements, the temperature factors of the carbon, oxygen, and nitrogen atoms were made anisotropic. Tests were made to show that the use of increased parameters was significant.[63] Refinement with full-matrix least squares and minimizing $\sum\omega(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error ratio was ~0.1. Secondary extinction was applied by using the method of Larson.[64] Scattering factors were taken from work by Cromer and Waber.[65] The final positional parameters and temperature factors are given in Table VII. All calculations were carried out on a Cyber 170/730 computer.[66]

Photoreaction of 2,3-Dimethyl-2-butenyl (1-Cyano-4-naphthyl)methyl Ether (2) in Benzene. 2,3-Dimethyl-2-butenyl (1-cyano-4-naphthyl)-methyl ether (**2**) (0.395 g, 1.5 mmol) in benzene (50 mL) was purged with argon and irradiated with 14 RPR-3000 lamps through Pyrex for 40 min. VPC analysis (6 ft × $^1/_4$ in. of 3% OV-1 on Chromosorb WHP at 215 °C) showed the presence of two products with retention times of 12.2 and 15.8 min in a ratio of 4.8:1, respectively. The starting material had a retention time of 19.6 min and represented 48% of the mixture. The solution was dark yellow, and the UV absorption showed a maximum at 372 nm (OD = 1.39). Upon evaporation of the benzene, the dark yellow color faded.

The mixture was chromatographed as above. A 50-mm diameter column was used with 10% ethyl acetate in 30–60 °C petroleum ether as eluent; 50 mL fractions were collected. The fractions were assayed by TLC and VPC. Fractions 5–13 (0.139 g) contained the starting material (**2**). Fractions 19–27 gave 0.108 g of the major photoadduct (**13**), mp 120–130 °C. Recrystallization from absolute ethanol gave 0.080 g of 9-cyano-5,6,6-trimethyl-10,11-benzo-3-oxatricyclo-[5.4.0.0^{1,5}]-8,10-undecadiene (**13**) as white needles (0.038 g): mp 138.5–139.5 °C; IR ($CHCl_3$) 2220 cm^{-1} (CN); mass spectrum, *m/e* 265 (M^+). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.23. Found: C, 81.52; H, 7.37; N, 5.23.

Fractions 31–39 from the above column separation gave 0.040 g of a yellow oil. VPC analysis of this fraction indicated the presence of at least three components. Fractions 40–47 (0.058 g) showed a carbonyl stretch (1710 cm^{-1}) in the IR spectrum, idicating that oxidation products were formed. The column was then washed with 500 mL of ethyl acetate. Concentration of the ethyl acetate fraction gave 0.048 g of material. These last two fractions were not investigated further.

Photoreaction of 2,3-Dimethyl-2-butenyl (1-Cyano-6-naphthyl)methyl Ether (3) in Benzene. 2,3-Dimethyl-2-butenyl (1-cyano-6-naphthyl)-methyl ether (0.179 g, 0.68 mmol) in benzene (50 mL) was deoxygenated with argon and irradiated with 14 RPR-3000 lamps through Pyrex. The progress of the reaction was monitored by VPC (6 ft × $^1/_4$ in. of 3% OV-1 on Chromosorb WHP at 210 °C). After 90 min, one major product (retention time 6.0 min) was observed, representing 17% of the mixture. The irradiation was terminated after 6.5 h. The solution contained one photoproduct (retention time 6.0 min, 15%) and the starting material (**3**, retention time 11.0 min, 81%). The mixture was chromatographed as before.[52] A 35-mm diameter column was used with 10% ethyl acetate in 30–60 °C petroleum ether as eluent; 25 mL fractions were collected and were assayed by TLC and VPC. Fractions 4–13 (0.081 g) contained the starting material, fractions 14–17 (0.024 g) consisted of a mixture of photoproduct **15** and **3**, and frations 18–24 (0.024 g) contained 1,11,11-trimethyl-8,9-(6-cyanobenzo)-3-oxatricyclo[6.3.0.0^{5,10}]-6,8-undecadiene (**15**) as an oil in 95% purity. The major contaminant was the starting material, **3**. The IR spectrum had a band at 2219 cm^{-1} (CN), and the ^1H NMR spectrum is described in the text.

Quantum Yield Measurements. Absolute quantum yields for reactions were measured as described previously.[8] A monochromator, high-pressure mercury lamp, collimating lens, beam splitter, and quartz cells were used. Light intensities were measured by using ferrioxalate actinometry,[67] and the sample:reference beam ratio was usually about 10:1. When the quantum yield was high (e.g., with **1**) the ratio was altered (3.5:1) by using a neutral density filter (Oriel Corp., G-66-22) in the sample beam. Water from a Haake bath was circulated through the cell jackets to control temperature (23 °C). In runs at −15 °C (biacetyl quenching), methanol was circulated through an external cooling bath of liquid nitrogen, and the Haake bath heater was used to maintain −15 °C. The solutions were continuously purged with argon, introduced through fine capillaries. Entrance and exit slit widths of 5.7 and 3.2 mm were used, giving a band pass of 15 nm at 313 nm. Product assay was by UPC, using internal standards, and the detector was calibrated with standard solutions. For the methylnaphthonitrile–TME reactions, the standard was phenanthrene (retention time 5.5 min), and column a at 170 °C was used. For the bichromophoric molecules, 4,4′-dichlorobenzophenone was the standard (retention time 5.1 min), and column b at 210 °C was used.

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(63) W. C. Hamilton, *Acta Crystallogr.* **18**, 502 (1965).

(64) A. C. Larson, *Acta Crystallogr.* **23**, 664 (1967).

(65) D. T. Cromer and J. T. Waber in "International Tables for X-ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press: Birmingham, England, 1964, Table 2.2A, p 72 ff.

(66) Initial data treatments used the programs DATCO5, DATRDN from the X-ray 76 package (J. M. Stewart, Technical Report TR-446, Computer Science Center, University of Maryland, College Park, MD, 1976). Most data treatment used programs from the SHELX package (G. M. Sheldrick, 1976, SHELX "Program for Crystal Structure Solution and Refinement", University of Cambridge, England). Final data treatment used the internally written programs CUDLS (J. S. Stephens) and SYMFOU (J. S. Rutherford). Least-squares planes used NRC-22 (M. E. Pippy, F. R. Ahmed "Mean Plane and Torsion Angles", National Research Council of Canada, Ottawa, 1978). Diagrams were prepared with ORTEP II (C. K. Johnson, Report No. ORNL-5138, Oak Ridge National Laboratory, TN, 1976).

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Table VII. Atomic Positional Parameters and Temperature Factors, Å^2

atom	x (×10^4)	y (×10^4)	z (×10^4)	U_{11} (×10^3)	U_{22} (×10^3)	U_{33} (×10^3)	U_{12} (×10^3)	U_{13} (×10^3)	U_{23} (×10^3)
C(1)	2285 (2)	8534 (3)	4554 (2)	42 (1)	51 (2)	39 (1)	6 (1)	20 (1)	0 (1)
C(2)	1534 (2)	9914 (4)	4742 (2)	51 (2)	63 (2)	63 (2)	8 (1)	25 (1)	−11 (1)
O(3)	461 (1)	9746 (2)	4071 (1)	50 (1)	61 (1)	73 (1)	17 (1)	25 (1)	4 (1)
C(4)	241 (2)	8030 (4)	4023 (2)	45 (2)	67 (2)	65 (2)	4 (1)	22 (1)	2 (2)
C(5)	1384 (2)	7191 (3)	4063 (2)	41 (1)	42 (1)	51 (1)	4 (1)	21 (1)	7 (1)
C(6)	1819 (2)	7351 (3)	3173 (2)	44 (1)	40 (1)	40 (1)	−1 (1)	15 (1)	−3 (1)
C(7)	2702 (2)	8735 (3)	3654 (1)	34 (1)	38 (1)	32 (1)	5 (1)	12 (1)	1 (1)
C(8)	3963 (2)	8385 (3)	3734 (2)	37 (1)	42 (1)	39 (1)	3 (1)	14 (1)	−5 (1)
C(9)	4674 (2)	7792 (3)	4550 (2)	40 (1)	56 (2)	45 (1)	10 (1)	11 (1)	0 (1)
C(10)	4251 (2)	7655 (4)	5363 (2)	52 (2)	86 (2)	40 (1)	16 (2)	5 (1)	11 (2)
C(11)	3190 (2)	8016 (4)	5368 (2)	57 (2)	87 (2)	35 (1)	9 (2)	16 (1)	4 (1)
C(12)	5800 (2)	7381 (4)	4581 (2)	47 (2)	81 (2)	64 (2)	17 (2)	8 (1)	−1 (2)
C(13)	6220 (2)	7541 (4)	3824 (2)	40 (2)	95 (3)	76 (2)	11 (2)	17 (1)	−22 (2)
C(14)	5527 (2)	8167 (4)	3030 (2)	49 (2)	88 (2)	60 (2)	−8 (2)	30 (1)	18 (2)
C(15)	4406 (2)	8606 (3)	2985 (2)	47 (2)	64 (2)	43 (1)	−4 (1)	15 (1)	−6 (1)
C(16)	2433 (2)	10349 (3)	3229 (2)	42 (1)	41 (1)	50 (2)	1 (1)	13 (1)	0 (1)
N(16)	2240 (2)	11599 (3)	2886 (2)	73 (2)	49 (1)	94 (2)	10 (1)	30 (1)	19 (1)
C(17)	921 (3)	7923 (4)	2313 (2)	53 (2)	71 (2)	45 (2)	−9 (2)	4 (1)	−2 (1)
C(18)	2403 (3)	5822 (4)	2942 (2)	66 (2)	46 (2)	68 (2)	−3 (1)	29 (2)	−13 (1)
C(19)	1443 (3)	5507 (4)	4502 (2)	80 (2)	59 (1)	70 (2)	−3 (2)	31 (2)	16 (2)
	(×10^3)	(×10^3)	(×10^3)	U (×10^3)					
H(2a)	141 (2)	984 (3)	535 (2)	36 (8)					
H(2b)	184 (2)	1103 (3)	466 (2)	19 (7)					
H(4a)	−5 (2)	771 (3)	456 (2)	35 (8)					
H(4b)	−39 (2)	775 (3)	346 (2)	34 (8)					
H(10)	480 (2)	731 (3)	593 (2)	33 (8)					
H(11)	298 (2)	791 (3)	594 (2)	31 (7)					
H(12)	627 (2)	696 (3)	517 (2)	41 (8)					
H(13)	699 (2)	724 (3)	384 (2)	32 (8)					
H(14)	583 (2)	831 (3)	249 (2)	32 (7)					
H(15)	390 (2)	905 (3)	242 (2)	25 (7)					
H(17a)	50 (2)	896 (3)	246 (2)	42 (8)					
H(17b)	35 (2)	703 (3)	209 (2)	31 (7)					
H(17c)	136 (2)	821 (3)	186 (2)	51 (9)					
H(18a)	307 (2)	550 (3)	345 (2)	28 (8)					
H(18b)	188 (2)	490 (4)	278 (2)	42 (9)					
H(18c)	273 (2)	605 (3)	244 (2)	29 (7)					
H(19a)	89 (3)	474 (4)	412 (2)	56 (10)					
H(19b)	226 (3)	503 (4)	463 (2)	57 (10)					
H(19c)	130 (3)	559 (4)	511 (2)	58 (10)					

Peak areas were determined with the Tracor 560 and Varian integrator. Products were transparent at the irradiation wavelength, except for **3**, and in the case correction was made for product absorption. UV data (benzene) were as follows: 4-Me-1-NN, $\epsilon_{313\text{nm}} = 0.59 \times 10^4$; 2-Me-1-NN, $\epsilon_{313\text{nm}} = 0.47 \times 10^4$; 6-Me-1-NN, $\epsilon_{313\text{nm}} = 0.39 \times 10^4$; benzene (1-cm path); sharp cutoff 285 nm; OD was 0.04 at 296 nm and 0 at 313 nm.

Exciplex Fluorescence Quantum Yields. Fluorescence quantum yields were measured on an Aminco-Bowman spectrofluorimeter, which is constructed for 90° viewing. The relative quantum-yield method was employed by using either anthranilic acid or 1-naphthonitrile as the standard. The yield assumed for anthranilic acid indeoxygenated benzene was 0.58.[68] The reported yield for 1-naphthonitrile in deoxygenated hexane was 0.21.[4] The excitation wavelength was 296 nm, and all measurements were made at ambient temperature (23 °C).

The anthranilic acid was recrystallized 3 times from ethanol–water; mp 114.5–45.5 °C. The naphthonitriles were crystallized from ethanol and sublimed. The anthranilic acid had $\lambda_{\max}$ (benzene) 340 nm (log ϵ = 3.31). The fluorescence had $\lambda_{\max}$ at 398 nm, and the band was the same shape as the exciplex fluorescence. the optical densities of all solutions were matched to avoid inner-filter effects.[69] The 1-naphthonitrile concentration in all solutions was 1.25×10^{-4} M, OD = 0.91 at 296 nm. The tetramethylethylene concentration used in each solution was that which resulted in 98% naphthonitrile quenching. All solutions were deoxygenated, in the fluorescence cells, by purging with argon for 3 min. The intensities were integrated by cutting and weighing the recorded spectra and were corrected for solvent refractive index where necessary.[69] Data for the exciplexes are given in Table II. Fluorescence quantum yields (benzene) for the monomers were 4-Me-1-NN, 0.22; 2-Me-1-NN, 0.21; 6-Me-1-NN, 0.16.

Stern–Volmer Quenching Studies. Fluorescence cells fitted with a standard taper joint and a stopcock were used, and solutions were deaerated by purging with argon. The experiments were performed with the Aminco-Bowman spectrofluorimeter. The naphthonitrile was excited at 300 nm, where the optical density was ~1. The fluorescence was monitored near the maximum (340 nm) and was corrected for overlap with the exciplex fluorescence where necessary.

Triplet Counting of Exciplexes Using Biacetyl as Monitor. Samples were contained in a Helma Q5 high-vacuum fluorescence cell (1 cm) equipped with a side arm attached to a 10-mL pear-shaped reservoir. The cell assembly was equipped with a rotoflo Teflon stopcock and a standard taper joint for connection to a vacuum line. The sample was transferred to the reservoir for the freeze–pump–thaw cycles. The detection of the 2-methyl-1-naphthonitrile–TME exciplex triplet state in benzene was attempted with biacetyl phosphorescence as monitor.[25,26] Two solutions contained in the above fluorescence cells were used for the study. One cell contained a solution of 2.0×10^{-4} M 2-methyl-1-naphthonitrile and 1.0 1.0×10^{-4} M biacetyl in benzene. The other consisted of a benzene solution that was 2.0×10^{-4} M in 2-methyl-1-naphthonitrile, 2.0 M in tetramethylethylene, and 1.0×10^{-4} M in biacetyl. The TMC concentration used resulted in 95% naphthonitrile quenching. Each sample was degassed (six freeze–pump–thaw cycles) and was excited at 320 nm. In the cell containing only the naphthonitrile and biacetyl, the phosphorescence of biacetyl was observed with a maximum at 520 nm. No phosphorescence from biacetyl could be deteced from the cell containing the naphthonitrile, tetramethylethylene, and biacetyl.

In a similar experiment, two solutions, one containing 2.0×10^{-4} 2-methyl-1-naphthonitrile and 1.0×10^{-4} M biacetyl in benzene and the other consisting of 2.2×10^{-4} M, 2,3-dimethyl-2-butenyl (1-cyano-2-naphthyl)methyl ether (**1**) and 1.0×10^{-4} M biacetyl in benzene were degassed as above. The optical densities of the two naphthonitriles were both 0.56 at 320 nm. Biacetyl phosphorescence at 520 nm was observed from the 2-methyl-1-naphthonitrile solution, but not from the bichromophoric compound (**1**).

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Quenching of the 4-Methyl-1-naphthonitrile–TME Exciplex. Fluorescence Dependence on Temperature. Biacetyl (Aldrich) was freshly distilled before use, bp 85–88 °C. The fluorescence measurements were performed at −14.5 °C on the Aminco-Bowman spectrofluorimeter with an Aminco JA 8262 thermostable cell compartment. Cooling of the sample was carried out by using a stream of cold nitrogen gas. Samples were contained in a fluorescence cell (1 cm), with a standard taper joint fitted with a stopcock, and were equilibrated for 20 min before the emission spectrum was recorded. The temperature of the cell was monitored by a Leeds and Northrup temperature potentiometer and a copper-constantan thermocouple and was found to be constant (±0.2 °C) during acquisition of the fluorescence spectrum. The exciplex was quenched by 4.3×10^{-3} M biacetyl by a factor of 3 (see Figure 5). Cycloaddition from this exciplex was quenched similarly, by a factor of 2 (see above). The same equipment was used to determine the ratios of exciplex:monomer fluorescence quantum yields at different temperatures (Figure 4).

Measurement of Nanosecond Lifetimes. The technique employed for the determination of excited-state lifetimes was that of time-correlated single-photon counting. The technique is only described in outline, since details will be published later.[70]

The excitation light was provided by a lamp of original construction. The lamp body was of Pyrex while the face was a removable quartz disk (General Electric G151). The electrodes were $^1/_{16}$ in. thoriated tungsten welding rod and were usually set with a 2-mm gap. The lamp was filled with 400 mm of prepurified H_2 or N_2. The standard operating voltage was 7 kV, and the lamp was repetitively flashed at 18 kHz.

Wavelength selection for excitation was achieved with a Jarrell-Ash 0.25-m Ebert monochromator. Emission wavelengths were selected by using Corning glass filters. Samples were contained in a 1-cm diameter Suprasil quartz tube, equipped with a Rotaflo valve for degassing by the freeze–pump–thaw method.

The sample emission was detected by an Amperex 56 DUVP/03 photomultiplier that was tuned and mounted by Photochemical Research Associated Inc.

Signal procesing was achieved by using a series of ORTEC electronic modules. The TAC (Ortec Model 457) output was accumulated in a multichannel analyzer, and the time base of the TAC was calibrated. The counting rate was maintained at ≤5% of the lamp repetition rate. The lamp profile was obtained by using Ludox SM as scatterer. The lamp and sample decays were deconvoluted by using the ITCONV computer program, kindly supplied by Dr. T. Nemzek. A series of standards with lifetimes ranging from 2 to 450 ns were run, and agreement with literature values was excellent.

Acknowledgment. We thank Dr. A. J. Yarwood and D. Evans for help with the lifetime measurements. The work was supported by the Natural Sciences and Engineering Research Council of Canada.

Appendix 1

Exciplex-Decay Kinetics at Limiting [TME]. The processes are shown in Scheme VII and $k_f + k_d + k_{ic} = \lambda_0$ and $k_f' + k_d' + k_a = k_p$. In the "rapid equilibrium region", $k_q, k_{-q} \gg \lambda_0, k_p$. In this region, both (NN)* and (NN–TME)* show single exponential decay (A $\exp(-\lambda t)$), with the same decay constant, λ,[4,50] where λ is given by

$$\lambda = \frac{\lambda_0 + (k_q k_p/k_{-q})[\mathrm{TME}]}{1 + (k_q/k_{-q})[\mathrm{TME}]}$$

As [TME] → ∞,

$$\lambda = \frac{\lambda_0}{(k_q/k_{-q})[\mathrm{TME}]} + \frac{(k_q/k_{-q})k_p[\mathrm{TME}]}{(k_q/k_{-q})[\mathrm{TME}]}$$
$$= k_p = \tau_{\mathrm{lim}}^{-1}$$

Under these conditions, we use the following approximation:

$$[(\mathrm{NN{-}TME})^*]_t = [(\mathrm{NN{-}TME})^*]_0 e^{-k_p t}$$

Appendix 2

Temperature Dependence of Exciplex:Monomer Fluorescence Intensities. The ratio of quantum yields for exciplex (Φ_E^F) and monomer (Φ_M^F) is given by[28a]

$$\Phi_E^F/\Phi_M^F = \frac{k_f}{k_f'}\left(\frac{k_q[\mathrm{TME}]}{k_{-q} + k_p}\right)$$

Since k_{-q} is more temperature dependent than k_p, there will be a temperature range where $k_p \gg k_{-q}$. Therefore,

$$\Phi_E^F/\Phi_M^F = \frac{k_f}{k_f'}\left(\frac{k_q[\mathrm{TME}]}{k_p}\right)$$

At constant [TME],

$$\log(\Phi_E^F/\Phi_M^F) = \text{constant} + \log k_q - \log k_p$$
$$= \text{constant} - \left(E_{k_q}^{\mathrm{act}} - E_{k_p}^{\mathrm{act}}\right)/RT$$

by using the Arrhenius equation. Thus the low-temperature region (right-hand side of Figure 4) is linear and the slope gives the difference of two activation energies.

Registry No. 1, 76454-98-3; **2**, 76454-99-4; **3**, 76455-00-0; 4, 76455-03-3; **5**, 81940-31-0; **6**, 20944-85-8; **7**, 76455-01-1; **8**, 81940-32-1; 9, 81940-33-2; **10**, 76455-04-4; **11**, 76484-81-6; **13**, 81940-34-3; **15**, 81940-35-4; 1-bromo-2-methylnaphthalene, 2586-62-1; 4-methyl-1-naphthonitrile, 36062-93-8; 1-bromo-4-methylnaphthalene, 6627-78-7; 6-methyl-1-naphthamide, 81940-36-5; 6-methyl-1-naphthoic acid, 6315-19-1; 6-methyl-1-naphthonitrile, 71235-73-9; tetramethylethylene, 563-79-1; 2-(bromoethyl)-1-naphthonitrile, 67266-37-9; ethyl 2,3-dimethyl-2-butenoate, 13979-28-7; 2,3-dimethyl-2-buten-1-ol, 19310-95-3; 4-(bromomethyl)-1-napthonitrile, 41014-20-4; 1-cyano-4-(hydroxymethyl)naphthalene, 79996-90-0; 1-bromo-2,3-dimethyl-2-butene, 5072-70-8; 2,3-dimethyl-1,3-butadiene, 513-81-5; 6-(bromoethyl)-1-naphthonitrile, 81940-37-6.

Supplementary Material Available: Table of observed and calculated structure factors for $C_{18}H_{19}NO$ (13 pages). Ordering information is given on any current masthead page.

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[70] For a general description see: L. J. Clivelove and L. A. Shaver, *Anal. Chem.*, 48, 365A (1976).