Inter- and Intra-molecular Photocycloaddition of Enol Ethers to Naphthalene

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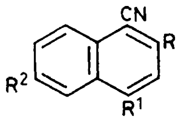
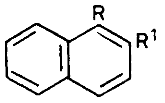
The isomeric non-conjugated naphthyl enol ether bichromophores (**6**) and (**7**) display markedly different photoreactivities. The former undergoes $[2_\pi + 2_\pi]$ cycloaddition from the S_1 state whereas the latter is relatively photostable. The two cyano derivatives (**4**) and (**5**) both yield intramolecular cycloadducts but the orientation of the addition is the opposite of that predicted from the reported intermolecular cyanonaphthalene–enol ether photoreactions. 2,3-Dihydrofuran undergoes specific 'head to head' *endo* photoaddition to naphthalene but in contrast the major adducts from 2,3-dihydrofuran and this arene have 'head to head' *exo* and 'head to tail' *endo* structures. The adduct (**18**) undergoes a facile 1,3-shift to yield the $(4_\pi + 2_\pi)$ *endo* adduct (**19**). The reactivities of the bichromophores and the regiochemistries of the additions are considered in relation to the relative charge densities at the 1- and 2-positions of the S_1 arene.

Naphthalene derivatives, particularly those having alkoxy or cyano substituents have been widely reported to undergo photodimerisation and photocycloaddition to a variety of ethenes and dienes.[1] In contrast, there are few accounts of the photochemical reactions of the parent hydrocarbon and in particular photocycloadditions of ethenes to naphthalene have been described only for *cis*- and *trans*-cyclo-octene,[2,3] acrylonitrile,[4] and dichlorovinylene carbonate.[5] The photochemistry of non-conjugated bichromophoric systems involving naphthyl groups has similarly received little attention. Indeed the only report of the photoreactions of such ethenyl-naphthyl bichromophores appeared in 1982 and all the systems described [*i.e.* (1), (2), and (3)] had trimethylethenyl (electron donor) and cyanonaphthyl (electron acceptor) chromophores linked by the CH_2OCH_2 unit.[6] We have investigated the photolability of 1-, and 2-isomers of naphthyl vinyl compounds in which the unit intervening between the chromophores was $(CH_2)_3$, $(CH_2)_2O$, CH_2O, CH_2OCH_2, CH_2COO, CH_2OCO, $COOCH_2$, and $OCOCH_2$.[7] In view of the facile intramolecular photocycloadditions of several of the corresponding phenyl vinyl systems,[8] it is noteworthy that the only naphthyl vinyl bichromophore which produced a cycloadduct isomer was the 1-naphthyl enol ether (**6**). Here we describe and discuss the intramolecular photoreactions of the naphthyl enol ether bichromophoric systems. In the course of this study we also investigated the intermolecular photoreactions of naphthyl enol ether systems: these had not previously been reported and our results illustrate that minor structural features of the addends can have a marked influence on the regiochemistry and selectivity of the cycloaddition process.



(**1**) $R = R^2 = H$, $R^1 = -CH_2OCH_2C(Me){=}CMe_2$
(**2**) $R^1 = R^2 = H$, $R = -CH_2OCH_2C(Me){=}CMe_2$
(**3**) $R = R^1 = H$, $R^2 = -CH_2OCH_2C(Me){=}CMe_2$
(**4**) $R = R^2 = H$, $R^1 = -(CH_2)_2OCH{=}CH_2$
(**5**) $R^1 = R^2 = H$, $R = -(CH_2)_2OCH{=}CH_2$



(**6**) $R = -(CH_2)_2OCH{=}CH_2$, $R^1 = H$
(**7**) $R = H$, $R^1 = -(CH_2)_2OCH{=}CH_2$
(**8**) $R = -(CH_2)_2OEt$, $R^1 = H$
(**9**) $R = H$, $R^1 = -(CH_2)_2OEt$

Results and Discussion

Use of 254 nm radiation or wavelengths longer than 290 nm gave essentially similar results for all systems studied. Solutions were degassed under nitrogen prior to irradiation.

Intramolecular Naphthyl Enol Ether Bichromophoric Systems.—Our preliminary investigation into the photochemistry of naphthyl-ethenyl non-conjugated bichromophoric systems had revealed that the unit intervening between the chromophores had a profound effect on their excited state interaction and subsequent photoproduct formation.[7] In particular the 1- and 2-isomers with $(CH_2)_3$ and CH_2OCH_2 units linking the naphthyl and ethenyl groups were photostable and very little quenching of the arene fluorescence by the ethenyl group was evident. These observations are in marked contrast to other bichromophoric systems where these connecting units have not hindered photoreaction and indeed the latter unit has actually been reported to promote the intramolecular dimerisation of 9,9′-bianthracenes.[9,†] Since only the ethenyl ether (**6**) of all the bichromophores we studied underwent intramolecular cyclisation, the photochemistry of this compound and its 2-isomer (**7**) has been investigated in detail: the cyano derivatives (**4**) and (**5**) were also studied for reasons outlined below.

The bichromophores (**6**) and (**7**) irradiated as 1% (w/v) solutions in cyclohexane displayed markedly different photochemical behaviour. Thus the 1-naphthyl compound (**4**) was photochemically very labile ($\Phi_{\text{disappearance}} = 0.5$) and gave only one photoisomer ($M^+ = 198$ m.u. $\Phi_{\text{formation}} = 0.45$) whereas (**7**) was relatively stable under the same conditions and was only converted into small amounts of a five-component product

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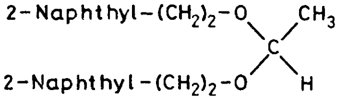
† Other bis aryls having the CH_2OCH_2 intervening unit also yield intramolecular excimers[10] and undergo intramolecular cyclisation.[11]

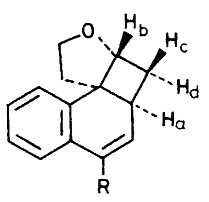
mixture of which two were isomers (M^+, 198 m.u.) of starting material. A preliminary investigation of (7) had suggested that a major photoproduct was the acetal (**10**) (m.p. 41—42 °C),[7]



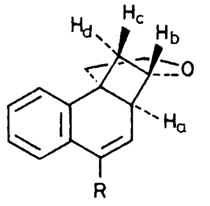
(**10**)

but this has now been shown to arise *via* a photoreaction of the bichromophore with 2-(2-naphthyl)ethanol which was an impurity in some preparations of (7) and which was also apparently formed from (7) on prolonged irradiation in non rigorously dried solvents. The photolabilities of (**6**) and (7) and the formation of photoisomers were not significantly affected by change in solvent from cyclohexane to acetonitrile and methanol.

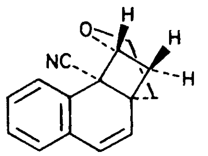
The photoisomer of compound (**6**) was isolated by flash chromatography[12] in >99.5% purity as a colourless oil. The ^{1}H n.m.r. spectrum of this product (see Experimental section) was consistent with a 1,2-dihydronaphthalene and a decision between the two possible intramolecular cycloadduct structures (**11**) and (**13**) was made in favour of the former from a detailed examination of the spectrum and $[Eu(fod)_3]$ shift studies. In particular, the allylic methine proton H_a shows weak *trans* 1,3-coupling to H_b (J 0.9 Hz) and is coupled to H_c and H_d with a J value of 8.5 Hz: in the alternative structure (**13**) the H_aH_b coupling would be expected to be of the order of 6 Hz and H_aH_c and H_aH_d considerably less than those observed. The formation of (**11**) was not sensitised by acetophenone or benzophenone and irradiation of xenon degassed solutions of (**6**) produced the intramolecular cycloadduct at 37% the rate of those degassed under nitrogen or argon.[13] From these observations it is deduced that the formation of (**11**) arises from the S_1 state of the bichromophore. It is not yet possible to comment on the involvement of intramolecular excited state complexes in the pathway to (**11**) or as an energy dissipation route for (7) since neither bichromophore showed emission attributable to an exciplex in the temperature range 20 to −60 °C,* and results of deuterium incorporation from irradiation of solutions of (**6**) and (7) in deuteriated methanol were not conclusive. The marked differences in the photochemical behaviour of (**6**) and (7), however, do reflect the differing interactions between the chromophores in the excited state since in the 1-isomer the arene fluorescence was quenched to 60% of that of the ethyl ether (**8**) whereas in the 2-isomer only 15% quenching was observed compared to (**9**).



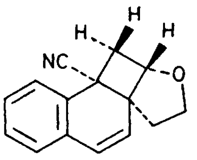
(**11**) R = H
(**12**) R = CN



(**13**) R = H
(**14**) R = CN



(**15**)



(**16**)

The possible origin of the differing behaviours of complex (**6**) and (7) requires comment. Calculation of the charge distribution of vinyl alcohol shows that the terminal carbon atom has a greater electron density than the carbon adjacent to the oxygen atom. Thus the present results can be rationalised if the 1-position of the S_1 naphthyl chromophore has a higher charge density than the 2-position: this would promote a parallel 1,2-, 1′,2′-interaction between the chromophores of (**6**) and facile formation of the photoisomer (**11**). Such charge distribution would, however, inhibit a similar interaction between the chromophores of the 2-isomer and a parallel approach of the naphthyl and the ethenyl ether groups in the alternative 1,2-, 2′,1′-orientation is, from molecular models, unlikely. It appears contrary to such charge distribution proposals for the excited state of naphthalene that nucleophilic photosubstitution occurs preferentially at the 1-position in this arene.[14] Unlike the formation of compound (**11**), however, 'most' of these substitution processes arise from the T_1 state of the arene[14] and charge densities of T_1 and S_1 states can differ appreciably.[15]

Polar substituents in the naphthyl entity will, of course, have a considerable effect on the charge distribution in the S_1 arene. In order to assess the importance of this feature on the reactions of (**6**) and (7) and also so that a direct comparison could be made between our results of intramolecular naphthyl enol ether systems and those described by McCullough *et al.* for compounds (**1**) and (**2**),[6] we studied the photoreactions of the cyano naphthyl ethenyl ethers (**4**) and (**5**). The electron donor-electron acceptor relationships between the chromophores in (**1**) and (**4**), and (**2**) and (**5**) may be expected to be similar but differences in photoreactivity between these systems are not unlikely since the ethenyl chromophores in (**4**) and (**5**) is polarised whereas for (**1**) and (**2**) this is not a significant feature. Further, the intermolecular $(2_\pi + 2_\pi)$ photocycloaddition of enol ethers to 1- and 2-cyanonaphthalenes is specifically a 'head-to-head' process,[16,17] and this reflects a higher electron density at the arene carbon atom which bears the cyano substituent than at the adjacent carbon atom. The operation of such a dipolar orienting effect on the chromophore in (**4**) and (**5**) would be expected to lead to the intramolecular cycloaddition products (**14**) and (**15**) respectively.

Unlike compounds (**1**) and (**2**), neither (**4**) nor (**5**) showed exciplex emission although the fluorescence of the cyanonaphthyl group was quenched by the ethenyl ether moiety by 96 and 93% respectively. On irradiation, compounds (**4**) and (**5**) disappeared with quantum yields of 0.20 and 0.25 respectively. The former bichromophore gave a clean conversion into one photoisomer (M^+ 223 m.u.) which was isolated in >99% purity and from its spectroscopic properties and their comparison with those of (**11**) was assigned the intramolecular cycloadduct structure (**12**). In contrast to (**4**), the composition of the product mixture from (**5**) was dependent upon the degree of conversion of the bichromophore. At conversions of (**5**) below 20% only one photoisomer (M^+ 223 a.m.u.) was evident but on continued irradiation other products were formed and these became increasingly significant until at 60% conversion of the bichromophore, the primary isomer comprised only 30% of the reaction mixture. The primary product was isolated by flash chromatography with a purity >99% and the ^{1}H n.m.r. spectral data were consistent with a 1,2-dihydronaphthalene but could not distinguish between the 'head-to-head' adduct (**15**) and the

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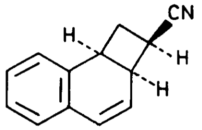
* Studies into photophysical aspects of compounds (**6**) and (7) are in progress in collaboration with Drs. A. Castellan and J.-P. Desvergne of the University of Bordeaux and these results will be reported elsewhere.

'head-to-tail' isomer (**16**). Examination of the undecoupled ^{13}C n.m.r. spectrum of this photoisomer, however, revealed that the carbon of the cyano substituent appeared as a triplet and was coupled (^{13}C–C–CH J 6 Hz) to two protons. This structural unit is present in (**16**) but not (**15**) and on this basis the photoisomer is assigned the former structure.

The intramolecular photocycloadditions of compounds (**4**) and (**5**) are noteworthy since neither occurs by the dipolar oriented route of the specific intermolecular photoreactions of cyanonaphthalene–enol ether systems.[16] In particular, the major product (**16**) from (**5**) represents the first example of cyanonaphthalene–enol ether ($2_\pi + 2_\pi$) photoreaction which has not involved a 'head-to-head' addition and thus provides a further illustration of the directing influence of the interconnecting chain on the reactions of non-conjugated bichromophoric systems.

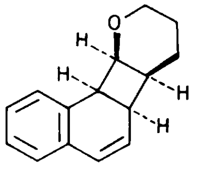
Intermolecular Naphthalene–Enol Ether Systems.—The differing photochemistries of compounds (**6**) and (**7**) have been suggested above to reflect the charge densities in the S_1 naphthyl chromophore. It was considered that this proposal could be substantiated or discounted from a determination of the regiochemistry of the [2 + 2] intermolecular photocycloadditions of polarised ethenes to naphthalene. Consistent with the above rationalisation, the major photoadduct of naphthalene and acrylonitrile has structure (**17**),[4] but no studies have been reported for the reactions of enol ethers with the parent hydrocarbon. We have, therefore, studied the irradiation of naphthalene in the presence of ethyl vinyl ether, 2,3-dihydropyran (DHP), 2,3-dihydrofuran (DHF), dihydro-1,4-dioxin, and of 1- and 2-methylnaphthalenes with DHP and DHF.



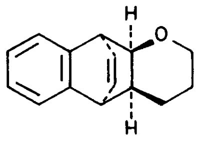
(**17**)

Naphthalene–Ethyl Vinyl Ether.—Irradiation of the addends in pentane gave only trace amounts of products and in acetonitrile although the yield was increased slightly the mixture was still complex and the composition time dependent. All major components were shown by combined m.s./g.c. analysis to be isomers of naphthalene–ethyl vinyl ether 1:1 adducts but isolation of individual products proved to be impracticable.

Naphthalene–DHP.—This system produced one primary 1:1 adduct (M^+ 212) and this rapidly reached a photostationary concentration. A second 1:1 adduct became evident after a short induction period and this isomer was subsequently shown to result from photorearrangement of the primary product. For preparative purposes, it was convenient to irradiate the mixture to a ratio of primary to secondary adducts of 1:4. The two isomers were isolated by preparative g.l.c. and it was deduced from their spectroscopic properties that the primary photoproduct had the *endo* 1,2-cycloadduct structure (**18**) and its photoisomer (m.p. 116—117 °C) the *endo* 1,4-structure (**19**). In particular, the *endo* stereochemistry for each isomer was assigned on the basis of a detailed analysis of the ^1H n.m.r. spectra and the effects on these of adding [Eu(fod)$_3$] shift reagent. Thus, in the spectra of both (**18**) and (**19**), a major feature on addition of the reagent was a shift of one of the aryl proton resonances to lower field: by comparison, the ethenyl protons suffered only a minor shift. It is of interest in view of the preferred *endo* stereochemistry of the [2 + 2] cycloadducts of 1-and 2-naphthonitriles with enol ethers, that the stereochemistry of the present reaction with the parent hydrocarbon should be specific.



(**18**)



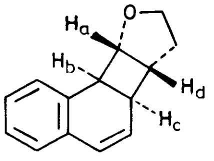
(**19**)

The formation of the 1,2-adduct (**18**) was quenched by 70% in solutions degassed under xenon compared to those under argon.[13] On 254 nm irradiation, compound (**18**) was cleaved to starting materials and formed the 1,3-shift isomer (**19**) with a respective ratio of the two processes of 9:1. The isomerisation process was relatively unaffected by degassing under xenon and was the sole route when (**18**) was irradiated at wavelengths longer than 290 nm in the presence of naphthalene. From these observations it is considered that the formation of the 1,2-cycloadduct (**18**) and the retro-process arise from singlet excited state intermediates whereas the photoinduced 1,3-shift is a triplet state reaction.

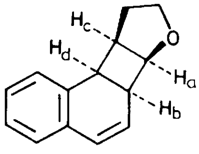
Naphthalene–DHF.—The specific formation of the particular 1,2-cycloadduct isomer (**18**) from naphthalene and DHP adds support to the proposal that the S_1 state of naphthalene has a higher electron density at the 1- than the 2-position. We have previously observed, however, that small structural differences in addends markedly affect photoproduct formation and, in particular, that the photoaddition reactions of DHP and DHF with benzene show significant differences in that the specificity observed for the 1,2-cycloaddition in the former system was lost in the latter.[18]

The irradiation of solutions of naphthalene and DHF in acetonitrile produced two major 1:1 adducts (M^+ 198 a.m.u.) in an initial ratio of 1:5 (increasing retention time on polar phase-bonded capillary column) which changed to a photostationary state of 1:9. Two minor 1:1 adducts were also detected but as these together constituted only *ca.* 5% of the total product mixture they were not considered further. The two major isomers were isolated in >99% purity by flash chromatography and 254 nm irradiation of each produced only starting materials with the minor adduct being the more labile by a factor of *ca.* 2. The retroadditions were not sensitised by naphthalene and hence as for (**18**) the process is deduced to arise from the S_1 state of the 1,2-adduct.

The ^1H n.m.r. spectra of the isolated adducts showed that each had arisen by [2 + 2] cycloaddition and from the vicinal coupling of the H_a proton to the benzylic protons (J 3 Hz) in the minor isomer and of H_a to the allylic proton (J 7 Hz) in the major adduct, the regioisomeric structures (**20**) and (**21**) are respectively assigned. The *exo* and *endo* stereochemistries of (**20**) and (**21**) respectively were deduced from the vicinal coupling constants of H_aH_b and H_cH_d in the two isomers. From molecular models, the dihedral angles of H_aH_b and H_cH_d are *ca.* 104° for the *exo* adduct and 0° for the *endo* isomer and for the



(**20**)



(**21**)

Table. Arene fluorescence quenching and quantum yield data for the naphthalene–DHP and naphthalene–DHF systems

	$10^{-9}k_q/M^{-1}\ s^{-1}$		Φ Product formation[b]		
Solvent	DHP[a]	DHF[a]	(18)	(20)	(21)
Acetonitrile	0.008	0.130	0.055	0.02	0.1
Iso-octane	0.008	0.015	0.01	0.01	0.055

[a] 5×10^{-3}M Naphthalene witn λ excitation = 303 nm and monitoring at λ = 339 nm. [b] λ > 290 nm, 0.3M naphthalene and 2.8M enol ether.

minor and major isomers these coupling constants were respectively 3 and 4.8 Hz and 7 and 12 Hz. The regio- and stereo-chemical deductions were reinforced by the effects on the ^{1}H n.m.r. spectra of adding [Eu(fod)$_3$] shift reagent. In particular, the effect of the reagent on the ethenyl and allylic protons in the minor isomer was small compared to the shift of the benzylic proton and unlike the observations with the *endo* adduct (**18**), the effect on the aryl protons was minor. The chemical shifts of the two ethenyl protons and one of the aryl protons in the major isomer were significantly affected and approximately to the same extent by addition of [Eu(fod)$_3$]. Thus, although in the addition of DHF to naphthalene, the *endo* isomer is preferred, surprisingly, the regiochemistry is the opposite of that observed for the addition of DHP. Further, a preliminary examination of photophysical aspects of the naphthalene–DHP and naphthalene–DHF systems revealed that while both enol ethers quench the arene fluorescence they do so with appreciably different efficiencies and that for DHF is, in contrast to that of DHP, significantly influenced by solvent polarity: these results along with the quantum yields of adduct formation are given in the Table. Neither system showed emission attributable to that of an exciplex in either polar or non-polar solvents. Enol ether additions to naphthonitriles have been proposed to arise from exciplex intermediates and the selectivity of these reactions is considered to reflect preferred orientations in such species.[17] The present results do not necessarily conflict with the involvement of excited state complexes in naphthalene–enol ether additions but further studies are required to assess the participation of non emissive exciplexes in these systems.[19] It is, however, noteworthy that irradiation of the dihydro-1,4-dioxine–naphthalene system in iso-octane, 1,4-dioxane, or acetonitrile yielded no photoadducts and in the last named two solvents exciplex emission is evident at $\lambda_{max.}$ 420 and 448 respectively.

The regiochemistry of the major DHF–naphthalene cycloadduct does not support the proposal concerning the charge densities in the S_1 arene and it is remarkable that the appreciable differences in photochemical behaviour noted above arises from addends with such small differences as those evident in DHP and DHF. In order to assess how minor structural differences in the arene might affect reaction selectivity, 1- and 2-methylnaphthalenes were irradiated in the presence of DHP and DHF. All four systems yielded multicomponent reaction mixtures containing at least three 1:1 adducts in each case.

To summarise, the differing photochemical behaviours of the naphthyl enol ether bichromophores (**6**) and (**7**) can be rationalised in terms of a higher charge density at the naphthyl 1-position than the 2-position. The regiochemistry of the photocycloaddition of 2,3-dihydropyran and of acrylonitrile[4] to naphthalene support this rationalisation but the reaction of 2,3-dihydrofuran with naphthalene does not and shows that minor structural features of the addends markedly influence the regio- and stereo-chemistries of the addition process. Intramolecular ($2_\pi + 2_\pi$) photocycloaddition does occur with both bichromophores which have an aryl cyano substituent but the observed 'head-to-tail' orientation of the reaction is the opposite of that reported for the intermolecular cycloaddition of enol ethers to 1- and 2-cyanonaphthalenes.

Experimental

Photochemical and Analytical Methods.—Irradiations of the bichromophores were carried out as 1% (w/v) solutions in cyclohexane, methanol, or acetonitrile in 50 × 1-cm silica tubes under nitrogen using two 60-cm low-pressure mercury arcs or in 10 × 1-cm Pyrex tubes using a water cooled 125-W medium-pressure mercury arc. Studies of the intermolecular systems were of 0.3M naphthalene and 2.8M enol ether in nitrogen degassed iso-octane, methanol, or acetonitrile. Quantum yield determinations and the study of solvent effects used 10 × 1-cm tubes in a 'merry-go-round' apparatus holding eight such tubes.

Flash chromatography was carried out with Silica Woelm 32—63,[12] and t.l.c. with Camlab Polygram G/U.V. pre-coated sheets. Analytical. g.l.c. was performed on a Hewlett Packard 5790A instrument fitted with a flame-ionisation detector and with either a 12m BPI (OV1 equivalent) or BP20 (CW20M equivalent) S.G.E. phase-bonded capillary column and using nitrogen carrier gas. Hexadecane was used as the internal g.l.c. standard. Mass spectra were obtained using a V.G. Micromass 2S8-controlled A.E.I. M.S.12 Spectrometer coupled to a Perkin-Elmer Sigma 3 g.l.c. fitted with either of the two capillary columns above. Accurate mass data were recorded using a V.G. Micromass 70-70 spectrometer (P.C.M.U., Harwell). ^{1}H N.m.r. spectra were obtained of $CDCl_3$ solutions with tetramethylsilane as internal reference using a Perkin-Elmer R-32 spectrometer and ^{13}C spectra were determined on a Joel FX90Q. Fluorescence spectra were determined on a Perkin-Elmer MPF-2A spectrometer in spectroscopic grade iso-octane and acetonitrile.

Synthesis of the Bichromophores (**6**) *and* (**7**).—The corresponding naphthylethanol (6 g) and freshly distilled ethyl vinyl ether were sealed in a base-washed tube with anhydrous sodium acetate (0.4 g) and mercuric acetate (0.3 g) and maintained at 155 °C for 44 h. Ethanol and unchanged ethyl vinyl ether were removed by rotary evaporation and the unchanged naphthylethanol was removed by eluting the concentrated reaction mixture through an alumina column with light petroleum (b.p. 30—40 °C). The resulting solution was concentrated and the crude naphthyl enol ether (*ca.* 4 g, *ca.* 60%) was purified by vacuum distillation: (**6**), b.p. 104—108 °C at 0.03 mmHg, δ 8.1—7.2 (7 H, m), 6.43 (1 H, dd, *J* 7 and 14 Hz), 4.3—3.8 (4 H, m), and 3.34 (2 H, m); $\nu_{max.}$ 3 040w, 2 950w, 2 870w, 1 640w, 1 615m, 1 510w, 1 020m, 960m, 800s, 790s, and 725s cm^{-1}; $\lambda_{max.}$(iso-octane) absorption 282nm, $\lambda_{max.}$ emission 327 nm (Found: *M*, *m/z* 198.1045. Calc. for: M^+, 198.1045); (**7**), b.p. 92—97 °C at 0.02 mmHg; δ 7.9—7.2 (7 H, m), 6.48 (1 H, dd, *J* 7 and 14 Hz), 4.4—3.8 (4 H, m), and 3.10 (2 H, t, *J* 6 Hz); $\nu_{max.}$ 3 040w, 2 950w, 2 870w, 1 640w, 1 615m, 1 510, 1 020m, 960m, 820s, and 750s cm^{-1}; $\lambda_{max.}$(iso-octane) absorption 276, $\lambda_{max.}$ emission 334 nm (Found: *M*, *m/z* 198.1044. Calc. for: M^+, 198.1045).

Synthesis of the Bichromophores (**4**) *and* (**5**): *General Procedure.*—The appropriate 1-bromomethylnaphthalene was converted into the corresponding acid by the method outlined by Newman and Kosak.[20] The acid (40 g) was reduced to the alcohol by diborane (6.5 g, 10% excess) in dry tetrahydrofuran and was subsequently acetylated with acetyl chloride. The acetyl compound (32 g) was obtained as a colourless oil and dissolved in dimethyl sulphoxide (100 ml). Cuprous cyanide

(15 g) was added to the solution under nitrogen and the mixture maintained at 165 °C for 24 h after which it was poured into 40% (w/v) aqueous potassium cyanide. The mixture was extracted with diethyl ether (3 × 75 ml) and the resulting oil was purified by flash chromatography. The cyano compound (26 g) in ethanol (75 ml) was treated with a 10% (v/v) solution concentrated hydrochloric acid (75 ml) and refluxed for 2.5 h. After removal of the solvent (rotary evaporation) and ether extraction, the 2-(1-cyanonaphthyl)ethanol (20 g) was obtained. The alcohol was converted into the enol ether by the same method as that employed for the synthesis of compounds (**6**) and (**7**). Compound (**4**), m.p. 45—46 °C [light petroleum (b.p. 40—60 °C)]; δ 8.5—7.2 (6 H, m), 6.7—6.3 (1 H, dd, *J* 7 and 14 Hz), 4.3—3.8 (4 H, m), and 3.5 (2 H, t, *J* 5 Hz); $\nu_{max.}$ 3 080w, 2 915m, 2 890m, 2 225s, 1 620s, 1 520m, 1 200s, 825s, and 770s cm^{-1}; $\lambda_{max.}$(iso-octane) absorption 298 nm, $\lambda_{max.}$ emission 344 nm; (Found: C, 80.8; H, 5.9; N, 6.4. $C_{15}H_{13}NO$ requires C, 80.7; H, 5.6; N, 6.3%). Compound (**5**), m.p. 32.5—33 °C [light petroleum (b.p. 30—40 °C]; δ 8.5—7.0 (6 H, m), 6.6—6.2 (1 H, dd, *J* 7 and 14 Hz), 4.3—3.9 (4 H, m), and 3.4 (2 H, t, *J* 5 Hz); $\nu_{max.}$ 3 110w, 3 080m, 2 915m, 2 890m, 2 220s, 1 620s, 1 510m, 1 200s, 830s, and 760s cm^{-1}; $\lambda_{max.}$(iso-octane) absorption 298 nm, $\lambda_{max.}$ emission 344 nm (Found: C, 80.5; H, 5.8; N, 6.3%. $C_{15}H_{13}NO$ requires C, 80.7; H, 5.6; N, 6.3%).

Photoproducts of the Bichromophores.—The isomer (**11**) from (**6**) was isolated as a colourless oil in >99.5% purity (g.l.c. and one spot on t.l.c.) by flash chromatograph using 10% diethyl ether in light petroleum (b.p. 30—40 °C) as the eluting solvent: δ 7.30—6.85 (4 H, m), 6.25 (1 H, dd, J_{vic} 10 and $J_{allylic}$ 1.5 Hz), 5.80 (1 H, dd, *J* 10 and 5 Hz), 4.52 (1 H, t with fine splittings, *J* 4.5 and 0.9 Hz), 4.45—4.20 (2 H, m), 2.80 (1 H, dd with fine splittings, *J* 8.5, 5, 1.5, and 0.9 Hz), 2.25 (2 H, dd, *J* 8.5 and 4.5 Hz), and 2.20—1.90 (2 H, m); ^{13}C spectrum ($SiMe_4$ standard) δ 136.82—123.62 (8 signals), 89.35, 68.74, 50.05, 42.92, 38.30, and 35.83 p.p.m.; $\nu_{max.}$ 3 070w, 3 030m, 2 980m, 2 940m, 1 600w, 1 495m, 1 065s, 810s, 790s, and 760s cm^{-1} (Found: *M*, *m/z* 198.1046. Calc. for *M*, 198.1045).

Prolonged irradiation of compound (**7**) in the presence of 2-(2-naphthyl)ethanol produced compound (**10**), m.p. 41—42 °C, δ 7.95—7.15 (14 H, m), 4.65 (1 H, q, *J* 5.5 Hz), 3.85—3.55 (4 H, ABq of t, *J* 9.5 and 7 Hz), 2.92 (4 H, t, *J* 7 Hz) and 1.25 (3 H, t, *J* 5.5 Hz); δ_C 136.57, 133.54, 132.13, 127.74, 127.47, 127.09, 125.79, 125.14, 65.88, 36.57, and 19.61 p.p.m. (Found: *M*, *m/z* 370.1933. Calc. for: *M*, 370.1930].

The isomer (**12**) from (**4**) (respective relative g.l.c. retention times on BP1 of 1.0:0.97) was isolated as a colourless oil in >99% purity (g.l.c. and on spot on t.l.c.) by flash chromatography using diethyl ether–light petroleum (b.p. 40—60 °C) (1:1) as the eluting solvent; δ 7.52—7.12 (4 H, m), 6.67 (1 H, d, *J* 6 Hz), 4.57—4.48 (1 H, m, *J* 6, 3, and 1 Hz), 4.45—4.10 (2 H, cm), 3.08—2.90 (1 H, m, *J* 10, 8.5, 6, and 1 Hz), 2.50—2.30 (2 H, cm, *J* 14, 6, and 3 Hz), and 2.30—2.10 (2 H, cm); $\nu_{max.}$ 2 220 cm^{-1}; (Found: M^+, *m/z* 223.0995. Calc. for: *M*, 223.0998).

The isomer (**16**) from irradiation of (**5**) (respective relative retention times on BP1 of 0.96:1.0) was isolated as colourless crystals, m.p. 70—72 °C in >99% purity (g.l.c. and one spot on t.l.c.) by flash chromatography using diethyl ether–light petroleum (b.p. 40—60 °C) (1:1) as the eluting solvent: δ 7.4—7.32 (1 H, m), 7.32—7.20 (2 H, m), 7.12—7.04 (1 H, m), 6.4 (1 H, d, *J* 9.7 Hz), 5.62 (1 H, d, *J* 9.7 Hz), 4.6—4.52 (1 H, dd, *J* 6.5 and 3.5 Hz), 4.46—4.34 (2 H, m, *J* 10.3, 8.5, 5.3, and 2 Hz), 3.02—2.76 (2 H, d of dd, *J* 14, 6.5, 3.5 Hz), 2.66—2.54 (1 H, d of dd, *J* 13.5, 5.3, and 2 Hz), and 2.02—1.84 (1 H, 8 lines, *J* 13.5, 10.3, and 8.5 Hz); δ_C ($SiMe_4$ standard) 132.18, 129.80, 128.98, 128.56, 128.01, 127.74, 127.53, 126.44, 120.92, 84.57, 69.18, 53.85, 46.59, 38.30, and 35.05 p.p.m.; $\nu_{max.}$ 3 040w, 3 020w, 2 980m, 2 950m, 2 860s, 2 220s, 1 540w, 1 495s, 1 425s, 1 360s, 1 093s, 785s and 760s cm^{-1}; $\lambda_{max.}$(cyclohexane) 260 nm (ε 11 500 l mol^{-1} cm^{-1}) (Found: *M*, *m/z* 223.0996. Calc. for *M*, 223.0998).

Photoproducts from Intermolecular Naphthalene–Enol Ether Systems Naphthalene–DHP.—The primary and secondary photochemical 1:1 adducts (respective relative retention times on a BP20 capillary column of 1.9 to 1.0) were isolated in >99% purity (g.l.c., one spot on t.l.c.) by preparative g.l.c. (**18**), δ 7.40—6.95 (4 H, m), 6.42 (1 H, dd, *J* 10 and 1 Hz), 5.92 (1 H, dd, *J* 10 and 4.5 Hz), 4.48 (1 H, dd + fine splitting *J* 6.5, 6.0, and 2 Hz), 3.74 (1 H, dd, *J* 10 and 6.5 Hz), 3.72—3.52 (1 H m), 3.42—3.25 (2 H, m), 2.88 (1 H, dd), 2.0—1.6 (2 H, m), and 1.6—1.0 (2 H, m); $\nu_{max.}$ 1 590w, 1 080s, 790s, and 755m cm^{-1}; $\lambda_{max.}$(iso-octane) 275 (ε 9 300 l mol^{-1} cm^{-1}) (Found: *M*, m/z 212.1196. Calc. for: *M*, 212.1202). Compound (**19**), m.p. 116–117 °C, δ 7.4—7.1 (4 H, m), 6.7—6.6 (1 H, 7 lines, *J* 8, 7, and 1 Hz), 6.5—6.4 (1 H, 7 lines, *J* 8, 6.5, and 1 Hz), 4.15—4.05 (1 H, m, *J* 6.5, 3.5, and 1 Hz), 3.8—3.5 (3 H, m, *J* 8, 7, 3.5, and 1 Hz), 3.45—3.3 (1 H, m), 1.95—1.70 (1 H, m), 1.7—1.55 (3 H, m), and 0.65—0.4 (1 H, m); $\nu_{max.}$ 1 610w, 1 090s, and 705m cm^{-1}; $\lambda_{max.}$(iso-octane) 265 nm (ε 350 l mol^{-1} cm^{-1}) (Found: *M*, *m/z* 212.1203. Calc. for: *M*, 212.1202).

Naphthalene–DHF.—The two 1:1 adducts were isolated in >99% purity (g.l.c. and one spot on t.l.c.) by flash chromatography using 20% (v/v) diethyl ether–light petroleum (b.p. 30—40 °C). Compound (**20**), δ 7.40—6.90 (4 H, m), 6.33 (1 H, d, *J* 10 Hz), 5.90 (1 H, dd, *J* 10 and 4.8 Hz), 4.56 (1 H, dd, *J* 6 and 3 Hz), 4.35 (1 H, m, J_{gem} 9.5 Hz), 4.22 (1 H, d + fine splitting, J_{gem} 9.5 Hz), 3.55 (1 H, dd, *J* 11 and 3 Hz) 2.98 (1 H, m, *J* 6, 4.8, and 0.5 Hz), 2.77 (1 H, m, *J* 11, 4.8, 4.8, and 0.5 Hz), and 1.88 (2 H, m); $\nu_{max.}$ 3 080w, 3 030w, 2 950s, 2 800m, 1 120s, 1 075s, 785m, 770m, and 755m cm^{-1}; $\lambda_{max.}$(iso-octane) 274 nm (ε 10 400 l mol^{-1} cm^{-1}) (Found: *M*, *m/z* 198.1038. Calc. for: *M*, 198.1045). Compound (**21**) δ 7.40—6.90 (4 H, m), 6.35 (1 H, d, *J* 10 Hz), 5.60 (1 H, dd, *J* 10 and 4.5 Hz), 4.96 (1 H, t with fine coupling, *J* 7 and 7 Hz), 4.10—3.80 (2 H, m, *J* 18, 11.5, 9, 7, and 3 Hz), 3.76—3.60 (1 H, m, *J* 18 and 6.5 Hz), 3.57—3.33 (2 H, m, *J* 13, 7, and 4.3 Hz), 2.22—2.02 (1 H, q + fine splitting, *J* 12, 6.5 and *ca.* 1 Hz), and 1.88—1.62 (1 H, m, *J* 12 and 9 Hz); $\nu_{max.}$ 3 080w, 3 020m, 2 960s, 2 890m, 1 490m, 1 445m, 1 085s, 795s, 790m, and 760s cm^{-1}; $\lambda_{max.}$(iso-octane) 276 nm (ε 10 600 l mol^{-1} cm^{-1}) (Found: *M*, *m/z* 198.1033. Calc. for *M*, 198.1045).

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