Substituent Effects on the Intramolecular Photochemical Reactions of Phenyl–Ethenyl Non-conjugated Bichromophoric Systems

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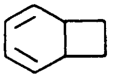
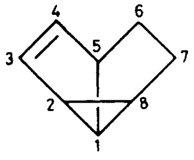
The effects of substitution on the photochemistry of phenyl–ethenyl bichromophoric systems are reported. Methyl substitution at the 2-, 3-, 5-, and 1,1,2-positions in the pentene moiety of 5-phenylpent-1-ene reduces both reaction efficiency and selectivity but in contrast to intermolecular analogues the photoreaction of 3-phenethylcyclohexene is comparable with that of the corresponding cyclopentene. Incorporation of ester units in the connecting unit between the chromophores or on the ethene inhibits intramolecular cyclisation as does the presence of *para* OMe, CN, or COMe groups in 5-phenylpent-1-ene. In contrast reaction selectivity and efficiency are greatly promoted by *ortho* Me or OMe groups and the products reflect exclusive 1,3-cycloaddition. The presence of a *para* Me group in 5-phenylpent-1-ene leads to specific 2,6-intramolecular cyclisation but the reaction of the *meta*-Me derivative leads to four products derived from 1,3- and 1,5-intramolecular cycloaddition. The observations are discussed in terms of mechanisms of arene–ethene photoreactions and preferred conformations of the bichromophores.

Factors which have a significant effect on the preferred modes and efficiencies of intermolecular photocycloaddition of ethenes to benzene and its alkyl, alkoxy, and cyano derivatives have been the subject of several studies and have now largely been elucidated.[1—10] Thus systems in which the reactants have an obvious electron donor–acceptor relationship (*e.g.* anisole–acrylonitrile,[2] benzonitrile–enol ethers[3]) yield mainly or solely bicyclo[4.2.0]octa-2,4-diene derivatives (*ortho* cycloadducts) (**1**) whereas in other cases the *meta* cycloaddition leading to the tricyclo[3.3.0.$0^{2,8}$]oct-3-ene system (**2**) is preferred.[1,4—8] With only one exception, the *para* cycloaddition reaction to give bicyclo[2.2.2]octadienes is that least favoured.[11] For systems in which the ethene and arene moieties are linked (*i.e.* intramolecular analogues) other features such as the number and type of units intervening between the addends, and the ethene geometry, have a marked effect on the position and efficiency of reaction. These features are illustrated by the photoproducts from 5-phenylpent-1-ene and 6-phenylhex-1-ene.[12] In the former case the ethene reacts at the phenyl 2,6- and 1,3-positions but for the hex-1-ene only the 1,3-positions are involved and the quantum efficiencies are respectively 0.11 and 0.045, and < 0.005. Further, phenethyl vinyl ether undergoes intramolecular addition principally at the 2,5-positions (*para*) but for 3-phenylpropyl vinyl ether the attack is at the 1,3- and 2,4-arene positions, and although *cis*- and *trans*-6-phenylhex-2-enes both yield intramolecular *meta* cycloadducts, reaction occurs only at the 1,3-positions in the former isomer and the 2,6-positions in the latter.[13] Inspection of space-filling molecular models of the bichromophores allows rationalisation of these results in terms of preferred conformations which dictate the relative orientations of the phenyl and ethenyl groups and thence lead to specific or highly selective positions of reaction. These considerations can give predictability to the photoreactions of such bichromophores: this is most important as illustrated by the studies of Wender and co-workers who have made elegant use of the intramolecular *meta* photocycloaddition as the key step in the synthesis of the polyquinanes cedrene,[14] isocomene,[15] and hirsutene.[16]

In order to gain a fuller appreciation of the factors which control modes and efficiencies of these intramolecular processes, and thereby to improve the ability to predict the synthetic usefulness of particular bichromophores, it is essential to elucidate the effects of substituents in the arene, the ethene, and the interconnecting unit on the excited-state chemistry of such systems. In the present paper we describe the results of such substituent effects on the interactions and reactions between the two chromophores and discuss our findings in terms of mechanisms of ethene–arene photoaddition processes and preferred conformations of the bichromophores. The synthetic implications of our results are also considered.


(1)



(2)

Results

5-Phenylpent-1-ene (**3**) was chosen as the 'standard' bichromophore in this study since, first, it has three connecting units between the chromophores and this feature maximises their interaction,[17] secondly it has the basic molecular structure of the polysubstituted systems that have been used in the three successful synthetic applications of the intramolecular *meta* cycloaddition process,[14—16] and thirdly its photochemistry is well established.[8,12] We have studied the photochemistries of the bichromophores (**6**)—(**22**) in order to determine the effects on (**3**) of (*a*) methyl substitution on the ethene and its incorporation into a cyclic system [(**6**)—(**12**)], (*b*) methyl substitution at the three positions in the propane connecting unit [(**13**)—(**15**)], (*c*) methyl, methoxy, cyano, and acetyl substitution in the phenyl group [(**16**)—(**20**)], and (*d*) replacement of the propane unit by an ester grouping [(**21**) and (**22**)].

All irradiations were carried out with 1% w/v solutions of the bichromophore in cyclohexane using low-pressure mercury arc lamps. Degassing under nitrogen or change to more polar solvents had no significant effect on photoproduct formation. The reactions were monitored by g.l.c. (W.C.O.T. Carbowax 20M) and t.l.c., and the photoproducts were isolated by preparative g.l.c. and flash chromatography. Purities of photoproducts > 99% (g.l.c.) were achieved in some cases but

Table 1. Intramolecular photoreactions of phenyl–ethenyl bichromophoric systems

Bichromophore [Φ disappearance]	Product[a]	Arene positions involved	Ratio of products	Chromatographic retention time[b]	Total Φ of product
(**3**)[8,12]	5,6-Bridged isomer (**27**)	1,3	1.15	0.67	0.15
	7,8-Bridged isomer (**28**)	1,3	1.00	0.53	
	1,6-Bridged isomer (**29**)	2,6	4.80	0.85	
(**4**)[13]	*exo*-7-Methyl-5,6-bridged isomer (**27**)	1,3	1.00		0.26
	exo-6-Methyl-7,8-bridged isomer (**28**)	1,3	1.00		
(**5**)[13]	*endo*-7-Methyl-1,6-bridged isomer (**29**)	2,6			Not given[13]
(**6**) [0.35]	*endo*-6-Methyl-5,6-bridged isomer (**27**)	1,3	1.00	0.52	0.06
	endo-7-Methyl-7,8-bridged isomer (**28**)	1,3	1.65	0.44	
	endo-6-Methyl-1,6-bridged isomer (**29**)[c]	2,6	1.65	0.58	
(**7**) [0.075]	(**32**)	2,5	1.90	0.37	0.03
	6,7,7-Trimethyl-4,6-bridged isomer[d]	2,4	1.00	0.41	
	6,7,7-Trimethyl-5,6-bridged isomer (**27**)	1,3	1.00	0.48	
	6,6,7-Trimethyl-7,8-bridged isomer (**28**)	1,3	1.25	0.44	
	+ two minor uncharacterised isomers				
(**8**) [0.30]	(**40**)	1,3	1.00	0.65	0.12
	(**41**)	2,6	9.00	0.85	
(**9**) [0.20]	(**42**)	1,3	1.35	0.56	0.15
	(**43**)	1,3	1.00	0.63	
(**10**)[g]	Very low yield of one isomer; uncharacterised			0.73	<0.001
(**11**)[g]	Very low yield of five isomers; uncharacterised		7:1:1:3.5:5	0.73, 0.78, 0.81, 0.90, 0.93	< 0.001
(**12**) [0.20]	Major: (**44**) + 9 other photoisomers	2,6 (major)	1:2.8:1.25:1:8.5:6.5:4.5:20:4.5:2.5	0.39, 0.40, 0.42, 0.48, 0.50, 0.52, 0.54, 0.59, 0.63, 0.72	0.03 (major)
(**13**) [0.50]	Methyl-substituted[e]				
	5,6-bridged isomer (**27**)	1,3	1.2	0.66	0.055
	7,8-bridged isomer (**28**)	1,3	2.3	0.57	
	1,6-bridged isomer (**29**)[c]	2,6	4.8	0.96	
	1,7-bridged isomer (**30**)[d]	2,6	1.0	0.84	
	4,6-bridged isomer	2,4	2.6	1.14	
(**14**) [0.15]	*exo*-Methyl-1,6-bridged isomer (**29**)[c]	2,6	1.0	0.79	0.035
	endo-Methyl-1,6-bridged isomer (**29**)[c]	2,6	1.4	0.85	
	+ 3 minor non-isolated isomers		0.8 combined	0.54, 0.60, 0.69	
(**15**) [0.40]	Methyl-substituted[e]				
	5,6-bridged isomer (**27**)	1,3	1.0	1.02	0.055
	1,6-bridged isomer (**29**)[c]	2,6	3.5	0.97	
	1,7-bridged isomer (**30**)	2,6	1.0	1.06	
	+ 2 minor non-isolated isomers		0.7 combined	0.88, 93	
(**16**) [0.90]	1-Methyl-1,5-bridged isomer (**27**)	1,3	1.60	0.73	0.60
	1-Methyl-7,8-bridged isomer (**28**)	1,3	4.25	0.60	
	(**48**)	1,4	1.00	0.68	
(**17**) [0.08]	8-Methyl-5,6-bridged isomer (**27**)	1,3	3.25	0.44	0.07
	5-Methyl-7,8-bridged isomer (**28**)	1,3	3.70	0.38	
	3-Methyl-5,6-bridged isomer (**27**)	1,5	10.00	0.54	
	3-Methyl-7,8-bridged isomer (**28**)[f]	1,5	1.00	0.80	
(**18**) [0.45]	3-Methyl-1,6-bridged isomer (**29**)[c,e,f]	2,6		0.43	0.06

[a] Numbering of *meta* cycloadducts as given in structure (**2**). [b] Relative to the starting bichromophore of 1.0 on a W.C.O.T. Carbowax 20M column. [c] Thermal 1,5-sigmatropic shift isomer[24] formed from the photoproduct during analysis by g.l.c. and/or separation by preparative g.l.c. [*e.g.* (**45**), (**46**), and (**47**) from photoadduct isomers of (**14**), (**15**), and (**18**) respectively.] [d] Structure tentative. [e] Stereochemistry of the methyl group not determined. [f] Four other isomers formed (M^+, m/z 160; mass spectrometry–g.l.c.) but structural elucidation inhibited by low purity from chromatographic procedures. [g] $\Phi_{\text{disappearance}}$ inaccurate owing to rapid polymer formation but assessed to be > 0.3.

Table 1. (*continued*)

Bichromophore [Φ disappearance]	Product[a]	Arene positions involved	Ratio of products	Chromatographic retention time[b]	Total Φ of product
(19) [0.80]	1-Methoxy-5,6-bridged isomer **(27)**	1,3	5.60	0.48	0.5
	1-Methoxy-7,8-bridged isomer **(28)**	1,3	4.65	0.42	
	+ two minor non-isolated isomers		1.00 combined	0.37, 0.76	
(20)	No significant volatile products; varying amounts of polymeric material				
(21)[g]	Much polymer, $Ph[CH_2]_nOH$, dicyclohexyl. Evidence in the 300—360 nm region for tetraene absorptions.				
(22)	Traces of photoproducts but largely photostable				
(35)	*cis* ⇄ *trans*-interconversions				

$Ph[CH_2]_3CH{=}CH_2$

(3)

$Ph[CH_2]_3CH{=}CHMe$

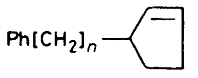
(4) *cis*
(5) *trans*

$Ph[CH_2]_3CMe{=}CH_2$

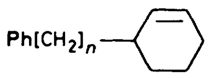
(6)

$Ph[CH_2]_3CMe{=}CHMe_2$

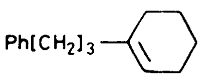
(7)



(8) $n = 2$
(10) $n = 3$



(9) $n = 2$
(11) $n = 3$



(12)

$Ph[CH_2]_2CHMeCH{=}CH_2$

(13)

$PhCH_2CHMeCH_2CH{=}CH_2$

(14)

$PhCHMe[CH_2]_2CH{=}CH_2$

(15)

$XC_6H_4[CH_2]_3CH{=}CH_2$

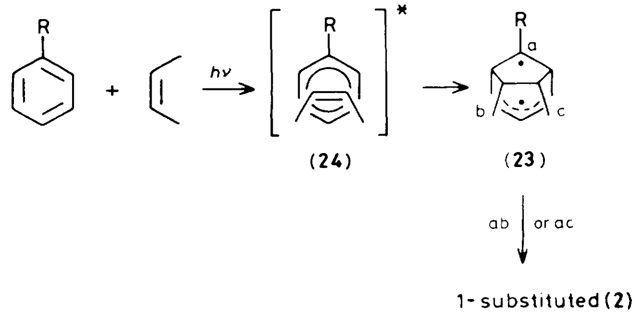
(16) X = *o*-Me
(17) X = *m*-Me
(18) X = *p*-Me
(19) X = *o*-OMe
(20) X = *p*-CN, -OMe, or -COMe

$Ph[CH_2]_n{-}O{-}COCH{=}CH_2$

(21) n = 1, 2 or 3

$Ph[CH_2]_n{-}CO{-}O{-}CH{=}CH_2$

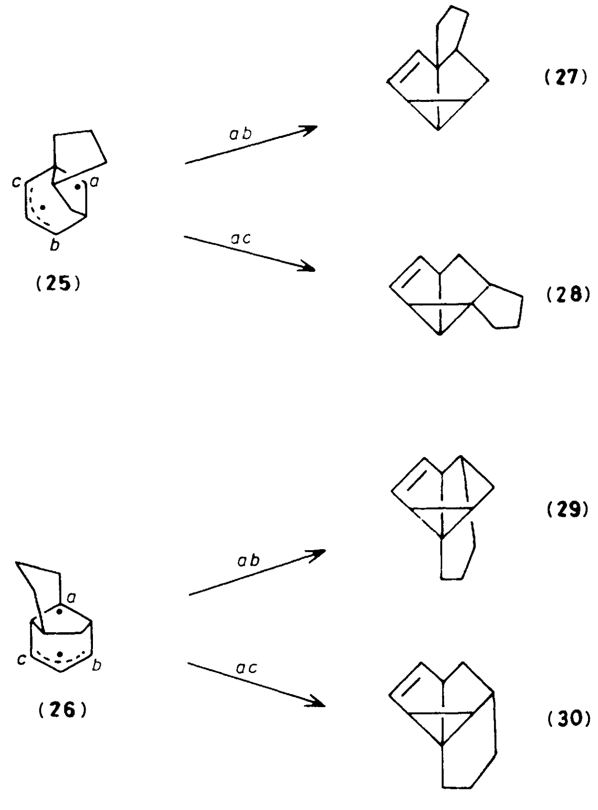
(22) n = 1, 2 or 3



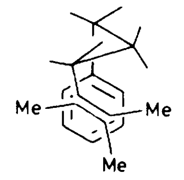
for other systems the chromatographic procedures gave purities of 75—90% which could not realistically be bettered; the impurities were other photoisomers. Structural elucidation of the photoproducts is based on their spectral data and chemical properties but as such features of arene–ethane adducts which allow conclusive assignments to be made have been extensively discussed and are well documented elsewhere,[18] these aspects of the present systems are not considered here, but relevant ^1H n.m.r. data of the photoadducts are summarised in the Experimental section. The results of irradiation of the bichromophores **(6)**—**(22)**, along with those from 5-phenylpent-1-ene **(3)**[8,12] and *cis*- and *trans*-6-phenylhex-2-ene [**(4)** and **(5)** respectively],[13] are summarised in Table 1. The numbering used for the intramolecular *meta* cycloadducts is based on that of **(2)** and it will be noted that the unit originally connecting the chromophores must, for the present systems, lie between the 1,6-, 1,7-, 4,6-, 5,6-, or 7,8-positions in the photoisomer.

Discussion

It can be seen from the tabulated results that intramolecular *meta* cycloadducts are the most common volatile products from 254 nm radiation of the bichromophores **(3)**—**(9)** and **(12)**—**(19)**. Study of the intermolecular photoreactions of substituted benzenoid compounds with ethenes has revealed that the *meta* cycloaddition process shows remarkable regioselectivity giving principally the 1-substituted isomers of **(2)**;[4–6] the exception to this is the formation of the 4-cyano isomer from benzonitrile and *trans* 1,2-dichloroethane.[10] These observations have been interpreted in terms of substituent stabilisation of the radical centres of the intermediate **(23)** which is considered to arise by 2,6-addition of the ethene to the arene on collapse of the sandwich exciplex **(24)**. Only for the *meta* cycloaddition of dioxoles to benzene, however, has the involvement of excited-state complexes been firmly established in these reactions.[9] Assuming that this basic mechanism of *meta* addition followed by formation of the ethenyl-cyclopropane operates for intramolecular systems then it must be realised that the two



Scheme.



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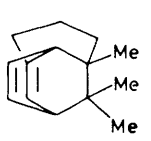
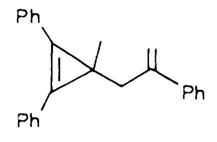


(32)



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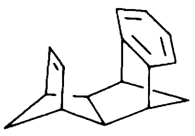
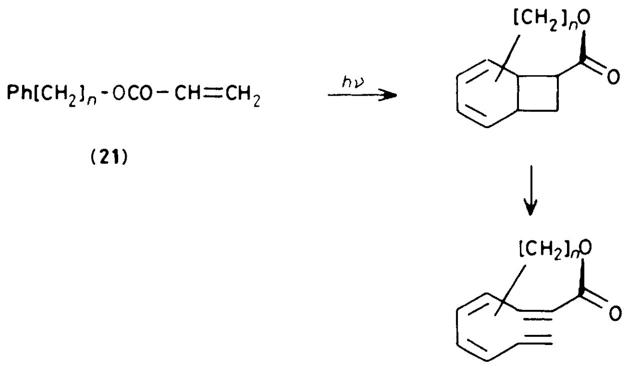


(34)

$Ph[CH_2]_3CH{=}CHCO_2Me$

(35)



(36)

modes of closure (*i.e. ac* and *ab*) in the intermediate diradical species can result in the formation of two isomers of the intramolecular cycloadduct. The two likely positions of ethene attack onto the arene from steric considerations are 1,3 and 2,6. These modes of reaction would give the intermediates (**25**) and (**26**); (**25**) may then yield the 5,6- and 7,8-bridged isomers (**27**) and (**28**), and (**26**) the 1,6- and 1,7-bridged isomers (**29**) and (**30**) as shown in the Scheme. If radical stabilisation of the intermediate is the important feature in the intramolecular additions then for phenyl compounds the latter process is expected to be preferred. In other cases substituent radical stabilisation may be provided by groups originally on the arene *ortho* and *para* positions which then reside respectively on the *a* and/or *c* and *b* positions in (**25**). Molecular models show that the 1,7-bridged isomer (**30**) is far more strained than the 1,6-isomer (**29**) but there is no obvious feature to differentiate between the closures from the 1,3-reaction and from such a pathway (**27**) and (**28**) might be expected to be formed with similar efficiencies. The results in Table 1 clearly show the preference for the 1,6-bridged isomer formation but the relative quantum efficiencies of 7,8- and 5,6-bridged isomer production are very variable. Similar inequality of formation of the two isomers has also been observed by Wender and co-workers for two of the bichromophores used in their synthetic studies.[15,16] Very small energy differences between the pathways may, however, lead to one isomer being greatly favoured (ΔE_a for a 10:1 factor *ca.* 5.7 kJ mol^{-1}) and it is thus unrealistic to expect equal quantities of (**27**) and (**28**). This reaction pathway implies interaction between the S_1 arene and S_0 ethene whereas the alternative mechanism of prior arene rearrangement to the bicyclo[3.1.0]hexenyl diradical and intramolecular trapping of this species by the ethene does not. For all the systems under study, the arene fluorescence was $<10\%$ that of the corresponding reduced compound and for (**7**) and (**18**) a broad longer wavelength emission was observed. The *ortho* methyl compound (**16**) has substituent stabilisation for (**25**) and the quantum yields of formation of the 7,8- and 5,6-bridged isomers are 0.38 and 0.15 respectively. The relative fluorescence of the bichromophore to the reduced derivative is 1:10; and hence, in this case at least, the products most reasonably result from the S_1 arene—S_0 ethene excited-state interaction. In this, as for other bichromophores, minor energy differences in the two modes of closure to the cyclopropanes must account for the non-equal formation of the two isomers. These differences do not apparently result from the environment of the spiro carbon atom for in the generally favoured 7,8-bridged adduct C_3–C_5 rings are involved while a C_5–C_5 system is present in the 5,6-isomer. Unfortunately the inability to determine and predict these influencing factors does render the reaction less attractive as a synthetic procedure.

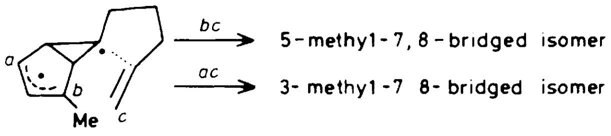
The effect of methyl substitution in the pent-1-ene moiety on the photochemistry of (**3**) is considerable both in terms of efficiency and modes of cyclisation. We have noted previously that the *meta* adduct isomers formed from (**3**) and the phenylhexenes (**4**) and (**5**) are understandable in terms of preferred conformations of the bichromophores which to some considerable extent control the relative orientation of the phenyl and ethenyl groupings.[8] The present study shows that a methyl group in the 2-position of (**3**) does not fundamentally affect the photochemistry although quantum yields are lowered and the 1,3-attack becomes preferred over the 2,6-process. Minor steric interactions evident from molecular models suggest that these differences between (**3**) and (**6**) may have been expected and a similar analysis of the trimethylethenyl

Table 2. Arene fluorescence emission of (**21**) ($\lambda_{max.}$ 287 nm)

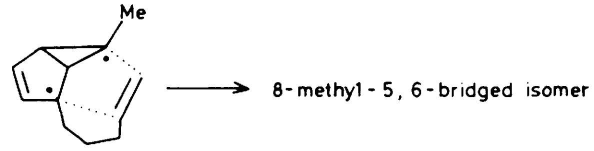
'n' Value	Relative fluorescence intensity of (**21**)	Relative fluorescence intensity of propionate	Relative intensities (**21**):propionate
0	—	1	—
1	6.5	11	1:5
2	2	18	1:26
3	1	17	1:50

compound (**7**) again provides understanding of the reaction modes followed. Thus, 2,6-attack appears unlikely for (**7**) but the conformational distortion of this orientation produced by the proximity of the *cis*-methyl group and the hydrogens on the 4-position [a feature which is considered to disfavour 2,6-attack with (**4**)[8.13]] causes the ethene unit in (**7**) to lie over the phenyl 2,5-positions [see structure (**31**)] and this is reflected in the photoreaction which yields the *para* cycloadduct (**32**) as the major product. The other likely orientation of attack appears to be 1,3 which is observed, but a 2,4-reaction, also observed, does seem somewhat unlikely for systems with only three units between the chromophores. Methyl substitution on the ethene will increase the electron-donor properties of this chromophore and from this feature and the precedent of the intermolecular reaction of 2,3-dimethylbut-2-ene and benzene,[7] it may have been expected that (**7**) would yield an intramolecular *ortho* cycloadduct probably by 1,2-attack. Despite no apparent serious steric barrier to this addition, no evidence for such reaction was obtained but it is noteworthy here that with the exception of 1,2-cycloaddition of the cyclopropene moiety to the phenyl group in (**33**),[19] the only intramolecular *ortho* photocycloadditions that have been reported result from systems such as (**34**) in which molecular geometry dictates the occurrence of this mode of reaction.[20] Our attempts to promote the *ortho* cycloaddition by using the intramolecular benzene–acrylate systems[2a] (**21**) and (**35**) failed. The bichromophore (**35**) simply underwent *cis–trans* interconversions and much polymeric material resulted from (**21**), although in these systems evidence was obtained from absorption spectroscopy that the tetraenes (**36**) (absorptions in the 300—360 nm region[21]), produced on ring opening of the *ortho* cycloadducts, may be present during the early stages of the irradiation. Likewise the intramolecular benzene–vinyl acetate systems[2a] (**22**) produced no isolable monomeric products and so despite the frequent use of the ester grouping as a convenient link between the bichromophores in polynuclear aromatic hydrocarbon systems,[22] for phenyl–ethenyl compounds such units effectively quench the photochemistry. The arene fluorescence intensity measurements of (**21**) compared with those of the corresponding propionates (see Table 2) suggest that for $n = 1$ quenching of the arene fluorescence has a 'through-bond' component with the ester grouping whereas for $n = 3$ the low emission intensity results from quenching by the vinyl group.

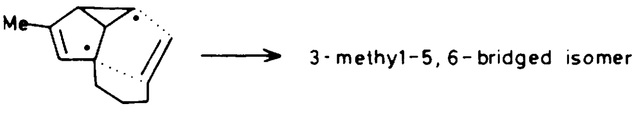
As evident from the data in Table 1, methyl substitution on the $-[CH_2]_3-$ unit of (**3**) causes a drop in quantum efficiency of *meta* cycloaddition and lowers the reaction selectivity but it is noteworthy that products having 1,7-bridged units are observed for the first time. Methyl substitution of the benzylic or allylic positions appear to have the most detrimental effects on selectivity but for (**14**) this feature is improved over (**3**). The cause of such perturbations of the reactions of (**3**) is not obvious but it is evident that subtle changes in molecular geometry induced by minor steric interactions have marked effects on the photochemistry of these bichromophoric systems.



(**37**)



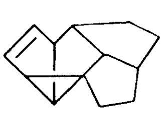
(**38**)



(**39**)

The intermolecular photoreactions of cyclopentenes and cyclohexenes with benzene and its simple derivatives differ markedly.[4,7] In the former case *meta* cycloadducts are formed with reasonable efficiencies but from cyclohexene very low yields of dimers of the ethene[23] and 1:1 adducts are produced. The present results show that for the intramolecular analogues (**8**) and (**9**) of these systems, the currently undetermined features which cause such differences between the intermolecular photoreactions of these cycloalkenes are not evident. Again, however, minor conformational and/or steric factors in the two systems result in the preference for 2,6-addition with (**8**) and 1,3- for (**9**). The changes observed between (**8**) and (**10**), and (**9**) and (**11**), result simply from the differing facility of excited-state interactions between the chromophores as a result of the numbering of intervening units. This feature is also shown by the efficiencies of intramolecular arene fluorescence quenching by the ethene which are very similar for (**8**) and (**9**) but for (**10**) and (**11**) are *ca.* 2.0 and 2.5 times smaller respectively. Structural change of the cyclohexene moiety to that in (**12**) has a dramatic effect on reaction selectivity and produces ten photoisomers. The major product results from 2,6-ethene attack which is probably directed by the same feature as that which dictates this as the exclusive mode of addition for *trans*-6-phenylhex-2-ene.

Substitution into the aromatic ring of (**3**) causes large but very different effects on its photochemistry. Irradiation of the *p*-OMe, *p*-CN, and *p*-COMe derivatives (**20**) yielded no volatile products but variable amounts of polymeric materials were formed. In marked contrast *o*-Me and *o*-MeO substituents have a significant promoting effect on both the efficiency and selectivity of the reaction of (**3**). Thus for both (**16**) and (**19**) essentially only 1,3-attack with respect to the connecting chain is observed and this with good chemical and quantum yields. It is most noteworthy here that the three examples of successful synthetic use of the *meta* photocycloaddition of such bichromophores have all involved systems having *o*-Me or *o*-MeO substitution.[14-16]. These systems also had substituents on the ethene and/or $-[CH_2]_3-$ chain, features which as noted above do not promote an efficient or selective reaction. It thus appears from our studies on individual substituent effects and those described in refs. 14—16 that the detrimental perturbing features of substitution in the pent-1-ene moiety may be favourably outweighed by the presence of Me or OMe groups in the phenyl *ortho* position(s). If the effect of such arene substitution is to



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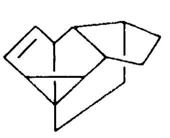

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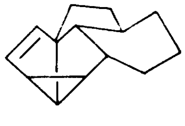

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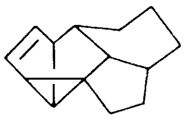

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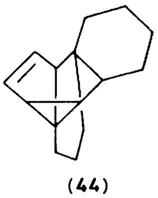

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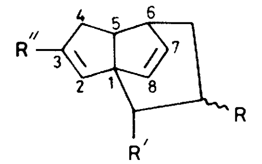
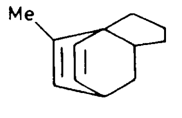


(45) R = Me, R' = R'' = H

(46) R = R'' = H, R' = Me

(47) R = R' = H, R'' = Me



(48)

direct the addition towards the reaction intermediate with the greatest degree of radical stabilisation then the high selectivity of the reactions of (**16**), (**18**), and (**19**) is understandable in terms of the mechanism involving initial addition of the ethene at the 1,3-positions [structure (**25**)] for (**16**) and (**19**) and 2,6-[structure (**26**)] for (**18**). This pathway does not, however, account for the apparent 1,3- or 1,5-attacks of the ethene onto the arene observed for (**17**) as neither would yield intermediates having radical stabilisation by the methyl group or interconnecting chain. On the present arguments, 2,6-addition may have been expected for (**17**) with the resultant formation of the 2- and 4-methyl 1,6- (and possibly 1,7-) bridged isomers. Alternatively intermediates (**37**)—(**39**) derived by initial *meta* bonding in the arene have stabilisation of radical centres and trappings of such species by the ethene would give the observed products. Thus it is possible to rationalise the products formed from the phenyl-substituted systems in terms of substituent radical stabilisation of intermediates formed by one of two plausible mechanistic pathways; this, however, proves the existence of neither and it is clear from the other results of the present study that seemingly minor steric and/or conformational differences between systems can lead to quite varied reaction efficiencies and selectivities of positions of ethene attack onto the arene.

From the synthetic point of view the intramolecular *meta* photocycloaddition reaction of phenyl–ethenyl systems may offer a convenient key step into polycyclic systems but it would seem that acceptable efficiencies and selectivities of the photoprocess are only achieved for compounds which have *ortho* Me or OMe substituents. This feature not only overcomes the perturbing aspects of substitution in the pent-1-ene unit but also directs the reaction with high selectivity to give the 5,6- and 7,8-bridged adduct isomers in relative yields very dependent on the particular system. It must, however, be realised that, for synthetic pathways which require other orientations of reaction, despite the highly selective reactions of (**5**), (**8**), and (**18**) to give 1,6-bridged adducts, there is no clearly discernible feature of the bichromophores which may be confidently used to predict this course of reaction.

To summarise, we have shown that the intramolecular photocycloaddition reactions of 5-phenylpent-1-ene are markedly modified by methyl substitution of the pent-1-ene moiety and by incorporation of the ethene into a C_5 or C_6 ring. In the latter case the intramolecular system does not show the reluctance for photoaddition as is observed in intermolecular benzene–cyclohexene systems. The presence of *o*-Me and *o*-OMe groups on the arene has a highly promoting effect on the efficiency and selectivity of the reaction and this effect can apparently overcome the detrimental effects of substitution in the pent-1-ene moiety.

Experimental

Photochemical and Analytical Methods.—Irradiations were carried out for 1% solutions of the bichromophores in 50 × 1 cm silica tubes under air or nitrogen using low-pressure mercury arc lamps. Quantum yield determinations used 10 × 1 cm silica tubes and a merry-go-round apparatus holding eight such tubes. Measurements were made relative to those of (**3**).[8,12]

Flash chromatography[25] was carried out with Silica Woelm 32—63 and t.l.c. with Camlab Polygram G/U.V. precoated sheets. Analytical g.l.c. was performed on a Hewlett Packard 5840A instrument fitted with a flame-ionisation detector and with a 17 m W.C.O.T. Carbowax 20M column and using nitrogen carrier gas. *cis*- and *trans*-decalins were used as the internal g.l.c. standard for the quantum yield experiments. Preparative g.l.c. was performed on a Perkin-Elmer F-21 gas chromatograph fitted with either 3 ft × 1 in or multiples of 3 ft × $\frac{1}{4}$ in stainless steel columns packed with 15% Carbowax 20M on 85—100 mesh Chromosorb P.

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 a Carbowax 20M W.C.O.T. column. Accurate mass data were recorded using a V.G. Micromass 70—70 spectrometer (P.C.M.U., Harwell), or an A.E.I. M.S. 902 spectrometer (N.I.R.D., Reading). ^1H N.m.r. spectra were obtained of $CDCl_3$ solutions with tetramethylsilane as internal reference using a Varian HA100, Perkin-Elmer R-32, or Bruker WH250 spectrometer. Fluorescence spectral measurements were determined using a Perkin-Elmer MPF-2A fluorescence spectrometer for 8mM solutions of the bichromophores in spectroscopic grade iso-octane, dioxane, and acetonitrile.

Synthesis of the Bichromophores (**3**), (**6**), (**8**)—(**11**), *and* (**13**)—(**20**).—These bichromophores were synthesised by a common route which involved reaction of the appropriate arylalkylmagnesium bromide with the allyl halide. To avoid undue repetition only the procedure for (**3**) is described here.

Phenethyl bromide (28 g, 0.151 mol; Aldrich) in sodium-dried diethyl ether (80 ml) was added dropwise over 1 h to magnesium (4.04 g, 0.165 mol) and a crystal of iodine (*ca.* 0.2 g) in sodium-dried ether (20 ml) under nitrogen and with stirring. The mixture refluxed gently initially without external heating and was refluxed after completion of the addition for a further 1 h. The mixture was cooled to room temperature and allyl bromide (18.3 g, 0.152 mol) was added in sodium-dried diethyl ether (80 ml) over 1 h with periodic cooling. The mixture was refluxed for a further 1 h and aqueous ammonium chloride added. The ethereal layer was separated off and added to the combined three portions (each 50 ml) of diethyl ether used to extract the aqueous layer. The ethereal solution was dried ($MgSO_4$), the diethyl ether removed under reduced pressure (water pump), and the oily residue distilled (65—70 °C at 6 mmHg) to give 5-phenylpent-1-ene (**3**) (20 g, 89%).

Using the same synthetic method (**6**) was produced from the

Grignard coupling of phenethyl bromide and 2-methylallyl chloride, (**8**) from phenethyl bromide and 3-chlorocyclopentene (produced from the addition of HCl to cyclopentadiene at −77 °C[26]), (**9**) from phenethyl bromide and 3-bromocyclohexene, (**10**) from 1-bromo-3-phenylpropane and 3-chlorocyclopentene, (**11**) from 1-bromo-3-phenylpropane and 3-bromocyclohexene, (**13**) from phenethyl bromide and but-2-enyl bromide, (**14**) from 1-bromo-1-methyl-2-phenylethane and allyl bromide, (**15**) from 2-methylphenethyl bromide and allyl bromide, (**16**) from 1-bromo-2-*o*-tolylethane and allyl bromide, (**17**) from 1-bromo-2-*m*-tolylethane and allyl bromide, (**18**) from 1-bromo-2-*p*-tolylethane and allyl bromide, (**19**) from 1-bromo-2-(*o*-methoxyphenyl)ethane and allyl bromide, and (**20**; R = OMe) from 1-bromo-2-(*p*-methoxyphenyl)ethane and allyl bromide. The *o*-, *m*-, *and p*-methylphenethyl bromides were synthesised by reaction of the appropriate bromotoluene (0.14 mol) with magnesium (0.16 mol) followed by ethylene oxide (0.30 mol). The mixture was decomposed with dilute HCl and the methylphenethyl alcohol extracted with diethyl ether. Conversion of the alcohol into the required bromide was achieved with fuming hydrogen bromide. Yields in excess of 95% were generally obtained.

Syntheses of the Bichromophores (**7**) *and* (**12**).—The bichromophores (**7**) and (**12**) were synthesised from 1-bromo-3-phenylpropane and the appropriate ketone [3-methylbutan-2-one for (**7**) and cyclohexanone for (**12**)] in the following manner. The bromo compound (20 g, 0.10 mol) in dry diethyl ether was added to magnesium turnings (2.65 g, 0.11 mol) in dry diethyl ether (20 ml) under nitrogen with stirring at such a rate to keep a mild reflux (*ca.* 1.5 h). The mixture was refluxed for a further 30 min and the ketone (0.1 mol) in dry diethyl ether (40 ml) was added at such a rate to maintain a steady reflux. The mixture was refluxed for a further 7 h, cooled in ice, and the Grignard complex decomposed with hydrochloric acid (20%; 80 ml). The product was extracted with diethyl ether, and the extract washed with aqueous sodium hydrogen sulphite (50 ml) and water (2 × 50 ml) and dried ($MgSO_4$). Iodine (100 mg) and hydroquinone (10 mg) were added to the crude alcohol (*ca.* 20 g) and the mixture was heated to 150 °C under nitrogen for 2.5 min. The resulting mixture was chromatographed on silica gel using light petroleum (b.p. 40—60 °C) as eluant. Removal of the solvent gave the bichromophore (**12**) which was distilled: b.p. 80—82 °C at 0.015 mmHg (10.0 g, 40% yield overall); this, however, was found to contain 15% of the exocyclic ethenyl isomer which was removed by preparative g.l.c. The bichromophore (**7**) contained *ca.* 8% impurities following two distillations and was purified by preparative g.l.c.

Synthesis of the Bichromophore (**20**; R = CN *or* COMe).—Bromine (28.4 g, 0.18 mol) in dichloromethane (50 ml) was added dropwise over 1.5 h to (**3**) (26 g, 0.178 mol) in dichloromethane (50 ml) at −55 °C in the dark. A solution of sodium hydrogen carbonate and sodium thiosulphate was added and the mixture was washed with water and dried ($MgSO_4$). The volume was increased to 300 ml with dichloromethane. Aluminium chloride (28.7 g) and acetyl chloride (14 g, 0.18 mol) were mixed in dichloromethane and cooled in an ice-bath, and the dibromide solution was added over 15 min. The mixture was stirred for 1 h, poured onto crushed ice–HCl, and extracted with chloroform. The chloroform layer was washed with water and dried, and the solvent removed under vacuum. The crude dibromo compound was divided for the synthesis of (**20**; R = COMe and R = CN). For the former case a portion (3.56 g) of the dibromo compound was refluxed in ethanol (10 ml) containing acetic acid (2 drops). Zinc powder (3 g) was added and a vigorous reaction ensued. Refluxing was continued for a further 75 min, the mixture diluted with water (20 ml), and the product extracted with ether. The resulting crude oil was chromatographed on silica gel to give, after distillation (b.p. 88—90 °C at 0.03 mmHg) pure (**20**; R = COMe).

For (**20**; R = CN), the dibromo compound (21.64 g) in dioxane (60 ml) was added to a solution of sodium hypobromite [Br_2 (30.8 g); NaOH (22.4 g); H_2O (180 ml)]. The acid (**20**; R = CO_2H) (18.5 g) was obtained from the aqueous layer by acidification and ether extraction, and then dissolved in benzene (60 ml) to which thionyl chloride (10 ml) was added and the whole refluxed for 2 h. Following removal of the excess of reagent and solvent, the crude acid chloride was added to ice-cold aqueous ammonia (*d* 0.880) and the amide extracted into benzene. The amide was purified by passage down a silica gel column with benzene–methanol (4:1) as eluant. The product was refluxed in benzene (30 ml) containing thionyl chloride (20 ml) for 6 h in order to dehydrate the amide. Chromatography on silica gel gave the dibromo nitrile (4.1 g), which was refluxed in ethanol (10 ml) containing acetic acid (3 drops) and zinc powder (5 g) for 75 min. Work-up as above and distillation (b.p. 55—58 °C at 0.01 mmHg) gave pure (**20**; R = CN) (2.0 g, 18.7% from the dibromo compound).

Syntheses of the Bichromophores (**21**), (**22**), *and* (**35**).— The acrylates (**21**) were synthesised from acryloyl chloride with the appropriate alcohol in the presence of sodium carbonate and copper(I) chloride. In all cases some unchanged alcohol remained and the esters were purified by flash chromatography. The bichromophores (**22**) were obtained by transesterification using vinyl acetate and $Ph[CH_2]_nCO_2H$ in the presence of mercury(II) acetate. Methyl 6-phenylhex-2-enoate (**35**) was synthesised as follows. 4-Phenylbutyric acid (25 g) was reduced to the alcohol (14.35 g, 63%) with $LiAlH_4$ (4.74 g) in sodium-dried diethyl ether under nitrogen. The alcohol (14.35 g) was oxidised to the aldehyde (9.4 g, 66%) using pyridinium chlorochromate by the method described by Corey and Suggs.[27] The final step involved the Horner–Emmons modification of the Wittig reaction using methyl diethyl phosphonoacetate.[28] These bichromophores were purified by flash chromatography.

Structural Evidence for the Bichromophores.—The bichromophores were purified where necessary (*i.e.* to purities > 99%) by preparative g.l.c. and/or flash chromatography. The ^1H n.m.r. data ($CDCl_3$) given refer to the centre of the signals; structurally significant i.r. absorptions for liquid smears are also given: (**6**), δ 7.2 (5 H), 4.7 (2 H), 2.6 (2 H), 2.2—1.6 (4 H), and 1.7 (3 H); $\nu_{max.}$ 3 060, 3 020, 1 640, and 1 605 cm^{-1}; $\lambda_{max.}$ 261 nm (ε 330 l mol^{-1} cm^{-1}); M^+, calc. 160.1252, found *m*/*z* 160.1260. (**7**), δ 7.15 (5 H), 2.56 (2 H), 2.3—1.5 (4 H), and 1.64 (9 H); $\nu_{max.}$ 3 080, 3 060, 3 020, and 1 605 cm^{-1}; $\lambda_{max.}$ 248 nm (ε 682 l mol^{-1} cm^{-1}); M^+, calc. 188.1565, found *m*/*z* 188.1566. (**8**), δ (360 MHz) 7.26 (2 H), 7.17 (3 H), 5.70 (1 H), 5.62 (1 H), 2.65 (2 H), 2.10 (1 H), 2.98 (2 H), 1.82 (1 H), 1.78—1.45 (4 H), and 1.27 (1 H); $\nu_{max.}$ 3 085, 3 056, 3 014, and 1 604 cm^{-1}; M^+, calc. 172.1252, found *m*/*z* 172.1244. (**9**), δ (360 MHz) 7.27 (2 H), 7.20 (3 H), 5.73 (2 H), 2.70 (1 H), 2.65 (2 H), 2.30 (2 H), 2.07 (1 H), 1.74 (1 H), 1.60 (1 H), and 1.46 (1 H); $\nu_{max.}$ 3 087, 3 062, 3 013, and 1 605 cm^{-1}; M^+, calc. 186.1409, found *m*/*z* 186.1417. (**10**), δ 7.14 (5 H), 5.46 (2 H), 2.59 (3 H), 2.40—2.14 (2 H), 2.14—1.77 (1 H), and 1.77—1.16 (5 H); $\nu_{max.}$ 3 087, 3 055, 3 030, and 1 607 cm^{-1}; M^+, calc. 186.1409, found *m*/*z* 186.1412. (**11**), δ 7.17 (5 H), 5.58 (2 H), 2.60 (2 H), 2.2—1.84 (3 H), 1.84—1.48 (5 H), and 1.48—1.12 (3 H); $\nu_{max.}$ 3 084, 3 068, 3 015, and 1 605 cm^{-1}; M^+, calc. 200.1565, found *m*/*z* 200.1566 (**12**), δ 7.17 (5 H), 5.40 (1 H), 2.56 (2 H), 2.1—1.74 (6 H), and 1.74—1.4 (6 H); $\nu_{max.}$ 3 090, 3 067, 3 030, and 1 607 cm^{-1}; M^+ calc. 200.1565, found *m*/*z* 200.1551. (**13**), δ 7.15 (5 H), 5.78 (1 H), 5.0 (2 H), 2.8—1.4 (5 H), and 1.0 (3 H); $\nu_{max.}$ 3 080, 3 060, 3 015, 1 640, and 1 605 cm^{-1}; $\lambda_{\text{max.}}$ 259 nm (ε 312 l mol^{-1} cm^{-1}); M^+, calc. 160.1252, found *m*/*z* 160.1260. (**14**), δ 7.2 (5 H), 5.84 (1 H), 5.0 (2 H), 2.52 (2 H), 2.2—1.6 (3 H), and 0.86 (3 H); $\nu_{\text{max.}}$ 3 080, 3 060, 1 640, and 1 605 cm^{-1}; $\lambda_{\text{max.}}$ 253 (ε 625 l mol^{-1} cm^{-1}); M^+, calc. 160.1252, found *m*/*z* 160.1264. (**15**), δ 7.2 (5 H), 5.84 (1 H), 5.0 (2 H), 2.72 (1 H), 2.2—1.5 (4 H), and 1.24 (3 H); $\nu_{\text{max.}}$ 3 080, 3 060, 1 640, and 1 605 cm^{-1}; $\lambda_{\text{max.}}$ 248 (ε 682 l mol^{-1} cm^{-1}); M^+, calc. 160.1252, found *m*/*z* 160.1244. (**16**), δ 7.08 (4 H), 5.88 (1 H), 5.05 (2 H), 2.60 (2 H), 2.28 (3 H), and 2.3—1.6 (4 H); $\nu_{\text{max.}}$ 3 140, 3 060, 3 020, 1 635, and 1 615 cm^{-1}; $\lambda_{\text{max.}}$ 263 (ε 515 l mol^{-1} cm^{-1}); M^+, calc. 160.1252, found *m*/*z* 160.1257. (**17**), δ 7.0 (4 H), 5.84 (1 H), 5.05 (2 H), 2.60 (2 H), 2.33 (3 H), and 2.2—1.5 (4 H); $\nu_{\text{max.}}$ 3 080, 3 060, 3 020, 1 640, and 1 610 cm^{-1}; $\lambda_{\text{max.}}$ 253 nm (ε 539 l mol^{-1} cm^{-1}); M^+, calc. 160.1252, found *m*/*z* 160.1246. (**18**), δ 7.03 (4 H), 5.84 (1 H), 5.0 (2 H), 2.60 (2 H), 2.3 (3 H), and 2.3—1.4 (4 H); $\nu_{\text{max.}}$ 3 080, 3 060, 3 020, and 1 640 cm^{-1}; $\lambda_{\text{max.}}$ 266 nm (ε 779 l mol^{-1} cm^{-1}); M^+ calc. 160.1252, found *m*/*z* 160.1258. (**19**), δ 7.0 (4 H), 5.85 (1 H), 5.0 (2 H), 4.75 (3 H), 2.6 (2 H), 2.05 (2 H), and 1.7 (2 H); $\nu_{\text{max.}}$ 3 080, 3 020, 1 640, and 1 605; $\lambda_{\text{max.}}$ 275 nm (ε 2 190 l mol^{-1} cm^{-1}); M^+, calc. 176.1201, found *m*/*z* 176.1202. (**20**; R = OMe), δ 7.8—7.10 (4 H), 5.85 (1 H), 5.0 (2 H), 4.70 (3 H), 2.6 (2 H), and 2.1—1.6 (4 H); $\nu_{\text{max.}}$ 3 080, 3 020, 1 645, and 1 600; $\lambda_{\text{max.}}$ 272 nm (ε 2.2 × 10^3 l mol^{-1} cm^{-1}); M^+, calc. 176.1201, found *m*/*z* 176.1211. (**20**; R = CN), δ 7.6—7.1 (4 H), 5.80 (1 H), 5.0 (2 H), 2.5 (2 H), and 2.2—1.6 (4 H); $\nu_{\text{max.}}$ 3 020, 2 225, 1 640, and 1 610 cm^{-1}; $\lambda_{\text{max.}}$ 267 nm (ε 812 l mol^{-1} cm^{-1}); M^+, calc. 171.1048, found *m*/*z* 171.1053. (**20**; R = COMe), δ 7.9—7.1 (4 H), 5.85 (1 H), 5.0 (2 H), 2.70 (2 H), 2.58 (3 H), and 2.2—1.5 (4 H); $\nu_{\text{max.}}$ 3 040, 1 680, and 1 640 cm^{-1}; $\lambda_{\text{max.}}$ 252 nm (ε 2.9 × 10^3 l mol^{-1} cm^{-1}) Found: C, 82.7; H, 9.0. $C_{13}H_{16}O$ requires C, 82.9; H, 8.6%). (**21**; *n* = 1), δ 7.26 (5 H), 6.40 (1 H), 6.08 (1 H), 5.74 (1 H), and 5.11 (2 H); $\nu_{\text{max.}}$ 1 725 cm^{-1}. (**21**; *n* = 2), δ 7.16 (5 H), 6.35 (1 H), 6.03 (1 H), 5.71 (1 H), 4.29 (2 H), and 2.92 (2 H); $\nu_{\text{max.}}$ 1 725 cm^{-1}. (**21**; *n* = 3), δ 7.13 (5 H), 6.35 (1 H), 6.04 (1 H), 5.73 (1 H), 4.11 (2 H), 2.69 (2 H), and 1.96 (2 H); $\nu_{\text{max.}}$ 1 725 cm^{-1}. (**22**; *n* = 1), δ 7.3 (5 H), 7.25 (1 H), 4.9 (1 H), 4.66 (1 H), and 3.7 (2 H); $\nu_{\text{max.}}$ 1 755 cm^{-1}. (**22**; *n* = 2), δ 7.25 (5 H), 7.30 (1 H), 4.85 (1 H), 4.55 (1 H), and 2.85 (4 H); $\nu_{\text{max.}}$ 1 755 cm^{-1}. (**22**; *n* = 3), δ 7.2 (5 H), 7.25 (1 H), 4.85 (1 H), 4.55 (1 H), 2.65 (2 H), 2.35 (2 H), and 1.95 (2 H); $\nu_{\text{max.}}$ 1 755 cm^{-1}. (**35**), δ 7.20 (5 H), 7.0 (1 H), 5.8 (1 H), 3.65 (3 H), 2.66 (2 H), and 2.5—1.6 (4 H); $\nu_{\text{max.}}$ 1 728 cm^{-1}.

Photoproducts of the Bichromophores.—The bichromophores were irradiated as 1% w/v solutions in cyclohexane. Change to polar solvents (*e.g.* MeCN) or degassing of the solutions under nitrogen prior to irradiation had no significant effect on product formation. The reactions were monitored by t.l.c. and g.l.c. and the products separated by preparative g.l.c. and/or flash chromatography. The spectral features which allow unambiguous structural determinations of arene–ethene adducts to be made are given fully in reference 18 and so only structurally relevant ^{1}H n.m.r. data for the photoproducts are given here. The spectra of the photoisomers produced from (**6**) are, however, given in more detail in order to illustrate the typical features of the commonly encountered 7,8-, 5,6-, and 1,6-bridged intramolecular *meta* photoadducts of phenyl–ethenyl nonconjugated bichromophoric systems. In cases where it was realistically practical the isomers were isolated pure (g.l.c.) and for such products mass measurements of the molecular ions are given; the impurities in the other photoproducts were invariably their isomers (mass spectrometry–g.l.c.).

Products from (**6**). *endo*-7-Methyl-7,8-bridged isomer (**28**), δ 5.71 (H-3, dd, $J_{3.4}$ 6, $J_{3.2}$ 2.5, $J_{3.5}$ 0.5 Hz), 5.42 (H-4, br. dd, $J_{4.3}$ 6, $J_{4.5}$ 2.5, $J_{4.2}$ 1.0 Hz), 3.13 (H-5, td, $J_{5.4}$ 2.5, $J_{5.1}$ 6, $J_{5.6exo}$ 6, $J_{5.3}$ 0.5 Hz), 2.23 (H-1, t, $J_{1.2}$ 7, $J_{1.5}$ 6 Hz), 2.14 (H-6$_{exo}$, dd, $J_{6.5}$ 6, $J_{6.6'}$ 12 Hz), 1.95 (H-2, br. dd, $J_{2.1}$ 7, $J_{2.3}$ 2.5, $J_{2.4}$ 1 Hz), 1.8—1.2 (H-6$_{endo}$, H-7$_{endo}$, and –[CH$_2$]$_3$– chain, unresolved), and 1.10 (Me, s); $\nu_{\text{max.}}$ (liquid smear) 3 030, 3 020, 2 940, 2 860, 1 450, 1 370, 1 340, 810, 760, and 720 cm ^{1}; M^+, calc. 160.1252, found *m*/*z* 160.1250; major fragment ions at *m*/*z* 145, 131, 117, 105, 104 (base), and 91. *endo*-6-Methyl-5,6-bridged isomer (**27**), δ 5.62 (H-3, dd, $J_{3.4}$ 5, $J_{3.2}$ 2 Hz), 5.33 (H-4, d, $J_{4.3}$ 5 Hz), 2.30 (H-1, t, $J_{1.2} = J_{2.8}$ = 7 Hz), 1.80 (H-2, dd, $J_{2.1}$ 7, $J_{2.3}$ 2 Hz), 2.0—1.0 (H-6$_{endo}$, H-7$_{endo}$, H-8, and –[CH$_2$]$_3$– chain, unresolved), and 0.71 (Me,. s); $\nu_{\text{max.}}$ (liquid smear) 3 020, 2 980, 2 970, 1 460, 1 450, 1 380, 1 360, 790, 775, and 740 cm^{-1}; M^+, calc. 160.1252, found *m*/*z* 160.1246; major fragment ions at *m*/*z* 145, 131, 117, 105, 104 (base), and 91. *endo*-6-Methyl-1,6-bridged isomer (**29**), δ 5.77 (H-3, dd, $J_{3.4}$ 6.0, $J_{3.5}$ 2.5 Hz), 5.62 (H-4, br. dd, $J_{4.3}$ 6.0, $J_{4.2}$ 2.25, $J_{4.5}$ 1.0 Hz), 2.43 (H-5, split d, $J_{5.8}$ 6.25, $J_{3.5}$ 2.5, $J_{5.4}$ 1.0 Hz), 1.99 (H-2, t, $J_{2.8} = J_{2.4}$ = 2.25 Hz), 2.2—1.3 (H-7$_{exo}$, H-7$_{endo}$, H-6$_{endo}$, and –[CH$_2$]$_3$– chain, unresolved), 0.87 (Me, s), and 0.78 (H-8, dt, $J_{8.7exo} = J_{8.5}$ = 6.25, $J_{8.2}$ 2.25 Hz); $\nu_{\text{max.}}$ (liquid smear) 3 060, 3 020, 3 010, 2 930, 2 900, 2 850, 1 455, 1 445, 1 370, 780, 730, and 700 cm^{-1}; M^+, calc. 160.1252, found *m*/*z* 160.1257; major fragment ions at *m*/*z* 105, 104 (base), and 91.

Products from (**7**). Compound (**32**), δ 5.95 (1 H, m), 5.68 (1 H, m), 5.17 (1 H, br. s), 2.73 (2 H, m), 2.1—1.3 (6 H, unresolved), and 1.08, 0.86, and 0.88 (each Me, s); M^+, calc. 188.1565, found *m*/*z* 188.1562. 6,7,7-Trimethyl-4,6-bridged isomer, structure tentative owing to incomplete ^{1}H n.m.r. spectral assignment, major feature; only one ethenyl proton (d, δ 5.45), and hence bridge must be between 4- and 6-position in a *meta* adduct. 6,7,7-Trimethyl-5,6-bridged isomer (**27**), M^+, *m*/*z* 188; δ 5.75 (H-3, d of d), 5.57 (H-4, d), 2.38 (H-1, t), 2.13 (H-2, m), 1.8—0.8 (7 H), and 1.06, 1.00, and 0.65 (each Me, s). 6,6,7-Trimethyl-7,8-bridged isomer (**28**), M^+, *m*/*z* 188; δ 5.75 (1 H, dd), 5.58 (H-3, br. dd), 2.65 (H-4, m), 2.32 (H-5, t), 2.08 (H-1, dd), 1.9—0.8 (6 H, overlapping multiplets), and 1.14, 1.02, and 0.76 (each Me, s).

Products from (**8**). 7,8-Bridged isomer (**40**), M^+, *m*/*z* 172; δ 5.61 (H-3, dd), 5.41 (H-4, br. dd), 3.04 (H-5, dd), 2.05 (H-1, dd), 2.02 (H-2, dd), and 2.0—1.2 p.p.m. (11 H, overlapping multiplets). 1,6-Bridged isomer (**41**), M^+, *m*/*z* 172; δ 5.78 (H-3, dd), 5.57 (H-4, ddd), 2.75 (H-5, dd), 2.43 (H-2, ddd), and 2.1—1.1 (11 H, overlapping multiplets).

Products from (**9**). 5,6-Bridged isomer (**42**), M^+, *m*/*z* 186; δ 5.56 (H-3, dd), 5.48 (H-4, br. d coupled to H-3 and H-2, *i.e.* no H-5), and 2.1—1.0 p.p.m. (overlapping multiplets). 7,8-Bridged isomer (**43**), M^+, *m*/*z* 186; δ 5.63 (H-3, dd), 5.41 (H-4, ddd), 2.94 (H-5, dd), 2.24 (H-1, t), 1.84 (H-2, dd), and 2.1—1.0 (overlapping multiplets).

Products from (**12**). 1,6-Bridged isomer (**44**), M^+, *m*/*z* 200; δ 5.82 (H-3, H-4, m), 2.43 (H-5, ddd), 2.12 (H-2, m), 2.1—1.0 (overlapping multiplets), and 0.92 (H-8, t).

Products from (**13**). Methyl-substituted 5,6-bridged isomer (**27**), M^+, *m*/*z* 160; δ (ethenylic protons) 5.52 (H-3, dd) and 5.37 (H-4, d), only $J_{3.4}$ coupling of H-4, no H-5 proton, remainder of spectrum very similar to that of the same isomer from (**3**). Methyl-substituted 7,8-bridged isomer (**28**), M^+, *m*/*z* 160; δ (ethenylic protons) 5.41 (H-3, dd) and 5.26 (H-4, dd); both protons have vicinal couplings, to H-2 and H-5, respectively, and H-4 has allylic coupling to H-2; H-5 appears as a multiplet at δ 3.1. Methyl-substituted 1,6-bridged isomer (**29**), M^+, calc. 160.1252, found *m*/*z* 160.1258; δ values for H-5 and H-2 not wholly typical for 1,6-structures, δ 5.90 (H-3, dd, $J_{3.4}$ 6, $J_{3.2}$ 2.5 Hz), 5.58 (H-4, dd, $J_{4.3}$ 6, $J_{4.5}$ 2.5 Hz), 2.36 (H-5, overlapped m), 2.3—2.5 (H-6$_{endo}$, H-7$_{exo}$, H-7$_{endo}$, m), 2.22 (H-2, overlapped m), 1.8—1.5 (bridge protons), 1.12 (Me, d, *J* 7 Hz), and 0.83 (H-8, br. t, $J_{8.2}$ 6, $J_{8.5}$ 7, $J_{8.7} < 1$ Hz). Methyl-substituted 1,7-bridged isomer (**30**), M^+, *m*/*z* 160; δ (ethenylic protons) 5.54 (H-3, dd) and 5.21 (H-4 dd); protons have vicinal couplings, to H-2 and H-5, respectively, but structure tentative since complete n.m.r. spectral analysis was hindered by presence of other isomers. 4,6-

Bridged isomer, M^+, m/z 160; δ 5.24 (H-3, br. s, $J_{3,2}$ 1 Hz), 2.67 (H-5, t, $J_{5,1}$ 5, $J_{5,6exo}$ 6 Hz), 2.34 (H-1, overlapped m), 2.2 (H-6, m, $J_{5,6}$ 6, $J_{6,7exo}$ 9 Hz), 1.78 (H-2, t, $J_{2,1}$ 2, $J_{2,8}$ 7 Hz), 1.70—1.30 (2 × H-7 and chain protons, multiplets), 1.15 (H-8, t, $J_{8,2} = J_{8,1} =$ 7 Hz), and 1.06 (Me, d, J 7 Hz).

Products from (**14**). Attempts to isolate the 1,6-bridged isomers from this bichromophore always produced heavy contamination with the thermally rearranged isomers.[24] Data of thermally arranged isomers proved their structures and hence those of the photoproducts. Rearranged *exo*-methyl-1,6-bridged isomer (**45**), M^+, calc. 160.1252, found m/z 160.1248; δ 5.7 (H-8, m), 5.65 (H-2 and H-3, br. s), 5.17 (H-7, br. d), 2.29 (H-6, br. t), 2.1—1.0 (H-4 and chain protons, unresolved), and 0.94 (Me, d). Rearranged *endo*-methyl-1,6-bridged isomer (**45**), M^+, calc. 160.1252, found m/z 160.1249; δ 5.74 (H-2 and H-3, br. s), 5.67 (H-7, dd), 5.24 (H-8, d), 2.61 (H-6, m), 2.4—1.0 (2 × H-4 and chain protons, unresolved), and 0.90 (Me, d).

Products from (**15**). Methyl-substituted 5,6-bridged isomer (**27**), M^+, m/z 160; δ 5.59 (H-3, dd), 5.48 (H-4, dd), 2.25 (H-1, t), 2.15 (H-2, overlapped), 2.15—1.5 (H-6, H-7, bridge protons, unresolved multiplets), 1.21 (H-8, ddd), and 0.96 (Me, d). The structures of the 1,7- and 1,6-bridged isomers (M^+, m/z 160, mass spectrometry–g.l.c.) were deduced largely from their ready thermal conversion[24] into (**46**): M^+, calc. 160.1252, found m/z 160.1257; δ 5.73 (H-2, H-3, br. s), 5.64 (H-8, m), 5.33 (H-7, br. d), 2.60 (H-6_{endo}, dd), 2.3—2.1 (H-4, m), 2.0—1.1 (H-5 and chain protons, unresolved), and 0.9 (Me, d).

Products from (**16**). 1-Methyl-5,6-bridged isomer (**27**), M^+, m/z 160; δ 5.47 (H-3, dd), 5.31 (H-4, d), 2.10—1.4 (overlapping multiplets; H-5 or H-1), and 1.26 (Me, s). 1-Methyl-2,8-bridged isomer (**28**), M^+, calc. 160.1252, found m/z 160.1260; δ 5.64 (H-3, dd), 5.37 (H-4, dd), 2.83 (H-5, dd), 2.56 (H-2, dd), 2.2—1.2 (H-6_{endo}, H-7, and bridge protons), and 1.21 (Me, s); (**48**), M^+, m/z 160; δ 6.13 (d), 5.83 (d), 5.63 (br. s), 2.87 (d), 2.3—1.1 (overlapping multiplets), 1.21 (s), and 0.85 (t).

Products from (**17**). The ^{1}H n.m.r. spectra of two of the photoisomers (M^+, m/z 160; relative retention times 0.38 and 0.44) were closely similar, showing H-3 (dd) and H-4 (d) resonances, with no evidence for 5- or 8-protons, but which had two 6-protons; the presence of two 7-protons could not be conclusively established. These isomers are assigned the 8-methyl-5,6-bridged isomer (**27**) and 5-methyl-7,8-bridged-isomer (**28**) structures. 3-Methyl-5,6-bridged isomer (**27**), M^+, 160.1252, found m/z 160.1255, δ 5.0 (H-4, br. s), 2.7 (H-2, H-8, overlapping multiplets) 2.26 (H-1, t), 2.0—1.5 (H-6_{endo}, 2 × H-7, and bridge protons), and 1.8 (Me, finely split s). 3-Methyl-7,8-bridged isomer (**28**), M^+, m/z 160; δ 5.39 (H-4, br. s), 3.48 (H-5, br. d), 2.55 (H-1, dd), 2.08 (H-6_{exo}, m), 1.95 (H-2, br. d), 2.7—1.2 (H-6_{endo}, H-7_{endo}, and bridge protons, overlapping multiplets), and 1.71 (Me, br. s).

Products from (**18**). 3-Methyl-1,6-bridged isomer (**29**), M^+, m/z 160; δ 5.09 (H-4, br. s), 2.34 (H-5, dd), 2.2—1.5 (H-6_{endo}, H-7_{endo}, and bridge protons, multiplets), 1.76 (Me, dd), 1.65 (H-2, m), and 0.78 (H-8, t d). Thermal product (**47**), M^+, calc. 160.1252, found m/z 160.1258; δ 5.62 (H-7, dd), 5.34 (H-2, br. s), 5.25 (H-8, d), 2.56 (H-6, m), 2.2—1.3 (2 × H-4, H-5, and bridge protons, multiplets), and 1.69 (Me, br. s).

Products from (**19**). 1-Methoxy-7,8-bridged isomer (**28**), M^+, calc. 176.1201, found m/z 176.1195; δ 5.66 (H-3, dd), 5.49 (H-4, ddd), 3.35 (OMe, s), 2.24 (H-5, m), 2.07 (H-2, m), and 2.05—1.3 (H-6_{endo}, 2 × H-7, and bridge protons, multiplets). 1-Methoxy-5,6-bridged isomer (**27**), M^+, calc. 176.1201, found m/z 176.1197; δ 5.5 (H-3, H-4, br. s), 3.36 (OMe, s), 2.16 (H-2, m), 2.1 (H-6, m), 2.1—1.6 (H-6_{endo} and bridge protons, multiplets), 1.78 (H-7_{endo}), 1.6 (H-8, m), and 1.51 (H-7_{exo}, dd).

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