# Intramolecular Photocyclizations of o,o'-Bis-(2-arylvinyl)biphenyls

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In a series of o,o'-bis-(2-arylvinyl)biphenyls (1a—f) the quantum yields of the photocycloaddition to give trans,-trans,trans,-1,2-diaryl-1,2,2a,10b-tetrahydrocyclobuta[l]phenanthrene (2a—f) (ϕ_{cb}), of their photocyclization to 4,9-diaryl-4,5,9,10-tetrahydropyrene (3a—f) (ϕ_{thp}), of trans–cis photoisomerization (ϕ_{tc}), and of fluorescence (ϕ_t) have been determined. An explanation, based on the different properties of the aryl groups, is given for the differences in product formation, which arise on irradiation of compounds (1a—f). For the p-methoxyphenyl (1e) and p-dimethylaminophenyl (1f) derivatives an enhanced internal conversion from the singlet $n \longrightarrow \pi^*$ state to the ground state is responsible for the low values of ϕ_{cb}. o,o'-Divinylbiphenyl (1g) cannot be converted into the cyclobutane derivative (2g). This is caused by the absorption characteristics of (1g) and (2g). The stereoselective formation of the cyclobutane derivatives (2a—f) takes place in a concerted [$_\pi2_s + _\pi2_s$] photocycloaddition via the S_1 state of the trans,anti,trans,anti-conformers of (1). The photocyclization to the tetrahydropyrenes (3a—f) also arises from the S_1 state.

In a previous paper [1] we reported that irradiation of 2,2'-distyrylbiphenyl (1a) under nitrogen can give two products depending on the wavelength used. On irradiation at 350 nm intramolecular cycloaddition between the olefinic groups is apparently the faster
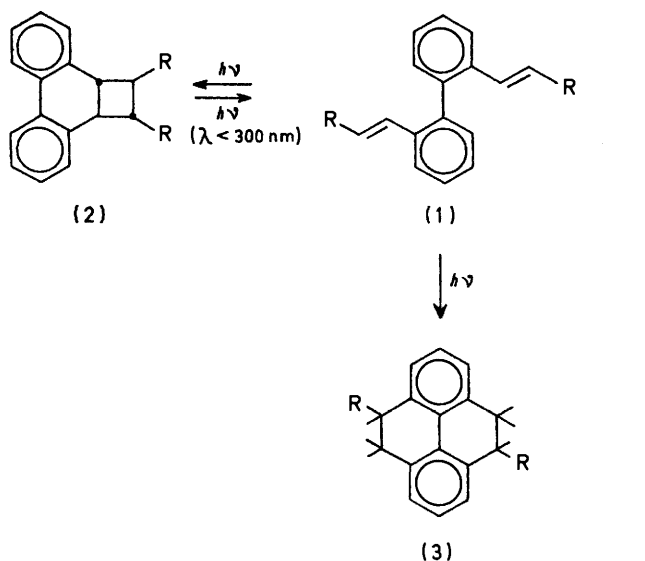
a ; R =Ph
b ; R =β-C₁₀H₇
c ; R = 2-benzo[c]phenanthryl
d ; R = p- NO₂C₆H₄

e ; R = p - MeOC₆H₄
f ; R = p - Me₂NC₆H₄
g ; R = H

SCHEME 1

reaction since a high yield of trans,trans,trans-1,2,2a,10b-tetrahydro-1,2-diphenylcyclobuta[l]phenanthrene (2a) is obtained (Scheme 1). At wavelengths below 300 nm this photocycloaddition becomes reversible, as shown by the detection at low temperature of (1a and b) in irradiation mixtures of pure (2a and b), respectively.[2] The apparently regiospecific cleavage in this reverse reaction was recently ascribed to a preference for that bond breaking which is accompanied by the highest release of steric strain.[3] The photolysis of (1a) at

[1] W. H. Laarhoven and T. J. H. M. Cuppen, J.C.S. Perkin I, 1972, 2074.

300 nm gives as the main photoproduct 4,5,9,10-tetrahydro-4,9-diphenylpyrene (3a), which is more stable than (2a).

The influence of sensitizers and quenchers on the product formation has now been investigated and quantum yields have been measured for a further elucidation of mechanistic details of the photoreactions of (1a). Moreover, the photochemistry of several related compounds (1b—g) has been studied and will be discussed.

RESULTS

Irradiation of (1a) in the presence of the triplet sensitizers benzil (E_T 54), Michler's ketone (E_T 61), or benzophenone (E_T 69 kcal mol⁻¹) did not lead to the formation of (2a) or (3a). On the other hand, triplet quenchers such as trans-piperylene (E_T 59) or azulene (E_T 31 kcal mol⁻¹) had no noticeable influence on the product formation from (1a); (2a) as well as (3a) were formed in the same amounts either with or without these quenchers.

TABLE 1

Photoproducts from substituted trans,trans-2,2'-divinylbiphenyls (1) in benzene solution [a] under nitrogen

	Product		
	λ 350 nm	λ 300 nm	
Compound	6 h	15 min	6 h
(1a)	(2a) 90%	(2a) 80%	(3a) 70%
(1b)	(2b) 90%	(2b) 85%	(3b) 60%
(1c)	(2c) 80%	(2c) 85%	(2c) [d] 80%
(1d)	(2d) [b] 80%		(2d) [e] 80%
(1e)	(2e) 35%		(2e) 30%
	(3e) 25%		(3e) 20%
(1f)	(2f) Trace, (3f)		(2f) Trace, (3f)
(1g)		(3g) [e] 70%	(3g) 90%

[a] Concentration ca. 10⁻³M. [b] After 40 h. [c] Accompanied by the intermediate, 4-vinylphenanthrene. [d] Accompanied by traces of (3c). [e] Even after 40 h (3d) could not be detected.

The nature and yields of the reaction products, formed on irradiation of several other o,o'-bis-(2-arylvinyl)biphenyls are given in Table 1. It appears that they all give cyclobutane derivatives (2) at 350 nm. The cycloaddition of (1d) is apparently much slower than that of (1a). With

[2] G. Kaupp and W. H. Laarhoven, Tetrahedron Letters, 1976, 941.

[3] G. Kaupp, Angew. Chem. Internat. Edn., 1974, 13, 817.

(1e and f) the corresponding tetrahydropyrene derivative is obtained as a second product, indicating that its formation rate is not much slower than that of the cycloaddition product. The photoreactivity of (1f) is, however, very low.

Irradiation experiments at 300 nm show that only (1b) gives a similar result as (1a). With (1c) formation of traces of (3c) at this wavelength could only be demonstrated by oxidation of the reaction mixture with dichlorodicyano-quinone. The characteristic pattern of the pyrene chromophore could then be observed in the u.v. spectrum. The substituted phenyl derivatives (1d—f) gave similar results

between 260 and 330 nm, quite different from that of biphenyl (see Table 3). Therefore, it may be expected that the triplet energy (E_T) of (1a) will be about equal to that of trans-stilbene $(E_T$ 50 kcal mol^{-1}). From the absence of any influence on product formation of three sensitizers with higher E_T values and of the quencher azulene with a lower E_T value it can then be concluded that the cycloaddition (1) $\longrightarrow$ (2) as well as the photo-cyclisation (1) $\longrightarrow$ (3) proceed from the first excited singlet state.

TABLE 2

Quantum yields for cyclobutane (ϕ_{cb}) and tetrahydropyrene formation (ϕ_{thp}) and for trans–cis-isomerisation (ϕ_{tc}) at 325 nm, and for fluorescence (ϕ_{fl}) at 25° in methanol at 320 nm

Compound	Solvent	ϕ_{cb}	ϕ_{thp}	ϕ_{tc}	ϕ_{fl}
trans,trans-(1a)	Methanol	0.27	<0.003	0.10	0.05
trans,trans-(1a)	Benzene	0.32	<0.003	0.09	
trans,cis-(1a)	Benzene	0.14 a			
cis,cis-(1a)	Benzene	0.04 a			
trans,trans-(1b)	Benzene	0.27	<0.003	0.07	0.09
trans,trans-(1c)	Benzene	0.22	<0.003	<0.1	0.15
trans,trans-(1d)	Benzene	0.004 b			0.00
trans,trans-(1e)	Methanol	0.027	~0.002	0.08	0.02
trans,trans-(1e)	Benzene	0.022	~0.002	0.10	
trans,trans-(1f)	Benzene	<0.02	<0.003		
trans,trans-(1g)	Benzene		~0.002		
trans-Stilbene e	Methylcyclohexane–isohexane			0.50	0.06
trans-4-Nitrostilbene e	Methylcyclohexane–isohexane			0.15	0.00
trans-4-Methoxystilbene e	Methylcyclohexane–isohexane			0.46	0.03
trans-4-Dimethylamino-stilbene e	Methylcyclohexane–isohexane			0.52	0.05
trans-β-styrylnaphthalene d	n-Hexane			0.13	0.75

a Dependent on the number of quanta absorbed. The value for trans,cis-(1a) is after absorption of 1 quantum molecule^{-1} for cis,cis-(1a) after absorption of 4 quanta molecule^{-1}. b Determined by comparison with (1a and e) in a Rayonet reactor at 350 nm. e D. Gegiou, K. A. Muszkat, and E. Fischer, J. Amer. Chem. Soc., 1968, 90, 3907. d P. Bortolus and G. Galiazzo, J. Photochem., 1973—1974, 2, 361.

at 300 and at 350 nm. When R is hydrogen [(1g)] formation of a cycloaddition product (2g) cannot be observed. At 350 nm this compound does not absorb, at shorter wavelengths only (3g) is formed.

For an interpretation of the varying photochemical behaviour of these related compounds the quantum yields have been measured for cyclobutane (ϕ_{cb}) and tetrahydropyrene formation (ϕ_{thp}) as well as for trans–cis-isomerisation (ϕ_{tc}) and fluorescence (ϕ_{fl}) under conditions where the photoproduction of (2) is irreversible (Table 2). Therefore, the measurements had to be done at a wavelength where (2) does not absorb (325 nm). The values of ϕ_{thp} are always very low (Table 2). For the parent compound (1a) the three geometrical isomers were investigated separately. Some relevant data from the literature have been included in Table 2 for comparison.

DISCUSSION

The Multiplicity of the Photoreactions.—It is known that the two halves of biphenyl derivatives containing large ortho-substituents behave independently towards light as a consequence of large deviations from the planar conformation by rotation around the central bond.[4] In accordance with this the u.v. spectrum of trans,trans-(1a) is qualitatively similar to that of trans-stilbene. It shows a broad, strong absorption band

Stereochemistry of the Cycloaddition.—The values of ϕ_{cb} for trans,cis- and cis,cis-(1a), especially their dependence on the amount of light absorbed, strongly suggest that formation of (2a) from these compounds occurs

TABLE 3

U.v. data, measured in methanol

| Compound	$\lambda_{max.}/$ nm	$10^{-3}\varepsilon$	$\lambda_{max.}/$ nm	$10^{-3}\varepsilon$	$\lambda_{max.}/$ nm	$10^{-3}\varepsilon$
(1a)	295	45.3			225	43.2
trans-Stilbene	296	29.0			228	16.4
(1g)	295	0.84	287	1.1	245	22.2
Styrene	291	0.57	283	0.74	248	15.0
(2a)	297	5.0	265	15.5		
Biphenyl					247	17.0

after a preceding isomerisation to the trans,trans-isomer. In Scheme 2, projections of the main conformations of trans,trans-(1a) are given together with the respective photoproducts to be expected from concerted $[_{\pi}2_s + _{\pi}2_s]$ or $[_{\pi}2_a + _{\pi}2_a]$ cycloadditions.[5] It appears that the only product found in the stereoselective cycloaddition of (1a) is that corresponding with the

4 G. H. Beaven, ' Steric Effects on Conjugated Systems,' ed. G. W. Gray, Butterworths Scientific Publications, London, 1958, p. 22.

most stable *anti,anti*-conformation (A). Similar stereo-selectivity is found in cycloadditions of related compounds. *E.g.* the intermolecular photocycloaddition of *trans*-stilbene yields *cis,trans,cis*-tetraphenylcyclobutane *via* a 'head-to-head' and the *trans,trans,trans*-isomer *via* a

These authors also gave evidence that the singlet excited state of (1g) is the reactive state for the photocyclisation.

The Influence of the R *Groups.*—Replacement of both phenyl groups in (1a) by β-naphthyl residues (1b)

(A)(*anti,anti*)   (B)(*syn,anti*)   (C)(*syn,syn*)

(2)   (4)   (5)
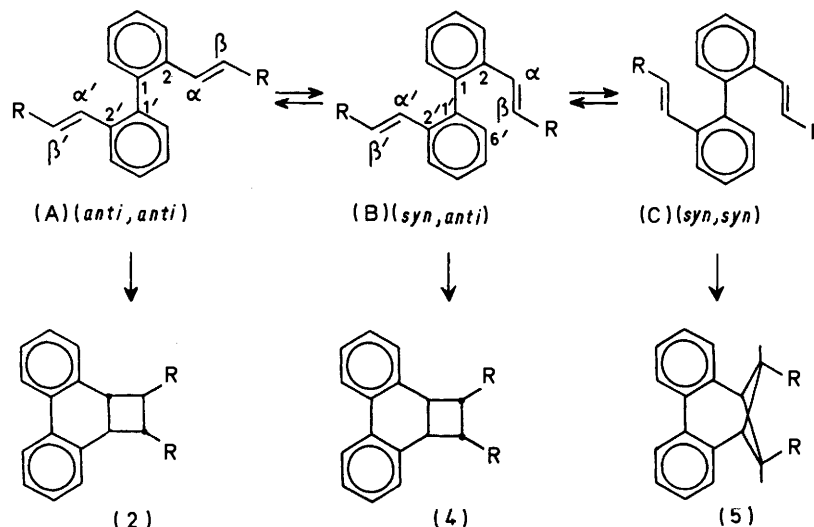
SCHEME 2   Projections of the main conformations of *trans,trans*-(1) and corresponding products from intramolecular [$_\pi 2_s + _\pi 2_s$] photocycloadditions

' head-to-tail ' addition; [6] and the intramolecular photocycloaddition of *trans,trans*-tetrabenzo[*a,c,g,i*]cyclododecahexaene [7] which has a fixed conformation corresponding to the *anti,anti* conformation (A) of (1a) yields only a *trans,trans,trans*-cyclobutane derivative. The antara-antara-interaction in these cases is sterically less favoured. Therefore, we assume that the photocycloadditions of compounds (1) proceed as concerted [$_\pi 2_s + _\pi 2_s$] reactions.

The Mechanism of Tetrahydropyrene Formation.—In a forthcoming paper devoted to the photochemistry of 2-styrylbiphenyl (6) it will be shown that its photoconversion into the dihydrophenanthrene derivative (8) occurs in two steps: a light induced cyclisation, previously found with several diarylbutadienes,[8] followed by a thermally allowed, suprafacial 1,5-hydrogen shift [9] (Scheme 3). It seems quite reasonable to accept that the formation of tetrahydropyrene derivatives (3) from compounds (1) is effected by two successive, similar reaction sequences (Scheme 4), as has previously been suggested.[1,9] The demonstration [10,11] of the occurrence of 4-vinyl-9,10-dihydrophenanthrene (10; R = H) as an intermediate in the photoconversion of (1g) into (3g) is in accordance with this scheme. Padwa and Mazzu [10] measured the quantum yields for the individual cyclisation steps: their values, $\phi_{(1g)\rightarrow(10g)} = 0.074$, $\phi_{(10g)\rightarrow(3g)} = 0.026$, are in good accordance with our value (*ca.* 0.002) for the overall reaction (1g) ⟶ (3g).

does not lead to differences in photochemical behaviour. Therefore, the formation of (2b) and (3b) must be analogous to the corresponding photoreactions of (1a).

(6)   (7)

(8)
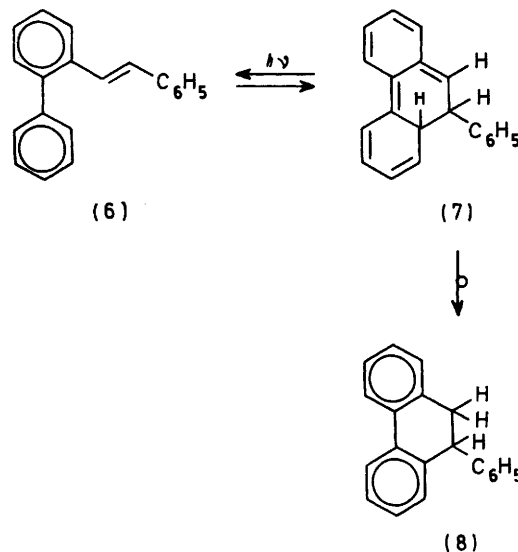
SCHEME 3

On further extension of the aryl residues (1c) the tetrahydropyrene derivative expected on irradiation at

[5] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[6] H. Shechter, W. J. Link, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1963, **85**, 1601.

[7] G. Wittig and G. Skipka, *Annalen*, 1975, 1157.

[8] R. J. Hayward and C. C. Leznoff, *Tetrahedron*, 1972, **27**, 2085.

[9] P. H. G. op het Veld, J. C. Langendam, and W. H. Laarhoven, *Tetrahedron Letters*, 1975, 231.

[10] A. Padwa and A. Mazzu, *Tetrahedron Letters*, 1974, 4471.

[11] J. C. Langendam and W. H. Laarhoven, unpublished results.

300 nm is hardly detectable; (2c) remains the main product at this wavelength. Since ϕ_{cb} and ϕ_{thp} for (1c) do not differ much from the corresponding quantum yields of (1a and b) the different behaviour seems to be caused by a higher photostability of (2c) in comparison with (2a and b). The photocleavage of compounds (2)
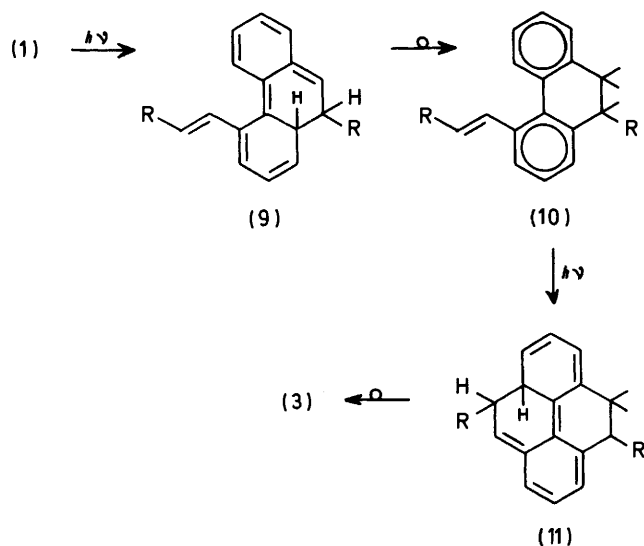
SCHEME 4

is probably caused by excitation of the biphenyl system of these compounds.[2] Absorption of light above 250 nm by (2c) will, however, mainly occur in the large aryl residues, and this will reduce the reversible character of the photocycloaddition (1c) ⟶ (2c). Another explanation might be that in the series phenyl, naphthyl, benzo[c]phenanthryl internal conversion from S_1 into S_0 and fluorescence become more important.[12] This should also lower the efficiency of the photolysis of (2).

The slow photocycloaddition of (1d), in full accord with the very low ϕ_{cb} value, is certainly caused by the efficient intersystem crossing which is characteristic for many nitro-compounds.[13] The same argument is used to explain that p-nitrostilbene does not undergo photodehydrocyclisation[14] which should proceed from the S_1 state.[15] As expected, neither (1d) nor p-nitrostilbene show fluorescence (Table 2). The competition between intersystem crossing and possible photoreactions reduces both ϕ_{cb} and ϕ_{thp} to an extremely low value and will also lower the quantum yield for the reaction (2d) ⟶ (1d). By this, formation of (3d) cannot be observed.

The quantum yields measured for (1e and f) reveal that only ϕ_{cb} is substantially lowered for these compounds in comparison with (1a). For (1e) trans–cis-

[12] J. B. Birks, ' Photophysics of Aromatic Molecules,' Wiley, London, 1970, p. 155.

[13] M. Kasha, Discuss. Faraday Soc., 1950, 9, 14.

[14] (a) C. S. Wood and F. B. Mallory, J. Org. Chem., 1964, 29, 3373; (b) E. V. Blackburn and C. J. Timmons, J. Chem. Soc. (C), 1970, 172.

[15] (a) Th. J. H. M. Cuppen and W. H. Laarhoven, J. Amer. Chem. Soc., 1972, 94, 5914; (b) C. H. Goedicke and H. Stegemeyer, Chem. Phys. Letters, 1972, 17, 492.

isomerisation appears to be the more efficient process. This explains that the formation rates at 350 nm of (3e) which arises from all isomers of (1e), and of (2e), which can only be obtained from trans,trans-(1e), are much less different than with (1a). On long irradiation of (1e) until complete conversion (40 h) the limiting product ratio (2c) : (3e) appeared to be ca. 1.0 at this wavelength; a similar experiment at 300 nm, where formation of (2e) is reversible gave (3e) in 60% yield as the only product. Irradiation at 350 nm in the presence of the quencher azulene led to a higher product ratio (2.7 after 16 h); however, with piperylene an unaltered ratio (1.4 after 16 h) was found. As neither formation of (2e) nor of (3e) was observed in the presence of adequate sensitizers, indicating that both photoreactions proceed from the S_1 state, the effect of azulene must be ascribed to quenching of the trans–cis-isomerisation.

Several possible explanations for the low efficiency of the cycloaddition with (1e) [and (1f)] could be excluded. (i) Differences in the Mulliken electronic overlap populations[16] (Δ_{nrs}) resulting from the promotion of an electron from the highest occupied to the lowest unoccupied molecular orbital appeared nearly equal for relevant pairs of atoms in (1a and e) (Table 4). With

TABLE 4

Differences in Mulliken overlap populations for relevant atoms in (1a, e, and g), calculated for conformations (A) and (B)

	(A)	(B)
Torsion angle	C_1–$C_{1'}$ = 55°	C_1–$C_{1'}$ = C_α–C_2 = 45°
	C_α–C_2 = $C_{\alpha'}$–$C_{2'}$ = 47°	$C_{\alpha'}$–$C_{2'}$ = 0°
Distances	C_α–$C_{\alpha'}$ = 2.69 Å	C_β–$C_{6'}$ = 2.69 Å
	C_β–$C_{\beta'}$ = 2.70 Å	

	(1a)	(1e)	(1g)
$\Delta_{n\alpha\alpha'}$ [in (A)]	0.031 2	0.030 8	0.041 7
$\Delta_{n\beta\beta'}$ [in (A)]	0.023 6	0.023 5	0.032 4
$\Delta_{n\beta_6'}$ [in (B)]	0.007 3	0.007 9	0.010 3

both compounds the values decrease in the order $\Delta_{n\alpha\alpha'}$, $> \Delta_{n\beta\beta'}$, $> \Delta_{n\beta_6'}$, indicating that cyclobutane formation should be favoured above tetrahydropyrene formation for both compounds to the same degree.[17,18]

(ii) Differences between (1a and e) in the conformation equilibria (see Scheme 2) could be excluded by analysis of their n.m.r. spectra. It appeared that the δ values of the olefinic protons at room temperature show equal differences when (1a) is compared with (1e) [$\Delta\delta(H_\alpha)$ 0.17; $\Delta\delta(H_\beta)$ 0.06] as for trans-stilbene compared with trans-p-methoxystilbene (0.13 and 0.05, respectively[19]). Moreover, the temperature dependences of $\delta(H_\alpha)$ and $\delta(H_\beta)$ are nearly equal for (1a and e). According to the Frank–Condon principle there is no difference between the conformations in the ground state and the initial excited state.

(iii) Finally, no indication was found for any particular

[16] R. S. Mulliken, J. Chem. Phys., 1955, 23, 1833, 1841.

[17] K. A. Muszkat and S. Sharafi-Ozeri, Chem. Phys. Letters, 1973, 20, 397.

[18] K. A. Muszkat, G. Seger, and S. Sharafi-Ozeri, J.C.S. Faraday II, 1975, 1529.

[19] H. Güsten and M. Salzwedel, Tetrahedron, 1967, 23, 173.

energy barrier along the reaction co-ordinate [20] on the excited state surface of (1e), which might cause a larger activation energy for cyclobutane formation from (1e) in comparison with (1a). Irradiation of (1a) for 15 min above 300 nm gives the same product ratio when performed at room temperature in ethanol, at room temperature in ethanediol, or at 195° in ethanediol [90 ± 5% (2a) and 7 ± 2% (3a)]. The same is true, however, for (1e); in all three similar experiments 35 ± 5% (2e) and 25 ± 5% (3e) was found. Apparently product formation from both compounds is independent of solvent and temperature.

The only remaining explanation for the low ϕ_{cb} value of (1e) might be the occurrence of enhanced internal conversion caused by mixing of an $n \longrightarrow \pi^*$ state with the $\pi \longrightarrow \pi^*$ state.[13] This phenomenon is not uncommon for aromatic methoxy-compounds. We tried to eliminate the $n \longrightarrow \pi^*$ contribution by protonation of the methoxy-group, but neither trifluoroacetic acid nor strong mineral acids had any influence on the absorption
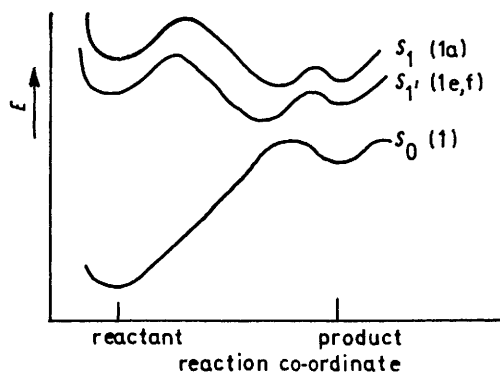
Potential energy curves for ground (S_0) and excited states (S_1 and S_1') of compounds (1)

spectrum, and addition of trifluoroacetic acid did not increase ϕ_{cb} for (1e).

Addition of hydrochloric acid, however, to a benzene solution of (1f), which is more basic than (1a) and whose S_1 state has more $n \longrightarrow \pi^*$ character,[21] led to a dramatic increase of ϕ_{cb}. After protonation the same value was found as for (1a) (0.3). A similar effect has previously been found in the photoreduction of p-dimethylamino-benzophenone.[22] So, it is probable that the different photochemical behaviour of (1e and f) in comparison with (1a) must be ascribed to increasing $n \longrightarrow \pi^*$ contributions to the first excited state. The effect of this mixing-up is qualitatively shown in the Figure, in which supposed energy surfaces [23] for the ground state and first excited state of (1e) [or (1f)] and (1a) are given. The competition between radiationless relaxation to the product side or the reactant side determines the

quantum yield of the reaction.[24] The central well, from which relaxation must occur is shifted to the reactant side in S_1' relative to S_1. Therefore, excitation to S_1' will give mainly unchanged reactant, whereas via S_1 a high yield of product will arise.

2,2'-Divinylbiphenyl (1g) cannot be converted into a cyclobutane derivative (2g). The same has been found for compounds (1), in which the residues R are alkyl groups.[9,10] As the u.v. spectra of these compounds correspond with that of styrene instead of stilbene (Table 3), absorption above 300 nm is weak and these compounds must have rather low photoreactivities in this region. At lower wavelengths (260—300 nm) the absorption of cyclobutane derivatives (2), which is due to their biphenyl system, is stronger than that of (1g). Therefore, (2g), if formed from (1g), should absorb a considerable fraction of the incident light and undergo fast photolysis. The equilibrium (1g) ⇌ (2g) is under all circumstances far to the left. This conclusion is supported by the values of the Mulliken overlap populations for (1g) (Table 4).

EXPERIMENTAL

For the obtaining of spectral data were used: a Varian MAT SM2B mass spectrometer, a Beckman DK2A or a Cary 15 u.v. spectrophotometer, a Perkin-Elmer MPF-4 fluorescence spectrophotometer, and a Varian HA-100 n.m.r. instrument. M.p.s were determined with a Leitz m.p. microscope and are uncorrected.

Substrates.—The syntheses of the o,o'-bis-(2-arylvinyl)-biphenyls were carried out by a previously described method.[25] The last step, a Wittig synthesis, was performed in boiling methanol or in boiling dimethylformamide (DMF) with sodium methanolate as base, and the respective aromatic aldehydes in 10% excess. The method using DMF gave slightly better yields. The overall yields, after separation by column chromatography on an SiO_2 column, ranged from 60 to 80%. In order to get the pure *trans,trans*-isomers we refluxed a mixture of isomers in CCl_4 with 5 mol % I_2.[26] After washing with a 5% water solution of $Na_2S_2O_5$ to remove iodine the *trans,trans*-isomers were purified by column chromatography over Al_2O_3 using a gradient of hexane–toluene as eluant. The pure isomers were recrystallized from ethanol.

trans,trans-o,o'-Bis-(2-β-naphthylvinyl)biphenyl (1b) had m.p. 166—168 °C (from ethanol), $\lambda_{max.}$ (CH$_3$OH) 358 (log ε 3.46), 343 (4.02), 319 (4.27), 305 (4.29), 276 (4.52), 270 (4.54), and 223 nm (5.10), δ (CS$_2$) 8.35—7.10 (22 H, m) and 7.02 and 6.89 (4 H, 2AB, J 16 Hz), m/e (290 °C) 458 (10%, M^+), 454 (6, M − 4H), 329 (7), 318 (7), 280 (100, M − C$_{14}$H$_{10}$), 265 (6), 178 (80, C$_{14}$H$_{10}$), and 141 (35). *trans,trans-o,o'*-Bis-{2-(2-benzo[c]phenanthryl)vinyl}biphenyl (1c) had m.p. 231—234 °C (from ethanol), $\lambda_{max.}$ (CH$_3$OH) 375 (log ε 3.80), 364 (4.06), 343 (4.25), 323 (4.42), 307 (4.55), 285 (4.74), 274 (4.75), 264 (4.71), and 227 nm (4.68), δ (CS$_2$)

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[21] C. J. Seliskar, O. S. Khalil, and S. P. McGlynn, ' Excited States,' ed. E. C. Lim, Academic Press, New York, 1974, vol. I, pp. 231*ff*.

[22] N. J. Turro, ' Techniques of Organic Chemistry,' ed. A. Weisberger, Wiley, New York, 1969, vol. XIV, pp. 219*ff*.

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[24] J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, 1969, **7**, 149.

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8.98 (2 H, s, α_4H), and 8.13—6.99 (32 H, m), m/e (240 °C) 658 (<1%, M^+), 480 (1, $M - C_{14}H_{10}$), 178 (100, $C_{14}H_{10}$), and 151 (6). *trans,trans-o,o'*-Bis-(2-p-nitrophenylvinyl)-biphenyl (1d) had m.p. 246—248 °C (from ethanol), $\lambda_{max.}$ (benzene) 350 nm (log ε 4.60), δ (AsCl$_3$) 8.74 and 8.02 (8 H, $2A_2B_2$, J 8 Hz), 8.64—8.47 (2 H, m), 8.34—8.09 (6 H, m), and 7.70 (4 H, s), m/e (230 °C) 448 (23%, M^+), 402 (3, $M - NO_2$), 326 (6, $M - C_6H_4NO_2$), 299 (17), 278 (10), 265 (65), and 178 (100, $C_{14}H_{10}$). *trans,trans-o,o'*-Bis-(2-p-methoxyphenylvinyl)biphenyl (1e) had m.p. 129—130 °C (from ethanol), $\lambda_{max.}$ (CH$_3$OH) 343 (log ε 4.21), 326 (4.49), 299 (4.54), 237 (4.44), and 228 nm (4.50), δ (CS$_2$) 7.68—7.54 (2 H, m), 7.37—6.90 (10 H, m), 6.62 and 6.53 (4 H, B$_2$ part of $2A_2B_2$), 6.78 and 6.53 (4 H, 2AB, J 16 Hz), and 3.62 (6 H, s, 2CH$_3$), m/e (290 °C) 418 (<1%, M^+), 414 (1, $M -$ 4H), 300 (1), 240 (16, $M - C_{14}H_{10}$), 225 (4, 240 $-$ CH$_3$), 178 (100, $C_{14}H_{10}$), and 152 (5), and 151 (5). *trans,trans-o,o'*-Bis-(2-p-dimethylaminophenylvinyl)biphenyl (1f) had m.p. 162—167 °C (from ethanol), $\lambda_{max.}$ (CH$_3$OH), 345 (log ε 3.48), 312 (3.81), 292 (4.08), 264 (4.56), 258 (4.58), 252 (4.58), 243 (4.47), and 212 nm (4.81), δ (CS$_2$) 7.73—7.50 (2 H, m), 7.20—7.00 (6 H, m), 6.93 and 6.40 (8 H, $2A_2B_2$, J 8 Hz), 6.74 and 6.47 (4 H, 2AB, J 15 Hz), and 2.85 (12 H, s, CH$_3$), m/e (160 °C) 444 (1%, M^+), 265 (100, $M - C_{14}H_{10}$), 251 (5, 265 $-$ CH$_3$), 236 (3, 265 $-$ 2CH$_3$), 222 (5, M^{2+}), and 178 (2, $C_{14}H_{10}$).

Irradiations.—All irradiations were carried out in oxygen-free benzene or ethanol solutions under nitrogen in order to prevent formation of oxidation products.[1] The presence of each type of product in the irradiation mixture could easily be established from n.m.r. spectra. All cyclobutane derivatives (2) showed the same characteristic AA'BB' pattern for the cyclobutane protons, which belongs to the *trans,trans,trans*-isomer as has previously been demonstrated[1] for (2a) by ozonolysis. The tetrahydropyrenes (3) could be recognized by the ABX pattern of their non-aromatic protons. In general, the signals of cyclobutane and tetrahydropyrene derivatives were sufficiently separated for a straightforward analysis of the spectra.

Products.—The cyclobutane (2) and tetrahydropyrene (3) derivatives were obtained by preparative irradiations of 10^{-3}M solutions of (1) in ethanol. These irradiations were carried out in a Rayonet photochemical reactor, fitted with 300 or 350 nm lamps. By using the appropriate conditions (see Table 1) in most cases could either the cyclobutane or the tetrahydropyrene be obtained in good yield. After separation by column chromatography over Al$_2$O$_3$ these compounds were purified by crystallization from ethanol.

trans,trans,trans-1,2,2a,10b-Tetrahydro-1,2-di-β-naphthylcyclobuta[l]phenanthrene (2b) had m.p. 179—183 °C (from ethanol), $\lambda_{max.}$ (CH$_2$Cl$_2$) 320 (log ε 2.96), 291 (4.09), 278 (4.36), 267 (4.40), 230 (4.64), and 228 nm (4.60), δ (CS$_2$) 8.26—7.62 (10 H, m), 7.62—7.10 (12 H, m), 4.10—3.76 (2 H, m), and 3.50—3.26 (2 H, m), m/e (240 °C) 458 (4%, M^+), 328 (4), 315 (5), 302 (4), 280 (100, $M - C_{14}H_{10}$), and

178 (35, $C_{14}H_{10}$). *trans,trans,trans*-1,2,2a,10b-Tetrahydro-1,2-bis-(2-benzo[c]phenanthryl)cyclobuta[l]phenanthrene (2c) had m.p. 215—218 °C (from ethanol), $\lambda_{max.}$ (CH$_2$Cl$_2$) 376 (log ε 2.97), 357 (3.17), 319 (4.36), 288 (5.02), 278 (5.03), 268 (4.85), 234 (4.84), and 223 nm (4.89), δ (CS$_2$) 9.21 (2 H, s, α-H), 8.97 and 8.89 (2 H, d, α-H), 8.14—7.70 (16 H, m), 7.58—7.06 (10 H, m), 4.34—4.14 (2 H, m), and 3.56—3.36 (2 H, m), m/e (300 °C) 658 (2%, M^+), 480 (8, $M - C_{14}H_{10}$), and 178 (100, $C_{14}H_{10}$). 4,5,9,10-Tetrahydro-4,9-di-β-naphthylpyrene (3b) had m.p. 279—280 °C (from ethanol), $\lambda_{max.}$ (CH$_3$OH) 320 (log ε 3.25), 297 (4.05), 282 (4.32), 276 (4.36), and 230 nm (5.04), δ (CS$_2$) 8.08—7.28 (14 H, m), 7.24—6.74 (6 H, m), 4.54—4.30 (2 H, X part of ABX, J 7.0 Hz), and 3.56—3.36 (4 H, AB part of ABX), m/e (270 °C) 458 (65%, M^+), 330 (41, $M - C_{10}H_8$), 203 (100), 202 (100, $M - 2C_{10}H_8$), 141 (47), and 128 (88, $C_{10}H_8$). 4,5,9,10-Tetrahydro-4,9-bis-p-methoxyphenylpyrene (3e) had m.p. 240—243 °C (from ethanol), $\lambda_{max.}$ (CH$_3$OH) 295 (4.03), 285 (4.23), 278 (4.28), and 269 nm (4.23), δ (CS$_2$) 7.1—6.8 (8 H, m), 6.8—6.5 (6 H, m), 4.03 (2 H, t, X part of ABX, J 7 Hz), 3.09 (4 H, d, AB part of ABX, J 7 Hz), and 3.69 (6 H, s), m/e (240 °C) 418 (58%, M^+), 403 (1, $M -$ CH$_3$), 385 (3), 309 (100, $M - C_6H_5OCH_3 -$ H), 294 (15, 309 $-$ CH$_3$), 203 (63), 202 (65, $M - 2C_5H_5OCH_3$).

The cyclobutane derivatives (2d—f) could not be obtained sufficiently pure to measure all relevant spectral data. Therefore, only the n.m.r. data for these compounds are given. *trans,trans,trans*-1,2,2a,10b-Tetrahydro-1,2-bis-(p-nitrophenyl)cyclobuta[l]phenanthrene (2d) had δ (C$_6$D$_6$) 7.8 and 6.8 (8 H, $2A_2B_2$, J 14 Hz), 7.8—7.5 (2 H, m), 7.3—6.5 (6 H, m), 3.43—3.10 (2 H, m), and 3.00—2.67 (2 H, m). *trans,trans,trans*-1,2,2a,10b-Tetrahydro-1,2-bis-(p-methoxyphenyl)cyclobuta[l]phenanthrene (2e) had δ (CS$_2$) 7.77—7.55 (2 H, m), 7.35—6.60 (14 H, m), 3.67 (6 H, s, 2CH$_3$), 3.53—3.35 (2 H, m), and 3.10—2.91 (2 H, m). *trans,trans,trans*-1,2,2a,10b-Tetrahydro-1,2-bis-(p-dimethylaminophenyl)-cyclobuta[l]phenanthrene (2f) had δ (CS$_2$) 7.86—7.70 (2 H, m), 7.36—6.30 (6 H, m), 6.75 and 6.37 (8 H, $2A_2B_2$, J 9 Hz), 4.14—3.94 (2 H, m), 3.88—3.68 (2 H, m), and 2.81 (12 H, s).

Quantum Yields.—The quantum yields were measured using a similar black box to that described by Zimmerman,[27] fitted with a Philips SP-900 lamp and a filter system, consisting of solutions of CoSO$_4$, NiSO$_4$, and SnCl$_2$ in Pyrex cells of 2 cm path length. The transmission of this filter system is <1% below 305 nm and above 345 nm, and has a maximum of 18% at 325 nm. Ferrioxalate actinometry[28] was used to measure the light intensity, in the modification described by Murov.[29]

To determine the quantum yields the conversions were calculated from the ^{1}H n.m.r. spectra. Conversions were measured up to 20%. Under these conditions the deviation in the given values for ϕ_{cb} is <10%, for ϕ_{thp} <25%, and for ϕ_{tc} <10%. The quantum yields of fluorescence are measured by a relative method,[30] using *trans*-stilbene as standard.

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