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PHOTODEHYDROCYCLIZATIONS IN STILBENE-LIKE COMPOUNDS—III

EFFECT OF STERIC FACTORS

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Abstract—Photodehydrocyclizations in stilbene-like compounds take place only if the sum of the free valence numbers of the atoms concerned in the cyclization step exceeds in the excited state, a value of 1. If more than one cyclization is possible the photoconversion follows the pathway for which ΣF^* is maximal; if $\Delta\Sigma F^*$ for various cyclizations is smaller than 0·1 a second product is sometimes formed.

These rules also hold if only non planar and no planar products can arise. If planar as well as non planar compounds can be formed the main product is as a rule a planar polycyclic aromatic, even if ΣF^* for its formation is lower than for other cyclizations. Sometimes but not always, a non planar product (with higher ΣF^*) is found as a side product.

The applicability of these rules in the planning of synthetic procedures for polycyclic aromatics is illustrated in the preparation of several new compounds (e.g. the four isomeric benzo hexahelicenes).

In part I we demonstrated[1] that photodehydrocyclizations of stilbene-like compounds appear to occur only if the sum of the free valence numbers of the proper atoms in the excited state exceeds a critical barrier ($\Sigma F^* > 1{\cdot}0$).

If two cyclization routes appear possible according to this rule, both will take place if the difference in ΣF^* is small. For large values of $\Delta\Sigma F^*$ only the most favourable cyclization pathway is followed.

Since then several new examples have been reported, e.g. cyclization of 4-styrylphenanthrene[2] to benzo[*c*]chrysene ($\Sigma F^* = 1{\cdot}059$) and 1-phenylpyrene ($\Sigma F^* = 1{\cdot}087$), and the formation of tribenzo[*c.i.o*]triphenylene ($\Sigma F^* = 1{\cdot}127$) and 4-phenylnaphtho[1.2-*a*]pyrene† ($\Sigma F^* = 1{\cdot}064$) from 13-styrylbenzo[*c*]chrysene.[3] Moreover, we found[2] that apparent exceptions in the photocyclizations of *ortho* and *para* distyrylbenzene[4] to picene ($\Sigma F^* = 0{\cdot}946$ in the first step) and 1:12-benzperylene ($\Sigma F^* = 0{\cdot}954$ in the first step) respectively, do not conflict with the rule, because these products only arise from dimers of the starting compounds.

In all cases studied the products formed consist of planar polycyclic aromatic systems or nearly so. We therefore investigated whether or not steric factors interfere with the rule if serious crowding should prevent the product from taking a planar structure. Such will be the case in cyclizations from which dibenzo[*c.g*]phenanthrene derivatives (pentahelicenes) or higher helicenes may result.

In Table 1 several relevant 1,2-diarylethylenes have been listed together with all possible cyclization products, the proper ΣF^*-values and the yields found experimentally.

Products isolated were identified by comparison of physical data with values from literature; compounds not described previously (III; V; VI; VIII; XIV; XXI; XXVII;

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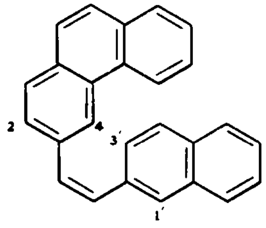
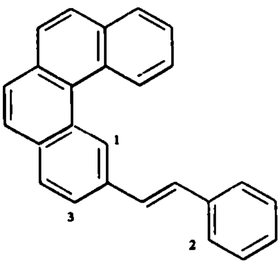
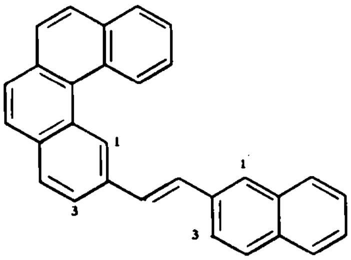
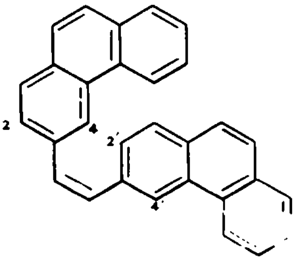
† The numbering of the polycyclic compounds is according to the IUPAC rules.

TABLE 1†

Compound	ΣF^*_{rs}	Product	Yield	Ref
1 1-(β-Naphthyl)-2-(3-phenanthryl)ethylene(I)			—	*a*
	2,3' = 0·916			
	4,3' = 1·020		— (np)	
	2,1' = 1·083	benzo[*a*]-naphtho[1.2-*h*] anthracene (III)	50%(p)	
	4,1' = 1·187	hexahelicene (II)	22%(np)	
2 2-Styrylbenzo[*c*]phenanthrene				
	3,2' = 0·955		—	*b*
	1,2' = 1·117	hexahelicene (II)	80%(np)	
3 1-(β-Naphthyl)-2-(2-benzo[*c*]phenanthryl)ethylene				*b*
	3,3' = 0·910		--	
	1,3' = 1·046		— (np)	
	3,1' = 1·080	dinaphtho[*a.h*]anthracene	65%(p)	
	1,1' = 1·216	heptahelicene (X)	20%(np)	
4 1,2-Di(3-phenanthryl)ethylene (IX)				
	2,2' = 0·927		—	*a*, *c*
	2,4' = 1·027	dinaphtho[1.2-*b*; 1.2-*g*] phenanthrene	— (np)	
	4,4' = 1·126	heptahelicene (X)	50%(np)	

Abbreviations: p = planar compound

np = non planar compound

[a] = this work

[b] = see Ref 5 and personal communication of Prof. R. H. Martin

[c] = see Ref 6

[d] = see Ref 1

† The romans correspond with formulae in the schemes I–VII.

TABLE 1—*continued*

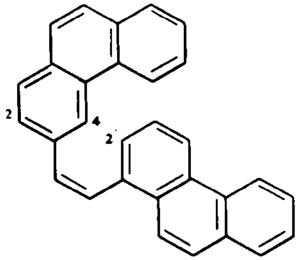
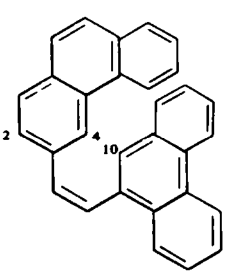
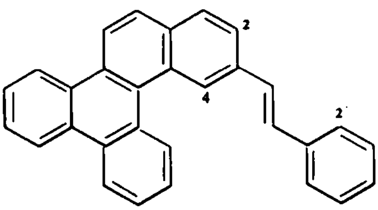
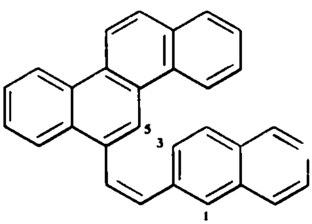
5	1-(1-Phenanthryl)-2-(3-phenanthryl)ethylene (IV) 	2,2′ = 0·972		—	*a*
		4,2′ = 1·069	naphtho[1.2-*a*]picene (V) ($\xrightarrow{h\nu}$ naphtho[1.2-*b*]-benzo[*ghi*] perylene) (VI)	(np) 80%	
6	1-(3-Phenanthryl)-2-(9-phenanthryl)ethylene (VII) 	2,10′ = 1·095	naphtho[1.2-*b*]-benzo[*g*] chrysene (VIII)	75%(p)	*a*
		4,10′ = 1·188	benzo[*a*]hexahelicene (XXI)	-- (np)	
7	3-Styrylbenzo[*c*]triphenylene (XX) 	2,2′ = 0·941	naphtho[1.2-*b*]-benzo[*g*] chrysene (VIII)	—	*a*
		4,2′ = 1·111	benzo[*a*]hexahelicene (XXI)	60%(np)	
8	1-(β-Naphthyl)-2-(6-chrysyl)ethylene (XIII) 	5,3′ = 1·032		— (np)	*a*
		5,1′ = 1·164	benzo[*d*]hexahelicene (XIV)	90%(np)	
9	8-Styrylbenzo[*c*]chrysene (XVII)	7,2′ = 1·097	benzo[*d*]hexahelicene (XIV)	66%(np)	*a*

TABLE 1—*continued*

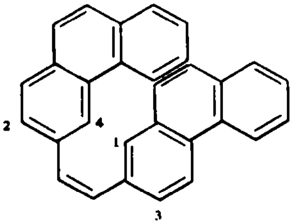
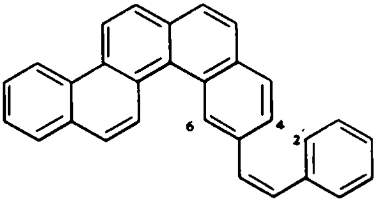
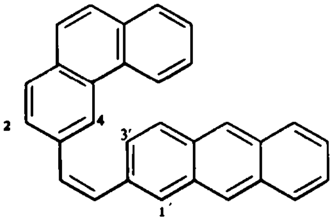
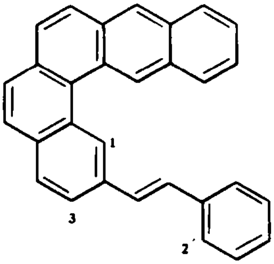
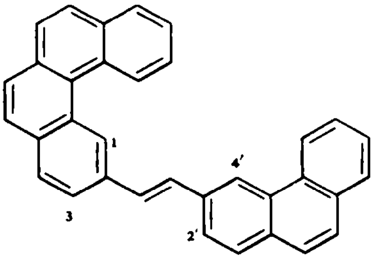
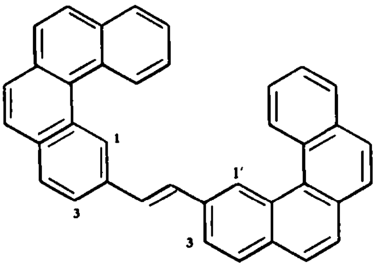
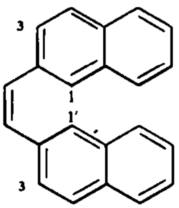
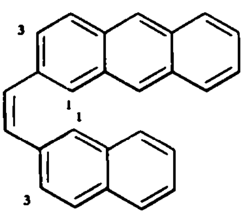
10	1-(2-Phenanthryl)-2-(3-phenanthryl)ethylene (XXVIII)				
		2,3′ = 0·938		—	*a*
		2,1′ = 1·048	dinaphtho[1.2-*b*; 2.1-*g*]-phenanthrene (XXIX)	75%(p)	
		4,3′ = 1·049		— (np)	
		4,1′ = 1·160	benzo[*m*]hexahelicene (XXVII)	— (np)	
11	5-Styrylbenzo[*c*]chrysene (XXVI)				
		4,2′ = 0·959		—	
		6,2′ = 1·083	benzo[*m*]hexahelicene (XXVII)	65%(np)	*a*
12	1-(2-Anthracyl-2-(3-phenanthryl)ethylene (XXXI)				
		2,3′ = 0·911		—	*a*
		4,3′ = 0·983		—	
		2,1′ = 1·074	dinaphtho[1.2-*b*; 2.3-*g*]-phenanthrene (XXXII)	60%(p)	
		4,1′ = 1·146	benzo[*n*]hexahelicene (XXXIII)	22%(np)	
13	2-Styryl dibenzo[*b*.*g*]phenanthrene (XXXVI)				
		3,2′ = 0·915		—	*a*
		1,2′ = 1·035	benzo[*n*]hexahelicene (XXXIII)	10%(np)	
14	1-(3-Phenanthryl)-2-(2-benzo[*c*]phenanthryl)ethylene				
		3,2′ = 0·922		—	*b*
		3,4′ = 1·023		— (np)	
		1,2′ = 1·050		— (np)	
		1,4′ = 1·150	octahelicene	62%(np)	

TABLE 1—*continued*

15	1,2-Di(2-benzo[*c*]phenanthryl)ethylene  	3,3′ = 0·916	---	*b*
		1,3′ = 1·046	— (np)	
		1,1′ = 1·176 nonahelicene	70%(np)	
16	1,2-Di(β-naphthyl)ethylene  	3,3′ = 0·904	—	*d*
		1,3′ = 1·082 dibenzo[*b.g*]phenanthrene	— (p!)	
		1,1′ = 1·260 dibenzo[*c.g*]phenanthrene	80%(np)	
17	1-(2-Anthracyl)-2-(β-naphthyl)ethylene (XXXVII)  	3,3′ = 0·907	—	*a*
		3,1′ = 1·012	— (p)	
		1,3′ = 1·071 benzo[*b*]-naphtho[2.3-*g*]-phenanthrene (XXXVIII)	5%(p)	
		1,1′ = 1·176 benzo[*b*]-naphtho[1.2-*g*]-phenanthrene	— (np)	

XXIX; XXXII; XXXIII and XXXVIII) were characterized by UV, NMR and mass spectra as given in the Experimental.

In one of the experiments (I) in which two cyclization products were isolated the dependence of the product ratio on solvent and temperature was tested. It appeared that the ratio II:III in ether, benzene and methanol at 15° as well as 60° was always 0·4 within the limits of experimental error.

In all cases where the number of possible products appeared to be higher than that of the compounds isolated the mother liquor which remained after the isolation of the main products was carefully examined by means of TLC, followed by several spectroscopic techniques (UV, IR, NMR and mass spectroscopy). Usually it consisted of a brown tar of polar nature; the presence of absorptions in the CO and OH ranges of its otherwise badly defined IR spectrum indicated the presence of oxidation products.

Sometimes, however, side products could be isolated. Frequently they appeared to be dimers of the starting compound. Especially with sparingly soluble diaryl-olefins these were even found upon irradiation of solutions with concentrations as low as 10^{-3} molar. Such dimerizations can mask possible cyclizations: 1-(β-anthracyl)-2-(β-naphthyl) ethylene (XXXVII) is converted into XXXVIII upon irradiation in benzene or xylene, in which it is sparingly soluble; however, in diglyme, in which XXXVII is more soluble ($c = 5{\cdot}10^{-3}$) only a mixture of dimers is formed.

The diphenanthrylethylenes (VII and IX) afforded dihydro derivatives of the starting compounds as side products. The very low yields prevented definite elucidation of their structures by NMR spectrometry; from the UV and mass spectra it seemed, however, that the reductions concerned the olefinic bond, not the phenanthrene moiety.

From the irradiation mixture of the diphenanthrylethylene (IX) in benzene with added iodine we isolated a greenish-brown substance, which lost iodine when an ethereal solution was shaken with sodium bisulphite. The mass spectrum of the residue clearly indicated the presence of iodine containing compounds.

In several cases (6 and 10) the absence of expected products (benzohexahelicenes) could be assured by the availability of authentic samples from other experiments (7 and 11, respectively).

In short it has been quite definitely ascertained that no cyclization products have been formed other than those indicated in Table 1.

DISCUSSION

I. The new results definitely confirm the general rule that photocyclization or otherwise in stilbene-like compounds depends on the ΣF^*-values of the compounds concerned: Products from cyclizations, for which $\Sigma F^* < 1$, have never been found; compounds, in which $\Sigma F^* > 1$ for properly chosen atoms, always provide one or more photocyclization products. The latter also holds in cases where only a non planar product is possible: In cases 2, 5, 7, 9, 11 and 13, in which only one cyclization route is considered, the expected products although non planar are obtained in yields of 60–80%. Only in 13 is the yield substantially lower, probably due to low quantum yield (long irradiation time) and substantial oxidation of the anthracene moiety of the molecule.

II. If more than one, but only non planar cyclization products can be formed (cases 4, 8, 14 and 15) only one product corresponding to the largest ΣF^*-value is obtained in a yield of about 50% or higher. In all these cases the difference of ΣF^* for two possible cyclization pathways is rather high (0·099, 0·132, 0·100 and 0·130 respectively). Also in the formation of planar cyclization products such differences always lead to only one product.[1] The same is true in the synthesis of tridecahelicene.[11]

III. In the remaining experiments (1, 3, 6, 10, 12, 16 and 17) planar as well as non planar products are possible. Although in all these cases the highest ΣF^*-value concerns the formation of a non planar compound, generally a planar polycyclic aromatic compound is the main product. In several cases (6, 10 and 17) the expected formation of benzohelicenes did not occur, in the others a non planar compound was isolated only as a side product. Case 16 is an exception; on irradiation of 1,2-di-(β-naphthyl)ethylene only the non planar dibenzo[*c*.*g*]phenanthrene and its second cyclization product could be isolated.

In Table 2 these experiments are arranged according to increasing ΣF^*-values of the non planar products. It is clear that no simple correlation exists between these values nor $\Delta\Sigma F^*$-values and product formation. On the whole non planar products are found as side products if the relative ΣF^* is high and at the same time much larger than the value for cyclization to a planar compound, but experiment 12 forms a striking exception.

TABLE 2

No.	Planar	Non planar	$\Delta\Sigma F^*$
	ΣF_p^* (yield %)	$\Sigma F_{n,p}^*$(yield %)	
12	1·074 (65)	1·146 (22)	0·072
10	1·048 (75)	1·160 (--)	0·112
17	1·071 (5)	1·176 (--)	0·105
1	1·083 (50)	1·187 (22)	0·104
6	1·095 (75)	1·188 (--)	0·093
3	1·080 (65)	1·216 (20)	0·136
16	1·082 (—)	1·260 (60)	0·178

In conclusion it can be stated that overcrowding during product formation is an interfering factor in photodehydrocyclizations of stilbene-like compounds, if planar as well as non planar products are possible. Simple rules as presented in the foregoing discussion may be a guide in the planning of the synthesis of polycyclic aromatic compounds by photocyclizations.

Without calculating the ΣF^*-values the preferred photocyclization pathway can be predicted in a simple way by counting the number of benzene rings in the formulae of the dihydrophenanthrene derivatives.[1] The compound with the largest number of benzene rings is formed if only planar or only non planar compounds are possible. If both planar and non planar products are possible, the planar one arises as the main product.

In the preparation of overcrowded compounds a pathway via a proper styryl aromatic as the last intermediate is generally preferable to one via another diaryl-olefin, in spite of the fact that the latter route includes fewer steps. Illustrative examples are the syntheses of hexahelicene via 1 or 2, of benzo[*m*]hexahelicene via 10 or 11, and especially the quite different results of 6 and 7.

EXPERIMENTAL

All diarylethylenes used in irradiation experiments, for the greater part new compounds, were obtained by Wittig syntheses.

For the preparation of the bromides required properly Me substituted aromatics were brominated with N-bromosuccinimide (NBS). Because 2-methylphenanthrene, obtained by irradiation of 3-methylstilbene and required for the synthesis of XXVI, could not be separated completely from 4-methylphenanthrene, separation on an Al_2O_3 column was carried out after bromination.

Especially in the bromination of compounds containing an anthracene moiety side products arose by ring substitution (Scheme VI).

In all cases the bromides were converted into arylmethyl triphenyl phosphonium bromides by treatment with triphenylphosphine in xylene.

The Wittig syntheses were carried out in DMF or alcoholic solutions using NaOMe as a base. Products were isolated and purified by column chromatography on Al_2O_3 or silicagel, followed by crystallization, yields varied from 50–90%.

Irradiations were performed in hexane, benzene or xylene with added iodine as an oxidant. To reduce the formation of oxidation products during irradiation sometimes the solns were boiled previously and air removed by passing a stream of N_2.

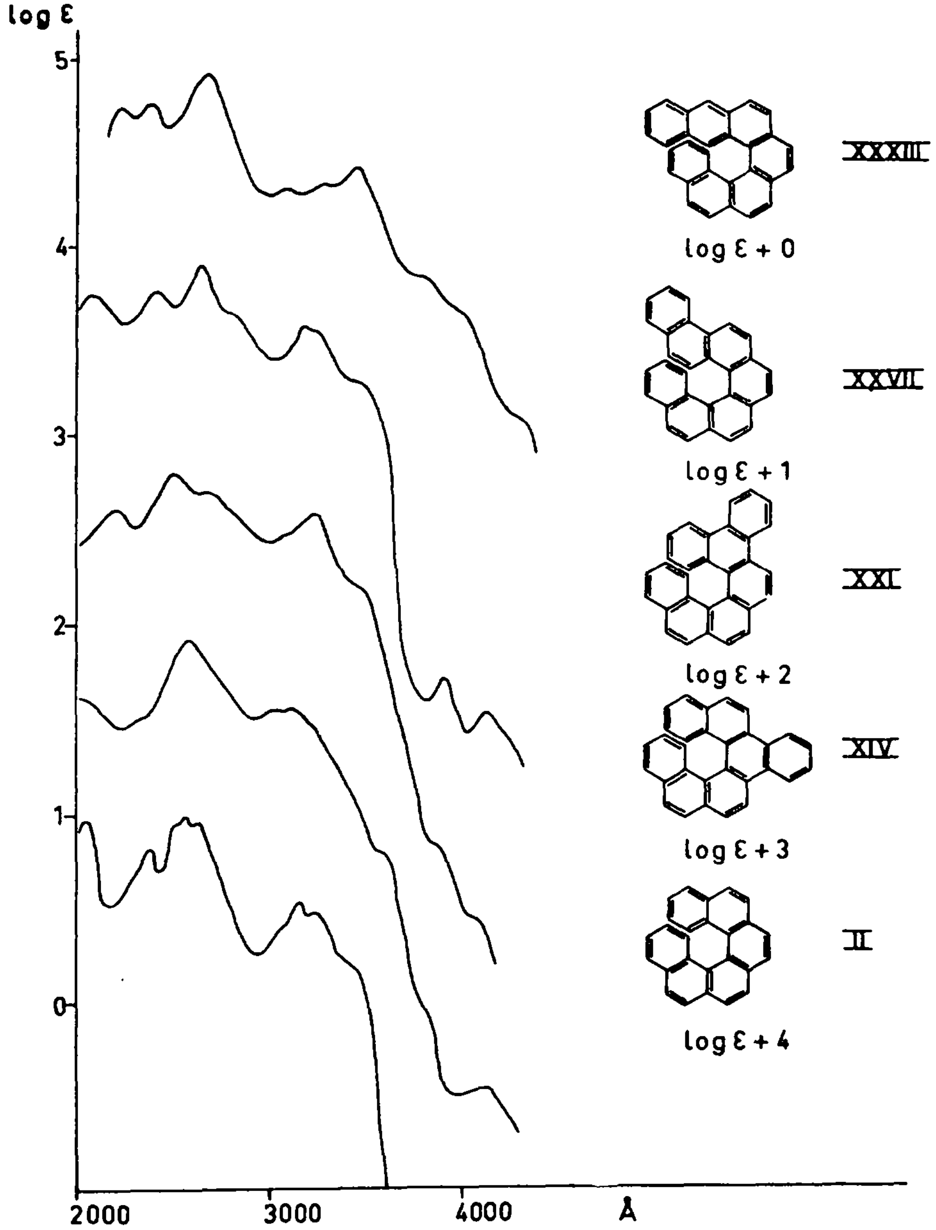
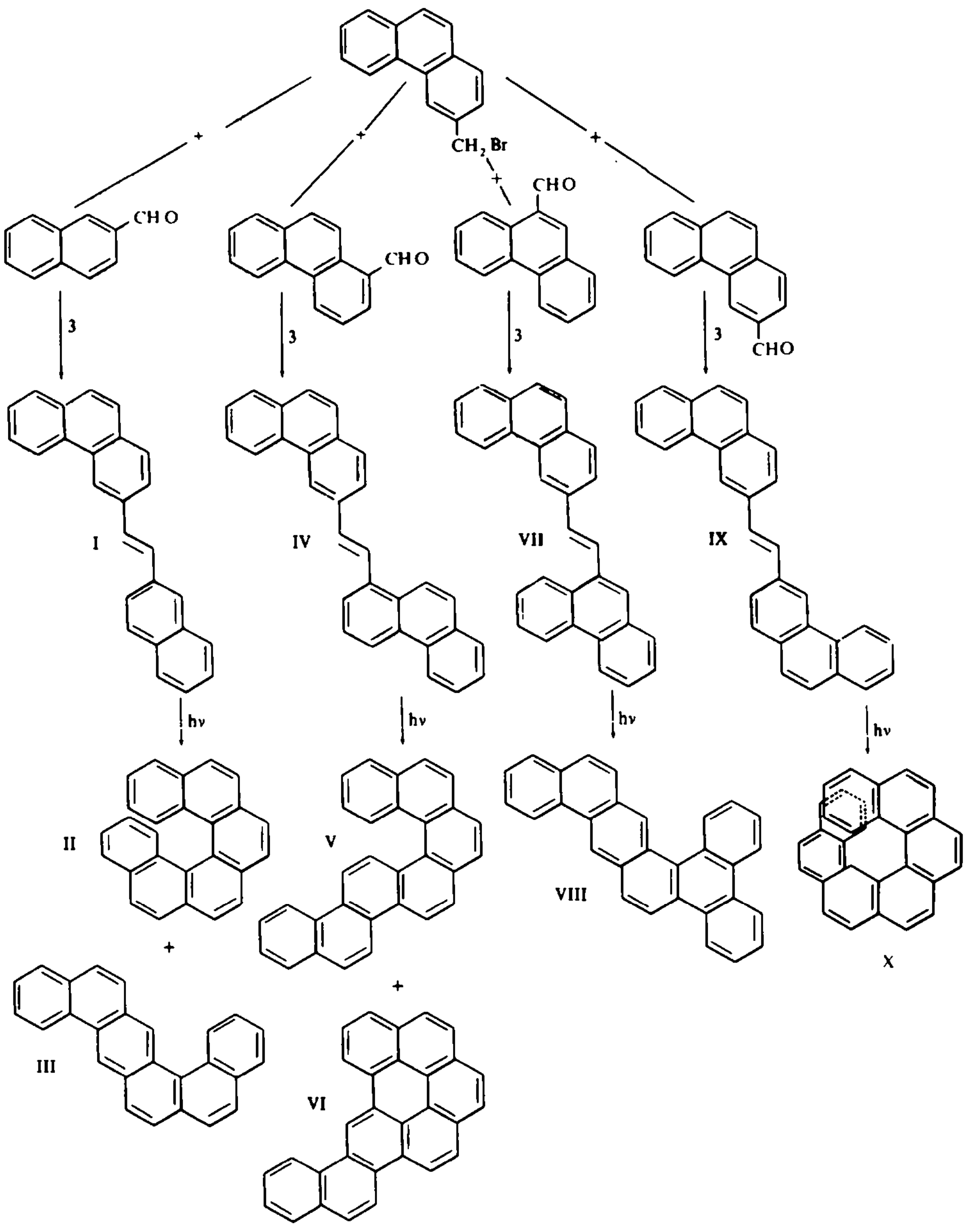
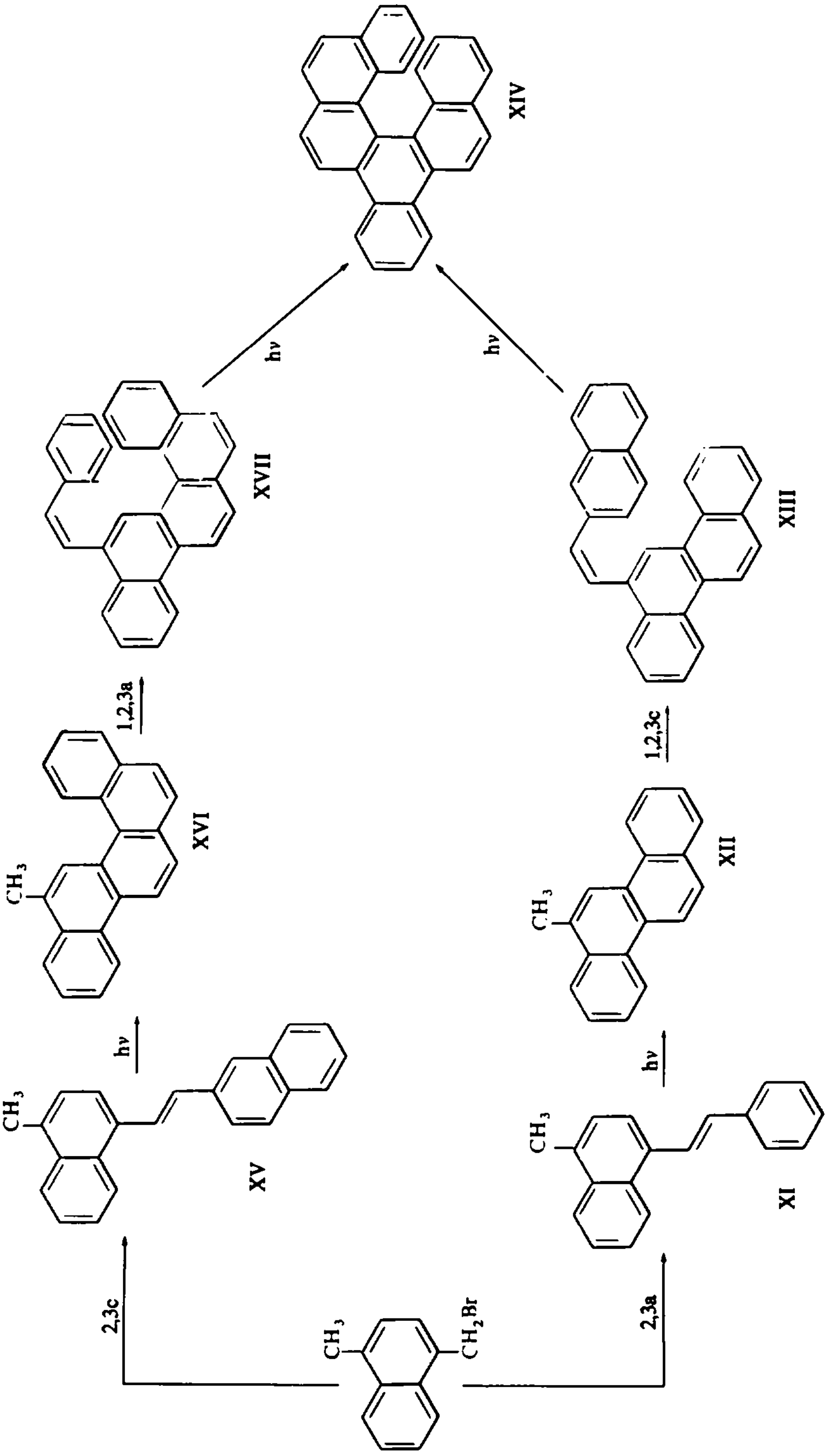


FIG 1. UV spectra of hexahelicene and benzohexahelicenes

SCHEME I. Synthetic pathway in experiments 1, 4, 5 and 6 (Table 1).



In this and the following schemes
1 = bromination by NBS
2 = reaction with $(C_6H_5)_3P$
3 = Wittig reaction
  a = with benzaldehyde
  b = with p.tolualdehyde
  c = with β-naphtaldehyde



SCHEME II. Synthetic pathway in experiments 8 and 9 (Table 1).

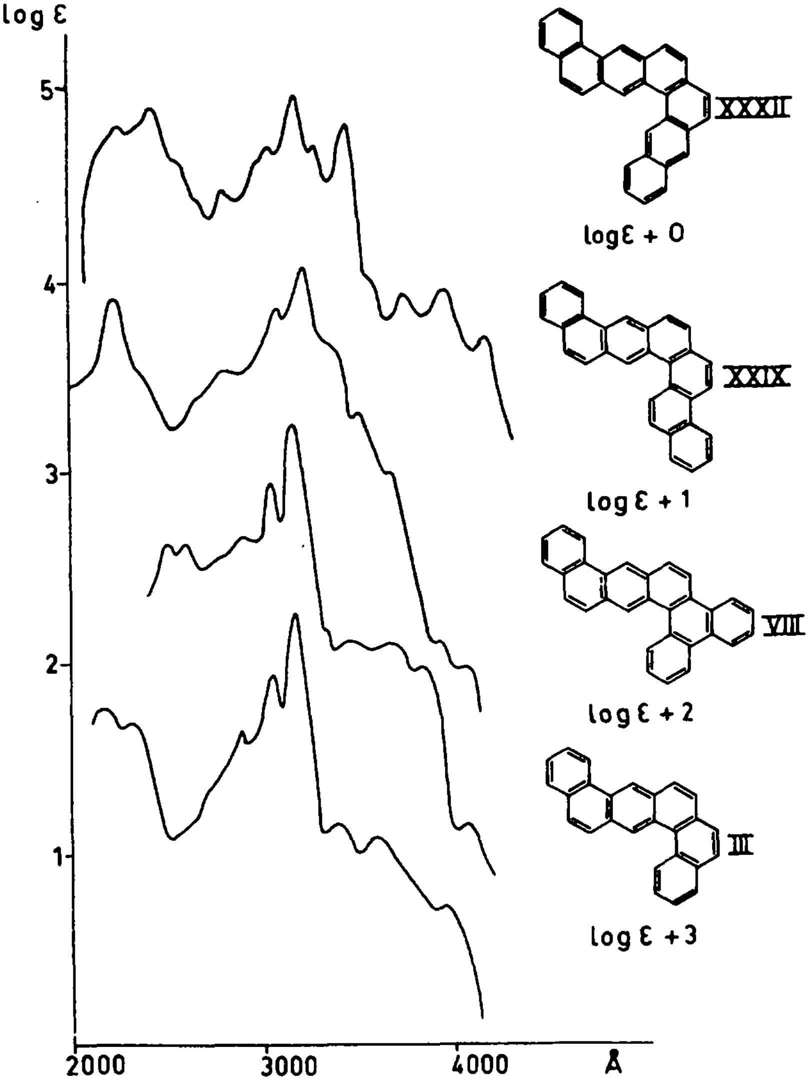
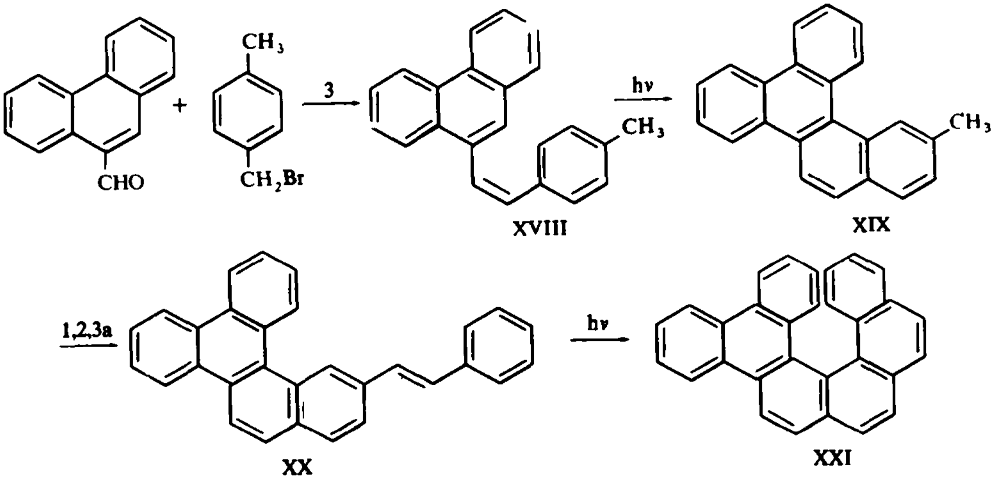
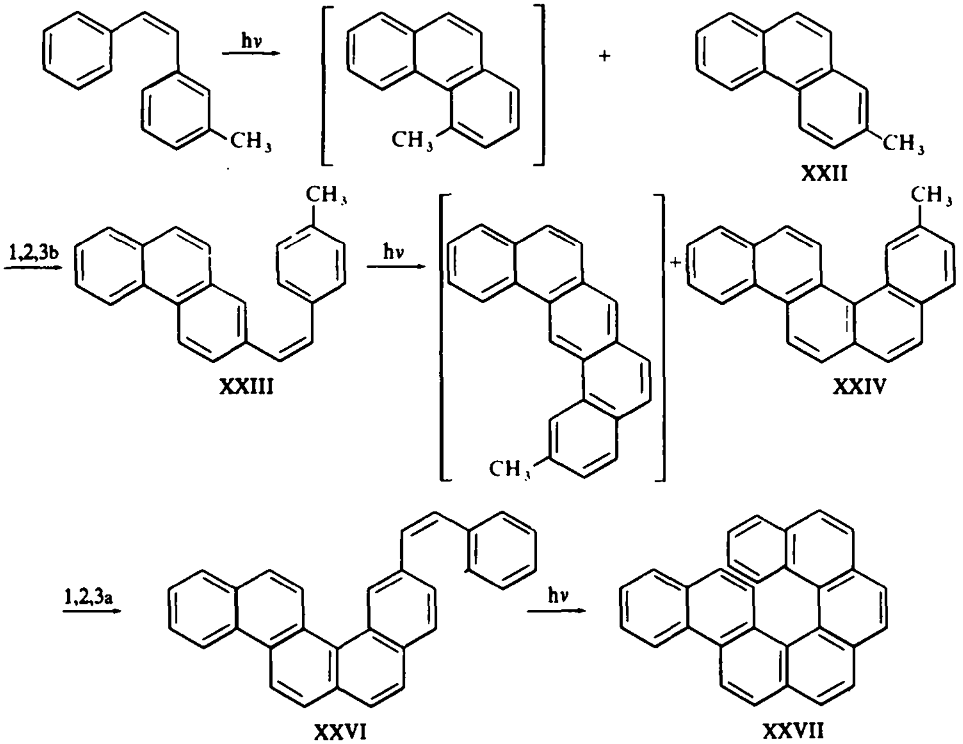


FIG 2. UV spectra of dibenzo[*a.h*]anthracene derivatives

SCHEME III. Synthetic pathway in experiment 7 (Table 1).



SCHEME IV. Synthetic pathway in experiment 11 (Table 1).



As light sources we used a Philips HP125 lamp, fitted in an irradiation vessel,[1] four Sylvania blacklite F8T5 lamps, surrounding a quartz or Pyrex tube of 250 ml, or a Rayonet photochemical reactor with 3000 or 3500 Å lamps.

In view of the strong relationship between the syntheses of individual compounds, synthetic procedures have been collected in Schemes I–VII.

Intermediates and products were identified by mass spectroscopy, (Varian MAT SM1B), UV spectrophotometry (Beckmann DK2A) and NMR spectrometry (Varian HA100).

Because UV spectra are simple aids in the recognition of the basic part of polycyclic aromatics, several spectra of new compounds, collected according to their basic structure, are reproduced in Figs 1–3.

Calculations of free valence numbers were carried out on an IBM 360/50 computer.

I 1-(β-*Naphthyl*)-2-(3-*phenanthryl*)*ethylene*. *trans*: m.p. 213–216°; UV (MeOH) λ_{max} (log ε): 339 (4·46); 326 (4·46); 269 (4·62); 247 (4·64); 225 (4·68); 213 (4·68). *cis*: m.p. 127–128°; UV (MeOH) λ_{max} (log ε): 322 (4·36); 265 (4·60); 246 (4·61); 226 (4·77). Irradiation of I in benzene for 4 hr gave 22% II and 50% III. This ratio was not essentially changed by varying solvent or temp. II was eluted from an alox column with a pentane–benzene (60–40) mixture, III with benzene. A mixture of dimers (MW 660) eluted with ether showed NMR peaks at δ 5·16 and 4·4 (CCl_4, HMDS).

II *Hexahelicene*, m.p. 231°; UV, (Fig 1) as given by Newman;[7] NMR as reported by Martin.[12]

III *Benzo*[*a*]*naphtho*[1.2-*h*]*anthracene*, m.p. 124°; MW 328; UV(MeOH) (Fig 2)λ_{max} (log ε): 356·5 (4·08); 341 (4·15); 337 (4·12); 315 (5·21); 301 (4·96); 289 (4·64); 233 (4·68); 216·5 (4·77); NMR† (CCl_4, HMDS): 9·7 (s), 1H-γ_4; 9·42 (m). 1H-α_4; 9·26 (s), 1H-γ_3; 8·99 (m), 1H-α_3.

IV 1-(1-*Phenanthryl*)-2-(3-*phenanthryl*)*ethylene*, *trans*: m.p. 285–287° (benzene); UV (dioxan) λ_{max} (log ε): 342 (4·60); 265 (4·72); 260 (4·71); 241 (4·82); 234·5 (4·72); 216·5 (4·68). *cis*: m.p. 221–224°; UV (dioxan) λ_{max} (log ε): 321 (4·40); 307 (4·34); 253 (4·82); 214 (4·71). The phenanthrene-1-aldehyde used in the synthesis

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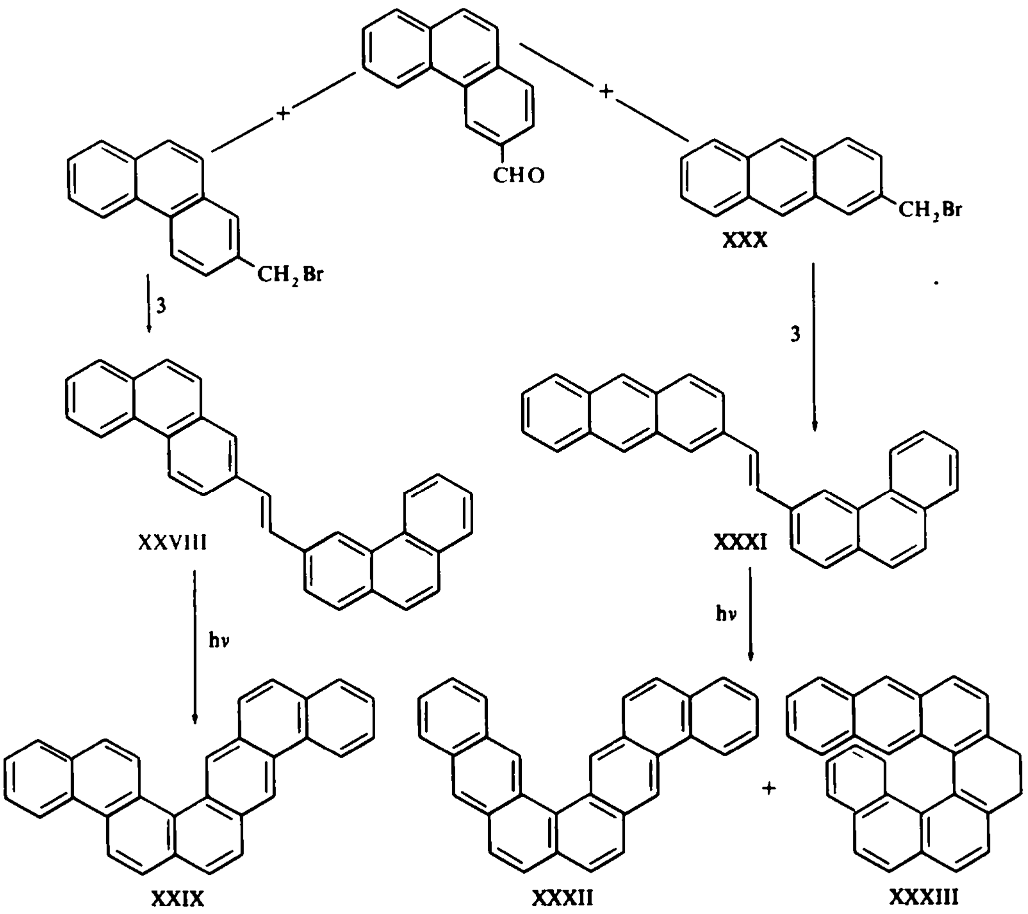
† The symbols used in the description of the NMR spectra are from R. H. Martin, *Tetrahedron* **20**, 897 (1964).

SCHEME V. Synthetic pathway in experiments 10 and 12 (Table 1).



of IV was made by a Rosenmund reduction of the corresponding acid chloride. The phenanthrene-1-carboxylic acid (m.p. 234–235°) was obtained by photocyclization of *o*-stilbene carboxylic acid in 30% yield. Synthesis of the latter compound (m.p. 161°) was according to Natelson and Gottfried.[8]

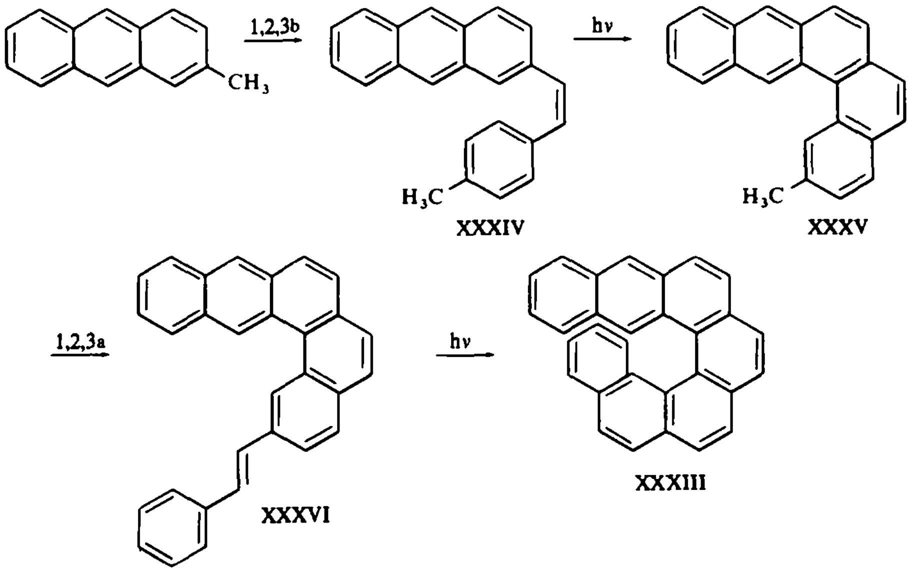
Irradiation of IV in benzene for 2 hr gave 12% V, 68% VI and 10% unreacted IV.

V *Naphtho*[1.2-a]*picene*, m.p. 290° (benzene); MW 378; UV (dioxan) (Fig 3) λ_{max} (log ε): 344 (4·43); 324·5 (4·64); 314 (4·67); 298 (4·68); 289·5 (4·78); 280 (4·64); 262·5 (4·68); 253 (4·77); 247 (4·72); 231 (4·67); 223 (4·70); 215 (4·61). The NMR spectrum was recorded in $AsCl_3$ because of low solubility in common solvents. Below δ 8·2 six angular protons are present in accordance with the given structure and in contrast with expectation for the isomeric cyclization product. Irradiation of V in benzene gave VI as the sole product.

VI *Naphtho*[1.2-b]*benzo*[g.h.i]*perylene*, m.p. 290–292°; MW 376; UV (dioxan) (Fig 3)λ_{max} (log ε): 429 (3·41); 410·5 (4·57); 387·5 (4·49); 367 (4·15); 327 (4·64); 314 (4·78); 300·5 (4·68); 286·5 (4·56); 276·5 (4·56); 267 (4·47); 248·5 (4·67); 238 (4·62); 221 (4·84); 214 (4·81). The solubility in common solvents was too small to record an NMR spectrum. In $AsCl_3$ a dark-green soln is obtained due to complex formation. This soln gave an unresolved NMR spectrum but a strong ESR signal.

VII 1-(3-*Phenanthryl*)-2-(9-*phenanthryl*)*ethylene*, *trans*: m.p. 186–187° (benzene); UV (MeOH) λ_{max} (log ε): 346 (4·54); 300 (4·29); 265 (4·72); 249·5 (4·79).

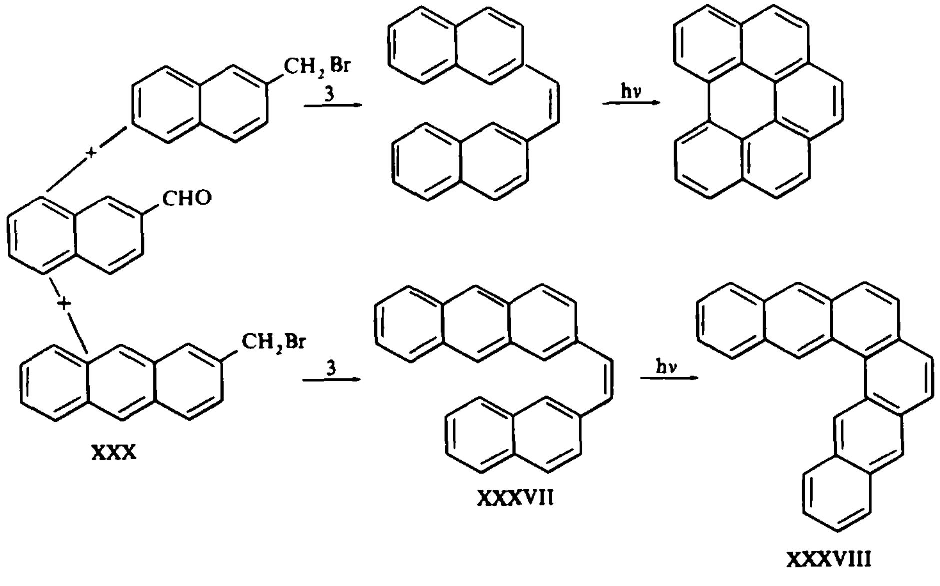
SCHEME VI. Synthetic pathway in experiment 13 (Table 1).



The 9-phenanthrene aldehyde required was prepared by a Rosenmund reduction of the corresponding acid chloride. 9-Phenanthrene carboxylic acid was prepared by photocyclization of α-stilbene carboxylic acid in 72% yield.

Irradiation of VII in benzene for 1 hr gave VIII in 75% yield, isolated by column chromatography on alox. The remainder consisted of 3% VII and a residue that on TLC gave rise to at least nine isolated spots. None of these spots showed an UV spectrum corresponding with that of XXI. One of the spots showed MW 382, corresponding to a diphenanthrylethane.

SCHEME VII. Synthetic pathway in experiments 16 and 17 (Table 1).



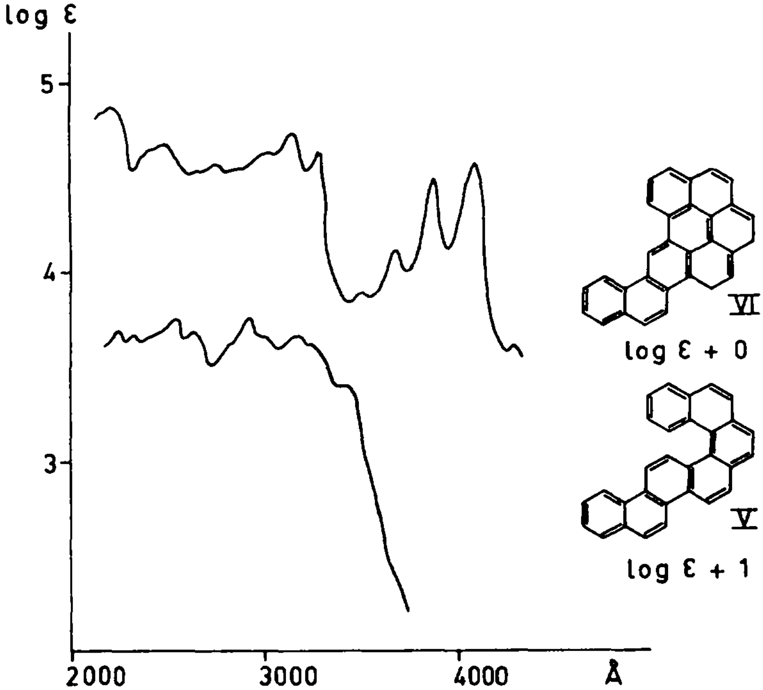


FIG 3. UV spectra of naphtho[1.2-*a*]picene and its cyclization product

VIII *Naphtho*[1.2-b]*benzo*[g]*chrysene*, m.p. 210–212°; MW 378; UV (MeOH) (Fig 2) λ_{max} (log ε): 405 (3·15); 382 (3·91); 368 (4·07); 348 (4·12); 335 (4·13); 318 (5·22); 305 (4·95); 292 (4·60); 283 (4·57); 260 (4·61); 251 (4·60); NMR (CS_2, HMDS) $\delta = 9{\cdot}58$ (s), 1H-γ_4; 9·35 (s), 1H-γ_3; 9·25 (m), 1H-α_4; 8·9 (m), 5H-α_3; 8·35 (d), 1H; 8·1 – 7·8 (m), 9H.

IX 1,2-*Di*(3-*phenanthryl*)*ethylene*, *trans*: m.p. 289–291°; UV (dioxan) λ_{max} (log ε): 357 (4·65); 342 (4·59); 302 (4·23); 288 (4·43); 270 (4·65); 250 (4·81); *cis*: m.p. 237–241°; UV (dioxan) λ_{max} (log ε): 328·5 (4·43); 300 (4·34); 265 (4·77); 249·5 (4·89).

X *Heptahelicene*, m.p. 254°; MW 378; UV and NMR in accordance with data given by Martin.[6]

XI 1-*Styryl*-4-*methylnaphthalene*, *trans*: m.p. 69–70°; UV (MeOH) λ_{max} (log ε): 326 (4·23); 260 (4·03); 232 (4·58); 207 (4·50). The starting compound 1-bromomethyl-4-methylnaphthalene was prepared by bromomethylation of α-methylnaphthalene according to Lock and Schneider.[9] Irradiation of XI for 5 hr in benzene gave XII in 70% yield.

XII 6-*Methylchrysene*, m.p. 159–162°; MW 242; UV (MeOH) λ_{max} (log ε): 322 (4·14); 308 (4·18); 296 (4·06); 284 (4·04); 268 (5·15); 258·5 (4·89); 250 (4·53); 242 (4·26); 221 (4·47).

XIII 1-(β-*Naphthyl*)-2-(6-*chrysyl*)*ethylene*, *trans*: m.p. 213–215°; UV (MeOH) λ_{max} (log ε): 352 (4·47); 268 (4·81); 224 (4·78). Irradiation of XIII in benzene for 4 hr gave benzo[*d*]hexahelicene in 90% yield.

XIV *Benzo*[d]*hexahelicene*†, m.p. 212–214° (CCl_4); UV (MeOH) (Fig 1) λ_{max} (log ε): 412 (2·56); 362 (3·79); 316 (4·55); 305 (4·56); 259 (4·92); 233 (4·57).

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† A detailed analysis of the NMR spectra of the benzohexahelicenes XIV, XXI, XXVII and XXXIII will be given in a subsequent paper.

XV 1-(4-*Methylnaphthyl*)-2-(β-*naphthyl*)*ethylene*, *trans*: m.p. 130–132°; UV (MeOH) λ_{max} (log ε): 333 (4·20); 294 (3·95); 283 (3·45); 261 (4·19); 227 (4·53); 211 (4·50). Irradiation of XV in benzene gave about 80% XVI.

XVI 8-*Methylbenzo*[c]*chrysene*, m.p. 151–153°; UV (MeOH) λ_{max} (log ε): 321 (4·49); 292·5 (4·89); 282 (4·72); 263 (4·30); 245 (4·32); 232·5 (4·46); 222 (4·47); 205 (4·74).

XVII 8-*Styrylbenzo*[c]*chrysene*, *trans* m.p. 163–164°; MW 380; UV (MeOH) λ_{max} (log ε): 358 (4·43); 348 (4·53); 327 (4·83); 311 (4·67); 299 (4·64); 279 (4·78); 217 (4·64).

XVIII 9-p-*Methylstyryl phenanthrene*, *trans*: m.p. 135–136°; UV (MeOH) λ_{max} (log ε): 325 (4·38); 274 (4·51); 257 (4·57); 219 (4·41); 208 (4·62). Irradiation of XVIII in benzene for 2 hr gave 95% XIX.

XIX 3 *Methylbenzo*[c]*triphenylene*, m.p. 143–145°; UV (EtOH) λ_{max} (log ε): 333 (3·95); 318 (4·09); 308 (4·09); 286 (4·85); 276 (4·81); 256 (4·72); 245 (4·54); NMR (CS_2, TMS) δ = 8·75 (m), 1H-α_4; 8·3–8·5 (m), 1H-α_4 and 4H-α_3; 7·2–7·8 (m), 7H; 2·5 (s), 3H—CH_3.

XX 3-*Styrylbenzo*[c]*triphenylene*, *trans*: m.p. 218–220°; MW 380; UV (EtOH) λ_{max} (log ε): 386 (3·48); 356 (4·38); 341 (4·45); 315 (4·76); 303 (4·70); 277 (4·57); 260 (4·62); 239 (4·44); 204 (4·50). Irradiation of XX in benzene for 7 hr gave 60% XXI; no trace of VIII could be detected.

XXI *Benzo*[a]*hexahelicene*, m.p. 247–253°; MW 378; UV (MeOH) (Fig 1) λ_{max} (log ε): 346 (4·19); 322 (4·58); 307·5 (4·48); 294 (4·46); 267 (4·69); 248 (4·80); 275 (4·58); 218 (4·60).

XXII 2-*Methylphenanthrene*. In view of the low yields in syntheses of this compound by known methods, we used photocyclization of *m*-methylstilbene. The irradiation mixture contained equal amounts of 2- and 4-methylphenanthrene as revealed by the NMR spectrum. The isomers could not be separated by crystallization, distillation or chromatography. After bromination of the mixture by NBS separation of 2- and 4-bromomethylphenanthrene appeared to be possible by silicagel column chromatography. 4-Bromomethylphenanthrene (m.p. 75–76°) was eluted with pentane–benzene; 2-bromomethylphenanthrene (m.p. 113–114°) with benzene.

XXIII 2-p-*Methylstyrylphenanthrene*, *trans*: m.p. 198–202°; UV (MeOH) λ_{max} (log ε): 365 (2·68); 300 (4·35); 292 (4·57); 278 (4·65); 270 (4·61); 247 (4·60); 211 (4·57). Irradiation of XXIII in benzene for 4 hr gave 80% XXIV and 2% XXV.

XXIV 5-*Methylbenzo*[c]*chrysene*, m.p. 121–122°; UV (MeOH) λ_{max} (log ε): 321 (4·48); 292 (4·92); 283 (4·78); 263 (4·49); 247 (4·34); 252 (4·50); 234 (4·49); 208 (4·66); NMR (CS_2, TMS) δ = 9·02 (d), 1H-α_4; 8·85 (m), 2H-α_3; 8·74 (s), 1H-α_4; 8·10–7·40 (m), 9H; 2·76 (s), 3H-CH_3.

XXV 2-*Methyldibenzo*[a.j]*anthracene*, m.p. 178–181°; MW 292; UV (MeOH) λ_{max} (log ε): 393 (2·42); 383 (2·64); 371 (2·80); 350 (3·82); 336 (4·26); 323 (4·26); 302 (4·98); 298 (5·07); 286 (4·91); 275 (4·59); 258 (4·68); 248 (4·59); 225 (4·76); NMR (CS_2, TMS) δ = 9·72 (s), 1H-γ_3; 8·76 (m), 1H-α_3; 8·54 (s), 1H-α_3; 8·06 (s), 1H-γ; 7·8 – 7·2 (m), 9H; 2·58 (s), 3H-CH_3.

XXVI 5-*Styrylbenzo*[c]*chrysene*, m.p. 179–180°; MW 380; UV (MeOH) λ_{max} (log ε): 358 (4·48); 327 (4·68); 311 (4·67); 299 (4·64); 279 (4·78); 217 (4·64). Irradiation of XXVI in benzene for 5 hr gave 65% of benzo[*m*]hexahelicene.

XXVII *Benzo*[m]*hexahelicene*, m.p. 252–253°; MW 378; UV (MeOH) (Fig 1) λ_{max} (log ε): 412 (2·55); 390 (2·74); 346 (4·30); 327 (4·55); 320 (4·58); 281 (4·65); 265 (4·90); 242 (4·77); 207 (4·74).

XXVIII 1-(2-*Phenanthryl*)-2-(3-*phenanthryl*)*ethylene*, *trans*: m.p. 225–230°; MW 380; UV (MeOH) λ_{max}: 372; 345; 330; 291; 276; 250. Irradiation of XXVIII in benzene for 5 hr gave 75% XXIX. Neither benzo[*m*]hexahelicene nor any other hydrocarbon could be detected.

XXIX *Dinaphtho*[1.2-b; 2.1-g]*phenanthrene*, m.p. 218–220°; MW 378; UV (MeOH) (Fig 2) λ_{max} (log ε): 413 (3·05); 392 (3·15); 371 (4·05); 354 (4·35); 340 (4·49); 321 (5·08); 309 (4·88); 298 (4·60); 284 (4·58); 248 (4·44); 226 (4·92); 204 (4·49); NMR (CS_2, TMS) δ = 9·43 (s), 1H-γ_4; 9·1 (m), 2H-α_4 + γ_3; 8·7 (m), 3H-α_3; 8·1 – 7·2 (m), 12H.

XXX 2-*Bromomethylanthracene*. 2-Methylanthracene was prepared according to Martin[10] by reduction of the condensation product of 2-p-tolyl benzoic acid; m.p. 210–212°. Bromination of this compound with NBS resulted in a mixture of XXX and ring substituted anthracyl derivatives, from which XXX could not well be isolated in pure form. On bromination at a low temp it was possible to restrict the formation of the side products. Crystallization from EtOH resulted in a rather pure product; m.p. 160°.

XXXI 1-(2-*Anthracyl*)-2-(3-*phenanthryl*)*ethylene*, *trans*: m.p. 294–301° (xylene); MW 380; UV (benzene) λ_{max} (log ε): 400 (4·50); 380 (4·48); 344 (4·83); 328 (4·71); 292 (4·60); 282 (4·52). After purification by crystallization purity was checked by mass spectroscopy to be sure that no bromo compound was present. Irradiation of XXXI in xylene for 45 hr gave rise to 60% of XXXII and 22% XXXIII.

XXXII *Dinaphtho*[1.2-b; 2.3-g]*phenanthrene*, m.p. 232–235°; MW 378; UV (MeOH) (Fig 2) λ_{max} (log ε): 419 (3·69); 396 (3·95); 376 (3·92); 358 (4·01); 345 (4·81); 329 (4·70); 318 (4·96); 304 (4·70); 281 (4·48); 269

(4·42); 258 (4·61); 243 (4·90); 226 (4·80); NMR (CS_2, HMDS) δ = 10·25 (s), 1H-γ_4; 10·20 (s), 1H-γ_4; 9·68 (s), 1H-γ_3; 9·62 (m), 1H-α_3; 8·88 (s), 1H-γ; 8·70–7·95 (m), 13H. This compound is oxidized rapidly in air. Purification is best done by chromatography on alox.

XXXIII *Benzo*[n]*hexahelicene*, m.p. 272–277°; MW 378; UV (MeOH) (Fig 1) λ_{max} (log ε): 430 (3·08); 399 (3·66); 379 (3·84); 361 (3·98); 344 (4·42); 329 (4·34); 309 (4·31); 268 (4·92); 238 (4·76); 223 (4·73).

XXXIV 2-p-*Methylstyrylanthracene, trans*: m.p. 294–296°; MW 294; UV (benzene) λ_{max} (log ε): 394 (4·17); 373 (4·27); 355 (4·14); 329 (4·86); 314 (4·82); 302 (4·62). Irradiation of XXXIV in xylene for 60 hr gave XXXV in about 15% yield. The remainder was a tar of polar nature. From the mass spectrum it was concluded that oxygen containing compounds were present. Strict exclusion of oxygen during irradiation did not result in a higher yield of XXXV.

XXXV 2-*Methyldibenzo*[a.g]*phenanthrene*, m.p. 166–170°; UV (MeOH) λ_{max} (log ε): 397 (3·18); 390 (3·59); 370 (3·76); 353 (3·68); 337 (3·47); 325 (3·91); 308 (4·87); 295 (4·77); 248 (4·68); 241 (4·46); 225 (4·79); 206 (4·32); NMR (CS_2, HMDS) δ = 9·88 (s), 1H-γ_4; 9·33 (s), 1H-α_4; 8·68 (s), 1H-γ; 8·40 – 7·60 (m), 10H; 3·00 (s), 3H-CH_3. Bromination of this compound with NBS was accompanied by ring substitution, even more so than with XXX. The best results were obtained when the reaction was carried out at low temp.

XXXVI 2-*Styryldibenzo*[b.g]*phenanthrene, trans*: m.p. 70°; MW 380; UV (MeOH) λ_{max}: 421, 404, 347, 335, 315, 273, 221. Irradiation of this compound in benzene for 20 hr gave about 10% benzo[*n*]hexahelicene. XXXII was completely absent.

XXXVII 1-(2-*Anthracyl*)-2-(β-*naphthyl*)*ethylene, trans*: m.p. 326–327°; UV (benzene) λ_{max} (log ε): 395 (4·37); 375 (4·40); 358 (4·29); 334 (4·90); 319 (4·78); 306 (4·48); 293 (4·64); 282 (4·48). Irradiation of this compound could only be carried out in very low concentration because of its low solubility. Moreover, the cyclization proceeded very slowly. From the reaction mixture XXXVIII could be isolated only as an impure product, but its UV and NMR spectrum made the presence of other cyclization products unlikely.

XXXVIII *Benzo*[b]*naphtho*[2.3-g]*phenanthrene*. This compound could not be purified because of rapid oxidation in air. The UV spectrum was analogous with those of Fig 2. λ_{max} (MeOH) 348, 322, 308, 294, 285; NMR (CS_2, TMS) δ = 9·6 (s), γ_4; 8·3 (s), γ; 8·1 – 7·1 (m).

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