PHOTODEHYDROCYCLIZATIONS OF STILBENE-LIKE COMPOUNDS VII[1]

Synthesis and properties of the double helicene, diphenanthro[3,4-*c*;3′,4′-*l*]chrysene

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A description of two alternative routes (Schemes 1 and 2) for the synthesis of the title compound (I) is given. Only the second route resulted in the formation of the two diastereomers of I. The physical properties of both isomers are given. The racemization is discussed.

In a preliminary communication[2] we described the synthesis of a first "double" helicene, diphenanthro[3,4-*c*;3′,4′-*l*]chrysene (I). In this paper we present full experimental details about the synthetic procedure used, and physical and chemical properties of both stereoisomers of the compound in relation to their structure and conformation.

Two relatively simple routes (Schemes 1 and 2) can be envisaged for the preparation of I. Generally, in the synthesis of overcrowded polyaromatics *via* photodehydrocyclizations, a pathway *via* styrylaromatics (Scheme 1) is preferable to one *via* another diarylolefin (Scheme 2) in spite of the fact that the latter procedure involves fewer steps[3]. The reason is that ring closure of styryl aromatics leads quite specifically to the desired product; for cyclizations leading to side-products relevant ΣF^*-values[4] are too low (compounds III, V, VI and VIII in Table I). A point of uncertainty in Scheme 1 is, however, the photocyclization

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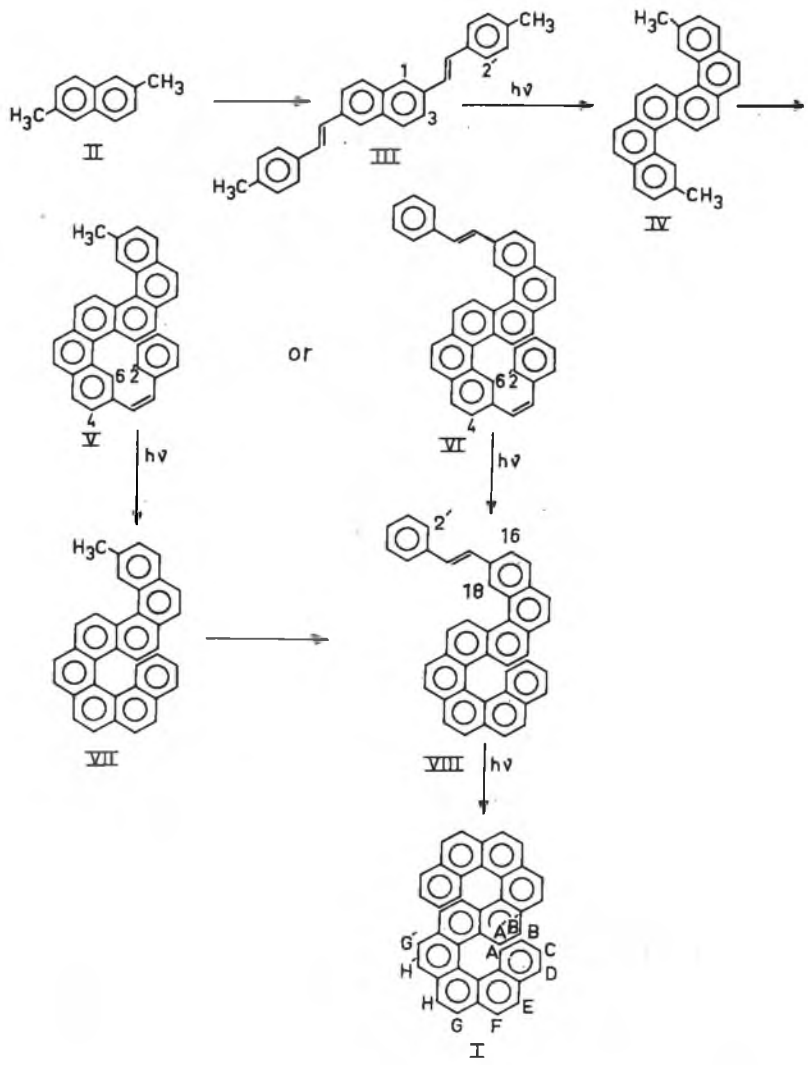
[1] Part VI: *W. H. Laarhoven* and *Th. J. H. M. Cuppen*, J. Am. Chem. Soc. **94**, 5914 (1972).

[2] *Idem*, Tetrahedron Letters **1971**, 163.

[3] *W. H. Laarhoven, Th. J. H. M. Cuppen* and *R. J. F. Nivard*, Tetrahedron **26**, 4865 (1970).

[4] *Idem*, Rec. Trav. Chim. **87**, 687 (1968).

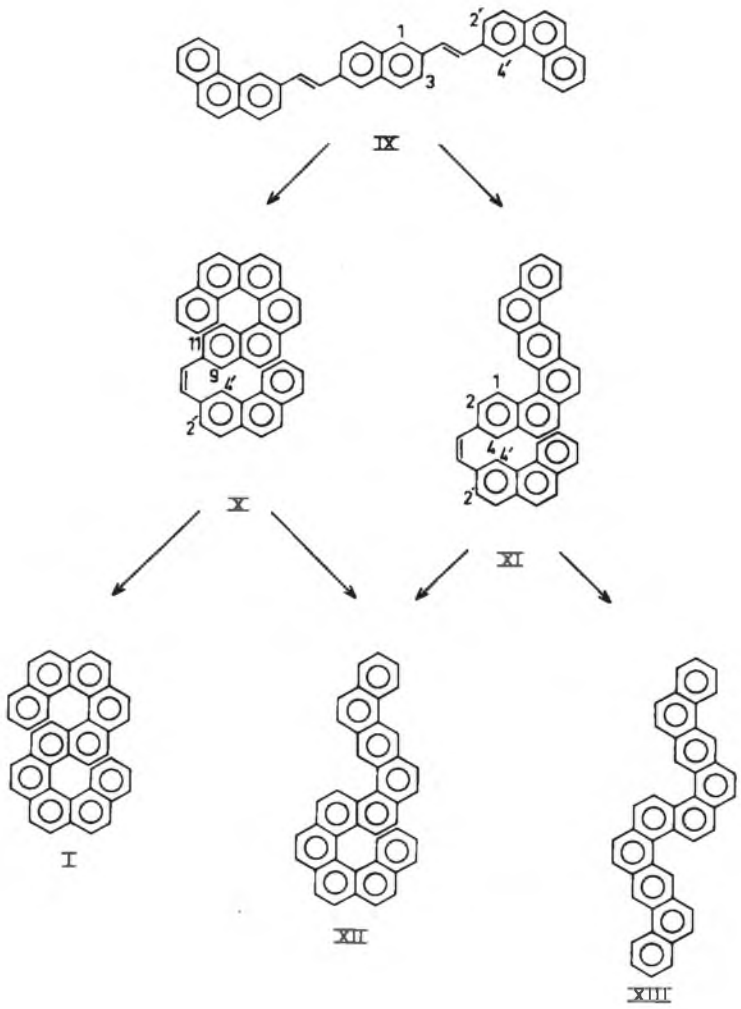


Scheme 1.

Tentative scheme for the synthesis of the double helicene I.

of VIII into I. Especially for the formation of a non-planar product the ΣF^*-value (1.003) of VIII is marginal[3].

The shorter pathway in Scheme 2 contains only one irradiation step (with IX). In view of previous results[3] it was uncertain whether the



Scheme 2.

Reaction scheme for the synthesis of the double helicene I.

hexahelicene derivative X or the nearly planar compound XI would be the main initial intermediate. The cyclization of X, if formed at all, underlies the same uncertainty. Hence, the overall yield of I *via* this route might be very low. With these considerations in mind we decided to investigate both synthetic procedures.

Table I

Sum of the free valence numbers in the excited state of the atoms r and s ($\Sigma F^*_{r,s}$) of the diarylethylenes in Schemes 1 and 2.

	Compound	r-s	$\Sigma F^*_{r,s}$
III	2,6-bis(*p*-methylstyryl)naphthalene[a]	1–2′	1.053
		3–2′	.897
V	13-methyl-5-styryldibenzo[*c*;*l*]chrysene[a]	6–2′	1.089
		4–2′	.951
VI	5,13-distyryldibenzo[*c*;*l*]chrysene	6–2′	1.016
		4–2′	.922
VIII	17-styrylnaphtho[1,2-*m*]hexahelicene	18–2′	1.003
		16–2′	.914
IX	2,6-bis{2-(3′-phenanthryl)ethenyl}naphthalene	1–4′	1.090
		1–2′	1.017
		3–4′	.976
		3–2′	.907
X	8-{2-(3′-phenanthryl)ethenyl}hexahelicene	9–4′	1.148
		9–2′	1.049
		11–4′	1.024
		11–2′	.925
XI	3-{2-(3′-phenanthryl)ethenyl}benzo[*a*]naphtho[1,2-*h*]-anthracene	4–4′	1.110
		4–2′	1.029
		2–4′	.994
		2–2′	.964

[a] ΣF^*-values are of the compound without methyl subsituent(s).

The diarylolefins required (III, V, VI, IX) were obtained by Wittig reactions as described in the experimental part. All three isomers of 2,6-bis(*p*-methylstyryl)naphthalene (III) gave in 60% yield, 5,13-dimethyldibenzo[*c*;*l*]chrysene (IV) upon irradiation in xylene.

With 5,13-distyryldibenzo[*c*;*l*]chrysene (VI) complete separation of the *cis-trans* isomers did not succeed. The pure *trans, trans* isomer could be obtained, however, by isomerization of the other isomers in an isomer mixture with iodine in carbon tetrachloride followed by sublimation at 260°.

Irradiation of *trans, trans*-VI, dissolved in benzene, for varying times did not yield the desired "double" helicene I. In the NMR spectrum of the irradiation mixture aromatic protons at relatively high field ($\delta = 6$ ppm) were found as in the hexahelicene spectrum; in the mass spectrum peaks at *m/e* 532 (starting compound) and 530 were present but not at *m/e* 528. These data indicated that VIII and not I had been

formed. In addition, a lot of polymeric products with molecular weights above 532 were present as appeared from the mass spectrum.

A pure sample of VIII was obtained from IV *via* 13-methyl-5-styryldibenzo[*c*;*l*]chrysene (V, as *cis-trans*-mixture) and the 17-methylnaphthohexahelicene (VII). Irradiation of this sample yielded the same reaction mixture as obtained from VI. Using short reaction times we isolated mainly unchanged VIII. So, it appeared that photocyclization of VIII, if possible at all, must be very slow in comparison with other photoconversions of this compound.

The pathway traced in Scheme 2 appeared to be more successful. Irradiation of 2,6-bis{2-(3′-phenanthryl)ethenyl}naphthalene yielded a mixture of three cyclization products (I, XII and XIII), in addition to a dimer of the starting compound*.

Surprisingly the desired double helicene (I) was the main product (60%). It could be separated from red-brown polymeric material and other side products (each present to the extent of 20%) by column chromatography on alox and silica. In this purification procedure the two diastereoisomers of I were separated too.

One of them is soluble in benzene, carbon disulfide, chloroform and carbon tetrachloride. It crystallizes in fine needles from ethyl acetate. Depending on the rate of temperature increase it softens at about 280°, but at 320° all needles are transformed into prisms, which melt at 400°–402°. This is also the melting point of the second isomer, which is poorly soluble in most of the organic solvents, and can be crystallized from a very dilute solution in carbon tetrachloride.

The UV spectra of the isomers are very similar; only the low intensity band at 320 nm for the higher melting compound is much broader than for the other isomer. On heating of the latter at 350° for some time, its spectrum becomes identical with that of the isomer.

It is known that *d*- and *l*-helicenes racemise at their melting points[6]. Racemisation of *d*- and *l*- I should probably proceed *via* the diastereomeric *meso*-form. Therefore, we suppose that our low-melting compound is the racemic form and the more stable high-melting isomer is the *meso* form.

We tried to separate the low-melting compound into enantiomers by crystal picking, but single crystals from solutions in carbon tetrachloride, dichloroethane or *d*-β-pinene showed no optical rotation in

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* *Martin*[5] has shown that the formation of the side-products XII and XIII can be prevented by the introduction of bromine atoms in the 2′-positions of the phenanthryl residues in IX.

[5] *R. H. Martin, Ch. Eijndels* and *M. Defay*, Tetrahedron Letters **1972**, 2731.

[6] *M. S. Newman* and *D. Lednicer*, J. Am. Chem. Soc. **78**, 4765 (1956); *R. H. Martin* and *M. J. Marchant*, Tetrahedron Letters **1972**, 3707.

a Jasco ORD instrument. Complexation of the compound with (−)tetranitrofluoreneaminopropionic acid[7] (TAPA) gave after five recrystallizations a product with a small signal, significantly different from that of (−)TAPA. This corroborates the supposition that the low-melting compound is racemic.

Irradiation of both isomers under similar conditions as used in their preparation revealed that they are photolabile. In both cases, however, in addition to new products only the starting compound, and not its diastereomer, was found on chromatography of the irradiation mixture. Apparently, isomerization cannot be induced by irradiation.

NMR spectra have been measured with the low-melting form in carbon disulfide, and with the high-melting form in arsenic trichloride because of its low solubility. Frequencies were determined with the side-band technique, and the assignment of the signals was done by decoupling experiments and by comparison with the spectrum of hexahelicene. In Table 2 frequencies (in ppm) have been tabulated, together with those of hexahelicene and of benzo[*m*]hexahelicene[8].

Table II

Chemical shifts in ppm of *dl*- and *meso*-I*, and some related compounds.

proton**	*dl*-I		*meso*-I	hexahelicene		benzo[*m*]-hexahelicene
	CS_2	$CDCl_3$	$AsCl_3$	CS_2	$AsCl_3$	CS_2
A	8.42	8.59	7.02	7.47	7.57	7.49
B	7.02	7.12	6.40	6.53	6.70	6.42
C	7.21	7.29	7.30	7.08	7.26	7.04
D	7.80	7.92	7.82	7.67	7.86	7.71
E	7.60	7.70		7.77	7.96	7.84
F	7.81	7.89		7.77	7.96	7.84
G	7.89	7.98	8.01	7.82	8.02	7.92
H	7.89	7.98		7.82	8.02	7.92
A′	7.60	7.75	7.78			7.43
B′	7.00	7.10	7.21			6.85
G′	7.89	7.98	8.06			7.93
H′	7.89	7.98	8.06			7.93

* Complete spectra have been given in ref. 2.
** For designations of protons, see formula I in Scheme 1.

[7] *M. S. Newman* and *W. B. Lutz*, J. Am. Chem. Soc. **78**, 2469 (1956); Organic Synthesis, vol. 48, 120.
[8] *W. H. Laarhoven* and *R. J. F. Nivard*, Tetrahedron **28**, 1803 (1972).

It appears that protons A, and to a lesser extent also B, in the isomer demonstrated to be the racemic one, are at very low field in comparison with the *meso* form.

We have attributed[2] the downfield shifts to a reduced ring-current of the opposite ring. We assumed that this was due to strong torsions of the terminal rings out of the plane of the central naphthalenic moiety. From calculations by *Haigh*[9] on this kind of molecules it appears that the position of the signal of proton A in hexahelicene is the resultant of two effects; an upfield shift by ring currents of opposite rings and a downfield shift by steric influences. On this basis it is our opinion now that especially in the racemic component steric effects, much larger than in hexahelicene, will cause a large downfield shift for protons A. This is in accordance with the assignment of the racemic configuration to the low-melting isomer. The same conclusion has been drawn by *Martin*[5] for the corresponding racemic dibromo derivative, for which the assignment of configuration was based on the results of the NOE technique applied to B and C protons in different terminal rings.

Experimental

U.V. spectra were measured with a Beckman DK2A or a Cary 15 spectrophotometer.

Mass spectra were measured with a Varian MAT SM1B, and NMR spectra with a Varian HA100 apparatus.

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

All diaryl ethenes used in irradiation experiments were obtained by Wittig syntheses. The required bromides were synthesized by bromination of the proper substituted methyl aromatics with *N*-bromosuccinimide (NBS). The bromides were converted into the arylmethyl(triphenyl)phosphonium bromides by treatment with triphenylphosphine in xylene or DMF. The Wittig reactions were carried out in DMF solutions using NaOMe as a base. Products were isolated and purified by column chromatography on silicagel or Al_2O_3, followed by crystallization.

Irradiations were performed in benzene or xylene with added iodine as an oxidant. To reduce the formation of oxidation products during irradiation, the solutions were boiled previously and cooled by leading a stream of nitrogen through them. As light source we used four Sylvania blacklite F8 T5 lamps surrounding a 600 ml pyrex tube.

II *2,6-Bis(bromomethyl)naphthalene* was obtained from 2,6-dimethylnaphthalene in 79% yield, and had m.p. 188–189°.

III *2,6-Bis(*p*-methylstyryl)naphthalene* could be separated into three isomers by column chromatography on silicagel. *cis,cis*, m.p. 150–155°; U.V. λ max (log ε) (benzene): 334 (4.44); 281 (4.46). *cis,trans*, m.p. 208–210°; U.V. λ max (log ε) (benzene): 350 (4.69); 292 (4.54); 283 (4.54). *trans,trans*, m.p. 384°; U.V. λ max (log ε) (xylene): 383 (4.72); 364 (4.84); 293 (4.49).

[9] *C. W. Haigh* and *R. B. Mallion*, Mol. Physics **18**, 767 (1970).

IV *5,13-Dimethyldibenzo*[c;l]*chrysene*

Irradiation of each of the isomers of III dissolved in xylene ($c = 10^{-4}$) gave IV as the sole photocyclization product in 60% yield. Irradiation of *cis,cis*-III and *cis,trans*-III was also possible in benzene; *trans,trans*-III is poorly soluble in this solvent. The product had m.p. 210–212°; molecular weight 356 (from the mass spectrum); U.V. λ max (log ε) (methanol): 404 (2.56); 385 (2.70); 339.5 (4.48); 310 (4.98); [300 (4.74)]; 255 (4.16); [230 (4.51)]; 221 (4.89); 213 (4.87); 200 (4.66); NMR (CS_2) (HMDS) δ = 9.7 (d) $J = 9$ cps 2H, α_4; 9.4 (s) 2H, α_4; 8.5–7.8 (m) 10H; 3.0 (s) 3H(CH_3).

V *13-Methyl-5-styryldibenzo*[c;l]*chrysene*

Bromination of IV with one equivalent of NBS gave the monobromomethyl derivative. It was converted into V by the usual procedure for Wittig reactions. The isomer mixture formed could not be separated well into its components. $M/e = 444$; U.V. λ max (366); 340; 313; 302.

VII *17-Methylnaphtho*[*1,2*-m]*hexahelicene*

Irradiation of V in a benzenic solution ($c = 10^{-3}$) during 40 hours gave VII in 60% yield. It had m.p. 256–258°; M = 442; U.V. λ max (log ε) (methanol) [450 (2.78)]; [420 (3.21)]; 398 (3.36); [360 (4.33)]; 343 (4.54); 329 (4.57); [317 (4.49)]; 284 (4.76); 257 (4.51); [234 (4.63)]; 221 (4.80); 204 (4.78). NMR (CS_2) δ = 9.08 (d) 1H α_4; 8.95 (s) 1H α_4; 7.95–6.78 (m) 16H; 6.39 (m) 1H helicenic B; 2.68 (s) 3H(CH_3).

VI *5,13-Distyryldibenzo*[c;l]*chrysene*

Bromination of IV with two equivalents of NBS gave the bisbromomethyl derivative in 75% yield with m.p. 229–231°. By the Wittig reaction it was converted into VI; m.p. 271–274°; M: 432; U.V. λ max (log ε) (CH_2Cl_2): 378 (4.63); 351 (4.78); 333 (4.86); 285 (4.71). NMR (CS_2) δ = 9.45 d (2H); 9.35 s (2H); 8.4–8.1 m (10H); 8.1–7.5 m (14H).

VIII *17-Styrylnaphtho*[*1,2*-m]*hexahelicene*

This compound was formed by a Wittig reaction from V *via* 17-bromomethylnaphtho-[1,2-*m*]hexahelicene (m.p. 286–288°). It could be detected by TLC and NMR in the irradiation mixture of VI but not well separated from other compounds in the mixture. M.p. 340–342°; M: 530; U.V. λ max (log ε) (CH_2Cl_2): [375 (4.54)]; 355 (4.65); 330 (4.68); [315 (4.63)]; 273 (4.82); [233 (4.66)]; 227 (4.17).

IX *2,6-Bis*{*2-(3'-phenanthryl)ethenyl*}*naphthalene*

A Sommelet reaction of 2,6-bis(bromomethyl)naphthalene gave 2,6-naphthalenedi-aldehyde (m.p. 178°) in 70% yield. A Wittig reaction of the dialdehyde with the triphenyl-phosphonium salt of 3-bromomethylphenanthrene and sodium methoxide in dimethyl-formamide gave a mixture of the three isomers of IX in 70% yield. The *trans,trans*-isomer was filtered from the reaction mixture. After evaporation of the solvent the residue was taken up in benzene. Chromatography on silicagel gave the *cis,cis*-isomer in a pure form. The *cis,trans*-isomer could not be isolated free from the *cis,cis* isomer.

cis,cis-IX. M.p. 192°; M = 532; U.V. λ max (log ε) (xylene) [372 (4.67)]; 358 (4.75); [350 (4.73)]; [303 (4.40)]; 289 (4.58).

trans,trans-IX. M.p. 370°; M = 532. Because of its low solubility it was not well possible to trace a quantitative U.V. spectrum. λ max (xylene): 407; 388; 370; 335; 302; 288.

Irradiation of 2,6-bis{2-(3'-phenanthryl)ethenyl}naphthalene (IX)

55 mg of *cis,cis*-IX was dissolved in 600 ml of benzene and placed in a quartz tube. The solution was boiled for some minutes in a water bath, and cooled while a slow stream of oxygenfree nitrogen was passed through the solution for about 20 minutes. After adding 60 mg of iodine the tube was closed, placed in the irradiation box and irradiated for 4 hours. The solutions from four identical runs were combined and filtered to remove a precipitate. The latter (12 mg) consisted of *trans,trans*-IX as was shown by melting point and U.V. spectrum. The filtrate was evaporated to remove the solvent. The brown coloured residue was dissolved in 20 ml of boiling xylene, the hot solution filtered through an Al_2O_3 column and eluted with:

a. hot xylene giving 140 mg of residue after evaporation of the solvent;
b. chloroform giving 63 mg of a second fraction.
   Fraction a. was treated with carbon tetrachloride, in which 20 mg (*meso*-I) did not dissolve. The solution was chromatographed on silica and eluted with carbon tetrachloride giving two new fractions.
c. 102 mg of *d,l*-I;
d. a mixture of several compounds.
   With benzene, chloroform and a mixture of chloroform and 50% methanol 9 mg of another fraction (e) was eluted.
   The combined fractions b, d and e were rechromatographed on alox. Elution with carbon tetrachloride produced four fractions.
f. 19 mg consisting of a mixture of *d,l*- and *meso*-I;
g. 14 mg containing *d,l*-I and XII;
h. 8 mg of XIII;
i. 3 mg of XIII contaminated with a dimer of IX.
   Finally, with dichloromethane a fraction containing only 15 mg of the dimer was isolated.
   From the several mixtures left, pure substances were isolated by crystallization.
   From this experiment the following yields can be derived based on the reacted compound IX:
   meso-I: 12% and *d,l*-1: 58%, together 70% I.
   XII: ~5%; XIII: ~5%; dimer: 7% and not identified polar products: 13%.

Physical data of the main products are given below.

I *Phenanthro[3,4-c; 3',4'-l]chrysene*

d,l The product was crystallized from ethyl acetate. At about 280° the fine needles began to lose their structure and started then to reform. This process went on till at about 320°, when all needles were reformed. At 400–402° (the melting point of the *meso* form) the compound melted.

With the aid of a Jasco ORD instrument used with a scale width of 0.02° no optical rotation could be observed on solutions of single crystals in carbon tetrachloride. With the same solution good U.V. spectra were obtained. U.V. λ max (log ε) (CH_2Cl_2): [431 (3.01)]; [407 (3.58)]; 375 (4.46); 354 (4.60); 338 (4.59); 312 (4.61); 277 (4.82); 259 (4.82); 242 (4.80). *M/e* 528; other peaks at 500, 300. The NMR spectrum has been reproduced previously[1]; the chemical shifts are given in Table II.

meso M.p. 400–402°. The substance is very slightly soluble in most of the common organic solvents. It was crystallized from carbon tetrachloride. U.V. λ max (log ε) (CH_2Cl_2): 432 (3.38); [406 (3.79)]; 383 (4.32); 360 (4.54); 348 (4.59); 336 (4.59); [321 (4.49)]; 276 (4.93); 259 (4.90); 228 (4.81). The NMR spectrum (in $AsCl_3$) has been reproduced before[1], the chemical shifts are given in Table II.

XII *Diphenanthro[3,2-c; 3',4'-l]chrysene*

M.p. 335–342°, M: 528; U.V. λ max (log ε) (CH_2Cl_2): [450 (2.42)]; [433 (2.98)]; 379 (4.61); 350 (4.78); [334 (4.72)]; 310 (4.85); 274 (4.71); 239 (4.90). NMR (CS_2) δ = 9.56 (s) 1H, α_4; 9.24 (d) 1H, α_4; 9.07 (s) 1H, α_3; 8.75 (m), 1H, α_3; 8.0–7.58 (m) 16H; 7.46 (d) 1H, A; 6.97 (m) 1H, C; 6.95 (d) 1H,B'; 6.44 (m) 1H, B.

XIII *Diphenanthro[3,2-c; 3',2'-l]chrysene*

M.p. 380°; M: 528; U.V. λ max (log ε) (benzene): 433 (3.07); [400 (4.00)]; 385 (4.41); [366 (4.60)]; 353 (4.91); 337 (4.73); 322 (4.49); 303 (4.43); 291 (4.43); 270 (4.17).

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