Tetrahedron. Vol. 30, pp. 3339 to 3342. Pergamon Press 1974. Printed in Great Britain

DOUBLE HELICENES: DIPHENANTHRO[4,3-a; 3′,4′-o]PICENE AND BENZO[s]DIPHENANTHRO[4,3-a; 3′,4′-o]PICENE

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(*Received in the UK* 8 *April* 1974; *Accepted for publication* 6 *May* 1974)

Abstract—The synthesis and NMR spectra of the title compounds are described. An X-ray diffraction study, carried out by Dr. J. D. Dunitz (ETH, Zurich), showed that the only product isolated from the photocyclisation of **6** has the *dl* configuration.

Following earlier work,[1] we have synthesised a new double helicene system, diphenanthro[4,3-a; 3′,4′-o]picene **7**, as well as a benzo-derivative, benzo[s]diphenanthro[4,3-a; 3′,4′-o]picene **12**, of this basic structure. Three different types of double helicenes, **1**[2], **2**[3] and **3**[4] are thus presently known.

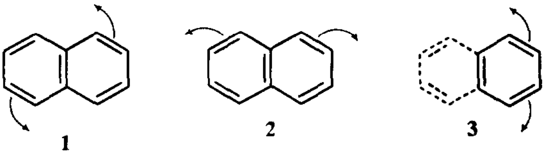
1 **2** **3**

Fig 1.

The hydrocarbons **7** and **12** have been prepared according to Schemes 1 and 2 respectively.

The required 4-methyl[6]helicene **5** and 6-methyl[7]helicene **9** were synthesised by the photocyclisation of **4** and **8**, respectively. In the case of **8**, the introduction of the methyl group seems to have a slight effect on the regioselectivity of the cyclisation process: 30% **9** + 54% **10** versus 20% **9** (CH_3=H) + 67% **10** (CH_3=H) in the case of the corresponding unsubstituted 1,2-diarylethylene **8** (CH_3=H)[5].

The photo-induced cyclodehydrogenation of **6** and **11** gave the desired double helicenes **7** (mp 452–454°) and **12** (mp 454–459°) in 73% and 26% yields, respectively. The relatively small yield of the last reaction (irradiation of a toluene solution during 2 h) may be due to the photodecomposition of the final product.†

Structure determination

The relative simplicity of the ^{1}H-NMR spectra proves that the cyclised products (M^+ 578 and 628, respectively) are symmetrical from the NMR point of view.

Diphenanthro[4,3-*a*; 3′,4′-*o*]*picene* **7** (Table 1). The four spins system H_1, H_2, H_3, H_4 is located at high field. The two heptuplets at 6·7 ppm and 6·13 ppm are assigned to H_2 and H_3, respectively, on account of the J's *ortho* and *meta* which, in the helicene series, are always larger for H_2 than for H_3.[6] In the present case, $(J_{1,2}+J_{2,3}+J_{2,4})-(J_{1,3}+J_{2,3}+J_{3,4}) = 0{\cdot}7$ Hz. H_1 (7·19 ppm), H_4 (7·39 ppm), H_{12} (8·84 ppm) and H_{26} (6·72 ppm) were then assigned by the following Indor experiments:

$$\begin{tikzcd} H_4 & H_1 \arrow[l, "Jp"'] \arrow[r, "Jo"] \arrow[d, "Jm"] & H_2 \\ & H_3 & \end{tikzcd} \qquad \begin{tikzcd} H_{26} \arrow[r, "Jepi", "({}^5J^{ttt})"'] & H_{12}\ddagger \end{tikzcd}$$

H_1 monitored at 641·9 Hz H_{26} monitored at 600·8 Hz

The relatively broad doublet at 7·6 ppm is assigned to H_5 on account of the well-known *epi* coupling (${}^5J^{ttt}$) of the corresponding proton in [6]helicenes. From these assignments, it follows that the doublets at 7·71 ppm and 8·05 ppm belong to H_6 and H_{11}, respectively. The remaining AB systems (H_7, H_8 and H_9, H_{10}) have not been formally assigned for lack of experimental proof.§

The most characteristic NMR features are: (a) the extra shielding of H_2 (0·4 ppm) in the double helicene as compared to H_2 in [6]helicene. High field shifts due to the overlap of the second helix diminish progressively from H_2 to H_6 (cf. Table 1), (b) the relative shielding of the two protons of the middle ring ($H_{25,26}$).

The *dl* configuration of the sole product isolated

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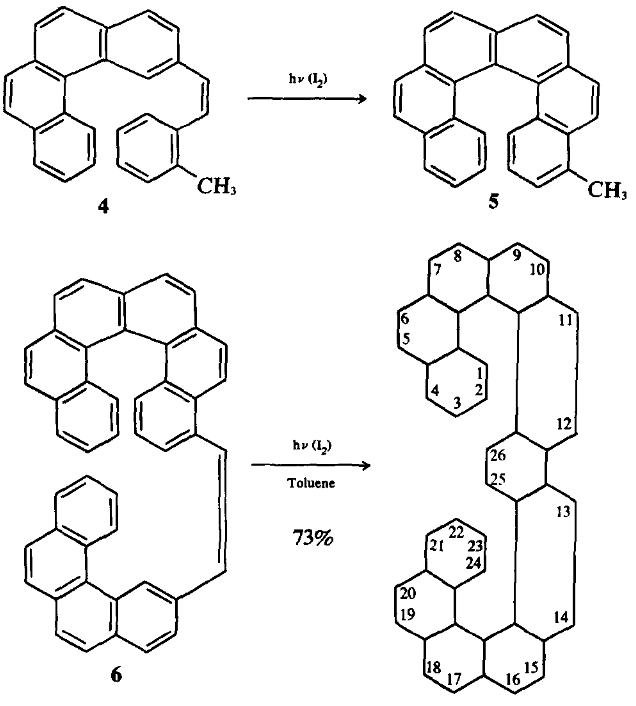
†The rapid photodecomposition of [7] helicene has been observed in our laboratory by A. Fisch (unpublished results).

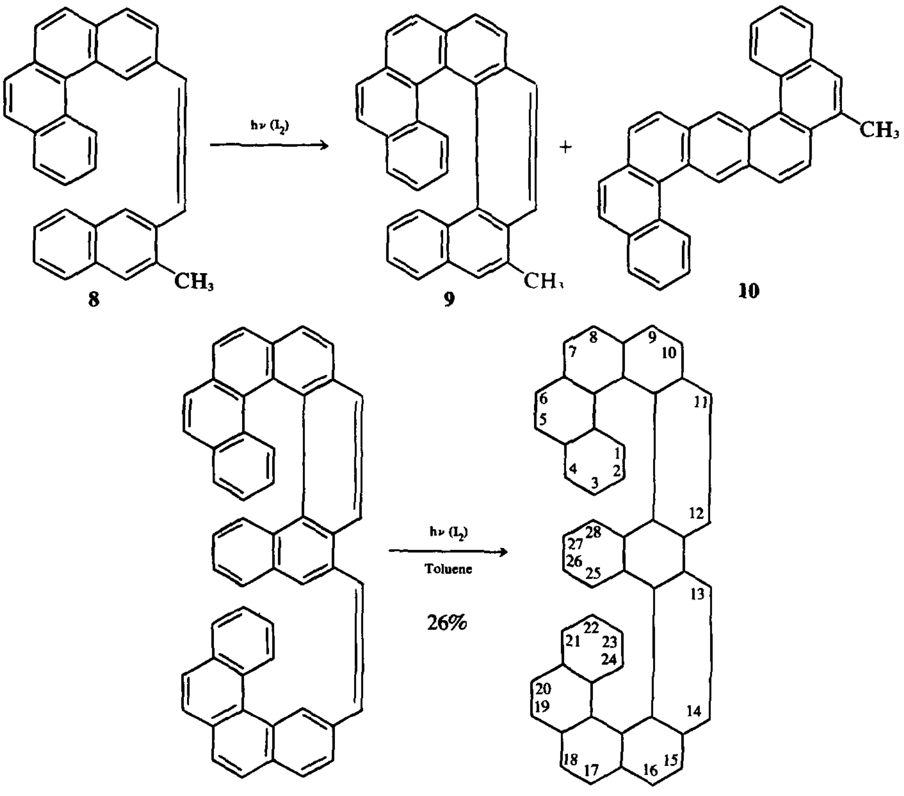
‡The low field signals are assigned to the $H\alpha_3$ proton H_{12}.

§We have not yet attempted to observe cross-ring *peri* couplings (${}^4J^{cc}$) by the Indor technique in this case.[7]



4 5 6 7

SCHEME 1



8 9 10 11 12

SCHEME 2

from the photocyclisation of **6** has been unambiguously assigned by an X-ray diffraction study.*

Benzo[s]*diphenanthro*[4,3-a; 3′,4′-o]*picene* **12** (Table 1). Because of the great insolubility of this hydrocarbon, we have been unable to study its NMR spectrum by the Indor technique. The given assignments are therefore based on analogies.[6] A four spins system ($H_{1,2,3,4}$), typical of a helicene structure, is clearly visible at high field.

The signals located at 5·37 ppm, which belong to the AA′BB′ four spins system $H_{25,28,26,27'}$ are provisionally assigned to $H_{26,27}$. These protons are the most strongly shielded protons yet observed in a non substituted benzenoid helicene structure.

It is interesting to recall that the protons of the middle ring of [13]helicene ($H_{15,16}$) resonate at 6·1 ppm.[8]

Symmetry arguments based on the NMR spectrum and the high field shift of $H_{26,27}$ strongly suggest that the isolated double helicene **12** has the *dl* configuration, with the two end rings on opposite sides of the central naphthalene system.

EXPERIMENTAL

1-(*o-tolyl*)-2-(2-*benzo*[*c*]*phenanthryl*)*ethylene* **4**

Solutions of K (0·3 g) in EtOH (20 ml) and 2-formylbenzo[c]phenanthrene (1 g) in C_6H_6 (10 ml) are added successively to o-triphenylphosphoniomethyltoluene bromide (1·8 g) in EtOH (20 ml). After standing 18 h at room temperature, the mixture is refluxed during 2 h. The reaction products are purified by column chromatography [alumina, CH_3CO_2Et/petrol bp 60–70° 20:80]. Yield: 90%. (*cis* + *trans* **4**); M$^+$ 344.

4-*Methyl*[6]*helicene* **5**

A solution of *cis* + *trans* **4** (0·25 g) and I_2 (0·02 g) in C_6H_6 (800 ml) is irradiated with a Hanovia 450 W medium pressure Hg lamp for 2 h. 4-Methyl[6]helicene is purified by chromatography (alumina; petrol bp 60–70°). Yield: 82%, mp 291–294° (C_6H_6/C_6H_{12}) with a phase modification between 200–250°; M$^+$ 342. The structure was confirmed

Table 1. ^1H chemical shifts in **7** and **12** (ppm; TMS = 0)

	7[a]	$\Delta^{[6]}$[b]	**12**[c]	**12**[d]	$\Delta^{[7]}$[e]
H_1–H_{24}	7·18	0·27	6·77	6·837	0·24
H_2–H_{23}	6·12	0·41	5·80	5·846	0·46
H_3–H_{22}	6·70	0·39	~6·3	6·369	~0·45
H_4–H_{21}	7·38	0·38	6·80	6·878	0·34
H_5–H_{20}	7·61	0·20	7·13	7·203	0·24
H_6–H_{19}	7·70	0·11	7·43	7·525	0·19
H_7–H_{18}	7·83[f]	(0·05)	7·68	7·762	0·14
H_8–H_{17}	7·83[f]	(0·05)	7·79	7·884	0·11
H_9–H_{16}	7·87[f]		7·88	7·967	0·04
H_{10}–H_{15}	7·91[f]		7·92	8·017	
H_{11}–H_{14}	8·06		8·01	8·113	
H_{12}–H_{13}	8·84		8·70	8·835	
H_{25}–(H_{28})	6·67		~6·3	6·377	
H_{26}–(H_{27})	6·67		5·39	5·450	

[a] 90 MHz (Bruker) in CS_2, internal lock and reference TMS–CAT (3 and 6 Hz/cm–195 scans)

[b] $\Delta^{[6]} = \delta$[6]helicene–δ**7**. ^1H-NMR spectrum of [6]Helicene in CS_2, cf.[1]

[c] 90 MHz (Bruker) in CS_2, internal referenceTMS–external lock C_6F_6–Fourier transform (spectral window 1000 Hz–15000 scans)

[d] 270 MHz (Bruker) in CS_2–CD_3COCD_3, internal reference TMS, internal lock CD_3–CO–CD_3–Fourier transform (spectral window 3000 Hz–51000 scans). We express our gratitude to Prof. G. Van Binst (VUB, Brussels) for recording this spectrum

[e] $\Delta^{[6]} = \delta$[6]helicene–δ**12**. ^1H-NMR spectrum of [7]helicene in CS_2, cf[7]

[f] not yet formally assigned

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*We express our gratitude to Dr. J. D. Dunitz (ETH, Zurich) who carried out this determination. W. H. Laarhoven and coll. arrived independently at the same conclusion by resolving the hydrocarbon 7 (cf. this issue of Tetrahedron). We are grateful to Dr. W. H. Laarhoven for the communication of his manuscript prior to publication.

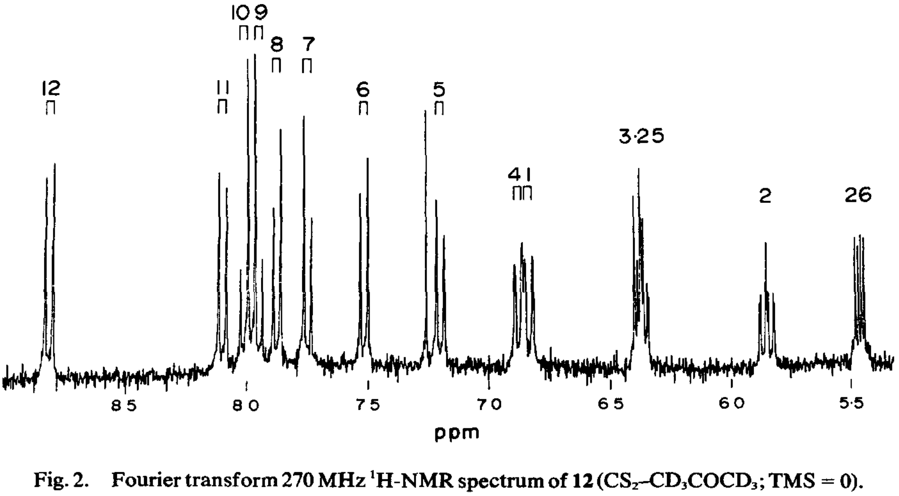

Fig. 2. Fourier transform 270 MHz ^1H-NMR spectrum of **12** (CS_2–CD_3COCD_3; TMS = 0).

by NMR spectroscopy. δ_{CH_3}: 2·77 ppm, $\nu_{1/2}$ 1·9 Hz ($CDCl_3$).

1-(2-*Benzo*[*c*]*phenanthryl*)-2-(4-[6]*helicyl*)*ethylene* **6**

A sol. of 4-triphenylphosphoniomethyl[6]helicene bromide (0·16 g) (prep. by treating 4-methyl[6]helicene with NBS in CCl_4 in the presence of $(C_6H_5COO)_2$ followed by $P(C_6H_5)_3$ in boiling xylene), 2-formylbenzo-[c]phenanthrene (0·065 g) and EtOLi in $EtOH/C_6H_6$ (80:20) is refluxed during 2 h and kept 14 h at room temp. The ppt. is filtered and dried. Yield: 82% (*cis* + *trans* **6**); M^+ 580.

Diphenanthro[4,3-a; 3′, 4′-o]*picene* **7**

A solution of **6** (0·1 g) and I_2 (0·01 g) in toluene (800 ml) is irradiated for 2 h. The reaction product is purified by column chromatography (alumina; C_6H_6). Yield: 73% m.p. 452–454°; M^+ 578.

1 - (2 - *Benzo*[*c*]*phenanthryl*) - 2 - (3 - *methyl* - 2 - *naphthyl*)*ethylene* **8**

The Wittig reaction is carried out by mixing 2-formylbenzo[c]phenanthrene (0·475 g) and 3 - methyl - 2 - triphenyl-phosphoniomethylnaphthalene bromide (1 g) in CH_3OH/C_6H_6 (10 ml/5 ml) and adding a solution of Li (0·02 g) in CH_3OH (10 ml). The stirred reaction mixture is kept 15 h at room temp. and the reaction product is purified by column chromatography [alumina; petrol bp 60–70°/CH_3CO_2Et (80:20)]. Yield: 75% (*cis* + *trans* **8**); M^+ 394.

6-*Methyl*[7]*helicene*

A solution of **8** (0·25 g) and I_2 (0·02 g) in C_6H_{12} (800 ml) is irradiated during 30 min. The reaction products are purified by column chromatography [alumina; petrol bp 60–70°]. First fraction: 6-methyl[7]helicene **9** (30%), mp 274–276° (C_6H_{12}), M^+ 392, δ_{CH_3} 2·82 ppm doublet J = 0·9 Hz ($CDCl_3$). Second fraction: 6-methyldinaphtho[1,2-a; 1′,2′-h]anthracene **10** (54%) m.p. 216–218° (C_6H_6/EtOH), M^+ 392, δ_{CH_3} 2·83 ppm doublet J = 0·9 Hz ($CDCl_3$). The structures of **9** and **10** were confirmed by NMR spectroscopy.

1-(2-*Benzo*[*c*]*phenanthryl*)-2-(6-[7]*helicyl*)*ethylene* **11**

The Wittig reaction, carried out as above, gave a 51% yield of **11** (*cis* + *trans*); M^+ 630.

Benzo[s]*diphenanthro*[4,3-a; 3′,4′-o]*picene* **12**

A solution of **11** (0·053 g) and I_2 (0·008 g) in toluene (800 ml) is irradiated during 2 h. The product is purified by column chromatography (alumina; C_6H_6). Yield: 26%, m.p. 454–459°; M^+ 628.

Acknowledgements—The financial support of the "Fonds de la Recherche Fondamentale Collective" is gratefully acknowledged. One of us (Ch.E). expresses his gratitude to the "Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture" for the award of a Fellowship.

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