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PHOTODEHYDROCYCLIZATIONS OF STILBENE-LIKE COMPOUNDS—XI

SYNTHESIS AND RACEMIZATION OF THE DOUBLE HELICENE DIPHENANTHRO[4.3-a; 3'.4'-o]PICENE

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Abstract—The synthesis of a new double helicene, diphenanthro[4.3-a;3'.4'-o]picene, is described. Of the two possible diastereoisomers only one was obtained as a racemate. The compound was partly resolved with TAPA yielding fractions enriched with one or the other enantiomer. They could not be converted into the other diastereomer by heating, but racemized under these conditions at a relatively low temperature and with a rate comparable to that of the racemization of hexahelicene at the same temperature.

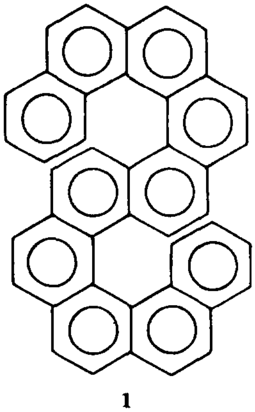
The NMR spectrum is discussed.

For many single helicenes such as pentahelicene,[2] hexahelicene,[3] heterohelicenes[4] and even hepta-, octa- and nonahelicene,[5] which exist in enantiomeric forms racemization of optically active samples has been observed on heating. The double helicenes **1–3** can theoretically occur in three forms: besides two enantiomeric forms, a *meso*-modification is also possible in these cases. Racemization of the enantiomers of these compounds will be a two step reaction; independent of its mechanism† the *meso*-compound will be an intermediate.

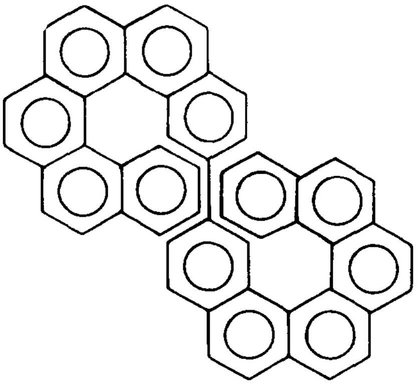
With diphenanthro[3.4-c;3'.4'-l]chrysene (**1**) which was synthesized in a racemic and a *meso*-modification, it has however, been shown that a partially resolved sample of the racemic form did not racemize at all on heating but isomerized into the *meso*-form.[6] Apparently the isomerization is irreversible owing to the lower energy content of the *meso*-compound.

Similar results[7] have been obtained with 2,2'-bishexahelicyl (**2**). Heating of the racemic form supplied the *meso*-form which itself appeared to be thermostable.

Hexaheliceno[3.4-c]hexahelicene (**3**) was only obtained in one form, presumably the racemic modification.[8] As a consequence of the low yield of the synthetic procedure the sample was too small to attempt resolution. So racemization could not be



1



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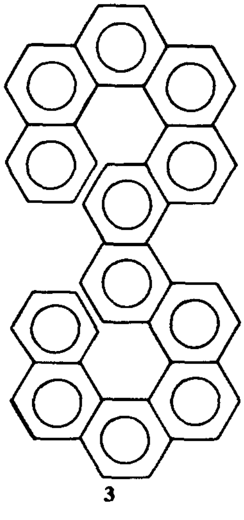

3

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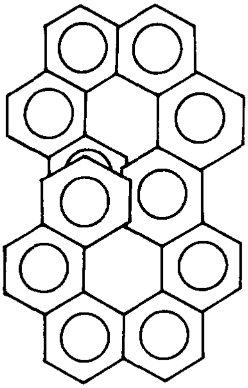
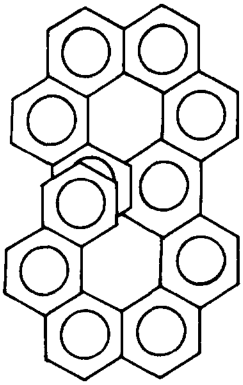
†Very recently Martin and Marchant[5] argued that the racemization of the [6] and higher helicenes proceeds *via* a conformational pathway and not *via* bond breaking or an internal Diels-Alder reaction.

investigated. However, the compound did not isomerize on heating. In **3** the racemic form has the terminal rings at different sides of the central part of the molecule, whereas in **1** the *meso*-form has this conformation. Apparently this conformation has the lower energy content.

In this paper investigations on a new double helicene, diphenanthro[4.3-a;3′.4′-o]picene (**4**), are described. It can be conceived as the lower benzolog of **3** in which the distinct helical parts have a common ring. The increased crowding in the central part of the molecule may mean that four instead of three stereoisomers are possible, since the presence of a plane of symmetry seems less probable in the steroisomer **4b** in which, as in *meso* **3**, both terminal rings are at the same side of the central ring.



4a



4b

Furthermore, it can be envisaged that the energy difference between **4b**, whether a racemic or a *meso*-form, and **4a** may be larger than that between racemic and *meso*-**3**. Racemization of the enantiomers of **4a**, which has to proceed *via* **4b**, might than appear to be a very slow reaction.

Synthesis and resolution. 4-Methylhexahelicene (**5**)[9] was converted into 1 - (2 - benzo[c]phenanthryl) - 2 - (4 - hexahelicyl)ethylene (**6**) *via* well-known reactions (Eq 1).

Irradiation at 360 nm for 1 h of a 10^{-3} molar solution of **6** in oxygen-free benzene containing an equimolar amount of iodine produced **4** in 90% yield.

Purification by column chromatography and crystallization yielded only one isomer, to which the structure **4a** was assigned in view of its NMR spectrum (see further). No trace of a diastereomeric form could be detected in the crude mixture after irradiation, nor during chromatography nor in the mother liquor after crystallization.

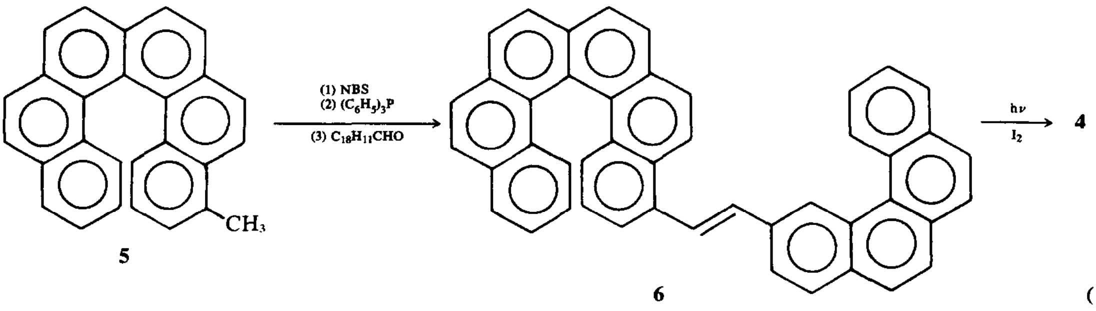
A solution of the product (**4a**) in benzene was percolated over a column of silicagel impregnated with (-)-TAPA ((-)-α-(2,4,5,7-tetranitrofluorenylideneaminooxy)-propionic acid[10]) according to the method of Klemm.[11]

On careful elution with benzene the first fractions containing the double helicene showed a positive Cotton effect. The highest specific rotations found were $[\alpha]_{380}$: 32300; $[\alpha]_{545}$: 9900 but the optical purity of this fraction is unknown. By evaporation of the solvent *in vacuo* optically active samples of **4** were obtained.

Racemization experiments. According to Martin[3b] hexahelicene racemizes in naphthalene solution at 205° (28° below its melting point) with a half life time of 48 min.

A preliminary experiment with **4a** revealed that the double helicene began to darken on heating even below its mp: on melting (440°) a brown oil was left which contained, besides unchanged **4a**, a number of destruction products. An isomeric form (**4b**) could not be detected by NMR.

Melting of an optically active fraction showed the same phenomena; moreover the optical activity of the sample was completely lost. In several experiments in which the heating temperature was progressively reduced we found that at 210° (230° below the mp) racemization proceeded at a rate such that residual optical activity was found after heating for 20 min. At this temperature the rate constant of racemization was determined by measuring the specific rotation after different time intervals of heating. From the first order plot the rate constant of racemization was found to be $1{\cdot}9\ 10^{-2}\ \mathrm{min}^{-1}$; and $t_{1/2} = 38$ min. The racemization rate is thus of about the same magnitude as that of hexahelicene. This unexpected result shows that flipping of one of the helical parts in **4** is not noticably hindered by the presence of the other helix. In view of this result **4b** accepted as an intermediate in the racemization should have a symmetrical *meso*-structure.



(1)

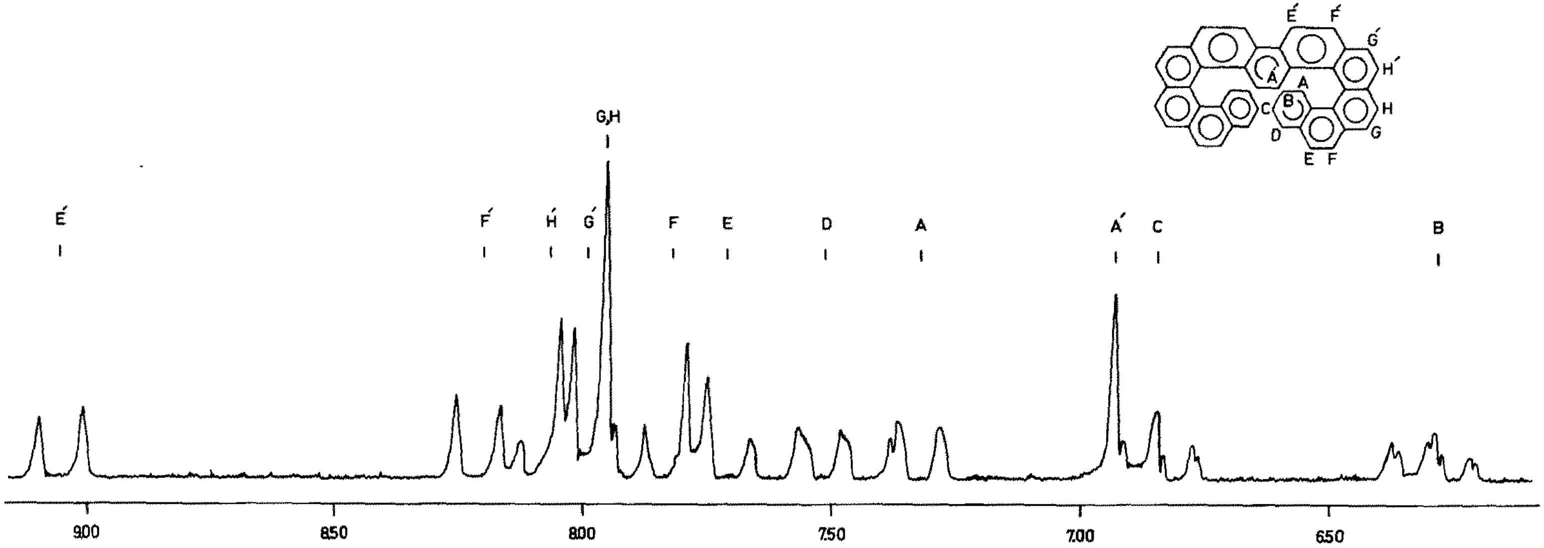


Fig. 1. NMR spectrum of diphenanthro[4.3-a;3′.4′-o]picene (**4**) in $AsCl_3$ (Varian HA 100).

NMR spectrum. An analysis of the NMR spectrum of the double helicene **4** seems to be of interest in order to investigate the magnitude of mutual shielding effects between the rather distant terminal rings. Such effects have been observed in multilayered cyclophanes[12] in which three or four layered rings are completely centered, and in [13]-helicene[13] having two complete turns. In **4a** the terminal rings overlap the middle ring only partly.

The NMR spectrum of **4a** was recorded in $AsCl_3$ solution with a Varian HA-100 apparatus. Frequencies were determined with the side band technique (Fig 1). For comparison with other helicenes the spectrum was also recorded in CS_2 solution with a XL-100 instrument with Fourier Transformer. (The solubility of **4a** in CS_2 is very low). By decoupling experiments and comparison with spectra of known helicenes all NMR signals of **4a** could be assigned. The chemical shifts in CS_2 are given in Table 1 together with those of corresponding protons in other helicenes in the same solvent.

As it has been shown that the helical conformation in hexahelicene remains rather undisturbed as long as no substituents are introduced at C_1,[9] and the same helical conformation will also be found in double helicene I if the terminal rings are at different sides of the central part of the molecule,[6] it may be accepted that all compounds in Table 1 have rather similar helix conformations. Some of the larger differences between chemical shifts of comparable protons are caused by differences in their character as a consequence of additional rings; e.g. the B′-protons in benzo[m]hexahelicene, **3** and **4** have higher values than the B-proton in hexahelicene, because they are α,β-protons; similarly the E′-protons in the same compounds are considerably shifted to lower field in comparison with E in hexahelicene because E′ is an α_3-proton in benzo[m]hexahelicene and **4** but an α_4-proton in **3**.

The upfield shifts found for some other protons of **3**, **4** and [13]-helicene when compared with hexa- and benzohexahelicene have mainly to be ascribed however, to the influence of the terminal ring in the second helical part. In **3** the effect is found for protons B, C and B′, in **4** also for the protons A, A′, D and even E as could be expected as a consequence of larger overlap of the terminal rings in the latter case. For the same reason the magnitude of the upfield shifts of protons B and C also increases in going from **3** to **4**. In [13]-helicene the shielding effects of protons A-C are again much larger than in **4**. Apparently the mutual influences of the terminal rings in [13]-helicene are more pronounced than in **3** and **4** due to a larger overlap of these rings with the central benzene ring.

From the relative simplicity of the spectrum of **4** it can be deduced that it belongs to structure **4a**. In structure **4b** the terminal rings are not equivalent and if **4b** were to be a *meso*-compound the protons of the terminal rings certainly would be shifted downfield as in dl-I[6].

The general similarity of the NMR spectra of the compounds **3** and **4** as well as the consistent differences in the chemical shifts of comparable protons in the central region of both compounds have been used as strong arguments for their configurational relationship. Indeed **3** must then have the configuration of a racemic isomer.

EXPERIMENTAL

For spectral data a Varian SM2B mass spectrometer, a Cary 15 UV spectrophotometer, and Varian HA-100 and XL-100 NMR apparatus were used.

Mps were measured with a mp microscope; that of the

Table 1. Chemical shifts in ppm of protons in several helicenes measured in CS_2

Protons[a]	Hexahelicene	Benzo[m]hexahelicene[14]	Hexaheliceno hexahelicene[8] 3	Diphenanthropicene 4	[13]-Helicene[13]
A	7·47	7·49	7·51	7·22	6·10
B	6·53	6·42	6·24	6·15	5·82
C	7·08	7·04	6·82	6·74	6·55
D	7·67	7·71	7·68	7·42	
E	7·77	7·84	7·72	7·63	
F	7·77	7·84	7·72	7·74	
G	7·82	7·92	7·92	7·86	
H	7·82	7·92	7·92	7·86	
A′		7·43	7·41	6·70	
B′		6·85	6·58	6·70	
C′		—	—	—	
D′		—	—	—	
E′		8·74	9·11	8·88	
F′		8·07	7·98	8·09	
G′		7·93	7·87	7·92	
H′		7·73	7·87	7·92	

[a] The use of capitals for the ring protons is explained in the formula in Fig 1.

double helicene **4** with a melting point block heated with a flame. They are uncorrected.

Irradiations were carried out in pyrex tubes surrounded by four Sylvania blacklite F8T5 lamps with $\lambda_{max} = 360$ nm.

1 - (4 - Hexahelicyl) - 2 - (2 - benzo[c]phenanthryl) - ethylene (**6**). 4-Methylhexahelicene[9] was brominated with an equiv amount of N-bromosuccinimide in CCl_4. After filtration of the succinimide and evaporation of the solvent the crude product was treated with triphenylphosphine in xylene. The triphenylphosphonium salt separated from the mixture and was isolated in 90% yield by filtration (mp 316–318°).

A Wittig reaction of this salt and 2-benzo[c]-phenanthraldehyde in DMF with NaOMe as a base gave the desired product **6** in 80% yield.

trans-isomer: mp 245–248°; Mass m/e: 580.

Diphenanthro[4.3-a;3'.4'-o]*picene* (**4**). The previous compound (**6**) was dissolved in deaerated benzene (10^{-3} molar) and irradiated in the presence of an equimolar amount of iodine. After one hour most of the solvent was evaporated and the residue was separated by column chromatography on silicagel. **4** was eluted with benzene; mp 440° (CH_2Cl_2); Mass m/e 578; UV (CH_2Cl_2) λ_{max} (log ϵ): 433 (3·04); 420 (2·95); 375 (4·29); 356 (4·43); [326 (4·57)]; 315 (4·61); 269 (4·82); 248 (4·68); 232 (4·77); for NMR data see Table 1 and Fig 1.

Resolution of dl **4**. A soln of **4** in benzene was brought on a column packed with silicagel impregnated with tetranitrofluorenylideneaminooxy propionic acid (TAPA)[10] according to Klemm.[13]

By very slow elution with CH_2Cl_2 every 12 h a fraction of about 25 ml was collected. During the elution the column was shielded from light. The first two fractions containing **4** showed optical activity. The optical rotation was measured with the aid of a Jasco ORD apparatus with a scale width of 0·05°. In order to evaluate the specific rotation the concentration was determined spectrophotometrically. The ORD curve in CH_2Cl_2 showed maxima at 545, 480 and 380 nm and minima at 500, 450 and 330 nm. With (+)-TAPA a small fraction of (−)-**4** was obtained in a similar way.

Racemization experiments. Weighed samples of optically active **4** (0·2–0·5 mg) with known specific rotation were brought into small heating tubes together with analytically pure, resublimed naphthalene (10–25 mg). The tubes were evacuated ($5 \cdot 10^{-6}$ mm Hg), sealed, and heated until clear solutions were obtained. They were then heated in an electrical furnace for different times at known temperatures. After cooling, the tubes were opened. From those in which the contents had not been discoloured the naphthalene was sublimed off. The residues were taken up in methylene chloride. The concentration of the solutions was determined by UV-spectroscopy, the optical rotation by measurements of ORD.

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