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CHEMICAL ASSIGNMENT OF ABSOLUTE CONFIGURATIONS IN THE HELICENE AND HETEROHELICENE SERIES. PART XXXIV[1].

1. *Hexahelicene*

2. *Benzo [d] naphtho [1,2-d'] benzo [1,2-b; 4,3-b'] dithiophene.*

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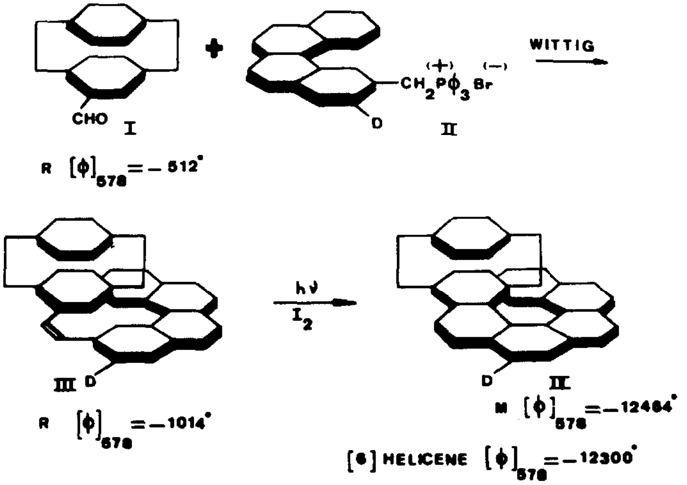
Lightner and co-workers have recently established the absolute configuration of hexahelicene by X-ray diffraction[2].

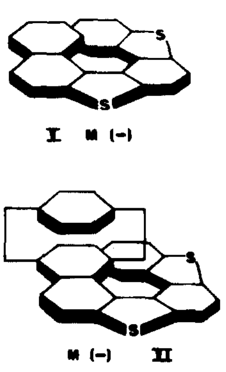
We wish to report the first chemical assignment of an absolute configuration in the helicene series. The conclusion of our work, namely that (-) hexahelicene has the left-handed (M) configuration, was reached independently[3] from the X-ray diffraction study.

The scheme outlined below was used successfully, starting from resolved [2,2] paracyclophane-4-carboxylic acid of known absolute configuration[4] [b].

It is obvious, for steric reasons, that the cyclisation which gives rise to the helicene structure IV *can only lead to the left-handed helix.*

In view of the fact that the photo-induced cyclodehydrogenation of III could take place in two different positions (1 or 3) of the benzo [c] phenanthrene system, we have applied the deuterium labelling method described in a previous publication[5]. (-) [2,2] Paracyclophane-4-carboxylic acid, m.p. 211-213°; $[\alpha]^{25}_{589} = -150°$[c] (lit.[6] m.p. 211-212°; $[\alpha]^{25}_{546} = -198°$) was esterified with diazomethane in quantitative yield. The methyl ester, m.p. 171-173°; $[\alpha]^{25}_{578} = -170°$ (lit.[7] m.p. 171-175°; $[\alpha]^{25}_{D} = -153°$) was reduced ($H_4LiAl$) in





75% yield to the corresponding alcohol, m.p. 151-153°; $[\alpha]^{25}_{546}$ = -71°d) (lit.8) m.p. 152-153°; $[\alpha]^{25}_{546}$ = -78.5°) which was oxidized with NiO_2 in benzene at room temperature (70% yield) to the R aldehyde, m.p. 146-148° (rac. aldehyde m.p. 140-144°)9); $[\alpha]^{25}_{578}$ = -217°, $[\alpha]^{25}_{546}$ = -280°, $[\alpha]^{25}_{436}$ = -844°, $[\alpha]^{25}_{364}$ = -1365°; $[\phi]^{25}_{578}$ = -512°. Found : C, 86.2; H, 7.0. $C_{17}H_{16}O$ requires : C, 86.4; H, 6.8%.

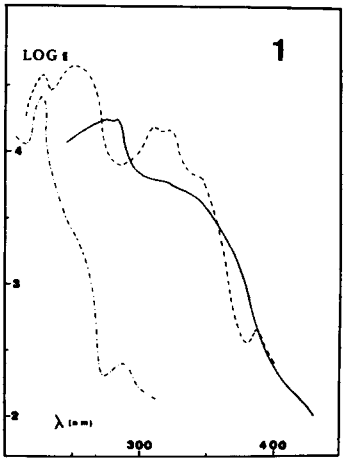
A Wittig reaction between II and optically active I ($[\alpha]^{25}_{578}$ = -217°) gave *cis* + *trans* III, $[\alpha]^{25}_{578}$ = -220°; $[\phi]^{25}_{578}$ = -1012°. Found : (non-deuteriated) C, 94.0; H, 5.8. $C_{36}H_{28}$ requires : C, 93.9; H, 6.1%. M.p. *trans* > 350°.

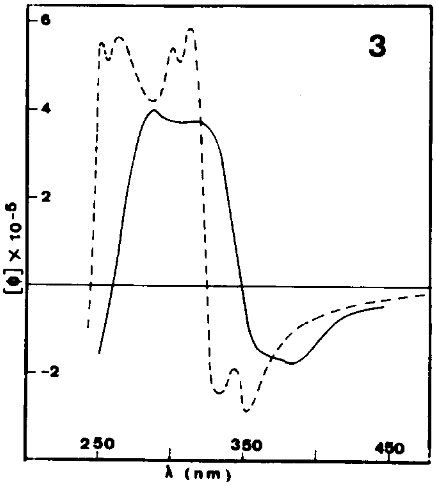
After 30 min. irradiation of III (100 mg, C_6H_6 1000 ml, I_2 1.5 mg; Hanovia 450 W medium pressure mercury lamp, pyrex well, stirring), the optical rotation of the solution, which had increased from $[\alpha]^{25}_{578}$ = -220° to $[\alpha]^{25}_{578}$ = -339° (2 mg/2 ml $CHCl_3$), remained practically constant. The reaction product was purified by column chromatography (alumina-petroleum ether 60-70°/benzene 98:2). The first fraction (blue fluorescence; 5.8 mg) was shown to be IV, $[\alpha]^{25}_{578}$ = -2716°; $[\phi]^{25}_{578}$ = -12464° ± 200°. Found : C, 93.70; H, 6.40. $C_{36}H_{25}D$ requires : C, 94.04; H, 5.96%. (-) Hexahelicene : $[\alpha]_{578}$ = -3750°; $[\phi]_{578}$ = -12300°10). The UV spectra of IV, hexahelicene and [2,2]paracyclophane are shown in Fig. 1.

The mass spectra of IV and of the corresponding non-deuteriated (dl) hydrocarbon (M^+ 459 and 458), recorded under identical conditions (Hitachi Perkin-Elmer PMU-6D), showed that the isotope purity (^2H) of the first mentioned (IV) is ⩾ 92.5%.

The NMR spectrum (Fig. 2) confirms the proposed structure. Comparison of the ORD curves (Fig. 3) of (-) hexahelicene[10)] and (-) IV, provides convincing evidence that the two compounds have the same chirality. The observed differences can be attributed to a probable modification of the geometry of the helix and/or to extra "vertical conjugation" in IV[e)].

In collaboration with H. Wynberg and M. Doyle, we have obtained a rigorous proof of the validity of the above method, by the synthesis of the *laevo* rotatory [2,2]paracyclophano-heterohelicene VI, starting from R(-) [2,2] paracyclophane-4-carboxylic acid. The UV and the ORD (590-290 nm region) spectra of the final product VI (M^+ = 470) show overall similarities with the UV and ORD spectra[f)] of the corresponding (-) heterohelicene V, whose left-handed (M) configuration had been determined previously by X-ray diffraction[11)].





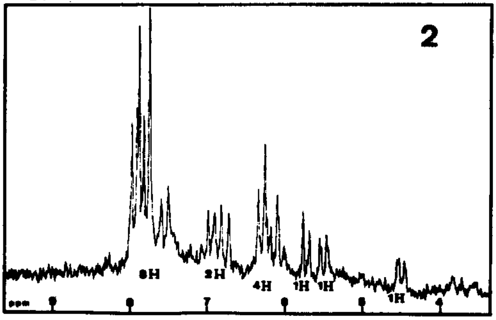


Fig. 1. UV spectra. I V (———) in methanol, hexahelicene (----) in methanol, [2,2] paracyclophane (-·--·-·) in dioxane.

Fig. 2. NMR spectra of IV, 90 Mz (CS_2) 69 scans. - Brücker HX90

Fig. 3. ORD spectra of (-) IV (———) and (-) hexahelicene (----) in methanol.

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Footnotes.

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b) The chemical assignment of the absolute configuration of [2,2]paracyclophane-4-carboxylic acid has been confirmed recently by X-ray crystal analysis; we express our gratitude to G.W. Frank, University of Los Angeles for this personal communication.

c) All the rotations were measured in $CHCl_3$ at 25-26°.

d) The NMR spectrum of *dl* 4-hydroxymethyl [2,2]paracyclophane shows diastereotopic protons : $\delta_{AB} = 4.5$ ppm, $J = 12.7$ Hz, $\Delta_{AB} = 0.32$ ppm ($CDCl_3$; 60 MHz; TMS = 0).

e) The CD curve of an impure specimen of the final product IV which unfortunately turned out to be unstable, is fully compatible with the assigned configuration. We are very grateful to Prof. G. Snatzke and to Dr. I. Pinter (University of Bonn) for the recording of the CD curve and for valuable comments.

f) Unfortunately compound VI was unstable, solutions turning yellow and the solid turning brown before satisfactory NMR and CD measurements could be made.

References.

1) Part XXXIII. R.H. Martin and J.J. Schurter, Tetrahedron 28, 1803 (1972).
2) D.A. Lightner, D.T. Hefelfinger, G.W. Frank, T.W. Powers and K.N. Trueblood, Nature, Phys. Sc., 232, 124 (1971).
3) Cf. W. Hug and G. Wagnière, Tetrahedron, 28, 1241 (1972), ref. 9.
4) O.E. Weigang, Jr. and M.J. Nugent, J. Amer. Chem.Soc., 91, 4555 (1969); M.J. Nugent and O.E. Weigang, Jr., J. Amer. Chem. Soc., 91, 4556 (1969); H. Falk and K. Schlögl, Angew. Chem. Int. Ed. Engl., 7, 383 (1968). H. Falk, P. Reich-Rohrwig and K. Schlögl, Tetrahedron, 26, 511 (1970).
5) R.H. Martin and J.J. Schurter, Tetrahedron Letters, 3679 (1969). R.H. Martin and J.J. Schurter, Tetrahedron, 28, 1749 (1972).
6) D.J. Cram and N.L. Allinger, J. Amer. Chem. Soc., 77, 6289 (1955).
7) H. Falk, P. Reich-Rohrwig and K. Schlögl, Tetrahedron, 26, 511 (1970).
8) D.J. Cram and L.A. Singer, J. Amer. Chem. Soc., 85, 1075 (1963).
9) A. Burger, Monatsh. Chem., 95, 1721 (1964).
10) M.S. Newman, S.R. Darlak and L. Tsai, J. Amer. Chem. Soc., 89, 6191 (1967).
11) M.B. Groen, G. Stulen, G.J. Visser and H. Wynberg, J. Amer. Chem. Soc., 92, 7218 (1970).