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PREPARATION OF (-)-(M)-[2.2]PARACYCLOPHANO-HEXAHELICENE FROM (-)-(M)-1,4-DIMETHYLHEXAHELICENE AND ABSOLUTE CONFIGURATION OF 4-SUBSTITUTED [2.2]PARACYCLOPHANES

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Photo-cyclization of a cis-trans mixture of the 1,2-diarylethylene precursor 1 gave 1,4-dimethylhexahelicene (2) whose levorotatory enantiomer with (M)-helicity was converted into (-)-(M)-[2.2]paracyclophano-hexahelicene (7), mp 236-237°C, $[\alpha](abs)_{577}$ -5520°[1] confirming the (R)-configuration previously assigned to (-)-[2.2]paracyclophanecarbaldehyde (8).

In 1972, Martin et al.[2] reported preparation of (-)-[2.2]paracyclophano-hexahelicene (7) from (-)-(R)-[2.2]paracyclophanecarbaldehyde (8) whose unique stereochemistry should force the final product 7 to have (M)-helicity; comparison of ORD cuve of (-)-7 with that of (-)-hexahelicene (3) enabled them to assign (M)-helicity to (-)-3. Since the (M)-helicity of (-)-3 had been well established by various methods,[3] Martin's work can rather be regarded as a most reliable chemical correlation to assign (R)-configuration[4] to the (-)-aldehyde 8. Unfortunately, however, their specimen of (-)-7, apparently impure, was poorly characterized seemingly because of its reported instability.

Our recent experimental study[5] which has revised the absolute configurations of the closely related 4-substituted [2.2]metacyclophanes prompted us to prepare this doubly layered hexahelicene 7 in optically active modification from 1,4-dimethylhexahelicene (2) with known configuration.

A ca. 1:1 cis-trans mixture of the 1,2-diarylethylene precursor 1[6] prepared by the Wittig reaction between 2,5-dimethylbenzaldehyde and 2-benzo[c]phenanthrylmethyltriphenylphosphonium bromide, was dissolved in benzene containing a small amount of iodine and was irradiated with a medium pressure mercury lamp for 4 hr. Column chromatography (Al_2O_3) of the product furnished 1,4-dimethylhexahelicene (2) (64% yield), mp 252-253°C, characterized by its two $C\underline{H}_3$ nmr signals at δ 0.45 and 2.42 corresponding to the inner and outer methyl groups respectively.

Optical resolution of 2 was accomplished by column chromatography over chiral poly(triphenylmethyl methacrylate)[7]; elution with hexane afforded a specimen of (-)-2, mp 241-243°C, $[\alpha]_{577}$ -432° whose ca. 12% optical purity[8] was estimated from the reported $[\alpha]_{578}$ -3756°[9] for (-)-hexahelicene (3) (Figure 1).

Photochemical NBS bromination in CCl_4 with benzoyl peroxide converted (-)-2 into the crude bromide 4 which was directly transformed to the ammonium salt 5, $[\alpha]_D$ -465°. Starting from a 2:1 mol equivalent mixture of p-methylbenzyltrimethylammonium bromide (6) and (-)-5, the Cram's method afforded a complex mixture of

doubly layered cyclophanes whose column chromatography (SiO_2) followed by preparative TLC (SiO_2) gave a 4% yield of (-)-7, which was recrystallized from ethyl acetate to yield yellow prisms, mp 236-237°C, $[\alpha]_{577}$ -662°.[8)]

Comparison of the CD spectrum of (-)-7 (Figure 1) with that of (-)-(M)-hexahelicene (3) led us to conclude that (-)-7 possesses the same (M)-helicity, and this coupled with Martin's experiment should provide a convincing evidence to support the (R)-configuration of (-)-[2.2]paracyclophanecarbaldehyde (8).

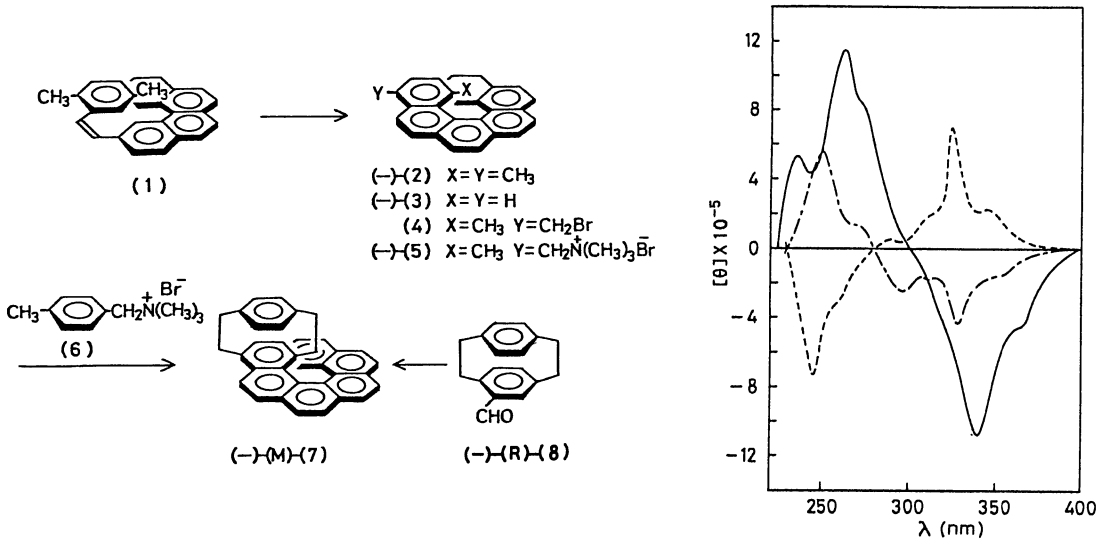

Figure 1.[8)] CD spectra of (-)-1,4-dimethylhexahelicene (2) (— - —), (-)-double layered hexahelicene (7) (———), and (+)-hexahelicene (------) in hexane.

References and Notes

1) All optical rotations reported in this communication refer to the $CHCl_3$ solution at 27°C.
2) J. Tribout, R. H. Martin, M. Doyle, and H. Wynberg, Tetrahedron Lett., 1972, 2839.
3) D. A. Lightner, D. T. Hefelfinger, T. W. Power, G. W. Frank, and K. N. Trueblood, J. Am. Chem. Soc., 94, 3492 (1972); Nature, Phys. Sc., 232, 124 (1971); W. S. Brickel, A. Brown, C. M. Kemp, and S. F. Mason, J. Chem. Soc. A, 1971, 756; W. Hug and G. Wagniere, Tetrahedron, 28, 1241 (1972).
4) H. Falk and K. Schlögl, Angew. Chem. Intern. Ed. Engl., 7, 383 (1968); O. E. Weigang, Jr. and M. J. Nugent, J. Am. Chem. Soc., 91, 4555 (1969); J. Am. Chem. Soc., 91, 4556 (1969); H. Falk, P. Reich-Rohwig, and K. Schlögl, Tetrahedron, 26, 511 (1970); A. Guest, P. H. Hofmann, and M. J. Nugent, J. Am. Chem. Soc., 94, 4241 (1972); Martin[2)] cited Dr. G. W. Frank's X-ray analysis of (-)-[2.2]paracyclophanecarboxylic acid, but this seems to have never been published.
5) M. Nakazaki, Y. Hirose, T. Shimizu, T. Suzuki, A. Ishii, and M. Makimura, Chem. Lett., 1979, 1507; J. Org. Chem., 45, 1428 (1980).
6) Recrystallization from hexane-benzene afforded a 31% yield of the pure trans isomer 1, mp 129-130°C.
7) Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, and H. Yuki, J. Am. Chem. Soc., 101, 4763 (1979); We thank Professor Yuki and Dr. Okamoto in our Department for providing us a valuable sample of optically active poly(triphenylmethyl methacrylate).
8) The 12% optical purity of (-)-2 permitted us to calculate $[\alpha]_{577}$ -5520° for the absolute rotation of (-)-7, and the CD spectra of (-)-2 and (-)-7 in Figure 1 are all adjusted to 100% optical purity based on this assumption.
9) M. S. Newman and D. Lednicer, J. Am. Chem. Soc., 78, 4765 (1956).

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