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PREPARATION OF OPTICALLY ACTIVE 1,6,12c,12d-TETRAMETHYL-12c,12d-DIHYDROCORONENE WITH KNOWN ABSOLUTE CONFIGURATION

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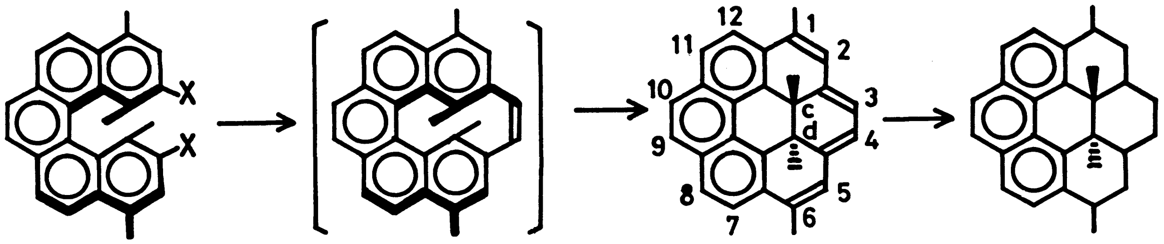
Starting from (M)-(-)-dibromopentahelicene derivative, the novel optically active dihydrocoronene with known absolute configuration was synthesized.

Recently we have reported a number of dissymmetrically condensed aromatic molecules1) as a series of synthetic studies of chiral molecules with high symmetry and with twisted and strained π-electron systems.2) Here we report the preparation of optically active 1,6,12c,12d-tetramethyl-12c,12d-dihydrocoronene (C_2 symmetry) with known absolute configuration.

Optical resolution of (±)-1 3) was achieved by column chromatography over chiral poly(triphenylmethyl methacrylate)(PTrMA).4) Elution with acetonitrile afforded a specimen of (M)-(-)-1,5) mp 234-236 °C, $[\alpha]_D^{25}$ -1206°($CHCl_3$). Lithiation of (M)-(-)-1 with n-BuLi in THF followed by formylation with DMF gave the dialdehyde (M)-(-)-2 (86% yield),7) mp 277-279 °C, $[\alpha]_D^{24}$ -689°($CHCl_3$).



(M)-(-)-(1) X=Br
(M)-(-)-(2) X=CHO
3
(12cS,12dS)-(-)-(4)
5

Although our first object of this study was the synthesis of highly strained bridged-pentahelicene (3) (the valence tautomer of dihydrocoronene (4)), intramolecular reductive coupling of 2 was found to afford directly dihydrocoronene (4). The transannular reductive coupling of (M)-(-)-2 according to Baumstark's procedure ($TiCl_3$-$LiAlH_4$),8) followed by silica gel chromatography and recrystallization from hexane gave (12cS,12dS)-(-)-4 9) (35% yield, red prisms, mp 229-230 °C, $[\alpha]_D^{24}$ -1077°

($CHCl_3$) whose 45% optical purity was determined by HPLC with a column packed with (+)-PTrMA (elution with methanol).$^{10)}$ The ^{1}H-NMR spectrum of 4 showed resonances at δ(ppm) -0.97(s,6H,CH_3), 2.85(d,6H,J=1.1 Hz,CH_3), 7.00(s,2H,=CH-), 7.36(d,2H,J=1.1 Hz,=CH-), and 8.33-8.41(m,6H,ArH). The ^{13}C-NMR spectrum exhibits thirteen peaks corresponding to the molecular symmetry; δ(ppm) 19.99, 21.12($\underline{C}H_3$), 37.24($\underline{C}^{12c}$,$\underline{C}^{12d}$), 120.3, 123.1, 125.1, 125.8, 126.0(=$\underline{C}$H-), 129.7, 129.9, 132.2, 132.4, 137.7(=$\underline{C}$<). In the electronic spectrum (λ_{max}(nm) 256(ε 60400), 265(69100), 274(89900), 294(73400), 320(30900), 336(35600), 353(33500), 372(37400), 445(7800), 471(10100), and 498(7800) in hexane), the presence of three absorption bands in longer wavelengh regions supported the structure of 4 containing phenanthrene ring with conjugated olefinic bonds. Isolation of the octahydro derivative (5) (mp 42-44 °C) from the catalytic hydrogenation (PtO_2, AcOH-EtOAc; r.t.; 0.5 h) of 4 also confirmed the proposed structure 4.

Finally, an attempted photochemical transformation$^{11)}$ of 4 to 3 failed, 4 being recovered unchanged. The equilibrium between 3 and 4 seems to lie almost completely in favor of the dihydrocoronene isomer 4.

References

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9) Optically pure (-)-4 was obtained by HPLC with a column packed with (+)-PTrMA (elution with methanol);$^{10)}$ $[\alpha]_D^{25}$ -2406°($CHCl_3$), mp 226-227 °C; CD(hexane) 10^{-4}[θ](nm) +9.42(255), +12.64(265), +8.07(272), -11.83(282), +5.65(318), +5.38 (335), -3.49(366), -1.85(422), -2.07(467), and -1.24(495).

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