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Short Communication

Chirality due to Deuterium Substitution: Synthesis and Circular Dichroism of (+)$(R)_p$-2,7-Dideuterio-1,6-methano[10]annulene

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Summary. The title compound was prepared from (−)$(S)_p$-2,7-dibromo-1,6-methano[10]annulene by treatment with *n-Bu*-Li and subsequent quenching with D_2O. The optical rotations at four wavelengths and the circular dichroism spectrum are reported.

Keywords. Enantioselective chromatography; Planar chirality; Circular dichroism.

Chiralität durch Deuterium-Substitution: Synthese und Circulardichroismus von (+)$(R)_p$-2,7-Dideuterio-1,6-methano[10]annulen (Kurze Mitt.)

Zusammenfassung. Die Titelverbindung wurde aus (−)$(S)_p$-2,7-Dibrom-1,6-methano[10]annulen durch Umsetzung mit *n-Bu*-Li und nachfolgende Reaktion mit D_2O dargestellt. Optische Rotationen bei vier Wellenlängen und das Circulardichroismus-Spektrum wurden bestimmt.

Introduction

Optical activity that arises from isotopic substitution has fascinated chemists since the discovery of deuterium by Urey in 1932 [1]. It was first accomplished by Eliel in the synthesis of (−)(*R*)-2-^{2}H-ethylbenzene [2]. Although many deuteriosubstituted compounds of C_1 symmetry are known, there are only few planar- or axial-chiral structures which exhibit this phenomenon [3]. Stimulated by our investigations of chiral 1,6-methano[10]annulenes [4], we decided to synthesize optically active 2,7-$^2H_2$-1,6-methano[10]annulene (**2**) and to study its chiroptical properties.

Results and Discussion

The enantiomers of 2,7-dibromo-1,6-methano[10]annulene (**1**) can be separated by enantioselective chromatography on triacetylcellulose in ethanol [5]; their ab-

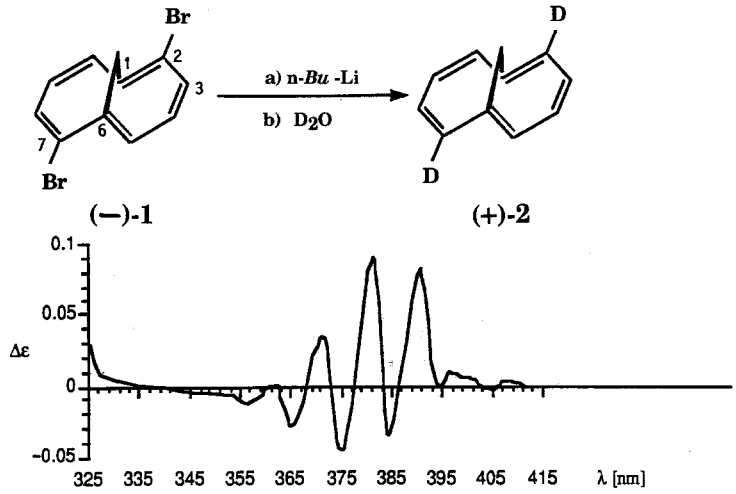

Fig. 1. CD Spectrum of (+)$(R)_p$-2,7-Dideuterio-1,6-methano[10]annulene (**2**)

gations of chiral 1,6-methano[10]annulenes [4], we decided to synthesize optically active 2,7-$^2H_2$-1,6-methano[10]annulene (**2**) and to study its chiroptical properties.

Results and Discussion

The enantiomers of 2,7-dibromo-1,6-methano[10]annulene (**1**) can be separated by enantioselective chromatography on triacetylcellulose in ethanol [5]; their absolute chirality had been established as (+)$(R)_p$ and (−)$(S)_p$, respectively [6]. Reaction of (−)-**1** in dry ether with an excess of *n-Bu*-Li followed by treatment with D_2O gave the desired (+)$(R)_p$-2,7-$^2H_2$-1,6-methano[10]annulene (**2**) in 78% yield [7]. **2** was purified by distillation (b. p. 64−68°C at 0.01 Torr; Kugelrohr; single GC peak) and identified by TLC, UV-, ^{1}H- and ^{13}C-NMR- as well as by mass spectroscopy.

Assuming a statistical replacement of the bromine atoms by D or H, the compound **2** according to MS corresponds to a mixture of 72% of the title compound, 20% of $(R)_p$-2-^{2}H-1,6-methano[10]annulene and 8% of unsubstituted 1,6-methano[10]annulene. The level of deuteration, however, is not easily evaluated, as − even under mild conditions (19.2 eV, 200 μA) and in the case of the undeuterated compound − the $M^+ = 140$ peak is accompanied by relatively strong $M+1$ and $M-1$ peaks. But as chiral 2- and 2,7-substituted 1,6-methano[10]annulenes are known to have qualitatively identical chiroptical properties (the effects for the latter C_2-symmetrical compounds being approximately twice as strong [6]) no great influence is to be expected in the present case.

The chiroptical properties were recorded in *iso*-octane. (+)$(R)_p$-**2** shows a remarkably high specific optical activity $[\alpha]^{20} = +6.3°$ (589 and 578 nm), +8.0° (546 nm) and +19.6° (436 nm; $c = 0.48$). Its CD-spectrum between 320 and 420 nm exhibits an unusual fine-structure (see Fig. 1): [Δε, λ(nm)] −0.01(356), +0.005(362), −0.024(366), +0.035(371), −0.044(375), +0.089(380), −0.033(384), +0.082(390), +0.01(397), +0.006(400), −0.004(404), +0.004(407).

It is of interest to compare this CD-spectrum with the MCD of unsubstituted 1,6-methano[10]annulene. Briat et al. found a positive sign for the MCD between 330 and 380 nm (with small local minima at 385, 387 and 396 nm) [8].

A theoretical study of the CD-properties of (+)-$(R)_p$-**2** is now planned.

Acknowledgements

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References and footnotes

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