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0040-4039(95)00361-4

Synthesis and Characterization of Both Enantiomers of a Chiral C₆₀ Derivative with C₂ Symmetry

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Abstract: The addition of chiral diamines to C_{60} allows the synthesis of the two enantiomers of a chiral C_{60} derivative with C_2 symmetry. The circular dichroism spectra of the two isomers show a very intense chirospectroscopic response.

Although several aspects of the fullerene research have been studied in detail, in this area there have been thus far very few reports on enantiomerically pure compounds. Vasella, Diederich and co-workers synthesized chiral sugar-methanofullerenes.¹ The Hawkins group at Berkeley has conducted a systematic study on the chiral osmylation of C₆₀ and higher fullerenes,²⁻⁴ unveiling exciting properties of these novel chiral π -systems. Finally, Wilson, Schuster and co-workers have separated the enantiomers of the *cis* and *trans* [2 +2] cycloadducts of C₆₀ and a cyclic enone.⁵ The circular dichroism (CD) spectra showed a remarkable difference between the *cis* couple of enantiomers and the *trans* couple of enantiomers. In particular, the *trans* enantiomers were found to give a much greater chirospectroscopic response than the *cis* enantiomers, probably due to a skewed π system with local C₂ symmetry. In the light of these previous results, it is evident that the synthesis of a fullerene derivative with C₂ symmetry would be highly desirable in order to investigate its chiroptical properties. We report herein the synthesis and CD spectrum of the enantiomeric couple of the first chiral C₆₀ derivative with C₂ symmetry.

In order to achieve an easy preparation of both enantiomers in a pure form, the addition of diamines to C_{60} recently reported by Kampe *et al.* was exploited,⁶ owing to the commercial availability of chiral diamines. For the purposes of the present work, the two enantiomers of *trans*-1,2-diaminocyclohexane [S,S-1 (from Fluka, ee>99.5%) and R,R-1 (from Fluka, ee>99.5%), Scheme] were separately subjected to N-methylation *via* reaction with ethyl chloroformate and subsequent reduction with LiAlH4⁷ (Scheme, only the S,S isomer shown).



a, ClCOOEt, NEt₃; b, LiAlH₄, THF; c, C₆₀, toluene, reflux

The resulting N,N'-dimethylated diamines S,S and R,R-2 were independently heated to reflux in a toluene solution of C₆₀. After a week, each reaction mixture was fractioned on a silica column affording S,S-3 and R,R-3 in 10% yield.⁸ The ¹H-NMR spectrum of both enantiomers shows a singlet at 3.48 ppm for the two methyl groups, and a broad signal at 4.18 ppm for the two methine protons. The ¹³C-NMR exhibits 30 signals for the fullerene moiety, thus confirming the C₂ symmetry of the new molecules. Most interestingly, the CD of S,S and R,R-3 displays strong bands which extend to 750 nm. The complete CD spectrum of S,S and R,R-3, along with the UV-Vis spectrum of R,R-3 for comparison, is reported in the Figure.



Figure. (a) (left): UV-Vis spectrum of R,R-3 in CHCl₃ (c = $2.6 \cdot 10^{-5}$ M). λ_{max} =314 (37,200 M⁻¹·cm⁻¹), 698 (360 M⁻¹·cm⁻¹). Inset: UV-Vis spectrum of R,R-3 in cyclohexane (arbitrary units for absorption). (b) (right): CD spectra for R,R-3 and S,S-3 in CHCl₃ (c = $5 \cdot 10^{-4}$ M).

It can be seen that very strong bands in the CD correspond to very weak absorptions in the UV-Vis spectrum. Finally, the specific optical rotation was measured at 589 nm, and found to be: $[\alpha]^{20}D = -803$ deg·cm²·dkg⁻¹ (c = 0.01, CHCl₃) for the R,R isomer, and $[\alpha]^{20}D = +796$ deg·cm²·dkg⁻¹ (c = 0.01, CHCl₃) for the S,S isomer.

Acknowledgments: the authors wish to thank Dr. R. Seraglia for MALDI-MS data. This work was in part developed within the *Progetto Strategico Materiali Innovativi* of the C.N.R.

References and Notes

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(Received in UK 6 December 1994; revised 20 February 1995; accepted 24 February 1995)