Supplementary Material (ESI) for New Journal of Chemistry

Electronic Supplementary Information

First Enantiomerically Pure C_{70}-Adducts with a Non-inherently Chiral Addition Pattern

Agnieszka Kraszewska, Pablo Rivera-Fuentes, Carlo Thilgen and François Diederich*

Laboratorium für Organische Chemie

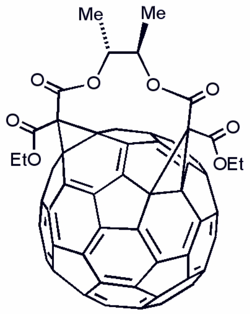
ETH Zürich

Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland

Index

Calibration of ZINDO Calculations for Fullerenes with an Inherently Chiral Addition Pattern

A conformational search was done for *cis*-3 bis-adduct $(R,R,{}^{\mathrm{f},s}A)$-**21** of C_{60} with an inherently chiral addition pattern,[1,2] using the standard Monte Carlo method implemented in Spartan '02,[3] keeping all conformers with an energy ≤10 kcal/mol above the global minimum.



Scheme S1 Structure of $(R,R,{}^{\mathrm{f},s}A)$-**21**.

The search yielded only one relevant structure which is a C_2-symmetric conformer. Although the solid state structure found by X-Ray diffraction is not C_2-symmetric, *Harada* and co-workers[2] proposed on the basis of NMR data that a C_2-symmetric conformation is actually present in solution. The single C_2-symmetric structure obtained at the semi-empirical quantum mechanical (AM1) level was used in the present work. The harmonic vibrational analysis at the same level of theory proved that the structure is a minimum of the PES (Potential Energy Surface).

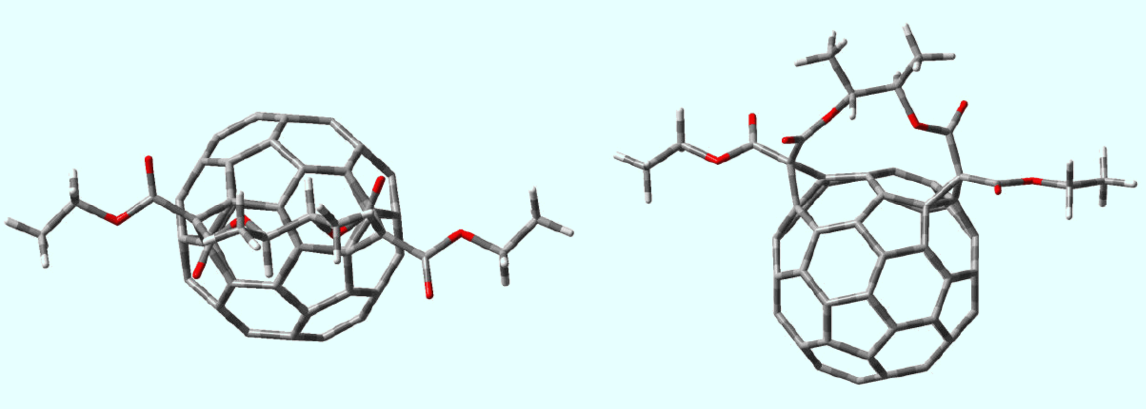


Figure S1 C_2-symmetrical AM1-optimized conformer of (R,R,$^{f,s}A$)-**21**.

This conformer (Figure S1) was taken to be the only one that determines the macroscopic properties and used for the calculation of the excited states.

Using the ZINDO data, the CD spectrum was simulated using the following equation:[4]

$$\Delta\varepsilon(E) = \frac{1}{2.297 \cdot 10^{-39}} \cdot \frac{1}{\sqrt{2\pi\sigma}} \sum_i^A \Delta E_i R_i e^{-\left(\frac{E-\Delta E_i}{2\sigma}\right)^2}$$

A σ value of 0.15 eV. was used for the simulation of the spectrum. The experimental spectrum, as reported by *Diederich* and co-workers,[1] was superimposed for comparison.

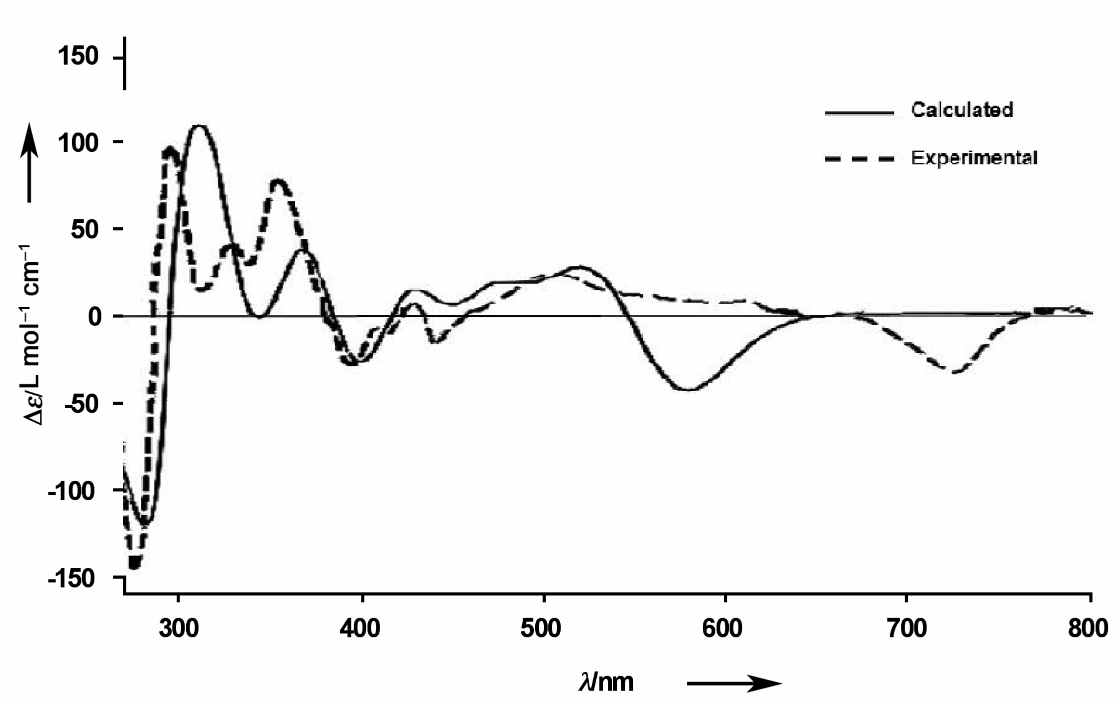


Figure S2 Superposition of the calculated (solid line) and the experimental[1] (dotted line) CD spectra of [CD(+)491]-(*R*,*R*,^{f,s}*A*)-**21**.

In general, the position, relative intensities, and signs of the Cotton effects are accurate in the region between 500 nm and 250 nm. The intensity of every calculated value was multiplied by 2 for a better comparison. Nevertheless, the intensity of the band around 380 nm is somewhat underestimated in the calculation. The biggest discrepancy is found in the excitation energy of the negative Cotton effect at higher wavelengths. The absorption that is located around 715 nm in the experimental spectrum appears blue-shifted by more than 100 nm in the calculated one. Despite of this discrepancy, the methodology used here confirms the absolute configuration assigned by *Diederich*[1] and *Harada*[2] and co-workers.

Based on the success of this methodology to confirm the absolute configuration of a fullerene with an inherently chiral addition pattern, the same sequence of calculations was used for the assignment of the absolute configuration of the enantiomers of 3′-benzoylisoxazolo[4′,5′:7,22](C_{70}-$D_{5h(6)}$)[5,6]fullerene (**20**).

The DFT geometry optimizations for (^{f,s}*A*)-**20** and (^{f,s}*C*)-**20** were done in each case starting from the geometry found in the conformational search at the AM1 level. The two minima found at the AM1 were further optimized at the B3LYP/6-31G(d) level of theory and the convergence was achieved through two different criteria for the different enantiomers. For the (^{f,s}*C*)-**20** enantiomer the optimization completed on the basis of negligible forces (RMS force = 0.00000), for (^{f,s}*A*)-**20** the optimization completed by convergence of all four criteria (Maximum Force, RMS Force, Maximum Displacement and RMS Displacement). It is expected, then, that the two enantiomers will have a slightly different geometry and will consequently show CD spectra that are not exact mirror images (see main text, Figure 6). Nevertheless, the computed difference in energy between the two enantiomers was extremely small (-3180.30126325 a.u. for (^{f,s}*C*)-**20** and -3180.30126315 a.u. for (^{f,s}*A*)-**20**) and although this slight difference might be magnified in the simulation of the CD spectra, it does not affect the sense of the assignment of the absolute configuration. Elimination of this minor inconsistency by the use of tighter convergence criteria or a modified GDIIS algorithm would lead to much longer computation times and the result would not be different from the one obtained in terms of assignment of the absolute configuration.

References

1 R. Kessinger, C. Thilgen, T. Mordasini and F. Diederich, *Helv. Chim. Acta*, 2000, 83, 3069–3096.

2 S. Kuwahara, K. Obata, K. Yoshida, T. Matsumoto, N. Harada, N. Yasuda, Y. Ozawa and K. Toriumi, *Angew. Chem., Int. Ed.*, 2005, 44, 2262–2265.

3 *Spartan `02,* Wavefunction Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612, USA, www.wavefun.com.

4 N. Harada and K. Nakanishi, *Circular Dichroic Spectroscopy, Exciton Coupling in Organic Stereochemistry*, University Science Books, Oxford University Press, 1983.