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Resolution and circular dichroism of an asymmetrically cage-opened [60]fullerene derivative

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The enantiomers of the first cagewise *inherently* asymmetric C₆₀ derivative, *i.e.* N-MEM (MEM = 2-methoxyethoxy-methyl) keto lactam **1**, have been separated by HPLC and their chiroptical properties compared with data obtained from C₆₀ derivatives that are dissymmetric or asymmetric due to chiral addends.

N-MEM keto lactam **1** (Fig. 1) is the first example of a well-defined open-cage derivative of C₆₀.¹ It is obtained from C₆₀ in two synthetic steps, and (±)-**1** serves as the key intermediate in the synthesis of azafullerenes, *e.g.* (C₅₉N)₂,² C₅₉NH³ and K₆C₅₉N.⁴ Stereochemically, **1** is an interesting molecule, because it can be regarded as a (highly symmetrical) sphere with a chiral orifice. A larger version could be envisioned as a chiral selector, operating by enantioselective endohedral complexation.

Various chiral C₆₀ derivatives have been prepared thus far.^{5,6} Chirality can be introduced into C₆₀ derivatives *via* chiral addends, either asymmetric^{7,8} or C₂-symmetric,⁹ as well as *via* an inherently asymmetric addition or substitution pattern, such as in 2:1 adducts with C₂-symmetry.^{10,11} Higher fullerenes and carbon nanotubes can be inherently chiral.¹² C₂C₇₆, D₃C₇₈ and D₂C₈₀ have been obtained in enantiomerically pure form *via* kinetic resolution by asymmetric osmylation, providing optically active forms of carbon.¹³ Since keto lactam **1** is the first open-cage C₆₀ derivative with an inherently asymmetric cage functionalization pattern, it is of interest to determine a possible resemblance of the chiroptical properties of **1** with those of the chirally modified C₆₀ compounds. Here we present the successful resolution of (±)-**1** and the chiroptical properties of the individual enantiomers.

Chromatography of racemic **1** as a 0.3 mg ml⁻¹ solution in toluene–1,2-dichlorobenzene (2:1 v/v) on an analytical chiral stationary phase HPLC column [Bakerbond Pirkle Type DNBPG 5 μm (4.6 × 250 mm)], using *n*-hexane–CHCl₃–PrⁱOH (70:30:1 v/v/v) as the eluent (flow rate 1 ml min⁻¹) and UV detection at λ = 328 nm, gave enough separation to yield the enantiomers in 80 and 92% ee (as inferred from a second HPLC experiment, Fig. 2), respectively. The two fractions were

Fig. 1 Molecular structure of the two enantiomeric forms of **1** with configurational description ¹C and ¹A according to ref. 6

assigned to (+)-**1** and (–)-**1**, respectively, by determining their specific rotations at 589 nm.

The UV–VIS spectrum of (±)-**1**, the circular dichroism (CD) spectrum and the resulting *g* value ($g = \Delta\epsilon/\epsilon \approx \Delta A/A$) of (+)-**1** are shown in Fig. 3. The CD spectrum of (–)-**1** was found to have a mirror image relation to that of (+)-**1**. Similar to the UV–VIS absorption, the CD spectrum of (+)-**1** extends throughout the 200–700 nm spectral range. The strongest Cotton effect is found at λ = 325 nm ($\Delta\epsilon = +29 \text{ M}^{-1} \text{ cm}^{-1}$), coinciding with the lowest energy dipole-allowed transition of **1** (λ = 328 nm). Comparison with, for example, (+)-hexahelicene, which has a *g* value of $+7.0 \times 10^{-3}$ at λ = 325 nm for the π–π* transition, shows however that the *g* value of (+)-**1** ($g_{325} = +6.4 \times 10^{-4}$) is an order of magnitude lower and represents a typical value for a noninherently dissymmetric chromophore.¹⁴ Various chirally modified [6,6]-dihydrofullerene derivatives show a diagnostic CD band at about λ = 430 nm, whose sign has been taken as an indicator for the absolute configuration.^{8,15–17} For (+)-**1**, a local extreme in the CD spectrum is found at λ = 426 nm, where the Cotton effect is negative. Tentatively applying the sector rule of Wilson *et al.* to **1** suggests that (+)-**1** corresponds to the ¹A configuration (Fig. 1).¹⁵ The largest *g* values of (+)-**1** are found in the wavelength range λ = 600–700 nm, with a maximum of $g = -1.7 \times 10^{-2}$ at 659 nm, a typical value for a magnetically-allowed dipole-forbidden transition.

In summary, we have separated the two enantiomers of the C₆₀ derivative (±)-**1** using chiral HPLC, providing a first example of an open-cage fullerene with a chiral orifice. The inherently chiral functionalization of the eleven-membered ring causes a dissymmetric perturbation on the π system of the fullerene, resulting in optical activity extending over the entire

Fig. 2 Chiral HPLC chromatogram of separated samples of (a) (+)-**1** and (b) (–)-**1** (Bakerbond Pirkle Type DNBPG, eluent: *n*-hexane–CHCl₃–PrⁱOH (70:30:1 v/v/v), flow rate 1 ml min⁻¹, UV detection at λ = 328 nm)

Fig. 3 (a) UV–VIS absorption spectrum of (±)-**1** ($c = 7.6 \times 10^{-6}$ M) [$\lambda_{\text{max}}/\text{nm} = 204$ ($\epsilon = 1.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, n -hexane), 260 (1.2×10^5 , CHCl_3), 328 (4.5×10^4 , CHCl_3), 428 (4.7×10^3 , CHCl_3) and 688 (4.2×10^2 , CHCl_3)]. (b) CD spectra (left axis) and g value (right axis) of (+)-**1** ($c = 7.6 \times 10^{-6}$ M). The UV–VIS and CD spectra were recorded using a solution in n -hexane for the region $\lambda = 200\text{--}248$ nm and in CHCl_3 for the region $\lambda = 248\text{--}800$ nm. The CHCl_3 spectra were recorded at higher concentrations and mathematically scaled to the spectrum in n -hexane for representation.

absorption spectrum, with high g values in the low-energy region.

Dedicated to Professor Dr Hans Wynberg on the occasion of his 75th birthday on 28th November 1997.

Footnote and References

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