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. (C90N)2,5 C90NH3 and K2C80N.6 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.3–6 Chirality can be introduced into C60 derivatives via chiral addends, either asymmetric7–8 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, D4C78 and D4C80 have been obtained in enantioselectively 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 11 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–PrOH (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 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 = ΔαΔε = ΔA/Δλ) 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 (Δε = +29 m⁻¹ 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 × 10⁻² at λ = 325 nm for the π–π⁻ transition, shows however that the g value of (+)-1 (g325 = +6.4 × 10⁻²) 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.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 A 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 × 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 wavelength range.

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

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

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

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Footnote and References

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