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Resolution of Enantiomers of *Cis*- and *Trans*-Fused C_{60}-Enone [2 + 2] Photoadducts

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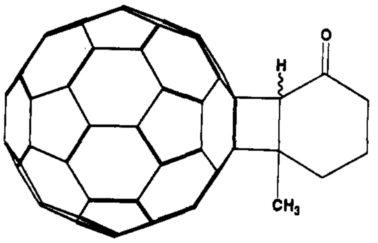
Summary: Enantiomers of the mixture of *cis* and *trans* photocycloadducts of C_{60} and 3-methylcyclohexenone were separated by HPLC on the chiral stationary phase (*S,S*)-Whelk-O; chiroptical properties indicate that the fullerene moiety in the strained *trans* cycloadducts has a skewed π-system with local C_2 symmetry.

The incredible burst of research on C_{60}[1] and related fullerenes over the last few years may be traced to the work of Krätschmer et al.[2] who described a method for preparation of C_{60} in quantity. The present scope of C_{60} reaction chemistry, which is still in its infancy, has been reviewed.[3] We have recently reported several new aspects of C_{60} chemistry,[4] including the preparation of [2 + 2] photocycloadducts of C_{60} and cyclic enones, typified by structure 1.[5]



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The resolution of enantiomers and characterization of their physical and biological properties is a topic of considerable current interest.[6,7] Chiral structures have been proposed for several higher fullerenes[8] and carbon nanotubes,[9] and there is a report of the preparation of an enantiopure adduct of C_{60} and a sugar.[10] Hawkins and Meyer recently reported the elegant kinetic resolution of C_{76}, a chiral allotrope of carbon, by asymmetric osmylation.[11] However, there have been no previous reports of the separation and characterization of enantiomers of a racemic derivative of the highly symmetric buckminsterfullerene molecule, C_{60}, which is an object of great current interest. We report here the successful resolution of the enantiomers of both *cis* and *trans* diastereoisomers of compound 1 and assignments of structure to these materials.

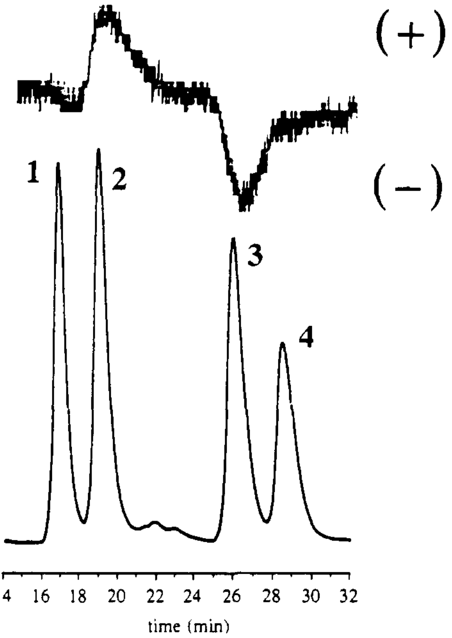

Figure 1. Enantiomeric separation and polarimetric response on injection of a mixture of the *cis* and *trans* isomers of 1 on the (*S,S*)-Whelk-O column. Peaks 1 and 4 are the enantiomers of *cis*-1 and 2 and 3 are the enantiomers of *trans*-1.

Both *cis*- and *trans*-1 are formed in a 40/60 ratio in the [2 + 2] photocycloaddition of 3-methylcyclohexenone to C_{60} and can be separated to near homogeneity on a "Buckyclutcher" HPLC column.[12] Upon injection of the individual diastereomers on a chiral stationary phase (*S,S*)-Whelk-O HPLC column,[13] each isomer is well resolved into its respective enantiomers. The separation factor α is larger for the *cis* (1.90) than for the *trans* (1.45) diastereomer. Indeed, injection of the 40/60 *cis/trans* mixture of 1 on the chiral stationary phase gave resolution into all four stereoisomers, as shown in Figure 1. The

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enantiomers of *trans* 1 show a much greater polarimetric response than do those of *cis*-1 (Figure 1), prompting a further investigation of the chiroptical properties of these materials.

Semipreparative HPLC separation on the (*S*,*S*)-Whelk-O HPLC column resulted in purification of each of the four stereoisomers of 1 to homogeneity. The enantiomers of *trans*-1 (peaks 2 and 3 in Figure 1) were crystalline and sparingly soluble, even in benzene, whereas the enantiomers of *cis*-1 (peaks 1 and 4) were noncrystalline and quite soluble in hexane. While the enantiomers showed identical spectroscopic properties, the NMR, IR, and UV spectra of the *cis* and *trans* series were significantly different. As previously reported,[5] the NMR and IR spectral differences between *cis* and *trans* 1 were critical to assignments of structure to these materials. We now find that *trans* 1 shows two maxima in its UV absorption spectrum at 320 and 340 nm, while *cis*-1 shows only a single maximum at 320 nm. Similar differences were noted in their circular dichroism spectra, shown in Figure 2. The mirror image CD curves for the *trans*-1 enantiomers (Figure 2a) show two maxima (or minima) at 337 and 368 nm, while the curves for the *cis*-1 enantiomers (Figure 2b) show only a single maximum (minimum) at 337 nm. Both isomers also show sharp UV absorption and a CD peak (trough) at 431–435 nm which we find to be characteristic, and even diagnostic, of "6,6-dihydrofullerenes".

We suggest that the longer wavelength CD response and the enhanced optical rotation of the enantiomers of *trans*-1 is due to an induced twist of the fullerene portion of the molecule in the more strained *trans*-fused cycloadduct. Molecular mechanics (MM2) calculations indicate that in *trans*-1 *the fullerene* π-*system is skewed and* C_2 *symmetric*.[14] It is this element of dissymmetry which we believe is the basis of the extra peaks seen in the UV and CD spectra and the relatively large optical rotation of the isomers of *trans*-1.

Application of the classic octant rule[15] to the stereoisomers of 1 suggests that they have the following configurations, in order of their elution from the chiral column (Figure 2): (2*R*,3*S*), (2*R*,3*R*), (2*S*,3*S*), and (2*S*,3*R*). This assignment is consistent with a mechanistic rationale developed to account for the separation of enantiomers of several pharmaceuticals on this chiral stationary phase.[13] However, because of the unusual nature of the stereoisomers of 1, an unambiguous assignment of their absolute configuration is needed. Experiments to achieve this goal, as well as further applications of chiral stationary-phase technology to fullerenes, will form the basis of subsequent reports.

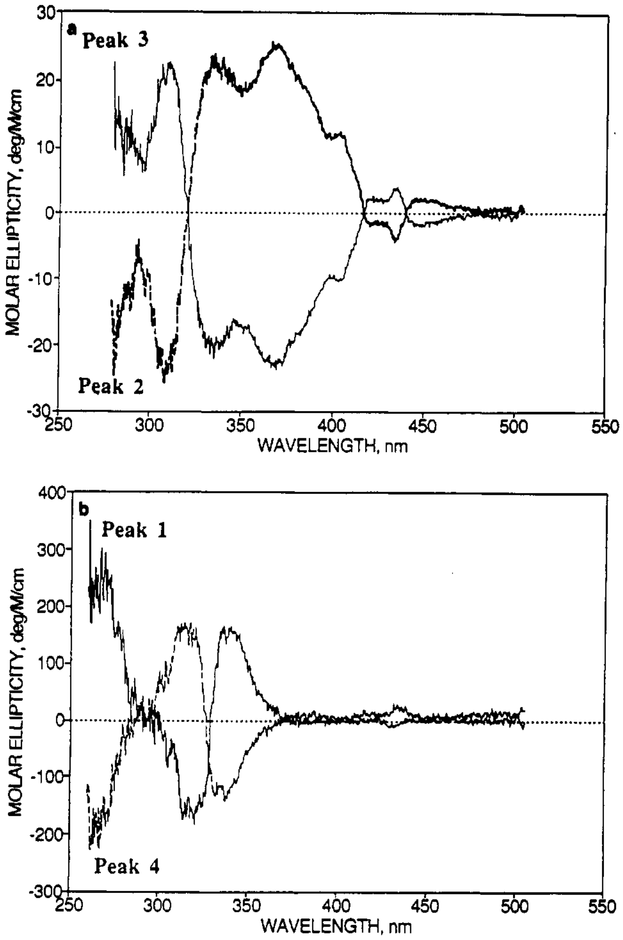

Figure 2. Circular dichroism curves for enantiomers of *trans*-1 (A) and *cis*-1 (B).

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(14) Details of these calculations will be reported separately.

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