to the isomerization of the *cis* and *trans* forms of the aldimine. To prevent the isomerization, the aldimine derived from cyclohexanecarbaldehyde and 2-amino-3-methylphenol was used. It was exciting to find that the enantiomeric excess of the corresponding pyridone derivative improved to 86 %.

In summary, the first catalytic, enantioselective aza-Diels–Alder reactions of imino dienophiles with Danishefsky's dienes have been achieved on using our original chiral zirconium catalyst. Optically active 2,3-dihydro-4-pyridone derivatives were prepared in high yields with good to high enantiomeric excesses. Further investigations to use the zirconium catalyst in other enantioselective reactions as well as to apply the present enantioselective reactions for the synthesis of biologically active compounds are now in progress.

Experimental Section

A typical experimental procedure is described for the reaction of the aldimine obtained from *o*-tolualdehyde and 2-aminophenol with **3**: 6,6′-Dibromo-1,1′-bi-2-naphthol (0.088 mmol) in toluene (0.5 mL) and *N*-methylimidazole (0.12 mmol) in toluene (0.25 mL) were added to $Zr(OtBu)_4$ (0.04 mmol) in toluene (0.25 mL) at room temperature. The mixture was stirred for 1 h at the same temperature, and then cooled to −45 °C. Solutions of the aldimine (0.4 mmol) and **3** (0.6 mmol) in toluene (0.75 mL each) were successively added. The mixture was stirred for 35 h at the same temperature, and saturated $NaHCO_3$ was added to quench the reaction. The aqueous layer was extracted with CH_2Cl_2, and the crude adduct treated with THF/1N HCl (20/1) at 0 °C for 30 min. After a usual work-up, the crude product was purified by chromatography on silica gel to give the desired adduct (83 %). ^1H NMR ($CDCl_3$): $\delta = 2.10$ (s, 3H), 2.68 (dd, 1H, $J = 7.6$, 16.6 Hz), 3.06 (dd, 1H, $J = 7.6$, 16.6 Hz), 5.15 (d, 1H, $J = 7.5$ Hz), 5.52 (t, 1H, $J = 7.5$ Hz), 6.57 (t, 1H, $J = 7.0$ Hz), 6.76–7.00 (m, 6H), 7.38–7.43 (m, 2H), 9.57 (brs, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 19.0$, 42.7, 58.6, 98.2, 117.1, 119.6, 126.1, 126.2, 126.6, 127.7, 128.3, 130.9, 131.5, 134.8, 136.6, 151.8, 156.8, 192.0; HR-MS calcd for $C_{18}H_{17}NO_2$ [M^+]: 279.1259, found: 279.1271. The optical purity was determined to be 82 % *ee* after methylation (MeI, K_2CO_3/acetone) by HPLC analysis with a chiral column. HPLC (Daicel Chiralcel OD, hexane/*i*PrOH (24/1), flow rate 1.0 mL min^{-1}): $t_R = 44.2$ (major enantiomer), $t_R = 50.6$ min (minor enantiomer).

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C_{60} and C_{70} Compounds in the Pincerlike Jaws of Calix[6]arene[**]

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Construction of supramolecular architectures involving electron-deficient fullerenes is of interest in crystal engineering, the synthesis of novel nanostructures, and the development of host–guest chemistry for use in the purification of fullerenes.[1–17] Host molecules that form discrete, albeit inherently weak, complexes with C_{60} and/or C_{70} include

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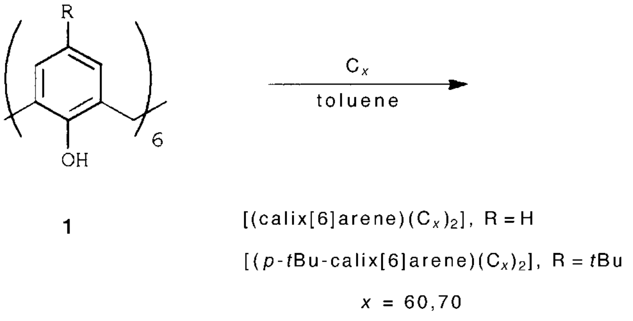
calix[5]-, calix[6]-, and calix[8]arenes,[5–11] cyclotriveratrylene (CTV),[14, 15] γ-cyclodextrin,[16] and azacrown ethers.[17] Two complexes based on the rigid cup-shaped CTV with C_{60} have been structurally authenticated, and both contain "ball and socket" local host–guest structures dominated by fullerene–fullerene interactions. For calix[6]- and calix[8]arenes the nature of the local structures is difficult to predict[11] because of possible preorganization of the calixarene molecules through torsion along the C_{Ar}-CH_2-C_{Ar} bonds prior to complexation.

The calix[6]arenes **1** (R = H, *t*Bu) form fullerene-rich complexes with C_{60} and C_{70}, all of which were isolated as 1:2 complexes (Scheme 1). The synthesis of two of these compounds has been reported;[6] the two new compounds [(*p*-*t*Bu-calix[6]arene)(C_{60})$_2$] and [(calix[6]arene)(C_{70})$_2$] were prepared analytically pure in a similar way, but in more concentrated solutions in toluene. Of the four complexes, crystals suitable for X-ray diffraction studies were obtained only for [(calix[6]arene)(C_{60})$_2$] and [(calix[6]arene)(C_{70})$_2$].[18a] These were grown by controlled slow evaporation of a 1:1 mixture of toluene and dichloromethane containing 5 mg each of the fullerene and the calixarene. Large black crystals deposited over the course of several days as the mixtures became depleted in the chlorinated solvent. Dichloromethane itself blocks the complexation of calixarenes with C_{60} and C_{70}, possibly due to the formation of symmetrical nonclassical hydrogen bonds between hydrogen atoms of the solvent and the π electron clouds of the calixarene aromatic rings.[6, 7] There is little or no discrimination in complexation of C_{60} relative to C_{70} for calix[6]arene, but C_{70} binds preferentially with *p*-*t*Bu-calix[6]arene. Subsequent decomplexation with dichloromethane leads to C_{70} with a purity as great as 95%.



Scheme 1. Reaction of calixarenes with C_{60} and C_{70}.

The complexes [(calix[6]arene)(C_{60})$_2$] and [(calix[6]arene)(C_{70})$_2$] are isostructural despite the anisotropic shape of C_{70}, and both crystallize in the space group $P4_12_12$. The calixarenes are in the double-cone conformation, and each of the associated shallow cavities is occupied by a fullerene. The overall arrangement resembles the jaws of a pincer acting on two adjacent spheres/ellipsoids (Figure 1).

In both structures, the fullerene molecules are positioned unsymmetrically above their associated calixarene cavities. The C_{60} molecule is situated with its center at distances of 7.06(7), 6.91(7), and 6.65(8) Å from the closest ring centroids. In the C_{70} complex the principal axis of the ellipsoidal C_{70} molecule is not directed toward the calixarene cavity. Its center is positioned at distances of 6.85(6), 7.23(7), and 7.46(7) Å from the closest ring centroids.

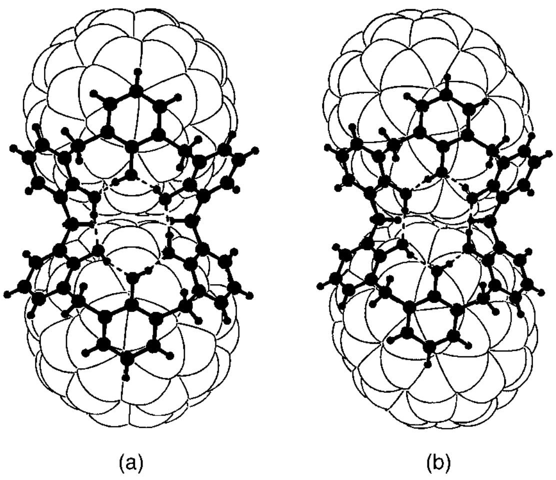


Figure 1. Projection of the structures of [(calix[6]arene)(C_{60})$_2$] (a) and [(calix[6]arene)(C_{70})$_2$] (b) as viewed from below the calixarene double cone. Atoms and bonds of the calixarene molecules are shown in shaded ball-and-stick representation, whereas fullerene molecules are shown as van der Waals surfaces. Hydrogen bonds are indicated by dashed lines.

Each fullerene molecule is in close proximity to six other fullerene molecules and is situated at the common vertex of two fullerene tetrahedra; individual fullerene molecules are less than 11 Å apart. These vertex-sharing tetrahedra form a three-dimensional array interspersed with molecules of calix[6]arene and solvent. Distances between independent centers are 10.04(7), 10.11(7), 10.21(8), and 10.76(7) Å for C_{60} and 10.53(7), 10.56(8), 10.60(7), and 10.66(8) Å for C_{70}. The distances between calixarene and fullerene molecules are somewhat greater than typical van der Waals distances, as are the distances between fullerene molecules in the supermolecules and between fullerenes in the gross structure. All hydroxyl groups of the calixarene units are situated on one side of the molecule and peripherally about the double cone. This is a similar arrangement to that found in solid-state structures of *p*-*t*Bu-calix[6]arene.[19] The OH stretching bands for both of the calix[6]arene complexes are shifted from about 3260 to 3080 cm^{-1}, which indicates a significant increase in the number of hydrogen bonds between hydroxyl groups. In contrast, *p*-*t*Bu-calix[6]arene complexes of the two fullerenes show no significant change in OH stretching bands relative to uncomplexed calixarene.

In solution, dimerization of fullerenes through the pincer/polarizing influence of calix[6]arene and *p*-*t*Bu-calix[6]arene may lead to higher order fullerene aggregates that are perhaps similar in structure to a portion of the solid-state structures described here. Another possibility is a micelle-like species with a central core of fullerene molecules surrounded by a sheath of calixarenes. Solutions in toluene of C_{60} and these calixarenes mobilized in the 5.4-nm pores of a mesoporous silica display a new absorption band at 450 nm, which is assigned to interfullerene electronic transitions.[13] No analogous bands have been identified for the C_{70} system, although spectral evidence suggests that aggregation of C_{70} molecules occurs in acetonitrile/toluene mixtures.[20]

For both calix[6]arene and *p-t*Bu-calix[6]arene it appears that fullerene dimerization is favored over a single fullerene residing in a single calixarene cavity. An interaction of this type would disrupt some of the H bonds. This is not the case for calix[5]arene complexes of C_{60} and C_{70}, for which a cone conformation is generally favored.[21, 22]

Our findings represent a major step forward in the construction of supramolecular assemblies based on calixarene-mediated interlocking of fullerenes. Furthermore, the results have implications in the rational design of host molecules for fullerenes and other large clusters such as icosahedral carboranes, for which the first host–guest species was recently established.[23]

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[18] a) Crystal data for $[(\text{calix[6]arene})(C_{60})_2]\cdot C_7H_8$: crystal dimensions $0.20 \times 0.20 \times 0.15$ mm^3, tetragonal, space group $P4_12_12$, $a = b = 18.8262(6)$, $c = 25.6416(12)$ Å, $V = 9088.0(6)$ Å^3, $\rho_{\text{calcd}} = 1.586$ g cm^{-3}, $\lambda(\text{Mo}_{K\alpha}) = 0.71070$ Å, $T = 173$ K; of 49124 reflections, 9311 were independent and used in the refinement. Final refinement against F^2 converged with $R_1 = 0.1193$ ($wR_2 = 0.2821$) for 6309 unique reflections ($I > 2\sigma(I)$, $1.34 \leq \theta \leq 26.40°$), 788 parameters and 90 restraints. Maximum residual electron density was 0.49 e$^-$ Å^{-3}. Crystal data for $[(\text{calix[6]arene})(C_{70})_2]\cdot C_7H_8$: dimensions $0.50 \times 0.40 \times 0.30$ mm^3, tetragonal, space group $P4_12_12$, $a = b = 19.5897(7)$, $c = 26.1122(14)$ Å, $V = 10020.7(7)$ Å^3, $\rho_{\text{calcd}} = 1.598$ g cm^{-3}, $\lambda(\text{Mo}_{K\alpha}) = 0.71070$ Å, $T = 173$ K; of 58301 reflections collected, 11096 were independent and used in the refinement. Final refinement against F^2 converged with $R_1 = 0.1260$ ($wR_2 = 0.3911$) for 8628 unique reflections ($I > 2\sigma(I)$, $1.30 \leq \theta \leq 27.16°$), 884 parameters and 105 restraints. Maximum residual electron density was 0.61 e$^-$ Å^{-3}. The structures were solved and refined with the Siemens SHELX-TL package. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions with their thermal parameters fixed at values 1.2 times those of the atoms to which they were bound. Difference electron density maps revealed the positions of all fullerene atoms included in the final model, and these were refined with full site occupancy. However, during all stages of refinement, relatively weak peaks of electron density were observed dispersed over the surfaces of the fullerene molecules. This is indicative of a small amount of disorder that was not modeled. As a further indication of possible fullerene disorder, the anisotropic thermal parameters of several of the fullerene atoms were negative. All fullerene bond lengths were constrained to values of 1.45(1) Å for the 6:5 ring fusions and 1.38(1) Å for the 6:6 ring fusions.[18b] A toluene molecule situated on a twofold rotation axis was located in each structure. Owing to disorder, the toluene methyl group was not located in the structure of the C_{60} complex, and hydrogen atoms were therefore not generated for this molecule. Crystallographic data (excluding structure factors) for the structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100886. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). b) M. Fedurco, M. Olmstead, W. R. Fawcett, *Inorg. Chem.* **1995**, *34*, 390–392.

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