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CHIRAL NON-RACEMIC C_{60} DERIVATIVES: A PROPOSED SECTOR RULE FOR FULLERENE ABSOLUTE CONFIGURATION

Stephen R. Wilson,* Qingyi Lu, Jingrong Cao, Yunhui Wu, Christopher J. Welch and David I. Schuster
Department of Chemistry
New York University
New York, NY 10003

ABSTRACT

A number of higher fullerenes as well as carbon nanotubes have been predicted to be chiral. Our lab has recently reported the resolution and CD spectra of several enantiomeric C_{60} derivatives. It appears that chromatographic resolutions using Whelk-O columns are rather general. Using optically active enones and dienes, non-racemic C_{60} adducts can also be formed. Recently we have discovered that fullerene CD spectra appear to arise from a UV band diagnostic for reaction at the C-C bond between two six membered rings, the most common site for mono-addition. A Cotton effect is observed in the CD associated with this chromophore and allows proposal of a sector rule for fullerene chirality. Preparation of chiral (non-racemic) fullerene adducts of known absolute configuration allows assignment of the sign to each of the sectors. These CD bands are due to *asymmetric perturbation of an intrinsically symmetric chromophore* and provide a new tool for *a priori* determination of absolute configuration.

Fullerene chemistry has attracted the interest of a wide cross-section of scientists.[1] Based on cost analysis, commercial applications of fullerenes and fullerene derivatives are envisioned initially in the areas of pharmaceuticals and optics.[2] In both these areas, chiral fullerenes are likely to play an important role. We have been studying chiral fullerene derivatives for several years and report herein a survey of our results. The chiroptical properties of non-racemic fullerene C_{60} mono-addition products allow us to propose a sector rule for assignment of absolute configuration to such molecules.

A number of higher fullerenes[3] as well as carbon nanotubes[4] have been predicted to be chiral. The intrinsic chirality of C_{76} was proven in a most elegant manner by the kinetic resolution of C_{76} by Hawkins,[5] who also studied the kinetic resolution of C_{78} and C_{84}.[6]

For C_{60}, derivatization is generally necessary to introduce chirality.[7] Mono-substituted derivatives C_{60} -R* with a chiral center in the R* group were first reported by Diederich, who prepared a glucose derivative attached to C_{60} and reported its circular dichroism spectrum.[8] The synthesis and CD spectra of peptides attached to C_{60} were reported recently by Prato[9] and co-workers, as well as by Diederich.[10] Our lab was the first to report direct resolution of enantiomeric C_{60} derivatives on a chiral HPLC column.[11] When two groups are attached to the C_{60}

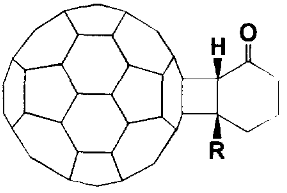
framework, a number of isomers are possible, some of which are chiral. Hawkins and coworkers prepared certain adducts from bis-osmylation of C_{60} in non-racemic form via kinetic resolution.[12]

There are two types of chiral non-racemic fullerene C_{60} derivatives. The first type, wherein the attached R group contains chiral centers is actually quite common and is the result of C_{60} simply serving as a substituent. The C_{60} chromophore in this case is still symmetric but could be asymmetrically perturbed by the attached R group. The second type of chiral C_{60} derivative has two groups dissymmetrically placed on the fullerene core. Hirsch has reported characterization of 7 of the 8 possible isomeric bis-adducts derived from addition of diethylbromomalonate to C_{60}, although he did not resolve the chiral isomers.[13] In this case, the C_{60} chromophore itself is chiral and can lead to very large $[\alpha]_D$ values for the optical rotation as shown by Hawkins for bis-osmate esters.[12]

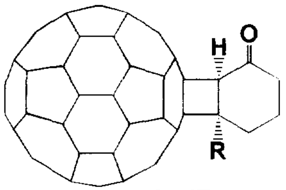
RESULTS

We report herein the preparation of several new adducts of C_{60} and their resolution by chiral HPLC. In addition, we report some reactions of C_{60} with optically active substrates leading to separable diastereomers. Using a facially selective Diels-Alder reaction we have also prepared an optically pure adduct of known absolute configuration. Correlation of circular dichroic spectra of a series of compounds leads to a proposal of a new sector rule for determination of fullerene absolute configuration. The rule is consistent with asymmetric pertubation of the C_{60} chromophore by the substituent groups.

Our first set of chiral HPLC resolutions of C_{60} derivatives has already been reported.[11] From the study of the [2+2] photocycloaddition of cyclic enones to C_{60}, several sets of isomeric C_{60}-enone photoadducts were available.[14]



1a (R = H)
1b (R = CH_3)



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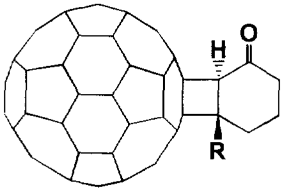
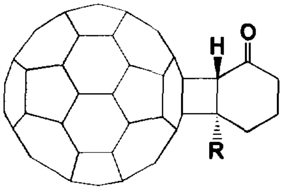
2b (R = CH_3)



3a (R = H)
3b (R = CH_3)



4a (R = H)
4b (R = CH_3)

When compounds **1a**-**4a** (R = H) and **1b**-**4b** (R = CH_3) were injected on a chiral Whelk-O HPLC column,[15] the resolutions shown in Figures 1A and B were achieved.

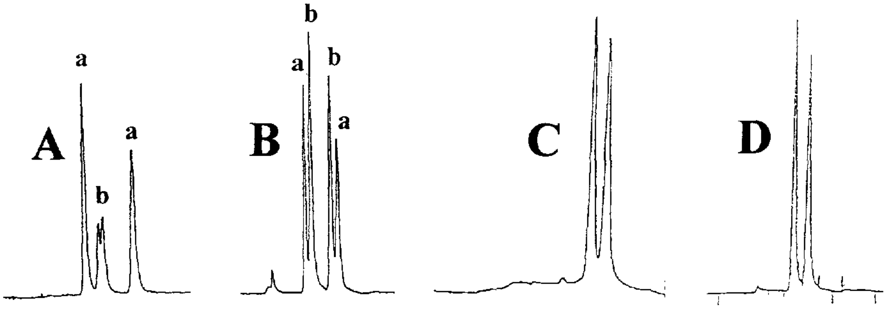


Figure 1. Chiral separations by Whelk-O HPLC chromatography.[11]
A. a. *Cis*-compounds **1a/2a** b. *Trans*-compounds **3a/4a** (toluene, Rt = 5.22, 6.07, 6.27, and 8.01 min). **B.** a. *Cis*-compounds **1b/2b**. b. *Trans*-compounds **3b/4b** (toluene, Rt = 5.43, 5.89, 7.29, and 7.83 min.) **C.** Compound **7**. (toluene, Rt = 4.58 and 5.00 min). **D.** Compound **8**. (1:1 toluene/hexane, Rt = 2.47 and 2.87 min). Flow rate = 1 mL/min, UV detection at 340 nm.

Preparative separation of compounds **1b-4b** on the chiral Whelk-O HPLC column allowed us to obtain CD spectra for each peak as reported in reference 11 and showed that we had resolved both the *cis* isomers **1b/2b** and the *trans* isomers of **3b/4b**. We did not isolate compounds **1a-4a** but HPLC analysis suggests similar isomer assignments since NMR and IR data indicate about a 60:40 ratio of *cis*/*trans* isomers.[16]

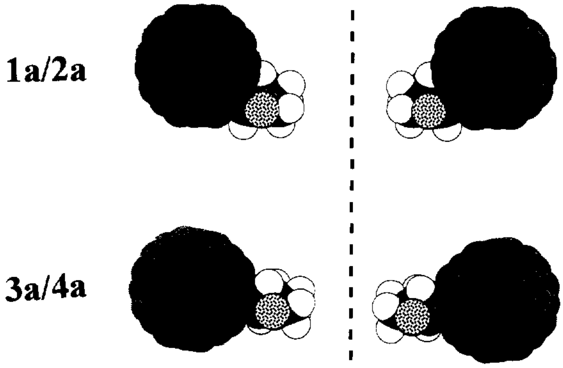
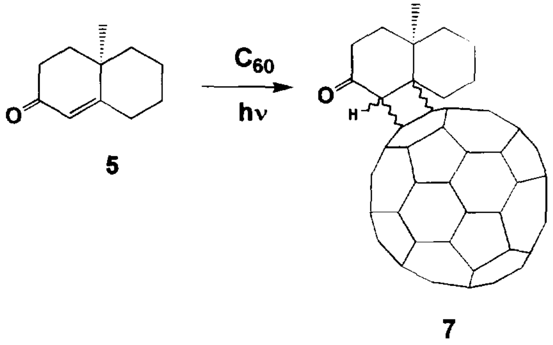


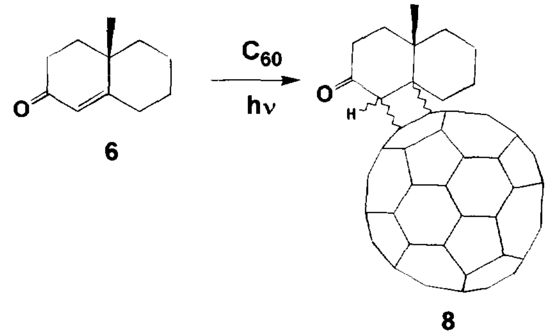
Figure 2. Computer models of *cis* enantiomers **1a/2a** and *trans* enantiomers **3a/4a**.

It is interesting to note from the model of enantiomers **1a/2a** and **3a/4a** that the *trans* (minor) isomers have the ketone group in the plane bisecting the C_{60} core and passing through the cyclobutane ring, while the *cis* (major) isomers have the ketone group well out of the plane bisecting the C_{60}. If the chiral recognition for the Whelk-O column involves coordination to the ketone, the *trans* isomers may present a less well defined chiral structure for molecular recognition than the *cis* isomers. In any case, it is observed that the Whelk-O separations are greater for the *cis* isomers for both **1a-4a** (Figure 1A) and **1b-4b** (Figure 1B) under the same experimental conditions.

We also prepared [2+2]-photoadducts of C_{60} with enantiomeric enones **5** and **6** as shown in equation 1.



(1)



(2)

Cis/trans isomers of [2+2]-photoadducts **7** and **8** are formed, as judged by Buckyclutcher HPLC analysis. Since enones **5** and **6** were enantiomerically pure, each isomer is non-racemic. The major diastereoisomers from each reaction were separated on a Buckyclutcher HPLC column, and tentatively assigned a *trans*-fused structure in analogy with the major [2+2]-photoadduct of testosterone and cyclopentene.[17] The CD spectra of the major [2+2]-photoadducts **7** and **8** are shown in Figure 3.

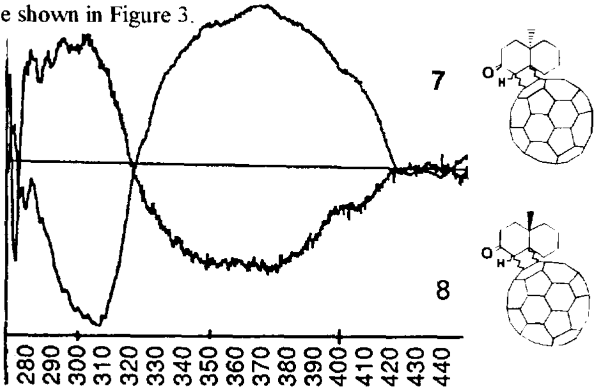
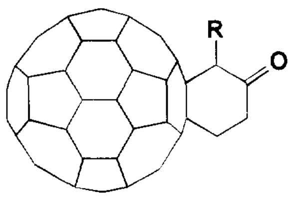
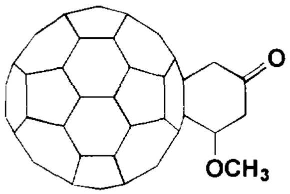


Figure 3. Circular dichroism spectra of major [2+2]-photoadduct isomers of **7** and **8**. (Deviation from exact mirror symmetry is due to experimental difficulties in measuring the very small amounts of compound available.)

Another approach to enantiomeric C_{60} derivatives is available via the Diels-Alder reaction. Cycloaddition of C_{60} with 3-(trimethylsilyl)oxy-1,3-pentadiene and 1-methoxy-3-(trimethylsilyl)oxy-1,3-butadiene leads after hydrolysis to ketones **10** and **11**, respectively.[18] Rubin has reported the related cyclohexanone/ C_{60} adduct **9** and has shown



9 R = H
10 R = CH_3



11

that it has a temperature dependent NMR spectrum due to slow cyclohexanone ring inversion.[19] The inversion process interconverts enantiomeric conformers for compound **9** but such inversion is prevented for substituted ketones **10** and **11** (cf. the model for one enantiomer of **10** in Figure 4A). The NMR spectrum of compound **10** (Figure 4B) is very similar to the low temperature spectrum for compound **9** reported by Rubin where ring flipping has been frozen out.[19] Compounds **7** and **8** and are enantiomerically resolved on the Chiral Whelk-O HPLC column (see Figures 1C and D.)

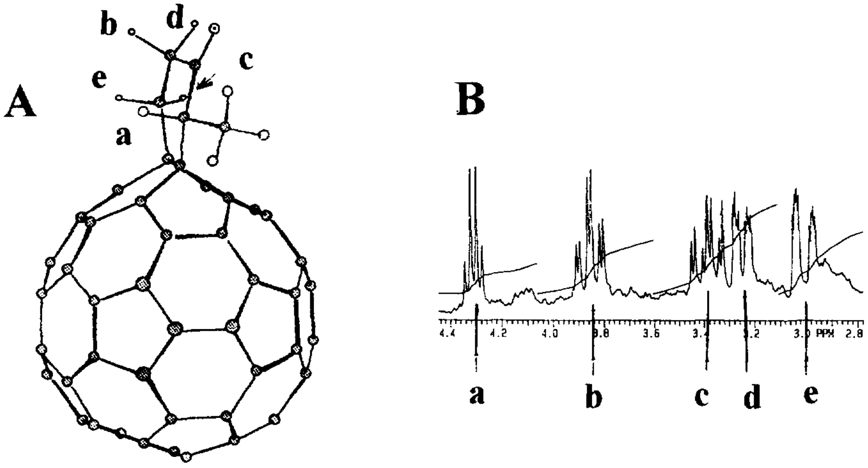
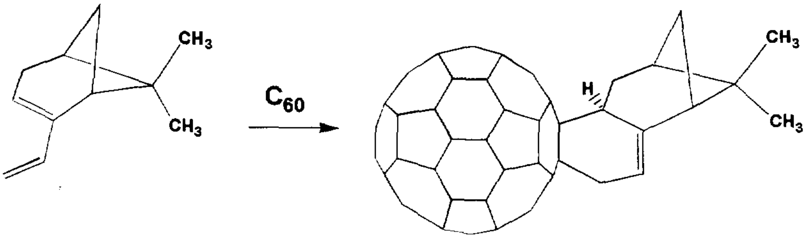


Figure 4. A. Computer model (CSC Chem 3D) of one enantiomer of compound **10**. Without the α-methyl group (i.e. compound **9**), slow ring flipping occurs on the NMR time scale.[19] **B**. Expansion of the methylene NMR spectral region for compound **10** (cf. Figure 1 in reference 19.)

In order to avoid the need for tedious chromatographic resolution of C_{60} derivatives, we have been studying diastereofacially selective Diels-Alder chemistry. One of the best dienes for this process is optically active *R*-nopadiene **12**, which can be prepared from 1-(*R*)-(+)-α-pinene.[20] Diels-Alder attack of C_{60} was expected to occur from the face of *R*-nopadiene **12** opposite from the methyl groups, leading to compound **13**. Indeed, only one product (64 % yield) is obtained when diene **12** is heated with C_{60} in benzene at reflux. The structure of this single



12 **13**

diastereoisomer of **13** was deduced by 1D- and 2D-NMR, electrospray MS, and UV-Vis spectroscopy. Buckyclutcher HPLC also shows a single peak at 9 min (40/60 toluene/hexane). NMR assignments clearly demonstrate the expected facial selectivity of the cycloaddition as opposite to the gem-dimethyl substituted bridge.

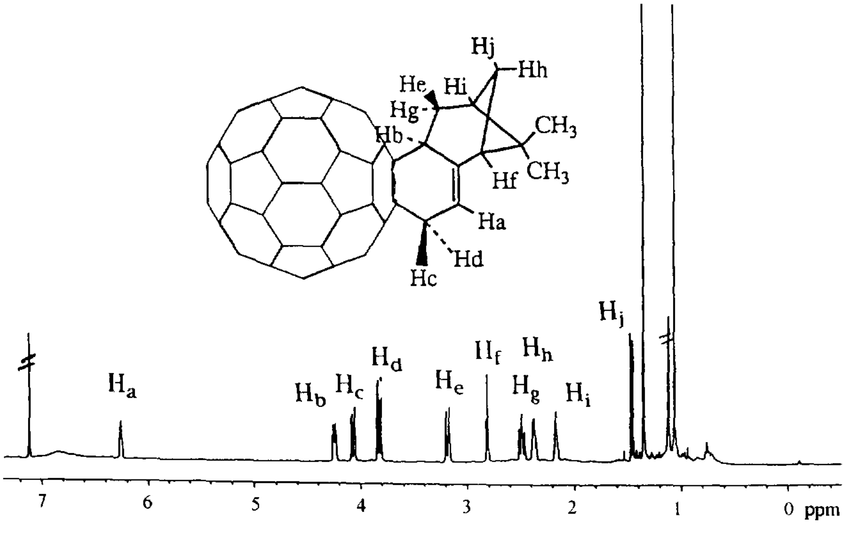


Figure 5. NMR spectrum of *R*-nopadiene-C_{60} adduct **13** (impurities at δ 1.1 and 7.2 are marked.)

Interpretation of the ^{1}H-NMR spectrum in Figure 5 was facilitated by the H-H COSY 2D-NMR spectrum (data not shown).[21] A safe entry point is the downfield vinyl proton quintet at δ 6.27 for H_a. Four coupling partners could be located in the H-H COSY spectrum. All three protons adjacent to C_{60}, unlike those in the fluctional case of compound 9 reported by Rubin,[19] have well-resolved J values. This phenomenon is attributed to the rigidity of the adduct and the shielding effect of the C_{60} moiety. The doublet of triplets at δ 3.24 assigned to proton H_e at the exo position, which is coupled to the geminal proton H_g with J=14.4 Hz and to the two vicinal protons H_h and H_i with J=3.6 Hz. The endo proton H_g is shifted upfield to δ 2.50 and the signal is split into a triplet of doublets. The triplet at δ 2.84 is assigned to the bridgehead proton H_f, which is more shielded than the other bridgehead proton H_i. The H_i resonance appears at δ 2.18 as a broad peak because of the multiple couplings. Long range coupling occurs between the two protons H_f and H_i. Consistent with the reported upfield shifts of the endo proton of the methylene group on the four-membered ring, H_j appears at δ 1.53 as a doublet while the exo-positioned proton H_h is centered at δ 2.40 as a doublet of triplets. Torsional angles of about 90° for H_i-C-C-H_j and H_j-C-C-H_f explain the lack of coupling of endo proton H_j with the two bridgehead atoms H_i and H_f. The data clearly indicates that an enantiomerically pure fullerene adduct is formed. It is interesting to note the wide separation of proton signals as a result of the C_{60} core. which functions as an NMR shift reagent.

A Sector Rule for Fullerene Absolute Configuration

Continuing work in our lab has lead to the discovery that the CD spectra for optically active fullerene derivatives appear to arise from the same chromophore. A "1,2-dihydrofullerene" UV band[29] diagnostic of reaction at the C-C bond between two six membered rings has been recognized by many workers.[22-24] This band at ~430 nm (shifted from 408 nm in C_{60}) is present in $C_{60}H_2$,[25] $C_{60}(t\text{-}C_4H_9)H$,[26] cyclopropanated fullerenes,[27] and in four,[14] five,[28] and six-membered[18,19] ring-fused compounds. Indeed, while the UV spectrum of C_{60} derivatives is generally quite similar to C_{60} itself, this band serves as a fingerprint for 6-6 substitution.[29] It therefore may not be surprising that a Cotton effect[30] associated with this chromophore is observed in the CD spectrum. Since this chromophore is symmetric around the 6-6 bond we propose a sector rule for fullerene chirality that uses the 6-6 bond as the origin (Figure 6).

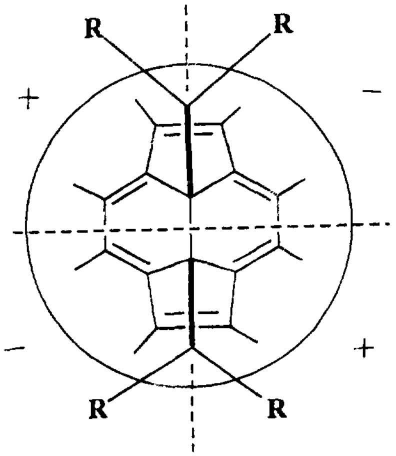


Figure 6. Sector Rule for C_{60} Derivatives. The vertical axis is drawn through the 6-6 $C(sp^3)$-$C(sp^3)$ bond. Location of atoms in + or - sectors defines the sign of the Cotton effect at 430 nm which is used to determine the absolute configuration of attached groups.

One plane is defined by a tangent to the sphere, a second plane goes through the 6-6 single bond and a third plane bisects the 6-6 single bond. This axis system defines positive and negative regions of space for which asymmetric perturbation of the intrinsically symmetric chromophore may be defined.

In order to assign the sign to the sectors, we required a *rigid* chiral (non-racemic) derivative of known absolute configuration. For this purpose the Diels-Alder adduct **13** was employed. A stereoscopic model of this cycloadduct is shown in Figure 7.

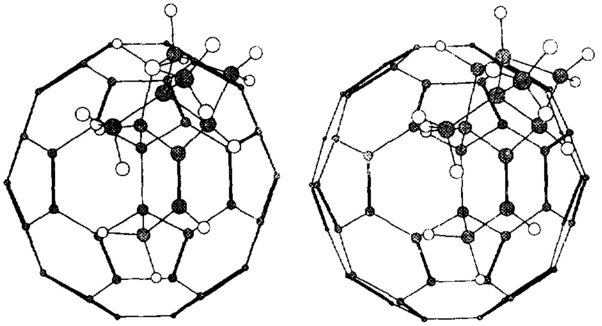


Figure 7. Stereo view of a sector projection of compound **13**. The greatest number of atoms are located in the upper right sector (cf. Figure 6) causing a negative sign of the Cotton effect at 430 nm.

The CD spectrum of compound **13** is shown in Figure 8 along with the CD of one enantiomer of the *trans*-C_{60} -[2+2]-photocycloadduct of 3-methyl-2-cyclohexenone (compound **2**)[11,14] and the major [2+2]-photocycloadduct 7 from equation 1. Clearly, each compound shows an identical Cotton effect near 430 nm. Additional support for this Cotton effect rule may also be found in literature reports of CD spectra of enantiomerically pure C_{60} derivatives of known absolute configuration. The CD spectra of a D-glucose derivative of C_{60}[10] and a phenylalanine derivative of C_{60}[9] shows similar Cotton effects near 430 nm whose sign is consistent with the sector rule model in Figure 6. Recently, Prato and coworkers reported the preparation of an enantiomeric pair of C_2-symmetric C_{60}-derivatives.[31] Their CD spectra show similar strong Cotton effects near 430 nm.

A Cotton effect in the CD can arise from either of two sources. The first is the asymmetry of an *intrinsically chiral chromophore*. Chiral C_{76}[5] and Hawkins' bis-osmylated C_{60} derivatives[12] are examples of this type of chirality. The second source is due to *asymmetric perturbation of an intrinsically symmetric chromophore*. The C_{60} chromophore due to mono-adducted C_{60} derivatives is intrinsically symmetric. Since the sign of the Cotton effect for C_{60} derivatives defines the absolute configuration of the attached derivative, perturbation of the intrinsically symmetric C_{60} chromophore by its interaction with a chiral molecule could serve as a new method for determination of absolute configuration of attached ligands.

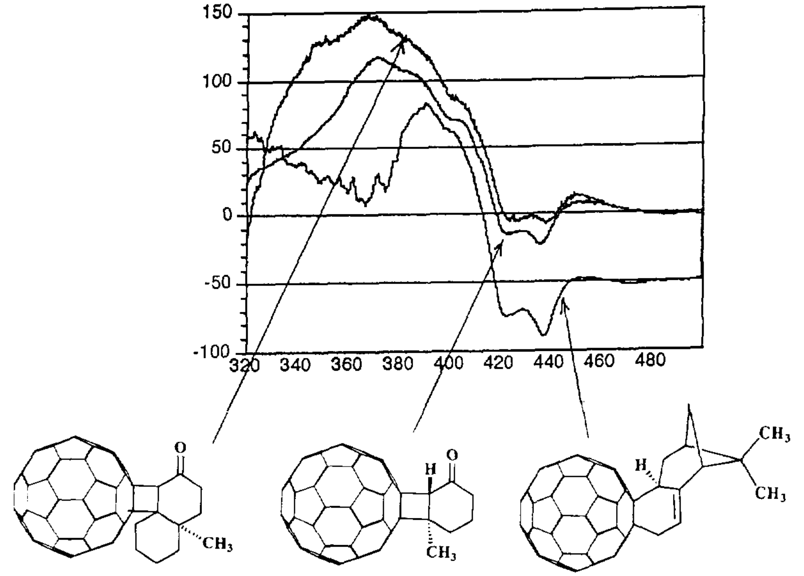


Figure 8. CD spectra of compounds **2**, **7**, and **13**. The negative Cotton effect near 430 nm requires related absolute configurations (cf. sector projection in Figure 6).

EXPERIMENTAL

5',6'-dihydrobenzo-3'-methyl-[1,9][5,6]-fullerene-C_{60}-I_h-4'(3'H)-one 10

To 100 mg (0.139 mmol) of C_{60} in 50 ml toluene, under N_2, 40 ml of 3-(trimethylsilyl)oxy-1,3-pentadiene was added. The reaction mixture was stirred at 105° C for 28 hr. The silyl enol ether was hydrolysed by passing the solution through a silica gel flash chromatography column with toluene to afford compound **10** (40 mg, 35%) as a brown solid. TLC: R_f = 0.35 (toluene). HPLC (Whelk-O chiral column, toluene): R_t = 4.58 and 5.00 min. ^1H NMR ($CS_2/CDCl_3$ = 1:2, see Figure 4): δ 1.80 (doublet, 2H), 2.9 (doublet of multiplets, 1H), 3.24 (doublet of multiplets, 1H), 3.38 (multiplet, 1H), 3.85 (doublet of triplets, 1H), 4.31 (quartet, 1H). ESI-MS[32] (KOAc-MeOH/toluene, m/z) M^+ = 804, X=400 (tagging reagent), MXK^+ =1243.

5',6'-dihydrobenzo-6'-methoxy-[1,9][5,6]-fullerene-C_{60}-I_h-4'(3'H)-one 11

To C_{60} (102 mg, 0.14 mmol) in toluene (27 ml) was added *trans*-1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (24.2 mg, 0.14 mmol) under nitrogen. The resulting mixture was warmed to 45°C for 15 hours. After the mixture was cooled to room temperature, dilute hydrochloric acid in THF (0.0375 N, 40 μl) was added and stirring was continued for 30 minutes. The product was purified by flash column chromatography with toluene/hexane (2:3 to 9:1) to afford compound **11** (44 mg, 38% yield) and the bis-adduct (33 mg, 26%) as a dark brown solid. TLC: R_f=0.49 (toluene). Buckyclutcher HPLC (toluene/hexane 1:1): R_t =21 min. HPLC (Whelk-O chiral column, toluene/hexane 1:1): R_t =2.47 and 2.87 min. IR (CS_2): 1725 cm^{-1} (C=O). ^{1}H-NMR (acetone-d_6/CS_2) δ: 5.00 (s, 1H); 4.80 (bs, 1H); 3.92 (d, 1H, J=14.4 Hz); 3.58 (s, 3H); 3.41 (d, 1H, J=18.3 Hz); 3.43 (dd, 1H, J=18.9, 4.2 Hz). ESI-MS[32] (toluene/MeOH/KOAc): M=820, X=400 (tagging reagent), MXK^+=1259.

R-(+)-Nopadiene **12**

To a dried flask containing methyl triphenylphosphonium bromide (1.18 g, 3.3 mmol) in freshly distilled ether/THF (20 ml, 1.5:1) was added phenyllithium (1.8 M, 3.7 mmol) dropwise under nitrogen at room temperature. The resulting clear brown solution was stirred for 4 hours and myrtenal (450.7 mg, 3.0 mmol) was then added in one portion. After stirring for an additional 3 hours, the reaction mixture was quenched by adding 25 ml of H_2O. The organic layer was separated and the aqueous layer was extracted with ethyl ether (30 ml x 3). The combined organic layers were washed with H_2O (30 ml) and brine (30 ml), dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by vacuum distillation under water pump to afford (+)-**12** (310.7 mg, 70% yield) as a clear colorless liquid (bp 65-75^{0}C/~20 mm Hg). TLC: R_f=0.21 (hexanes/EtOAc 20:1). $[\alpha]^{20}_D$ +33.2^0 ($CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 6.38 (dd, 1H, J=17.4, 10.8 Hz); 5.57 (bs, 1H); 5.07 (d, 1H, J=17.4 Hz); 4.90 (d, 1H, J=10.8 Hz); 2.60 (dt, 1H, J=11.4, 1.6 Hz); 2.44 (dt, 1H, J=11.4, 8.8 Hz); 2.38 (d, 1H, J=3.5 Hz); 2.35 (d, 1H, J=3.5 Hz); 2.14 (bs, 1H); 1.35 (s, 3H); 1.15 (d, 1H, J=8.8 Hz); 0.81 (s, 3H).

(*S*)-1',2',3',4',4a',7'-hexahydro-2',2'-dimethyl[1,3]methanonaphtho[5',6':1,9][5,6]fullerene-C_{60}-I_h **13**

A solution of C_{60} (19.3 mg, 0.027 mmol) and nopadiene (+)-**12** (7.8 mg, 0.053 mmol) in toluene (8.0 ml) was heated at 70^{0}C under nitrogen for 20 hours, at which time HPLC analysis (toluene/hexane 40:60) showed 64% producct yield. The crude mixture was then concentrated and washed with a large amount of methanol to remove excess diene. The methanol was decanted and the solid was redissolved in chloroform. Most of the C_{60} was removed by filtration. The product enriched chloroform solution was then concentrated to dryness. Separation of the residual C_{60} and adduct **13** by flash chromatography proved to be difficult. 1D and 2D NMR were obtained without further purification. The CD spectrum (Figure 8) was obtained from a sample purified by HPLC. TLC: R_f=0.74 (toluene/hexane 2:1). HPLC (toluene/hexane 2:3): R_t=18 min. ^{1}H-NMR ($CDCl_3$) δ: 6.27 (ddd, Ha, Ja-d=7.2, Ja-c=3.6, Ja-b=3.3 Hz); 4.26 (dt, Hc, Jb-e=10.5, Jb-a,g=3.3 Hz); 4.06 (dd, Hc, Jc-d=14.4, Jc-a=3.6 Hz); 3.81 (dd, Hd, Jd-c=14.4, Jd-a=7.2 Hz); 3.24 (dt, He, Je-g=14.7, Je-b,i=3.6 Hz); 2.84 (t, Hf, Jf-h,i=5.4 Hz), 2.50 (td, Hg, Jg-e=14.7, Jh-c=3.3 Hz); 2.40 (dt, Hh, Jh-j=9.9, Jh-if=5.4 Hz); 2.18 (bs, Hi), 1.54 (d, Hj, Jj-h =10.2 Hz); 1.37 (s, 3Hk); 1.10 (s, 3Hl) (see Figure 5). ESI-MS[32] (toluene/MeOH/KOAc) M=869, X=400 (tagging reagent), MXK^+= 1308.

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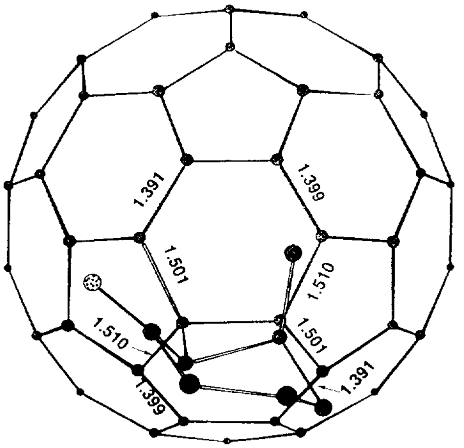

MM3- computed bond lengths (MacroModel) for *trans*-fused enone [2+2]photoadduct **4b**

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