Derivatization of Fullerene Dimer C_{120} by the Bingel Reaction and a ^{3}He NMR Study of ^{3}He@C_{120} Monoadducts

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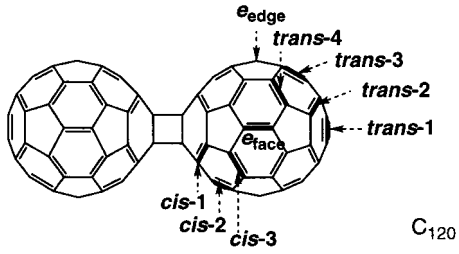
Abstract: Cyclopropanation with diethyl bromomalonate and base (the Bingel reaction) was conducted on fullerene dimer C_{120} to give a mixture of "monoadducts" (45% yield) and "bisadducts" (≤37% yield), while 18% of the C_{120} remained unchanged. The "monoadducts" were separated into five positional isomers, i.e., e_{face}, e_{edge}, *trans*-4, *trans*-3, and *trans*-2, by preparative HPLC. Assignments were made based on ^{1}H (and ^{13}C) NMR and confirmed by theoretical calculations of the addends' ^{1}H NMR chemical shifts. The relative yields of these isomers were in fair agreement with those observed for the Bingel bisaddition of C_{60}. The Bingel reaction was also carried out on the dimer C_{120} encapsulating ^{3}He in one of the C_{60} cages. Each positional isomer of the "monoadduct" exhibited a pair of ^{3}He NMR signals corresponding to an isomer with functionalization on the ^{3}He-containing cage and the other isomer with functionalization on the empty cage. Using the ^{3}He NMR spectroscopy, a pair of signals for the *trans*-1 isomer, which eluded detection by ^{1}H NMR, were observed, in addition to pairs of signals for e_{face}, e_{edge}, *trans*-4, *trans*-3, and *trans*-2 isomers. The ^{3}He NMR signals for isomers with functionalization on the ^{3}He-containing cage were spread out over a 1.82-ppm range reflecting the direct effects of the addition pattern on the C_{60} surface. In contrast, the isomers with functionalization on the empty cage exhibited ^{3}He NMR signals that appeared over a 0.14-ppm range, which was shown to be primarily due to changes in the diamagnetism of the functionalized cage based on theoretical calculations of ^{3}He NMR chemical shifts for the model system in which the C_{60} cage encapsulating ^{3}He was removed.

Introduction

We have previously reported a highly selective synthesis of the fullerene dimer C_{120} by the solid-state reaction of C_{60} using a high-speed vibration-milling technique.[1] This simplest fullerene dimer, C_{120}, is regarded as the essential subunit of fullerene polymers,[2] and the study of its chemical reactivity is of great interest, particularly with respect to the problem of how one of the C_{60} cages would affect the reactivity of the other. Upon the chemical functionalization of C_{120}, the monofunctionalization can be looked upon as bisfunctionalization of one of the C_{60} cages, and there are in principle nine possible reaction sites.



A ^{3}He atom encapsulated in a C_{60} cage is sensitively influenced by the π-electronic ring current of the C_{60} cage,[3] and the use of ^{3}He NMR[4] has proved to be a valuable tool for investigating isomers of C_{60} multiadducts.[3b,5−9] Although the content of a C_{60} molecule encapsulating ^{3}He out of all the empty C_{60} is only approximately 0.1%,[3a] each isomer or derivative gives a single and specific ^{3}He NMR resonance. For example, in the "Bingel" bisaddition, i.e., the biscyclopropanation reaction with a bromomalonate ester and base, for which eight isomers

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(4) The natural abundance of ^{3}He is 1.3×10^{-4} %, but we used 100% enriched ^{3}He to prepare ^{3}He@C_{60}. For ^{3}He, $I = 1/2$ and the NMR sensitivity is 0.44 relative to ^{1}H. The ^{3}He NMR was taken at 381 MHz tuned on a Bruker 500 MHz NMR spectrometer.

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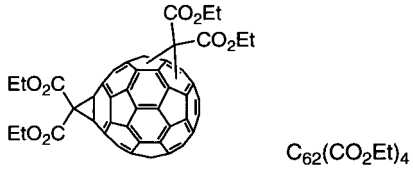
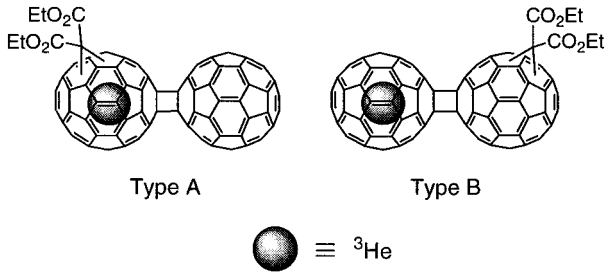
in total can be conceived as products ($^3He@C_{62}(CO_2Et)_4$), ^3He NMR signals for seven bisadduct isomers have been observed[6] and seven isomers have actually been isolated.[10] From the relative intensities of the ^3He NMR signals, relative amounts of each isomer can be estimated even without separation of the isomers.[6] Similar studies have been successfully utilized for the azomethine ylide addition reaction,[6] hydrogenation,[6,7] fluorination,[8] and 9,10-dimethylanthracene cycloaddition,[9] on $^3He@C_{60}$.



$C_{62}(CO_2Et)_4$

We have previously synthesized the fullerene dimer C_{120} encapsulating ^3He in one of the C_{60} cages, i.e., $^3He@C_{120}$.[1b] Herein we wish to report the results of the Bingel cyclopropanation reaction on the fullerene dimer with and without encapsulation of ^3He. Particularly in the case of $^3He@C_{120}$, the derivatization is expected to give two types of isomers, Type A and Type B, for each regioisomer having an addend at a different position. When viewed from the ^3He-containing C_{60} cage, the Type A derivatives can be considered as "bisfunctionalized," while the Type B derivatives are regarded as "monofunctionalized" by another C_{60} cage that is cyclopropanated. The ^3He atom encapsulated in the cage would directly perceive the influence of cyclopropanation for the Type A derivatives, while the influence is indirect for the Type B derivatives. Hence, ^3He NMR measurements of the Type B regioisomers will provide valuable information regarding not only identification of each isomer but also examination of the interaction between the two C_{60} cages.



Results and Discussion

Bingel Cyclopropanation Reaction on C_{120}. First, the Bingel reaction was performed on C_{120} containing no ^3He atom. The reaction was conducted with diethyl bromomalonate (1.3 equiv) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU; 2.2 equiv) in *o*-dichlorobenzene (ODCB) at room temperature for 30 min (eq 1). The reaction mixture produced the HPLC chromatogram (Buckyprep column) shown in Figure 1. A mixture of "monoadducts" was separated from "bisadducts"[11] and from unchanged C_{120} by preparative HPLC through the use of a Cosmosil 5PBB column eluted with ODCB. The yields of "monoadducts" and "bisadducts" were 45% and ≤37%, respectively, while 18% of C_{120} was recovered unchanged. The identification of "mono-" and "bisadducts" fractions was based on the appearance of atmospheric-pressure chemical ionization mass spectra (APCI MS). It is known that the central cyclobutane ring of C_{120} is cleaved under mass spectral conditions.[1] The APCI MS measurements of "monoadducts" gave rise to peaks for C_{60} and $C_{61}(CO_2Et)_2$, whereas measurements of "bisadducts" exhibited peaks for C_{60}, $C_{61}(CO_2Et)_2$, and $C_{62}(CO_2Et)_4$.

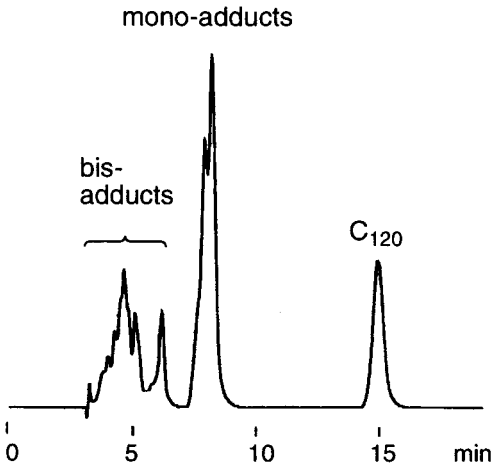
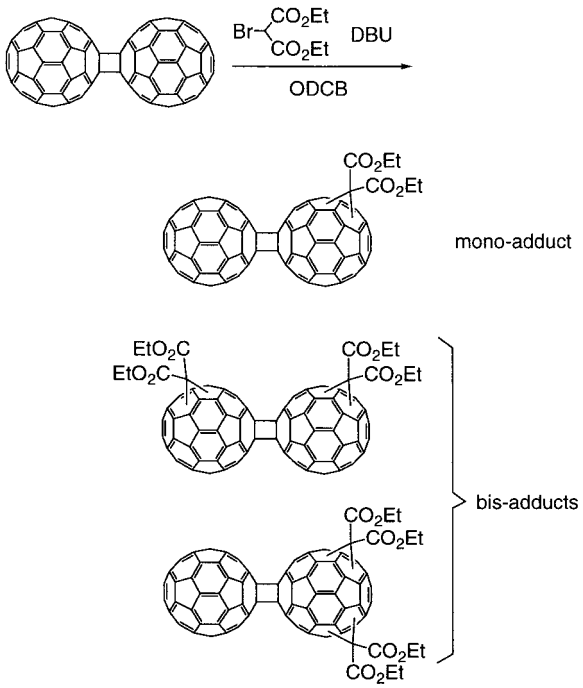


Figure 1. HPLC chart of the Bingel reaction mixture on C_{120}. Conditions: 250 × 4.6 mm Buckyprep column eluted by toluene at 1 mL/min. UV detection at 326 nm.



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(11) As judged from the appearance of the APCI-MS spectra and the elution pattern of the HPLC analysis, there is a possibility that this fraction contains some amount of "tris-adducts".

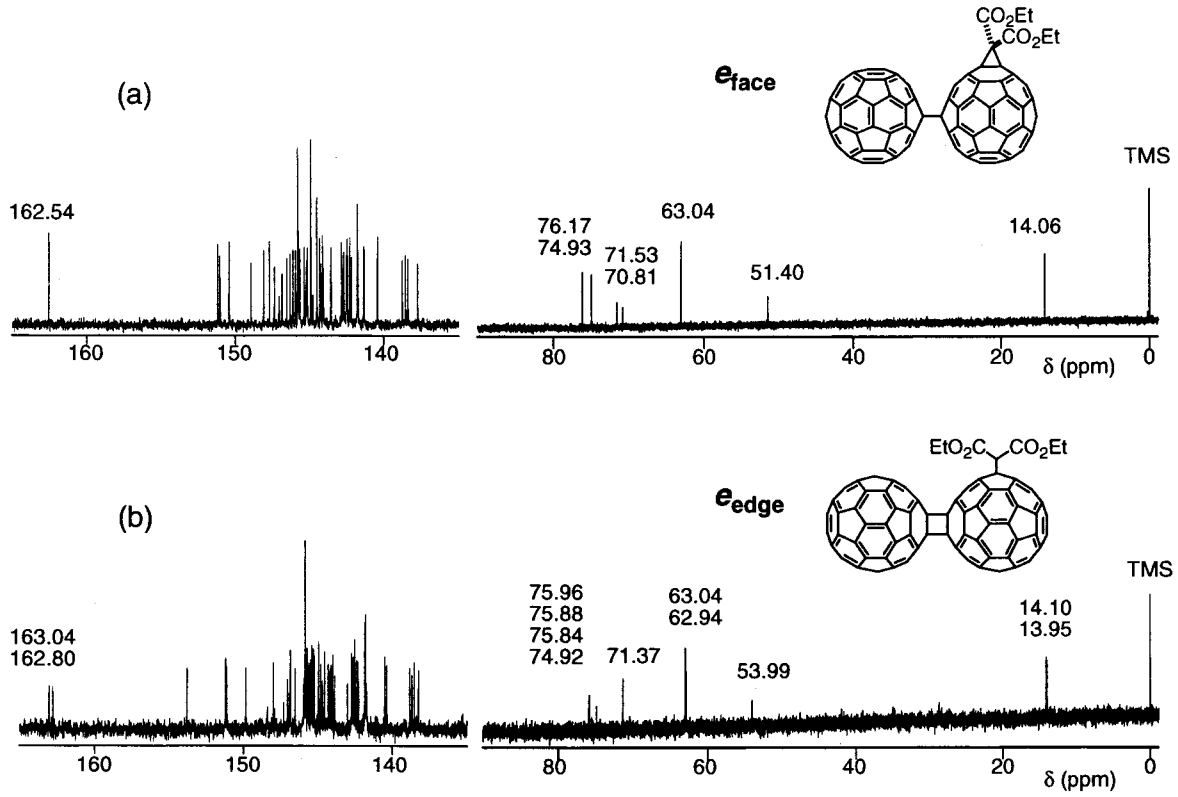

Figure 2. ^{13}C NMR spectra of (a) Fraction 1 ("e_{face}" isomer) and (b) Fraction 3 ("e_{edge}" isomer) of the Bingel monoadduct on C_{120}.

Table 1. Relative Yields and ^1H NMR Chemical Shifts of Bingel Monoadducts of C_{120}

		^1H NMR, ppm						deshielding	
fraction	rel yield, %	δCH_2		δCH_3		δ_{calc} CH_3[a]		order	assignment
1	36.4	4.38		1.26		1.58		4	e_{face}
2	6.9	4.51	4.44	1.39	1.31	1.70	1.65	3	*trans*-4
3	22.5	4.44	4.23	1.32	1.14	1.67	1.60	4	e_{edge}
4	26.9	4.55	4.40	1.42	1.31	1.84	1.70	2	*trans*-3
5	7.3	4.74	4.48	1.57	1.37	1.83	1.77	1	*trans*-2

[a] Calculated by using the HF/3-21G//PM3 geometry.

The mixture of "monoadducts" was separated into five fractions by preparative HPLC through the use of a Yamazen prepacked silica gel column eluted with ODCB. Each fraction was found to contain only one isomer by ^1H NMR analysis (see below). The product distribution was 36.4% (Fraction 1), 6.9% (Fraction 2), 22.5% (Fraction 3), 26.9% (Fraction 4), and 7.3% (Fraction 5) in the order of elution.

In principle, altogether nine positional isomers, that is, "*cis*-1", "*cis*-2", "*cis*-3", "e_{face}", "e_{edge}", "*trans*-4", "*trans*-3", "*trans*-2", and "*trans*-1", are conceivable for the "monoadduct" of C_{120}. The symmetry of these isomers is C_{2v} for "*trans*-1", C_s for "e_{face}" and "e_{edge}", and C_1 for the rest of them. In the ^{13}C NMR spectra, Fractions 1 and 3 exhibited 51 peaks in the typical sp^2 carbon range of C_{60} derivatives (135−155 ppm), as shown in Figure 2. Supposing an accidental overlap of six or eight peaks, these spectra can be assigned to the equatorial isomers with C_s symmetry. Of these two isomers, the spectrum for Fraction 1 exhibited only one set of signals for the ethoxycarbonyl group at δ 162.54, 63.04, and 14.05 ppm, and signals for the cyclopropane rings at δ 71.53, 70.81, and 51.40 ppm. The carbons of the central cyclobutane rings were observed as two signals at δ 76.17 and 74.93 ppm. These results clearly indicate that this isomer is "e_{face}", with the cyclopropane ring located on the mirror plane and the cyclobutane ring perpendicular to it. In contrast, the ^{13}C NMR spectrum of Fraction 3 exhibited two sets of signals for the ethoxycarbonyl groups (δ 163.04, 162.80, 63.04, 62.94, 14.10, and 13.95 ppm) and four signals for the cyclobutane rings at δ 75.96, 75.88, 75.84, and 74.92 ppm. The cyclopropane carbons appeared as two signals at δ 71.37 and 53.99 ppm. Fraction 3 is therefore considered to be "e_{edge}", with the cyclobutane ring located on the mirror plane and the cyclopropane ring perpendicular to it. In good agreement with this, the ^1H NMR spectra exhibited only one set of signals for the ethyl group for Fraction 1 and two sets of the ethyl signals for Fraction 3 (Table 1).

The ^1H NMR chemical shifts of all the fractions are given in Table 1. With respect to the ^1H NMR spectra of bisadducts obtained by Bingel cyclopropanation and Prato azomethine-ylide addition, it is known that the addends' signals appear from downfield in the following order: "*trans*-1", "*trans*-2", "*trans*-3", "*trans*-4", "*e*", and "*cis*-3".[12] The yield of "*cis*-2" and "*cis*-1" isomers is so low possibly because of steric hindrance so that no NMR data are available. In the ^1H NMR spectra of Fractions 2, 4, and 5, signals for two sets of methyl and methylene protons can be observed, which are shifted downfield compared with those of equatorial isomers. We can assume that the "*trans*-1" isomer is formed in the least amount among the *trans*-isomers for a statistical reason: there is only one reaction site for "*trans*-1" as compared with four for the rest of the *trans*-

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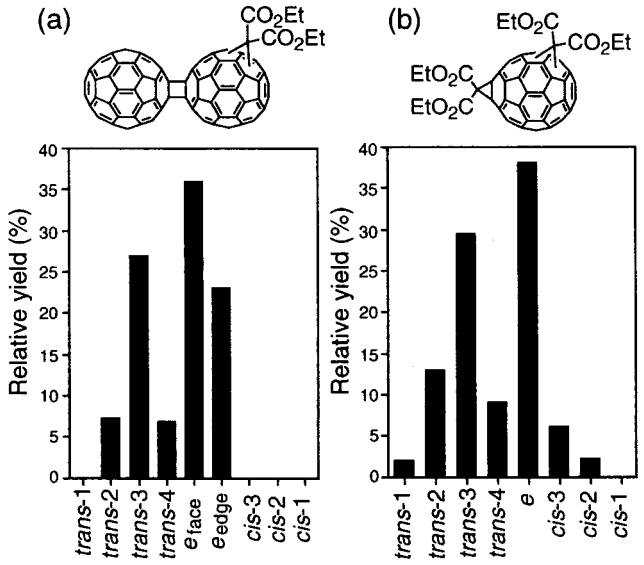

Figure 3. Relative yields of the isolated positional isomers of Bingel addition (a) to C_{120} and (b) to Bingel monoadduct.[12]

Table 2. Relative Heat of Formation Calculated by PM3 for Bingel Monoadducts of C_{120}, in kcal mol^{-1}

cis-1	*cis*-2	*cis*-3	e_{face}	e_{edge}	*trans*-4	*trans*-3	*trans*-2	*trans*-1
26.19	3.15	3.09	0.00	0.07	0.27	0.95	0.41	0.64

isomers. Then, based on the deshielding order of the chemical shifts, Fractions 2, 4, and 5 are assigned to "*trans*-4", "*trans*-3", and "*trans*-2" isomers, respectively (Table 1), by analogy to the reported tendency of the downfield shift of the bisadduct NMR signals.[12] Formation of the "*trans*-1" isomer could not be confirmed by ^{1}H NMR.

To confirm the validity of the above assignments, GIAO-SCF/3-21G calculations (PM3 geometry) were conducted to obtain the chemical shifts of methyl protons of each ethoxycarbonyl group. As shown in Table 1, the general trend in the observed deshielding order of methyl signals was in agreement with the calculated results, although the calculated chemical shifts were 0.3−0.4 ppm more downfield-shifted.

The relative yields of each isolated isomer are shown in Figure 3a, and these are in fair agreement with the results obtained for the Bingel bisaddition reaction[10,13] (Figure 3b). The calculated relative stabilities (the values of the heat of formation relative to the value for the most stable isomer, e_{face}, calculated by the semiempirical PM3 method) for all possible isomers of the "bisadducts" are shown in Table 2. The instability of the *cis*-isomers is possibly due to the steric hindrance caused by the presence of a bulky C_{60} unit, and is reflected in the absence of these isomers in the experimentally obtained Bingel addition product. Among the equatorial addition products, the yield of the "e_{edge}" isomer is apparently lower than that of the "e_{face}" isomer (see also the ^{3}He NMR study described below). This might be taken as evidence that the bulky C_{60} unit is located at a position close to one of the ethoxycarbonyl groups in the "e_{edge}" isomer.

Bingel Cyclopropanation Reaction on ^{3}He@C_{120}. We next proceeded to conduct the Bingel reaction on the fullerene dimer containing a ^{3}He atom in one of the C_{60} cages, i.e., ^{3}He@C_{120}, to examine the ^{3}He NMR for each "monoadduct". The reaction was carried out exactly in the same way as described above for the empty C_{120}. A mixture of "monoadducts" was separated by preparative HPLC through the use of a Cosmosil 5PBB column eluted with ODCB. However, due to the limited amount of reaction product, the subsequent separation by preparative HPLC using a prepacked silica gel column afforded only four fractions, Fractions A, B, C, and D, in the order of elution. On the basis of the ^{1}H NMR and HPLC analyses, the content of each fraction was found to be as follows: Fraction A, "e_{face}"; Fraction B, "e_{face}", "*trans*-4", and "e_{edge}"; Fraction C, "*trans*-3"; and Fraction D, "*trans*-3" and "*trans*-2".

The ^{3}He NMR measurements were then conducted on these four fractions dissolved in ODCB-d_4 containing chromium(III) acetylacetonate as a relaxation reagent to give the spectra shown in Figure 4.

As is most clearly shown by the spectrum of Fraction A, each isomer exhibited a pair of characteristic ^{3}He NMR signals. It has been shown in previous studies that the ^{3}He NMR signals for "bisadducts" generally undergo a considerable upfield shift.[3b,6,14] Thus, between a pair of ^{3}He NMR signals, the upfield signal is assigned to the one corresponding to Type A, which has an addend on the ^{3}He@C_{60} cage, and the downfield signal to the one corresponding to Type B, which has an addend on the empty C_{60} cage. The intensities of the two signals, typically in Fraction A, are equal. This result provides direct experimental evidence that there is no difference in the chemical reactivity of a C_{60} cage based on whether it contains a helium atom.

The assignment of each pair of signals is shown in Figure 4. In the spectrum of Fraction C, an unidentified pair of signals can be observed at δ −8.66 and −8.79 ppm beside the downfield signal of the "*trans*-3" isomer. These signals are assignable to either the "*trans*-1", "*cis*-3", or "*cis*-2" isomer, which eluded isolation in the experiment described above involving the ^{1}H NMR measurements, and "*trans*-1" is considered to be the most probable candidate as judged from the PM3 calculations shown in Table 2.

To confirm these assignments shown in Figure 4, the chemical shift of the incorporated ^{3}He atom was computed by the GIAO-SCF/3-21G calculations for the PM3-optimized structures for all isomers. The results are shown in Table 3. The predicted chemical shift was calculated to be 1−2 ppm further upfield than the experimental value, but when we examined the difference in the chemical shift, $\Delta\delta$, relative to the most upfield shift, that is, the one for the "e_{face}" isomer, there seemed to be qualitatively fair agreement between the observed and calculated values for both Type A and Type B isomers. These results demonstrate that the ^{3}He NMR measurement as well as a calculated estimation of the ^{3}He NMR chemical shift is a useful tool for identification of complicated signals for positional isomers of C_{60} multiadducts either as a mixture or as separated isomers. Among the calculated values of $\Delta\delta$ for "*trans*-1", "*cis*-2", and "*cis*-3", the values for "*trans*-1" are closest to the observed values of $\Delta\delta$, i.e. −8.79 and −8.66 ppm, for the signals of both Type A and Type B, thus confirming the assignment of the ^{3}He signals for this isomer as "*trans*-1". The detection of "*trans*-1" signals only by ^{3}He NMR demonstrates the advantage of this method over the ^{1}H NMR method, by which this isomer eluded detection.

The most notable advantage in the use of ^{3}He NMR is that, for an isomeric mixture like the one in the present work, the signals for individual isomers should be clearly observed, even without separation of each isomer. For the isomeric mixture of the Bingel "monoadducts" of ^{3}He@C_{120}, the ^{3}He NMR mea-

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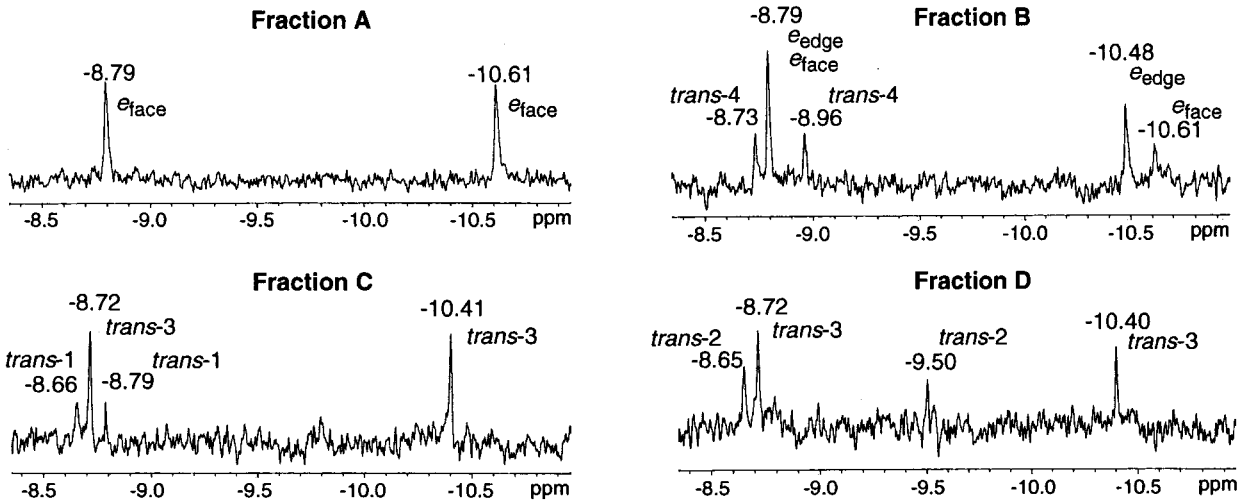


Figure 4. ^{3}He NMR spectra of fractions A, B, C, and D. Chemical shifts are relative to free ^{3}He.

Table 3. ^{3}He NMR Chemical Shifts of Endohedral ^{3}He Fullerene Compounds (ppm)

	Type A			Type B			Type C	Type D
	δ	$\Delta\delta$	$\Delta\delta_{calc}$[a]	δ	$\Delta\delta$	$\Delta\delta_{calc}$[a]	$\Delta\delta_{calc}$[a]	$\Delta\delta_{calc}$[a]
e_{face}	−10.61	0.0	0.0[b]	−8.79	0.0	0.0[c]	0.0[d]	0.0[e]
e_{edge}	−10.48	0.13	0.02	−8.79	0.0	−0.01	−0.02	−0.03
trans-4	−8.96	1.65	1.01	−8.73	0.06	0.02	1.06	0.0
trans-3	−10.41	0.20	−0.08	−8.72	0.07	0.04	−0.13	0.03
trans-2	−9.50	1.11	0.64	−8.65	0.14	0.09	0.60	0.07
trans-1	−8.79	1.82	1.50	−8.66	0.13	0.12	1.45	0.10
cis-3			1.02			0.04		
cis-2			−0.08			0.01		

[a] Computed chemical shifts relative to that for the e_{face} isomer (employing GIAO-SCF/3-21G//PM3 geometry). [b] The calculated δ value is −11.93 ppm relative to free ^{3}He. [c] The calculated δ value is −10.73 ppm relative to free ^{3}He. [d] The calculated δ value is −12.37 ppm relative to free ^{3}He. [e] The calculated δ value is 0.15 ppm relative to free ^{3}He.

surement before separation produced the spectrum shown in Figure 5. The Type A isomers having an organic addend on the ^{3}He@C_{60} cage exhibited ^{3}He NMR signals in a wide chemical-shift range from −8.79 to −10.61 ppm. The order of each signal from downfield is the following: "*trans*-1", "*trans*-4", "*trans*-2", "*trans*-3", "e_{edge}", and "e_{face}". This order is the same as that observed for the case of Bingel bisadducts,[6] except for the downfield shift of the "*trans*-1" signal observed in the present work. It can also be seen that the relative intensity of each signal is in good agreement with the product distribution of each component shown in Table 1.

For the Type B isomers, as the distance between the bis(ethoxycarbonyl)methylene addend and the ^{3}He-containing C_{60} cage increased, the ^{3}He signal was found to be more downfield-shifted. Consequently, the chemical shift of the ^{3}He signal ranged from −8.79 to −8.65 ppm over a width of 0.14 ppm, even though the organic addend was not directly attached to the ^{3}He-containing cage. This can be taken as evidence for an electronic or magnetic interaction between the two C_{60} cages in the C_{120} molecule.

To examine the effects of the presence of a C_{60} cage upon the ^{3}He NMR chemical shifts, calculations of the chemical shift of the encapsulated ^{3}He atom were performed by the GIAO-SCF/3-21G method for the PM3-optimized structures for hypothetical compounds of Type C, in which a C_{60} cage was removed from Type A isomers. In exactly the same way, the chemical shift calculations were conducted for an imaginary Type D system, in which an encapsulating C_{60} cage was removed from the PM3-optimized structures of Type B isomers

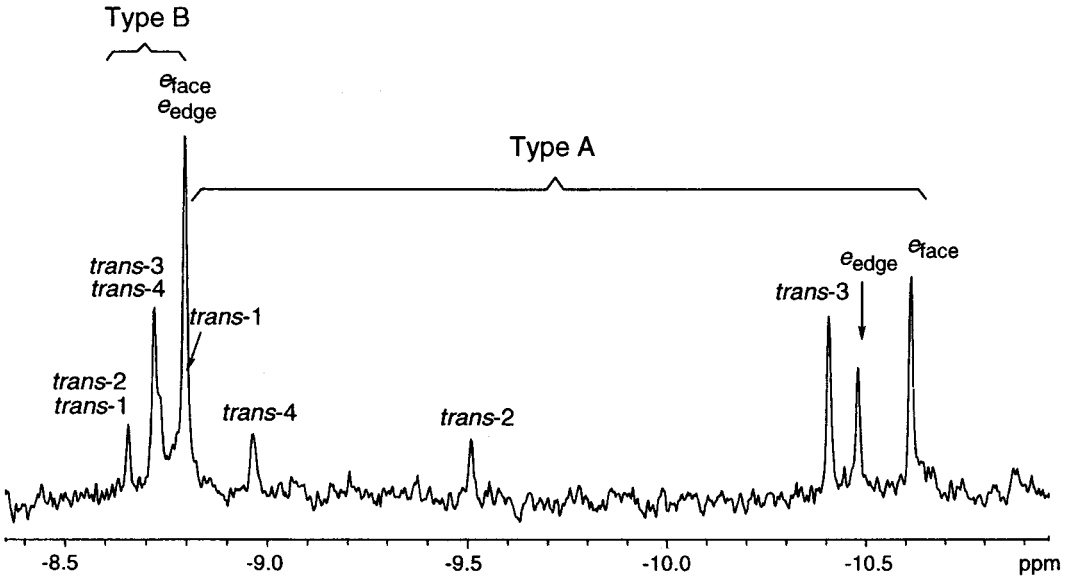
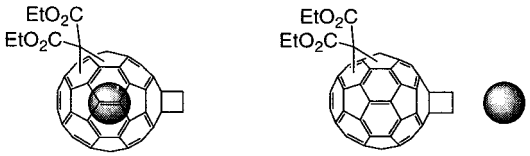


Figure 5. ^{3}He NMR spectrum of a mixture of Bingel monoadducts on ^{3}He@C_{120}.

so that the naked ^{3}He atom was located close to the cyclobutane ring. The results are shown in Table 3. The calculated ^{3}He chemical shift for "e_{face}" of Type C (−12.37 ppm) is 0.44 ppm upfield-shifted as compared with the calculated value for that of Type A. However, the calculated chemical-shift difference relative to "e_{face}", $\Delta\delta_{calc}$, showed fair agreement with the observed values of $\Delta\delta$ for Type A. Thus, the considerably wide range of scattered ^{3}He signals observed for Type A isomers can be attributed to the electronic effects of both the cyclopropane and cyclobutane rings fused to the ^{3}He@C_{60} cage, and the presence of an empty C_{60} cage does not seem to exert much additional effect. In the case of the Type D system, the ^{3}He chemical shift for "e_{face}" was calculated to be 0.15 ppm downfield from the signal for free ^{3}He. Again, the calculated chemical-shift difference relative to "e_{face}", $\Delta\delta_{calc}$, was in fair agreement with the observed values of $\Delta\delta$ of Type B, despite the ^{3}He atom no longer being encapsulated by the C_{60} cage. Thus, this chemical shift difference observed in Type B isomers is considered to have been caused by the diamagnetic effect of the cyclopropanated C_{60}.



Type C Type D

Conclusion

The "monoadducts" of the Bingel cyclopropanation reaction on the fullerene dimer C_{120} were found to contain six positional isomers, i.e., e_{face}, e_{edge}, *trans*-4, *trans*-3, *trans*-2, and *trans*-1. The *cis*-isomers were not formed, possibly due to the steric effect of the opposing C_{60} cage. When the reaction was conducted on the dimer C_{120} encapsulating ^{3}He in one of the C_{60} cages, each isomer was found to consist of one component with functionalization on the ^{3}He-containing cage and another component with functionalization on the empty cage. From the ^{3}He NMR measurement, it was found that there is no difference in reactivity beween the C_{60} cages with or without encapsulation of a ^{3}He atom. Assignments of ^{3}He NMR signals were made for all the isomers. The ^{3}He NMR signals for isomers with functionalization on the ^{3}He-containing cage were spread out over a 1.82-ppm range, reflecting the direct effects of the addition pattern on the C_{60} surface. In contrast, the isomers with functionalization on the empty cage exhibited ^{3}He NMR signals that appeared over a range of 0.14 ppm, mostly due to the diamagnetic effect of the functionalized C_{60} cage. Thus, ^{3}He NMR was shown to be quite useful for the identification of each derivative of products obtained by C_{120} functionalization.

Experimental Section

General. ^{1}H NMR spectra were recorded at 300 MHz on a Varian Mercury-300 spectrometer in *o*-dichlorobenzene-d_4 (ODCB-d_4). ^{13}C NMR spectra were recorded at 100 MHz on a JEOL JMN-AL-400 spectrometer in ODCB−C_6D_6 (5:1). ^{3}He NMR spectra were obtained on a Brucker AM-500 NMR spectrometer in ODCB-d_4 containing Cr(acac)$_3$ as a relaxation agent with ^{3}He gas bubbled in as an internal standard. The high-performance liquid chromatography (HPLC) was conducted on a Shimadzu LC10A liquid chromatograph with a UV detector at 326 nm, using a Cosmosil Buckyprep column (4.6 mm × 250 mm) with toluene as an eluent for analytical purposes and using a Cosmosil 5PBB column (10 mm × 250 mm) with ODCB as an eluent and a prepacked SiO_2 column (Yamazen Ultra Pack SI40B; 26 mm × 300 mm) with ODCB as an eluent for preparative purposes. Fullerene dimer C_{120} was prepared following the literature method.[1b]

Computational Methods. All calculations were conducted with the GAUSSIAN 98 program. Geometries of C_{120} derivatives were fully optimized by using the semiempirical PM3 method. The position of the ^{3}He atom for each isomer of ^{3}He@C121$(CO_2Et)_2$ was determined by optimization at the restricted Hartree−Fock (HF) level by using a standerd 3-21 G basis set. The all chemical shifts of ^{3}He and ^{1}H were computed by the GIAO-SCF method by using a HF/3-21G basis set over PM3 geometries.

Typical Procedure for the Preparation of $C_{121}(CO_2Et)_2$. To a stirred solution of C_{120} (17.5 mg, 0.0121 mmol) in ODCB (16 mL; distilled over CaH_2 before use) was added diethyl bromomalonate (3.64 mg, 0.0152 mmol) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU; 4.07 mg, 0.0267 mmol) under nitrogen and the mixture was stirred for 30 min. The reaction mixture was treated with excess trifluoroacetic acid (0.10 mL, 1.3 mmol) and was concentrated to ca. 4 mL under reduced pressure. The concentrated solution was separated by preparative HPLC by using a 5PBB column eluted with ODCB to afford a mixture of bisadducts, $C_{122}(CO_2Et)_4$ (8.0 mg, 38%), a mixture of monoadducts, $C_{121}(CO_2Et)_2$ (8.7 mg, 45%), and unchanged C_{120} (3.1 mg, 18%): the mixture of bisadducts, APCI MS (negative ion mode) *m*/*z* 720 (C_{60}), 878 ($C_{61}(CO_2Et)_2$), 1036 ($C_{62}(CO_2Et)_4$); the mixture of monoadducts, APCI MS (negative ion mode) *m*/*z* 720 (C_{60}), 878 ($C_{61}(CO_2Et)_2$).

Separation of Monoadduct Isomers. The monoadduct mixture (29.0 mg) was separated by preparative HPLC by using a prepacked silica gel column eluted with ODCB with five recyclings to afford e_{face} isomer (10.0 mg, 34.5%), *trans*-4 isomer (1.9 mg, 6.6%), e_{edge} isomer (6.2 mg, 21.4%), *trans*-3 isomer (7.4 mg, 25.5%), and *trans*-2 isomer (2.0 mg, 6.9%). For the ^{1}H NMR data, see Table 1. The e_{face} isomer: ^{13}C NMR (100 MHz, ODCB−C_6D_6 (5:1)) δ 162.54, 151.16, 151.03, 150.41, 150.39, 148.92, 148.07, 147.68, 147.34, 147.02, 146.82, 146.52, 146.29, 146.10, 145.93, 145.77, 145.72, 145.63, 145.34, 145.21, 145.18, 145.11, 144.88, 144.73, 144.48, 144.29, 144.21, 144.10, 144.03, 143.55, 143.52, 142.82, 142.78, 142.69, 142. 65, 142.49, 142.47, 142.43, 142.26, 142.25, 142.15, 141.76, 141.73, 141.68, 141.31, 141.30, 140.40, 140.39, 138.73, 138.51, 138.35, 137.68, 76.17, 74.93, 71.53, 70.81, 63.04, 51.40, 14.06. The e_{edge} isomer: ^{13}C NMR (100 MHz, ODCB−C_6D_6 (5:1)) δ 163.04, 162.80, 153.81, 151.20, 151.13, 149.82, 148.37, 147.97, 147.88, 147.27, 147.02, 146.87, 146.82, 146.51, 145.93, 145.82, 145.71, 145.64, 145.53, 145.44, 145.39, 145.35, 145.29, 145.21, 144.92, 144.79, 144.67, 144.53, 144.51, 144.29, 144.24, 144.12, 144.10, 143.97, 143.84, 142.97, 142.70, 142.64, 142.57, 142.49, 142.47, 142.35, 142.28, 142.23, 141.81, 141.75, 141.70, 140.47, 140.34, 138.80, 138.67, 138.51, 138.22, 75.96, 75.88, 75.84, 74.92, 71.37, 63.04, 62.94, 53.99, 14.10, 13.95.

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