Theoretical Studies of the Structures and Stabilities of Dumbell-like Fullerene Dimers: C_{121}

Hidekazu Shimotani,*,† Nita Dragoe,†,‡ and Koichi Kitazawa†,‡

Department of Applied Chemistry, The University of Tokyo, Tokyo 113-8656, Japan, and CREST, Japan Science and Technology Corporation (JST)

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Three possible isomers of C_{121}, i.e. [6,6]−[6,6] (**1**, D_{2d}), [6,6]−[6,5] (**2**, C_s), and [6,5]−[6,5] (**3**, C_2), were examined by ab initio MO calculations and a hybrid method of Hartree−Fock and DFT. The geometry optimizations gave closed-bond structures (methanofullerene) for all 6,6-bridge and open-bond structures (homofullerene) for all 6,5-bridge structures. Calculations of energies revealed that **2** is the most stable, while **1** is slightly less stable than **2** by $\Delta(\Delta G_f°(298.15\ K)) = 2.521$ kJ mol^{-1}, and **3** is much less stable than **2** by $\Delta(\Delta G_f°(298.15\ K)) = 21.777$ kJ mol^{-1}. That is explained by the difference of energy between a methanofullerene and a homofullerene, and the strain energy of the spirojunction at the central bridging carbon atom of C_{121}. The predicted IR and Raman spectra of **1**, **2**, and **3** indicate that all of **1**, **2**, and **3** have the same six cage−cage vibrational modes. By comparing the predicted ^{13}C NMR spectra of **1**, **2**, and **3,** and the experimental ^{13}C NMR spectra of C_{121} isolated by HPLC, we concluded that the structure of the C_{121} is **2**, which is the first C_{60} dimer that has both a methanofullerene and a homofullerene moiety.

1. Introduction

Since the discovery of polymerized C_{60}, polymerized C_{60} has been a subject of interest from the viewpoint of electronic interactions between adjacent C_{60} cages as well as promising candidates for new materials.[2] For these reasons, C_{60} dimers have been intensely studied as models for fullerene polymers, in addition to being interesting on their own.

We are interested in all-carbon dimeric fullerenes for several reasons: to study how the close contact of curved π-conjugated structures influences the properties of the molecules and to use dimeric fullerenes as a starting point for growing larger all-carbon clusters. Along these lines, we mention the interesting synthesis of C_{119}, an "odd-numbered" fullerene.[3]

As a consequence, we have studied the synthesis of C_{121}.[4,5] In the previous studies,[4,5] we proposed that the C_{121} dimer has a structure like that of **1** in Figure 1. This structure was been earlier proposed by Osterodt and Vögtle following mass-spectroscopic studies of dibromo-methano[60]fullerene.[6] However, we recently found experimental indications for the existence of a lower-symmetry dimer, C_{121}.[7] For C_{121}, there are three possible structural isomers because of the position of methanobridges. There are two different positions on a C_{60} cage that can make a methanobridge, namely a connection at the junction between two six-membered rings (Figure 2(a)) and that at the junction between a six- and a five-membered ring (Figure 2(b)), called 6,6- and 6,5-junctions, respectively. It is known that, without exception, there is a bond between the bridgehead carbon atoms of a 6,6-junction, while there is no bond between those of 6,5-junctions.[8] These structures are called methanofullerene and homofullerene, respectively. As in the case of carbon-bridged fullerene derivatives, there are three possible structural isomers of C_{121} depending on the bridged positions, named [6,6]−[6,6] (**1**), [6,6]−[6,5] (**2**), and [6,5]−[6,5] (**3**) (Figure 1), whose symmetries are D_{2d}, C_s, and C_2, respectively. Although there is no asymmetric carbon atom, **3** has two optical isomers (**3(a), 3(b)** in Figure 1). To the best of our knowledge, there are no fullerene dimers such as **2**, which contains both a methanofullerene and a homofullerene. The comparison between a methanofullerene and a homofullerene has attracted much attention from the viewpoint of the π-bonding pattern; in other words, a methanofullerene has fewer π-electrons (58 π-electrons) than C_{60} (60 π-electrons), while a homofullerene retains the same π-bonding pattern as C_{60}.

The characterization of the fullerene dimers by experimental methods (^{13}C NMR, IR, and Raman spectroscopy) is greatly impeded by low symmetry and extremely low solubility, particularly in the case of all-carbon derivatives. Consequently, theoretical investigations of their structures, stabilities, and properties are of prime importance. For instance, the power of theoretical models has been used to distinguish among several possible isomers of C_{119}.[9,10] Here, we report the structures and relative stabilities of the three possible isomers of C_{121}, the calculated IR, Raman, and ^{13}C NMR spectra, and the experimental ^{13}C NMR spectrum of C_{121}.

2. Computational Methods

All calculations were carried out using the Gaussian98 program (Revision A.7).[11] The Cartesian *d* function was employed for all calculations. Geometry optimizations were performed with Becke's three parameter hybrid functional[12] (B3) in combination with the correlation functional of Lee, Yang, and Parr[13,14] (LYP) using 6-31G(d) basis set (B3LYP/6-31G(d)), ab initio Hartree−Fock calculation using 6-31G(d) basis set (HF/6-31G(d)), and *semiempirical* calculation using the PM3 Hamiltonian.[15] For all geometry optimization, the symmetries of **1**,

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* Author to whom correspondence should be addressed.

† The University of Tokyo.

‡ CREST, Japan Science and Technology Corporation (JST).

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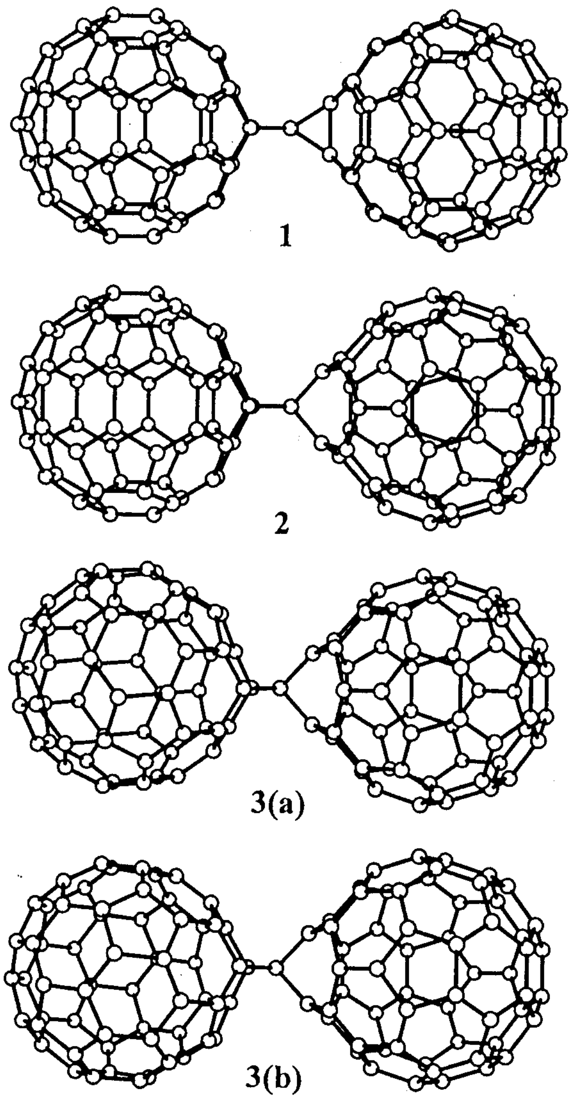

Figure 1. Three possible isomers of C_{121}: **1** [6,6]−[6,6], **2** [6,6]−[6,5], and **3(a,b)** [6,5]−[6,5].

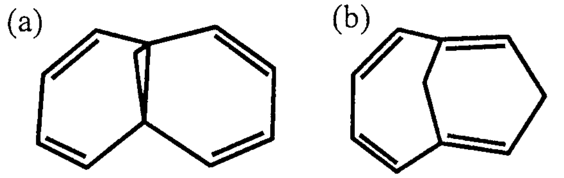

Figure 2. Two positions of methanobridge: (a) 6,6 position and (b) 6,5 position.

2, and **3** were constrained to be D_{2d}, C_s, and C_2, respectively. The optimized structures were confirmed as the local minima by frequency analyses at the HF/STO-3G level of theory; none of them showed imaginary frequencies. Total energies were computed with the B3LYP/6-31G(d) method. Because of the size of the systems, we used smaller basis sets for the frequency analyses and prediction of ^{13}C NMR chemical shifts. Frequency analyses were done with the HF/STO-3G method by analytic evaluation of the second derivative of the energy with respect to nuclear displacement. ^{13}C NMR shielding tensors were computed with the HF/3-21G//B3LYP/6-31G(d) method using the gauge-independent atomic orbital (GIAO) method.[16]

Because of the finite basis set and the neglect of anharmonicity effects and electronic correlation, Hartree−Fock harmonic vibrational frequencies have uniform error relative to the experimental fundamental frequencies and experimental harmonic vibrational frequencies. To correct this error, we determined the scaling factors for predicting the fundamental frequencies, zero-point vibrational energy (ZPVE), thermal contributions of vibration to enthalpy ($\Delta H_{\mathrm{vib}}(T)$), and entropy ($S_{\mathrm{vib}}(T)$) at 298.15 and 750 K, which are listed in Table 1. We followed the method of Scott and Radom[17] to determine these scaling factors from the experimental fundamentals of a total of 128 individual vibrations of 15 molecules that consist of atoms H through F and harmonic frequencies and anharmonic corrections of a set of 20 diatomic molecules (see Supporting Information).

The scaling factor for fundamental frequencies was tested by comparing the computed and experimental IR and Raman frequencies of C_{60}.[18] The rms of error in the test was 39 cm^{-1}.

TABLE 1: Scaling Factors Used in This Study

	scaling factor	rms of error
fundamental frequency	0.8287	83 cm^{-1}
ZPVE	0.8353	1.28 kJ mol^{-1}
ΔH_{vib}(298.15 K)	0.8865	0.053 kJ mol^{-1}
ΔH_{vib}(750 K)	0.8394	0.177 kJ mol^{-1}
S_{vib}(298.15 K)	0.9103	0.299 J K^{-1} mol^{-1}
S_{vib}(750 K)	0.8503	0.558 J K^{-1} mol^{-1}

TABLE 2: Selected Structural Parameters of 1, 2, and 3[a]

	PM3	HF[b]	B3LYP[c]
	1		
C1−C2	0.1482	0.1468	0.1476
C2−C2′	0.1564	0.1596	0.1663
C2−C1−C2′	63.7	65.9	68.5
	2		
C1−C2	0.1480	0.1471	0.1476
C2−C2′	0.2225	0.2224	0.2220
C2−C1−C2′	97.5	98.2	97.6
C1−C3	0.1504	0.1489	0.1500
C1−C4	0.1503	0.1487	0.1494
C3−C1−C4	62.2	63.9	65.8
	3		
C1−C2	0.1500	0.1491	0.1493
C1−C3	0.1502	0.1493	0.1496
C2−C1−C3	94.6	94.4	94.0

[a] Bond lengths in nm, bond angles in degree. [b] HF/6-31G(d). [c] B3LYP/6-31G(d).

3. Results and Discussion

3.1. Geometries of Possible Structures. For C_{121}, there are three possible structures whose selected structural parameters are shown in Table 2, in which carbon atoms were numbered as in Figure 3. For all structures, the distance between the two bridgehead carbon atoms is significantly different between the 6,6-junctions and the 6,5-junctions. For the 6,6-junctions of **1** and **2**, the distances at B3LYP/6-31G(d) are 0.1663 and 0.1628 nm, respectively. On the other hand, for the 6,5-junction of **2** and **3**, the distances at B3LYP/6-31G(d) are 0.2220 nm and 0.2186 nm, respectively. This is consistent with the fact that all 6,6-junctions of the possible structures are closed and all 6,5-junctions are open, as in the case of all known carbon-connected [60]fullerene derivatives.

Theoretical method dependences of structures were also examined and are shown in Table 2. Three theoretical methods give different lengths of the 6,6-junction although they give similar lengths of the 6,5-junction. The order of lengths of the 6,6-junctions is the same for all cases, namely B3LYP/6-31G(d) > HF/6-31G(d) > PM3.

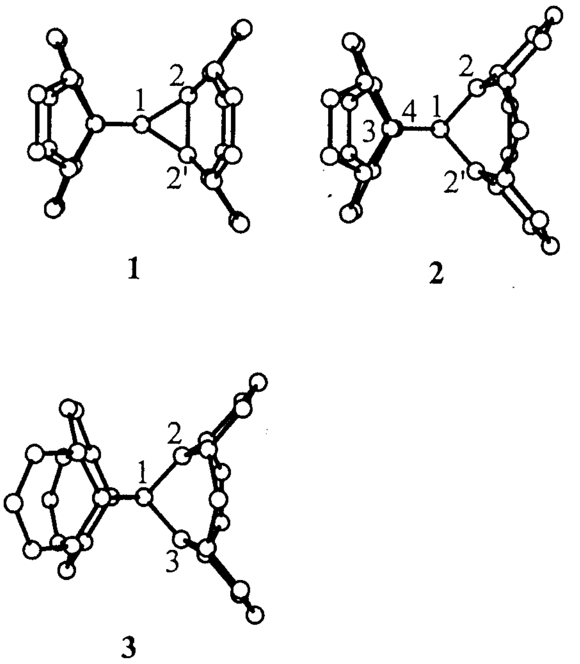

Figure 3. Numbering systems of the carbon atoms in the bridging moiety of (a) **1**, (b) **2**, and (c) **3**.

TABLE 3: Energies, Enthalpies, and Entropies of 1, 2, and 3

isomer	E_{tot} (kJ mol^{-1})	ΔE_{tot} (kJ mol^{-1})	ZPVE (kJ mol^{-1})
1	−12104652.663	0	1922.149
2	−12104649.515	3.148	1918.911
3	−12104627.515	25.148	1915.588

isomer	ΔH_{vib} (298.15 K) (kJ mol^{-1})	S_{vib} (298.15 K) (kJ mol^{-1} K^{-1})	$\Delta(\Delta H_f)°$ (298.15 K) (kJ mol^{-1})	$\Delta(\Delta G_f°)$ (298.15 K) (kJ mol^{-1})
1	103.413	0.53625	0	2.521
2	103.940	0.53481	0.436	0
3	104.449	0.53199	19.623	21.777

isomer	ΔH_{vib} (750 K) (kJ mol^{-1})	S_{vib} (750 K) (kJ mol^{-1} K^{-1})	$\Delta(\Delta H_f°)$ (750 K) (kJ mol^{-1})	$\Delta(\Delta G_f°)$ (750 K) (kJ mol^{-1})
1	910.527	2.12129	0	7.887
2	912.217	2.12258	1.600	0
3	913.997	2.12275	22.057	24.733

The distances of 6,6-junctions obtained with the B3LYP/6-31G(d) method are somehow longer than the typical C−C single-bond length. However, X-ray crystal structure determinations of other methano[60]fullerenes showed that the bond lengths of the 6,6-junction were 0.1614(7) nm and 0.1606(4) nm for (3,4-dimethoxyphenyl)phenylmethano[60]fullerene[19] and diethoxycarbonylmethano[60]fullerene, respectively.[20] These are also longer than the usual C−C bond length but maintain good agreement with the computed bond lengths in **1** and **2** with the B3LYP/6-31G(d) method. Thus, the B3LYP/6-31G(d) method gives better predictions of structures than the two other calculation methods we employed.

3.2. Energetic. *3.2.1. Relative Stability of Isomers.* Total energies(E_{tot}), ZPVE, $\Delta H_{vib}(T)$, and $S_{vib}(T)$, relative standard enthalpies of formation ($\Delta(\Delta H_f°(T))$), and relative standard Gibbs's free energies ($\Delta(\Delta G_f°(T))$) are listed in Table 3. The total energies were computed with the B3LYP/6-31G(d) method, while frequency analyses were done with the HF/STO-3G method. The contributions of rotations and translations were treated as rigid rotor and ideal gas, respectively. Rotational constants (A, B, C) were derived from the structures optimized with the B3LYP/6-31G(d) method and are listed in Table 4. $\Delta(\Delta H_f°(T))$ and $\Delta(\Delta G_f°(T))$ were computed at 298.15 and 750 K (the synthesis of C_{121} was done around this temperature[4,5]).

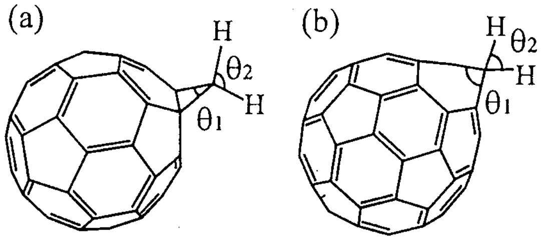

Figure 4. $C_{60}CH_2$ (a) methanofullerene and (b) fulleroid.

TABLE 4: Rotational Constants of 1, 2, and 3 Derived from the Structures Optimized at B3LYP/6-31G(d)

isomer	*A* (MHz)	*B* (MHz)	*C* (MHz)
1	41.8171	10.7713	10.7713
2	41.8082	10.9989	10.9777
3	41.8212	11.1283	11.1281

Comparing the total energies, **1** is the most stable while **2** is slightly less stable (3.148 kJ mol^{-1}). **3** is much less stable than either of the other isomers at both the standard temperature and the reaction temperature. However, comparing $\Delta(\Delta G_f°(T))$, **2** is more stable than **1**, although by a small difference (2.521 kJ mol^{-1}). That is because of the consideration of $\Delta H_{vib}(T)$ and $S_{vib}(T)$. Because these contributions are significant at the reaction temperature, the difference of stability between **2** and **1** at the reaction temperature is larger than that at room temperature. These results suggest that **2** should be stable and isolable. Indeed, we recently succeed in isolating and characterizing **2**, a compound embodying both methanofullerene and homofullerene.[7]

3.2.2. Strain Energy of Spiro Moieties. The relative stability of **1** and **2** seems to be contrary to the general tendency that [6,6]-closed methanofullerenes are more stable than [6,5]-open homofullerenes.[8] The stability of **2** can be explained by the strain energy involved in the central bridge carbon atom of C_{121}, a spirojunction structure. Even though all methanofullerenes and homofullerenes have strained methanobridges (Figure 4), the geometries of their additional groups are not restricted. Therefore, the spirojunction of two methanobridges leads to additional strain.

To evaluate the strain energy (SE), we presumed that the strain energy of a coupled methanobridge moiety of C_{121} is approximately the summation of the strain energies of two C_{60} methanobridges ($SE(\theta_{n,n'})$ for the bridge angle $\theta_{n,n'}$ that is on the n,n'-junction) and the strain energy that is produced by the combination of two methanobridges ($SE_{spiro}(\theta_1,\theta_2)$), whose bond angles are θ_1 and θ_2.

For the evaluation of $SE_{spiro}(\theta_1,\theta_2)$, $C_{60}CH_2$ in a methanofullerene and in a homofullerene form (Figure 4) were employed as model compounds and θ_2 dependencies of their total energy were computed with the B3LYP/6-31G(d) method. In order for SE ($\theta_{n,n'}$) of C_{121} to be included in the total energy of $C_{60}CH_2$, θ_1 was restricted to its value in C_{121} optimized with the B3LYP/6-31G(d) method. As an example, we will show the evaluation of the difference of SE_{spiro} of **1** and **2**.

The total energy of 6,6-closed $C_{60}CH_2$ ($E_{tot,C_{60}CH_2}(\theta_1,\theta_2)$) was computed, where θ_1 was fixed to 68.5°, i.e., $\theta_{6,6}$ of **1**, for the unrestricted case of θ_2 ($E_{tot,C_{60}CH_2}(68.5°,\theta_2{}^{u})$) and for the fixed case of θ_2 at 67.2° ($E_{tot,C_{60}CH_2}(68.5°,67.2°)$), which is the average of $\theta_{6,6}$ of **1** and **2**. The difference between them ($\Delta E_{tot,C_{60}CH_2}$

TABLE 5: Total Energies (E_{tot}) of $C_{60}CH_2$ at Specified Bond Angles

structure	θ_1 (degree)	θ_2 (degree)	E_{tot} (kJ mol^{-1})	ΔE_{tot} (kJ mol^{-1})
6,6-closed	68.5	114.1	−6105520.285	
6,6-closed	68.5	67.2	−6105359.770	160.515
6,6-closed	65.8	114.9	−6105520.915	
6,6-closed	65.8	95.8	−6105496.570	24.345
6,5-open	97.6	109.3	−6105508.285	
6,5-open	97.6	67.2	−6105372.113	136.172
6,5-open	94.0	110.4	−6105528.209	
6,5-open	94.0	95.8	−6105482.323	14.896

TABLE 6: The Difference of SE_{spiro} of 1, 2, and 3

isomer	ΔSE_{spiro} (kJ mol^{-1})
1	33.792
2	9.449
3	0

$(68.5°,\theta_2{}^u \rightarrow 67.2°) = E_{tot,C_{60}CH_2}(68.5°, 67.2°) - E_{tot,C_{60}CH_2}(68.5°,\theta_2{}^u))$ was expressed into

$$\Delta E_{tot,C_{60}CH_2}(68.5°,\theta_2{}^u \rightarrow 67.2°) \approx SE_{spiro}(68.5°, 67.2°) + SE(67.2°)$$

In the same way, for 6,5-open $C_{60}CH_2$,

$$\Delta E_{tot,C_{60}CH_2}(97.6°,\theta_2{}^u \rightarrow 67.2°) \approx SE_{spiro}(97.6°, 67.2°) + SE(67.2°)$$

was computed.

The difference between these two sums is approximately equal to the difference between SE_{spiro} values of **1** and **2**, which are expressed by $SE_{spiro}(\mathbf{1}) = SE_{spiro}(68.5°, 68.5°)$ and $SE_{spiro}(\mathbf{2}) = SE_{spiro}(97.6°, 65.9°)$, respectively.

$$\begin{aligned} SE_{spiro}(\mathbf{1}) - SE_{spiro}(\mathbf{2}) &= SE_{spiro}(68.5°, 68.5°) - SE_{spiro}(97.6°, 65.9°) \\ &\approx SE_{spiro}(68.5°, 67.2°) - SE_{spiro}(97.6°, 67.2°) \\ &\approx \Delta E_{tot,C_{60}CH_2}(68.5°,\theta_2 \rightarrow 67.2°) - \\ &\qquad \Delta E_{tot,C_{60}CH_2}(97.6°,\theta_2 \rightarrow 67.2°) \end{aligned}$$

The same method was applied to evaluate the difference of SE_{spiro} between **2** and **3**. The total energies of $C_{60}CH_2$ at specified bond angles and ΔSE_{spiro} are summarized in Table 5 and Table 6, respectively.

For comparison ΔSE_{spiro} with the difference of thermodynamical stabilities between methanofullerenes and homofullerene, the total energies of some experimentally accessible methanofullerenes (i.e., $C_{60}CH_2$, $C_{60}CCl_2$, $C_{60}CBr_2$, $C_{60}CPh_2$, and $C_{60}CMe_2$) and their homofullerene isomer were computed using the B3LYP/6-31G(d) method. The total energies are summarized in Table 7. The differences of the total energies of homofullerenes from that of methanofullerenes are from 12 to 38 kJ mol^{-1}. On the other hand, the SE_{spiro} of **2** is smaller than that of **1** by 24.343 kJ mol^{-1}, which is comparable to the difference of the total energies of homofullerenes from that of methanofullerenes. Therefore, the cost of having a homofullerene moiety is compensated for by the strain energy of the spirojunction. Thus, the difference of SE_{spiro} is the reason that **2** is more stable than **1**, even though the former has a homofullerene moiety.

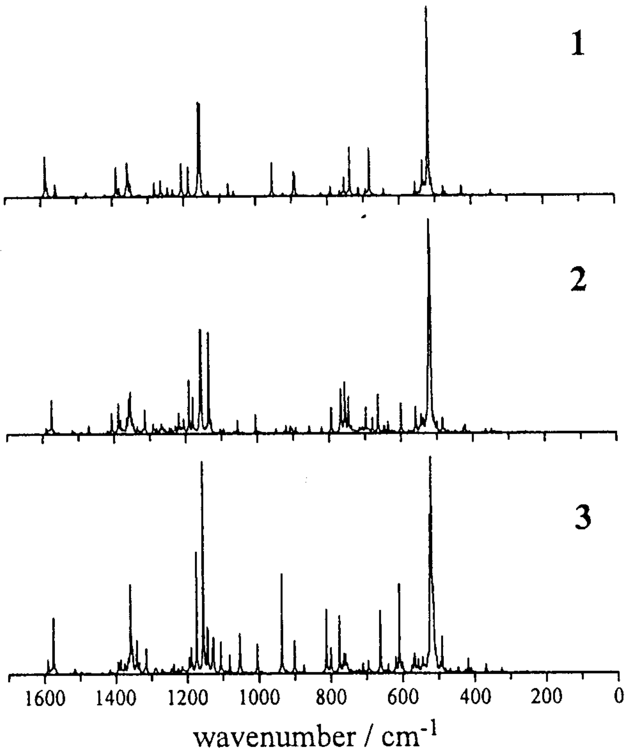

Figure 5. Calculated IR spectra of three isomers of C_{121}.

SE_{spiro} of **3** is smaller than **1** by 33.792 kJ mol^{-1}, but this does not compensate for the presence of two homofullerene moieties (ca. 24−76 kJ mol^{-1}). That is the reason that **3** is much more less stable than either **1** and **2**.

3.3. Calculated IR and Raman Spectra. The point groups, symmetry species of normal vibration modes, and IR and Raman activity for the three isomers are listed in Table 8. Because of the increase of the number of atoms and the significant decrease of symmetry in comparison with C_{60}, all isomers show many more IR and Raman active modes than C_{60}, which has only four IR and ten Raman active modes. The number of IR and Raman active modes are 134 and 223, 351 and 357, and 351 and 356 for **1**, **2**, and **3**, respectively.

IR and Raman spectra were predicted with the HF/STO-3G method. Vibrational frequencies were scaled by the values given in Table 1. Calculated IR and Raman spectra for the three structures are shown in Figure 5 and Figure 6, respectively. All

TABLE 7: The Calculated Total Energies[a](E_{tot}) of Methanofullerenes and Their Fulleroid Isomers

molecular formula	E_{tot} of methanofullerene isomer (kJ mol^{-1})	E_{tot} of fulleroid isomer (kJ mol^{-1})	relative E_{tot} of fulleroid isomer to that of methano fullerene isomer (kJ mol^{-1})
$C_{60}CH_2$	− 6105520.943	−6105509.080	11.863
$C_{60}CCl_2$	−8518804.780	−8518786.173	18.607
$C_{60}CBr_2$	−19606351.063	−19606335.712	15.351
$C_{60}CMe_2$	−6311969.280	−6311935.531	33.749
$C_{60}CPh_2$	−7318758.907	−7318721.385	37.522

[a] Calculated using B3LYP/6-31G(d) method.

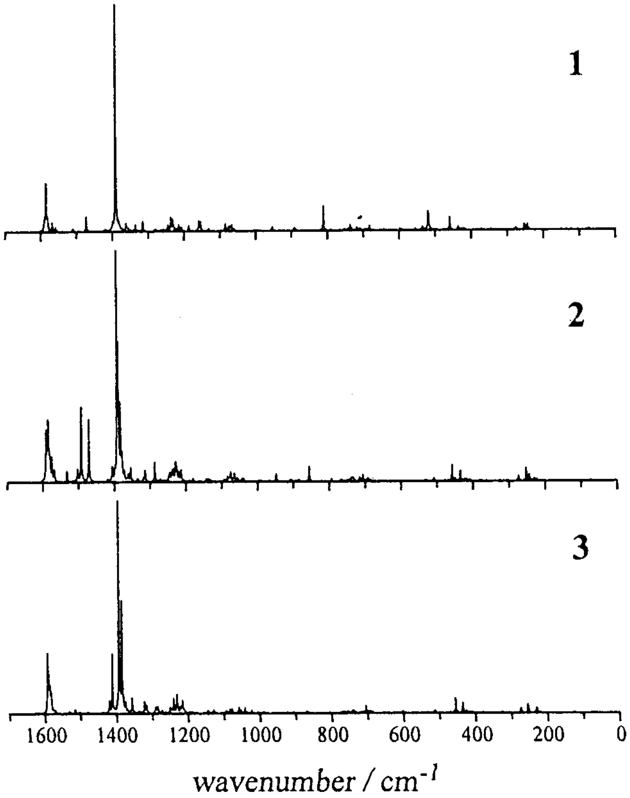

Figure 6. Calculated Raman spectra of three isomers of C_{121}.

TABLE 8: The Point Groups, Symmetry Species of Normal Mode, and Their IR and Raman Activity of Three Structural Isomers

isomer	point group	symmetry species of normal mode	IR active mode	Raman active mode
1	D_{2d}	$47A_1 + 42A_2 + 43B_1 + 47B_2 + 89E$	$47B_2$, 87E	$47A_1$, $41B_1$, $46B_2$, 89E
2	C_s	$183A' + 174A''$	$183A'$, $168A''$	$183A'$, $174A''$
3	C_2	$179A + 178B$	174A, 177B	179A, 177B

TABLE 9: Symmetry, Wavenumber, and IR and Raman Activities of the Cage−Cage Vibrational Modes

isomer	vibration	symmetry	wavenumber	IR active	Raman active
1	ν_1, ν_2	E	13.00	yes	yes
	ν_3	B_1	17.59	no	no
	ν_4	A_1	72.68	no	yes
	ν_5, ν_6	E	100.64	yes	yes
2	ν_1	A'	14.20	yes	yes
	ν_2	A''	16.63	yes	yes
	ν_3	A''	19.48	yes	yes
	ν_4	A'	72.58	yes	yes
	ν_5	A'	107.23	yes	yes
	ν_6	A''	114.86	yes	yes
3	ν_1	B	19.10	yes	yes
	ν_2	A	19.53	yes	yes
	ν_3	B	21.81	no	yes
	ν_4	A	74.98	yes	yes
	ν_5	B	123.21	yes	yes
	ν_6	A	123.89	yes	yes

IR and Raman spectra were modified by Lorenzian broadening with HWHM of 1 cm^{-1}. The exact values of the peaks are listed in the Supporting Information. Because there are so many active modes in both IR and Raman spectra, it is more difficult to identify these dimers[21] experimentally only by comparing the calculated spectra with experimental ones.

Useful information can be collected by analyzing the low-energy regions for the IR and Raman spectra. All isomers of C_{121} have six vibrational modes in 0−130 cm^{-1} (**1** has four vibrational modes because of degeneration), although C_{60} has no vibrational modes in this region. These are cage−cage vibrations in which C_{60} moieties behave as rigid frameworks. These kinds of vibrations were calculated for C_{120}[22] and $C_{120}O$,[23] and the predicted spectra are in good agreement with the experimental ones.

These low-energy vibrational modes for **1**, **2**, and **3** are shown in Figure 7. The symmetry, wavenumber, and IR and Raman activities of these cage−cage vibrational modes of **1**, **2**, and **3** are listed in Table 9, and the calculated IR and Raman spectra of this region are shown in Figure 8 and Figure 9. As given in Table 9, the three isomers have different numbers of IR and

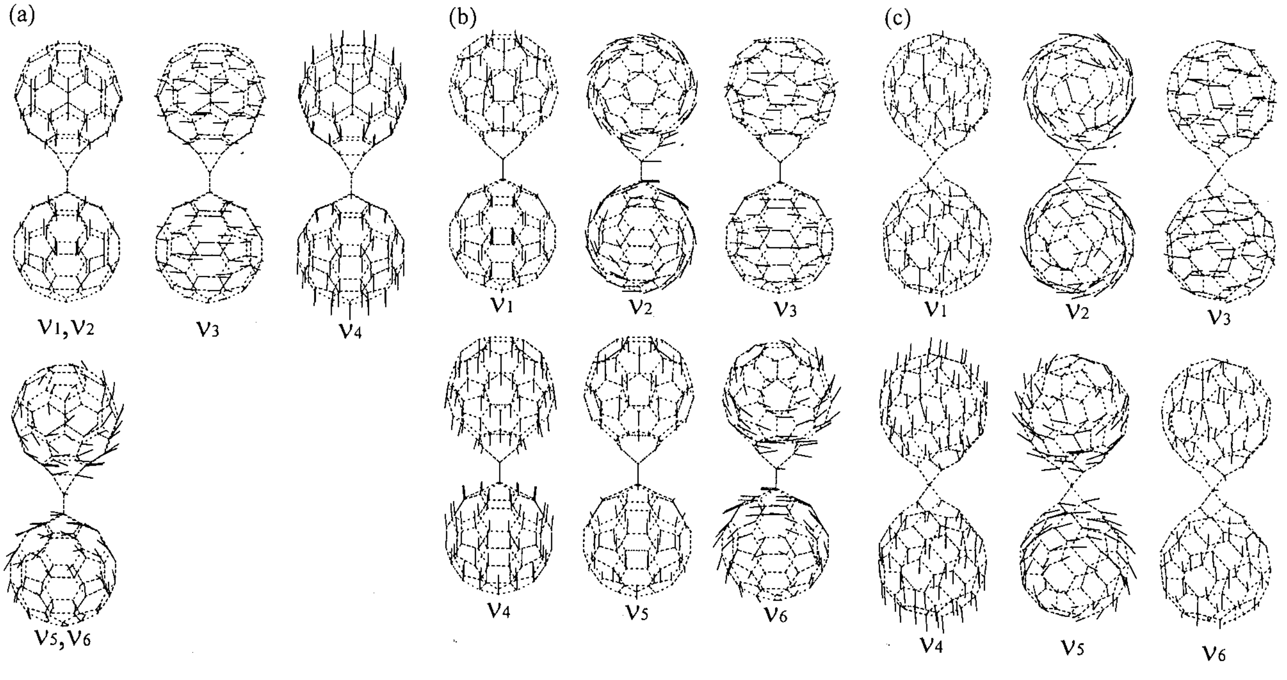

Figure 7. Cage−cage vibrational modes of **1**, **2**, and **3**.

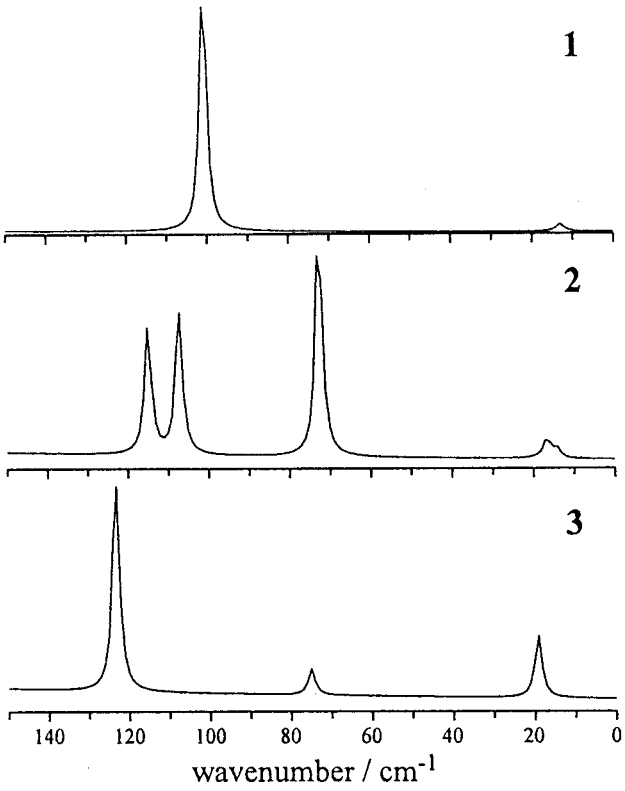

Figure 8. Low-energy portions of calculated IR spectra of **1**, **2**, and **3**.

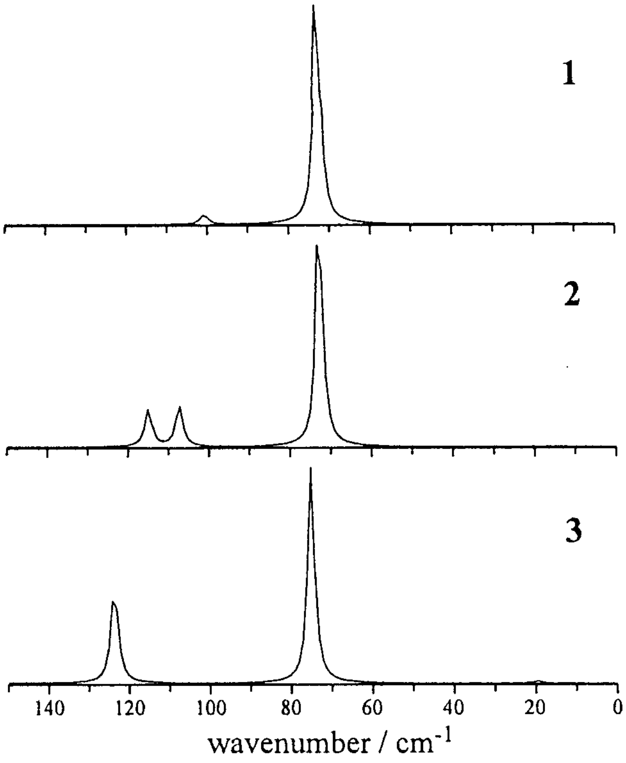

Figure 9. Low-energy portions of calculated Raman spectra of **1**, **2**, and **3**.

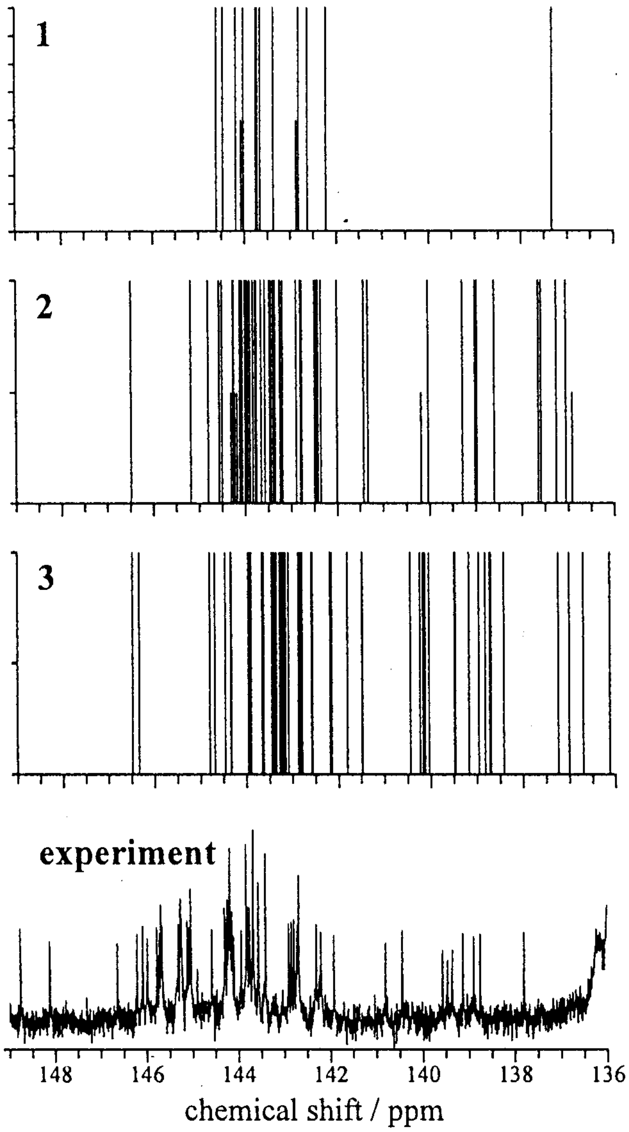

Figure 10. sp^2 region of calculated ^{13}C NMR spectra of **1**, **2**, and **3** and experimental ^{13}C NMR of the isolated C_{121}. A resonance of **2** (128.61 ppm) and three resonances of **3** (128.61, 133.88, 135.90 ppm) are out of the range.

Raman active modes, which should be useful for further structural analysis.

Another important point is that **3** has the largest wavenumber for all vibrational modes while **2** is the second. This shows that the order of rigidity of the spiro moiety of the three isomers is **3** > **2** > **1**, which agrees with the order of increase of the strain energy of the moiety of the three structures, **3** < **2** < **1**, which was discussed in section 3.2.2. The cage−cage stretching vibration for fullerene dimers, that is, ν_4 in Figure 7, can be seen as an indication of the “bond strength of a diatomic molecule”.

3.4. Calculated NMR Spectra. Magnetic shielding tensors were calculated with the HF/3-21G//B3LYP/6-31G(d) method using the GIAO method. Shielding constants were converted to chemical shifts by taking the signal of C_{60} in 1,2-dichlorobenzene with 5% (v/v) C_6D_6 (δ = 143.02 ppm)[24] as a reference. The calculated ^{13}C NMR spectra for **1**, **2**, and **3** are shown in Figure 10 (a)−(c) (136−149 ppm) and Figure 11 (a)−(c) (35−80 ppm). In these figures, the resonances of central carbon atoms and bridgehead carbon atoms are labeled by closed triangles and closed circles, respectively.

The three isomers can be distinguished by analyzing the number of single- and double-intensity resonances between 125 and 150 ppm (sp^2 region) or between 20 and 90 ppm (sp^3 region). **1**, **2**, and **3** have 16, 62, and 60 resonances in the sp^2 region and two, three, and one signals in the sp^3 region, respectively. However, there are many signals in the sp^2 region,

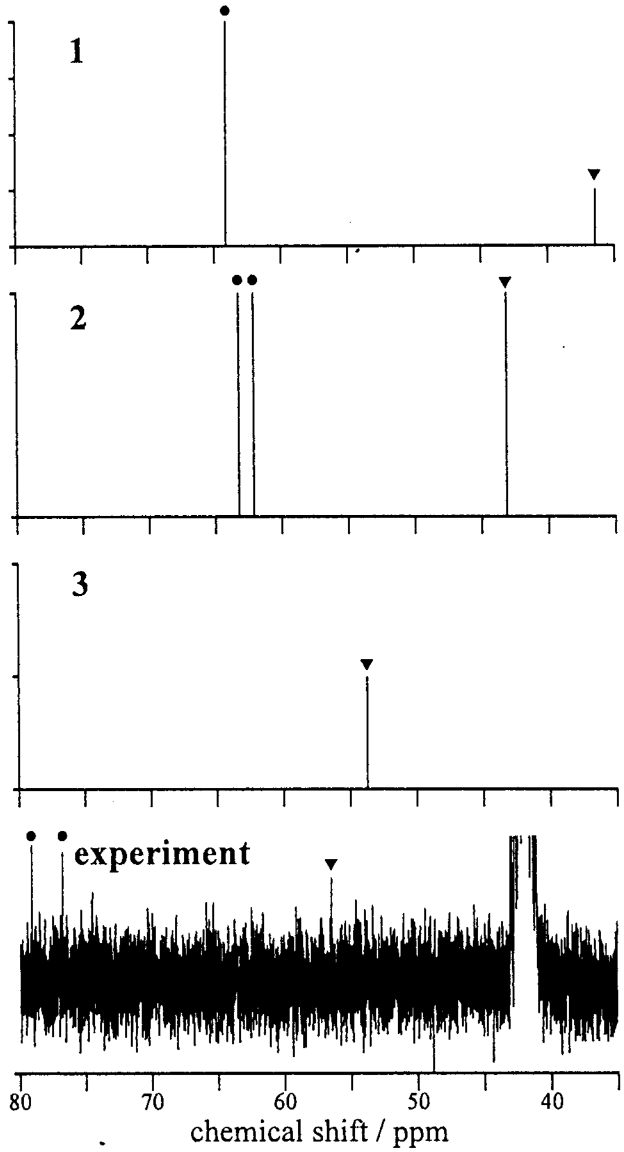

Figure 11. sp^3 region of calculated ^{13}C NMR spectra of **1**, **2**, and **3** and experimental ^{13}C NMR of the isolated C_{121}. Signals marked with a closed triangle (▼) and a closed circle (●) are resonances of central-bridge carbon atoms and bridgehead carbon atoms, respectively. The resonances around 42 ppm originate from dimethylsulfoxide-d_6 used as external lock solvent.

more than 10 over 1 ppm, which accounts for severe overlaps in the ^{13}C NMR spectrum. Qualitatively, the sp^2 ^{13}C NMR spectra can be used to distinguish between **1** and the other isomers but not between **2** and **3**. The sp^3 region of ^{13}C NMR should be useful for the distinction between all these isomers.

3.5. Experimental NMR Spectra. C_{121} was synthesized by the thermolysis reaction of $C_{60}CBr_2$ described in the previous papers[4,5] and isolated by HPLC (Cosmosil Buckyprep Column) using toluene as the eluent. ^{13}C NMR (67.8 MHz) spectra of the isolated C_{121} in 1-methylnaphthalene solution were measured with a JEOL JNM-EX270 using dimethyl sulfoxide-d_6 as external lock solvent. The resonance of a carbon atom in the methyl group of 1-methylnaphthalene (19.20 ppm) was used as a reference.

The obtained ^{13}C NMR spectrum of the C_{121} is shown in Figure 10 (136−149 ppm) and Figure 11 (35−80 ppm). There are 55 resonances in the sp^2 region (Figure 10), some of which probably consist of some overlapped peaks. The number of resonances is consistent with the symmetry of **2** (C_s) and **3** (C_2), but not with that of **1** (D_{2d}). In the sp^3 region, there are only three resonances, two of which are close to each other, while the last one is apart (ca. 20 ppm). The number of resonances in the sp^3 region is consistent only with the computed spectrum of **2**, and the computed spectrum reproduces the experimental peak pattern well.

To confirm the structure of C_{121} as **2**, a sample was synthesized from $C_{60}CBr_2$, in which the carbon atom of the top of the cyclopropane ring was 99% ^{13}C-enriched, while the carbon atoms of the C_{60} cage were at natural abundance. The ^{13}C NMR spectra of this sample showed that the intensity of the resonance at 56.46 ppm increased significantly in comparison with the other resonances. This suggests that the resonance at 56.46 ppm originates in the central carbon atom of C_{121}, which is also consistent with the predicted ^{13}C NMR spectrum of **2**. Therefore, ^{13}C NMR experiments and theoretical calculations support the structure of the isolated C_{121} as **2**. The details of experimental investigations of C_{121} are reported elsewhere.[7]

4. Conclusion

All methanobridge moieties of the three possible structures have either a 6,6-closed (methanofullerene) or a 6,5-open (homofullerene) structure, and there is no 6,6-open or 6,5-closed structure. This is the same behavior as in all known carbon-connected fullerene derivatives.

2 is the most stable isomer with **1** being close in stability, while **3** is much less stable than the other two isomers. The strain energy around the central carbon atom is probably the reason that **2** has comparable stability with **1** even though it has a homofullerene moiety, which is generally less stable than methanofullerenes. Thus, from the energetic viewpoint, it is probable that **2** and **1** coexist and experimental support of the stability of **2** has been found.

All isomers have cage−cage vibrational modes in 0−130 cm^{-1}, whose IR and Raman activities and wavenumber will assist in discerning between the possible structures. Interestingly, the low-energy vibrations are consistent with the bond strength of these "diatomic molecules".

The obtained ^{13}C NMR spectra of C_{121} isolated by HPLC are consistent with the calculated ^{13}C NMR spectrum of **2**, which is predicted as the most stable structure. **2** is the first fullerene derivative embodying both fundamental modes of connection of a carbon atom to C_{60}.

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Supporting Information Available: Computed harmonic frequencies and experimental fundamental frequencies of molecules used for determining scaling factors. Computed harmonic frequencies, and experimental harmonic frequencies and anharmonic corrections of diatomic molecules used for determining a scaling factor for ZPVE. Cartesian coordinates of structures of **1**, **2**, and **3** optimized with the B3LYP/6-31G(d) method. IR and Raman spectra of **1**, **2**, and **3** computed at the HF/STO-3G level of theory. ^{13}C NMR spectra of **1**, **2**, and **3** computed at the HF/3-21G//B3LYP/6-31G(d) level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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