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Preparation and Characterization of Novel Amphiphilic C_{60} Derivatives

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Amphiphilic C_{60} derivatives of [(ethoxycarbonyl)decylene]fullerene and bis[(ethoxycarbonyl)decylene]-fullerene, which are used to obtain organized molecular films by the LB technique, were prepared by the reaction of C_{60} with diazo compounds. They were characterized by IR, UV−vis, ^{1}H-NMR, ^{13}C-NMR, and FD-MS. Direct evidence confirmed that the [6,5]-fullerenoid is the thermodynamically more stable isomer. It was converted from the arrangement of a [6,6]methanofullerene rather than a reaction product in 6,5 double bonds. A carbene mechanism is suggested for the reaction.

Whereas initial fullerene research focused mainly on the physical properties of the pure carbon sphere, the potential utilities of fullerene derivatives as biologically active compounds or sources for material science have spurred intensive interest in achieving efficient functionalization of fullerenes[1], exemplified by the reactions of C_{60} with diazoalkanes,[1c,2] diazirine,[3] dienes,[4] nucleophiles,[5] and radicals.[6] Wudl has shown that water-soluble methano-bridged C_{60} compounds inhibit HIV enzyme protease (HIVP) and reverse transcriptase (HIVRT).[7] Subsequently, a number of C_{60} derivatives with peptide groups were synthesized. Recently, functionalizations have been developed to meet the requirements of special techniques, such as that involving Langmuir−Blodgett (LB) films.

The LB technique, which provides a method to fabricate thin films on a molecular level, is an effective technique for obtaining C_{60} thin films. Up to now, most research concentrated on the LB films of pure fullerenes.[8] However, spherical hydrophobic fullerene molecules are not suitable for the LB method. In most cases, the limiting molecular area obtained via a surface pressure−area isotherm was smaller than that calculated by the Corey−Pauling−Koltun molecular model. Such a reduced value of the limiting molecular area suggests that the floating film of pristine C_{60} is a condensed layer rather than a monolayer at the air/water interface. Thus, designing and synthesizing amphiphilic fullerene derivatives is a major goal to pursue in order to overcome the above-mentioned problems in the study of LB films.

There are some reports of Langmuir films of amphiphilic fullerene derivatives such as $C_{60}O$ and *N*-acetylfulleropyrrolidine molecules[9] and other amC_{60} derivatives,[10] which form monolayers at the air/water

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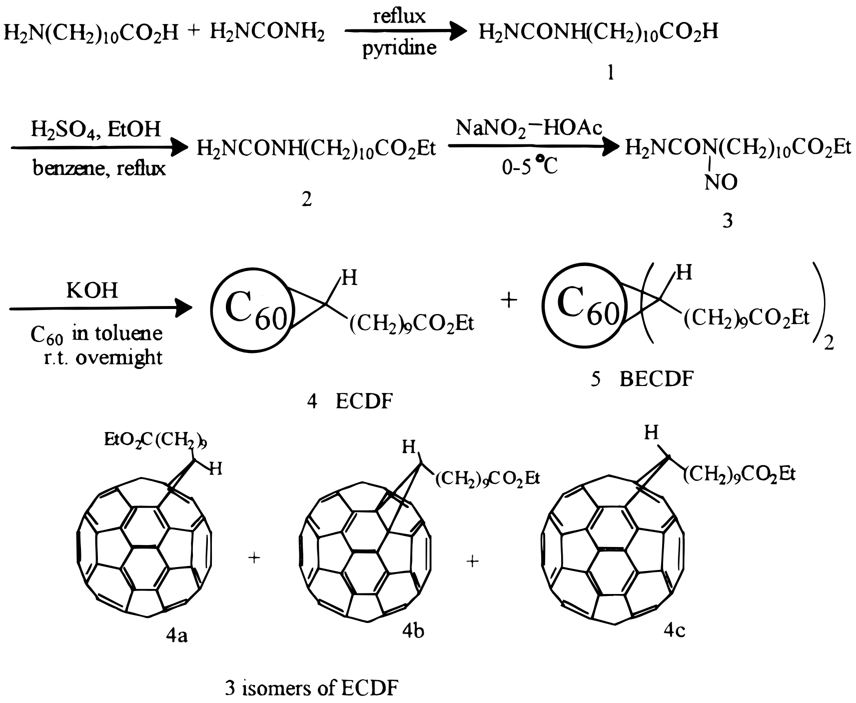
Scheme 1



interface. We have reported relatively uniform multilayer LB films of (dodecylamino)fullerene and polyhydroxy(dodecylamino)fullerene.[11] In this paper, we report the first synthesis of two amphiphilic C_{60} derivatives with a long chain having C_{60} as a hydrophobic moiety and the ester group as a hydrophilic moiety for the application using the LB technique. Their chemical structures were confirmed and discussed in terms of thermodynamic stability.

Experimental Section

General Methods. C_{60} was purchased from Beijing University. 11-Aminoundecanoic acid was purchased from Beijing Chemical Factory.

11-Ureidoundecanoic Acid (1). A mixture of 11-aminoundecanoic acid (4.2 g), urea (1.32 g), and pyridine (10 mL) was refluxed for 4.5 h. Cooling gave the crystalline product, which was filtered, washed with water, and recrystallized from 95% EtOH. Yield: 3.53 g (69.3%). Mp: 147−148 °C (lit.[12] mp 147 °C). IR: 3500−2500 (broad), 3322, 3123, 2920, 2850, 1720, 1623, 1480, 1449, 1372, 1320, 1285, 1265, 1190, 720 cm^{-1}. ^{1}H-NMR δ: 12 (m, 1H), 5.2−6.0 (m, 3H), 2.9 (t, 2H), 2.15 (t, 2H), 1.0−1.7 (m). MS *m/z*: 245 ($M^+ + 1$), 210, 201, 186, 169, 157, 142, 114, 110, 86, 73, 55, 41, 30. Anal. Calcd for $C_{12}H_{24}N_2O_3$: C, 58.99; H, 9.90; N, 11.46. Found: C, 59.11; H, 9.68; N, 11.22.

Ethyl 11-Ureidoundecanoate (2). A mixture of 0.73 g of compound **1**, 20 mL of anhydrous EtOH, 30 mL of benzene, and 1 mL of concd H_2SO_4 was refluxed until no benzene water azeotrope was being distilled off the reaction mixture. After cooling, 30 mL of water was added to the mixture and then benzene was removed by rotary evaporation and the product filtered. The filtrate was crystallized from 95% EtOH to give 0.73 g (90%). Mp: 103−105 °C. IR: 3400, 3340, 3200, 2920, 2840, 1730, 1658, 1650, 1480, 1470, 1420, 1380, 1345, 1290, 1170, 720 cm^{-1}. ^{1}H-NMR δ: 5.2−5.9 (m, 3H), 4.02 (q, 2H), 3.0 (t, 2H), 2.2(t, 2H), 1.0−1.7 (m). MS *m/z* 272 (M^+), 227, 210, 200, 185, 172, 157, 142, 129, 115, 101, 88, 73, 55, 41, 30. Anal. Calcd for $C_{14}H_{28}N_2O_3$: C, 61.73; H, 10.36; N, 10.28. Found: C, 61.90; H; 10.18; N, 10.14.

Ethyl 11-(*N*-Nitrosoureido)undecanoate (3). A solution of 0.29 g of $NaNO_2$ in 5 mL of water was added dropwise to the mixture of 0.283 g of compound **2** and 5 mL of HOAc at 0−5 °C followed by stirring for an additional 15 min. The mixture was poured into 50 mL of ice water. A white solid was obtained after filtration, which was entirely used for the preparation of compound **4** without any further purification.

Fullerene Derivatives ECDF(4) and BECDF (5). To a solution of 50 mg of C_{60} and freshly prepared compound **3** (see above) in 40 mL of toluene under N_2 was added dropwise 5 mL of an aqueous solution of 0.28 g of KOH. After the mixture was stirred overnight at room temperature, the reaction was quenched with AcOH. The resulting mixture was filtered to removed the participate. The brown toluene solution was separated from water, dried with anhydrous Na_2SO_4, and chromatographed on a silica gel column using toluene/ethyl acetate as the eluents. The second running fraction was compound **4** and then compound **5**. Yields were 23 mg (43.5%) and 20 mg (30.7%) (based on the 40 mg of C_{60} consumed), respectively. Compound **5** is a brown powder. ^{1}H-NMR δ: 5.75−5.85 (m), 5.35−5.45 (m), 4.85−5.05 (m), 3.9−4.3 (m), 2.2−2.3 (m) 1.95−2.05 (m), 0.8−1.7 (m). ^{13}C-NMR δ: 173.9, 139.1, 131.0, 129.6, 114.1, 71.8, 68.2,65.5, 64.3 60.1, 125−155 (broad), 10−40 (m). IR: 2925, 2854, 1733, 1462, 1178, 1094, 721, 527 cm^{-1}. FD-MS: 1145 ($M^+ + 1$).

Results and Discussion

The synthetic route to [(ethoxycarbonyl)decylene-]fullerene (ECDF) and bis[(ethoxycarbonyl)decylene-]fullerene (BECDF) is shown in Scheme 1. Aliphatic diazo compounds are of high activity and low selectivity. Controlling the reaction of diazo compounds with polyene fullerene becomes quite difficult. In addition, the aliphatic diazo compounds are unstable. The preparation yields are very low; e.g., the yield of diazododecane is only 4%.[13] To solve these problems, we started the reaction from the stable compound **2**. After nitrosylation with $NaNO_2$−HOAc, the resulting nitroso compound **3** was

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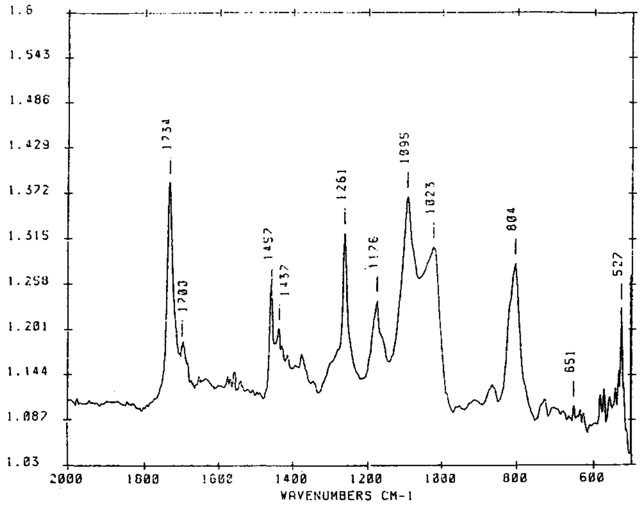

Figure 1. IR spectrum of compound **4**.

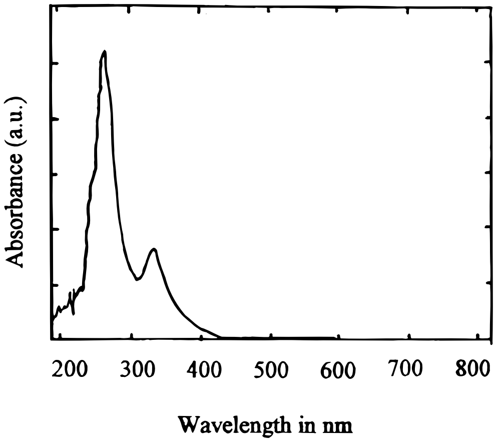

Figure 2. UV–vis spectrum of ECDF.

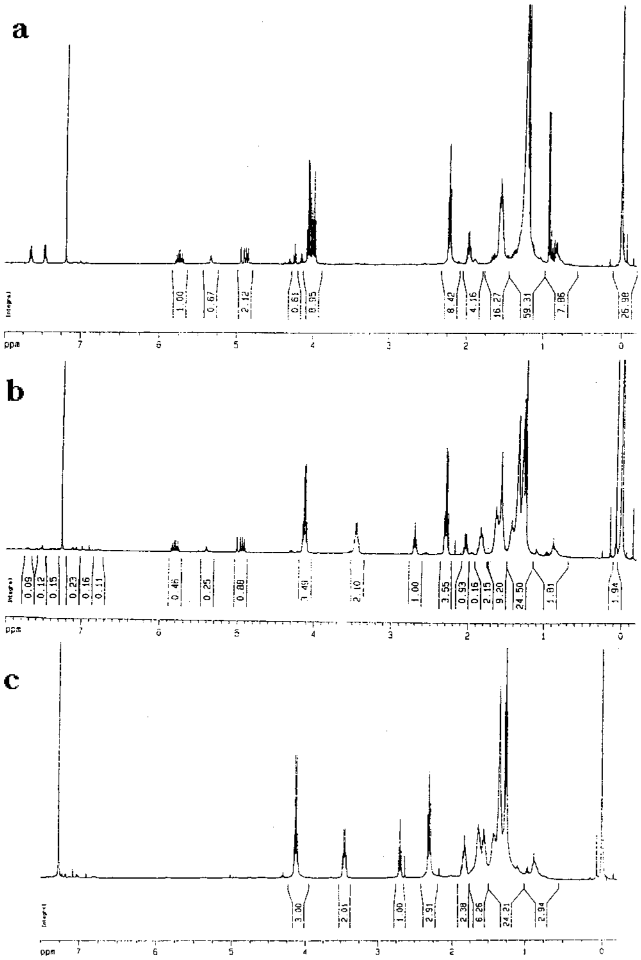

Figure 3. ^{1}H-NMR spectra of compound **4**: (a) initial product; (b) product after storage for 2 weeks; (c) product after storage for 6 mos.

used directly without any further purification. The rate and amount of diazo compound formation were controlled by the rate of addition of KOH. The diazo compound was generated and treated with C_{60} in situ by addition of excess 40% KOH solution or solid KOH to a mixture of compound **3** and C_{60}. TLC showed that the monoaddition products were produced immediately but the diaddition products appeared after 15 min. The amount of triaddition products was too small to be separated.

Figure 1 shows the IR spectrum of compound **4**. The bands at 1429, 1183, 578, 527 cm^{-1} as a result of the vibration of the C_{60} skeleton all appear in this spectrum. Only the bands at 1183 and 1429 cm^{-1} have shifted to 1176 and 1473 cm^{-1}, respectively. The band at 578 cm^{-1} got weaker. It is noteworthy that the strong absorption band at 1734 cm^{-1} confirms the presence of a carbonyl group in the molecule. Only the peak at 1176 cm^{-1} shifts to 1173 cm^{-1} after the conversion from compound **4** to **4a**. No other obvious changes for the characteristic peaks were observed.

The electronic absorption spectrum (Figure 2) of compound **4** in chloroform solution after standing for 6 mos is identical to that of C_{60} in the range of 190–400 nm. The absorption band at 213 nm red-shifted and mixed with the band at 275 nm to form a broad band. No bands appeared at 430 or 690 nm, which are observed in a variety of closed transannular C_{60} derivatives bridged at a 6,6 ring junction, indicating the absence of 6,6-methanofullerene.

The FD-MS spectrum of compound **4a**, which is the same as compound **4**, depicts a molecular ion peak at *m*/*z* 932 along with a very weak peak at *m*/*z* 948, which suggests the incorporation of oxygen. The oxidation properties of the nitroso compound may be responsible for this incorporation.

Figure 3 shows the ^{1}H-NMR spectra of compound **4**. After the compound was stored in chloroform solution at room temperature under N_2 atmosphere for 2 weeks, the spectrum changed from the original (Figure 3a) to the mediate (Figure 3b). Six mos later, the simple spectrum (Figure 3c) was obtained. The peaks in the region of 4.2–6.0 ppm in Figure 3b disappeared, which is consistent with a rearrangement. The less stable isomer slowly changed into the thermodynamically more stable one.

The ^{13}C-NMR spectrum of **4** (Figure 4) after the compound was stored for 6 mos in $CHCl_3$ exhibited 45 signals. The peak at 173.9 ppm was assigned to the carbonyl carbon. ^{13}C-DEPT experiments indicated that the signals for methine and methyl appeared at δ 49.1 and 14.3 ppm, respectively. The remaining nine peaks at high field are due to CH_2 groups. There were 32 lines (including shoulders) in the fullerene region. This is the appropriate number for a C_{60} adduct of C_s symmetry. No diagnostic sp^3 carbon atoms resonating at 70–80 and 90–110 ppm for [6,6]- and [6,5]-closed structures existed in the spectra. This excluded the structure of methanofullerene or [6,5]-closed ring junction. With the foregoing

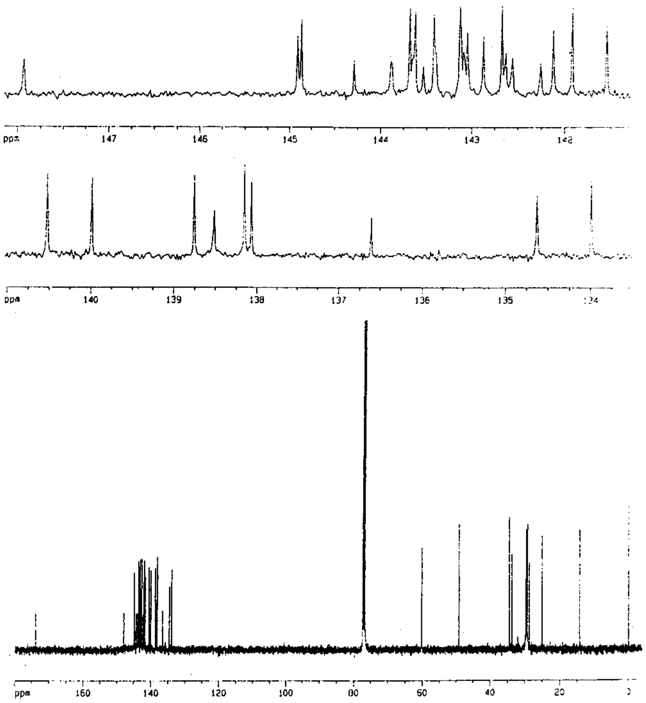

Figure 4. ^{13}C-NMR spectrum of compound **4** after storage for 6 mos.

evidence, we can draw the conclusion that the isomer has the [6,5]-fullerenoid structure.

Wudl prepared the parent fullerenoid $C_{61}H_2$.[2c] The methine bridge at the 6,5 double bond puts the two hydrogens in different environments. One is located above a 5-membered ring and the other one above a 6-membered ring of the fullerene surface. Local ring-current anisotropy effects will influence their chemical shifts. Calculations predict that a strong local paramagnetic ring current exists on the 5-membered rings, whereas a weaker diamagnetic ring current is present above the 6-membered rings.[2f] Thus, the proton above the 6-membered ring will be shielded weakly and the proton above the 5-membered ring in C_{60} will be strongly deshielded. In $C_{61}H_2$, the two hydrogens absorb at δ 2.87 ppm (above 6-membered ring) and 6.35 ppm (above 5-membered ring). In Figure 3c, there exists a peak at δ 2.7 ppm. It is very near δ 2.87 ppm, which indicates that it may be assigned to the methine proton over the 6-membered ring. Decoupling the triplet at δ 2.7 ppm collapsed the multiplet at δ 3.4 ppm to a triplet (Figure 5a). Irradiation of the multiplet at δ 3.4 ppm causes the triplet at δ 2.7 ppm to collapse to a singlet and the multiplet at δ 1.83 ppm to a triplet (Figure 5b), which illustrates that they are coupling CH proton and CH_2 protons. In addition, the ratio of the relative intensities of the peaks at δ 3.4 and 2.7 ppm is about 2:1. Thus, they may be ascribed to methine hydrogen over the 6-membered ring (at 2.7 ppm) and its neighbor CH_2 (at 3.4 ppm).

A C−H COSY spectrum (Figure 6) confirmed that the methine hydrogen and the attached carbon did appear at δ 2.7 ppm in the ^1H-NMR and 49.11 ppm in the ^{13}C-NMR spectra. FD-MS of **4a** also gave the molecular peak at *m/z* 932. This is consistent with a structure with the methine hydrogen above the 6-membered ring and $-CH_2(CH_2)_8CO_2Et$ over the 5-membered ring. In conclusion, the thermodynamically more stable isomer **4a** is a [6,5]-fullerenoid with hydrogen above the 6-membered ring and $-CH_2(CH_2)_8CO_2Et$ over the 5-membered ring in our experimental conditions.

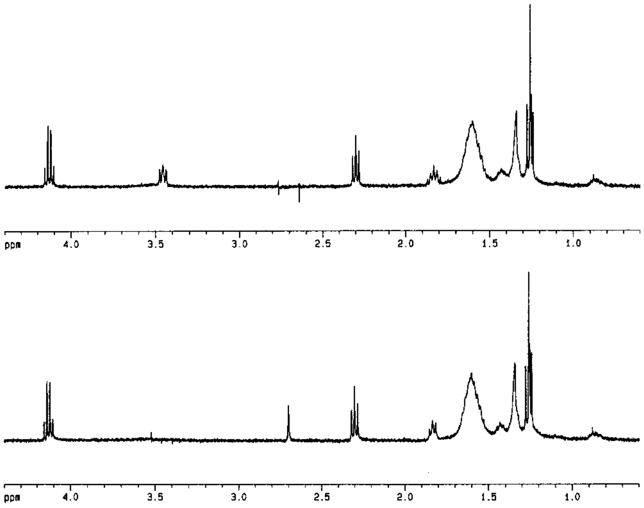

Figure 5. Decoupled ^1H-NMR spectra of **4a**: (a) proton at δ 2.7 ppm decoupled; (b) protons at δ 3.4 ppm decoupled.

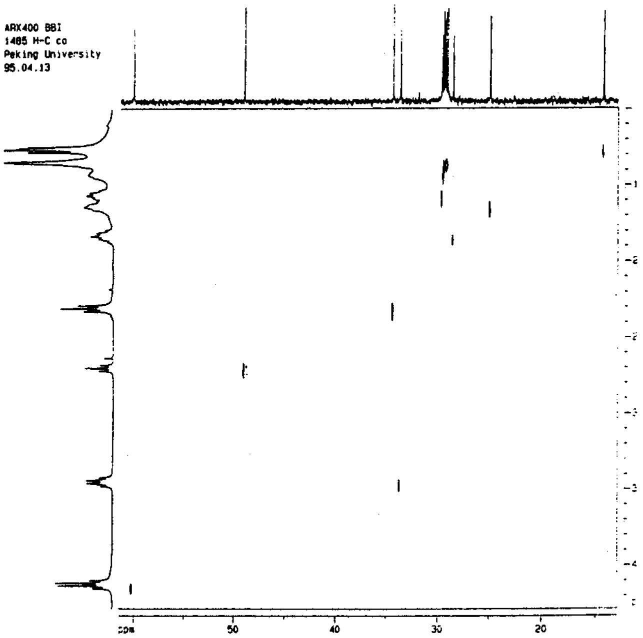

Figure 6. C−H COSY spectrum of ECDF.

Diederich has presented comprehensive computational studies of experimentally accessible methanofullerenes by the PM3 methods.[2e−h] The results show that the [6,6]-closed structure is more stable in most cases. This was confirmed experimentally by refluxing the mixture of three isomers in toluene for 24 h. Only the [6,6]-closed isomer was isolated.

Warner investigated a series of model systems by MMPI, RHF/AM1, and UHF/AM1 calculations.[14] His results show that the increasing curvature causes the [6,5]-bridged fullerenoid structure to become relatively more stable than the [6,6]-closed fullerene structure. Our result gives experimental evidence for the first time that the [6,5]-fullerenoid can become the thermodynamically more stable product. No [6,6] ⟺ [6,5] exchange was observed in its ^1H-NMR spectrum after reflux of the final [6,5]-fullerenoid in toluene for 24 h.

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This result is also reasonable. Although [6,6]-closed isomers avoid placing formal double bonds in 5-membered rings and avoid violation of Bredt's rule, this is fulfilled by creating sp^3-hybridized bridgehead carbon atoms in a strained cyclopropane. Fusing a strained 3-membered ring on a rigid fullerene frame is not particularly favorable, especially when it contains something bulky on the ring. This factor reduces its stability. On the other hand, the [6,5]-open isomer can also avoid placing formal double bonds within 5-membered rings, but the formal double bonds appear at the bridgehead carbon atoms. This may cause strain by distorting these double bonds out of planarity in violation of Bredt's rule. However, the transannular distance (0.220−0.225 nm) for the [6,5]-open isomers is longer than that of the corresponding [6,6]-closed isomers (0.157−0.161 nm)[15] and [6,5]-open isomers can avoid attaching the strained three-membered ring to the rigid fullerene skeleton. Both factors relieve the strain in the isomer and enhance its stability. Thus, which one is more stable depends on structure. In our structure, the [6,5]-fullerenoid is more stable. It is noteworthy that solvents play important roles in the conversion. In contrast with the result of **4a** in chloroform solution, no conversion or equilibrium has ever been observed in the ^{13}C-NMR of compound **5** when it was kept in the solid state for the same period of time. Temperature, solvents and substituent groups are three important factors which determine what products are thermodynamically stable.

The mechanism of the reaction may involve an intermediate carbene or 1,3-dipolar cycloaddition product or other mechanism. According to the initial report by Wudl, the reaction proceeds via a 1,3-dipolar cycloaddition reaction to give the 1-pyrazoline as an intermediate. It subsequently partitions to the bridged fullerene after loss of N_2. Diederich provided an example of the possible attack of a carbene, from which fullerene substituted sugars were prepared by the reaction of C_{60} with nucleophilic carbenes. In our reaction, although the 1,3-dipolar cycloaddition mechanism is possible, the carbene mechanism is preferable as based on the following consideration: alkyl diazo compounds without an electron-withdrawing group are very unstable; nitrogen escaped immediately when KOH was added to the reaction system; and no 1-pyrazoline intermediate was ever detected. The typical chemical shift at δ 3.93 in Figure 3a,b for the [6,6]-closed methine hydrogen and the diagnostic chemical shift for [6,6]-closed bridgehead carbon at δ 71.8 ppm in the ^{13}C-NMR of compound **5** (see the Experimental Section) strongly suggest that the reaction takes place at the [6,6]-double bond first. After a period of time, the [6,5]-fullerenoid was gradually produced (Figure 3). Eventually, it changed into a [6,5]-fullerenoid isomer completely. The mechanism for the interconversion of the isomers is complex and needs further work.

Conclusion

The reaction of a diazo compound is an effective way for the functionalization of fullerene. The [6,5]-fullerenoid **4a** is the thermodynamically stable isomer in this case. After hydrolysis to the corresponding acids, the amphiphilic compounds would be good materials, and research in this area is under way.

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