Fullerenes

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Addition of Carbene to the Equator of C_{70} To Produce the Most Stable $C_{71}H_2$ Isomer: 2a*H*-2(12)a-Homo(C_{70}-$D_{5h(6)}$)[5,6]fullerene**

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Unlike C_{60}, in which all carbon-atom environments are identical, C_{70} has five distinct carbon-atom environments, which give rise to eight distinct C–C bond types. Hence, the addition chemistry of C_{70} involves both chemo- and regioselectivity. The synthetic chemistry of C_{70} is centered on the areas near the poles,[1,2] as these areas have the highest curvature and hence high bond strain.[3,4] This relatively high bond strain in turn makes the polar regions the most reactive sites of the molecule. The equatorial region of C_{70}, on the other hand, has little curvature and hence lower bond strain. Thus, the carbon atoms at the equator are much less reactive, as there is a much higher activation barrier to be overcome before reactions can occur. For example, carbene (CH_2) has been added to the polar region of C_{70}, and several isomers of $C_{71}H_2$ have been synthesized and fully characterized.[5–8] However, the addition of carbene to the equatorial bond of C_{70} (to form C_{2v}-$C_{71}H_2$) has not been detected.

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We were prompted to synthesize this elusive C_{2v} $C_{71}H_2$ isomer for several reasons: 1) The hydrogen-atom chemical shifts of the carbene adducts are useful for probing the local ring currents of C_{70} and its hexaanion.[7,9–11] Computations show that the equatorial six-membered ring of C_{70} has the largest diamagnetic ring current,[11,12] but no solid experimental evidence exists. 2) Theoretical studies have indicated that the sidewall of nanotubes can be opened by chemical modifications of divalent groups, such as carbene,[13] as was also confirmed indirectly by Umeyama et al.[14] C_{70} can be considered as the shortest (5,5) nanotube; fully characterized C_{2v} $C_{71}H_2$ would provide us with direct hard evidence of the structure of nanotube carbene adducts. 3) The density functional computations in this study show that the C_{2v} structure has the lowest energy of all possible isomers of $C_{71}H_2$ and is an open [6,6] homofullerene. Addition at the [6,6] junction of fullerenes mostly results in [6,6] closed adducts;[15] [6,6] open homofullerenes are stable only in special cases.[16,17]

Herein we report the synthesis, characterization, and theoretical studies of the missing $C_{71}H_2$ isomer—a homofullerene with a CH_2 group attached to the C_{70} equator. Access to this elusive C_{2v} $C_{71}H_2$ isomer not only enabled satisfactory clarification of the local electron delocalization of the C_{70} equatorial rings and provided unambiguous support for nanotube-sidewall opening, but also provided a new member of the homofullerene family. Moreover, the pyrogenic synthesis proved to be a highly efficient approach to overcome the high activation barriers to the formation of the thermodynamically most stable isomers, as also demonstrated, for example, by the synthesis of $C_{60}Cl_8$ and $C_{60}Cl_{12}$, in which the C_{60} cage violates the isolated pentagon rule (IPR),[18] and by the synthesis of the stable unconventional fulleride $C_{64}H_4$.[19]

The structures of all chemically possible C_{70}-fullerene-based isomers of $C_{71}H_2$ were optimized by density functional calculations at the B3LYP/6-31G* level. There are eight different types of bonds in C_{70}: a–a, a–b, b–c, c–c, c–d, d–d, d–e, and e–e; among them, the a–b and d–d bonds are the shortest and exhibit chemical reactivity like that of a C=C double bond, for example, they may undergo [2+1] cycloaddition with an incoming carbene, whereas the bonds in the equatorial pentaphenyl belt are benzene-like (not quinoid-like) and far less reactive.[5–8,11,12] Topologically, there are potentially 16 isomers of $C_{71}H_2$: eight methanofullerenes (CH_2 adds across one of each of the eight C–C bonds) and eight homofullerenes (CH_2 replaces one of each of the eight C–C bonds).[6,20] Depending on which of the eight bonds undergoes reaction, and irrespective of whether the C–C bond is crossed or replaced, these isomers have C_s, C_s, C_1, C_s,

C_1, C_s, C_1, and C_{2v} symmetry, respectively (according to the list of bond types above). Our computations show that homofullerenes are formed when the CH_2 addend is attached to an a–a, b–c, c–d, d–d, or e–e bond, whereas methanofullerenes are obtained when the CH_2 group is attached to an a–b, c–c, or d–e bond (Figure 1).[21] Similar to the case of carbon

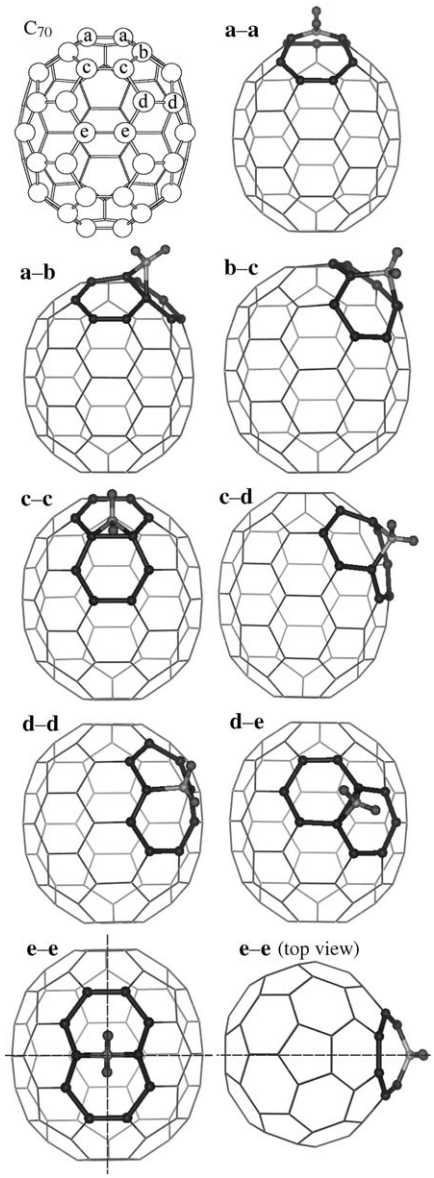

Figure 1. C_{70} and the eight computationally identified isomers of $C_{71}H_2$. The five different types of carbon atom in C_{70} are assigned as a, b, c, d, and e. The **e–e** isomer has two mirror planes marked with dashed lines. Isomers **a–a**, **b–c**, **c–d**, **d–d**, and **e–e** are homofullerenes; isomers **a–b**, **c–c**, and **d–e** are methanofullerenes.

nanotubes,[13] the enhanced stability of homofullerenes is due to homoaromatic stabilization and the avoidance of strain energy; the addition of CH_2 would otherwise result in the formation of a three-membered ring (as in methanofullerenes) and loss of the homoaromatic stabilization (as in bridged 1,6-X-[10]annulenes).[22]

Of the eight calculated $C_{71}H_2$ isomers, the **e–e** isomer has by far the lowest energy (Table 1). Thus, reactions at the poles are kinetically rather than thermodynamically controlled.

Table 1: Distances between the two C atoms attached to the CH_2 addend in the eight $C_{71}H_2$ isomers and relative energies of the isomers (calculated at the B3LYP/6-31G* level).

Bonds bridged by CH_2	C–C separation [Å]	Relative energy [kcal mol^{-1}]
e–e	2.315	0
a–b	1.647	9.9
d–d	2.154	11.5
c–c	1.611	11.9
a–a	2.184	12.6
b–c	2.181	15.3
c–d	2.179	22.8
d–e	1.709	24.8

Our calculations agree well with those of Smith et al.,[7] who obtained the kinetically favorable **a–a/b–c** and **a–b/c–c** isomers by thermolysis and irradiation of the precursor, respectively; these isomers were among those low in energy. The $C_{71}Cl_2$ isomer synthesized by Kiely et al. with CCl_2 bridging d,d carbon atoms[8] is the isomer of third-lowest energy. Considering the rather high relative energies, it is understandable that the **d–e** isomer of $C_{70}O$[23] and the **c–d** and **d–e** isomers of $C_{71}H_2$ have not been detected so far.

There are several possible methods for the synthesis of $C_{71}H_2$, such as solution chemical reactions,[6–8] the Krätschmer–Huffman method,[24] and a photochemical reaction.[20] The method[7,8] for the synthesis of **a–a**, **a–b**, **b–c, c–c**, and **d–d** isomers involves kinetically favorable [2+1] cycloaddition reactions in solution at relatively low temperature. To overcome the possible higher activation barrier and obtain the product of equatorial addition to C_{70}, pyrogenic synthetic methods were adopted in this study.

The C_{2v} $C_{71}H_2$ homofullerene was synthesized by a modified Krätschmer–Huffman method in the presence of methane (see the Experimental Section) and separated from other hydrogenated fullerene derivatives as well as C_{70} and $C_{70}O$ by recycling HPLC. The purity of the final sample was approximately 99%, as estimated from the HPLC profile (Figure 2) and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. The mass spectrum (see the Supporting Information) exhibited only one molecular-ion peak, at m/z 854, which corresponds to $C_{71}H_2$.

NMR spectroscopy is an effective tool for the structural characterization of fullerenes and their derivatives,[25] and symmetry considerations are critical in the correlation of NMR spectroscopic data with possible structures.[7] The ^{13}C NMR spectrum of the product obtained by this method exhibits 22 lines (14×4, 7×2, 1×1; Figure 3). This pattern can only be consistent with the C_{2v} homo or methano isomer since the symmetry of the other isomers is far too low. Although the C_{2v} homo and methano isomers have patterns of the same intensity, ^{13}C NMR spectroscopy can readily distinguish between the two isomers, as in general sp^3- and sp^2-hybridized carbon atoms have vastly different chemical shifts. The

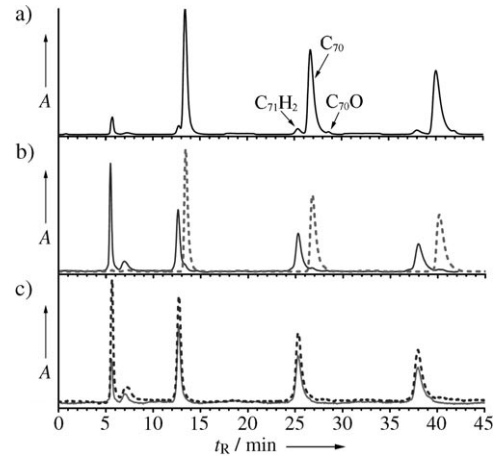

Figure 2. Recycling-HPLC profiles (three recycles) of a) the $C_{70}/C_{71}H_2$ mixture, b) pure $C_{71}H_2$ (solid line) together with pure C_{70} (dashed line), and c) pure $C_{71}H_2$ produced by the Krätschmer–Huffman method (solid line) and by the CVD method (dashed line). Conditions: Buckyprep-M column (20×250 mm^2); flow rate: 12 mL min^{-1}; eluent: toluene.

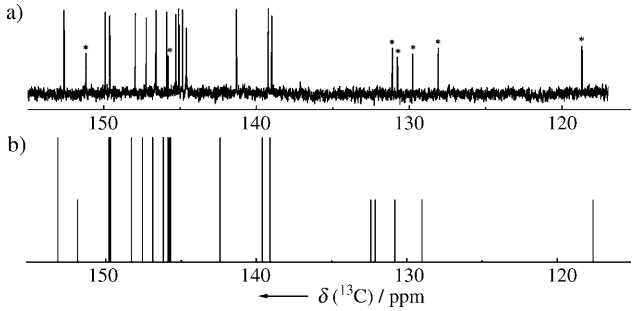

Figure 3. a) ^{13}C NMR spectrum (100 MHz) of $C_{71}H_2$ (CS_2/[D_6]acetone) in the range $\delta = 115$–155 ppm. b) Computed (B3LYP/6-31G* level) ^{13}C NMR spectrum of $C_{71}H_2$ with C_{2v} symmetry. Signals marked with * are single-intensity resonances (all others are double intensity).

equivalent hydrogen atoms. The resonances for the methylene hydrogen atoms of the **a**–**b** isomer were reported to occur at $\delta = 2.88$ ppm.[7] The singlet that we observed at $\delta = 1.27$ ppm for the C_{2v} $C_{71}H_2$ isomer indicated unambiguously that our spectrum was that of the **e**–**e** isomer. The high-field chemical shift of this signal indicates that the methylene hydrogen atoms are more shielded than those in the other experimentally accessible $C_{71}H_2$ isomers ($\delta = 2.91/6.52$ for **a**–**a**, 2.88 for **a**–**b**, 2.78/5.23 for **b**–**c**, and 2.56 ppm for **c**–**c**)[7] and provides strong evidence that the equatorial hexagonal rings of C_{70} are the most aromatic.[11,12]

UV/Vis spectra exhibit different absorption characteristics for different isomers as a result of changes in the molecular-orbital levels. According to Smith et al.,[7] the absorptions of the **a**–**a** isomer (homofullerene) are much more similar than those of the **a**–**b** isomer (methanofullerene) to those of C_{70}, as the homofullerene retains the π-electron conjugation system of the C_{70} skeleton to the maximum extent. The spectrum of our arc-produced **e**–**e** isomer exhibits similar absorptions to those of pristine C_{70} (Figure 4). This result is again consistent with a homofullerene structure.

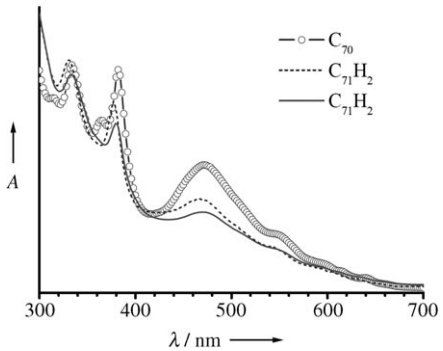

Figure 4. UV/Vis spectra (in toluene) of C_{70}, arc-produced $C_{71}H_2$ (dashed line), and CVD-produced $C_{71}H_2$ (solid line).

measured spectrum with 21 lines (14×4, 7×2) in the range $\delta = 115$–155 ppm (corresponding to sp^2-hybridized carbon atoms) and a single line (1×1) at $\delta = 30.2$ ppm (corresponding to the sp^3-hybridized methylene carbon atom) is only consistent with the **e**–**e** homofullerene isomer with C_{2v} symmetry, since the methano isomer should have 20 lines (14×4, 6×2) for the sp^2-hybridized carbon atoms and two lines for a twofold degenerate and a methylene sp^3-hybridized carbon atom. The ^{13}C NMR spectrum simulated at the B3LYP/6-31G* level for the **e**–**e** isomer agrees reasonably well with the experimental result (Figure 3). Notably, the e,e bridgehead carbon atoms have a chemical shift of 118.64 ppm, which is consistent with the computationally optimized structure, homofullerene, owing to homoaromaticity.[26]

The heteronuclear multiple quantum coherence (HMQC) NMR spectrum (see the Supporting Information) shows a ^{13}C–^{1}H correlation at the intersection of $\delta_C = 30.2$ ppm with $\delta_H = 1.27$ ppm; this correlation is consistent with a methylene functional group. Of all eight computationally predicted isomers of $C_{71}H_2$, only isomers **a**–**b** and **e**–**e** contain two

Three basic formation mechanisms can be envisioned for $C_{71}H_2$ in the direct-current (DC) arc. First, C_{70} and $C_{71}H_2$ form simultaneously under the conditions of the arc. Second, C_{70} forms initially in the arc and then reacts with CH_x to form several isomers of $C_{71}H_2$, which isomerize into the **e**–**e** isomer. The third mechanism is similar to the second except that the **e**–**e** isomer is the only survivor of the several isomers of $C_{71}H_2$ formed during the subsequent cooling collisions.

To confirm that high temperatures are required to overcome an activation barrier to produce thermodynamically stable e–e-bonded adduct, and to probe the formation mechanism, we produced $C_{71}H_2$ by another high-temperature technique. This technique was similar to chemical vapor deposition (CVD)[27] but involved the direct reaction of C_{70} with CH_4 in the gas phase at approximately 1100 °C. The $C_{71}H_2$ product obtained by the "CVD" method was essentially identical to that synthesized by the modified Krätschmer–Huffman method (Figures 2 and 4). As the temperature of the "CVD" method is about 3000 K lower than that of the arc method, it is likely that C_{2v}-$C_{71}H_2$ is produced by the second or

third mechanism; that is, C_{70} forms in the arc and subsequently reacts whilst hot with CH_4.

In conclusion, we synthesized the elusive but thermodynamically most stable carbene adduct of C_{70}: an isomer of $C_{71}H_2$ in which CH_2 has added across an e–e bond to form a C_{2v} homofullerene. The product was characterized by NMR and UV/Vis spectroscopy, as well as mass spectrometry. Theoretical studies (B3LYP/6-31G*) confirmed that this isomer is the most stable, although the direct addition of carbene at the equatorial sites is not kinetically favorable. This DC-arc production of the $C_{71}H_2$ **e**–**e** isomer appears to be thermodynamically controlled, as confirmed by a CVD-based method for the direct reaction of C_{70} with CH_4 in the gas phase.

The production and characterization of the thermodynamically most stable but kinetically unfavorable $C_{71}H_2$ isomer, together with the systematic theoretical studies, not only offer us direct experimental evidence in answer to some important chemical questions, such as the local aromaticity of C_{70} and the structure of divalent-group adducts of normal-diameter single-walled nanotubes, but also introduce a new member into the homofullerene family and provide a new route for the synthesis of novel stable fullerene derivatives that can not be obtained under routine synthetic conditions. More studies on this homofullerene and related systems are in progress.

Experimental Section

In the modified Krätschmer–Huffman method, helium and methane (ca. 100:1) were introduced into the DC-arc oven at a total pressure of 26.7 kPa. A spectroscopically pure graphite rod (length 30 mm, ø 8 mm) was used as the anode, a graphite disk as the cathode. The voltage and intensity of the current were maintained at 40 V and 160 A, respectively. The as-produced soot was extracted by Soxhlet extraction with toluene for 48 h, and the extracts were separated by HPLC (see the Supporting Information). The total amount of $C_{71}H_2$ obtained was approximately 3 mg (ca. 0.05 % in the produced soot). The retention time for $C_{71}H_2$ was approximately 19.5 and 12.2 min on Buckyprep and Buckprepy-M columns (20×250 mm^2, Cosmosil; detector: 310 nm), respectively, at a flow rate of 12 mL min^{-1} in toluene.

In the CVD-based method, C_{70} vapor, sublimed from the purified C_{70} powder at 800 °C, was brought into the reaction area (1100 °C) by a flow of CH_4. The products were deposited at the collection zone (room temperature), then extracted with toluene from a sootlike residue (amorphous carbon resulting from the decomposition of CH_4 and C_{70}), and then separated by recycling HPLC (Buckyprep-M column).

^{13}C NMR spectroscopy of $C_{71}H_2$ was carried out on a 100 MHz NMR spectrometer (Bruker AV400) with a BBO probe (5 mm). The sample was dissolved in CS_2, with [D$_6$]acetone in a capillary as an internal lock. The ^{1}H–^{13}C HMQC spectrum of $C_{71}H_2$ was acquired on a Bruker AV400 instrument (600 MHz) with a BBI probe (5 mm), with CS_2 as the solvent and [D$_6$]acetone as an internal lock. ^{13}C NMR (100 MHz, [D$_6$]acetone, 25 °C): $\delta = 30.2$ (1 C), 118.6 (2 C), 129.3 (2 C), 129.7 (2 C), 130.7 (2 C), 131.1 (2 C), 139.1 (4 C), 139.3 (4 C), 141.4 (4 C), 144.6 (4 C),144.9 (4 C), 145.2 (4 C), 145.4 (2 C), 145.9 (4 C), 146.0 (4 C), 146.7 (4 C), 147.3 (4 C), 148.0 (4 C),149.7 (4 C), 150.0 (4 C), 151.2 (2 C), 152.7 ppm (4 C).

^{1}H NMR (400 MHz, [D$_6$] acetone, 25 °C, Si(CH$_3$)$_4$): $\delta = 1.27$ ppm.

UV/Vis spectra of $C_{71}H_2$ and C_{70} were recorded on a UV spectrometer (Unico UV4802) in toluene. $C_{71}H_2$: $\lambda_{max} = 333$, 380, 471, 550, 600, 618, 640, 660 nm ($\varepsilon_{380} = 32\,970$ L mol^{-1} cm^{-1}); C_{70}: $\lambda_{max} = 316$, 335, 365, 383, 472, 550, 600, 620, 640, 660 nm ($\varepsilon_{383} = 36\,067$ L mol^{-1} cm^{-1}).

Full geometry optimization and ^{13}C NMR chemical-shielding computations were carried out for all possible $C_{71}H_2$ isomers at the B3LYP/6-31G* level of theory. ^{13}C NMR chemical-shielding values were evaluated by employing the gauge-independent atomic orbital (GIAO) method. They were calculated relative to C_{60} and converted to the tetramethylsilane scale. All calculations were carried out with the Gaussian 03 program.[28]

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