

Electronic Interactions in a New Fullerene Dimer: C₁₂₂H₄, with Two Methylene Bridges

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The isolation of a new fullerene dimer, C₁₂₂H₄, and its structural characterization by ¹³C NMR and ¹H NMR spectroscopy and by UV/vis and IR spectroscopy are reported. The structure of this dimer consists of two fullerene cages, which are directly connected through two C–C bonds and two methylene bridges. Consequently, adjacent hexagonal faces of the two fullerene cages are arranged in a face to face manner. Molecular orbital calculations indicate that the proximity of the fullerene cages results in significant through space overlap in both the HOMO and LUMO. As a consequence of this overlap, the electrochemistry of the dimer shows electronic communication with stepwise reduction of each cage.

Introduction

Dimeric fullerenes have attracted attention as models for fullerene polymers and as compounds where electronic interactions between cages can be examined. The study of these electronic interactions could lead to the design of electron acceptor systems and would allow theoretical modeling of intercage interactions in fullerene-based materials. Such “electronic communication” was indeed observed in the electrochemical reduction of C₁₂₀O,² and of (C₅₉N)₂.³ For these reasons we are interested in the synthesis and structural characterization of other fullerene dimers. We recently reported the synthesis of the novel fullerene dimers C₁₂₁ and C₁₂₂ whose synthesis probably takes place *via* an intermediate carbene, C₆₁.⁴ The existence of this intermediate was first proposed by Vogtle *et al.*⁵ and supported by a subsequent work of Strongin *et al.*⁶ Several other fullerene dimers have already been reported.⁷ In a continuation of our work on the thermolysis of methanofullerene derivatives, we describe here the isolation and characterization of a new fullerene dimer, C₁₂₂H₄.

Experimental Section

C₆₀ (>99.5% purity) was purchased and used without any further purification. ¹³C-enriched fullerenes were purchased from MER Corp., Tucson, AZ; the HPLC separation with toluene on a preparative Buckyprep column afforded pure [¹³C]-[60]fullerene. All the solvents used were reagent grade, and they were dried and distilled before use. The reactions were performed under argon atmosphere. UV/vis measurements were performed on either toluene or *o*-dichlorobenzene (ODCB) solutions. IR spectroscopy experiments were performed on KBr micropellets. ¹H and ¹³C NMR were done with either a Jeol JNM270 (¹H, 270 MHz) or a Varian (¹H, 300 MHz; ¹³C, 500 MHz) instrument with CS₂, ODCB, or 1-chloronaphthalene as solvent. Laser desorption and ionization time of flight mass spectroscopy (LDI TOF MS) and matrix-assisted LDI TOF MS (MALDI TOF MS) were performed with a Perseptive Biosystems instrument with either negative or positive ionization in linear or reflector mode. In the negative mode, a one-point calibration was performed with angiotensin I (MH⁺, 1296.685 Da; MH⁻, 1294.669 Da), whereas in the positive mode two-point calibrations of the spectrometer were performed. To ensure a high accuracy for the dimer peaks, the two-point calibrations were made with either angiotensin I and neurotensin (MH⁺, 1672.97 Da) in α -cyano 4-hydroxycinnamic acid or ¹²C₆₀ (720.0 Da in both isotopic and average mass) and neurotensin. For MALDI TOF MS experiments, either dithranol or 9-nitroanthracene was used as matrix.

Preparative HPLC was performed with a Cosmosil Buckyprep column (250 × 20 mm) at flowing rates of toluene between 15 and 21 mL/min. Gel permeation chromatography (GPC) with toluene as eluent was performed on preparative Jaigel 1H + 2H columns (40 × 600 mm) at 12 mL/min or on analytical Shodex KF810 + KF802 columns with a 1 mL/min flow of toluene. HPLC analyses were performed with an analytical Cosmosil Buckyprep column (4.6 × 250 mm) with toluene at 1 mL/min or a Cosmosil 5PBB column (10 × 250 mm) with toluene, chlorobenzene, or ODCB as eluent.

Ethoxycarbonylmethano-1,2-dihydro[60]fullerene was synthesized by the procedure described by Wilson *et al.*⁸ and bis-(ethoxycarbonyl)methano-1,2-dihydro[60]fullerene according to the method of Bingel.⁹ The purifications of the monoadducts were done with a preparative GPC or a GromSil HPLC column.

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Semiempirical calculations (AM1 and PM3) and *ab initio* calculations at the HF/3-21G level were done with the Gaussian 98W package.¹⁰

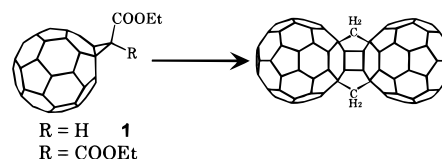
Electrochemistry of C₁₂₂H₄. *o*-Dichlorobenzene (Sigma-Aldrich) and tetra(*n*-butyl)ammonium perchlorate (Fluka) were used as received. For the electrochemical studies the samples of **2** were purified at least three times by HPLC and checked to produce single, symmetrical peaks in recycling HPLC on both Cosmosil Buckyprep and Cosmosil 5PBB columns. The solutions were 0.03 mM C₁₂₂H₄ and 0.11 mM C₆₀ with 0.01 M TBAP as supporting electrolyte. Details regarding the voltammetric experiments are given elsewhere.² All potentials are reported with the potential of the ferrocene/ferrocenium redox couple as the standard reference potential.

A Typical Procedure for the Synthesis of 2. In a controlled atmosphere furnace, 100 mg of pure **1** was placed and kept under vacuum at 10⁻⁴ Torr for 30 min, at 400 K. Then, under an argon flow of 50–100 mL/min, the furnace was heated to 700 K at a rate of 10 K/min and immediately cooled at 10 K/min as the temperature reached 700 K. The as-obtained dark-brown powder was dissolved in ODCB, giving a brown solution. Adding hexane to the ODCB solution of the reaction product induced precipitation of the less soluble material. (This procedure was used before for the separation of other fullerene dimers; see Kratschmer *et al.*¹¹) The mixture was filtered, and the precipitate was extracted with toluene in a Soxhlet extractor for one week. This procedure produced a dark-brown solution with a reduced content of [60]fullerene. Triple HPLC separation of the as-obtained solution afforded 5–10 mg of **2**. A better alternative than the precipitation is the separation of the ODCB solution of the thermolysis product using a Cosmosil 5PBB column with ODCB as eluent. In this case (Cosmosil 5PBB guard, 10 × 20 mm, and 5PBB, 10 × 250 mm) at a 2 mL/min flow of ODCB and 1 mL injection volume, [60]fullerene elutes at 9.8 min, the mixture of dimers as a broad peak at 13–15 min, and the higher oligomers at 19–23 min. After the broad peak was collected at 13–15 min, the solvent was evaporated *in vacuo* and the resulting powder dissolved in toluene. The toluene solution was further subjected to HPLC separation on a Cosmosil Buckyprep column (see below).

Results

After thermolysis of the methanofullerene **1**, which contains an ester group, several fullerene derivatives were observed which eluted during chromatography on a Cosmosil Buckyprep HPLC column with retention times between 15 and 45 min.¹² The main product, other than [60]fullerene, is a compound which elutes at 23.4 min. This compound was subsequently identified as the interesting fullerene dimer C₁₂₂H₄, **2** (Scheme 1). In a typical experiment, thermolysis of 100 mg of **1** under argon allows about 5–10 mg of pure **2**.¹³ On the basis of the data presented below, we propose that the structure of **2** involves two fullerene cages that are directly joined by two carbon–carbon bonds and by two bridging meth-

Scheme 1



ylene groups. The resulting ring CH₂–CC–CH₂–CC– has a rigid “boat” conformation.

MALDI TOF MS of **2**¹⁴ gave the molecular peak at 1468.96 Da (the expected value for C₁₂₂H₄ is 1469.33 Da¹⁵). Additionally, peaks at 720.87, 735.07, and 749.31 Da, which correspond to the fragments C₆₀, C₆₀CH₂, and C₆₀C₂H₄, were observed.

IR spectroscopy revealed the presence of C–H stretching and CH₂ bending vibrations at 2961, 2930, and 2875 cm⁻¹ and 1652 and 1594 cm⁻¹, respectively, as well as C₆₀ breathing mode vibrations at 524 and 569 cm⁻¹. As seen in Figure 1, the UV/vis spectrum of **2** is generally featureless, as has been reported for other fullerene dimers,¹⁶ except for a small band at 430 nm, which is characteristic of dihydrofullerenes. Accordingly, the color of a toluene solution of **2** is yellow-orange, while the saturated ODCB solution is orange-red. Analytical GPC data for **2** are consistent with a dimeric fullerene; the elution times for C₆₀, **1**, and **2** on Shodex analytical columns KF801 + KF802 at 1 mL/min toluene were 27.5, 23.8, and 22.2 min, respectively.

(12) With our HPLC system (Shodex ODS guard column, 4 × 20 mm, coupled with a Cosmosil Buckyprep, 4.6 × 250 mm) at 1 mL/min of toluene and 325 nm detection, [60]fullerene elutes at 8.1 min, whereas C₁₂₂H₄ elutes at 26 min. For preparative purposes we used a Cosmosil Buckyprep, 20 × 250 mm, and a guard Buckyprep column of 10 × 20 mm. The retention times quoted in the text refer to a flow of 21 mL/min of toluene on the preparative column (injection volume 7 mL, the volume of the UV detector being 0.5 mL). Using either bis-(ethoxycarbonylmethano)-1,2-dihydro[60]fullerene or ethoxycarbonylmethanol-1,2-dihydro[60]fullerene, the HPLC trace looks very similar. We identified the fraction corresponding to **2** in both thermolysis products of ethoxy- and bisethoxycarbonylmethanofullerene. Either one of the two methanofullerenes can be used for the synthesis of this dimer. Several fractions overlap between 19 and 30 min; among these we have identified after recycling HPLC separation (on the basis of the HPLC elution time, UV/vis, IR, ¹³C NMR and MALDI TOF MS experiments) C₁₂₀O, two isomers of C₁₂₀O₂, C₁₂₁, C₁₂₂, and C₁₂₂H₄. There are three fractions giving the C₁₂₂ peak in the MS (eluting at 21, 25.5, and 29 min), but we were unable to identify them by ¹³C NMR experiments. Minor peaks can be observed up to 45–50 min; we assigned them as belonging to fullerene trimers. The dimer **2** elutes on a Cosmosil 5PBB column (10 × 250 + 10 × 20 mm guard 5PBB column) at 28.2 min with toluene at 7.5 mL/min, at 16.1 min with 3 mL/min of chlorobenzene, and at 12.1 min with 2.5 mL/min of ODCB.

(13) To determine purity, we used recycling HPLC analysis. Elemental analysis is not suitable for some fullerene derivatives because of the poor combustion which systematically gives a lower content of carbon. Moreover, the hydrogen content of the fullerene dimer **2** (theor. 0.27%) is even smaller than the usual error limit for combustion analysis.

(14) The values discussed in the text for MALDI TOF MS of **2** refer to an experiment made in linear mode, negative ionization using dithranol as matrix (20 kV accelerating voltage, 70% grid voltage, 125 averaged scans).

(15) Within the error of the MALDI TOF experiments, the peak appearing at 1469 Da could correspond to a hypothetical C₁₂₁O as well as C₁₂₂H₄. On the basis of a ¹³C NMR resonance at 167 ppm, which appeared in our samples, we initially considered that **2** had a molecular formula of C₁₂₁O. However, we finally found that the resonance at 167 ppm was that of an unidentified impurity and systematically appears in samples previously purified by a Buckyprep column. This impurity interfered with the ¹³C NMR experiments since the sample had low solubility. Four other resonances were identified as belonging to impurities in the sample: 0.25 and 30.2, 54.1, and 68.1 ppm.

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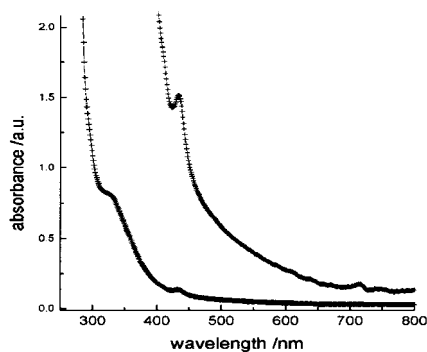


Figure 1. UV/vis spectrum of **2** in ODCB.

Several ¹³C NMR experiments on ¹³C-enriched samples of **2** provided definitive structural characterization of the new dimer.¹⁷ Four samples of **2** with different labeling patterns were made as follows:¹⁸ **A**, natural isotopic abundance was present for all carbon nuclei; **B**, the fullerene cage carbons were 10–15% enriched in ¹³C, and the cyclopropane carbon atoms were not enriched; **C**, the fullerene cage carbons were 10–15% enriched in ¹³C, and the cyclopropane carbon atoms were 99% enriched in ¹³C; **D**, the cyclopropane carbon atoms were 99% enriched in ¹³C, while the fullerene carbon atoms were not enriched. The ¹³C NMR spectra of samples **A** and **B** displayed 30 resonances in the sp² region. Four of these resonances had only half the intensity of the other 26. This pattern is consistent with a dimer with C_{2v} symmetry. The structures of four such dimers are shown in Figure 2. For the ¹³C NMR spectra of samples **A** and **B**, three resonances were detected in the sp³ region at 74.93, 63.52, and 57.35 ppm, and for sample **A** as seen in Figure 3a the relative intensity of these resonances is 2:2:1. Sample **C** (see Figure 3b) was notable in showing structural details for this compound: a doublet at 63.5 ppm and a triplet at 57.3 ppm with a J_{CC} of 34.2 Hz. These originate from the spin–spin coupling of fullerene sp³ carbon atoms with the carbon atoms of the bridging methylene groups, which in this case are 99% ¹³C-enriched. Two-dimensional ¹³C NMR INADEQUATE experiments confirmed that these carbons are directly connected. ¹³C NMR off-resonance decoupling experiments for samples **C** and **D** showed a characteristic triplet for the CH₂ group (J_{CHa} and J_{CHb} were determined to be 133.7 and 137.8 Hz, respectively).

The ¹H NMR spectrum for sample **A** revealed a quartet for the methylene protons with a characteristic AB pattern centered at 5.72 ppm and a coupling constant of 15.2 Hz (instrument frequency 269 MHz). ¹H NMR for sample **C** showed two quartets, the splitting arising from the spin–spin coupling with the bridging carbon atoms. The coupling constants J_{CHa} and J_{CHb} were determined to be 133.7 and 137.1 Hz, respectively.

(17) The resonance at 147.24 ppm was observed as a doublet in a subsequent measurement in d₄-ODCB. The resonance at 142.61 belonged to a minor impurity of C₆₀ (see the Supporting Information). Due to a solubility limitation the resolution of the spectra measured in solvents other than chloronaphthalene was rather poor, even after 48 h of measurements. When 1-chloronaphthalene was used as solvent, an upfield shift of about 0.3 ppm was observed, compared to the spectrum measured in d₄-ODCB. This effect was previously observed in the ¹³C-NMR of fullerenes; see: Scriven, W. A.; Tour, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1207.

(18) ¹³C-enriched mixed fullerenes were purchased from MER Corp. (Tucson, AZ); the quoted ¹³C content of the fullerene was 10–15%. Our LDI TOF MS experiments indicated that the average content of ¹³C was about 16%, with a distribution ranging from 10% to 20% ¹³C.

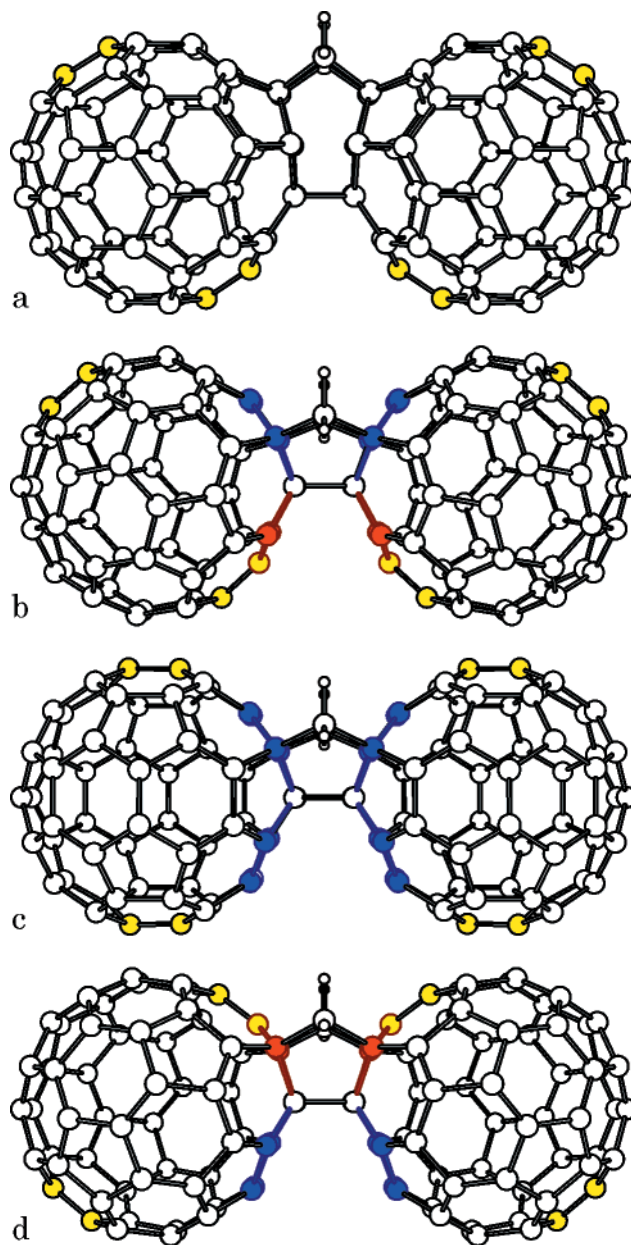


Figure 2. Possible structures for the dimer **2**, optimized at the HF/3-21G level. Note that, to agree with the observed ¹³C NMR spectra, in the dimer **2a**, two carbons from each connecting hexagon should not participate in the intercage bonding. The most unlikely structure is **2d**, which has four sp³ carbons in each of the connecting pentagons. The carbon atoms involved in the pentagons and hexagons adjacent to the bridge are marked in red and blue, respectively. The on-plane carbon atoms are marked in yellow; their position relative to the bridge can be used for a straightforward identification of dimeric fullerene structures. The most stable structure can be intuitively deduced as the one with the smallest number of [6, 5] connections (i.e., at the junction between a pentagon and a hexagon). The number of [6, 6] and [6, 5] connections for the **2b–d** structures are 2 and 4, 4 and 2, and 0 and 6, respectively.

Possible structures for the new dimer **2** are presented in Figure 2. These structures were separately optimized by *ab initio* calculations at the HF/3-21G level. One of these structures (**2a**) places the CH₂ bridges in a (1, 2) position while the other three structures (**2b**, **2c**, and **2d**) place the methylene bridges in a (1, 4) position. From these possible structures, **2d** can be discarded since each

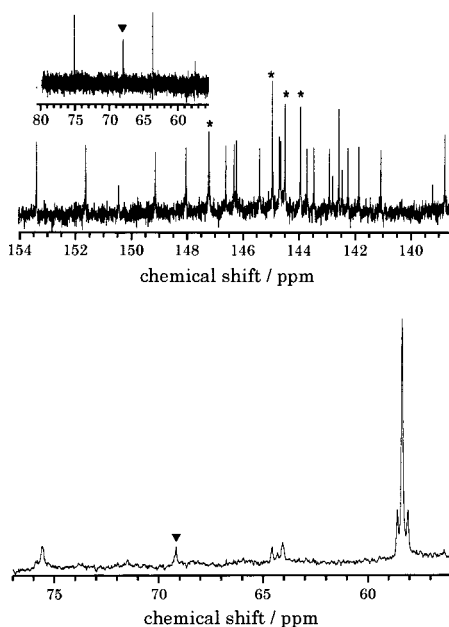


Figure 3. (a, top) ^{13}C NMR spectrum of **2** (experiment A). The resonance at 67 ppm, marked by a triangle, was detected to be of an impurity (see ref 15). An additional resonance at 134.5 ppm, covered by the solvent in this experiment, was detected when using CS_2 as solvent for experiment C (i.e., 15% ^{13}C -enriched C_{60} cage). There are four coincidental resonances at 147.2, 144.9, 144.4, and 143.9 (marked by asterisks); a resonance belonging to a minor impurity of C_{60} was observed at 142.61 ppm. (b, bottom) sp^3 region ^{13}C NMR of **2**, H-decoupling (15% ^{13}C -enriched C_{60} and 99% ^{13}C bridge carbon).

pentagon adjacent to the bridge has four sp^3 carbons. *Ab initio* calculations showed that **2b** is the most stable of these four isomers and that **2a**, **2c**, and **2d** are less stable by 283.7, 99.5, and 496.6 kJ/mol than **2b**, respectively. Additional data favoring the structure **2b** are given below. From previous work of Diederich *et al.*,¹⁹ it was observed that the ^1H NMR shifts of addends are strongly affected by local and ring currents and anisotropic effects of fullerene. Thus, in the case of [6,5] open ethoxycarbonylmethano-1,2-dihydro[60]fullerene, there are two possible isomers: the proton is adjacent either to a pentagon ring or to a hexagon ring. The chemical shifts for the two cases differ by as much as 3.5 ppm, because of the influence of the ring currents, particularly strong paramagnetic ring currents of the pentagon. Note that the ^1H NMR data of **2** showed that the environments of the protons are very similar, like they are in **2b** and **2c**. The difference in chemical shifts originates in their distinct location; one hydrogen atom faces away from the bridging unit, while the other is located on the inward side of the bridge structure. Their NMR shifts differ by 0.16 ppm. In the case of structure **2a**, one of the protons lies over a pentagon ring and the other over a hexagon. Accordingly, the ^1H NMR for **2a** should show a much larger difference between the proton chemical shifts. In a more quantitative approach, the expected ^1H NMR spectra for the **2a**, **2b**, and **2c** dimers were calculated at the HF/3-21G level using the GIAO method.²⁰ These calculations indicated that the isomers should have lines at 3.739 and 4.182

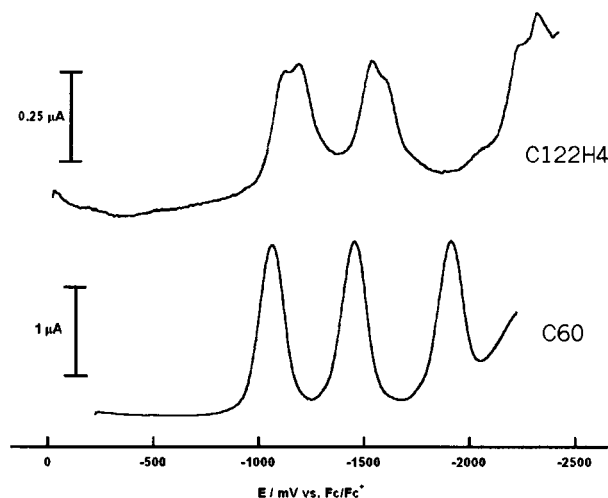


Figure 4. Square-wave voltammetry of (a, top) C_{122}H_4 and (b, bottom) C_{60} in ODCB with 0.10 M TBAP as supporting electrolyte vs ferrocene/ferrocinium as internal standard. Square-wave voltammetry parameters: pulse step 2 mV, square-wave frequency 15 Hz, square-wave amplitude 10 mV, and 256 samples per point for C_{122}H_4 ; pulse step 4 mV, square-wave amplitude 25 mV, square-wave frequency 15 Hz, and 256 samples per point for C_{60} .

ppm for **2a**, at 4.951 and 5.056 ppm for **2b**, and at 4.309 and 4.428 ppm for **2c** (neglecting the spin–spin coupling). These values are in good agreement with the experiment considering the strong deshielding due to the vicinity of the pentagon ring.²¹ Although these electronic effects were initially observed for fullerenes, they also are found to hold for methanofullerenes as well, albeit to a smaller extent. On the basis of these observations, we propose that the C_{122}H_4 dimer has structure **2b**, with two adjacent hexagons of the fullerene cages oriented in a “face-to-face” manner. This structure is similar to that proposed by Krätschmer *et al.*²² for the C_{120}O_2 dimer. Their reasoning in regard to the ^{13}C NMR shifts of the on-plane carbon atoms for two possible structures of C_{120}O_2 can also be applied here. Additionally, we analyzed the ^{13}C NMR shifts of **2** by the GIAO method for the structures **2a**, **2b**, and **2c**. For isomer **2b** good agreement was found between the computed ^{13}C NMR spectrum and the experimental spectrum. Agreement was particularly satisfactory for the resonances of the carbon atoms that were situated on the mirror plane (see the Supporting Information).

The C_{122}H_4 dimer seems to be stable as a solid under ambient conditions, in air and in the presence of light. However, although no decomposition of this dimer has been observed, completely insoluble golden-yellow films are formed on the flask surface after several weeks of storage of saturated ODCB solutions.

Trace a of Figure 4 shows the square-wave voltammogram for reduction of C_{122}H_4 , while trace b shows similar data for C_{60} itself. Notice that the reduction of C_{122}H_4 consists of three major peaks at ca. -1200 , -1600 , and -2300 mV with clear splitting on each peak. All pairs of waves are shifted to more negative potentials relative to C_{60} , and the shift for the waves at -2300 mV is largest.

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(21) A similar strong paramagnetic shift was observed in a CH_2 -bridged dimer, C_{121}H_2 , as was reported by A. B. Smith III *et al.*; see ref 16.

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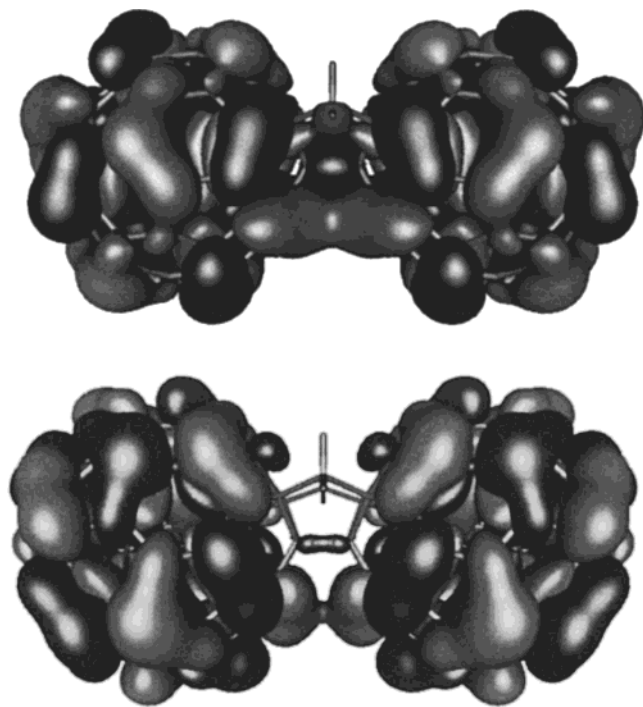


Figure 5. Contour plots for the HOMO (a, top) and LUMO (b, bottom), calculated for **2b** (0.005 e/au).

The splitting of the three major peaks is indicative of electronic communication between the two halves of the dimer. Thus, reduction occurs stepwise to form [C₁₂₂H₄]^{*n*} (*n* = [−1, −2] at −1200 mV, [−3, −4] at −1600 mV, and [−5, −6] at −2300 mV). Cyclic voltammograms reveal that the reductions are reversible. There is no evidence that the dimer dissociates to form free C₆₀ upon reduction. In contrast, the dimer C₁₂₀ undergoes dissociation to [C₆₀]^{*n*} upon electroreduction.²³ The electrochemical behavior of C₁₂₂H₄ parallels that of C₁₂₀O with three sets of pairwise reduction to form [C₁₂₀O]^{*n*} (*n* = [−1, −2], [−3, −4], and [−5, −6]).²

To understand the nature of the electronic communication between the two fullerene cages in **2**, semiempirical molecular orbital calculations were performed. Figure 5 shows the contours of the HOMO and LUMO of **2b**. There is a significant, through space overlap between the two cages in the immediate vicinity of the bridging connections, in both the HOMO and LUMO. As a result of this overlap, the two cages interact and the reduction of each cage occurs at a distinct potential as seen in Figure 4. Compared to that at the HOMO, the interaction at the LUMO level seems smaller. However, if the cages are independent, then the addition of the first and the second electrons would take place at the same potential.²⁴ We

presume that the addition of a third electron would not be influenced by the level of interactions between the cages. Considering the second electron addition, there are two possibilities: it is at the same potential as the first electron, thus showing that the cages are independent, or it occurs at a different potential, showing that the cages are interacting. The magnitude of this difference shows, to some extent, the level of interaction. Nevertheless, because of the different possible delocalization of the electrons in C₆₀ dimers (different from that for C₆₀) and a higher electron affinity of [C₆₀-dimer]^{1−} compared with [C₆₀]^{1−} it is expected that the potential difference between the first and the second reductions is smaller on C₆₀ dimers than on C₆₀. The effects of these interactions between the cages and their influence upon the optical properties of this remarkable dimer are currently under investigation.

The mechanism of formation of this dimer is still unclear. However, we do know that the cyclopropane carbon atom of **1** became a methylene bridge in the dimer **2**, as deduced from the results on ¹³C-enriched samples in both MS and NMR experiments. This fact implies that scission of the cyclopropane takes place, possibly with the formation of a biradical. The hydrogen abstraction might be done *via* a radical mechanism (thermogravimetry (TG)–mass spectroscopy coupled experiments showed the formation of methyl and methylene groups, and they might be involved in the formation of **2**). The fact that the cyclopropane carbon became a methylene bridge allows us to speculate that an intermediate in the formation of **2** might be a C₁₂₂ dimer, in one of the several possible forms inferred recently from ion-mobility studies by Jarrold et al.²⁵

Conclusions

A new fullerene dimer, C₁₂₂H₄, has been isolated and characterized. Electronic interactions between the C₆₀ cages have been observed by electrochemical methods.

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Supporting Information Available: Spectral data of the dimer **2**, a ¹³C NMR spectrum of **2** in *d*₄-ODCB, and charts of computed ¹³C NMR spectra for **2a–c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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