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The synthesis and characterization of 1′-bromo-1,2-methano[60]fullerene

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In this paper we report the synthesis and characterization of 1′-bromo-1,2-methano[60]fullerene. This methanofullerene was synthesized using the reaction of C_{60} with bromocarbene. The interest in this derivative is related to the possibility of its further functionalization *via* Suzuki coupling as well as it being a possible intermediate for the generation of a C_{61} unit.

Introduction

In the last ten years, since their first isolation,[1] fullerenes have attracted a great deal of attention as an interesting substrate for functionalization with organic groups. This is an active field of research and many reports and several monographs are devoted to this topic.[2] Among the possible strategies for the functionalization of fullerenes, carbene attack is one of the most studied. Dihalocarbene addition to C_{60}, which is of particular interest for further functionalization of fullerenes, was first reported by Ishida *et al.*[3,4] More recently, several other groups have tackled this class of derivatives,[5] in particular with relation to the possibility of synthesis of *all-carbon* allotropes containing C_{61} units.[6,7] It was also recently found that in the case of C_{70}, a homofullerene could be obtained as a result of CBr_2 addition by using a Seiferth reagent.[8] This was actually the first fully characterized homofullerene (also called fulleroid). Based on these works and on the perspectives offered by the functionalization of the C_{60}-haloderivatives we report here the first synthesis of a mono-halo methanofullerene derivative, 1′-bromo-1,2-methano[60]fullerene, **1**. We are interested in the synthesis of this compound because of the possibility of using it as a building block for C_{61} addition–substitution reactions.

Experimental

General

C_{60} (>99.5% purity) was purchased from Term Co. and used without further purification. The solvents were reagent grade, dried and distilled before use. All reactions were performed under a dry argon atmosphere. UV–VIS spectra were measured with a Hitachi 9000 spectrophotometer as toluene and *o*-dichlorobenzene (ODCB) solutions. IR spectroscopy experiments were performed with a Bruker FT-IR instrument on KBr pellets. ^1H and ^{13}C NMR spectra were run on a JEOL JNM270 (^1H 270 MHz) spectrometer in 1-chloronaphthalene with 25% 1,2-dichlorobenzene-d_4 or nitrobenzene-d_5 for field/frequency lock. FAB-MS were measured with a JEOL JMS-AX505H spectrometer in positive or negative ionization. HPLC analyses were performed with preparative (20 × 250 mm) or analytical Cosmosil Buckyprep (4.6 × 250 mm) columns with toluene and with a Cosmosil 5PBB column (10 × 250 mm) with chlorobenzene or ODCB as mobile phases. The HPLC system was a Jaigel-C_{60}-908 with automatic injecting–recycling JAR-2.

All theoretical calculations were made using the Gaussian 98W package.[9] Geometry optimizations were made at the HF/6-31* level and by using the Becke-style 3 parameter density functional theory, with the Lee–Yang and Parr correlation functional, at the 6-31G* basis set.[10]

Cyclic voltammetry experiments were carried out in ODCB using 0.05 M tetra-*n*-butylammonium tetrafluoroborate (Fluka) as supporting electrolyte. A standard three electrode cell was employed, using a 1.6 mm diameter disk Au electrode, a Pt counter electrode and a silver wire as reference. The potential was referenced against an internal Fc/Fc^+ couple.

Into a flame-dried two-necked flask, 36 mg C_{60} and 0.5 mL CH_2Br_2 were added. The flask was filled with argon, equipped with an Ar-gas flow inlet and a septum. 50 mL of dry toluene was added by using a transfer line. The flask was then cooled to −30 °C and the mixture stirred until the C_{60} was completely dissolved. Through a syringe, 0.5 mL of a toluene solution of $[(CH_3)_3Si]_2NNa$ (commercially available at a concentration of 35% from Wako) was slowly added. After another two hours the reaction was quenched with 10 mL water and the mixture was thoroughly extracted with toluene. The organic phase was filtered through a silica plug, dried over $CaCl_2$ and separated by using HPLC. Typically, about 30% yield was obtained. The reaction is very sensitive to the water content of the solvent and therefore a freshly distilled and dried solvent is recommended. Alternatively, the reaction can be scaled up with some loss in the yield. The use of dry-ODCB at 0 °C for 12 hours allows syntheses in batches of 720 mg C_{60}, the yield decreasing in this case to 10–15%.

HPLC separation

For the purification of **1** a semi-preparative Cosmosil 5PBB column (10 × 250 mm) with 6 mL min^{-1} toluene as mobile phase was used. The retention time of **1** in these conditions is slightly smaller than that of C_{60}, 6.5 *vs.* 6.9 minutes, and its separation requires recycling. An automatic injection–recycling system was used and typically a 360 mg C_{60} reaction batch requires about 200 injections of 2 mL and 3 recycle periods. The product is difficult to purify with other columns; on a Cosmosil Buckyprep column eluting with toluene only a slight asymmetry of the C_{60} peak can be observed. The presence of a broad peak eluting before **1** was also observed during HPLC analyses. This is presumably due to the formation of higher adducts such as $C_{60}(CHBr)_n$. The high number of possible isomers for these multiadducts as well as their difficult HPLC separation impeded further investigations.

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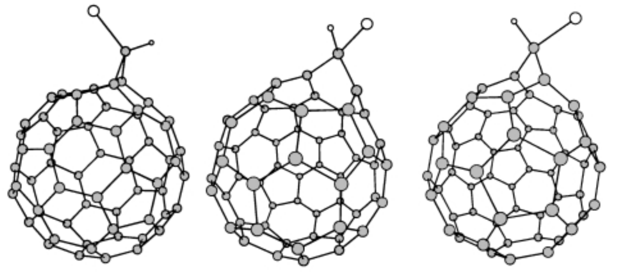

1a **1b** **1c**

Fig. 1 Energy minimized structures (HF/3-21G) of the possible isomers of $C_{60}CHBr$: **1a** has a [6,6] connection, *i.e.* is a methanofullerene, while **1b** and **1c** have [6,5] open structures, *i.e.* they are homofullerenes.

Results and discussion

Theoretical calculations

Following the pioneering work of Wudl and coworkers[11] and Smith III *et al.*[12] it was found that $C_{60}CH_2$ can adopt two geometries, depending upon the position of the addition to the fullerene core. Thus, for the bonding of a bridge carbon to a fullerene framework there are two possibilities for connection: closed [6,6] and open [6,5], where [6,6] and [6,5] denote a connection at the junction between two six-membered rings and at the junction between five- and six-membered rings, respectively. $C_{60}CH_2$ was found to be relatively stable in both [6,6] and [6,5] conformations.[13] $C_{60}CBr_2$ has the structure of a methanofullerene, *i.e.* a connection at a [6,6] position. However, it was reported that $C_{60}CBr_2$ with a [6,5] junction should be 4 kcal mol^{-1} more stable than the [6,6] one, based on PM3 calculations.[6] We reinvestigated the stability of the $C_{60}CBr_2$ isomers at the *ab initio* level of theory and found that, in contrast with the semi-empirical calculations, the methanofullerene should be more stable than the homofullerene. This result is in agreement with all experimental evidence obtained so far concerning $C_{60}CBr_2$.[14] For instance, $C_{60}CH_2$ in a [6,5] conformation was isolated and characterized but no report of $C_{60}CBr_2$ in the homofullerene form has been made.[15] Nevertheless a homofulleroid of C_{70} obtained *via* CBr_2 addition generated *in situ* from a Seiferth reagent has been reported recently by Kiely *et al.*[8] Since $C_{60}CH_2$ is stable in the homofullerene form and because of the precedent of $C_{70}CBr_2$ as a fulleroid, we performed quantum chemistry calculations in order to assess the most stable conformation for $C_{60}CHBr$. There are three possible structures, **1a**, **1b** and **1c**, whose HF/3-21G optimized geometries are presented in Fig. 1. The single-point energy calculations for the optimized geometries showed that **1b** and **1c** are less stable than **1a** by 3.9 and 6.4 kcal mol^{-1}, respectively. It is interesting to note that of the two possible isomers of the homofullerene derivatives, the one placing the bromine over the hexagon ring, **1c**, is significantly less stable than the other. Additional theoretical data have been obtained, in particular the calculated ^{13}C-NMR pattern using B3LYP model chemistry (see below). Selected connectivity data for **1a**, as obtained at the B3LYP/6-31G* level of theory, are shown in Fig. 4.

Synthesis

$C_{60}CHBr$ could be synthesized *via* dibromoderivative, $C_{60}CBr_2$. We initially chose this approach because $C_{60}CBr_2$ is relatively easy to synthesize and purify and was readily available from our previous studies. Thus, a first attempt at synthesizing **1** was made starting from $C_{60}CBr_2$ by treating it with $(tBu)_3SnH$ with or without the presence of AIBN. Although several different conditions have been tried we could not optimize this reaction because it was sluggish. Moreover, side reactions involving radical addition to C_{60} took place. Another alternative was to use directly bromocarbene addition to C_{60}. The addition of bromocarbene to olefins was reported to perform cleanly and to give high yields. A bromocarbene addition followed by dehydrobromination was outlined to be the key part in the synthesis of the triangulanes.[16] Bromocarbene addition to C_{60} was found to go in good to excellent yields with the addition of a strong base such as $[(CH_3)_3Si]_2NNa$ (NaHMSA) over a mixture of C_{60}–CH_2Br_2 at low temperatures.

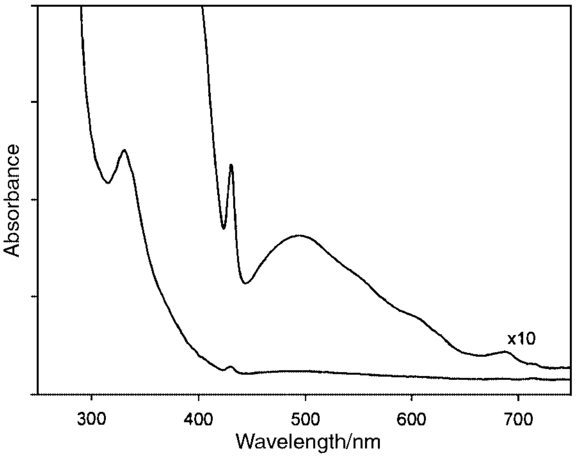

Fig. 2 UV–VIS spectrum of **1** in toluene.

Structural characterization

FAB-MS spectra in negative ionization showed the molecular peak of **1** at 812–814 Da (calc. 812 (84%), 813 (55), 814 (100), 815 (57), 816 (18)) and fragments at 720 and 732 Da. The procedure utilized for the FAB-MS was that described by Gross.[17]

A toluene solution of **1** is red, this alone being a strong indication that its structure is that of a methanofullerene rather than of a homofullerene. UV–VIS spectra of **1** in toluene (Fig. 2) are practically superimposable on those of other methanofullerenes, with typical absorption bands at 430 nm, some features in a broad band from 440 to 650 nm and with a small 690–700 nm absorption.

The ^{1}H-NMR of **1** gave a single peak located at 5.77 ppm, in agreement with a [6,6] closed structure as in **1a**. For a homofullerene (either **1b** or **1c**) only one peak in the ^{1}H-NMR should also be obtained. However, **1b** and **1c** should be very different in ^{1}H-NMR behavior considering the ring currents of the pentagons which should strongly deshield the proton in its immediate vicinity.[18]

^{13}C-NMR data of **1** (broadband decoupling) showed 31 resonances in the sp^2 region (with accidental overlap), four of them being half-intensity. Two additional resonances were located in the sp^3 region. This pattern is indicative of a C_S symmetry methanofullerene (**1a**). In the sp^3 region, the resonance at 75.05 ppm (2C) was assigned to the sp^3 carbon atoms of the fullerene cage while the other at 30.73 ppm (1C) was assigned to the cyclopropane carbon. The latter was observed as a CH doublet when measuring an off-decoupling ^{13}C-NMR spectrum. The coupling constant J_{CH} was determined from this experiment as 191.3 Hz. This apparently high value of the coupling constant is consistent with the structure **1a**, a cyclopropane derivative, because cyclopropanes show relatively high values for the coupling constants, the J_{CH} values being related to the interorbital angles and the influence of the electronegative substituents which increase the values of J_{CH}.[19] We assume that this value of J_{CH} is related to the presence of a halogen and not to the presence of C_{60}. In other fullerene derivatives the coupling constant J_{CH} in cyclopropanes is "normal", for instance in ethoxycarbonylmethano-1,2-dihydro-[60]fullerene we found it to be 167.7 Hz.

An interesting fact was observed in the ^{1}H-coupled ^{13}C-NMR experiment. The two most downfield resonances were significantly broadened (see Fig. 3) suggesting a long-range

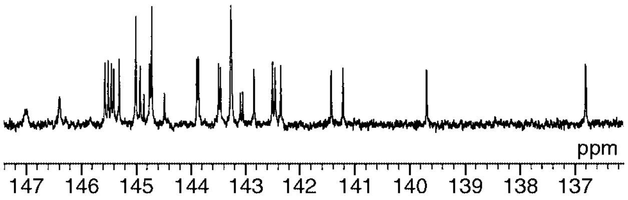

Fig. 3 ^{1}H-coupled ^{13}C-NMR spectrum of **1**.

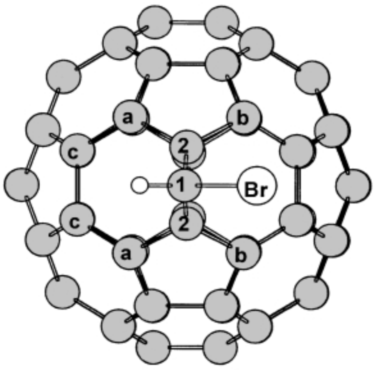

Fig. 4 Structural details of **1a**. The carbon atoms which are affected by the vicinity of the proton are marked **a**, **b** and **c** (see also Fig. 3 and Fig. 5a). Selected geometry data as obtained at B3LYP/6-31G* level: 2–2′ = 0.1640 nm, 1–2 = 0.1489 nm, 1–Br = 0.1933 nm, 2–**a** = 0.1491 nm, 2–**b** = 0.1489 nm, 1–**b** = 0.2676 nm, 1–**a** = 0.2644 nm and H–1–Br = 110.72°.

coupling between the proton and some of the sp^2 carbon atoms of the fullerene cage. Since the proton is facing a hexagonal ring and the broadening was observed only for two double-intensity carbon atoms, we initially considered that these two resonances belong to the four sp^2 carbon atoms of the hexagonal ring which faces the proton. Theoretical calculations suggested that these couplings originated from the closest four sp^2 carbon atoms relative to the cyclopropane. Thus, the two most downfield shifted resonances which were observed to broaden belong to the sets of nuclei **a** and **b** (see Figs. 4 and 5a). This long range coupling and its relation to the cyclopropane conjugation remain to be investigated. According to theoretical calculations, the cyclopropane is slightly distorted, *i.e.* is not perpendicular to the fullerene but slightly bent toward the H-facing hexagon (see Fig. 4). This is probably due to steric influences of the bromine substituent.

Concerning the ^{13}C-NMR spectra, four half-intensity resonances should be observed for each of the three possible C_S symmetry structures **1a**–**1c**. However, we note that their relative position in the spectrum alone is sufficient for the distinction between **1a** and **1b**/**1c**. The relative shift of these four carbon atoms depends greatly upon their distance from the sp^3 carbon atoms of the fullerene cage, which can be regarded as a *perturbation* of the conjugation. Thus, in the case of **1a** all four resonances should be relatively close one to another, considering the fact that they are far from the *perturbation*, *i.e.* the cyclopropane addend. In contrast, for either **1b** or **1c**, one resonance should be downfield shifted, another upfield shifted and the other two practically unaffected. These effects were initially proposed by Krätschmer and coworkers[20] for $C_{120}O_2$ and later found to hold for other fullerene derivatives, such as $C_{122}H_4$.[21] In the case of $C_{61}HBr$, all the four half-intensity resonances are found in close proximity, grouped in twos, in agreement with a C_S [6,6] structure of the molecule. Note that the relative position of the half-intensity resonances is important in discerning between structures that have non-equivalent addition units, such as $C_{61}AB$. This can be used in cases when the position of the resonances of the fullerene sp^3 carbon atoms and/or those of the connecting carbon cannot be observed because of accidental overlap with the solvent, *etc.*

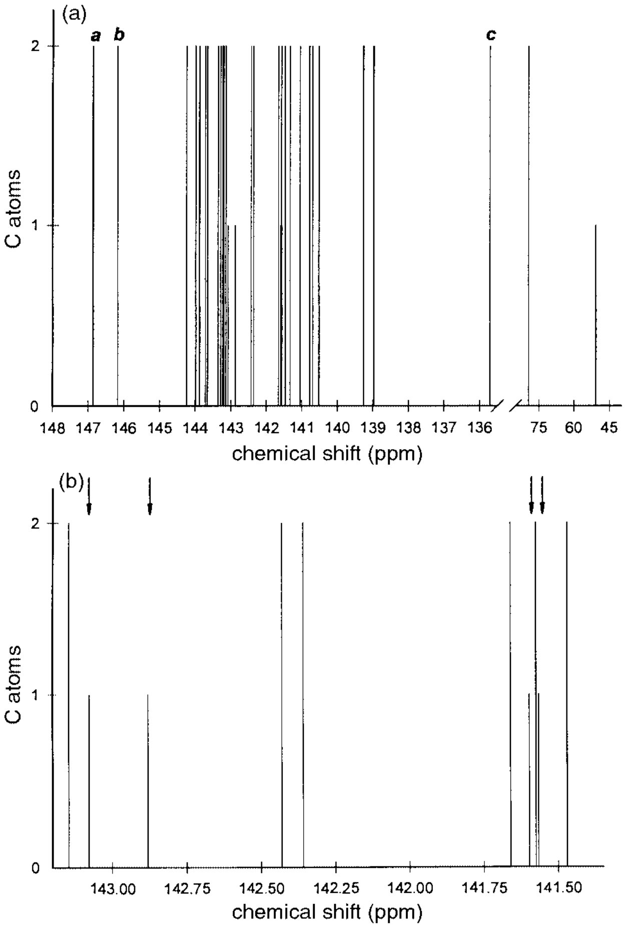

Fig. 5 (a) Computed ^{13}C-NMR data for **1a** and (b) detail concerning the half-intensity resonances, evidenced by arrows.

The relative positions of the four half-intensity resonances in this compound have been investigated by *ab initio* calculations. The magnetic shielding tensors were obtained by using the GIAO method,[22] at the B3LYP/6-31G* level with **1a** having the geometry optimized at the B3LYP/6-31G* level of theory. Figs. 5 (a) and (b) show the computed ^{13}C-NMR spectra of $C_{61}HBr$, using as a reference the resonance of C_{60} (143.15 ppm) obtained by a similar calculation. Except for the two sp^3 resonances, which have relatively large errors due to the reference used, the computed spectrum is in excellent agreement with the experimental one. Note the relative position of the half-intensity resonances which are strikingly similar to the experiment. To our knowledge this is the first experimental evidence concerning the position of the relative intensity resonances in a [60]fullerene derivative, other than qualitative considerations.

We also checked the electrochemical behaviour of **1** in order to compare it with the "parent" molecules, *i.e.* $C_{60}CBr_2$ and $C_{60}CH_2$. The first three reduction waves, reversible, were located at −1150, −1590 and −2070 mV, relative to the Fc/Fc$^+$ couple. The first reduction waves for $C_{60}CBr_2$ and $C_{60}CH_2$, measured in the same conditions,[23] were reported at 1130 and 1205 mV *vs.* Fc/Fc$^+$.[24] Thus, the first reduction potential of **1** occurs at values intermediate between those of $C_{60}CBr_2$ and $C_{60}CH_2$. This value correlates with the inductive effects of the substituents.

All the structural data support the methanofullerene structure for **1**, as obtained from a bromocarbene addition to C_{60}, **1a**.[25]

The formal generation of a C_{61} carbene *via* **1** would be possible depending upon the acidity of the proton and based on the fact that bromine is usually a good leaving group. Also, the dehydrobromination of **1** in the presence of Na–DMSO could also lead to the formation of a C_{61} group. Another interesting direction of synthetic utility is to control the coupling of this mono-haloderivative with boronic derivatives through Pd-catalyzed Suzuki reactions,[26] or to synthesize a boronic derivative of C_{60},[27] which could subsequently be used for these couplings. All these possibilities made attractive the first synthesis of a monohaloderivative of a methanofullerene, which is reported here. The use of such strategies should allow the coupling of C_{61} units yielding spiranes. These synthetic possibilities and in particular the incorporation of C_{60} units into oligospirocyclopropane systems, are now being explored in our laboratory.

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25 UV–VIS (toluene): 430, 690 nm; ^{1}H-NMR (1-chloronaphthalene locked with nitrobenzene-d^5, reference 8.1 ppm) 5.77 (s, 1H) ppm; ^{13}C-NMR (1-chloronaphthalene with 25% ODCB-d^4 and traces of CS_2; reference CS_2 192.8 ppm): 147.00 (2C), 146.38 (2C), 145.55 (2C), 145.50 (2C), 145.44 (2C), 145.39 (2C), 145.29 (2C), 144.99 (2 × 2C), 144.91 (2C), 144.84 (1C), 144.74 (2C), 144.70 (2 × 2C), 144.47 (1C), 143.88 (2C), 143.85 (2C), 143.48 (2C), 143.45 (2C), 143.26 (C_{60}), 143.25 (2 × 2C), 143.08 (1C), 143.04 (1C), 142.83 (2C), 142.49 (2C), 142.44 (2C), 142.34 (2C), 141.42 (2C), 141.20 (2C), 139.68 (2C), 136.80 (2C), 75.05 (2C), 30.73 (1C, $J_{CH} = 191.3$ Hz); IR (KBr pellet): 2962, 2922, 2852, 1628, 1464, 1428, 1384, 1377, 1260, 1251, 1185, 1162, 1095, 998, 799, 706, 575, 555, 525, 502 cm^{-1}.

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