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The First Trisaza-Bridged [60]Fulleroid: Drilling a Hole on the Fullerene

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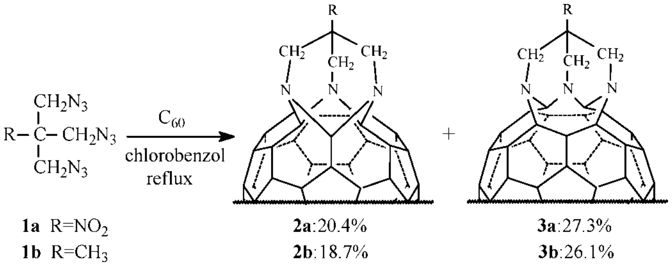
ABSTRACT



Two types of trisaza-bridged [60]fulleroids have been synthesized for the first time. By means of ^{13}C NMR, ^{1}H NMR, MALDI-TOF MS, FTIR, UV–vis, and 2D-NMR (gHSQC, gHMBC, and NOSEY) spectroscopy, they have been shown to be tris[6,5]-opened-aza-bridged adducts with substituents on the same five-membered ring with C_s symmetry. Some data of nonlinear optics and electrochemistry for the product are also reported.

Investigation of the regioselectivity of multiple additions to C_{60} and ring-opening of C_{60} are currently at the forefront of organic fullerene chemistry.[1] The reactions of C_{60} with azido compounds and their mechanism have been studied extensively.[2] The synthesis of bisaza-bridged [60]fulleroids has been also reported.[2d,e] For the first time, a trisaza-bridged [60]fulleroid with the substituent bonded to the same five-membered ring on the fullerene, and details of its characterization are reported. Some data of nonlinear optics and electrochemistry for the product are also reported in this letter. The structure of the product is interesting and somewhat unexpected. The reactions reported here are designed to expand the ring on the surface of the fullerene and enlarge the volume of the cage and thus carry out highly regioselective chemistry of C_{60}. There are similar to as drilling a hole on the surface of the fullerene in this reaction. It is possible to introduce practically any atom inside these hollow structures.

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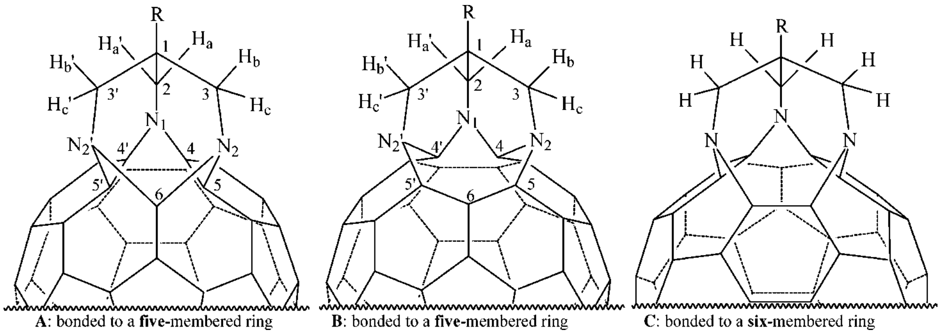
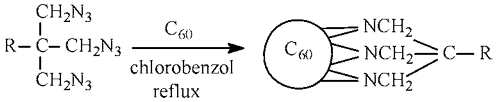


A: bonded to a **five**-membered ring **B**: bonded to a **five**-membered ring **C**: bonded to a **six**-membered ring

Figure 1. Possible structures for the product and the position of marked atoms in structure **A** and **B** (**a**, R = NO_2; **b**, R = CH_3).

We have successfully carried out two parallel reactions and obtained simillar compounds (see Scheme 1). The reaction of C_{60} with 2-nitro-2-azidomethylene-1,3-diazidopropane **1a** (2-methyl-2-azidomethylene-1,3-diazidopropane **1b**) synthesized according to the work of Ou[3] et al. results in two isolated compounds **2a**, 20.4% (**2b**, 18.7%), and **3a**, 27.3% yield (**3b**, 26.1%) (isolated yields based on the consumption of C_{60}).

Scheme 1. Reaction of **1** with C_{60}



1 **2** and **3**

a: R=NO_2, **b:** R=CH_3

The MS (MALDI-TOF) of the two compounds exhibit almost identical molecular ion peaks at m/z (M^+) 861.9 for **2a** (m/z 831.4 for **2b**) and (M^+) 861.8 for **3a** (831.4 for **3b**), which are in good agreement with the expected molecular mass m/z for **2** $C_{60}(NCH_2)_3C(NO_2)$ (**3** $C_{60}(NCH_2)_3CCH_3$).

Both the ^1H NMR and ^{13}C NMR for compound **2a**, **2b**, **3a**, and **3b** are explicit (see the Supporting Information). These spectra can be conformed to each other.

The ^1H NMR and ^{13}C NMR of the parallel compounds **2a** and **2b** exhibit similar patterns and show that **2a** and **2b** are tris[6,5]-open-ring adducts (fulleroid) with C_s symmetry. Among the three methylenes, one is on the mirror plane while the other two methylenes are symmetrically distributed about the plane according to their intensities. One methylene gives a singlet, and the other two exhibit an AB quartet in the ^1H NMR.

Interstingly, the ^{13}C NMR and ^1H NMR spectra of the second parallel compound **3a** and **3b** also show similar patterns, and it may be concluded that they are tris[6,5]-open-ring adducts with C_s symmetry.

By considering the bond lengths and strain using a ball-and-stick model, it can be concluded that the three nitrogen atoms may only be bonded to the same five-membered or six-membered ring. In light of the above analysis of the olefinic carbon region of the ^{13}C NMR spectra, the three structures shown in Figure 1 can be proposed. These structures have been initially optimized using the Hyperchem[4] semiempirical method and then by a Gaussian 98[5] ab initio calculation method. The energy of structure **C** is found to be lower by 89.0 and 143.1 kJ mol^{-1} for R = NO_2 in comparison to structures **A** and **B**, respectively. When R = CH_3, the energy of **C** is lower than that of **A** by 64.2 kJ mol^{-1} and **B** by 97.1 kJ mol^{-1}.

In structure **A**, the three N atoms are bonded to the same five-membered ring. The C-6 atom in the C_{60} moiety bonded to two N atoms is expected to give a signal at low field around δ 160[2c,j] with one carbon atom intensity. The lowest field signal in the ^{13}C NMR spectrum of **2a** is at δ 155.510 with one carbon atom intensity and the lowest field signal of **2b** is at δ 160.835 also with one carbon atom intensity. Thus, compound **2** can be assigned structure **A**.

On the basis of ^{13}C NMR, ^1H NMR, gHSQC, and gHMBC spectra, assignments of atoms marked in the side chain for structure **A** are given in Table 1. In the side chain of **A** shown in Figure 1, the methylene C-2, N_1, and the C-6 atom on the C_{60} sphere are on the plane of symmetry. H_a and H_a' of the C-2 methylene result in a singlet in the ^1H NMR spectrum. They are not correlated with C-6, which gives the lowest

Table 1. NMR Data of Atoms Marked in the Side Chain for Structure **A** for Compound **2**

assignment	δ/ppm (compd **2a**)	δ/ppm (compd **2b**)
H_a, H_a'	4.841	4.259
H_b, H_b'	4.744, 4.696	4.123, 4.096
H_c, H_c'	4.885, 4.837	4.348, 4.321
C-6	155.510	160.835
C-2	57.866	60.707
C-3, C-3′	54.810	58.697
C-1	82.319	35.573

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(4) Hyperchem 5.1 pro, Hypercube, Inc., 1998.

field signal in the ^{13}C NMR spectrum as there are five bonds between them. The coupled signals δ 4.744, 4.696 at relatively high field (coming from H_b and H_b') are correlated with the lowest field signal (C-6), namely H_b (also H_b') and C-6 have a correlation ($^3J_{C-H} \approx 5-7$) because they are in an *anti*-position (see Figure 1, structure **A**). H_c (also H_c') and C-6 are in a gauche position, and no correlation signal is observed between them in the gHMBC spectrum ($^3J_{CH} \approx 0$).

In structure **C**, the three N atoms are bonded to the same six-membered ring, and the side chain has a classical three-dimensional pyramidal structure. It has three mirror planes and should give only 12 signals in the ^{13}C NMR spectrum for the C_{60} moiety, and the three methylenes ($N-CH_2$) should have the same chemical shift in the ^{1}H NMR spectrum. This is not consistent with our NMR data. If the nitro group were unable to rotate freely as a consequence of a group effect, the molecule would have only one mirror plane. However, the rotational energy barrier of the nitro group is 8 kJ mol^{-1}, lower than the synperiplanar energy barrier 12.5 kJ mol^{-1} of ethane, according to calculations using DFT B3YLP/6-31g[5] method. The ^{1}H NMR spectrum of **3a** in o-$C_6D_4Cl_2$ at 393 K is identical to that in CS_2 at 293 K and does not show a singlet. Thus, the structure **C** may be ruled out, even though it is calculated to have the lowest energy.

In structure **B**, the three N atoms are also bonded to the same five-membered ring. In the side chain in structure **B** shown in Figure 1, the methylene C-2, N_1, and C-6 atoms on the C_{60} moiety are on the mirror plane. C-4 and C-4′ atoms in the C_{60} moiety, respectively, bonded to two N atoms are equivalent by symmetry and result in one signal at the lowest field[2c,j] with an intensity of two carbon atoms in the ^{13}C NMR spectrum. In our data, this signal is observed at δ 153.499 for **3a** and δ 157.747 for **3b**, both with two carbon atoms intensity. Assignment of atoms marked in the side chain for structure **B** are given in Table 2 on the basis of ^{13}C NMR, ^{1}H NMR, gHSQC, and gHMBC spectra. Furthermore, the NOESY spectrum of **3a** confirms the above assignment of signals from the side chain of structure **B**. H_a and H_b (also H_a' and H_b') are correlated as they are near each other in space (see Figure 1, structure **B**). Thus, compound **3** can be assigned structure **B**. It should be noted that the C-6 atom on the mirror plane in structure **B** will give a signal at the highest field position in the C_{60} moiety with one carbon atom intensity,[2e] which corresponds to the peak at δ 120.533 in the ^{13}C NMR spectrum of **3a** and to the peak at δ 120.202 in that of **3b** (see Table 2), both with one-carbon atom intensity.

Table 2. NMR Data of Atoms Marked in the Side Chain for Structure **B** for the Compound **3**

assignment	δ/ppm (compd **3a**)	δ/ppm(compd **3b**)
H_a, H_a'	4.238	4.281
H_c, H_c'	4.969, 4.997	4.412, 4.439
H_b, H_b'	5.257, 5.284	4.772, 4.799
C-4, C-4′	153.499	157.747
C-6	120.533	120.202
C-2	51.805	55.489
C-3, C-3	55.812	59.492
C-1	74.210	25.848

Actually, because of the equality of the methyl group in space, compound **3b** would be of C_{3v} symmetry and would give only 12 signals in the C_{60} moiety if it was of structure **C**. The NMR spectra of **3b** conclusively demonstrate the structure **B** and not structure **C** is present in **3**.

The five-membered rings of C_{60} exhibit a strong paramagnetic current while the six-membered rings support a mild diamagnetic current.[6,7] The effects of paramagnetic and diamagnetic currents may be employed to discuss the chemical shifts of the atoms in the methylene groups in the two structures. All of the methylenes are located above the junction of the five-membered and six-membered rings. The chemical shifts of all of the protons on the methylene groups are shifted downfield to about δ 5.

In structure **A**, the C-2 methylene on the plane of symmetry is slightly closer to the center of the five-membered ring than the other two methylenes according to the optimized structure using the Gaussian 98 program.[5] Its resonance is therefore shifted to lower field than that of other two methylenes in both ^{13}C and ^{1}H NMR spectra. In structure **B**, the C-2 methylene on the mirror plane is slightly farther from the center of the five-membered ring than the other two methylenes according to the optimized structure. Its resonance is therefore shifted to higher field than that of the other two methylenes in both ^{13}C and ^{1}H NMR spectra. In addition, the C-1 quaternary atom in structure **A** is closer to the center of the five-membered ring than that in structure **B**, and the NMR signals of the quaternary carbon atoms in compound **2** are at lower field than that in compound **3** about 10 ppm (see Tables 1 and 2).

The expected peaks are all observed in their FTIR, and the UV−vis spectra are similar each other for all compound **2a**, **2b**, **3a**, and **3b**.

We simply test the properties of nonlinear optic (NLO) for **2a** and **3a** by the Nd:YAG pulse system with a wavelength of 532 nm, pulse width of 8 ns, and 10 Hz repetition rate. Optical limiting measurements are carried out in DMF solution with a linear transmission 60%. The laser beam is divided into two equivalent beams in energy. One is used to monitor the incident laser energy, and the other is focused into the sample cell (5 mm thick). The input and

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(5) Gaussian 98, Revision A.3: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(6) Pasquarello, A.; Schluter, M.; Haddon, R. C. *Phys. Rev. A.* **1993**, *47*, 1783.

(7) Prato, M.; Suzuki, T.; Wudl, F.; Lucchini, V.; Maggini, M. *J. Am. Chem. Soc.* **1993**, *115*, 7876.

output energies of beams are measured with an energy meter (Laser Precision Corp. Rjp-735), while the incident energies are varied with a Newport Co. Attenuator (see the Supporting Information). The optical limiting behavior is measured. Similar results can be obtained from **3a** under the same conditions. At very low flunences the optical response of **2a** solution obeys Beer's law and the transmittance is roughly constant. At an input fluence of 250 μJ the transmittance begins to decrease markedly. When the incident fluence become very high, the transmitted fluence leveled off at ca. 350 μJ (**2a**, 8.8×10^{-5} M) and 320 μJ (**3a**, 2×10^{-4} M).

We use the Z-scan technique to study the third-order nonlinear optical susceptibility. The Z-scan setup is similar to that reported by Sheik-bahae et al.[8] The transmitance of a sample is measured through a finite aperture in the *far field* as the sample is moved along the propagation path (z) of a focused Gaussian beam. The linear transmission is 70%. The samples are also dissolved in DMF and placed in a 2-mm-thick glass cell. Third-order nonlinear optical susceptibility, $\chi^{(3)}$, is 3.226×10^{-12} esu for **2a** (8.8×10^{-5} M) and 3.529×10^{-12} esu for **3a** (2×10^{-4} M), respectively.

The cyclic voltammetry measurements of **2b** and **3b** are also carried out in toluene/acetonitrile solution with $(n\text{-Bu})_4NClO_4$ (TBAP) as the supporting electrolyte.[9] Peak reduction potentials are summarized in Table 3. The CV curves recorded for **2b** and **3b** indicate the three reductions are totally reversible and occur at slightly more negative valuse in comparison with C_{60}, in agreement with the expected behavior for organofullenes.[10]

In conclusion, two types of trisaza-bridged [60]fulleroids, **2** and **3**, both with substituents on the same five-membered ring have been successfully synthesized and shown to have structures **A** and **B** both with C_s symmetry. The energetically more stable structure has not been observed, and the investigation of the mechanism will be of interest. Detailed studies for the properties of the compounds and the reaction mechanism are in progress.

Table 3. Peak Reduction Potentials (V vs Ferrocene/Ferrocenium) for Compounds **2b** and **3b**

compd	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E^5_{red}
C_{60}[a]	−0.97	−1.38	−1.88	−2.34	−2.83
2b	−1.05	−1.43	−2.01		
3b	−1.12	−1.53	−2.12		

[a] C_{60} exhibits five reversible reductions in our experiment.

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Supporting Information Available: Detailed experimental procedure, characterization data, and copies of NMR, MS, IR, UV−vis, 2D-NMR (gHSQC, gHMBC, and NOESY) spectra for compounds **2** and **3**; the setup and the raw data of the NLO measurement for **2a** and **3a** and CV charts for **2b** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Sheik-Bahae, M.; Said, M.; Wei, A. A.; Hagan, D. J.; Stryland, E. W. V. *IEEE J. Quantum Electron.* **1990**, *26*, 760.

(9) CV conditions: 0.1 M TBAP in toluene/acetonitrile (v/v 4:1), 278 K. Working electrode: Pt disk (2 mm diameter). Counter electrode: Pt wire. Reference electrode: aqueous Ag/AgCl (Fc/Fc$^+$ internal stand). Potentiostat: CHI660A, scan rate 100 mV s^{-1}. The sample concentration is 1×10^{-4} M.

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