Experimental Evidence for Segregated Ring Currents in C_{60}

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The theoretical aspects of the magnetic susceptibility of C_{60} have been controversial.[1] The most recent contribution, due to Pasquarello, claims that the 5-membered rings of buckminsterfullerene exhibit strong paramagnetic currents, whereas the 6-membered rings support mild diamagnetic currents.[2] The intriguing question of the influence of the C_{60} sphere on NMR chemical shifts can be solved experimentally only by placing a spin-active probe in the vicinity of the fullerene. Since this cannot be done with C_{60} itself, it is necessary to use properly functionalized derivatives. We report herein *the first experimental evidence for the presence of ring currents* in some methanofullerenes and fulleroids-C_{61}.[3]

Compounds **1–3** were prepared, according to our reported procedure, by addition of diazo compounds to C_{60} (Scheme I),[4] and their structures were determined mainly by NMR spectroscopy.

The ^{1}H NMR spectrum of compound **1** shows a singlet at 7.49 ppm for the olefinic protons and only four signals for the two aromatic rings and is therefore consistent with a structure derived from a formal carbene addition across the symmetrical 6,6 junction of C_{60}.

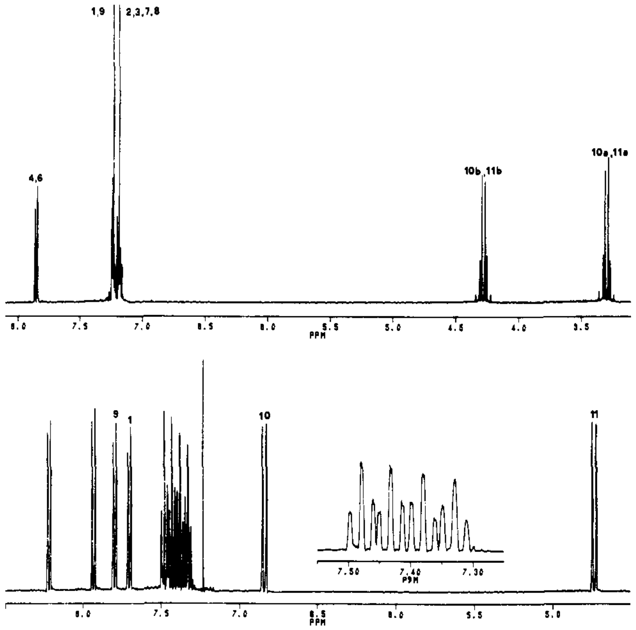
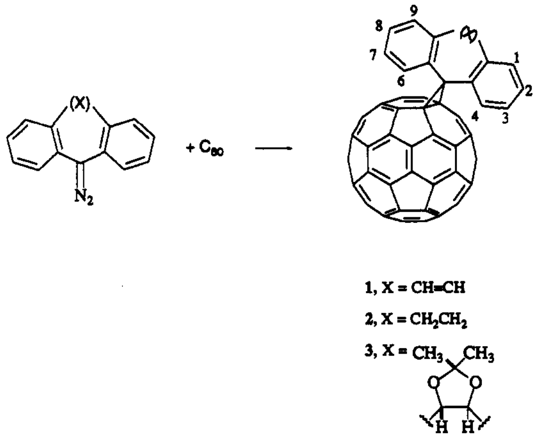


Figure 1. (Top) ^{1}H NMR spectrum of methanofullerene **2**. (Bottom) Relevant part of ^{1}H NMR spectrum of **3**.

Scheme I



The ^{1}H NMR spectrum of compound **2** (Figure 1, top) exhibits two multiplets at 3.33 and 4.41 ppm (intensity 2H each signal, an AA′XX′ system) for the ethano bridge protons, two multiplets at 7.21 (intensity 4H) and 7.26 ppm (intensity 2H), and a doublet at 7.87 ppm (intensity 2H). The analysis of the second-order AA′XX′ spin system gives $J_{AX} = J_{A'X'} = -16.4$ Hz, $J_{AA'} = 9.6$, $J_{XX'} = 8.8$, and $J_{AX'} = J_{A'X} = 6.5$ Hz. The J_{AX} constant is, from sign and magnitude, a geminal constant; thus the protons within a methylene moiety resonate at different frequencies (H-10a and H-11a vs H-10b and H-11b, see Figure 2a). This observation is compatible with a static boat conformation of the seven-membered ring, with an eclipsed ethylene bridge, or with fast interconverting twist-boat conformations, possessing a staggered ethylene bridge. The aromatic protons (H-1 and H-9) ortho to the ethylene bridge resonate at 7.26 ppm and display relevant NOE dipolar interactions with the high-field multiplet at 3.33 ppm but none with the low-field multiplet at 4.41 ppm. This finding supports the boat conformation (where the exo methylene protons 10a and 11a are in the plane of the adjacent aromatic ring) and rules out the twist-boat conformation (in the latter the aromatic rings bisect the geminal methylene group). The low-field aromatic doublet at 7.87 ppm, interacting with the multiplet at 7.21 ppm, is due to the ortho protons 4 and 6 vicinal to the spiro carbon.

Also in this compound, the equivalences of the exo ethylene protons 10a and 11a, of the endo ethylene protons 10b and 11b, and of the low-field aromatic ortho protons 4 and 6 are in agreement with a 6,6 adduct.

In complete agreement with the spectroscopic evidence, the computational optimization of this structure (at the semiempirical MNDO[5] level) yields a preferred boat conformation with rigorous C_s symmetry (Figure 2a). In this conformation, the deshielded endo ethylene protons 10b and 11b are oriented toward the adjacent pentagon of the fullerene sphere.

The ^{1}H NMR spectrum of methanofullerene **3** (Figure 1, bottom) shows that all eight aromatic resonances are differen-

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(2) Pasquarello, A.; Schluter, M.; Haddon, R. C. *Science* **1992**, *257*, 1660. Pasquarello, A.; Schluter, M.; Haddon, R. C. *Phys. Rev. A* **1993**, *47*, 1783.

(3) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157. IUPAC-recommended rules are "methanofullerene" for a cyclopropane structure and "fulleroid" for a methanoannulene structure.

(4) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991**, *254*, 1186.

(5) *Spartan 2.1* program running on an IBM RS/6000 workstation.

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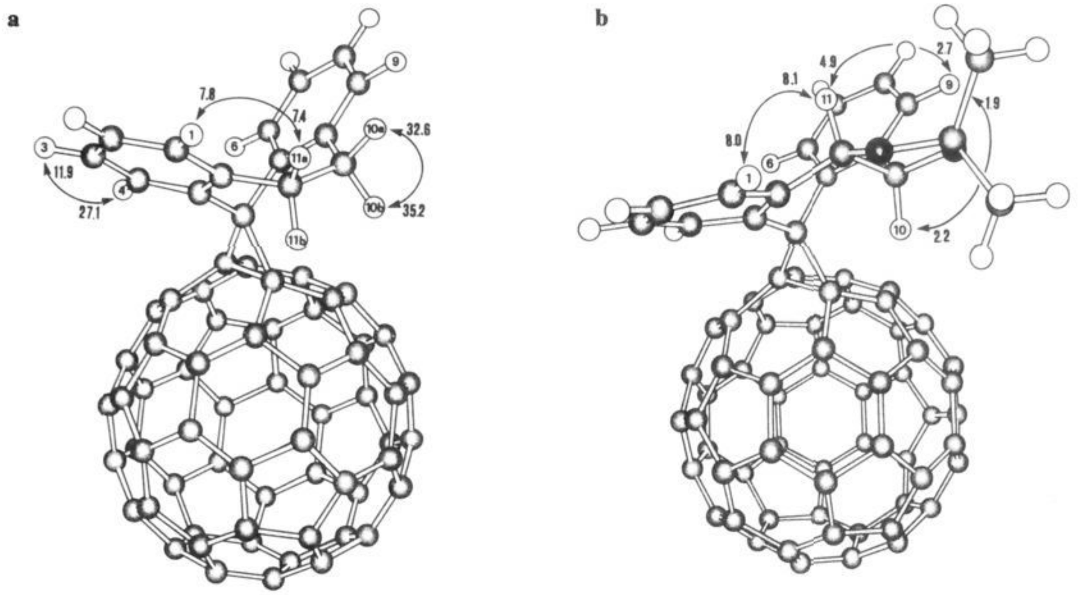

Figure 2. MNDO-minimized structures of compounds **2** (a) and **3** (b). The numbers at the tip of the arrows give the % NOE enhancements of the given proton upon irradiation of the connected proton.

tiated. The two methyne protons resonate as doublets at 4.67 and 6.77 ppm (J = 10.2 Hz). In this molecule, the acetonide bridge forces the seven-membered ring into a twist-boat conformation, with the endo bridge proton 10 pointing toward the ball and the exo proton 11 away. By spectral analogy with **1** and **2**, **3** has the structure depicted in the scheme.

The structure reported in Figure 2b, optimized at the MNDO level, shows that the exo proton 11 is 3.1 and 3.7 Å away from the ortho protons 1 and 9 of the geminal and vicinal aromatic rings, respectively. The distances of the endo proton 10 from protons 1 and 9 are 4.5 and 3.6 Å, respectively. The expected NOE dipolar interactions of exo proton 11 with both protons 1 and 9 and of endo proton 10 with only proton 9 are observed as shown in Figure 2b and lead to the assignments of doublets at 6.77 and 4.67 ppm from the endo 10 and to the exo 11 methyne protons, respectively.

Low solubility prevented recording reliable ^{13}C NMR spectra of **1** and **2**. The ^{13}C spectrum of **3** shows 70 aromatic resonances (some are isochronous), attributable to the 12 carbons of the nonequivalent phenyl rings and to 58 nonequivalent fullerene carbons. The two residual fullerene carbons resonate in the aliphatic region at 76.30 and 80.93 ppm, together with the adjacent spiro carbon at 53.09 ppm. These observations favor the methanofullerene structure for **3** (and by extension for **1** and **2**) and rule out the fulleroid isomer. The possibility of a methanofullerene–fulleroid equilibrium has been considered, but no significant change of the ^{13}C spectra was detected in the +30/−60 °C temperature range.[6] The MNDO-optimized structures of **2** and **3** give distances of 1.58 and 1.59 Å, respectively, for the transannular bond. The optimized geometries and the spectral assignments show that the most deshielded protons in **2** and **3** are those pointing toward a 5-membered ring. The most dramatic difference is between the ethano bridge protons in **3**, where the endo proton 10, pointing almost exactly toward the center of the adjacent 5-membered ring, is 2.1 ppm downfield-shifted with respect to the exo proton 11. *This constitutes the first experimental evidence for the theoretically postulated[2] strong paramagnetic currents associated with 5-membered rings in C_{60}.*

The effect of paramagnetic and diamagnetic currents[2] was employed in the structural assignments for 5,6 junction adducts

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with equal or different substituents.[7] For example, the methylene 2.87- and 6.35-ppm resonances of the parent fulleroid **4**[8] can be assigned, on the basis of similar arguments, to the proton over the 6- and 5-membered rings, respectively.

The diamagnetic shifts exerted by the 6-membered rings in C_{60} are modest when compared with those found in 1,6-methano[10]annulenes.[9] While the overall current in C_{60} is neutral, the paramagnetic component is concentrated in only 12 5-membered rings, and the diamagnetic component is distributed over 20 6-membered rings. Hence, the "current per ring effect" must be larger in the 5-membered rings.[2] As any external probe can sense mostly the current of the nearest ring (or rings), the average effect exerted by the C_{60} sphere on NMR chemical shifts is, as observed,[3] essentially deshielding.

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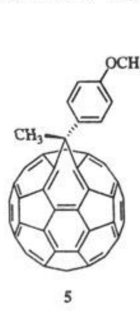

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[9] Cf. δ_{Me} = 1.32 in **5**[7] vs 0.5 in 11,11-dimethyl-1,6-methano[10]annulene; δ_H = 2.87 in **4** vs −0.5 in 1,6-methano[10]annulene: Vogel, E. *Pure Appl. Chem.* **1969**, *20*, 2375.