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Trends in Chemical Shift Dispersion in Fullerene Derivatives. Local Strain Affects the Magnetic Environment of Distant Fullerene Carbons

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^{13}C NMR chemical shift assignments for 1,2-$C_{60}H_2$ (**1**) and a series of ^{13}C-labeled fullerene derivatives with three-, four-, and five-membered annulated rings (**2**−**4**) were assigned using 2D INADEQUATE spectroscopy and examined for trends that correspond to the changes in strain in the fullerene cage. Chemical shifts of equivalent carbons from **1**−**4** show that eight carbons trend downfield (carbons 5, 7, 8, 9, 11, 15, 16, 17) and the remaining six carbons (4, 6, 10, 12, 13, 14) trend upfield with increasing ring size. While the *average* chemical shift is nearly constant, the dispersion is greatest when the local strain is the least, in 1,2-$C_{60}H_2$ (**1**). ^{13}C chemical shifts are not well correlated with trends in ring size, with strain as measured by the pyramidalization angle of nearby carbons, or with the geometry of the fullerene cage. We interpret the results as evidence that subtle geometrical changes lead to modulation of the strength of ring currents near the site of addition and, in turn, the magnetic field generated by these ring currents affects the chemical shift of carbons on the far side of the fullerene core. These results highlight ring currents as being critically important to the determination of ^{13}C chemical shifts in fullerene derivatives.

The conversion of C_{60} into $C_{60}H_2$ (**1**) results in a change in the ^{13}C NMR spectrum from a single resonance (143 ppm) to a set of 17 resonances, including 16 sp^2 resonances spread out over 13 ppm. For comparison, the conversion of benzene (128 ppm) to toluene results in less than a 3.6 ppm dispersion of sp^2 resonances for the *ortho*, *meta*, and *para* carbons,[1] even though the molecular weight has been increased by 18%. Contained in the chemical shift dispersion there is a wealth of information about the electronic structure and, therefore, the reactivity of fullerene derivatives. Understanding the factors that determine the chemical shifts of fullerene is an important step toward full utilization of the information contained in the ^{13}C NMR spectra of these compounds.
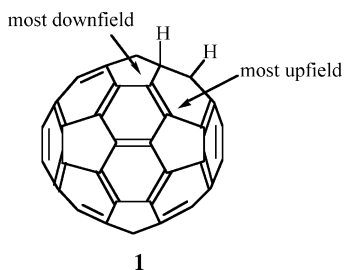
We have previously observed[2] some interesting trends within the chemical shifts of **1**. For example, the most downfield resonance (typically ca. 155 ppm) is due to the carbons immediately adjacent to the site of addition. This pattern is a bit surprising, since that carbon atom is bonded to an sp^3 carbon and is the least pyramidalized[3−5] carbon in the molecule. Both of these structural features normally move a resonance *upfield*, rather than downfield. Also surprising is the observation that the most downfield carbons are bonded to the most upfield carbons.

In this paper, we report the investigation of the NMR spectra of a set of fullerene derivatives that have different degrees of strain imposed by annulation of different sized rings. The compounds studied here are the $C_{61}H_2$ methanofullerene **2**, the benzyne adduct **3**, and the *N*-triphenylmethylpyrrolidine **4**. These compounds are compared to **1** as an example of an unstrained system.
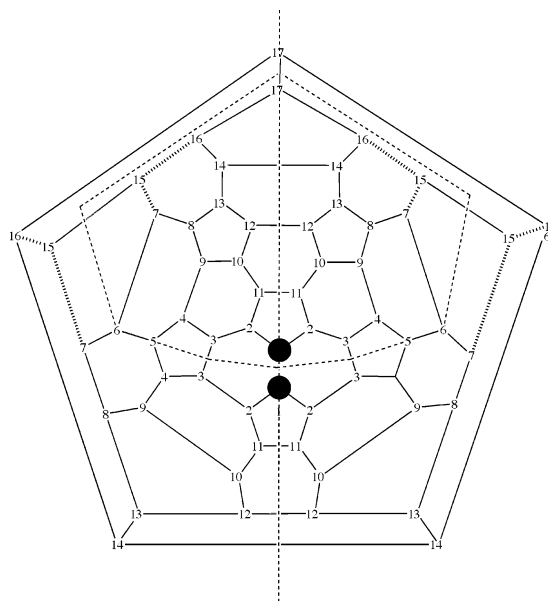

1

2   3   4
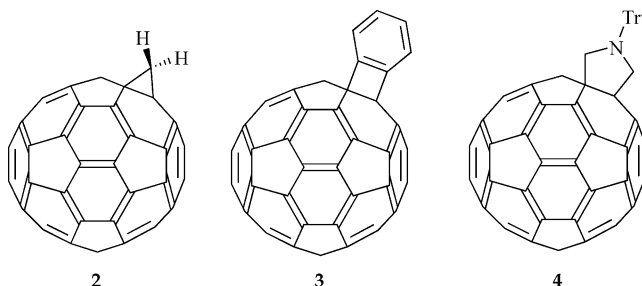
Starting with 13% ^{13}C-labeled C_{60}, we prepared samples of the $C_{61}H_2$ cyclopropane **2** via photolysis of the diazo-

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FIGURE 1. Planar projection of 1,2-disubstituted 1,2-dihydrofullerenes. The dark circles represent the substituents, and the dashed lines represent the two planes of symmetry in these C_{2v}-symmetrical structures.

methane adduct of C_{60} as described by Smith and co-workers,[6] the four-membered ring benzyne adduct of C_{60} **3** as described by Hoke and others,[7,8] and pyrrolidine **4** as described by Maggini and Scorrano.[9] Using similar methodology as used for $C_{60}H_2$ and for $C_{60}H_6$,[10] we made complete chemical shift assignments for the fullerene resonances and extracted the $^1J_{CC}$ coupling constants for all three adducts. A planar projection is shown in Figure 1, along with a numbering scheme that identifies the 17 symmetrically unique carbon atoms.

In Table 1 are the assigned chemical shifts for **2**, **3**, and **4**. For comparison purposes, the corresponding chemical shifts of **1**[10,11] are shown, providing an example of a system with no strain imposed by the addends. "Ring strain," in this context, is strain local to the site of addition due to the geometry of the annulated ring, rather than the strain inherent in the rest of the fullerene cage.

C_{60} has a ^{13}C chemical shift of 143 ppm.[12,13] The *average* chemical shift of carbons 3–17 (Figure 1) in each of the

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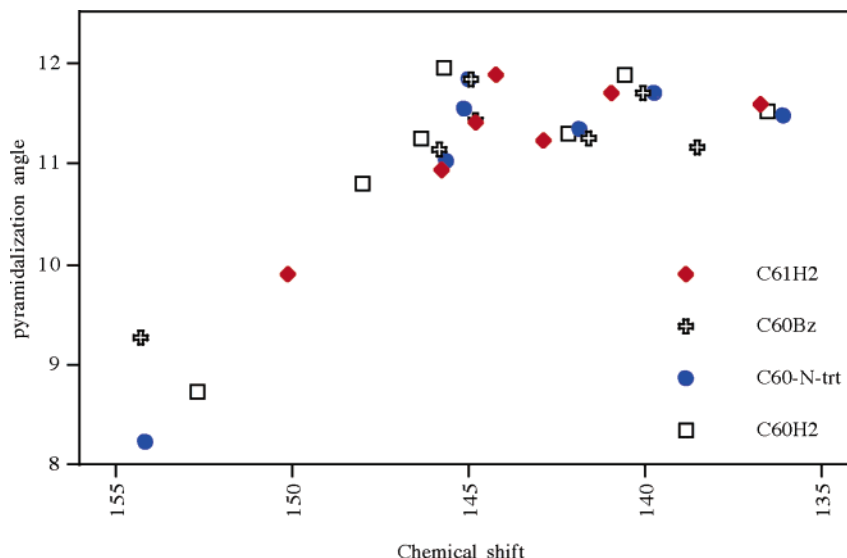
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(11) The chemical shifts of **1** in ref 10 were measured in CS_2 solution. There is a −0.68 ppm offset in chemical shifts due to the difference in solvents, so for comparison purposes the chemical shifts of **1** in Table 1 and Figure 2 have been adjusted by −0.68 ppm.

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TABLE 1. Assigned ^{13}C Chemical Shifts of Resonances in 2, 3, 4, and 1[a]

atom	2	3	4	1[b]
2	150.10	154.25	154.16	152.69
3	136.77	138.51	136.08	136.56
4	142.87	141.62	141.89	141.50
5	144.82	144.79	145.15	145.64
6	143.02	142.47	142.61	142.84
7	145.12	145.6	145.78	145.92
8	143.75	144.06	144.09	144.25
9	144.26	144.94	145.03	145.03
10	140.98	140.05	139.78	139.90
11	145.74	145.84	145.67	147.31
12	143.15	142.39	141.12	141.12
13	142.24	141.85	141.59	141.48
14	143.02	144.87	142.20	142.07
15	144.76	142.47	144.81	144.96
16	145.21	145.55	145.61	145.85
17	144.37	146.31	146.78	146.92

[a] Atom labels are as given in Figure 1. Chemical shifts were measured in CS_2/$CDCl_3$ solution, except as noted. [b] Measured in ODCB-d_4 solution,[10] and a 0.687 ppm solvent correction applied.[11]
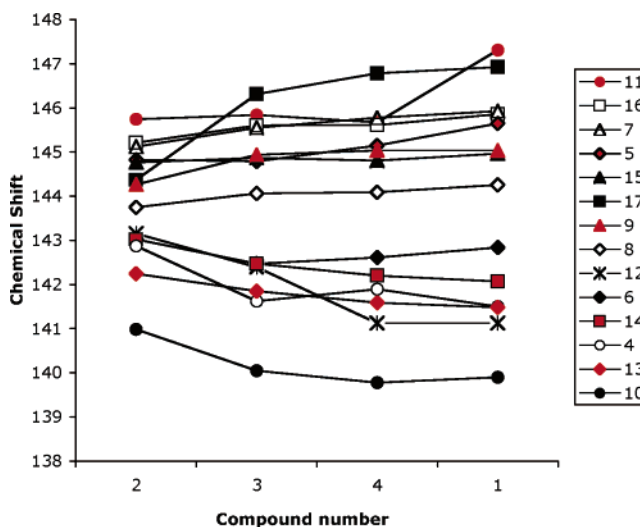
FIGURE 2. Chemical shifts of symmetry-related sp^2 carbon atoms across the series **2**, **3**, **4**, **1** (in order of decreasing strain). The chemical shifts of the carbons directly bonded to the sp^3 carbons are not included. The chemical shifts are numbered as in Table 1.

four adducts is very close to the C_{60} value, ranging from 143.72 to 143.92 ppm (See Table 1). The chemical shifts of fullerene sp^2 carbons that are directly bonded to the site of addition are likely to reflect a substituent effect that would complicate the understanding of subtle geometric and electronic effects on the chemical shifts. When we omit the fullerene sp^3 carbons and the sp^2 carbons directly attached to them, the remaining set of carbons still reflects a significant trend in dispersion. Plotting the chemical shifts of equivalent carbons from **1**–**4** shows that eight carbons trend downfield (5, 7, 8, 9, 11, 15, 16, 17) and the remaining six carbons (4, 6, 10, 12, 13, 14) trend upfield with increasing ring size (Figure 2). This figure shows that while the *average* chemical shift is nearly constant, there is a clear trend in the *dispersion* of chemical shifts. Interestingly, the dispersion is greatest when the local strain is the least, in 1,2-$C_{60}H_2$ (**1**).[14]

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FIGURE 3. Plot of pyramidalization angle (q_p) versus the experimental ^{13}C chemical shift in four adducts of differing ring size.

In the series **1−4**, the geometry of the sp³ carbons in $C_{60}H_2$ (**1**) is the least like that of C_{60}. The saturated carbons in **1** are capable of relaxing to sp³ geometry and are, therefore, unlike the pyramidalized sp² carbons of C_{60}. The chemical shift dispersion in **1** is the greatest of the series. On the other hand, **2** displays the smallest chemical shift dispersion of the series. The cyclopropyl ring in **2** does not allow the sp³ carbons in the fullerene core to relax into a less strained geometry, and they remain in geometries such as that of the carbons in C_{60}. The benzyne (**3**) and pyrrolidine (**4**) adducts have progressively less small-ring strain and therefore allow more distortion of the fullerene sp³ carbons away from the "ideal" $C_{60'}$ values.

With the chemical shift assignments in hand, we looked for correlations between trends in chemical shift and trends in strain. We anticipated that the carbon atoms near the site of addition would be the most affected and that carbons distant to the site of addition would be less affected. Examination of the chemical shifts of the carbons near the site of addition in these compounds reveals that there is some perturbation of the chemical shifts of carbons within two bonds of the site of addition, but there does not seem to be a consistent trend with appended ring size for any of the carbons examined (Table 1). Comparison of the calculated BLY3P/6-31G* structures of **2−4** to the calculated structure of C_{60} did not uncover any significant distortion of the cage at any site distant from the site of addition. This (not unexpected) result demonstrates that the observed trends in chemical shift dispersion are not due to changes in fullerene geometry due to changes in strain introduced by the small rings.[15]

We next examined the relationship of chemical shift to pyramidalization angle for these adducts.[16] The results are shown in Figure 3. In many molecular systems, including C_{70}, increasing pyramidalization results in a downfield shift in the ^{13}C NMR chemical shifts.[17] However, in the cases studied here, there is not a linear correlation between pyramidalization angle and chemical shift.

What then is responsible for the chemical shift dispersion in fullerene derivatives? Through-bond influences are clearly not responsible. In fact, the greatest dispersion is observed in the chemical shifts of C17, a pair of equivalent carbons located completely across the fullerene cage from the site of addition and the least likely to be affected by any through-bond influences. Field effects on NMR chemical shifts are well-known, particularly field effects due to induced ring currents.[18−20] NMR spectroscopy has provided evidence for segregated ring currents in fulleroids,[21] and calculations have recently suggested that a strong paramagnetic ring current that circulates around an [18]annulene in 1,2-$C_{60}H_2$.[10]

If this ring current influences the chemical shifts of fullerene sp² carbons, then it should have effects on the chemical shifts of addends as well. The addends (H, CH_2, etc., in **1−4**) sit just above this paramagnetic ring, and the resonances of these groups should appear downfield relative to model compounds that lack the ring current.[22]

The ^{13}C chemical shift of the methylene carbon in **2** is quite downfield (30.45 ppm) from the corresponding resonance of the simple model system **5**, which appears at 20.75 ppm.[23] In fact, examination of the chemical shifts

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(15) Burley et al. reported evidence that a cyclopropanated fullerene has a long bond at a position five bonds from the site of addition. The changes in bond length are small but large enough to change the $^{13}C-$ ^{13}C coupling constant. See: Burley, G. A.; Keller, P. A.; Pyne, S. G.; Ball, G. E. *Magn. Reson. Chem.* **2001**, *39*, 466−470.

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in the dehydro systems **6** and **7**[23] shows in an increasingly *upfield* shift for the bridging methylene. This trend suggests that field effects from the π-system of fullerenes are *opposite* of those in this simple series of methano bridged alkanes and alkenes.
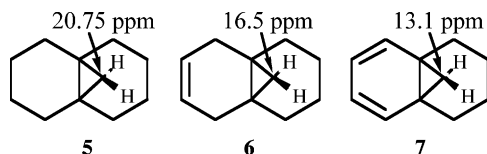
A similar situation is found when pyrrolidine models of **4** are examined. The ^{1}H chemical shift of the pyrrolidine protons in **4** is 4.13 ppm, nearly 2 ppm farther downfield the corresponding protons (2.25−2.40 ppm) in the simple *N*-tritylpyrrolidine **8**.[24]
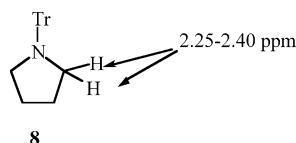
The [3]He chemical shifts of [3]He@fullerene derivatives show a downfield trend with increasing chemical modification of the cage. The [3]He chemical shifts of He@C_{70}, He@$C_{70}H_2$, He@$C_{70}H_4$, He@$C_{70}H_8$, and He@$C_{70}H_{10}$ are −28.81, −27.18, −25.33, −17.84, −17.17 ppm.[25] The downfield trend reflects the loss of aromaticity in the carbon shell and also reflects the changing nature of the ring current-induced magnetic fields. Ring currents resulting from different patterns of addition have been proposed to help explain different [3]He chemical shifts of different isomeric [3]He@C_{60} diadducts.[26]

Conclusions

We have fully assigned the fullerene ^{13}C NMR spectra of **2**−**4**, a series of compounds with decreasing ring strain.

There is no trend in fullerene sp^2 chemical shifts that correlates with the strain imposed by annulated rings, with pyramidalization, or with through-bond distance from the site of addition. These results suggest a counterbalancing influence that overpowers the influence of sigma bond issues (bond angles and lengths). There is strong evidence for a large paramagnetic ring current that circulates around the site of addition. This evidence includes significant downfield shifts for both ^{1}H and ^{13}C resonances for addend atoms above the site of addition in **2**−**4**. The influence of this ring current on ^{13}C resonances is less clear but is a prime candidate for the nonsigma influence mentioned above. It is clear that modification of selected bonds can lead to significant ring currents that are capable of perturbing the chemical shifts of nearby atoms, of atoms outside of the cage, of atoms inside of the cage, and of the cage atoms themselves.

Experimental Section

Samples of ^{13}C-enriched $C_{60}H_2$ (**1**),[2] *N*-triphenylmethylpyrrolidine adduct (**4**),[9] C_{60}-benzyne adduct (**3**),[7,27] and $C_{61}H_2$ (**2**)[6] were prepared from 13% ^{13}C-enriched C_{60} (MER Corp.) by literature methods and purified by preparative HPLC. 2D INADEQUATE NMR spectroscopy was carried out using methodology described earlier.[10] Calculations were preformed with Gaussian98[28] on an HP N-class computer at the University of Kentucky Computation Center, part of the National Computational Science Alliance.

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