Fullerene Anions: Unusual Charge Distribution in C_{70}^{6-}**

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C_{70}, the second most abundant fullerene,[1] has an ellipsoid structure with symmetry of D_{5h}.[2] Its ^{13}C NMR spectrum, consisting of five lines with intensities in the ratio of 1:2:1:2:1 provides very strong evidence for its structure and symmetry (Figure 1).[3]
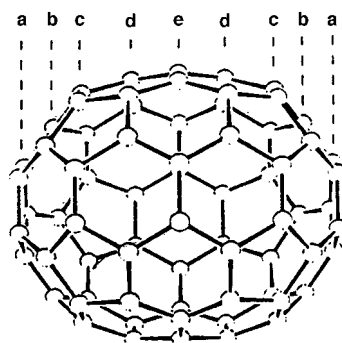

Figure 1. Schematic diagram of C_{70} depicting the different carbon sites **a–e** (reprinted from ref. [3]; copyright 1990 The Royal Society of Chemistry).

Reduction of C_{70} with lithium yields its hexaanion[4] where the ^{13}C NMR spectrum has the same pattern as the neutral compound, and a slight overall deshielding ($\Delta\delta = 0.9$ per carbon).[5] Although the reduction does not change the symmetry of C_{70}, it significantly changes the magnetic and electronic properties of the fullerene. The bulk and internal properties of charged C_{70} (that is C_{70}^{6-}) were previously investigated by the measurement of the ^3He NMR chemical shifts in the endohedral $He@C_{70}^{6-}$.[6] These experiments, as well as magnetic susceptibility calculations,[7] indicate a decrease in the aromaticity of C_{70}^{6-}. Studying the local properties of fullerenes can provide a deeper understanding of their aromatic character. The fullerenes consist of five- and six-membered rings (5-MRs and 6-MRs, respectively) that have different magnetic properties which define the overall character of the system.[8] Calculations indicate that the paramagnetic ring current of the 5-MRs disappears in C_{70}^{6-}. Moreover there is a decrease in the diamagnetic ring current of the 6-MRs, that results in an overall decrease of the C_{70}-fullerene diamagnetism.[9] We have previously studied the external and local magnetic properties by measuring the ^1H NMR chemical shifts of the fulleroids $C_{71}H_2$.[10] We concluded that the added electrons in C_{70}^{6-} are mainly located at the 5-MRs, thus converting them from paramagnetic into

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diamagnetic rings. The diamagnetism of the 5-MRs at the poles is much stronger than that of the 5-MRs far from the poles and also than that of the 6-MRs.

According to the above mentioned studies[9, 10] and because of the D_{5h} symmetry of C_{70}, it seems that the extra electrons of C_{70}^{6-} are not distributed evenly over the fullerene skeleton. Studying the carbon NMR chemical shifts can shed light on the magnetic properties of the fullerene surface, and help towards completing the C_{70}^{6-} puzzle. Therefore, a full assignment of the ^{13}C NMR spectrum is required, to determine the changes in the charge density on each set of carbons and the changes in the magnetic susceptibility.

To determine conclusively the chemical shift of each carbon type in C_{70}^{6-}, a 2D INADEQUATE (incredible natural abundance double quantum transfer experiment) NMR experiment was performed. This experiment correlates the ^{13}C NMR resonance of a carbon to that of its bonded neighbor.[11]

A sample of 4 mg of ^{13}C-enriched C_{70} ($\sim 13\%$)[12] was prepared by using [D_8]THF as solvent and in the presence of corannulene (1 mg), which acts as an "electron shuttle",[6] in a 5 mm NMR tube equipped with a top reduction chamber containing excess lithium metal.

The 2D INADEQUATE spectrum (Figure 2) of the sample shows, as expected, four interactions that make the assignment of the carbon connectivity possible.[13] The interaction
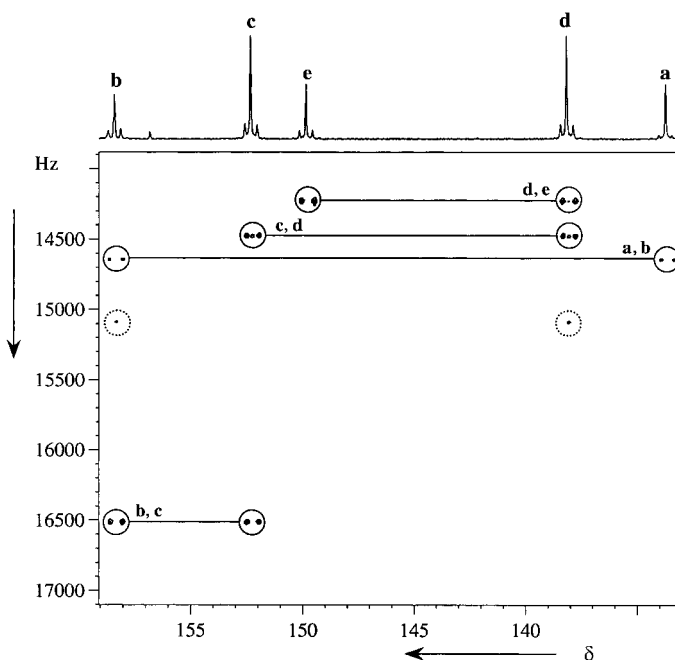

Figure 2. 2D NMR INADEQUATE spectrum of C_{70}^{6-}, short-range interactions: solid circles, long-range interactions: dashed circles.

between the signal that appears at $\delta = 133.6$ and the signal at $\delta = 158.3$, where both represent 10 carbon atoms, leads to the following assignment (Figure 1): carbons **a**: $\delta = 133.6$; carbons **b**: $\delta = 158.3$; carbons **c**: $\delta = 152.3$; carbons **d**: $\delta = 138.1$; carbons **e**: $\delta = 149.8$.

To understand the changes that occur as a result of the addition of electrons to C_{70} a comparison with the neutral molecule[14] is necessary (Table 1). Chemical shift changes,

Table 1. ^{13}C NMR chemical shifts (δ) and coupling constant ($^1J_{c,c}$ [Hz]) for the carbon atoms of C_{70}[a] and C_{70}^{6-}.

Carbon	C_{70}	C_{70}^{6-}
a	150.1 ($^1J_{a,b} = 68$)	133.6 ($^1J_{a,b} = 60.9$)
b	146.8 ($^1J_{b,c} = 55$)	158.3 ($^1J_{b,c} = 53.8$)
c	147.5 ($^1J_{c,d} = 55$)	152.3 ($^1J_{c,d} = 56.4$)
d	144.8 ($^1J_{d,e} = 62$)	138.1 ($^1J_{d,e} = 58.4$)
e	130.3	149.8

[a] Taken from ref. [14].

caused by the addition of electrons to the molecule, originate from the changes of the electron density, as well as changes of induced ring currents in the molecule.[15] Although in many polycyclic aromatic hydrocarbons the carbon atoms are not sensitive to anisotropic effects, in C_{70}^{6-} it is obvious that there is such an influence, as there is an overall deshielding. The anisotropic effect is also expressed by the K_c value (-0.15 ppm per electron) that was calculated by Equation (1).

$$\delta_c = \delta_N - K_c \Delta q_\pi \tag{1}$$

δ_c and δ_N are the chemical shifts of a carbon in the charged and the neutral species, respectively, K_c is a proportionality factor and q_π is the extent of π charge.[16] In C_{60}, the reduction to the hexaanion leads to a $\Delta\delta = 14$ deshielding of the ^{13}C NMR spectrum,[5] which results from increasing diamagnetism, as shown by calculation[7] and the ^{3}He NMR spectrum.[6]

As mentioned above, the local aromaticity or antiaromaticity of fullerenes is studied by examining the ring current of each ring. Each carbon is not only in the nodal plane of a π-ring system, where theory predicts small ring current effects, but is also adjacent to other rings, where the ring current effect may be significant. Therefore, it is difficult to distinguish between the different contributions to the chemical shifts.

Comparison between the chemical shifts in the ^{13}C NMR spectra of the neutral C_{70}[14] and the hexaanion (Table 1) shows a large change for the signals of carbon atoms **a** and **e**, which are located at the pole and the "equator" of the fullerene, respectively. The signal of carbon atoms **a** have a strong up field shift ($\Delta\delta = -17$). This shift is rationalized by the concentration of the negative charge on the polar 5-MRs, as was previously shown for charged $C_{71}H_2$.[10] Therefore, **a** type carbon atoms carry the highest negative charge. On the other hand, the signal of the **e** type carbon atoms have a strong low field shift ($\Delta\delta = 19$). Such a shift may originate from a decrease in the charge distribution[17] on the carbons at the equator of the C_{70}^{6-} surface as well as from global ring currents. Calculations by Haddon and co-workers[9a] show that in neutral C_{70} the **e** type carbons are the most affected by the ring current. The change in chemical shift of the signal of this carbon atom follows the same trend of that of the shifts in the ^{3}He NMR spectra of He@C_{70}[18] and He@C_{70}^{6-},[6] which might indicate similar ring current influences on the endohedral atom and the atoms at the equator. The chemical shifts of the signals of carbon atoms **b – d** show smaller changes. These shifts could result from the local effects of the magnetic ring currents of neighboring rings.[19] The low field shift of the signals of carbon atoms **b** and **c** can be explained by the diamagnetism of the 5-MRs in C_{70}^{6-}, since, the carbon atoms **b** and **c** are connected through one bond to the 5-MRs periphery, they are thus affected by the diamagnetic ring current of the 5-MRs. Moreover, each carbon of type **b** is near a polar 5-MR, so it is much more affected by the ring current, and thus shows a lower field chemical shift than **c** type carbon atoms.[10]

The high field of the signal of the **d** carbons can be explained in terms of a reduction of the diamagnetic ring current of some of the 6-MRs, since the **d** carbons are connected by one bond to those rings. This tendency was calculated by Bühl[9b] and by Haddon and co-workers,[9a] who independently showed a small aromatic character of 6-MRs in C_{70}^{6-}.

The $^1J_{c,c}$ for each interaction was also measured and was compared to the equivalent value in the neutral C_{70}[14] (Table 1). The most significant change of coupling constants is for $^1J_{a,b}$ that is reduced by 7 Hz. This result confirms that the location of the charge is at the poles, leading to increased bond lengths between the carbons of the 5-MRs at the poles(**a**) and their radially attached neighbors (**b**).

In addition to a full assignment of the ^{13}C NMR spectrum of C_{70}^{6-}, we have added another dimension to the study of the aromaticity of charged fullerenes and especially of C_{70}^{6-}. As has been shown,[6, 7, 9] the global aromaticity of C_{70}^{6-} is significantly weaker than that of C_{70}. Therefore, understanding the origin of the global magnetic properties requires an insight into the local characteristics of the anion. It can be concluded that the low aromatic character of C_{70}^{6-} results from the following causes; first, the charge distribution of the added electrons on the C_{70}^{6-} skeleton is not symmetrical and charge concentrates at the poles of the fullerene. The effect of the ring current is not equal over the entire fullerene, or the fullerene surface. Second, the addition of the electrons to the 5-MRs renders them diamagnetic. The global decrease in the aromaticity of C_{70}^{6-} could be accounted for by a reduced aromaticity in some of the 6-MRs.

Finally, this study represents a substantial addition to the understanding of the behavior of C_{70}^{6-}. Having studied the molecule from the inside[6] and the outside[10] we have now looked at it from the surface thus observing the molecule from every perspective.

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[11] The method is based on the excitation of a shared double quantum coherence by scalar *J* coupling, thus giving rise to a carbon connectivity map of the molecule. Two bonded carbons share a double quantum frequency in the vertical dimension, and peaks occur at their two chemical shifts in the horizontal dimension, allowing the correlation to be made. Each peak is split into a doublet by the relevant $^1J_{c,c}$ coupling constant; A. Bax, R. Freeman, *J. Magn. Reson.* **1980**, *41*, 507 – 511.

[12] ^{13}C-enriched C_{70} was purchased from MER Corp. (Tucson, AZ, USA).

[13] Additional weaker signals arising from multiple bond correlation were also observed.

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[17] For example: L. Zelikovich, R. E. Hoffman, A. Ayalon, M. Rabinovitz, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1785 – 1792.

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[19] These might be similar effects to those of systems such as pyrene (B. Eliasson T. Lejon, U. Edlund, *J. Chem. Soc. Chem. Commun.* **1984**, 591 – 593) and corannulene derivatives (A. Weitz, E. Shabtai, M. Rabinovitz, M. S. Bratcher, C. C. McComas, M. D. Best, L. T. Scott, *Chem. Eur. J.* **1998**, *4*, 234 – 239) where carbon atoms are affected by the ring current.

An Artificial Ion Channel Formed by a Macrocyclic Resorcin[4]arene with Amphiphilic Cholic Acid Ether Groups**

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Ion channels are naturally occurring molecular devices in the brains and nerve systems of all animals that generate large ionic fluxes with on – off gate control. An ion channel with a typical conductance of 10 pS allows the passage of 5×10^6 ions per second through a single molecular pore. Even at such high ionic fluxes, ion channels generally discriminate different ionic species, for example, cation/anion and Na$^+$/K$^+$.[1] These functions are of potential use as the basis for molecular ionic devices[2] that can transfer information across a thin membrane. If these functions are properly attributed to artificial ion channels, they should show great advantages with regard to handling, stability, and availability over large natural proteins, which are hardly expected to meet these demands.

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At the same time, construction of artificial ion channels by using simple molecular systems may provide important information with regard to understanding natural ion channels and to establishing structure – function relationships.

Several approaches to artificial ion channels have been reported by us[3] and others.[4] We have already obtained several nonpeptidic ion channels by two approaches: supramolecular and molecular half channels. Two important results were: 1) A macrocyclic resorcin[4]arene with four alkyl chains **1** (Figure 1) gave a single ion channel having only
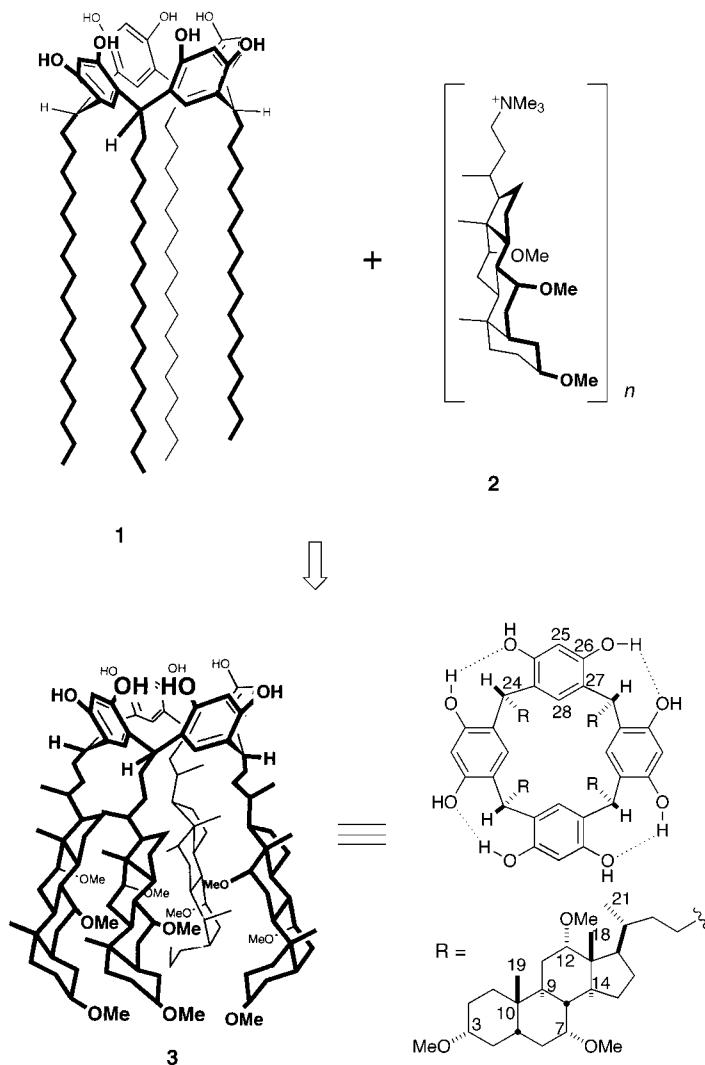

Figure 1. Structures of compounds **1** – **3**.

one conductance level.[3d] 2) A supramolecular ion channel obtained by using the rigid methyl cholate **2** with amphiphilic nature showed a long-lasting open state.[3e] We have now combined these two functions by synthesizing a macrocyclic resorcin[4]arene having four amphiphilic methyl cholate groups (**3**) in the hope of obtaining a fundamental molecular channel unit with a single conductance level and a stable open state. Then, refined design of the ion-transporting path by modifying the rigid molecular plane of the cholic acid residues is expected to modify the conductance and ion selectivities so that structure – function relationships can be established.