Metallofullerenes

2D NMR Characterization of the La@C_{82} Anion**

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Endohedral metallofullerenes have attracted special interest as new spherical molecules, and intensive effort has been made to disclose their structures and electronic properties.[1] Although NMR spectroscopy is a powerful tool for elucidating the structure of a given compound,[2] its application to endohedral metallofullerenes such as La@C_{82} is very difficult because of their paramagnetic nature.[3,4] Recently, we reported the determination of the cage symmetry in paramagnetic metallofullerenes such as La@C_{82}-A(C_{2v}),[5] La@C_{82}-B(C_s),[6] Pr@C_{82}-A(C_{2v}),[7] and Ce@C_{82}-A(C_{2v})[8] by ^{13}C NMR measurements on their anionic forms [M@C_{82}]$^-$. However, it remains an important goal to verify the bond connectivity and assign the NMR lines, as this is essential for full characterization of the structures of endohedral metallofullerenes. We now report the first mapping of the bond connectivity in the carbon cage of [La@C_{82}-A]$^-$ and definitive assignment of the NMR lines by 2D INADEQUATE (incredible natural abundance double quantum transfer experiment) NMR measurements.[9–11] The bonding nature

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of the carbon cage in $[La@C_{82}\text{-}A]^-$ was revealed from the carbon–carbon coupling constants $^1J_{CC}$. The position of La was also confirmed by measurements of relaxation time T_1.

Figure 1 shows the 2D INADEQUATE NMR spectrum of $[La@C_{82}\text{-}A]^-$. Two-bonded carbon atoms share a double

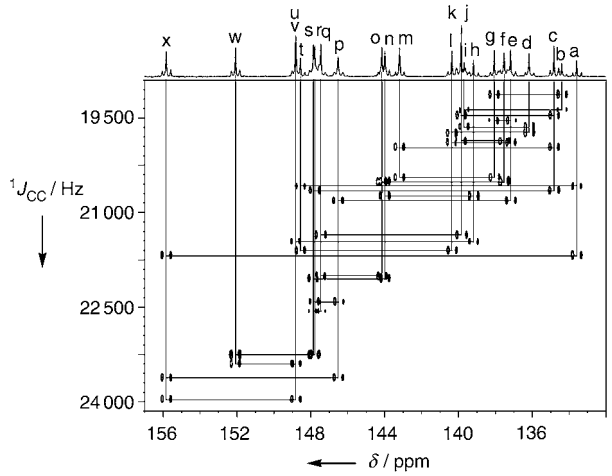
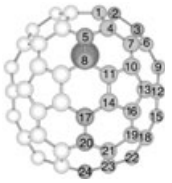


Figure 1. 2D INADEQUATE NMR spectrum of $[La@C_{82}\text{-}A]^-$.

quantum frequency in the vertical dimension, and each peak appears at the two respective chemical shifts in the horizontal dimension. To assign the 2D INADEQUATE NMR spectrum at an early stage, the ^{13}C NMR chemical shifts of $[La@C_{82}\text{-}A]^-$ were calculated at the B3LYP-GIAO/6-31G(d)//B3LYP/6-311+G(d) level. It was shown that the C atom designated no. 8 in Table 1 has the most upfield ^{13}C NMR signal. Therefore, we started the ^{13}C NMR assignment and bond

Table 1: Peak assignment and chemical shifts (δ) for the ^{13}C NMR spectrum of $[La@C_{82}]^-$.



Carbon no.[a]	Signal no.[b]	δ [ppm]	Carbon no.[a]	Signal no.[b]	δ [ppm]
1	d	136.5	13	r	148.1
2	i[c]	140.0	14	u	149.1
3	b[c]	134.7	15	k	140.1
4	l	140.6	16	w	152.4
5	t[c]	148.9	17	v[c]	149.1
6	g	138.4	18	q	147.8
7	e	137.5	19	s	148.2
8	a[c]	133.9	20	h[c]	139.5
9	m	143.5	21	n	144.3
10	p	146.8	22	o	144.4
11	x	156.1	23	f	137.8
12	c	135.1	24	j[c]	140.1

[a] Carbon atoms are numbered in order of distance from La atom. The optimized structure of $[La@C_{82}\text{-}A]^-$ was obtained at the B3LYP/6-311+G(d) level. [b] Assigned in Figure 1. [c] Half-intensity peak.

connectivity from the most upfield signal a in Figure 1, that is, from carbon no. 8. As shown in Table 1, all C atoms in $[La@C_{82}\text{-}A]^-$ are completely assigned, as the first example for fullerenes apart from C_{60}, C_{70}, and their derivatives.

In the 2D INADEQUATE NMR spectrum, each peak is split into a doublet by the relevant carbon–carbon coupling constant $^1J_{CC}$. It is well known that $^1J_{CC}$ increases with shortening bond length and increasing π-bond order.[12] The 5,6 and 6,6 ring-fusion bonds of empty fullerenes such as C_{60} and C_{70} are considered to have single- and double-bond character, respectively.[13] Figure 2a plots the C–C bond

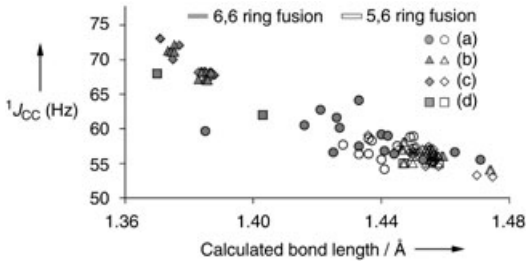


Figure 2. Plots of calculated carbon–carbon bond lengths [Å] vs $^1J_{CC}$ [Hz] for a) $[La@C_{82}\text{-}A]^-$, b) C_{60} *trans*-3 bis-adduct,[10b,c] c) C_{60} *trans*-4 bis-adduct,[10b,c] and d) C_{70}.[11b]

lengths calculated for $[La@C_{82}\text{-}A]^-$ at the B3LYP/6-311+G(d) level against the observed $^1J_{CC}$ values. To compare $[La@C_{82}\text{-}A]^-$ with empty fullerenes, the plots for *trans*-3 and *trans*-4 Bingel bis-adducts of C_{60}[10b,c] and pristine C_{70}[11b] are also shown in Figure 2b–d. For the empty fullerenes, the C–C bonds with larger $^1J_{CC}$ values and shorter calculated bonds correspond to the 6,6 ring-fusion bonds, and these plots do not overlap with those for the 5,6 ring-fusion bonds. However, the plots of 6,6 and 5,6 ring-fusion bonds for $[La@C_{82}\text{-}A]^-$ overlap with each other. In this context, it may be concluded that the 5,6 and 6,6 ring-fusion bonds in $[La@C_{82}\text{-}A]^-$ are shortened and elongated, respectively, and the classification of single- and double-bond character of $[La@C_{82}\text{-}A]^-$ is less clear than that of empty fullerenes. Shortening of the 5,6 ring-fusion bonds and the elongation of the 6,6 ring-fusion bonds were also calculated for $C_{82}(C_{2v})$ (Figure 3). However, the extent of shortening and elongation in $[La@C_{82}\text{-}A]^-$ is much larger than

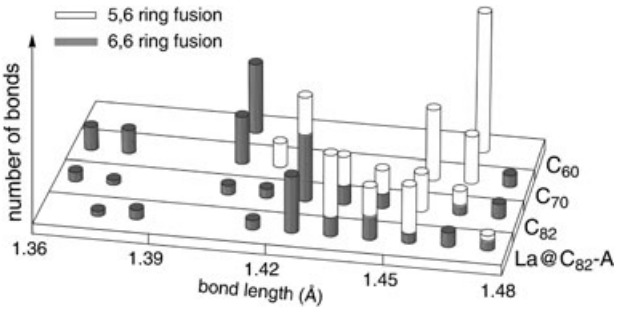


Figure 3. Histogram of 5,6 and 6,6 ring-fusion bond lengths calculated for C_{60}, C_{70}, $C_{82}(C_{2v})$, and La@C_{82}-A at the B3LYP/6-311+G(d) level.

that in pristine C_{82}, as a result of three-electron transfer from La to the LUMO and LUMO+1 of C_{82}, which have antibonding character.[4]

Important information about the position of La in $[La@C_{82}\text{-}A]^-$ is also obtainable from ^{13}C NMR measurements. Calculations on $[La@C_{82}\text{-}A]^-$ show that the C–C bonds in the vicinity of La are elongated (Figure 4) because of electron

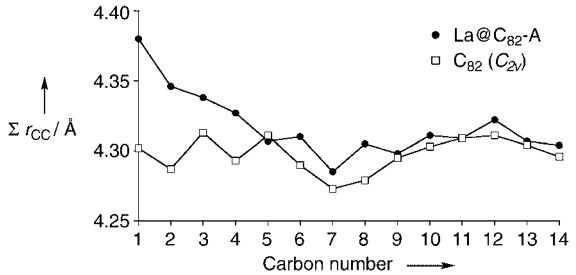


Figure 4. Plots of the sum of the calculated carbon–carbon distances to neighboring carbon atoms for $[La@C_{82}\text{-}A]^-$ and C_{82} (C_{2v}) at the B3LYP/6-311+G(d) level. Carbon atoms are numbered in order of distance from La atom, as shown in Table 1.

transfer from La to C_{82}.[4] It is known that the relaxation time T_1 governed by dipole–dipole relaxation is proportional to the sixth power of the internuclear distance.[14,15] It is noticeable that carbon no. 1 in Table 1, which is calculated to be the nearest to La in $[La@C_{82}\text{-}A]^-$, has the largest T_1 value and gives the largest value for the sum of the sixth power of the C–C bond lengths (see Supporting Information).[16] Thus, T_1 measurements support that La is located at the position predicted by calculations.[4,5]

In conclusion, the 2D INADEQUATE NMR spectrum of $[La@C_{82}\text{-}A]^-$ yields the bonding topology, coupling constants, and full assignment of the ^{13}C NMR spectrum. In other words, the 2D INADEQUATE NMR measurement can be used as an alternative method to X-ray crystallographic analysis for the structural characterization of endohedral metallofullerenes.

Experimental Section

A 13% ^{13}C-enriched $La@C_{82}$-A sample was prepared according to the reported procedure by using an arc vaporization method with a composite anode containing ^{13}C-enriched graphite and lanthanum oxide.[17] $[La@C_{82}\text{-}A]^-$ was prepared electrochemically as described before.[5] The 2D INADEQUATE NMR spectrum was measured in $[D_6]$acetone/CS_2 (1/1) at 125 MHz on a Bruker DRX 500 spectrometer with a CryoProbe system. All calculations were performed with Gaussian 03.[18]

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