An Insight into the Aromaticity of Fullerene Anions: Experimental Evidence for Diamagnetic Ring Currents in the Five-Membered Rings of C_{60}^- and C_{70}^-.

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Abstract: Reduction of the two “closed” [6,6] methanofullerenes, [6,6]C_{60}H_2 (1) and [6,6]C_{70}H_2 (5), to the corresponding hexaamions with lithium metal causes the bridgehead–bridgehead bonds to open, at least partially, and this change gives rise to diamagnetic ring currents in the resulting homoconjugated six-membered rings (6-MRs). These new ring currents shield the overlying hydrogen atoms on the methylene bridge and induce upfield shifts of 1.60 and 0.11 ppm in their ^1H NMR resonances, respectively. Analogous reduction of the already “open” [5,6] methanofullerenes, [5,6]C_{60}H_2 (2) and [5,6]C_{70}H_2 (3 and 4), only slightly enhances the shielding of the hydrogen atoms over the homoconjugated 6-MRs (upfield shifts of 0.13, 0.68, and 0.14 ppm, respectively) but leads to exceptionally strong diamagnetic ring currents in the homoconjugated five-membered rings (5-MRs), as evidenced by dramatic shielding of the hydrogen atoms situated over them (upfield shift of 5.01, 6.78, and 1.63 ppm, respectively). The strongest shielding is seen for the hydrogen atom sitting over the 5-MR at the pole of C_{71}H_2^− (δ = −0.255 ppm) indicating that the excess charge density is concentrated at the poles.

Introduction

Fullerenes occupy a unique place among aromatic compounds, and studies of their properties enhance and deepen our understanding of the principles of aromaticity. These carbon allotropes embody completely conjugated π systems of spheroidal shape, so that the carbon skeletons are boundaryless, and large numbers of Kekulé structures can be drawn. The aromaticity of fullerenes has been thoroughly investigated theoretically and substantiated experimentally by NMR studies. Calculations showed a modest aromatic character for C_{60} and a much greater aromaticity for C_{70}. This trend was confirmed by the ^3He NMR spectra of endohedral fullerenes.

More detailed characterization of the magnetic properties of each fullerene is possible by probing the separate contributions of individual rings. From the point of view of aromaticity, there is a distinct difference between the six-membered rings (6-MRs) and the five-membered rings (5-MRs). Ring current calculations have shown that the 6-MRs exhibit diamagnetic ring currents while the 5-MRs exhibit paratropicity. The low aromatic character of C_{60} has been attributed to a near cancellation of these two opposing contributions. The higher aromaticity of C_{70} compared to C_{60}, as was shown, results from an increase in the number of 6-MRs, while the number of 5-MRs remains the same. It is possible, however, to study these local ring currents by attaching a methylene bridge to the fullerenes. The protons on the bridge sit over either a “5-MR” or a “6-MR”, and their chemical shifts reflect the magnetic character of each ring. These hydrogen probes thus serve as “observers” that do not participate in the π-system.
Fullerenes can accommodate large numbers of electrons in their π-systems as can be deduced from their characteristic pattern of low-lying unoccupied molecular orbitals, their high electron affinity, and their electrochemistry.\(^7\) Since their shape and symmetry are not expected to be significantly modified by reduction, the effect of added electrons will be expressed mainly in their magnetic and electronic properties, i.e., their aromaticity.

The changes in the aromaticities of \(C_{60}\) and \(C_{70}\) upon reduction to their hexaanions are expressed by their \(^{13}\)C and \(^{3}\)He NMR chemical shifts.\(^10,11\) Unlike the neutral fullerene, the hexaion of \(C_{60}\) shows a high degree of delocalization and aromaticity. On the other hand \(C_{70}\) shows a change in the opposite direction upon reduction.

These trends were predicted and explained by magnetic susceptibility calculations.\(^6\) The added electrons were calculated to be located mostly on the 5-MRs, rendering them diamagnetic, and thus supplying more extended diamagnetism to \(C_{60}^\bullet\). In \(C_{70}\), the paramagnetic ring currents are also diminished, but there is an additional decrease in the diamagnetic ring currents, resulting in a large overall decrease of diamagnetism.

Here we report a comprehensive systematic study\(^12\) of local magnetic properties of charged fullerenes and methylene-bridged fullerenes. The motivation for this study is to understand the origins of the magnetic properties of fullerene anions using their aromatic properties as observed by NMR spectroscopy and magnetic susceptibilities.\(^6\) The investigation was carried out by monitoring the local ring currents of 5-MRs and 6-MRs in the neutral and reduced fullerenes, using carbon-bridged fullerenes to sense local contributions. The study includes an examination of the nature of the bonding in the bridged moiety vis-à-vis the fullerene π-system.

**Results and Discussion**

**Synthesis.** Homofullerenes \(C_{60}H_2\) (2),\(^7\)\(^13\)C\(_71\)H\(_2\) (3), and \(C_{71}H_2\) (4)\(^7\)\(^13\) were previously reported by the group of Wudl and Smith and synthesized according to ref 7c by addition of diazomethane to the respective fullerene, followed by thermal extrusion of dinitrogen from the resulting pyrazolofullerene. Methanofullerenes (3\(^7\)H-cyclopropafullerenes) \(C_{61}H_2\) (1) and \(C_{71}H_2\) (5) can be prepared in a similar sequence by photolysis of the intermediate pyrazolofullerenes.\(^7\)\(^13\) However, the [6,6]-closed adducts obtained by this method are generally ac-

**compared by the isomeric open homofullerenes\(^7\)\(^13\) from which they cannot be easily separated. For this reason, we were looking for a convenient and specific synthesis affording isomerically pure unsubstituted methanofullerenes. This search was inspired by the finding that controlled potential electrolysis of \(C_{60}\)\(^14\) or of Bingel-type adducts of \(C_{84}\)\(^15\) slightly below the third reduction potential of the starting compound, produced methanofullerenes when the experiment was run in \(CH_2Cl_2\). Substituted methano[60]fullerenes have been electro-synthesized by reaction of the mono- and dianion of \(C_{60}\) with dihalomethane derivatives.\(^16\) Furthermore, it was shown that diamions of \(C_{60}\), chemically generated by reaction of the fullerene with alkaliolithiates, can be bridged in the 1,2-position by alkylation with 1,3-diiodopropene and 1,4-diiodobutane.\(^17\) By applying the latter methodology to the reaction of \(C_{60}\) with diiodomethane we were able to obtain isomerically pure 1,2-methano[60]fullerene 1.

Direct cyclopropanation of fullerenes is also possible by reaction with ylides. Addition of various phosphonium ylides to \(C_{60}\) was reported by Bestmann et al.,\(^18\) whereas other authors used stabilized sulfonium ylides in the preparation of substituted methano[60]\(^19\) and methano[70]fullerenes.\(^20\) In neither case did


the authors prepare unsubstituted methanofullerenes. The ylide route was used in the present work to selectively synthesize the parent 3'H-cyclopentafullerene 1 and 5 by addition of dimethylsulfoxonimidemethane to C_{60} and C_{70}, respectively. In the latter case, 1,2-methano[70]fullerene, resulting from attack at the most reactive polar 6,6-bond, was obtained as the sole isomer.

The reduction process of all the detected fullerenes was achieved by adding a small amount of corannulene to the solution, making it possible to carry out the reaction under mild conditions, i.e., low temperature and without sonication. In this method, the corannulene monoanion radical serves as an "electron shuttle", which transfers electrons from the lithium metal to the fullerene in a more effective way than other charged \(\pi\)-systems.\(^{21}\)

**Bridged \(C_{60}\) and \(C_{70}\).** Several isomers of \(C_{61}H_2\) and \(C_{71}H_2\) were reduced and analyzed by NMR methods. We reduced the two isomers of \(C_{61}H_2\) (1 and 2) and the three isomers of \(C_{71}H_2\) (3, 4, and 5) where isomers 3 and 4 were reduced as a mixture and are distinguished according to their peak area ratio (6:1). In all these bridged fullerenes, the protons are located above the centers of rings of the fullerene skeleton, either above two 5-MRs and the other above a 6-MR, or one above a 5-MR and the other above a 6-MR, as in \([6,6]C_{61}H_2(1)\). The small changes in the 3\(^{\text{He}}\) chemical shifts between 3\(^{\text{He}}\)@C\(_{60}\) and 3\(^{\text{He}}\)@C\(_{70}\) route was used in the present work to selectively synthesize several isomers of \(C_{61}H_2\) and \(C_{71}H_2\). This confirms that the \(3^\text{He}\) chemical shifts of the neutral systems and their hexaanions allow the "electron shuttle", which transfers electrons from the lithium metal to the fullerene in a more effective way than other charged \(\pi\)-systems.\(^{21}\)

**Proton and Carbon NMR Data**

Table 1. Proton and Carbon NMR Data

<table>
<thead>
<tr>
<th>(\Delta \delta)</th>
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<tr>
<td>(\text{Ha} )</td>
<td>(\text{Hb} )</td>
<td>(\delta^{13}\text{C} )</td>
<td>(\delta^{13}\text{C} )</td>
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<tr>
<td>[6,6]C(_{61}H_2) (1)</td>
<td>3.94(^a)</td>
<td>30.4(^a)</td>
<td>166.5(^a)</td>
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\(^{a}\) Taken from ref 7b. \(^{b}\) Taken from ref 7a. \(^{c}\) Taken from ref 12a. \(^{d}\) Taken from ref 12c. \(^{e}\) Not observable.

The signal of the neutral compound.\(^7\) The nature of the skeleton of the bridged hexaanion, whether it is open or closed, is not obvious. The \(1^\text{JcH}\) of 1\(^\circ\), like those of 2\(^\circ\) to 6\(^\circ\), has a value that is typical for an open bond.\(^22,23\) On the other hand, the chemical shift of the carbon atom that is attached to the bridge appears at a higher field than that of the bridgehead carbon in other "open" fullerenes (77.6 ppm), which might be taken as evidence against an open bond.\(^23\) It is perhaps relevant that changing the temperature\(^23,27\) causes a slight change in the chemical shift of this peak (from 77.3 to 78.5 ppm for 165 and 298 K, respectively). Our suggestion is that like some other bridged annulene systems, 1\(^\circ\) may have a nonclassical structure,\(^25\) or alternatively that an equilibrium exists between the open and the closed bonds.\(^23\) In either case, the 6-MRs rings at the base of the bridge become highly conjugated, and therefore more aromatic than in neutral 1, which explains the high-field shift seen in the \(^{1}\text{H}\) NMR spectrum.

\[\text{[5,6]}C_{61}H_2(2)\]. The \(^{1}\text{H}\) NMR of 2\(^\circ\) shows two doublets at 2.74 and 1.34 ppm (Table 1), with \(^{2}\text{JHH} = 8.93\) Hz.\(^22\) On the basis of the \(^{1}\text{H}\) NMR spectrum of 1\(^\circ\), these two doublets of 2\(^\circ\) can be assigned as \(\text{Ha}\) and \(\text{Hb}\), respectively; one of them (\(\text{Ha}\)) resides above a 6-MR, as in 1\(^\circ\), in which both protons sit above 6-MRs. While there is almost no change in the chemical shift of \(\text{Ha}\) (\(\Delta\delta = -0.13\) ppm), the signal for \(\text{Hb}\) moves upfield dramatically (\(\Delta\delta = -5.01\) ppm). This leads to the conclusion that the added electrons are located mainly in the 5-MRs, converting them from paratropic to diatropic rings, while the ring currents of the 6-MRs experience little influence.

\[\text{[5,6]}C_{71}H_2\text{ Major Isomer (3)}\]. The \(^{1}\text{H}\) NMR spectrum of 3\(^\circ\) contains two doublets at 2.27 and \(-0.255\) ppm (Table 1), with coupling constant of \(^{2}\text{JHH} = 9.6\) Hz.\(^22\) These data are discussed below, together with those from isomer 4 of \(C_{71}H_2\).

\[\text{[5,6]}C_{71}H_2\text{ Minor Isomer (4)}\]. The \(^{1}\text{H}\) NMR spectrum of 4\(^\circ\) contains two doublets at 2.34 and 3.6 ppm (Table 1), with a coupling constant of \(^{2}\text{JHH} = 9.1\) Hz.\(^22\) A COSY experiment showed an absorption at 3.6 ppm under the solvent (THF-\(d_8\)) peak, which could only be observed directly in a 1D spectrum


by performing double quantum filter (DQF) and inversion recovery experiments simultaneously (see Experimental Section).

From the spectrum of the two isomers, a full assignment of the $^1$H NMR chemical shifts can be obtained, as proton H$_a$ of both isomers is located above the same 6-MR of the C$_{70}$ framework. Thus the absorptions appearing at 2.27 and 2.34 ppm can safely be assigned to H$_a$ in 3$^6$- and 4$^6$-, respectively, and the absorptions of H$_b$ appear at $-0.255$ and 3.6 ppm for 3$^6$- and 4$^6$-, respectively (Table 1). In these compounds, as in 2$^6$-, the added electrons are located mostly on the 5-MRs. The substantial upfield shifts of both H$_b$ peaks point to the increased diamagnetism of the 5-MRs in C$_{70}$$^6$$^-$. The different location of the bridge in 3 and 4 affords an insight into the charge distribution at different regions on the C$_{70}$ surface. While the chemical shifts of the H$_a$ probe protons are very similar in both 3$^6$ and 4$^6$-, those of the H$_b$ probes are quite different. In 3$^6$-, where the bridge is positioned at the C$_{70}$ pole, the chemical shift of H$_b$ is shifted to much higher field than in 4$^6$-.

These observations, when taken together with our recent finding from direct NMR measurement on C$_{70}$$^6$$^-$ (INADEQUATE), showing that the majority of the excess charge density in C$_{70}$$^6$$^-$ is concentrated at the poles, support the following general conclusions: (a) Reduction of fullerenes and homofullerenes to their hexaanions puts extra charge into the 5-MRs and renders them diatropic. (b) The strength of the diamagnetic ring currents in the 5-MRs of fullerene and methanofullerene anions increases as a function of excess charge in the individual 5-MRs.

[6,6]C$_{70}$H$_2$ (5). Following our results regarding to the nature of the bridge of 1$^-$, we wanted to examine the general behavior of bridges above two 6-MRs in reduced fullerenes, and therefore we reduced isomer 5. In this isomer the two protons are located over equivalent 6-MRs. The $^1$H NMR of 5$^6$- contains one singlet at 2.77 ppm, shielded by 0.11 ppm from the neutral 5. The $^1$C$_{CH}$ measured for 5$^6$- is much smaller than that of 5 (127.9 and 168$^7$ Hz, respectively, Table 1), and similar to that of 1$^-$, which is typical for an open bond. In addition, the low-field $^{13}$C NMR chemical shift of the methylene carbon of 5$^6$- indicates an opening of the cyclopropane ring.

Bis(4-methoxyphenyl)methanofullerene (6). In the fullerene derivatives 1–5 described above, where substituents are hydrogens, the methylene group interferes minimally with the fullerene $\pi$-system, and the electronic and magnetic properties retain their fullerene-like nature. In contrast, derivative 6 contains bulkier substituents, namely p-methoxyphenyls, which might affect the properties of the fullerene, both sterically and electronically. Reduction of 6 with lithium metal affords a $^{13}$C NMR spectrum of the resulting species that contains, apart from the phenyl signals, 14 peaks in the 130–160 ppm region that belong to the fullerene skeleton. From the $^{13}$C NMR spectrum it seems reasonable that the C$_{60}$ skeleton accepts six electrons, since the chemical shifts are in the same range as that of C$_{60}$$^6$$^-$. On the other hand, the chemical shifts of the phenyl carbons are similar to those of the neutral compound (113.77, 113.77, 131.46, 158.76 and 110.3, 130.8, 145.3, 155.4 ppm, respectively). The $^1$H NMR spectrum contains a singlet at 3.5 ppm belonging to the methoxy group, and two doublets at 8.21 and 6.33 ppm that are assigned to H$_2$ and H$_3$ of the phenyl ring, respectively. The increase in $\Delta$ between the doublets, compared to that in neutral 6 (1.9 vs 1.0 ppm), is a result of electron addition to the fullerene skeleton. As the phenyls rotate freely, the location of the protons and the influence of the magnetic anisotropy are averaged.

Conclusions

Methylen-bridge protons serve as sensors of the local contributions of the 5-MRs and 6-MRs to the aromaticity of fullerenes. The added electrons in both C$_{60}$$^6$$^-$ and C$_{70}$$^6$$^-$ are located mainly in the 5-MRs, rendering them diatropic. The lower symmetry of C$_{70}$$^6$$^-$ causes an asymmetrical charge distribution, with the extra charge concentrated mostly in the 5-MRs at the poles. Decreasing [6,6]methanofullerenes, which have closed bonds in the neutral state, causes partial opening of the bond between the 6-MRs; this phenomenon could be explained by either a nonclassical bond or an equilibrium between the open and the closed forms. Adding a carbon bridge to fullerenes causes a negligible effect on the $\pi$-system and on the ability of a fullerene to accept electrons.

Experimental Section

Materials. Reagents and solvents were purchased (reagent grade) and used without further purification. Solvents were dried over molecular sieves 3 Å (acetonitrile) and 4 Å (DMSO, toluene). All reactions were run under argon. C$_{60}$ was obtained from Materia Technologies Research—MTR Ltd., Cleveland, Ohio; C$_{70}$ was obtained from Hoechst AG. Solvent evaporation was done at water aspirator pressure and compounds were dried at 10$^{-2}$ Torr. Column chromatography: SiO$_2$ (60 230–400 mesh, 0.040–0.063 mm) from E. Merck and SiO$_2$:H from Fluka. The identity of all compounds was confirmed by comparison of their $^1$H and $^{13}$C NMR data with published spectra.

Syntheses. [6,6]C$_{60}$H$_2$ (1). Method 1: A suspension of C$_{60}$ (60 mg, 0.083 mmol) in dry acetonitrile (50 mL) was sonicated under Argon for 25 min. Sodium butanethiolate (933 mg, 8.32 mmol) was added, and the mixture turned dark red after a few minutes. After the mixture was stirred for 16 h, diiodomethane (2.7 mL, 33.3 mmol) was added and stirred continuing for 24 h. Toluene was added, the mixture was washed with water and dried (MgSO$_4$), and the solvent was evaporated in a vacuum. The residue was purified by flash chromatography (SiO$_2$:hexane/toluene 3:1) to yield a dark solid that was dissolved in toluene and precipitated by addition of MeOH. Final HPLC purification (SiO$_2$:hexane/toluene 4:6, flow rate 6 mL min$^{-1}$, $\lambda = 310$ nm, $t_R = 29$ min) afforded 8 mg (13%) of 1. Method 2: A solution of the ylide was generated by addition of NaH (25 mg, 1.041 mmol) to a solution of trimethylsulfonium iodide (229 mg, 1.041 mmol) in dry DMSO (30 mL). A tenth of this solution was added dropwise to a solution of C$_{60}$ (50 mg, 0.069 mmol) in dry toluene (50 mL) at 10$^\circ$C. After being stirred at room temperature for 2 h and at 50$^\circ$C for 1 h, the mixture was washed with water and concentrated in vacuo. The residue was purified by plug filtration (SiO$_2$:CS$_2$) and then by HPLC (trident-DNP “Buckyclutcher” (Regis), 500 × 25 mm, toluene/hexane/hexane (1:2:3)).

(30) The charge distribution was also shown by calculations, see ref 4a.

(31) We could not observe the $^{13}$C NMR chemical shifts of the bridgehead carbons (even with HMBC) on account of the low concentration and the broad peaks.

(32) Prior to the reported reduced state, another species was detected by $^1$H NMR (two doublets at 6.68 and 7.39 ppm, $J_{HH} = 9.1$ Hz). This may indicate an earlier charging state for 6.


(34) To determine a possible influence of corannulene on the properties of reduced 6, we reduced 6 with lithium, and without corannulene. The reduction process was carried out by contact of the solution with the lithium metal in an ultrasonic bath until the solution became colored (light brown). After the color change, the reduction was continued at room temperature and followed by NMR spectroscopy. This process resulted in the dissociation of 6 and the generation of C$_{60}$$^6$$^-$.
4:6, flow rate 8 mL min\(^{-1}\), \(\lambda = 310\) nm, \(t_R = 8.72\) min) affording 16 mg (31\%) of 1.

\[\text{[6,6]}C_{70}H_{2}\] (5) was prepared in analogy to 3 (Method 2). Final HPLC purification (trident-DNP “Buckyclutcher” (Regis), 500 \(\times\) 25 mm, toluene/hexane 4:6, flow rate 8 mL min\(^{-1}\), \(\lambda = 310\) nm, \(t_R = 15.55\) min) afforded 7 mg (14\%) of 5.

**General Method of Lithium Metal Reduction.** All fullerenes were reduced in 5 mm NMR tubes equipped with an upper reduction chamber. The fullerenes (2–5 mg) and a catalytic amount of corannulene were introduced into the lower chamber of the tube under an argon atmosphere. A lithium wire was introduced under argon to the reduction chamber, and the tube was attached to a vacuum line. THF-\(d_8\) (dried over sodium–potassium 1:5 alloy, under high vacuum) was vacuum transferred to the tube and degassed several times, and the extended tube was flame sealed. Reduction occurred on contact of the solution with the lithium metal, in dry ice, by repeated inversion of the tube. The formation of the anions was detected visually by the changing of corannulene color to green (that represents the monoanion of corannulene) and by \(^1\)H NMR and \(^{13}\)C NMR spectroscopies.

**NMR Data.** \(^1\)H, and \(^{13}\)C NMR spectra were recorded on a Bruker DRX-400 spectrometer. The chemical shifts were measured relative to the most downfield solvent peak (THF-\(d_8\) 3.57 ppm relative to TMS). All the reported spectra were recorded in the temperature range of 200–220 K, and analyzed by standard 2D NMR techniques.

\[\text{[6,6]}C_{70}H_{2}\] (1\(^+\)): \(^1\)H NMR 2.33 ppm (s, 2H). \(^{13}\)C NMR 32.5 (methylene, by HSQC), 77.6 (C\(_{60}\)-CH\(_2\)), 144.9 (benzene-like, by HSQC), 147.8, 148.4, 149.0, 150.7, 152.7, 153.0, 156.6, 156.8, 157.9, 159.6, 160.0, 162.2, 163.3 ppm.

\[\text{[5,6]}C_{70}H_{2}\] (2\(^+\)): \(^1\)H NMR 1.34 ppm (d, 1H, \(J = 8.93\) Hz), 2.74 ppm (d, 1H, \(J = 8.93\) Hz). \(^{13}\)C NMR: 37.1 (methylene), 138.2, 139.0, 143.7, 147.2, 147.5, 149.9, 152.1, 152.3, 154.5, 154.6, 154.7, 154.8, 155.1, 155.5, 155.7 (two peaks), 156.2, 156.7, 157.2, 158.0, 158.5, 159.6, 159.9, 160.1, 160.2, 160.9, 161.2, 161.5, 162.5, 164.8 ppm.

\[\text{[5,6]}C_{71}H_{2}\] (3\(^+\) and 4\(^+\)): \(^1\)H NMR –0.255 ppm (d, 1H, \(J = 9.6\) Hz), 2.27 ppm (d, 1H, \(J = 9.6\) Hz), 2.34 ppm (d, 1H, 3.6 ppm (d, 1H, \(J = 9.1\) Hz). \(^{13}\)C NMR 39.9 (methylene, by HSQC, \(4^+\)), 44.9 (methylene, \(3^+\)), 120–160 ppm (broad bands).

\[\text{[6,6]}C_{71}H_{2}\] (5\(^+\)): \(^1\)H NMR 2.77 ppm (s, 2H). \(^{13}\)C NMR 43.6 (methylene, by HSQC), 113–156 ppm.

**Hexaanion of bis(4-methoxyphenyl)methanofullerene (6\(^-\)):** \(^1\)H NMR 3.50 ppm (s, 6H, OCH\(_3\)), 6.33 ppm (d, 4H, \(J = 8.1\) Hz) 8.21 ppm (d, 4H, \(J = 8.1\) Hz). \(^{13}\)C NMR 53.5 (methylene, by HMBC), 91.4, 110.3 (C3), 130.8 (C2), 54.7 (OCH\(_3\)), 145.3 (C3), 148.0, 149.0, 149.1, 150.3, 151.0, 154.2, 155.4 (C4), 155.8, 157.5, 158.1, 158.4, 160.1, 160.2, 160.8, 161.1 ppm.

**Simultaneous Double Quantum Filter (DQF) and Inversion Recovery Experiments of C\(_{71}\)H\(_2\) (4\(^+\)).** COSY experiments showed a correlation between a doublet at 2.34 ppm and a peak at 3.6 ppm, which is under the solvent signal. The latter doublet was observed by performing double quantum filter (DQF) and inversion recovery experiments simultaneously; the signal was expected to have an intensity of 1\% of the solvent signal. A gradient-enhanced DQF experiment reduced the solvent signal. To observe the desired signal we also took advantage of the difference in relaxation times, preceding the DQF sequence by an inversion pulse. This suppressed the solvent signal by 3 orders of magnitude leaving the desired signal of 4\(^+\) clearly visible.

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