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# Theoretical $^{13}$C NMR Spectra of IPR Isomers of Fullerenes $C_{60}$, $C_{70}$, $C_{72}$, $C_{74}$, $C_{76}$, and $C_{78}$ Studied by Density Functional Theory

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Optimized geometries and $^{13}$C NMR chemical shifts of all the isolated-pentagon-rule (IPR) isomers of fullerenes $C_{60}$, $C_{70}$, $C_{72}$, $C_{74}$, $C_{76}$, and $C_{78}$, except $C_{76}$:2, have been calculated by density functional theory (B3LYP/6-31G*). $C_{60}$ has the highest value of total energy per atom. The total energy per atom of other fullerenes decreases when the size of fullerene increases. The unobserved $C_{72}$ is found to have higher total energy per atom while the also unobserved fullerenes $C_{74}$, $C_{78}$:4, and $C_{78}$:5 have similar values of total energy per atom compared to those already observed. The general patterns of the calculated $^{13}$C NMR spectra give good agreement with the experimental patterns. Peaks above 140 ppm agree better with experiment while chemical shifts below 140 ppm are generally overestimated by 1−2 ppm. Local geometry is shown to be determined largely by the connectivity and have some effect on chemical shifts although no direct relationship between the $\pi$-orbital axis vector (POAV) angles and chemical shifts is apparent.

## Introduction

Research on higher fullerenes has been an active field since the discovery[1] of the existence of fullerene $C_{60}$ and its following identification by IR[2] and NMR[3]. A number of isomers of various higher fullerenes have been characterized by NMR. These include one isomer of $C_{70}$,[3,4] one isomer of $C_{76}$,[5] three isomers of $C_{78}$,[6,7,8] one isomer of $C_{80}$[9], and four isomers of $C_{84}$.[10,11] Three isomers of $C_{82}$ exist, but cannot be assigned unambiguously.[7] Some minor isomers of $C_{84}$[12] and one high-symmetry isomer of $C_{90}$[8] also appear to exist, although their separation and identification has not been achieved experimentally.

All these isomers abide the isolated-pentagon-rule (IPR),[13] which dramatically reduces the number of possible isomers. On the other hand, it is still possible that a fullerene has more than one IPR isomers having the same symmetry, which are very likely to give similar NMR patterns. For example, four IPR isomers of $C_{84}$ have $D_2$ symmetry and all have 21 NMR peaks with equal intensity. Since the synthesized isomer is not necessarily the one with lowest energy, quantitative theoretical NMR patterns would facilitate their identification.

Few theoretical studies have been devoted to the NMR properties of fullerenes. Häser et al.[14] reported the chemical shifts of $C_{60}$ and $C_{70}$ with respect to that of benzene calculated at the GIAO−CPHF/DZP level (gauge-independent atomic orbital−coupled-perturbed Hartree−Fock). Schneider et al.[15] used GIAO−SCF/TZP theory to calculate the chemical shifts of three isomers of $C_{84}$. By comparing the calculated spans of the NMR spectra with the experimental values, they were able to eliminate isomers **1** and **5** (nomenclature after Manolopoulos and Fowler[16]) as the candidate for the observed $D_2$ isomer. In a recent study by Heine et al,[17] chemical shifts of $C_{70}$, $C_{76}$, $C_{78}$, $(C_{36})_2$, $(C_{60})_2$ and isomers **1**, **5**, **21**, **22**, and **23** of $C_{84}$ were calculated using the IGLO-DFTB (individual gauge for local orbitals−density-functional-based tight-binding) method. On the basis of the spectrum span and total energy, their calculations support the assignment of the two major isomers of $C_{84}$. NMR chemical shift predictions for $C_{70}$ were used to help selecting the best model for interpreting gas-phase electron diffraction (GED) experiments.[18] Bühl et al.[19] employed Hartree−Fock (HF) and density functional theory (DFT) methods to accurately calculate the chemical shifts of $C_{60}$ and $C_{70}$. We have recently[20] utilized the B3LYP method in combination with the 6-31G* and 6-311G** basis sets to predict the NMR spectra of isomers **21**, **22**, and **23** of $C_{84}$. The small rms values (less than 0.6 ppm) of our predicted NMR peaks for isomers **22** and **23** allowed us to confirm that isomers **22** and **23** are the experimentally obtained major isomers.

The excellent performance of B3LYP/6-31G* on the NMR chemical shifts of isomers **22** and **23** of $C_{84}$ sparked our interest in reproducing the NMR spectra of isomers of other higher fullerenes that are already experimentally observed and predicting the NMR spectra for a few unobserved ones. In this paper, we discuss our results for fullerenes up to $C_{78}$. We optimized the geometries of all the IPR isomers of fullerenes $C_{60}$, $C_{70}$, $C_{72}$, $C_{74}$, $C_{76}$ and $C_{78}$, except $C_{76}$:2, using DFT. Figure 1 shows all the fullerene isomers studied in this work. Total energy per carbon atom relative to that of $C_{60}$ is used to show the stability of these fullerene isomers. On the basis of the optimized geometries, we calculated $^{13}$C NMR chemical shifts of these fullerenes employing the same methodology and using the NMR peak of $C_{60}$ as reference. The effect of local geometry on chemical shifts was also considered.

## Computational Details

Full geometry optimization and NMR chemical shielding calculations were performed for all the IPR isomers of fullerenes $C_{60}$, $C_{70}$, $C_{72}$, $C_{74}$, $C_{76}$, and $C_{78}$, except $C_{76}$:2. Becke's three-parameter (B3) hybrid functional[21] incorporating exact exchange in combination with Lee, Yang and Parr's (LYP) correlation functional[22] was used throughout this study. Three basis sets, STO-3G, 3-21G and 6-31G*, were used in this sequence for geometry optimizations to obtain results at different theory levels as well as to minimize the computational cost. NMR chemical shielding values were evaluated employing the gauge-indepen-

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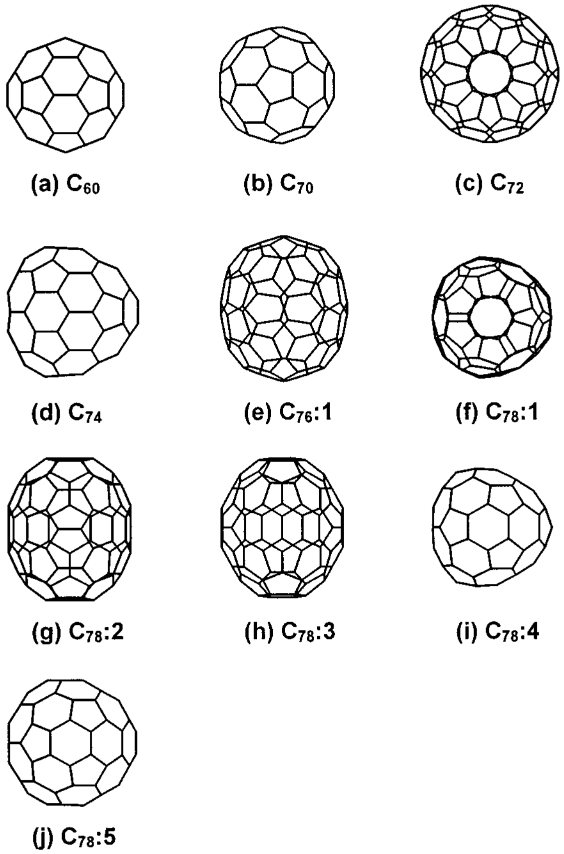
**TABLE 1: Bond Length Statistics and Relative Energies of IPR Isomers of Fullerenes $C_{60}$, $C_{70}$, $C_{72}$, $C_{74}$, $C_{76}$, and $C_{78}$ Calculated by Density Functional Theory**[a]

| | shortest $R_{cc}$[b] | longest $R_{cc}$[b] | average $R_{cc}$[b] | B3LYP/ STO-3G | B3LYP/ 3-21G | B3LYP/ 6-31G* | $\Delta E_{HOMO-LUMO}$[c] | DFTB[d] | TBMD[e] | BP86[f] | HF[g] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_{60}$ | 1.395 | 1.453 | 1.4244 | | | | 2.76 | | | | |
| $C_{70}$ | 1.389 | 1.471 | 1.4328 | | | | 2.69 | | | | |
| $C_{72}$ | 1.377 | 1.467 | 1.4336 | | | | 2.49 | | | | |
| $C_{74}$ | 1.388 | 1.472 | 1.4326 | | | | 0.71 | | | | |
| $C_{76:1}$ | 1.382 | 1.472 | 1.4328 | | | | 1.97 | | | | |
| $C_{78:1}$ | 1.380 | 1.471 | 1.4329 | 9.59 | 6.60 | 10.25 | 1.62 | 11.02 | 7.47 | 8.1 | 7.6 |
| $C_{78:2}$ | 1.365 | 1.470 | 1.4329 | 5.70 | 4.12 | 6.71 | 2.02 | 8.80 | 6.55 | 3.3 | 6.6 |
| $C_{78:3}$ | 1.372 | 1.471 | 1.4326 | 0.00 | 0.00 | 0.00 | 1.65 | 0.00 | 0.00 | 0.0 | 0.0 |
| $C_{78:4}$ | 1.357 | 1.468 | 1.4333 | 23.13 | 18.76 | 24.37 | 2.47 | 28.37 | 20.82 | 19.4 | 21.1 |
| $C_{78:5}$ | 1.367 | 1.473 | 1.4327 | 6.11 | 6.42 | 4.47 | 1.53 | 2.53 | 2.01 | 8.7 | 7.8 |

[a] Bond lengths in angstroms, energy in kcal/mol. [b] Bond length statistics of B3LYP/6-31G* geometries. [c] HOMO−LUMO gap (in eV) calculated by B3LYP/6-31G*, this work. [d] Density functional based tight-binding approach, taken from ref 17. [e] Tight-binding molecular dynamics, taken from ref 27. [f] BP86/3-21G, taken from ref 28. [g] SCF/DZ//MNDO, taken from ref 28.


(a) $C_{60}$ (b) $C_{70}$ (c) $C_{72}$

(d) $C_{74}$ (e) $C_{76}$:1 (f) $C_{78}$:1

(g) $C_{78}$:2 (h) $C_{78}$:3 (i) $C_{78}$:4

(j) $C_{78}$:5

**Figure 1.** IPR isomers of fullerenes $C_{60}$, $C_{70}$, $C_{72}$, $C_{74}$, $C_{76}$, and $C_{78}$ that are studied in this work. Isomer numbering are according to ref 13.

dent atomic orbital (GIAO) method[23] at the B3LYP/6-31G* optimized geometry. For NMR calculations, the 6-31G* basis set was used upon the recommendation by Cheeseman et al.[24] and our own experience.[20] Geometry optimizations were accomplished using Gaussian 98[25] and NMR calculations were performed using the PQS[26] suite of ab initio programs. The calculated chemical shieldings ($\sigma$) were then referenced to that of $C_{60}$ to obtain the calculated NMR chemical shifts ($\delta$) using the following formula:

$$\delta(i) = \delta(C_{60}) + \sigma(C_{60}) - \sigma(i) \tag{1}$$

where $\delta(C_{60})$ is taken as 143.15 ppm, after Avent et al.[12] $\sigma(C_{60})$ is the calculated chemical shielding of $C_{60}$ (50.59 ppm), and ($i$) is the carbon atom under consideration.

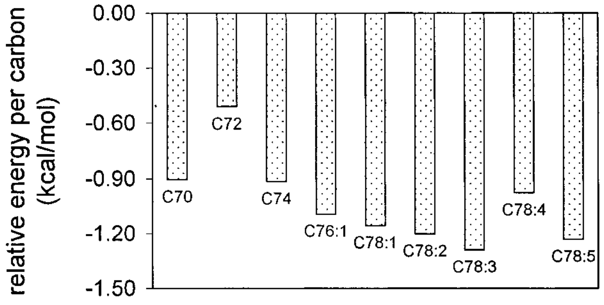


**Figure 2.** Energy per carbon atom for each fullerene isomer relative to that of $C_{60}$ calculated by B3LYP/6-31G*.

## Results and Discussion

**Geometry and Total Energy.** Table 1 lists the statistics of the B3LYP/6-31G* calculated bond lengths for all fullerene isomers studied in this work as well as the relative energies of $C_{78}$ isomers at different levels of theory. Also listed are the HOMO−LUMO gaps calculated at the B3LYP/6-31G* level of theory and relative energies of $C_{78}$ isomers as obtained by earlier theoretical studies.[17,27,28] All calculated bond lengths fall within the 1.36−1.48 Å range. The average bond lengths are also very similar, varying from 1.432 to 1.434 Å for fullerenes larger than $C_{60}$.

$C_{78}$ is the only fullerene that has more than one IPR isomers studied here. The orders of relative stability of the five $C_{78}$ isomers as calculated by different levels of theory are similar. From the most to least stable, the order of stability at the B3LYP/6-31G* level is **3** > **5** ∼ **2** ∼ **1** > **4**. Earlier theoretical studies, including TBMD[27] (tight-binding molecular-dynamics), HF,[28] BP86[28], and the DFTB[17] method, agree with this order in that all calculations predict isomer **3** is the most stable one, isomer **4** is the least stable one, and isomers **1**, **2**, and **5** are in between.

The question why some fullerene isomers form while others do not has attracted much attention. In an attempt to answer this question, we calculated the energy per carbon atom for each isomer relative to that of $C_{60}$ and the result is shown in Figure 2. It is interesting that all higher fullerene isomers have lower energy per atom than $C_{60}$, as indicated by the negative values. This is not unexpected since $C_{60}$ is the smallest thus has the highest strain. For the higher fullerenes that have been observed, $C_{70}$, $C_{76}$:1, $C_{78}$:1, $C_{78}$:2, and $C_{78}$:3, the calculated values of the energy per atom are 0.90, 1.09, 1.16, 1.20, and 1.29 kcal/mol lower than that of $C_{60}$, respectively. Generally, the larger the molecule, the lower the per carbon energy. The experimentally obtained difference of heat of formation per carbon atom

**TABLE 2: $^{13}$C Chemical Shifts of IPR Isomers of $C_{70}$, $C_{72}$, $C_{74}$, and $C_{76}$ Calculated at B3LYP/6-31G* Level of Theory**[a]

| $C_{70}$ | type[d] | $C_{72}$ | type[d] | $C_{74}$ | type[d] | $C_{76}$:1 | type[d] |
|---|---|---|---|---|---|---|---|
| 151.24[b] | pc | 148.94 | pc | 158.09[b] | pc | 149.77 | pc |
| 148.23 | pc | 146.09 | pc | 152.95 | pc | 147.52 | pc |
| 147.03[b] | pc | 142.61[b] | cor | 148.61 | pc | 147.51 | pc |
| 146.33 | cor | 131.81[b] | py | 146.01 | cor | 147.44 | pc |
| 132.07[b] | py | | | 139.76[b] | cor | 146.33 | cor |
| | | | | 138.41[b] | py | 146.27 | pc |
| | | | | 131.32[b] | py | 146.24 | pc |
| | | | | 131.18[c] | py | 144.47 | cor |
| | | | | 126.03 | cor | 143.69 | pc |
| | | | | | | 143.51 | cor |
| | | | | | | 143.03 | cor |
| | | | | | | 142.86 | pc |
| | | | | | | 142.17 | cor |
| | | | | | | 141.86 | cor |
| | | | | | | 140.93 | pc |
| | | | | | | 138.29 | py |
| | | | | | | 137.50 | py |
| | | | | | | 135.56 | py |
| | | | | | | 130.35 | py |

[a] Chemical shifts, in ppm, are referenced to that of $C_{60}$ at 143.15 ppm. [b] Half-intensity peak. [c]Peak of $C_{74}$ with one-sixth of full intensity. [d] pc, pyracylene; cor, corrannulene; py, pyrene.

**TABLE 3: $^{13}$C Chemical Shifts of IPR Isomers of $C_{78}$ Calculated at B3LYP/6-31G* Level of Theory**[a]

| $C_{78}$:1 | type[c] | $C_{78}$:2 | type[c] | $C_{78}$:3 | type[c] | $C_{78}$:4 | type[c] | $C_{78}$:5 | type[c] |
|---|---|---|---|---|---|---|---|---|---|
| 149.62 | pc | 147.90 | cor | 148.25[b] | pc | 147.42 | pc | 146.94[b] | pc |
| 148.07 | pc | 147.32 | pc | 147.16 | pc | 145.86 | cor | 146.22[b] | cor |
| 145.45 | pc | 146.55 | pc | 147.01 | pc | 145.36[b] | pc | 145.11 | cor |
| 144.16 | pc | 146.33 | cor | 146.59[b] | pc | 144.49 | pc | 142.20 | cor |
| 142.08 | pc | 146.04 | pc | 146.49[b] | cor | 143.49 | pc | 139.26 | py |
| 141.76 | py | 146.03 | pc | 146.36 | cor | 142.70[b] | cor | 137.74 | cor |
| 141.35 | cor | 145.29[b] | pc | 145.83[b] | pc | 135.68 | py | 134.93[b] | py |
| 141.12 | cor | 145.14 | cor | 145.27 | cor | 134.51[b] | py | 133.76 | pc |
| 140.74 | cor | 144.74 | pc | 145.09 | cor | | | | |
| 140.29 | pc | 143.98 | py | 144.00 | cor | | | | |
| 139.43 | cor | 143.58 | pc | 143.31 | pc | | | | |
| 134.65 | py | 143.54 | cor | 142.90 | cor | | | | |
| 133.09 | py | 142.90[b] | cor | 139.53 | cor | | | | |
| | | 140.00 | py | 139.49 | py | | | | |
| | | 138.36 | cor | 139.16 | py | | | | |
| | | 137.81 | cor | 137.85 | cor | | | | |
| | | 137.78 | py | 137.49 | py | | | | |
| | | 137.53 | cor | 136.20 | cor | | | | |
| | | 136.15 | py | 136.13 | pc | | | | |
| | | 134.84[b] | py | 134.73[b] | py | | | | |
| | | 133.40 | py | 133.80 | py | | | | |
| | | | | 133.57 | pc | | | | |

[a] Chemical shifts, in ppm, are referenced to that of $C_{60}$ at 143.15 ppm. [b] Half-intensity peak. [c] pc, pyracylene; cor, corrannulene; py, pyrene.

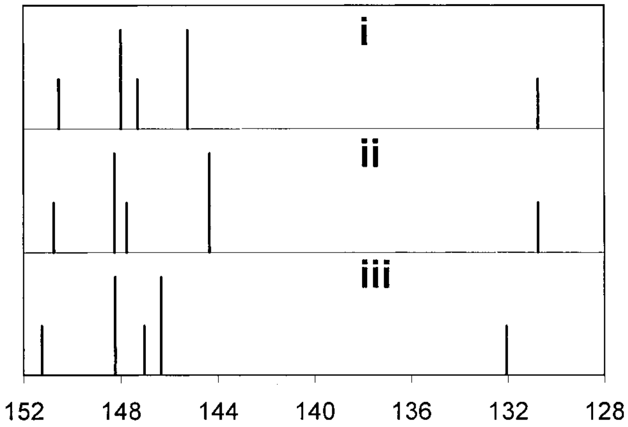


**Figure 3.** $^{13}$C NMR spectra of $C_{70}$ by (i) experiment[3], (ii) experiment,[6] and (iii) calculated by B3LYP/6-31G*. All spectra are referenced to $C_{60}$ at 143.15 ppm.

between $C_{60}$ and $C_{70}$[29] is 0.51 kcal/mol, which is in qualitative agreement with our result of 0.90 kcal/mol, as well as earlier HF and LYP calculations.[30] Fullerene $C_{72}$, which has not yet been observed, has a very high energy per atom compared with those of the observed ones. The other unobserved fullerenes, $C_{74}$, $C_{78}$:4, and $C_{78}$:5, have energy per atom values that are comparable to those of already observed ones. The reason these three isomers are not yet observed could lie either in kinetic factors or experimental conditions.

**NMR Chemical Shifts.** Fullerene $C_{60}$ has icosahedral symmetry, rendering all 60 carbon atoms chemically equivalent. The calculated chemical shielding of $C_{60}$ is 50.59 ppm. Earlier calculations yielded 40.43 ppm by Hartree−Fock (HF) approximation[15] and 51.3 ppm estimated by IGLO-DFTB.[17] As pointed out by Heine et al.,[17] the error in the theoretical chemical shielding values is mainly systematic for fullerenes and is significantly reduced once chemical shifts are used. Since the calculated $^{13}$C chemical shielding of TMS is 189.31 ppm at the B3LYP/6-31G* level of theory, our predicted chemical shift of $C_{60}$ is 138.72 ppm. The experimental chemical shift of $C_{60}$ has been reported by several groups, and the values range from 142.68[3,8] to 143.2[6] ppm. The differences between our calculated chemical shift of $C_{60}$ and the experimental values range from 3.96 to 4.48 ppm, which is of the same accuracy as earlier results[19] (∼6 ppm for HF-GIAO and ∼1 ppm for UDFT-GIAO−BPW91). We follow the experimental approach on higher fullerenes and reference the calculated chemical shieldings of other fullerenes relative to that of $C_{60}$ by using the chemical shift value of 143.15 ppm for $C_{60}$ and report the chemical shifts.

The calculated $^{13}$C NMR chemical shifts of the IPR isomers of fullerenes $C_{70}$, $C_{72}$, $C_{74}$, $C_{76}$, and $C_{78}$ are listed Tables 2 and 3. These results will be compared graphically below with the observed NMR spectra, when available. We note that it is possible that some NMR chemical shifts accidentally have similar values and the spectrum appears to have fewer peaks than required by symmetry. In that case, numerical chemical shifts can give a clearer picture.

The only IPR isomer of $C_{70}$ has $D_{5h}$ symmetry. Both 1D and 2D NMR studies[3,4] on $C_{70}$ have been reported and all the five peaks have been assigned. The five NMR peaks with the intensity ratio of 1:2:1:2:1 are correctly predicted in our calculation. Figure 3 shows the experimental[3,6] and theoretical $^{13}$C NMR spectra of $C_{70}$. The span of the calculated NMR spectrum, 19.17 ppm, is in good agreement with Taylor's experimental value of 19.79 ppm[3]. The calculated positions of the NMR peaks agree well with the experiments. The calculated peaks are at 151.24(a), 148.23(c), 147.03(b), 146.33(d), and 132.07(e) ppm, where a−e are the distinct sites from cap to equator. These values give 0.70, 0.24, −0.26, 1.09, and 1.32 ppm deviation with respect to the experimental values of Taylor et al.[3], respectively. Comparable errors were obtained for $C_{70}$ by Bühl et al.[19] using a comparable basis set. This leads us to expect errors in the order of up to 2 ppm in calculated chemical shifts for other fullerenes. This error is rather large considering that the span of NMR spectra of fullerenes is about 20−25 ppm. However, a general trend exists where peaks below 140 ppm are generally overestimated by 1−2 ppm while peaks over 140 ppm are well reproduced, as we will show later. This trend helps significantly to compare our theoretical spectra with the experimental ones.

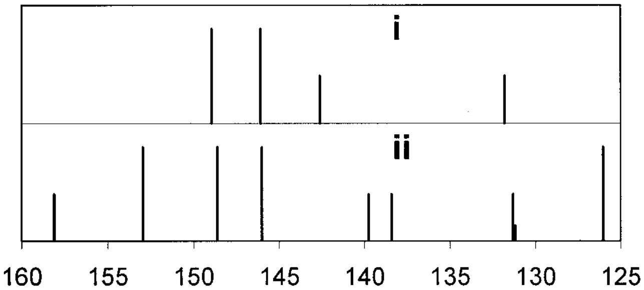


**Figure 4.** $^{13}$C NMR spectra of (i) $C_{72}$ and (ii) $C_{74}$ calculated by B3LYP/6-31G*. All spectra are referenced to $C_{60}$ at 143.15 ppm and the intensities are scaled so that the highest peaks in both spectra have same intensity.

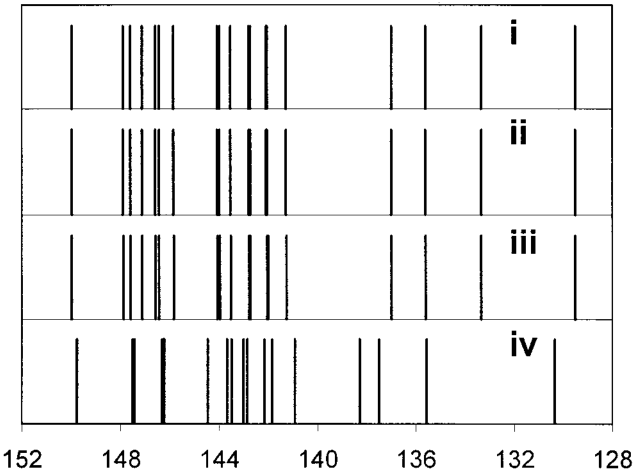


**Figure 5.** $^{13}$C NMR spectra of $C_{76}$:1 by (i) experiment,[5] (ii) experiment,[6] (iii) experiment,[8] and (iv) calculated by B3LYP/6-31G*. All spectra are referenced to $C_{60}$ at 143.15 ppm.

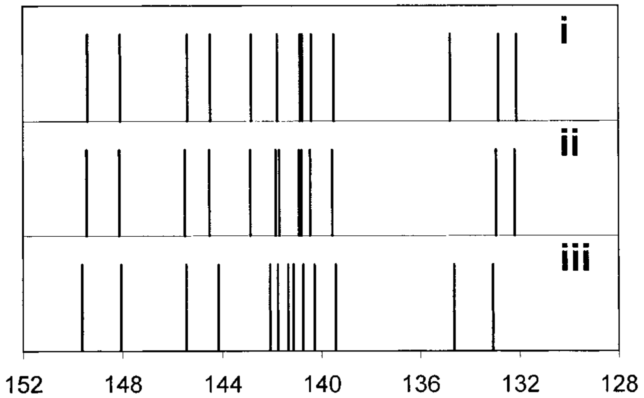


**Figure 6.** $^{13}$C NMR spectra of $C_{78}$:1 by (i) experiment,[6] (ii) experiment,[8] and (iii) calculated by B3LYP/6-31G*. All spectra are referenced to $C_{60}$ at 143.15 ppm.

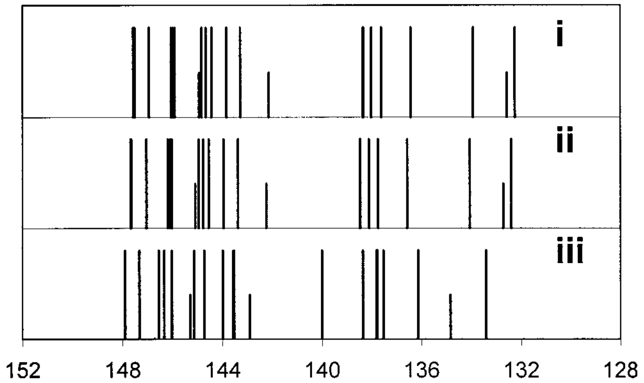


**Figure 7.** $^{13}$C NMR spectra of $C_{78}$:2 by (i) experiment,[6] (ii) experiment,[8] and (iii) calculated by B3LYP/6-31G*. All spectra are referenced to $C_{60}$ at 143.15 ppm.

The IPR isomer of fullerene $C_{72}$ has $D_{6h}$ symmetry and its NMR spectrum consists of 2 full-intensity peaks and 2 half-intensity peaks. The IPR isomer of $C_{74}$ has $D_{3h}$ symmetry and is the only one among the fullerenes studied here that has three sets of peak intensities: four full-intensity peaks and four half-intensity peaks and two $^1/_6$-intensity peaks. These two fullerenes have not yet been observed. Their calculated $^{13}$C NMR spectra are compiled in Figure 4 where the intensities are scaled so that the highest peaks have same height. In the calculated NMR spectrum of $C_{72}$, two full-intensity peaks and one-half-intensity peak occur in the 142−149 ppm, while the other half-intensity peak is predicted at 131.81 ppm. The span of the calculated NMR spectrum of $C_{74}$, 126−159 ppm, is much wider than any other fullerene studied in this work.

One of the two IPR isomers of $C_{76}$, $C_{76}$:1, is studied here. Figure 5 shows the experimental[5,6,8] and theoretical $^{13}$C NMR spectra of this molecule. This fullerene isomer has $D_2$ symmetry and 19 NMR peaks with equal intensity. Five groups, each containing 1, 6, 8, 3, and 1 peaks from downfield to upfield, exist in the calculated spectrum and agree well with the experimental spectra. Four peaks occur below 140 ppm and are overestimated by up to 2.22 ppm by DFT. Fifteen peaks occur in the range of 140−150 ppm, where the calculated peaks appear to agree better with experiment than peaks below 140 ppm. Because of the crowdedness of the peaks at the140−150 ppm region, however, we do not attempt a one-to-one assignment of the peaks.

Five isomers of fullerene $C_{78}$ are considered in this study. Isomer $C_{78}$:1 has $D_3$ symmetry thus shows 13 NMR peaks with equal intensity. The experimental[6,8] and theoretical $^{13}$C NMR spectra of isomer 1 of $C_{78}$ are shown in Figure 6. There is a discrepancy between the two experiments, where three peaks occur in the 132−135 ppm region in Diederich's result[6] as compared with only two peaks in Taylor's spectrum.[8] Our calculation predicts two peaks in this region and the nearest peak is 5 ppm away downfield. This leads us to conclude that the peaks at 132.20 and 132.95 ppm in Taylor's spectrum are from $C_{78}$:1. Similar to earlier cases of $C_{70}$, $C_{76}$, and $C_{84}$,[20] the general pattern of the calculated spectrum agrees well with experiments. In the calculated spectrum, four groups containing 2, 2, 7, and 2 peaks from downfield to upfield exist and each has a counterpart in the experimental spectra. In general at this level of theory, downfield peaks compare better with experimental ones than the upfield peaks. For instance, the two peaks at 132.95 and 132.20 ppm are overestimated by 1.70 and 0.89 ppm with respect to values in ref 8, respectively, while for the two peaks at 149.44 and 148.14 ppm, our predictions are off by only 0.18 and −0.07 ppm, respectively.

Isomer $C_{78}$:2 has $C_{2v}$ symmetry and 18 full intensity peaks plus 3 half-intensity peaks. The experimental[6,8] and theoretical $^{13}$C NMR spectra of isomer **2** of $C_{78}$ are shown in Figure 7. The positions of the three half-intensity peaks relative to that of full intensity peaks are correctly predicted. As to peak positions, these half-intensity peaks differ from the experimental values by 0.19, 0.65, and 2.12 ppm for the peaks at 145.10, 142.25, and 132.72 ppm, respectively. The full intensity peaks occurring within the range of 142−148 ppm are in good agreement with the experimental peaks. Full intensity peaks occurring below 140 ppm are overestimated by up to 2 ppm.

Although $C_{78}$:3 is predicted as the most stable one of the five IPR isomers of $C_{78}$, it is the least abundant one as

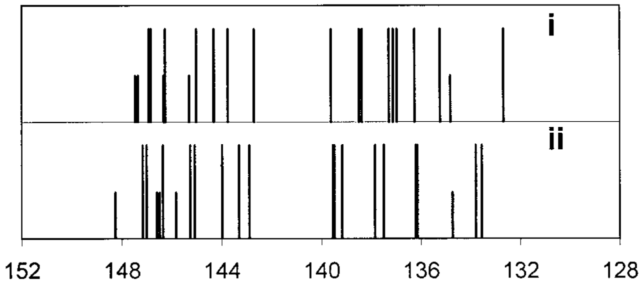


**Figure 8.** $^{13}$C NMR spectra of $C_{78}$:3 by (i) experiment[8] and (ii) calculated by B3LYP/6-31G*. All spectra are referenced to $C_{60}$ at 143.15 ppm.

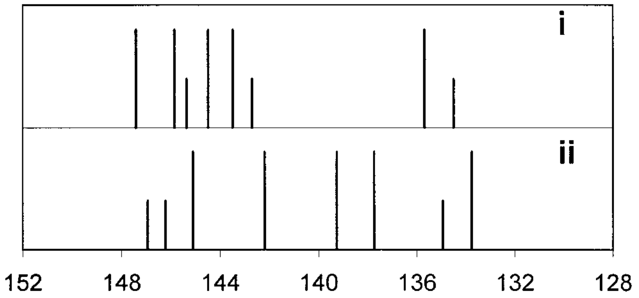


**Figure 9.** $^{13}$C NMR spectra of (i) $C_{78}$:4 and (ii) $C_{78}$:5 calculated by B3LYP/6-31G*. All spectra are referenced to $C_{60}$ at 143.15 ppm.

observed in the experiment.[8] The calculated $^{13}$C NMR spectrum of isomer $C_{78}$:3 is compared with experimental result[8] in Figure 8. The general pattern of our theoretical spectrum agrees with experiment. The predicted positions of the half-intensity peaks agree well with experiment in that four peaks occur at around 146 ppm and one peak at around 135 ppm. The 17 full intensity peaks form two groups, one with eight peaks at downfield and the other with nine peaks at upfield. The nine upfield peaks have larger deviations from experiment than the eight downfield peaks. The agreement between theoretical and experimental chemical shifts is the worst for this isomer among the fullerenes studied in this work.

The remaining two IPR isomers, $C_{78}$:4 and $C_{78}$:5, have $D_{3h}$ symmetry and each has five full intensity peaks plus three half-intensity peaks. Isomers **4** and **5** are 24.2 and 4.7 kcal/mol, respectively, less stable than isomer **3**. Although isomer **5** has similar total energy with isomers **1**, **2**, and **3**, it remains unobserved alike the high-energy isomer **4**. The calculated $^{13}$C NMR spectra of these isomers are shown in Figure 9. In the calculated NMR spectrum of $C_{78}$:4, four full-intensity peaks and two half-intensity peaks occur in the range of 142−148 ppm. The other full intensity peak and half-intensity peak occur in the 134−136 ppm region. The full intensity peaks in the calculated NMR spectrum of $C_{78}$:5 spread in the span of 132−146 ppm, while two out of three half-intensity peaks occur between 146 and 147 ppm and the other one is at 134.93 ppm. If these two isomers become available, the differences in their theoretical NMR spectra might facilitate their identification.

**Chemical Shifts and Local Geometry.** The relationship between chemical shift and local geometry in fullerenes has been studied by several groups. Three types of carbon sites[5,6] have been suggested to categorize the carbon atoms in fullerenes: pyracylene site (type 1, pc), corannulene site (type 2, cor) and pyrene site (type 3, py). The chemical shifts of these sites should appear in the 1 > 2 > 3 order. Heine et al.[17] correlated the chemical shifts to the local geometry quantitatively using Haddon's $\pi$-orbital axis vector (POAV) model.[31] They reported linear relationship between chemical shifts and POAV angles for types 1 and 2 carbons and no direct relationship for type 3 sites.

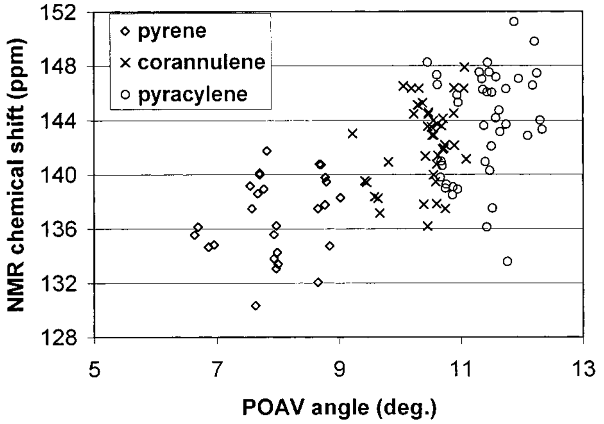


**Figure 10.** The relationship between the calculated $^{13}$C NMR chemical shifts and POAV angles for isomers of $C_{60}$, $C_{70}$, $C_{76}$:1, $C_{78}$:1, $C_{78}$:2, $C_{78}$:3, $C_{84}$:22, and $C_{84}$:23 calculated by B3LYP/6-31G*.

The type of carbon site is given for all NMR peaks in Tables 2 and 3. Type 1 sites generally have higher values of chemical shift than type 2 sites, and both have higher chemical shifts than type 3 sites. Few exceptions exist, e.g., the 126.03 ppm (cor) peak of $C_{74}$, the 136.13 (pc), and 133.57 ppm (pc) peaks of $C_{78}$:3 and the 133.76 ppm (pc) peak of $C_{78}$:5. These could be the "weak sites" of the corresponding isomer indicating why those isomers are unobserved or less abundant.

Utilizing the site[5,6] and the POAV[31] concepts, we plotted the calculated chemical shift vs POAV angle in Figure 10 for the fullerene isomers that have been experimentally observed, $C_{70}$, $C_{76}$:1, $C_{78}$:1, $C_{78}$:2, and $C_{78}$:3, as well as $C_{84}$:22 and $C_{84}$:23. The POAV angles are taken from geometries optimized at B3LYP/6-31G* level of theory. It is clear, from Figure 10, that each type of carbon atoms has a characteristic range of POAV angles. The ranges of POAV angles are 10.5° ~ 12.5° for type 1, 9.0° ~ 11.0° for type 2, and 6.5° ~ 9.0° for type 3 site. This suggests that the local geometry and hence the POAV angle is determined largely by the connectivity. The calculated chemical shifts range from 133 to 152 ppm for type 1 sites (with the majority of the points lying within 138−150 ppm), 136−148 ppm for type 2 sites, and 130−142 ppm for type 3 sites. Thus, the ranges of chemical shifts for different types of carbon sites overlap significantly with each other and the chemical shifts do not correlate with the POAV angle very well. Overall, the calculated chemical shifts generally increase when the corresponding POAV angles increase.

After this work was completed, we became aware of the work by Heine *et al.*[32] where the NMR chemical shifts of $C_{70}$, $C_{76}$, $C_{78}$, and $C_{84}$ were calculated by GIAO−CHF and IGLO-DFTB methods. Considering the isomers studied in both their work and ours, their results are of similar quality to ours for $C_{70}$. In other cases, however, the discrepancies of their results with respect to the experiment are larger than in our calculations.

## Conclusion

In summary, geometry optimization has been performed on IPR isomers of fullerenes $C_{60}$, $C_{70}$, $C_{72}$, $C_{74}$, $C_{76}$, and $C_{78}$ using density functional theory. Employing the GIAO method, the $^{13}$C NMR chemical shifts were evaluated at the B3LYP/6-31G* level of theory. For the fullerenes that have been characterized experimentally, our calculated spectra generally agree with experiments. Peaks above 140 ppm appear to agree better with experiment, while peaks below are overestimated by 1−2 ppm.

For isomers not yet identified, we expect that our theoretical NMR predictions will be helpful once they are synthesized. Chemical shifts generally increase when the corresponding POAV angles increase.

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