Letter

Theoretical evidence for the major isomers of fullerene C_{84} based on ^{13}C NMR chemical shifts

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Geometry optimizations for three isomers of fullerene C_{84}, 21, 22 and 23, have been performed by density functional theory (DFT) at the B3LYP/6-31G* level of theory. ^{13}C NMR chemical shifts were evaluated by the GIAO method employing 6-31G* and 6-311G basis sets. Isomers 22 and 23 are predicted to have essentially equal energies and isomer 21 to be 16 kcal mol^{-1} less stable. The calculated ^{13}C NMR chemical shifts of isomers 22 and 23 agree nicely with experimental data while the results of isomer 21 show large differences, indicating that isomer 22 is the experimentally observed D_2 isomer.**

C_{84} has been one of the most attractive higher fullerenes, not only since it is one of the main components[1] of fullerene soot besides C_{60} and C_{70}, but also because of its large number of isolated pentagon rule[2] (IPR) abiding isomers, numbering 24.[3] In pursuing an understanding of the ground state of C_{84}, two major isomers out of these 24 possible IPR isomers, having D_{2d} and D_2 point group symmetry, have been observed by ^{13}C NMR in a mixture.[4–6] Later, these two isomers were separated by means of recycling HPLC and characterized by NMR.[7] The D_{2d} isomer shows ten full-intensity peaks and one half-intensity peak, it is thus isomer 23.[3] The D_2 isomer showing 21 NMR peaks with equal intensity is either isomer 1, 5, 21 or 22 of C_{84}. Several minor isomers have also been characterized in mixtures by NMR,[8] followed by the separation and characterization of two high-symmetry isomers, 24 (D_{6h}) and 19 (D_{3d}).[9] Recently, the HPLC separation and NMR characterization of five minor isomers of C_{84} was reported.[10]

Earlier theoretical work has mainly focused on the prediction of the number of symmetry-based NMR peaks[3] as well as the relative energies[11–17] of the IPR isomers of C_{84}. Since several isomers have the same symmetry, it is not always possible to distinguish them solely from the symmetry-based patterns of one-dimensional NMR spectra. One early attempt to predict ^{13}C NMR chemical shifts of C_{84} by the Hartree–Fock (HF) approximation was made by Schneider *et al.*[18] By comparing the calculated spans of NMR spectra of isomers 5 (D_2), 22 (D_2) and 23 (D_{2d}) with the experimentally observed value, they eliminated isomers 1 and 5 as candidates for the observed D_2 isomer. Recent theoretical NMR studies using the individual gauge for local orbital-density functional-based tight-binding (IGLO-DFTB) method by Heine *et al.*[19,20] supported the assignment of 22 as the D_2 isomer over isomer 21 on the grounds of the energies and the spans of the NMR spectra.

In this work, we calculated ^{13}C NMR chemical shifts of isomers 21 (D_2), 22 (D_2) and 23 (D_{2d}) (see Fig. 1) by density functional theory (DFT). On the basis of the excellent agreement between our predicted NMR peaks and the experimental ones, we conclude that the experimentally obtained isomers are indeed 22 (D_2) and 23 (D_{2d}). We therefore expect theoretical prediction of NMR shifts to facilitate the identification of the numerous isomers of higher fullerenes.

Full geometry optimization and NMR chemical shielding calculations were done with the PQS program package[21] for C_{60} and three isomers of C_{84}, namely 21, 22 and 23. Becke's three-parameter (B3)[22] hybrid functional incorporating exact exchange in combination with Lee, Yang and Parr's (LYP)[23] correlation functional was used throughout this study. The standard double zeta quality basis set 6-31G* was used for geometry optimization. Using 6-31G* and 6-311G** basis sets, NMR chemical shieldings were evaluated at the B3LYP/6-31G* optimized geometry employing the gauge-independent atomic orbital (GIAO) method.[24] The calculated chemical shieldings were then referenced to that of C_{60} to obtain the calculated NMR chemical shifts. The experimental chemical shift of C_{60} at 143.15 ppm, after Avent *et al.*,[8] was used.

Right after the report of the existence of C_{84},[1] theoretical studies began to emerge to address the ground-state structures or major isomers of this fullerene.[11–17] Despite the issues of whether 22 or 23 has the lowest energy and by how much they are more stable than the others, these studies predicted 22 and 23 as essentially isoenergetic and significantly more stable than the other isomers (see Table 1).

The minimum, maximum and average bond lengths of the

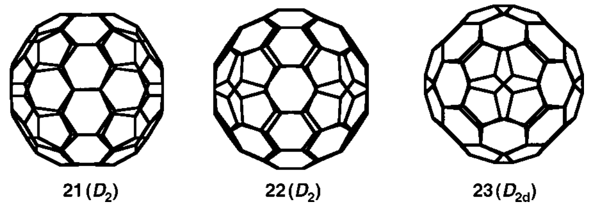

Fig. 1 Three isomers of C_{84} viewed down a C_2 axis.

Table 1 Bond length statistics and relative energies of isomers 21, 22 and 23 of fullerene C_{84} calculated by B3LYP/6-31G*[a]

	23 (D_{2d})	22 (D_2)	21 (D_2)
Minimum R_{cc}[b]	1.367	1.367	1.366
Maximum R_{cc}[b]	1.471	1.472	1.475
Average R_{cc}[b]	1.4324	1.4324	1.4325
PM3[c]	0.0	0.4	18.9
TB-MD[d]	0.0	−0.8	9.1
HF/3-21G[e]	0.0	0.5	26.6
HF[f]	0.0	0.4	—
DFTB[g]	0.0	−0.3	12.8
B3LYP/6-31G*[b]	0.00	0.08	16.12

[a] Bond lengths in Å. Energies in kcal mol^{-1} relative to that of 23 (D_{2d}). [b] This work. [c] Taken from ref. 12. [d] Tight binding molecular dynamics, taken from ref. 13. [e] Taken from ref. 17. [f] (7s4p)/[3s/2p] basis set, taken from ref. 18. [g] Density functional based tight-binding method, taken from ref. 19.

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optimized geometries[25] and relative energies of 21 (D_2), 22 (D_2) and 23 (D_{2d}) are summarized in Table 1 along with earlier theoretical results.[12,13,17–19] Our results are in agreement with the earlier reports. Isomers 22 and 23 have essentially the same energy, while isomer 21 is less stable by 16 kcal mol^{-1} relative to both.

The calculated ^{13}C NMR chemical shifts as well as the experimental values from Dennis *et al.*[7] are listed in Table 2. The experimental and B3LYP/6-311G** calculated values are listed in increasing order. The B3LYP/6-31G* values are listed in such a way that the atom giving rise to the chemical shift is the same as the atom in the B3LYP/6-311G** column. Fig. 2 compares the experimental NMR spectra and our predicted spectra. We would like to note that peaks in both experimental and theoretical spectra may have similar values and the spectra may appear to have fewer peaks than expected. In that case, the numerical values in Table 2 should give a clearer view.

Two out of the 24 IPR isomers of C_{84} have D_{2d} symmetry. Since isomer 4 (D_{2d}) should give 12 lines, including three at half intensity and nine at full intensity, the observed isomer must be 23 (D_{2d}), which gives 11 lines including one at half intensity.[3] Our calculated chemical shifts for 23 show excellent agreement with experiment. The rms deviation is 0.556 ppm by B3LYP/6-311G**. Fig. 2(a) also shows this agreement. Due to the crowding in the middle part of the spectra, we cannot assign every experimental peak with confidence. Experimental and theoretical values appearing in the same row in Table 2 do not necessarily mean that they correspond to the same carbon atom. The peaks can be grouped into five sets, with four sets each containing 1, 6, 2 and 1 full-intensity peaks from low to high chemical shift and one set having the half-intensity peak. It is clear that our calculated spectra match these groups nicely.

Two out of the four D_2 isomers of C_{84}, 21 and 22, which have lower energy than the other two according to earlier calculations,[12,13,17,19] are considered in this study. When compared with the experimental spectrum with 21 equal peaks, it is clear that the calculated spectral span of isomer 22 agrees within 1 ppm with the experimental value. The NMR spectral spans of isomer 21 calculated at both levels of theory are

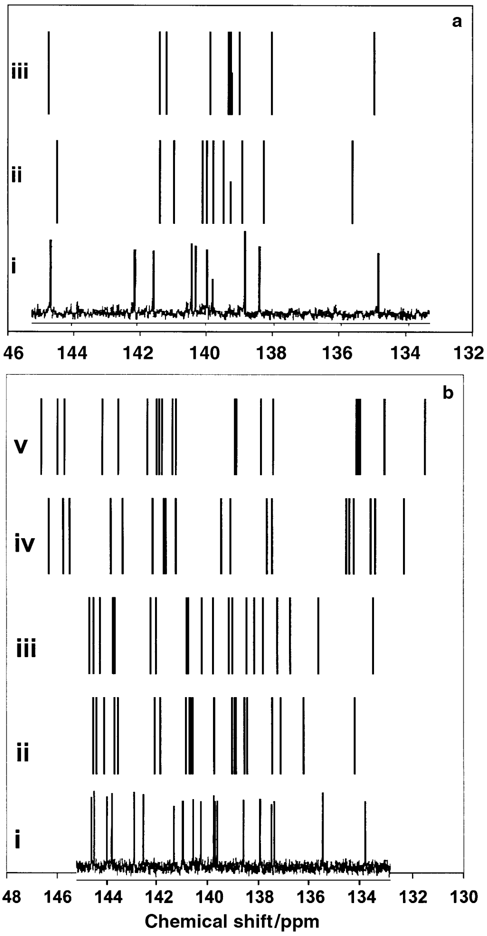

Fig. 2 Theoretical and experimental ^{13}C NMR spectra of C_{84}. (*a*) Spectra of 23 (D_{2d}) by experiment (*i*), B3LYP/6-31G* (*ii*) and B3LYP/6-311G** (*iii*). (*b*) Spectra of 22 (D_2) by experiment (*i*), B3LYP/6-31G* (*ii*) and B3LYP/6-311G** (*iii*), and of 21 (D_2) by B3LYP/6-31G* (*iv*) and B3LYP/6-311G** (*v*). Experimental spectra reproduced from ref. 7 by permission of the Royal Society of Chemistry.

Table 2 ^{13}C chemical shifts of isomers 21, 22 and 23 of fullerene C_{84} calculated at B3LYP/6-31G* geometries[a]

23 (D_{2d})				22 (D_2)				21 (D_2)	
n.c.[b]	Exp.[c]	B3LYP/6-31G*	B3LYP/6-311G**	n.c.[b]	Exp.[c]	B3LYP/6-31G*	B3LYP/6-311G**	B3LYP/6-31G*	B3LYP/6-311G**
8	134.98	135.59	134.94	4	133.81	134.25	133.53	132.33	131.51
8	138.48	138.25	138.01	4	135.48	136.25	135.67	133.63	133.08
8	138.87	138.91	138.99	4	137.39	137.16	136.79	133.46	133.10
8	138.88	139.47	139.26	4	137.50	137.50	137.30	134.29	134.05
4	139.82	139.26	139.22	4	137.91	138.60	137.86	134.58	134.10
8	140.00	139.79	139.29	4	138.58	138.93	138.21	134.45	134.18
8	140.37	140.11	139.33	4	139.63	138.48	138.51	137.50	137.46
8	140.50	139.98	139.88	4	139.74	138.98	139.07	137.70	137.93
8	141.57	140.97	141.20	4	139.77	139.09	139.22	139.50	138.91
8	142.13	141.40	141.41	4	139.79	139.80	139.83	139.14	138.97
8	144.60	144.51	144.77	4	140.32	140.73	140.28	141.31	141.31
				4	140.60	140.76	140.28	141.71	141.44
				4	141.00	140.91	140.82	141.74	141.85
				4	141.33	140.64	140.88	141.79	141.97
				4	142.58	141.93	142.10	142.22	142.07
				4	142.89	142.15	142.31	142.23	142.44
				4	143.78	143.60	143.73	143.41	143.58
				4	143.81	143.73	143.79	143.88	144.21
				4	143.98	144.14	144.31	145.50	145.71
				4	144.48	144.45	144.57	145.75	145.98
				4	144.58	144.58	144.73	146.32	146.62
rms deviation		0.464	0.556			0.512	0.420	1.944	2.155

[a] Chemical shifts, in ppm, are referenced to that of C_{60} at 143.15 ppm. [b] Number of carbon atoms. [c] Taken from ref. 7.

3.5–4 ppm larger than the experimental value of the D_2 isomer. This difference can also be seen in Fig. 2(b). More importantly, the distribution of the peaks in the spectra of isomer 21 completely disagrees with the experimental spectrum of the D_2 isomer. The B3LYP/6-311G** calculated chemical shifts of 22 yield an rms value of 0.420 ppm, while the rms deviation for 21 is 2.155 ppm. This indicates that the experimentally observed D_2 isomer is 22. Although it is not surprising that the low-lying isomer is the one observed, this is the first theoretical NMR evidence to confirm this.

Both 6-31G* and 6-311G** basis sets give similar results. The rms values of the 6-31G* calculations are 0.464 and 0.512 ppm for isomers 23 and 22, respectively. Unlike the spectra of 23, in which all the peaks are in the same order in both 6-31G* and 6-311G** calculations, the spectra of 22 calculated with the two basis sets have some switched peaks. For instance, the 137.86, 138.21 and 138.51 ppm peaks in the 6-311G** calculation for 22 are at 138.60, 138.93 and 138.48 ppm, respectively, in the 6-31G* calculation. Similar switching exists for isomer 21. If we rearrange the 6-31G* predicted chemical shifts of 22 and 21 in numeric order, the rms values will be reduced to 0.441 and 1.933 ppm, respectively. These values, as well as the previous ones, are comparable with those of the 6-311G** calculations, therefore the calculations using different basis sets are of similar quality. Since the latter calculations generally take 2–3 times longer than the former, without any obvious improvement, the smaller basis set is probably preferable because of concerns about the size of fullerene molecules.[26] Similarly to the case of 23, we cannot assign each peak unequivocally for isomer 22.

On the basis of this work, a detailed study of NMR chemical shifts of the minor isomers of C_{84} is under way.

In summary, we optimized the structures of three isomers of C_{84}, 21 (D_2), 22 (D_2) and 23 (D_{2d}), with B3LYP/6-31G*. Using the 6-31G* and the 6-311G** basis sets, ^{13}C NMR chemical shifts were calculated by the GIAO method. The calculated chemical shifts of isomers 22 and 23 show excellent agreement with experimental values. Our study confirms earlier assumptions[4–7,10] that the experimentally obtained isomers are 22 (D_2) and 23 (D_{2d}).

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References

1 F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. C. Khemani and A. Koch, *Science*, 1991, **252**, 548.
2 P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon, Oxford, 1995, pp. 73–80.
3 D. E. Manolopoulos and P. W. Fowler, *J. Chem. Phys.*, 1992, **96**, 7603.
4 K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho and Y. Achiba, *Nature* (*London*), 1992, **357**, 142.
5 D. E. Manolopoulos, P. W. Fowler, R. Taylor, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc*., *Faraday Trans*., 1992, **88**, 3117.
6 R. Taylor, G. J. Langley, A. G. Avent, T. J. S. Dennis, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc*., *Perkin Trans. 2*, 1993, 1029.
7 T. J. S. Dennis, T. Kai, T. Tomiyama and H. Shinohara, *Chem. Commun*., 1998, 619.
8 A. G. Avent, D. Dubois, A. Pénicaud and R. Taylor, *J. Chem. Soc*., *Perkin Trans. 2*, 1997, 1907.
9 N. Tagmatarchis, A. G. Avent, K. Prassides, T. J. S. Dennis and H. Shinohara, *Chem. Commun*., 1999, 1023.
10 T. J. S. Dennis, T. Kai, K. Asato, T. Tomiyama, H. Shinohara, T. Yoshida, Y. Kobayashi, H. Ishiwatari, Y. Miyake, K. Kikuchi and Y. Achiba, *J. Phys. Chem. A*, 1999, **103**, 8747.
11 P. W. Fowler and F. Zerbetto, *Chem. Phys. Lett*., 1995, **243**, 36.
12 D. Bakowies, M. Kolb, W. Thiel, S. Richard, R. Ahlrichs and M. M. Kappes, *Chem. Phys. Lett*., 1992, **200**, 411.
13 B. L. Zhang, C. Z. Wang and K. M. Ho, *J. Chem. Phys*., 1992, **96**, 7183.
14 E. Albertazzi and F. Zerbetto, *J. Am. Chem. Soc*., 1996, **118**, 2734.
15 K. Raghavachari, *Chem. Phys. Lett*., 1992, **190**, 397.
16 J. Aihara, *Bull. Chem. Soc. Jpn*., 1999, **72**, 7.
17 T. Nishikawa, T. Kinoshita, S. Nanbu and M. Aoyagi, *THEOCHEM*, 1999, **461**, 453.
18 U. Schneider, S. Richard, M. M. Kappes and R. Ahlrichs, *Chem. Phys. Lett*., 1993, **210**, 165.
19 T. Heine, G. Seifert, P. W. Fowler and F. Zerbetto, *J. Phys. Chem. A*, 1999, **103**, 8738.
20 T. Heine, M. Bühl, P. W. Fowler and G. Seifert, *Chem. Phys. Lett*., 2000, **316**, 373.
21 PQS version 2.1, Parallel Quantum Solutions, Fayetteville, AR, 1998.
22 A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648.
23 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
24 K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc*., 1990, **112**, 8251.
25 Fully optimized geometry is available upon request.
26 J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, *J. Chem. Phys*., 1996, **104**, 5497.