Physical Chemistry Chemical Physics

SUPPORTING INFORMATION

Fullerene C_{70} Characterization by ^{13}C NMR and the Importance of the Solvent and Dynamics in Spectral Simulations†

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Fullerene parameters

bond stretching	C	C	6.56	1.4200						
bond stretching (5-ring)	C	C	6.56	1.4540						
angle bending	C	C	C	0.45	120.80	108.00	0.00			
angle bending (5-ring)	C	C	C	0.45	108.00	108.00	0.00			
torsional	C	C	C	C	-0.67	0.0	1	10.30	138.0	2	0.00	0.0	3
torsional (5-ring)	C	C	C	C	-0.67	0.0	1	10.30	142.0	2	0.00	0.0	3

Definition and notation is identical to the MM3-200 (N. L. Allinger, Y. H. Yuh and J.-H. Lii, "Molecular Mechanics. The MM3 Force Field for Hydrocarbons. 1", J. Am. Chem. Soc., 111, 8551-8566 (**1989**)) force field, available in the Tinker program. Other parameters correspond to benzene carbon atoms.

Table S1 Basis set convergence of ^{13}C chemical shifts (in ppm) for C_{70}.

atom	pcS-0	pcS-1	pcS-2
C_a	152.8	153.9	154.3
C_b	149.5	150.6	151.2
C_c	148.6	149.3	149.6
C_d	147.4	147.6	148.0
C_e	132.6	130.5	130.5

Chemical shifts were calculated for BP86/def-TZVP optimized geometry. The BP86 Functional for ^{13}C Chemical Shifts was used.

Table S2 Performance of DFT functionals for ^{13}C chemical shifts (in ppm) in C_{70}. RMSD is the root-mean-square deviation from the experiment calculated for relative NMR peak positions ($C-C_e$). The BP86/def-TZVP optimized geometry and IGLO-III basis set were used. Experimental values were from ref. 15.

Functional	RMSD
BHandHLYP	0.3
BHandH	0.4
CAMB3LYP	0.5
B1LYP	0.8
wB97xd	0.8
M06L	0.8
X3LYP	0.9
B98	0.9
B3LYP	0.9
O3LYP	1.0
M06HF	1.1
HCTH	1.3
OLYP	1.3
BP86	1.6
BLYP	1.6
PBEPBE	1.7
SV5LYP	2.3

Table S3 Motion of the C_{70} carbon atoms. Average distance from the centre of mass r (in pm) and average atom fluctuation Δr from that position (in pm) as obtained from MM3 MD simulation.

Method		C_a	C_b	C_c	C_d	C_e
MD	r	421	407	392	368	360
	Δr	7	7	7	7	7
FPMD	r	418	405	391	370	359
	Δr	5	5	5	6	5
FPMD/CPCM	r	418	405	391	370	359
	Δr	3	3	3	3	3

Table S4 Temperature dependence of C_{70} ^{13}C NMR shifts (ppm). The force field was calculated at the HF/6-31G level, while the expansion of the NMR property was made at the HF/IGLO-II and BP86/IGLO-II levels.

		C_a	C_b	C_c	C_d	C_e
HF/IGLO-II// HF/6-31G	Δ_{273}	-8.4	-8.7	-8.5	-9.2	-10.7
	Δ_{373}	-9.1	-9.4	-9.3	-10.0	-11.6
	ΔΔ	**-0.7**	**-0.7**	**-0.8**	**-0.8**	**-0.9**
BP86/IGLO-II// HF/6-31G	Δ_{273}	-7.3	-7.2	-7.3	-7.9	-9.2
	Δ_{373}	-7.9	-7.7	-8.0	-8.6	-10.0
	ΔΔ	**-0.6**	**-0.5**	**-0.7**	**-0.7**	**-0.8**

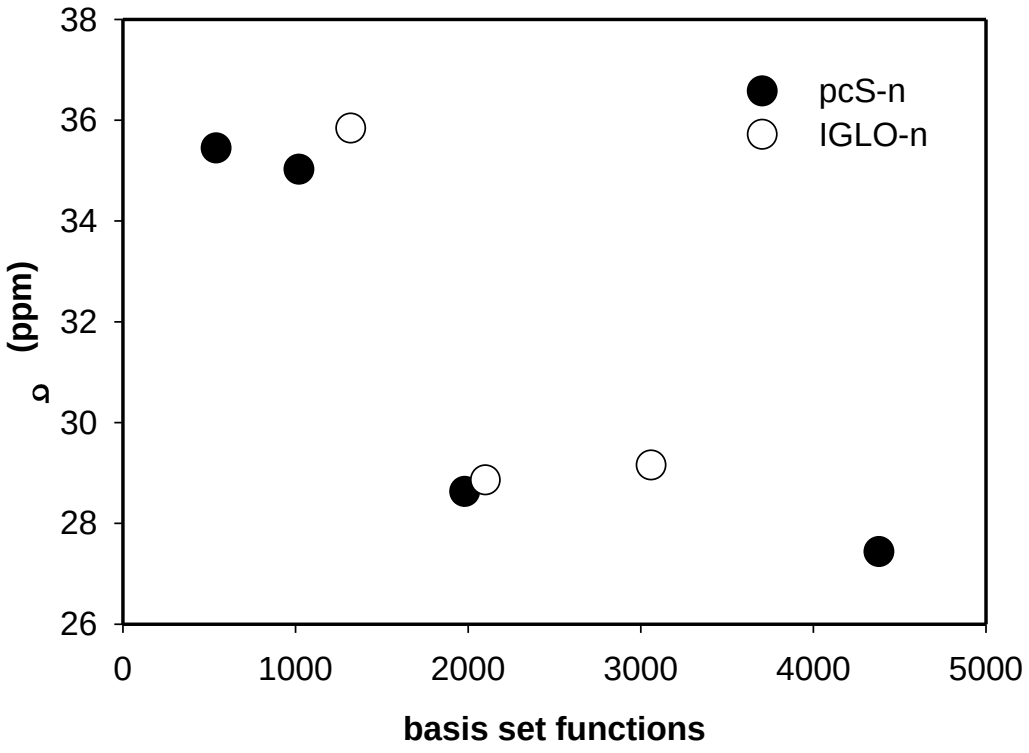

Fig. S1 The effect of increasing the basis set on calculated ^{13}C nuclear shieldings of C_{60}. Jensen's pcS-n (n = 0, 1, 2 and 3; full circles) and IGLO-n (n = II, III and IV; empty circles) basis sets were used. Shieldings were calculated for BP86/def-TZVP optimized geometry. The BP86 functional was used.

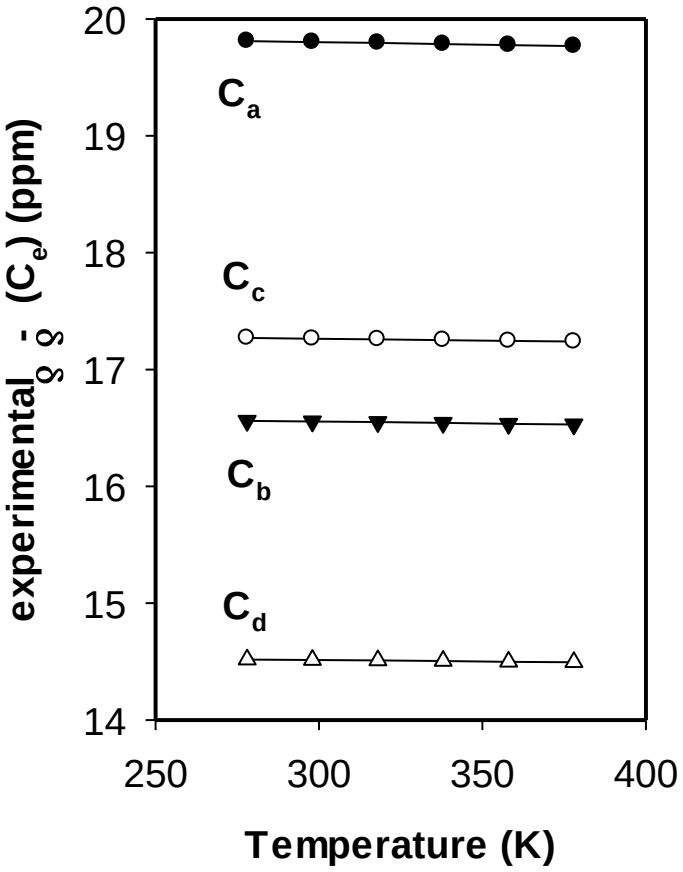

Fig. S2 Temperature effect on experimental NMR signals in C_{70}. Plot shows experimental chemical shifts (related to C_e) measured for six different temperatures.