

Supporting Information

Thermodynamic rearrangement synthesis and NMR structures of C₁, C₃ and T isomers of C₆₀H₃₆

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Part 1. Structure determination of C₁, C₃ and T isomers.

The key to solving the structure of the C₁ isomer was the identification of six CH groups interconnected in a six-membered ring (Table S1). Only one such combination was found: A2-K39-A3-K38-A4-K43, and only one placement was possible in the C₆₀ framework (Figure S1a). The discovery of this key fragment allows for step-by-step structure solution. Next was the identification of three CH-CH-CH(CH)₂ fragments attached to K39, K38 and K43 (all meta) positions of the six member ring. Again, only one possible placement of these three fragments was possible due to the fact that there was no additional inter-correlation between CH groups in these three fragments as well as between them and the A2-K39-A3-K38-A4-K43 fragment. This unique placement unveils three benzene rings in the structure. This was later confirmed by the structural analysis of the C₃ isomer (see discussion below).

Table S1. Signal correlations in the three C₆₀H₃₆ isomers

Signal	COSY-HSQC correlations	TOCSY-HSQC correlations ^a	Signal	COSY-HSQC correlations	TOCSY-HSQC correlations ^a
C ₁ isomer					
A2	K39, K43	H25, H26	G22	H26, J47	F7, C15
A3	K38, K39	H21, H25	G29	H21, J37	F9a, C18, K38
A4	K38, K43	H21, H26	H21	G29, K38	A3, A4
B40	L8, C14	E10, D27, J45; D16	H25	G20, K39	A3, J45
B41	C15, L17	E6, D28, D27	H26	G22, K43	
C14	B40, J45	L8, G20	I30	F11, E19	J45; D16, D27
C15	B41, J47	F7, L17, G22	31	D16, D28	L17, C18
C18	J37	F9a, 31, I34	I34	E6, F9a	L17, J37; C18, L33
D16	31, L33	E19, I30, B40	I36	F7, E10	J47; D27, D28
D27	L8	B40, E10; I30, I36, B41	J37	F9a, C18, G29	H21, I34
D28	L17, 31	E6, B41; I36	J45	F11, C14, G20	H25, I30
E6	L17, I34	D28	J47	F7, C15, G22	
E10	L8, I36	D27, B40	K38	A3, A4, H21	G29
E19	I30, L33	D16	K39	A2, A3, H25	G20, K43
F7	I36, J47	G22	K43	A2, A4, H26	K38
F9a	I34, J37	E6, C18	L8	E10, D27, B40	C14, I36
F11	I30, J45	E19, G20	L17	E6, D28, B41	I34, 31
G20	H25, J45	F11, C14	L33	D16, E19	31, I34
C ₃ isomer					
A1	K44	H24	G23	H24, J46	F5, C13, K44
B42	L9b, C13	E12, J46, D32	H24	G23, K44	A1, J46
C13	B42, J46	F5, L9b, G23	I35	F5	L9b, J46, D32
D32	L9b	I35, B42	J46	F5, C13, G23	H24, I35, B42
E12	L9b	D32, B42	K44	A1, H24	
F5	I35, J46	C13, G23	L9b	E12, D32, B42	
T isomer					
A	K	H			
H	K				
K	A, H				

^aOnly ⁵J, ⁴J and/or relay peaks are shown

At this stage complete analysis of all the possible locations of the remaining CH groups and the three double bonds (gray area, Figure S1b) become feasible. The task was further simplified by identification of two CH(CH)₃ fragments: L17(E6,D28,B41) and L8(E10,D27,B40) leading to only two^{S1} possible structures (Figure S2). From these two structures only one structure fit the connectivity data pattern (Figure S2a).

Final confirmation of this unique assignment has been made by evaluation of the results of the TOCSY experiments showing relayed and long-range (4J , 5J ,)^{S2} correlations (Table S1).

^{s2} Spielmann, H. P.; Weedon, B. R.; Meier, M. S. *J. Org. Chem.* **2000**, *65*, 2755-2756, and references 12, 13 and 15 therein.

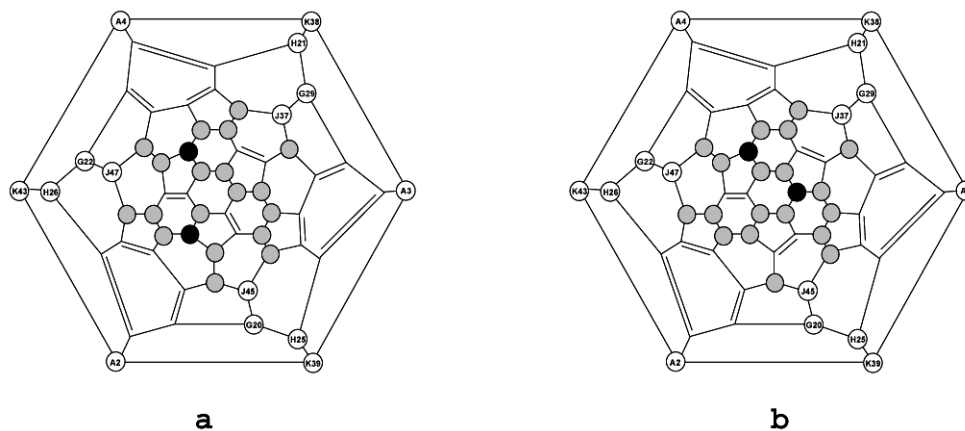


Figure S2. The only two possible structures of C_1 isomer having two additional $\text{CH}(\text{CH})_3$ fragments (centers of these two fragments are in solid black). One of these structures (left) corresponds to the actual structure of the C_1 isomer (see Figure S1c); the other was rejected on the basis of incompatibility with the COSY-HSQC spectrum.

Structure analysis of the C_3 isomer can be initiated by the identification of the signals of three identical $\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}(\text{CH})_2$ fragments as A1-K44-H24-G23-J46 (C13,F5) using the COSY-HSQC connectivity (Table S1, Figure S3). Due to C_3 symmetry there is only one possible placement of these three fragments in the C_{60} framework (Figure S4a).

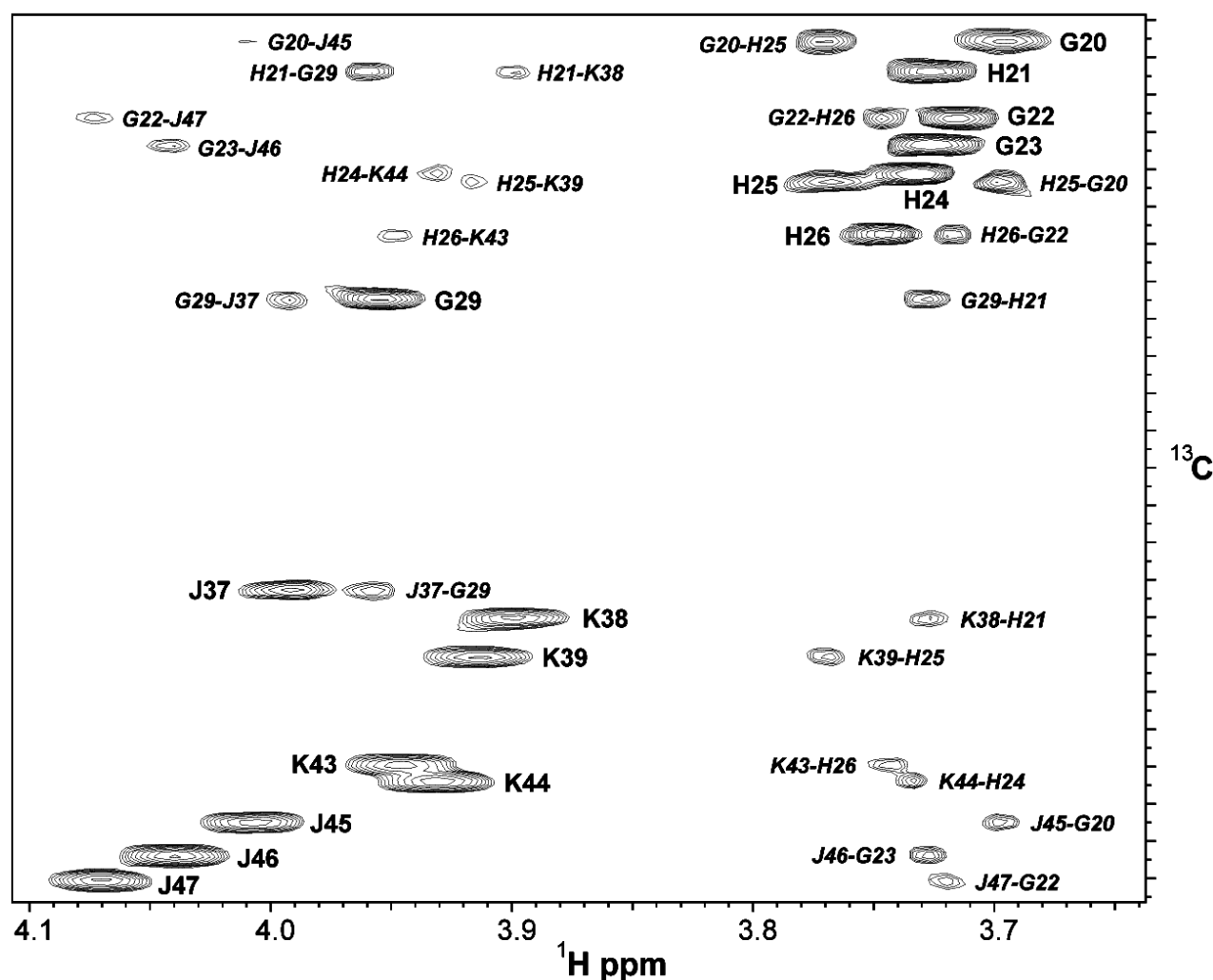


Figure S3. ^1H - ^{13}C COSY-HSQC spectra, expanded region of G, H, J and K signals. The diagonal resonances (one-bond ^1H - ^{13}C correlations) are phases absorptive in both dimensions; cross-peaks are antiphase in the ^1H dimension but are 90° out of phase, creating the appearance of narrow absorptive resonances when only positive contours are displayed. One-bond ^1H - ^{13}C connectivities are marked in regular font. Cross peaks are marked in italic. Blank regions in the ^{13}C dimension of the spectrum have been deleted for clarity, and the ^{13}C scale is therefore highly non-linear.

The unique placement confirms the similarity between the C_1 and C_3 structures: type A, K, J, H and G signals were found within the same areas of the 2D (^1H , ^{13}C) spectrum for both isomers (Figure 1). It also narrows the placement of the CH groups remaining within the gray area of Figure S4a. The final assignment (Figure S4b) was made after complete analysis of all the possible candidates to fit both the COSY-HSQC connectivity pattern and the C_3 symmetry requirements.^{s1} The structure was confirmed by the TOCSY-HSQC experiment (Table S1).^{s3}

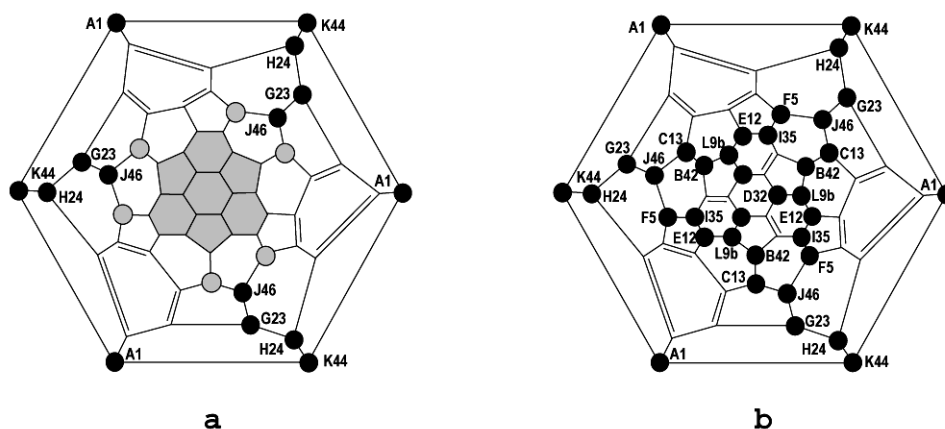


Figure S4. Structure elucidation of the C_3 isomer.

^{s3}The C_3 isomer has particularly strong COSY cross peaks associated with the CH groups surrounding the double bonds (such as D and I; D and B). A plausible explanation can be found in the unique symmetry-related structural features of the C_3 isomer: D groups are in both cis- and trans- positions relative to groups I and B, thus multiplying usually weak J^5 constants across a double bond π electron system. The same correlations across the isolated double bonds were found in the C_1 isomer, but they are much weaker. More details regarding long-range ^1H - ^1H constants (J^5 - J^7) in hydro[60]fullerenes can be found in references 7 and S2.

The structural elucidation of the elusive⁵ T C₆₀H₃₆ isomer was made by using the results of 2D NMR experiments and computer analysis. First, all the possible structures of T C₆₀H₃₆ isomers (the only two) were identified (Figure S5).^{s1} Both T isomers were found to be consistent with the COSY connectivity data (Table S1). The selection was made on the basis of the HSQC ¹H, ¹³C chemical shift analysis (Figure 1), and was further supported by calculations of relative thermodynamic stabilities (the T isomer **a** is almost 50 kcal/mol less thermodynamically stable than the selected one, **b**). Similar computational results have been reported previously.¹³

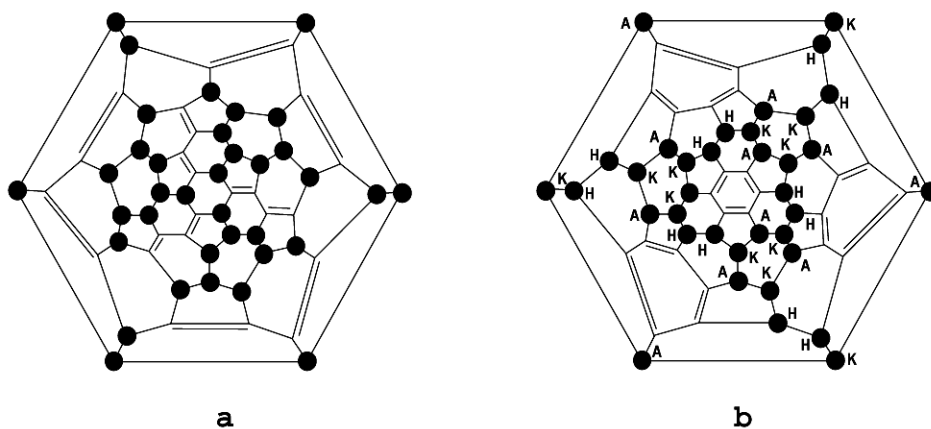


Figure S5. Structure elucidation of the T isomer.

Part 2. Compatibility studies of C_1 , C_3 , and T isomers of $C_{60}H_{36}$ and C_{3v} isomer of $C_{60}H_{18}$.

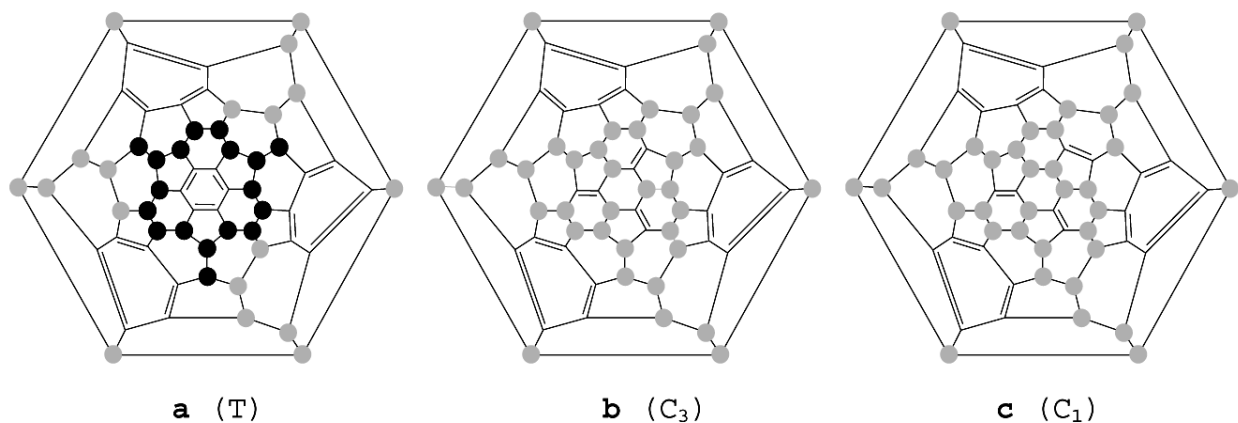


Figure S6. Compatibility/Incompatibility study of C_{3v} $C_{60}H_{18}$ versus T, C_3 and C_1 , isomers of $C_{60}H_{36}$. Compatible hydrogenated fragments of T $C_{60}H_{36}$ and C_{3v} $C_{60}H_{18}$ are presented as black dots (S6a). No compatible hydrogenated fragments were found for the other isomers (S6b, S6c).

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