

Formation of Hydrides of Fullerene-C₆₀ and Fullerene-C₇₀

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Fullerene-C₆₀ and fullerene-C₇₀ have been reduced by various methods to di- and tetra-hydro derivatives. Reduction by diimide is the most satisfactory method with regard to both yield and ease of carrying out of the reaction. The ¹H NMR chemical shifts are highly solvent dependent, and are *ca.* 1 ppm further downfield in carbon disulfide than in benzene; the shifts for C₆₀H_{*n*} compounds are downfield compared with those for C₇₀H_{*n*} compounds, due possibly to differences in strain between the cages and/or a field effect operating across the cage void. 1,2,3,4-Tetrahydrofullerene-C₆₀ is the main product from reduction of fullerene-C₆₀ with diimide, and all other tetrahydro derivatives that can be produced by addition across the high order bonds appear to be present, together with more highly hydrogenated derivatives. Eight products are obtained on diimide reduction of fullerene-C₇₀; two have been characterised as 1,5,6,9-tetrahydrofullerene-C₇₀ and 1,7,8,9-tetrahydrofullerene-C₇₀, and two others are the 1,9- and 7,8-dihydrofullerenes obtained by reduction with diborane. The other four derivatives may be the other tetrahydro isomers which can be obtained by addition across the 1,9-bond and its other equivalents. The hydrogenated fullerenes are more soluble in carbon disulfide than in either benzene or toluene, thus facilitating observation of the ¹³C satellites of 1,2-dihydrofullerene-60 in the ¹H NMR spectrum. The C–H and H–H coupling constants are 141.2 and 15.7 Hz respectively; a ¹³C–¹²C isotope shift of –17 ppb is also observed. Coupling constants for interhexagon (6:5) bonds range from 9.3–9.8 Hz, whilst those for interpentagon (6:6) bonds range from 13.9–16.3 Hz. The latter are exceptionally large, and the differentiation between the two types should prove a valuable aid in structure determination of hydrogenated fullerenes and derivatives thereof.

Interest in the fullerene hydrides arises not only because it has been suggested that they give rise to the diffuse interstellar bands¹ but also because they are the simplest derivatives, which should make structural identification less difficult than is normally the case in fullerene chemistry. Knowledge of the structures will aid understanding of the addition patterns that apply to these molecules. Most reductions (Birch,^{2,3} hydrogen transfer,⁴ and hydrogen radical-induced hydrogenation⁵) appear to produce C₆₀H₃₆ but this material (for which a tetrahedral, *T*, structure has been proposed)⁶ has yet to be fully characterised.

By contrast, Cahill and Henderson⁷ have prepared C₆₀H₂ *via* hydroboration and have confirmed by MS (*m/z* = 722) and by ¹H NMR { δ 5.93 (s) [²H₈]toluene} that it is the 1,2-isomer. (For nomenclature see ref. 8.) This compound is also produced *via* hydrozirconation, and exhibits a singlet at δ 5.85.⁹ We have also obtained preliminary evidence from MS for the existence of C₇₀H₁₂, although the origin of this species is unclear.¹⁰ We now describe the formation of a range of di- and tetra-hydrides of fullerene-C₆₀ and fullerene-C₇₀ and have identified the structures of some of them by ¹H NMR.

Experimental

Reduction with Hydrogen.—Saturated solutions of fullerene-C₆₀ in one of hexane, cyclohexene, or benzene (30 cm³) were placed in a 50 cm³ round-bottomed flask together with platinum on activated carbon (5%, *ca.* 10 mg) and a magnetic stirrer. The flask was evacuated and then filled with hydrogen, the process being repeated four times. A small positive pressure of hydrogen (*ca.* 80 mmHg) was then maintained in the flask, and the contents stirred until uptake of hydrogen ceased. The time taken for this varied with the solvent used (because of the concomitant reduction of the solvent) and also from batch to

batch for reasons not yet apparent; a time of 24 h was typical when hexane was used. The magenta solutions turned yellow-brown indicating the progress of reaction which, in hexane, was also monitored by UV spectroscopy. Upon completion of the reaction, the catalyst was separated by filtration, the solvent was removed, and the product analysed by ¹H NMR spectroscopy; in initial runs this was complicated by the presence of dioctyl phthalate plasticizer in the solvents. Obtaining satisfactory spectra was difficult, owing to the low concentration of material, to the irreversible absorption of the product on the catalyst, and to a change in structure of the product if solutions were evaporated to dryness. This was indicated by the fact that the product would no longer redissolve in the same solvent; the IR spectrum indicated the presence of OH groups. The product under these circumstances could be dissolved only in aq. acetone, pyridine and dimethyl sulfoxide (DMSO), and fullerol formation was believed to be responsible. Reactions carried out in hexane gave singlets at δ 5.9 and 6.1 (the latter peak being dominant) and were attributed to hydrogenated derivatives (see Discussion).

Adam's catalyst was ineffective in reduction, an observation which was utilised in stabilisation, through reduction, of cycloadducts. Here the addend, but not the cage, can be reduced by using hydrogen and Adam's catalyst, and this prevents the retro-Diels–Alder reaction.¹¹

Reduction with Chromium(II) Acetate.—A suspension of fullerene-C₆₀ in aq. *N,N*-dimethylformamide (DMF) was stirred for 12 h with excess of chromium(II) acetate, prepared from chromium(II) chloride as described in the literature.¹² No reaction was apparent (attributed to the insolubility of fullerene-C₆₀ in the solvent), so toluene (100 cm³) was added and the mixture was sonicated. The toluene layer became pink, and a colourless solid appeared at the solvent interface. This was

separated, washed with water, dried, and analysed by ^1H NMR spectroscopy. Only a small amount of reduction occurred, probably due to the heterogeneous conditions, but singlets at δ 6.13 (major) and 5.90 (minor) were detected.

Reduction with Diborane.—This was carried out as described in the literature.⁷

Reduction with Diimide.—Preliminary experiments carried out in reagent grade benzene were unsatisfactory due to the presence of dioctyl phthalate plasticizer. Benzene was therefore purified by triple fractional distillation before use. Even so, traces of this impurity (detected by ^1H NMR) were still present, although insufficient to create a problem with the NMR analysis. Nevertheless, we recommend that benzene should be fractionally distilled at least four times before use, or boiled under reflux with KOH to saponify the ester, then washed, dried and distilled. Care was taken to avoid any contact between any solvents used and plastic material, *e.g.* wash bottles, *etc.* These precautions are recommended for *general* work involving fullerenes because of their low solubility and the consequent need to use large volumes of solvents.

A solution of fullerene- C_{60} (20 mg, 0.028 mmol) in benzene (20 cm^3) was treated with glacial acetic acid (4 drops), saturated copper(II) sulfate solution (4 drops) and hydrazine hydrate (98%; 1.41 g, 28.2 mmol, 1.37 cm^3). The mixture was stirred vigorously under argon whilst a solution of sodium periodate (600 mg, 2.8 mmol) in water (6 cm^3) was added over 1 h, and this mixture was then stirred for a further 19 h. The benzene layer turned from magenta to brown and was separated, filtered and washed with water (2 \times 20 cm^3). Volatiles were removed under reduced pressure, the black residue was redissolved in benzene (20 cm^3) and the solution was passed down a short column of silica gel (60–120 mesh). The golden-brown eluate gave a black solid after removal of solvent.

The reduction of fullerene- C_{70} (20 mg, 0.024 mmol) in benzene (40 cm^3) by diimide, carried out by a similar method, gave a red-brown solid.

Mass Spectrometry.—Various attempts were made to obtain satisfactory mass spectra of the reaction products under fast atom bombardment (FAB) conditions. Although a range of peaks in the 720–728 u region were observed with some samples, these were accompanied by so many other peaks that we consider analysis of the data unsafe at this stage.

NMR Spectra.—These were obtained on a 500 MHz instrument.

Results and Discussion

We have duplicated the reported⁷ reduction of fullerene- C_{60} with diborane and find a singlet at δ 5.88 ($[\text{C}_6\text{H}_6]$ benzene). We also find (from the unchromatographed reaction product) a second singlet at δ 6.13 which we tentatively assign to 1,4-dihydrofullerene- C_{60} . Both singlets are produced by reducing fullerene- C_{60} with diimide, chromium(II) acetate, and with hydrogen over Pt/C catalyst (the δ 6.1 singlet was the more intense in some runs involving the latter two reagents). Reduction of fullerene- C_{60} by H_2S resulted in a product exhibiting a singlet at δ 6.03 ($[\text{C}_6\text{H}_6]$ toluene).¹³ We also find that the chemical shifts of the hydrogenated fullerenes are extremely sensitive to the solvent employed for the measurements. An early indication of this fact lay in the discrepancy between the reported chemical shifts for the proton in $\text{C}_{60}\text{Bu}^1\text{H}$ *viz* δ 6.08 ($[\text{C}_6\text{H}_6]$ toluene)¹⁴ and δ 6.67 (carbon disulfide).¹⁵ For the di- and tetra-hydrofullerenes, the downfield shift between measurements made in $[\text{C}_6\text{H}_6]$ benzene and carbon disulfide is *ca.* 1 ppm (Tables 1 and 2). In carbon disulfide, the

peak for 1,2-dihydrofullerene- C_{60} appears at δ 6.97 (1.07 ppm downfield shift) whilst the other singlet we observe on reduction appears at δ 7.23 (1.10 ppm downfield shift). These results support our view that this is another (symmetrical) dihydrofullerene- C_{60} isomer. There are, of course, other symmetrical isomers that could in principle be considered. However, these place more double bonds in pentagonal rings (a destabilising feature)¹⁶ than is the case for the 1,4-dihydro isomer, and moreover there is a precedent for 1,4-addition in $\text{C}_{60}\text{Bu}^1\text{H}$ (although here the greater eclipsing interaction in the 1,2-isomer provides a greater driving force for 1,4-addition). We believe that other symmetrical but more highly hydrogenated derivatives may be ruled out because there is accumulating evidence, reinforced by the data presented here, that these derivatives appear more upfield in the ^1H NMR spectrum.

From the results, we conclude that reduction with diimide is superior to other methods. For example, reduction with Pt/C (which involves lengthy reaction times) is difficult because the hydrofullerene becomes bound to, and is difficult to remove from, the catalyst. Moreover, the fullerene must be dissolved in a solvent compatible with the reduction conditions; hexane is a poor solvent, whilst cyclohexene (a better solvent for fullerenes) or benzene (better still) undergo concurrent reduction. Reduction with diborane involves a relatively bulky intermediate (prior to acidification with acetic acid to give the hydrofullerene); consequently there may be a limit to the number of hydrogens that can be added to the cage. Moreover, we find that fullerols can be the major product of this reaction.¹⁷ By contrast, diimide reduction (Scheme 1) is a concerted process, and this appears to favour multiple addition to the cage. This aspect is under further investigation.



Scheme 1

Interpretation of the data is aided by our finding that the hydrogenated fullerenes are appreciably more soluble in carbon disulfide than in benzene or hexane, so yielding enhanced ^1H NMR signals. In analysing the data the following criteria are used.

(i) The signals appear well downfield because of strong electron withdrawal by the cage, composed of sp^2 -hybridised carbons which have a $-I$ inductive effect.¹⁸ These carbons may also withdraw electrons by a field effect (which operates through space rather than through σ -bonds).¹⁹ In fullerenes, therefore, some electron withdrawal may operate within the cage, which is a true void. This proposal may account for the so far unexplained greater downfield shifts of the signals due to hydrogenated C_{60} compared with hydrogenated C_{70} ,²⁰ though greater strain in fullerene- C_{60} compared with fullerene- C_{70} could also be a factor. Either conjecture predicts that hydrogenated derivatives of smaller fullerenes may show even greater downfield ^1H NMR signals.

(ii) The ^1H NMR signals will be further upfield the more sp^3 carbons that are present and the nearer they are to the proton in question. It follows that the signals should tend to be more upfield the more hydrogenated the product.

Reduction of Fullerene- C_{60} by Diimide.—Fig. 1 shows the many-line ^1H NMR spectrum obtained (CS_2 solvent, CDCl_3 as lock signal), all of which lies upfield relative to the two singlets at δ 6.97 (due to 1,2-dihydrofullerene- C_{60}) and δ 7.23. Interpretation of the latter in terms of 1,4-dihydrofullerene- C_{60} (see above) is consistent with the expectation that the signals should be more downfield, because each hydrogen is adjacent to sp^2 -hybridised carbons, which is not the case for the 1,2-isomer. The greater solubility of the material in carbon disulfide

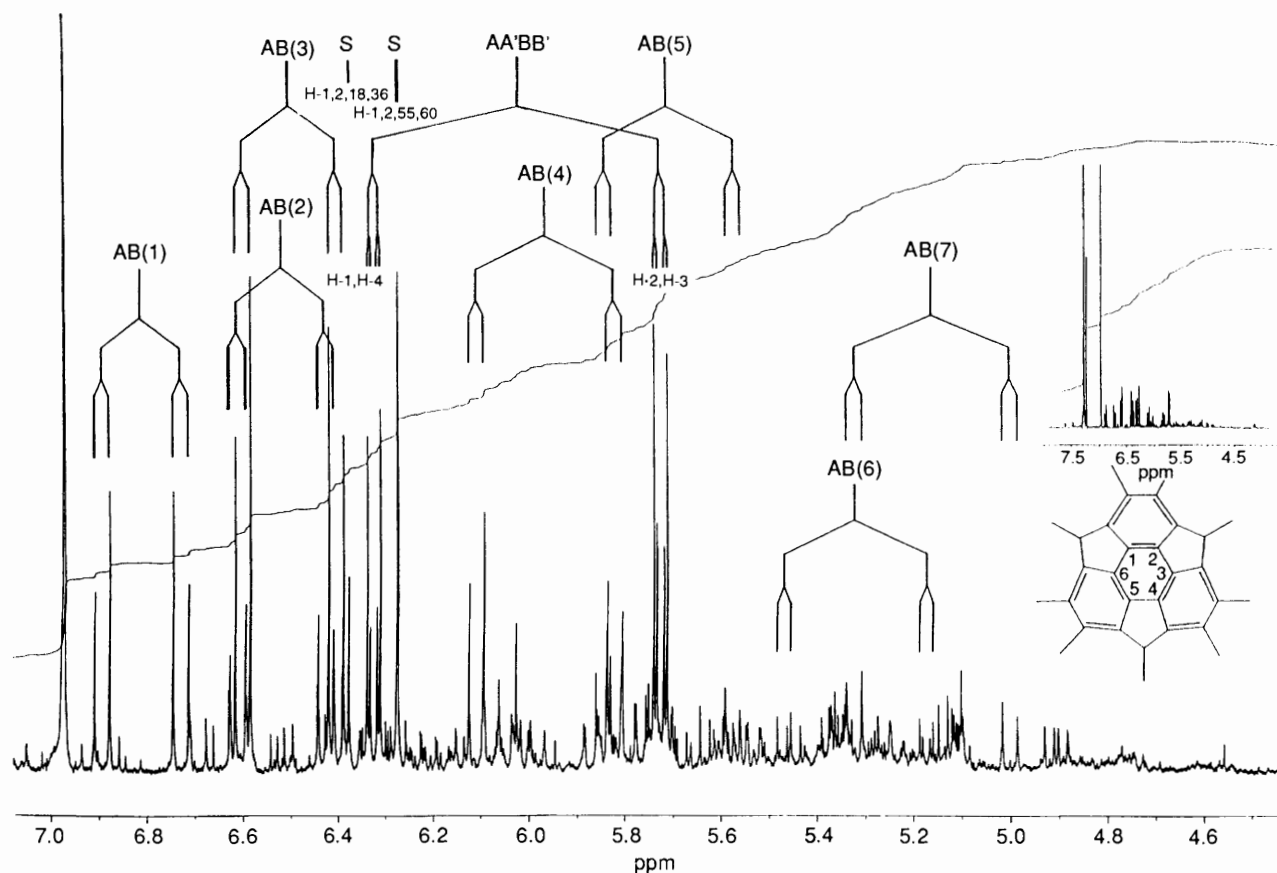


Fig. 1 ^1H NMR spectrum of diimide hydrogenated fullerene- C_{60} in CS_2 . Insets show high-field region and numbering system.

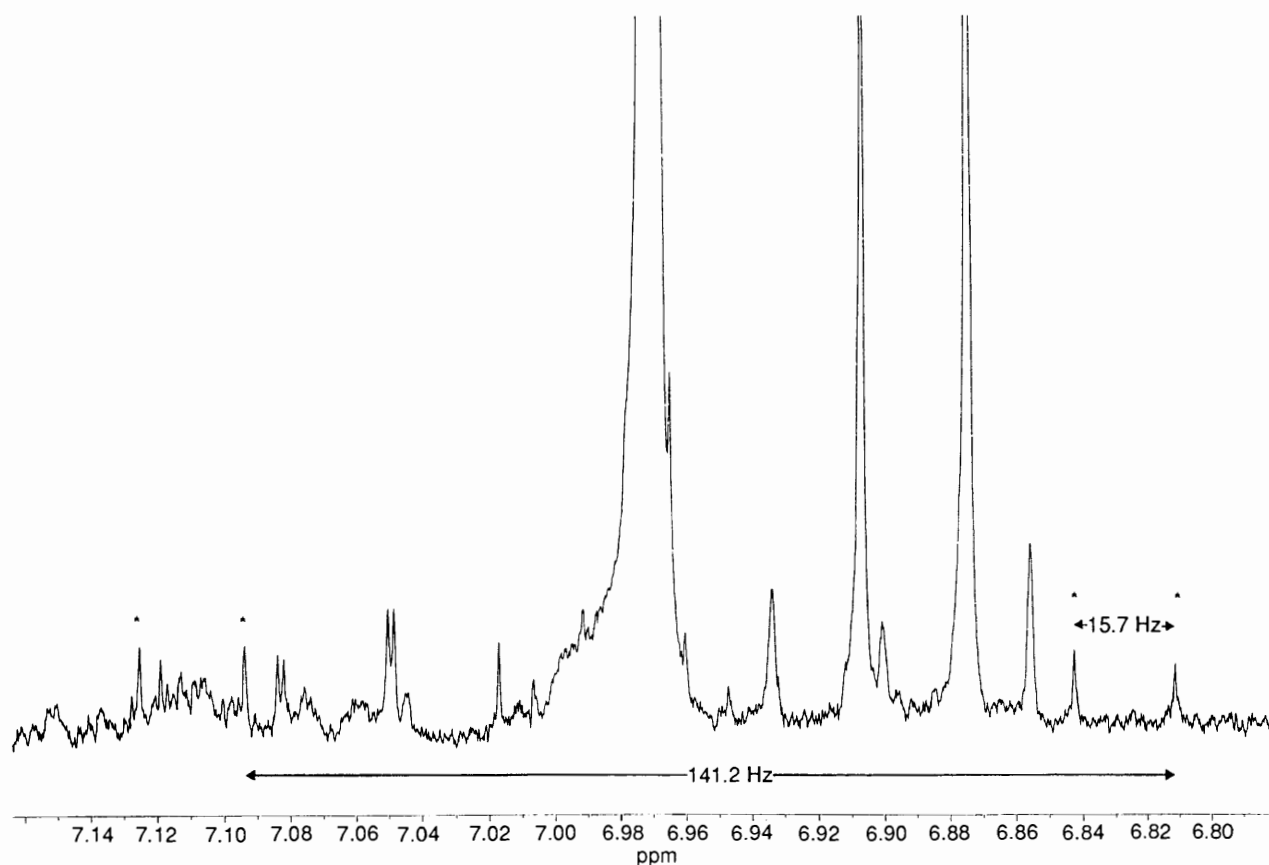


Fig. 2 ^1H NMR spectrum of the ^{13}C isotopomer of 1,2-fullerene- C_{60} , showing ^{13}C -H and H-H couplings

permitted observation of the ^{13}C -containing isotopomer of 1,2-dihydrofullerene- C_{60} (see Fig. 2). The C-H coupling constant,

141.2 Hz, is high for an sp^3 carbon with no electronegative substituents, but may be explained in terms of cage strain. The

Table 1 ^1H NMR data for hydrogenated fullerene- C_{60} , recorded in CS_2 or C_6D_6

$\delta(\text{CS}_2)$	J/Hz	$\delta'(\text{C}_6\text{D}_6)$	$\delta - \delta'$	Type	Position of H	Relative intensities
7.23		6.13	1.10	s	1, 4 ^a	5
6.97		5.89	1.07	s	1, 2	11
6.38		5.49	0.89	s	1, 2, 18, 36 ^b	1.5
6.27		5.34	0.93	coincident singlets	1, 2, 57, 58 ^a	3
6.891	15.95	5.909	0.982	AB q	—	4.5
6.728		5.751	0.977			
6.611	16.1	5.640	0.971	AB q ^c	—	4
6.425		5.498	0.928			
6.600	15.55	5.615	0.985	AB q	—	6
6.404		5.437	0.967			
6.323	14.1 (AB)	5.369	0.954	AA'BB' ^d	1, 2, 3, 4	10.5
5.726	9.8 (AA')	4.562	1.164			
	1.59 (BB')					
	-0.25 (AB')					
6.107	15.35	5.141	0.966	AB q	—	5
5.820		4.921	0.899			
5.844	15.3			AB q	—	1.5
5.575						
5.469	13.9			AB q	—	1
5.175						
5.323	15.35			AB q	—	1.5
5.002						

^a See text. ^b Associated with one of the unassigned AB quartets. ^c Secondary splitting of *ca.* 0.5 Hz can be seen. ^d See Fig. 4 for spectrum simulated (PANIC) using the couplings in this Table.

flattened character of the three C–C bonds increases their p character, thus increasing the s character (and hence the coupling constant) of the C–H bond. The H–H coupling constant is 15.7 Hz (*ca.* six times the $^3J_{\text{HD}}$ value of 2.4 Hz reported by Henderson and Cahill,⁷ as required by theory) and there is a ^{13}C – ^{12}C isotope shift of -17 ppb. The observation of ^{13}C satellites further confirms that the hydrogens are not migrating over the cage surface. ^{13}C Satellites were also visible for the component we believe to be 1,4-dihydrofullerene- C_{60} but, due to the lower concentration, were incompletely distinguishable from background signals.

All other signals in the spectrum (assigned using homonuclear spin coupling experiments) are upfield with respect to the δ 6.97 and 7.23 peaks and are thus likely to be due to more highly hydrogenated material. For C_{60}H_4 , 29 different isomers are theoretically possible assuming addition across the high order bonds, but symmetry reduces this number to eight. These should have the following hydrogen locations, where the number of equivalent structures and predicted ^1H NMR pattern are given in parentheses (for site numbering, see ref. 8): 1, 2, 55, 60 (1, s); 1, 2, 3, 4 (4, AA'BB' spin system); 1, 2, 51, 52 (4, AB q); 1, 2, 7, 21 (4, AB q); 1, 2, 16, 17 (4, AB q); 1, 2, 18, 36 (4, s + AB q); 1, 2, 34, 35 (4, AB q) and 1, 2, 33, 50 (4, AB q). The ^1H NMR data obtained in carbon disulfide, and in $[\text{H}_6]\text{benzene}$ as solvent, the relative intensities under the former conditions, and the solvent shift, are listed in Table 1. The spectrum recorded in the former solvent gives more detail and shows all of the predicted features—indeed, there is an extra AB quartet. However, two of these quartets are somewhat upfield of the others and may be due to symmetrical, more highly hydrogenated derivatives. The three most upfield AB quartets could not be clearly distinguished from background in the spectrum obtained using C_6D_6 as solvent and CDCl_3 as lock signal (Fig. 3).

The resonance at δ 6.38 (CS_2) consists of two almost identical singlets of equal intensity, which we suggest are due to the 1, 2, 55, 60 isomer, present in two conformations. The inability of the cage to flex may result in adjacent hydrogens being very slightly *trans* to each other. Thus when addition occurs at exactly opposite sides of the cage, two similar isomers [*meso* and (\pm)] are produced, and the distance between hydrogen atoms on opposite poles is such that the effect on the

chemical shift should be very small, as observed. If this explanation is correct, it follows that other isomers should be likewise affected, and it is therefore relevant that two other AB quartets show very small splittings.

The most abundant isomer is evidently 1,2,3,4-tetrahydrofullerene- C_{60} which gives rise to the AA'BB' spectrum shown together with the simulated spectrum in Fig. 4. The analysis yielded the following coupling constants, $J_{\text{AB}} = +14.1$, $J_{\text{AB}'} = -0.2$, $J_{\text{AA}'} = +9.8$ and $J_{\text{BB}'} = +1.6$ Hz. Note that the J_{AB} coupling is comparable with that found for 1,2-dihydrofullerene- C_{60} , and can thus be assigned to two protons on an interpentagonal (6:6) bond. The $J_{\text{AA}'}$ coupling therefore occurs between protons on an interhexagonal (6:5) bond; its significantly smaller magnitude is found in other tetrahydroderivatives of fullerene- C_{60} and fullerene- C_{70} . Additionally, the $J_{\text{BB}'}$ coupling (+1.6 Hz) further confirms our assignment of the four protons to a hexagon, as in this case $J_{\text{BB}'}$ is a five-bond interaction through a double bond for which +1.6 Hz is reasonable. Were these protons to be in a pentagon, then $J_{\text{BB}'}$ would be a four-bond interaction through single bonds which is known to be negligible, except where the four bonds are in the *W*-conformation which is certainly not the case here.

Further confirmation that we have correctly identified this isomer comes from the large difference in the chemical shifts of the hydrogens: H-1 and -4 (at δ 6.323) are adjacent to two sp^2 - and one sp^3 -hybridised carbons, where H-2 and -3 (at δ 5.726) are adjacent to one sp^2 - and two sp^3 -hybridised carbons. The two sets of hydrogens also show significantly different solvent shifts. This isomer is also the only one with adjacent hydrogens, and will possibly not be generated *via* hydroboration because of steric hindrance in the intermediate as noted above. The preferential formation of this isomer is reasonable, for although delocalisation of electrons is poor in any one hexagonal ring of fullerene- C_{60} , once addition has occurred across a 1,2-bond, the remaining π -electrons will be more localised so aiding further addition in the same ring. This suggests that formation of 1,2,3,4,5,6-hexahydrofullerene- C_{60} by diimide reduction may be possible and we are investigating this.

At present it is not possible to assign the AB quartets, but it is noteworthy that the chemical shift difference tends to decrease the more downfield the quartet. A possible interpretation of this

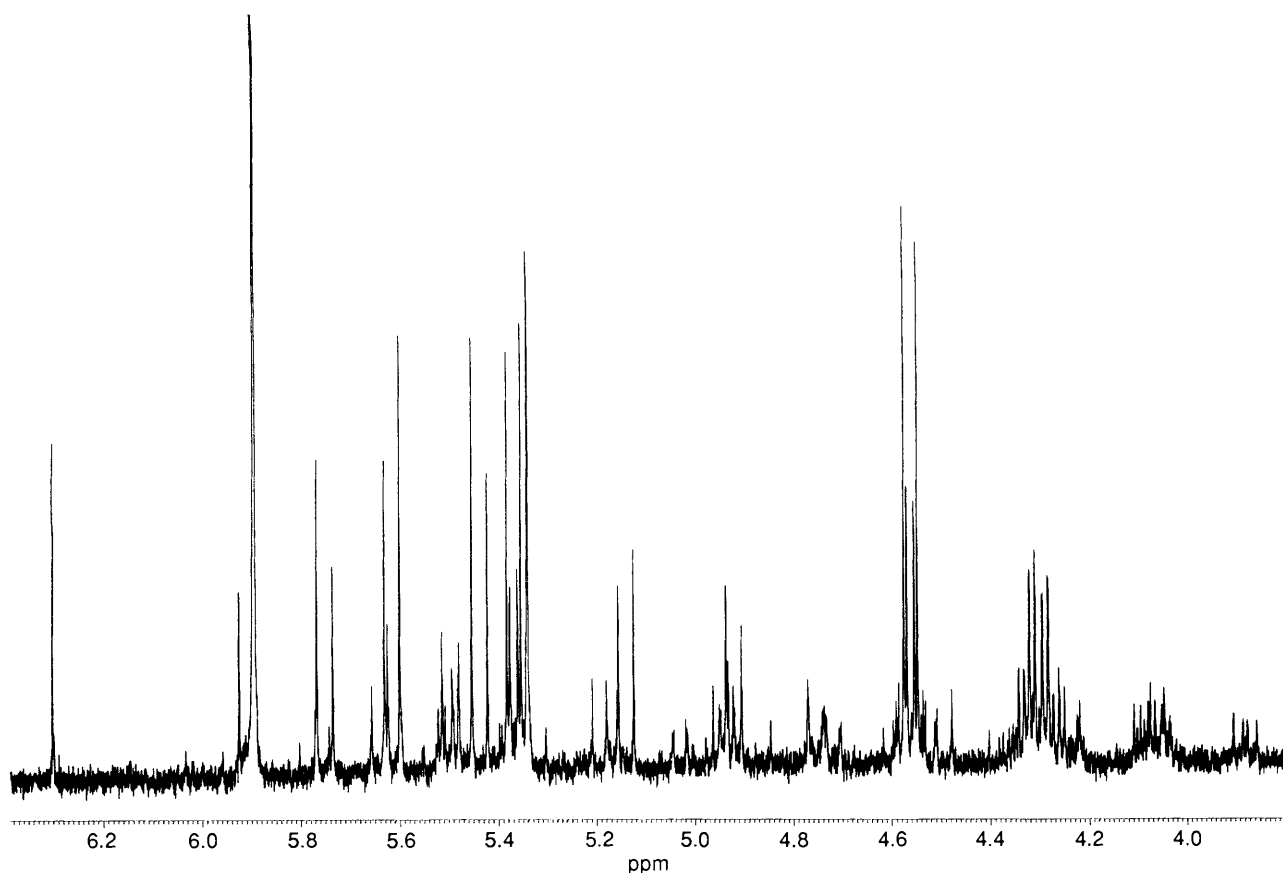


Fig. 3 ^1H NMR spectrum of diimide hydrogenated fullerene- C_{60} in C_6D_6

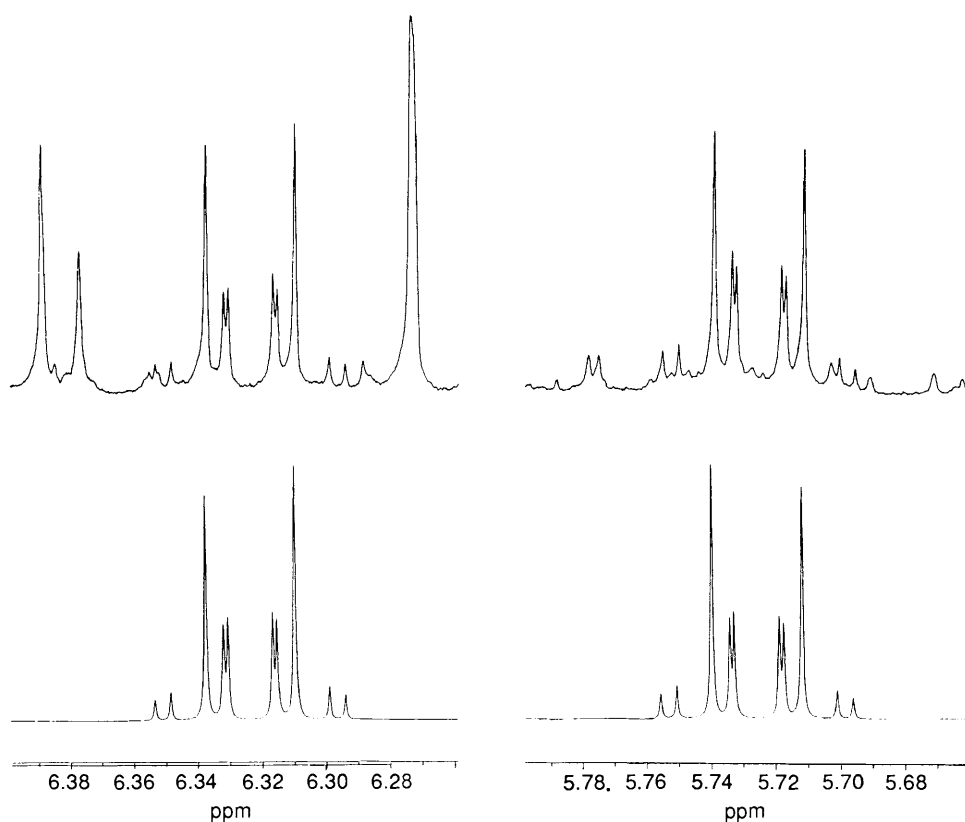


Fig. 4 Observed and simulated ^1H NMR spectrum for 1,2,3,4-tetrahydrofullerene- C_{60}

phenomenon is that the chemical shift difference is smaller the further apart are the hydrogen pairs, and this displacement in turn should generate a more downfield signal because

the sp^3 -hybridised carbons are more remote. The singlet at δ 6.38 may reasonably be attributed to the 1, 2, 18, 36 isomer (and equivalents) and seems, from the integrated intensity,

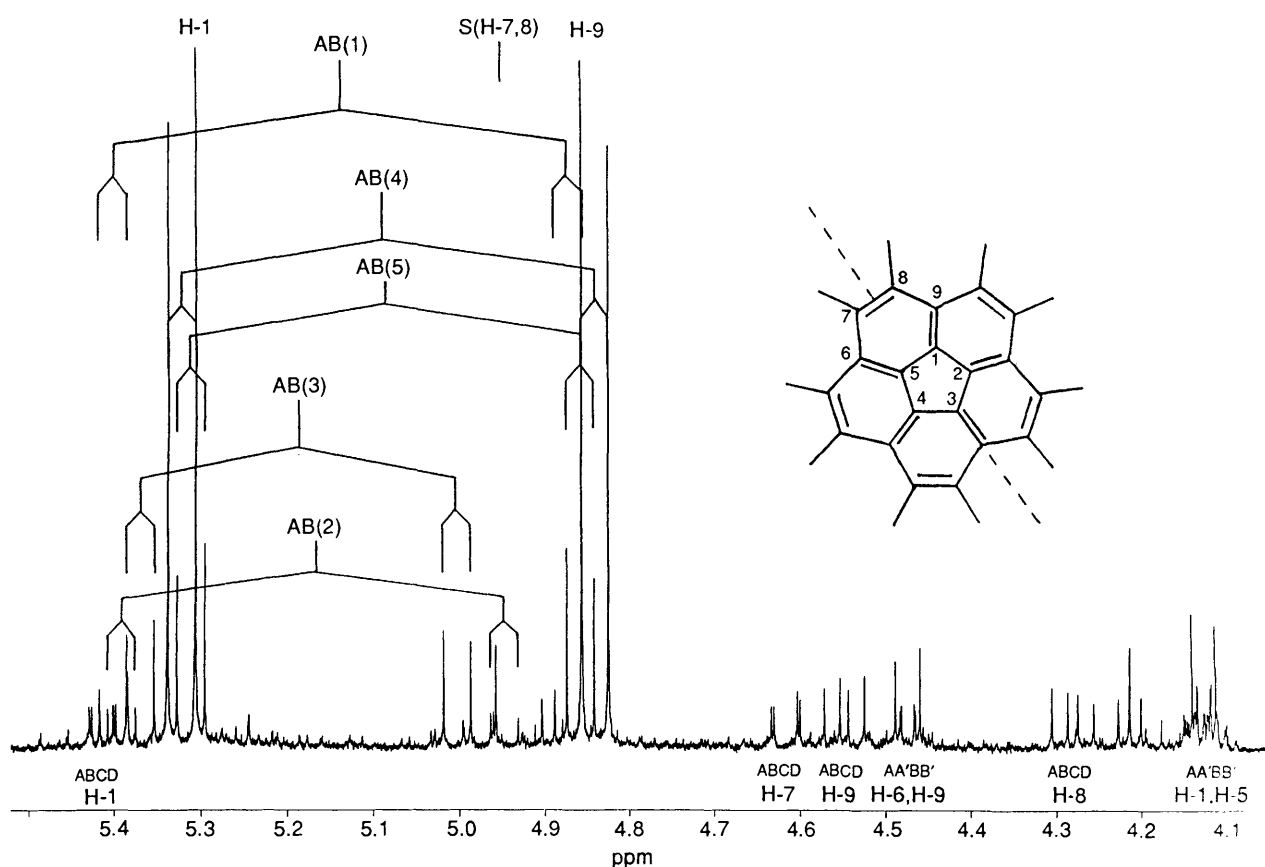


Fig. 5 ^1H NMR spectrum of diimide hydrogenated fullerene- C_{70} in CS_2

Table 2 ^1H NMR data for hydrogenated fullerene- C_{70} , recorded in CS_2 or C_6D_6

$\delta(\text{CS}_2)$	J/Hz	$\delta'(\text{C}_6\text{D}_6)$	$\delta - \delta'$	Type	Position of H	Relative intensity
4.96		3.87	1.09	s	7, 8	1
5.32 ^a	16.1	4.22	1.10	AB q	1, 9	25
4.84		3.71	0.93			
5.401 ^a	16.35					
4.873						
5.392 ^a	16.05					
4.948						
5.370 ^a	16.05					
5.003						
5.312 ^a	16.05					
4.859						
5.414 ^a	14.3, 1.6					
4.618	15.1, 1.6					
4.417	14.2, 9.3					
4.283	15.1, 9.3					
4.475	14.25					
4.127	9.8					
	1.6			AA'BB'	1, 5, 6, 9	9

^a These signals are assigned to hydrogens at the 1- and symmetry-equivalent positions.

to be associated with one of the three most upfield AB quartets.

Reduction of Fullerene- C_{70} by Diimide.—Fig. 5 shows the ^1H NMR spectrum obtained using CS_2 as solvent (CDCl_3 lock signal), the data are given in Table 2, and the two-dimensional analysis is presented in Fig. 6. The downfield spectrum ($>\delta$ 5.5) shows signals due to hydrogenated fullerene- C_{60} but of greater intensity than we would have expected from the concentration of fullerene- C_{60} in the sample used ($<2\%$). This result suggests

that fullerene- C_{60} is hydrogenated more readily than fullerene- C_{70} , as found by Cahill and co-workers in hydrogenation using diborane²⁰ (which we confirm). Resonances occur much more upfield for hydrogenated fullerene- C_{60} than for hydrogenated fullerene- C_{70} , indicating that the latter is appreciably less acidic. This may be due to field effects as described above, for here the fullerene- C_{70} cross-cage distances are greater. The triplet centred at δ 4.21 is associated with features at δ 7.24 and 1.69 and is due to an impurity.

The most intense feature of the spectrum is the AB quartet

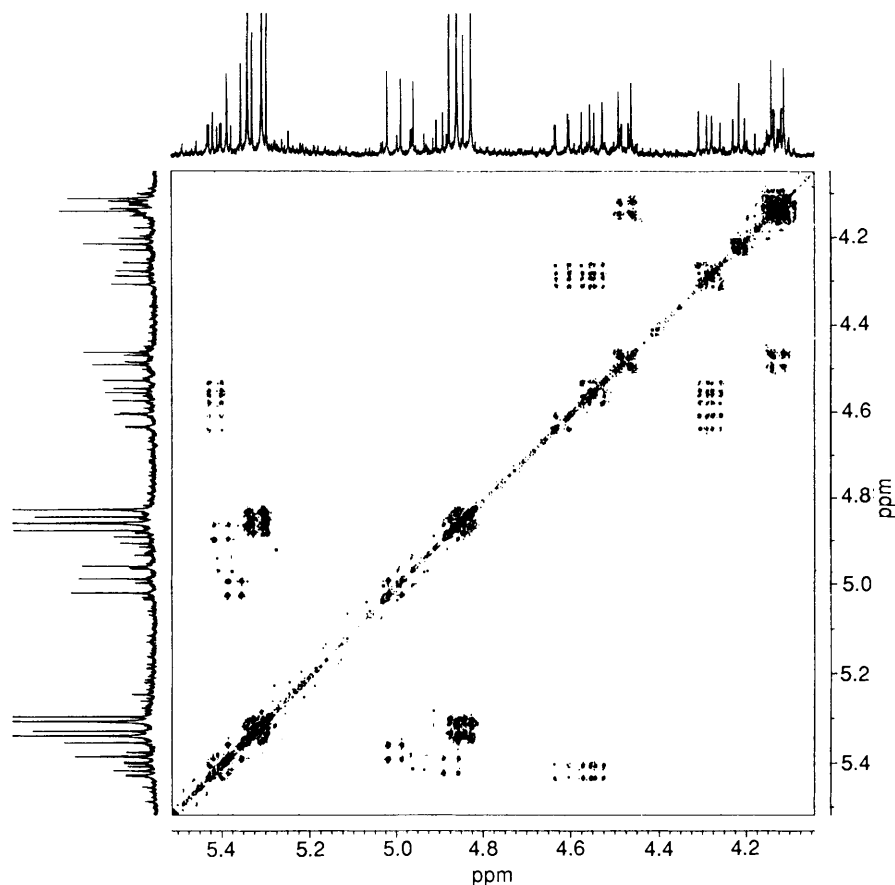


Fig. 6 Two-dimensional (COSY) analysis of the spectrum given in Fig. 5

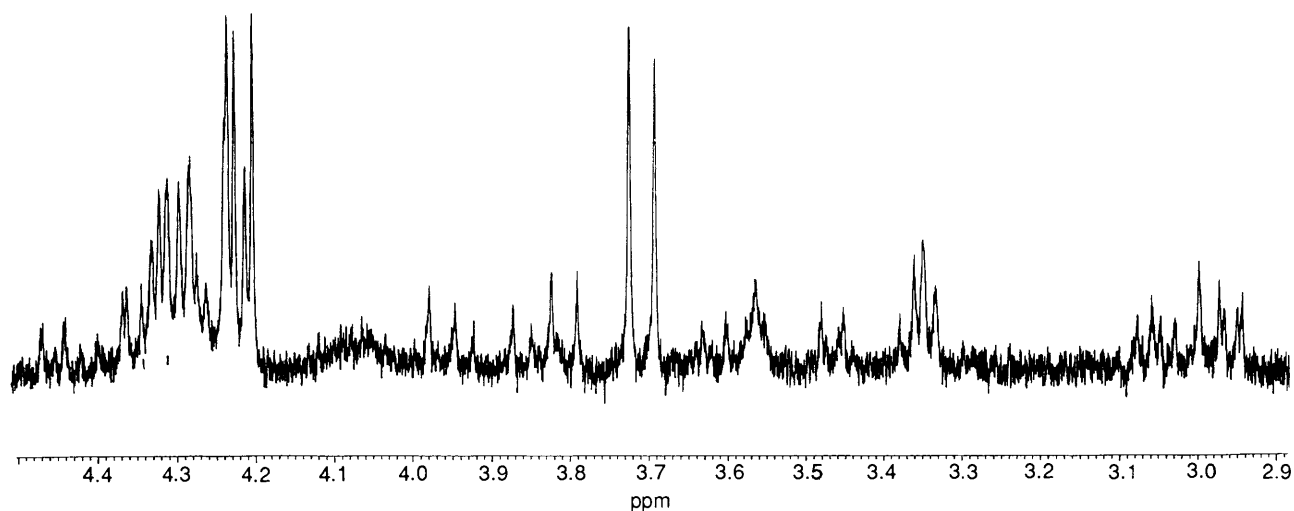


Fig. 7 ^1H NMR spectrum of diimide hydrogenated fullerene- C_{70} in C_6D_6

at δ 5.32 and 4.84 (these appear at δ 4.22 and 3.71, respectively, in C_6D_6 , Fig. 7). This quartet has also been observed by Cahill and co-workers (at δ 4.24 and 3.75 in $[\text{C}_6\text{H}_8]$ toluene) after reduction with diborane²⁰ and thus has been attributed to 1,9-dihydrofullerene- C_{70} , an assignment with which we concur. Further, given that due to strain effects, the ^{13}C NMR signal for C-1 appears appreciably more downfield than that for C-9,²¹ it seems probable that the doublet at δ 5.32 is due to the hydrogen at C-1 and that at δ 4.84 is due to the hydrogen at C-9. We also find a small singlet at δ 4.96 (δ 3.87 in C_6D_6) that they²⁰ observe with diborane reduction (at δ 3.91 in $[\text{C}_6\text{H}_8]$ toluene) and they have assigned it to 7,8-dihydrofullerene- C_{70}

(for numbering system, see ref. 8) with which we also agree. Theoretical calculations indicate that the 7,8- and 1,9-bonds should have the highest bond orders,²² however previous additions have been found to take place exclusively across the 1,9-bond (insofar as the experimental analysis permits).²³ For reduction by diimide, the reactivity ratio between the two sites is *ca.* 8:1; further hydrogenation (see below) makes this value somewhat uncertain as a quantitative measure.

The remainder of the spectrum consists of an AA'BB' spin system, an ABCD spin system (both systems of approximately equal intensity), and four AB quartets. Most of the elements of the spectrum are upfield of the peaks for dihydrofullerene- C_{70} ,

the difference from the case of hydrogenated fullerene-C₆₀ (where all are upfield) possibly reflecting the differences in trans-gage distances at different sites in fullerene-C₇₀.

The AA'BB' spin system, and moreover its similarity to that for 1,2,3,4-tetrahydrofullerene-C₆₀ is commensurate with 1,5,6,9-tetrahydrofullerene-C₇₀. As with fullerene-C₆₀, once addition has occurred to one hexagonal ring (adjacent to the terminal pentagon) and preferentially across the 1,9-bond, further addition will be favoured in the same ring because delocalisation will be interrupted. This addition can take place across either the 5,6- or 7,8-bonds. By the reasoning given for hydrogenated fullerene-C₆₀, we may assign the resonances due to H-6, -9, -1 and -5 as shown in Fig. 5.

The ABCD spin system shows couplings that are very similar to those found for the two AA'BB' systems, and must be due to an unsymmetrical tetrahydrofullerene. It follows from the foregoing discussion that this species must be 1,7,8,9-tetrahydrofullerene-C₇₀, produced either as described above, or it can be formed by further reduction of 7,8-dihydrofullerene-C₇₀. Again, reduction will preferentially take place in the same hexagon. At first sight, it may seem surprising that these two tetrahydro derivatives are formed in approximately equal amounts. However, it must be borne in mind that once addition has occurred across the 7,8-bond, there are two equivalent bonds (1,9 and 5,6) in the same ring, thus increasing the probability of forming the 1,7,8,9-tetrahydro product. The four hydrogens in this isomer can be assigned. First, we would expect H-8 and -9 to be the most upfield for the same arguments noted previously, a fact confirmed by the coupling constant of 9.3 Hz which is that which applies across a bond between a pentagon and a hexagon (sometimes referred to as a 6,5- or interhexagonal bond). Moreover, it appears from the data for 1,2,3,4-tetrahydrofullerene-C₆₀ and 1,5,6,9-tetrahydrofullerene-C₇₀ that the H-H coupling *exo* to the terminal pentagon is *ca.* 14.3 Hz. If one assumes that this criteria applies also to the 1,7,8,9-isomer, than H-1 and -9 may be located as shown on Fig. 5, and similar arguments allow one to locate H-7 and -8.

Given that addition across the 7,8-bond (and equivalents) is not very facile, the probability of obtaining isomers containing combinations of this bond and its equivalents is small, and can reasonably be discounted. Five tetrahydrofullerene-C₇₀ isomers can arise from combinations of addition across the 1,9-bond and its equivalents; one we have already identified, and the other possibilities are the 1,3,9,15-, 1,9,63,64-, 1,9,61,62- and 1,9,67,68-tetrahydrofullerene-C₇₀ isomers. Each should give rise to AB quartets and it is interesting therefore that we clearly observe four such quartets in our spectrum. No assignments are possible at this stage, though it is likely that each of the downfield doublets is due to the hydrogen pairs 1,3, 1,63, 1,62 and 1,67. Moreover, it is probable that the most upfield AB quartet is due to the 1,3,9,15-isomer as this is the one with all four sp³-hybridised carbons in close proximity.

¹H NMR Analysis of Hydrogenated Fullerenes and Derivatives.—In the course of this study, we have measured 17 coupling constants for ³J_{HH} interactions between protons on interpentagonal (6:6) bonds (which lie in the range 13.9–16.3 Hz) together with three coupling constant for protons on interhexagonal (6:5) bonds (which lie in the 9.3–9.8 Hz range). This clear differentiation will be useful in determining the structure of subsequent isomers. Further, we note that the

standard Karplus curves predict values for vicinal C–H couplings with a dihedral angle of 0°, as effectively here, of between 8.5 and 12.5 Hz, so although the interhexagonal bond couplings are typical, the interpentagonal couplings are very large. No reason for this is presently evident.

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