Pentamethylcyclopentadiene Adducts of [60]- and [70]-Fullerene

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Pentamethylcyclopentadiene reacts with [60]- and [70]-fullerene to form Diels–Alder monoadducts, characterised by ^{1}H and ^{13}C NMR spectroscopy, in which the methyl group attached to the single carbon bridge points away from the cage. Cycloaddition to [70]fullerene takes place across the 1,9-bond adjacent to the pentagonal cap. The pentamethyl adducts are less prone to undergo the retro Diels–Alder reaction than their non-methylated counterparts. The ^{1}H NMR spectra provide further confirmation that [70]fullerene is less electron withdrawing than [60]fullerene.

Diels–Alder cycloadditions to fullerenes provide a potential route to a wide variety of organofunctional derivatives, a fact that has resulted in intense activity in this field.[1-3] Unfortunately many Diels–Alder adducts readily undergo the retro reaction to regenerate the diene and the fullerene, thus making product analysis by mass spectrometry difficult. We have shown previously that this drawback can be circumvented by reduction of the adduct.[2]

We reasoned that adduct stability should be enhanced by increasing the electron supply in the diene, and for the purpose of the present investigation we have used the readily available pentamethylcyclopentadiene. Because [60]fullerene is a stronger electrophile than [70]fullerene (see e.g. the positions of the resonances of the reduced fullerenes),[4] the former yields Diels–Alder adducts more readily.[3] Adducts obtained from [70]fullerene are therefore likely to be less stable, and thus it was of interest to investigate stability of the product obtained from reaction of this fullerene with a more electron-rich diene.

Whereas addition to [60]fullerene has been shown in numerous investigations to take place across the 1,2-bond,[1,2] to date there have been only four determinations of the most reactive position in [70]fullerene.[4-7] Molecular orbital calculations indicated that the 7,8-bond should be marginally more reactive than the 1,9-bond, both being significantly more reactive than other bonds.[8,9] Experimental studies have involved either reduction,[4] formation of an iridium complex,[5] osmylation[6] or Michael-type addition of an α-halocarbanion.[7] In each case 1,9-addition was preferred, though in the case of reduction (in which byproducts are more easily detected) some 7,8-addition occurred as well.

The preference for 1,9-addition, first observed in the formation of the iridium complex, was provisionally attributed to a more favourable steric environment.[5] However, the hydrogenation result shows that the effect is independent of steric requirement of the added group, and relief of the highest points of strain in the molecule now seems the most probable cause. We used the concept of strain (arising from increased local curvature) in assigning, correctly, the ^{13}C NMR frequencies of [70]fullerene;[10] the most downfield signals were attributed to the carbons of the pentagonal cap (i.e., C-1 and equivalents), so that addition across the 1,9 bond becomes readily understandable.

We have now determined the most reactive site in [70]fullerene towards a Diels–Alder type cycloaddition, and have determined the stereochemistry of the addends on both [60]- and [70]-fullerene.

Experimental

A solution of pentamethylcyclopentadiene (0.06 mmol) in benzene was added to a solution of [60]fullerene (0.05 mmol) in the same solvent at 10 °C, and the mixture turned immediately red–brown. The mixture was stirred for a further 18 h at room temp. The solution was then passed through a short column of neutral alumina (0.5% H_2O) and the solvent removed from the eluate under vacuum to give 1,2-[1,3]epi(4,5-dimethyl-2,3-dihydro-1H-cyclopenta) [60]fullerene in 81% yield. A similar procedure using [70]fullerene gave 1,9-[1,3]epi(4,5-dimethyl-2,3-dihydro-1H-cyclopenta) [70]fullerene* in 83% yield.

Occluded solvent and other impurities were partially removed by heating each adduct at 200 °C/0.1 mmHg for 6 h. Significantly however, no change in the spectra of either adduct occurred during this process, whereas by contrast the adduct formed from [60]fullerene and cyclopentadiene partly decomposes during such treatment. This demonstrates that the pentamethyl adducts are more stable, as anticipated.

Structural Characterisation of the Adducts

Addition to [60]Fullerene.—The ^{1}H NMR spectrum of the adduct derived from [60]fullerene (500 MHz, CS_2, $CDCl_3$, Fig. 1) consists of the following main resonances: δ 1.30 (3 H, d, J 6.4 Hz, Me_c), 1.95 (3 H, s, Me_b), 2.095 (3 H, s, Me_a), 3.55 (1 H, q, J 6.4 Hz, H). (Other samples show up to 0.3 ppm upfield shifts of the peaks, owing to solvent and/or concentration effects.)

The simplicity of the spectrum shows that the product is symmetrical and that addition must therefore have taken place across the 1,2-bond of [60]fullerene, as in all other related cycloadditions so far investigated.[1] This conclusion is confirmed by the ^{13}C NMR spectrum (500 MHz, CS_2, $CDCl_3$, Fig. 2) which consists of six lines in the sp^3 region at δ 80.34 (C-1, -2 of the cage), 65.14 [$C(Me_b)$], 57.07 [$C(Me_c)$], 14.78 (Me_a), 12.09 (Me_b), 8.97 (Me_c) (each confirmed by proton-decoupling experiments). The carbons of the double bond of the addend were shown by their proton decouples to appear at δ 137.45. Of the 58 sp^2 carbons of the cage, four are on the symmetry axis and give unit intensity peaks at δ 144.95, 144.89, 142.72 and 142.68. The remaining 27 double intensity peaks are at δ 156.13, 154.35, 146.57, 146.56, 146.39, 145.87, 145.75, 145.66, 145.46, 144.94, 144.84, 144.79, 144.75, 144.12, 143.94, 142.30, 142.24, 142.17, 141.69, 141.68, 141.65, 141.33, 141.31, 139.28, 139.18, 136.72 and 136.61. It seems probable that the most downfield resonances of the on-axis carbons arise from those (C-18 and -36) that are on the side of the cage nearest to the double bond of

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* The numbering for the [70]fullerene cage is that given in ref. 9, and should be taken as provisional. A fully contiguous numbering scheme has now been devised in which the most reactive bond in [70]fullerene is numbered 1,2 and thus parallels the situation in [60]fullerene. According to this revision, positions 1, 9, 7, and 8 become positions 2, 1, 5 and 6, respectively. (R. Taylor and E. W. Godly, Report of the Fullerene Nomenclature Subcommittee to Commission II.3 of IUPAC.)
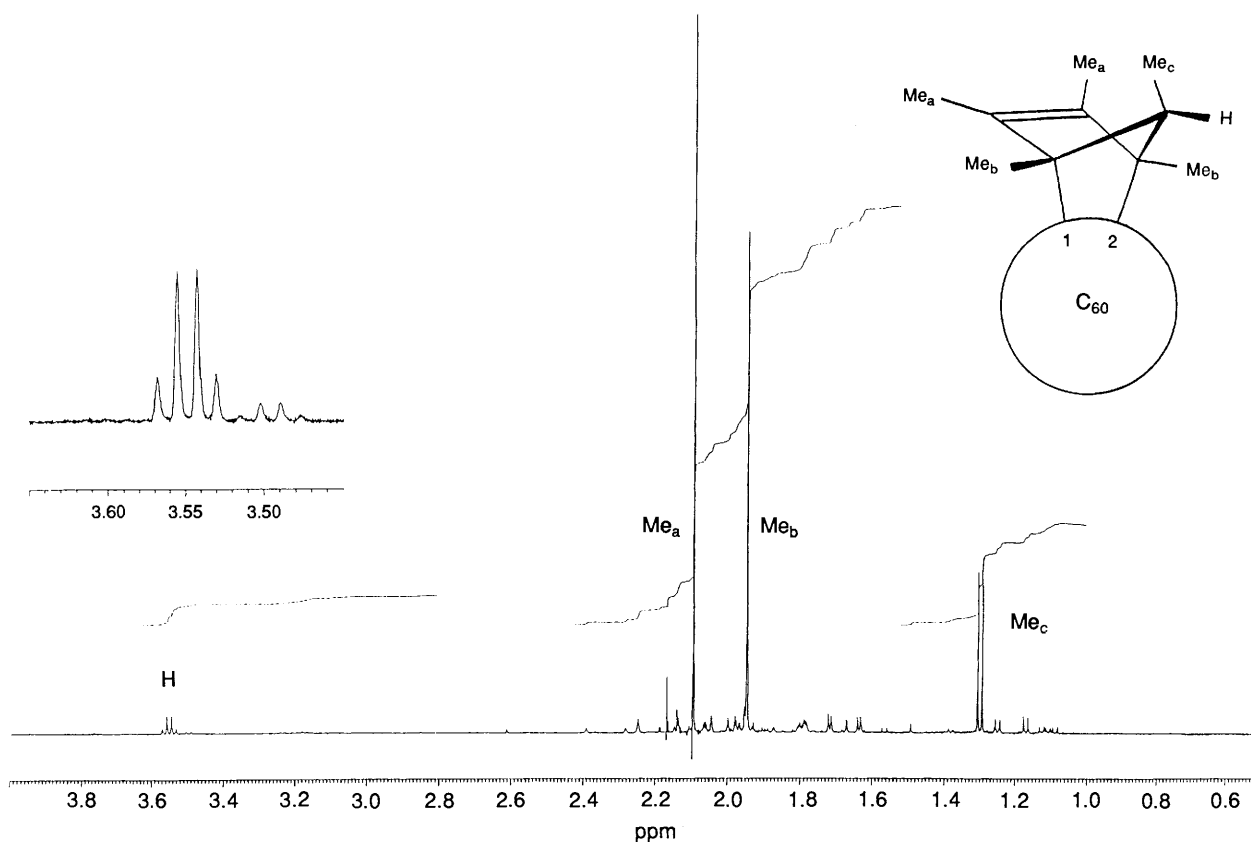
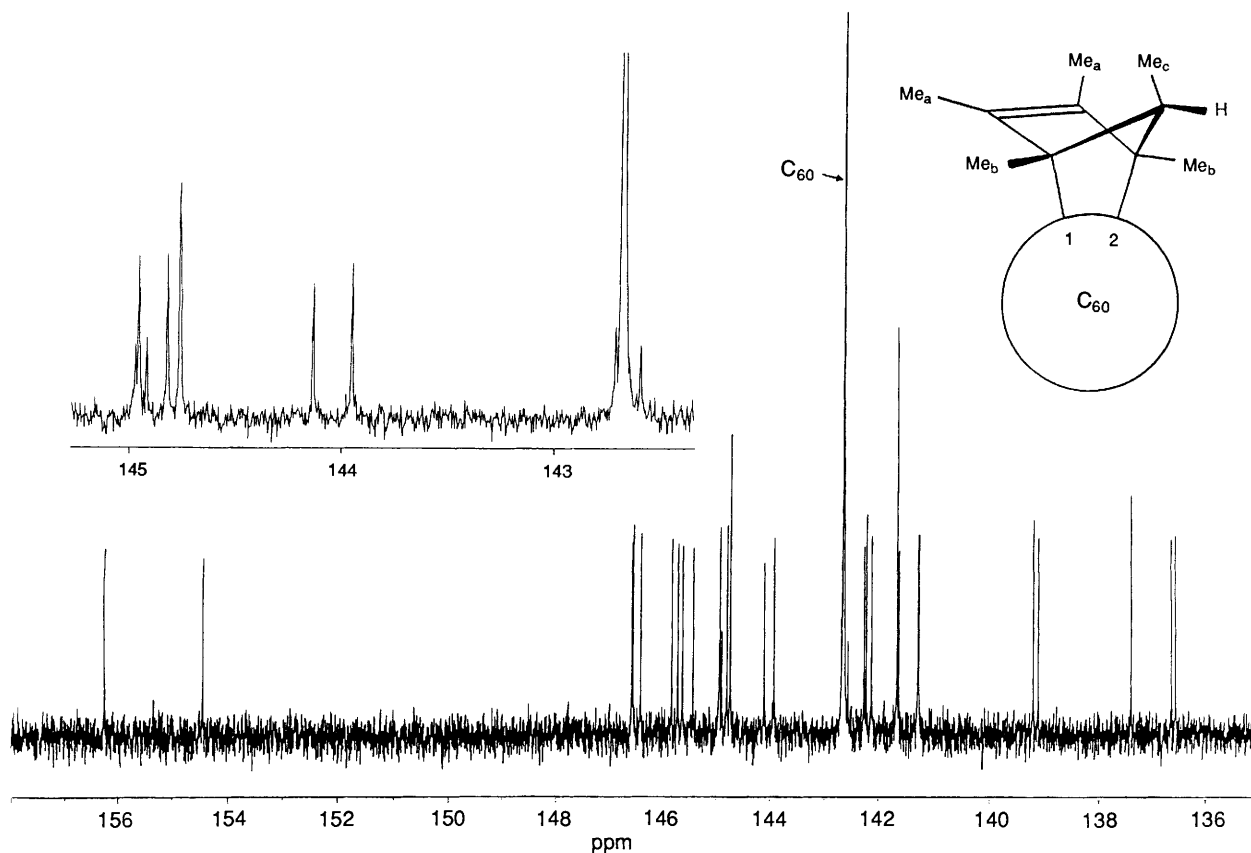**Fig. 1** ^{1}H NMR spectrum for 1,2-[1,3]epi(4,5-dimethyl-2,3-dihydro-1H-cyclopenta) [60]fullerene

Fig. 2 ^{13}C NMR spectrum for 1,2-[1,3]epi(4,5-dimethyl-2,3-dihydro-1H-cyclopenta) [60]fullerene

the addend (field effect). In due course we hope to assign the cage resonances for a range of [60]- and [70]-fullerene derivatives, through the use of ^{13}C-enriched material.

There is evidence in the ^{1}H NMR spectrum for the formation of a diadduct, in that a second quartet, appears at δ 3.495, upfield of the main one at δ 3.55 (see inset to Fig. 1). There are

several doublets around δ 1.2 that may be associated with this quartet. The upfield position is consistent with reduced electron withdrawal by the cage that accompanies increased addition and conversion of carbons from sp^2- to sp^3-hybridisation, with concomitant reduction in cage strain; similar effects are seen in the ^{1}H NMR spectra of fullerene hydrides.[4]

From the ^{1}H NMR data we have also determined the stereochemistry in the addend. There are two possibilities: Me_c can either be *exo* or *endo* to the cage. The marked downfield location of the quartet at δ 3.55 due to the single hydrogen provides very strong evidence that it possesses the conformation shown in Fig. 1. We have shown previously that the very strong electron withdrawal by the cage causes downfield shifts of hydrogens *endo* to the fullerene cage* relative to their *exo* counterparts.[2] [Note that on Fig. 2 of ref. 2, the labels (c) and (d) have been inadvertently interchanged; the associated text is correct.]

We have further confirmed the stereochemistry by NOE experiments: irradiation of the singlet at δ 2.095 (Me_a) gives a 0.5% enhancement of the signal at δ 1.95 (Me_b), a 0.2% enhancement of the doublet at δ 1.3 (Me_c) and no enhancement of the quartet at δ 3.55 (H). By contrast, irradiation of the singlet at δ 1.95 (Me_b), gives a 1.5% enhancement of the singlet at δ 2.095 (Me_a), a 2.25% enhancement of the doublet at δ 1.3 (Me_c) and a 5.2% enhancement of the quartet at δ 3.55 (H).

Cycloaddition to [70]Fullerene.—Addition to [70]fullerene across high-order bonds gives rise to two possibilities, shown in Figs. 3 and 4, in which the dotted lines indicate the plane of symmetry passing through the bond involved in the cyclo-addition. Addition across the 1,9-bond (Fig. 3) generates an unsymmetrical product, whereas addition across the 7,8-bond (Fig. 4) gives a symmetrical product (in which case the spectrum would be similar to that obtained in the [60]fullerene experiment).

The spectrum (500 MHz, [^{2}H$_4$]-1,2-dichlorobenzene, Fig. 5) consists of the following main resonances with provisional assignments: δ 1.06 (3 H, d, J 6.35 Hz, Me_c), 1.60 (3 H, s, $Me_{b'}$), 1.85 (3 H, q, J 1.1 Hz, $Me_{a'}$), 2.03 (3 H, q, J 1.1 Hz, Me_a), 2.04 (3 H, s, Me_b), 2.45 (1 H, q, J 6.35 Hz); there are also two singlets at δ 1.53 and 2.10, shown to be due to impurities by comparison with spectra obtained from other samples. (A spectrum subsequently obtained using CS_2 as solvent gave resonance positions identical within 0.02 ppm.)

The product is evidently unsymmetrical, and shows that addition takes place across the 1,9-bond. Some interesting features emerge from this spectrum and from comparison with that (Fig. 1) obtained with [60]fullerene. (*i*) The quartet due to the single hydrogen and the doublet due to Me_c lie upfield in the [70]fullerene derivative, and by 0.24 and 1.1 ppm, respectively. This upfield shift not only further confirms the lower electron-withdrawing character of [70]fullerene than [60]fullerene, but the fact that the shift is greater for the single hydrogen than for Me_c indicates that the hydrogen occupies the *endo* position in the addend (confirmed by NOE experiments, below). (*ii*) Whereas the signal for one of the methyl groups $Me_{b/b'}$ has shifted upfield compared to its [60]fullerene analogue, in line with expectation based on the foregoing observation, the signal for the other has moved downfield by a small amount. We believe this enables us to assign these methyl groups as shown on the inset of Fig. 5. Both methyl groups $Me_{b/b'}$ point slightly towards the cage, and one lies over the pentagonal cap, which we now believe is the most electron-deficient region of the molecule. For example, the ^{13}C NMR resonance for the carbons

* Note that groups *endo* to the cage are *exo* to the addend and *vice versa*.
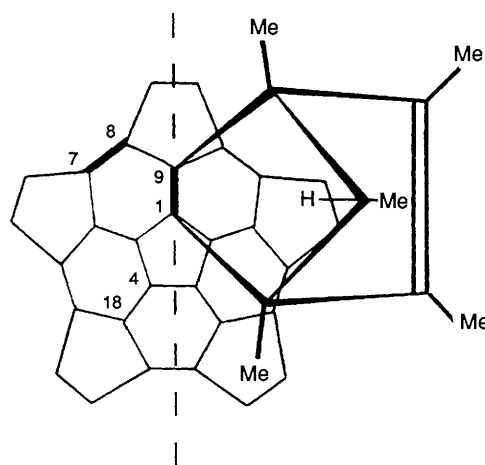

Fig. 3 Structure of 1,9-[1,3]epi(4,5-dimethyl-2,3-dihydro-1H-cyclopenta) [70]fullerene
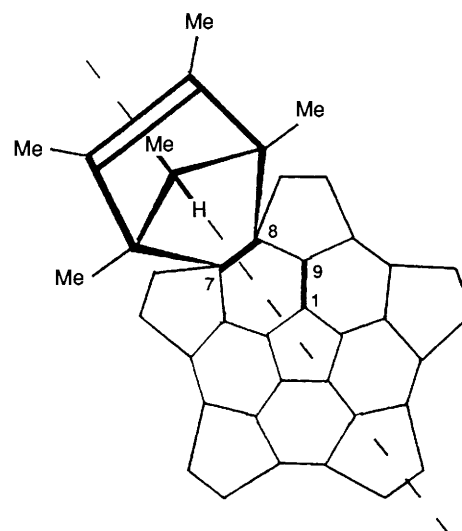

Fig. 4 Structure of 7,8-[1,3]epi(4,5-dimethyl-2,3-dihydro-1H-cyclopenta) [70]fullerene (one of two geometrical isomers)

of the pentagonal cap of [70]fullerene appear 7.3 ppm downfield from that for [60]fullerene. Thus that methyl which we assign in Fig. 5 as Me_b experiences greater electron withdrawal and the position of the resonance follows logically.

The resonances for the methyl groups $Me_{a/a'}$ are both more upfield compared to those in the [60]fullerene analogue. Since these methyls are further from the cage than methyls $Me_{b/b'}$, the upfield shift is smaller, and the shift between them (0.18 ppm) is less than that between $Me_{b/b'}$ (0.44 ppm). By the same reasoning given for the asignment of $Me_{b/b'}$, Me_a and $Me_{a'}$ are assigned as shown in Fig. 5.

NOE experiments confirmed the *endo* location of the single hydrogen. Irradiation of the resonance at δ 1.85 ($Me_{a'}$) produced a 1% enhancement at δ 2.03/2.04 (Me_a and Me_b, not resolved), a 0.7% enhancement at δ 1.60 ($Me_{b'}$), a 0.3% enhancement at δ 1.06 (Me_c) and no enhancement at δ 2.45 (single hydrogen).

The ^{13}C NMR spectrum (500 MHz, CS_2, $CDCl_3$) confirmed the asymmetry of the product. There are ten resonances in the sp^3 region as required, at δ 73.60, 71.67 (C-1 and C-9, respectively), 64.81 (CMe_b), 64.38 ($CMe_{b'}$), 56.66 $C(Me_c)$, 15.61 (Me_a), 14.84 ($CMe_{a'}$), 12.24 (Me_b), 11.96 ($Me_{b'}$), 8.31 (Me_c); in each case we have assigned the more downfield resonance to the carbon nearest to the pentagonal cap. Two other resonances appeared at δ 21 and 30 due to the impurity peaks evident on Fig. 5. In the sp^2 region there are 68 resonances as required for
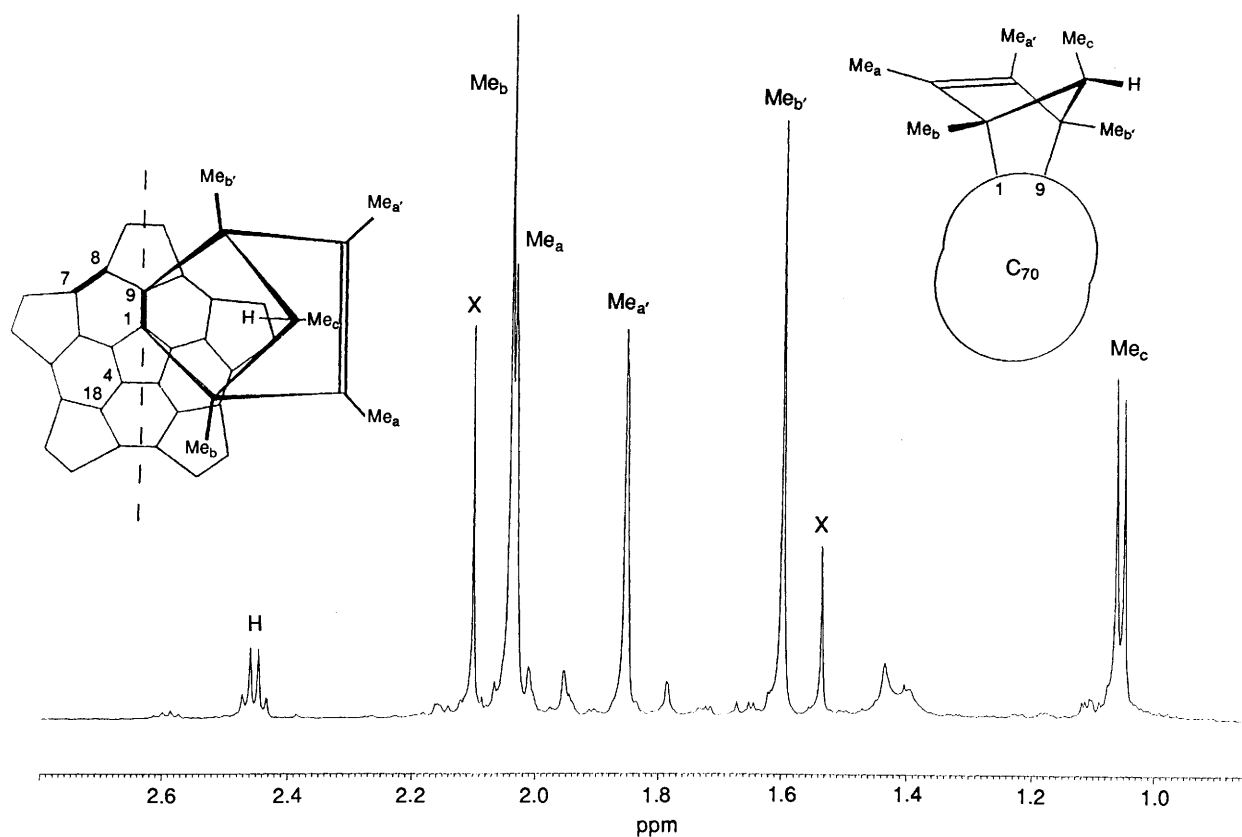
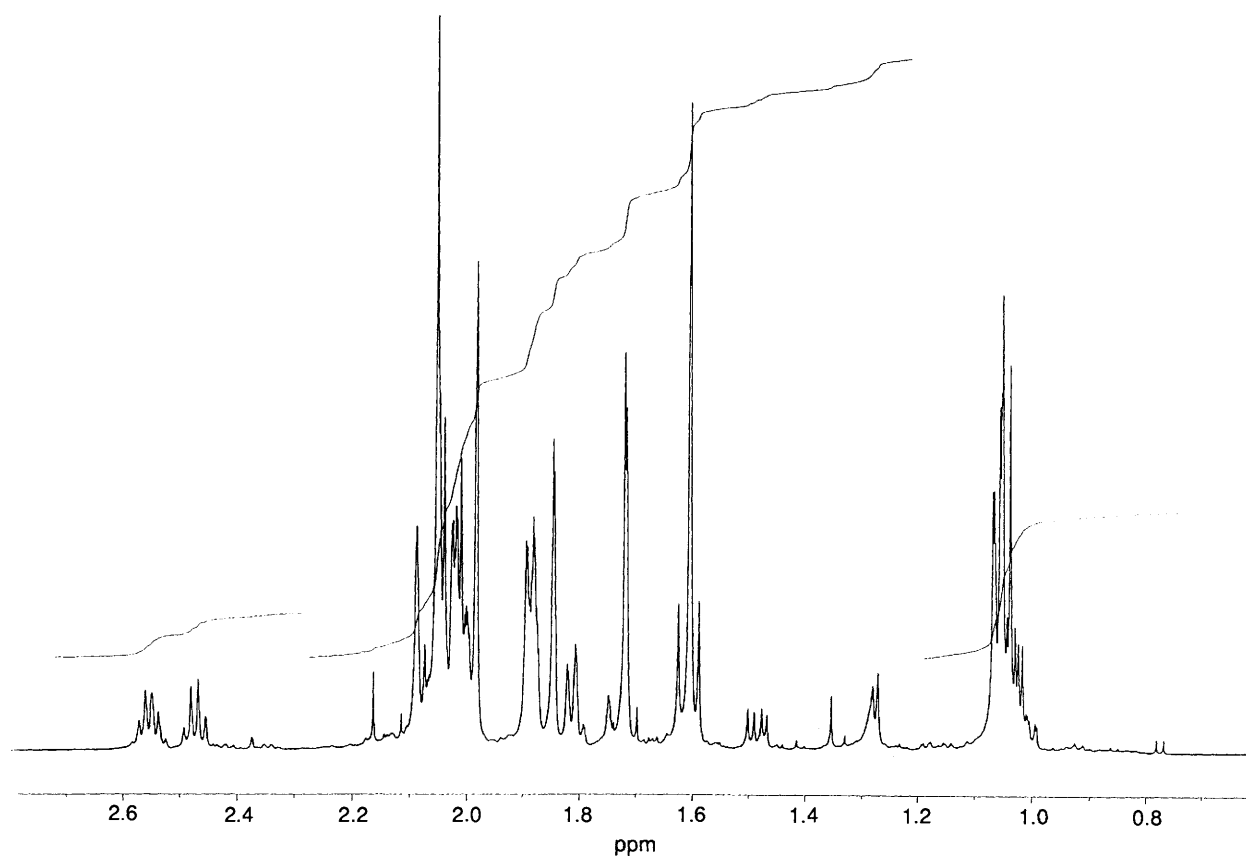Fig. 5 ^{1}H NMR spectrum for 1,9-[1,3]epi(4,5-dimethyl-2,3-dihydro-1H-cyclopenta) [70]fullerene

Fig. 6 ^{1}H NMR spectrum for 1,9-[1,3]epi(4,5-dimethyl-2,3-dihydro-1H-cyclopenta) [70]fullerene in the presence of another unidentified component

the asymmetric adduct, at δ 159.93, 157.98, 156.25, 155.94, 151.033, 151.017, 150.948, 150.935, 150.70, 150.51, 150.39, *150.24*, 150.18, 149.96, *149.38*, 149.36, *149.15*, 149.07, 148.97, 148.86, 148.84, 148.58, 148.56, 148.39, 148.33, 147.09, 147.05, 146.97, 146.71, 146.69, 146.65, 146.62, *146.55*, 146.51, *145.99*, 145.56, 145.41, 145.17, 144.82, 142.947, 142.935, 142.733, 142.722, 142.62, 142.40, 142.16, 141.31, 140.91, 139.82, 139.65, 137.85, 137.78, 137.32, 136.56, 133.33, 133.24, 133.16, 133.11, 130.88, 130.86, 130.83, *130.74*; italicised peaks are of double intensity due to coincidence of resonances.

In Fig. 5 the presence of a second quartet is evident, centred at ca. δ 2.59. Since this resonance is downfield from that for the quartet identified above, it seems unlikely that this is due to a diadduct, since an upfield shift would be expected (cf. hydrogenation[4]). It could be due to a trace of the 7,8-isomer in which the CHMe group sits over the pentagonal cap. However, in a further experiment, in which a longer reaction time was used, not only was the adduct shown in Fig. 5 obtained, with the resonances at exactly the same positions, but an additional component was present, and in greater concentration (see Fig. 6). This gave a quartet at δ 2.55 coupled (J 6.1 Hz) with a methyl doublet at δ 1.06, which in turn showed secondary splitting (J 1.5 Hz). Also present (together with a number of other peaks, Fig. 6) were singlets at δ 1.98 and a methyl doublet at δ 1.72 (J 1.5 Hz). This second component could also be due either to the 7,8 adduct (of which two geometric isomers are possible), or also a diadduct in which addition has occurred across the 1,9- and 4,18-bonds (see Fig. 3); the slight downfield shift of the quartet could then arise because steric interactions force the single hydrogen slightly nearer to the cage. Other conjectures are possible and considerable further work will be needed to resolve the problem. We do consider however, that any diadduct is more likely to involve further addition to the cage rather than to the addend, in view of the high electrophilicity of the former.

Acknowledgements

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