^{13}C NMR Spectroscopy of C_{76}, C_{78}, C_{84} and Mixtures of C_{86}–C_{102}; Anomalous Chromatographic Behaviour of C_{82}, and Evidence for $C_{70}H_{12}$

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Using high pressure liquid chromatography, the fullerenes C_{76}, C_{78}, C_{84} and C_{86}–C_{102} have been separated (in some cases partially) from soot produced by the arc-discharge procedure. The ^{13}C NMR spectrum for C_{76} confirms that reported previously, whilst the spectrum for C_{78} indicates the presence of C_{2v}, D_3, $C_{2v'}$ isomers in the approximate relative yields (there is a small batch dependence) of 52:30:18%. The spectrum for the D_3 isomer (confirmed from two separate batches) differs from that given in the literature with respect to the location of one peak. The relative peak heights in the C_{84} ^{13}C NMR spectrum are similar to those reported for samples produced under different conditions. The stabilities of the component isomers must therefore be similar and so produced in a similar ratio irrespective of conditions; this indicates them to be the D_2 and a D_{2d} isomers. The spectrum also contains over 70 minor peaks due to other isomers of C_{84}. Eleven of the peaks are more intense than the others, consistent with the presence of the D_{3d} and D_{6h} isomers, predicted to be of relatively high stability. Two fractions (giving yellow solutions in hexane) eluted after C_{84}: the first was separated into two components, shown by mass spectrometry to consist of minor amounts of C_{86}–C_{92}, and mainly C_{90} and C_{92} with lesser amounts of C_{94}–C_{102}, respectively. The ^{13}C NMR spectrum of the C_{94}–C_{102} component indicated the presence of a fullerene isomer of high symmetry. The second yellow fraction consisted largely of C_{82} together with traces of fullerenes up to C_{108}, but the quantity was insufficient for the ^{13}C NMR spectrum to be obtained. The retention time of C_{82} is inconsistent with values for the other fullerenes indicating that it consists of the C_{3v} isomer, predicted to be polar. C_{90} eluted with two different retention times suggesting that the second fraction is also a polar isomer. One sample of C_{84} contained a co-eluent, identified by mass spectrometry as $C_{70}H_{12}$; proposals are made concerning its possible origin, structure, and stability relative to other hydrogenated derivatives.

The mode of formation of fullerenes is not well understood. Any satisfactory theory must explain the mechanism of formation not only of C_{60} and C_{70}, but also of higher fullerenes, and why one particular isomer is formed in preference to another. A necesssary first step is to ascertain which fullerenes (and moreover which isomers) are readily formed. Isolation of the higher fullerenes is at present both very difficult and extremely time consuming. Moreover, their low solubility, coupled with the small amounts of material available makes the acquisition of good ^{13}C NMR spectra difficult. Satisfactory results require *ca.* 50 000 scans at 500 MHz resolution which corresponds to approximately 4–5 days of continuous operation. Consequently there have been very few reports to date.[1–4]

In a preliminary account of our results for C_{76} and C_{78},[4] a new isomer of C_{78} was identified and a discrepancy found between the spectrum for the D_3 isomer and that reported[1] in the literature. To evaluate this result, we have prepared another batch of the C_{76}/C_{78} mixture and obtained the ^{13}C NMR spectrum. In a preliminary account[5] results were presented for C_{84} which, taken together with other published data,[3] indicated that it consists mainly of a mixture of a D_2 and a D_{2d} isomer. We now present further results for C_{84}, and have obtained partial mass spectroscopic and ^{13}C NMR data for fullerenes C_{86}–C_{102}. We have also partially purified C_{82}, discovered that it behaves anomalously during chromatography, and obtained evidence for the existence of $C_{70}H_{12}$.

Experimental

The general method, described previously,[4] was modified in

order to overcome the difficulty encountered in obtaining sufficiently concentrated hexane solutions of the crude fullerenes (C_{84} and above) for HPLC processing. Two strategies were adopted: in the first, dilute solutions were prepared by allowing an excess of crude fullerene to stand during 24 h, with 250 cm^3 of hexane. (*NB.* Ultrasound agitation was counterproductive since it produced a fine suspension which was very slow to settle.) The solution was then concentrated on a rotary evaporator, the clear (super-saturated) solution allowed to settle, and then removed by pipetting. This process was repeated numerous times. In the second (quicker) process the material (*ca.* 1 mg) was dissolved in 20 cm^3 of dichloromethane, and then added to a large excess of hexane. This was then concentrated on a rotary evaporator (the dichloromethane was effectively removed) leaving a super-saturated solution of the fullerene. Occasionally, a temperature drop in the processing room caused the fullerene to precipitate from the saturated solutions and it was necessary to repeat either of the above processes. Each run through the HPLC took approximately 30 min, and some 300–400 runs were required for each of the *ca.* 2 mg samples of the fullerenes described in this work.

The approximate relative retention times of the various fullerenes were as follows: C_{60}, 1.0; C_{70}, 1.17; $C_{76/78}$, 1.35; C_{84}, 1.58; C_{88}, 1.77; C_{92}, 2.06; C_{94}, 2.23; C_{82}, 2.37. The retention time of C_{60} was generally 12–13 min.

In the preliminary report it was noted that a number of yellow fractions (hexane solution) were obtained after elution of C_{70}.[4] The first of these was shown by mass spectrometry and ^{13}C NMR to consist of a mixture of C_{76} and C_{78}, together with a little C_{60} and C_{70} which were retained as markers.[4] A second

(a)

C₇₆(D₂)

C₇₈(C₂ᵥ)

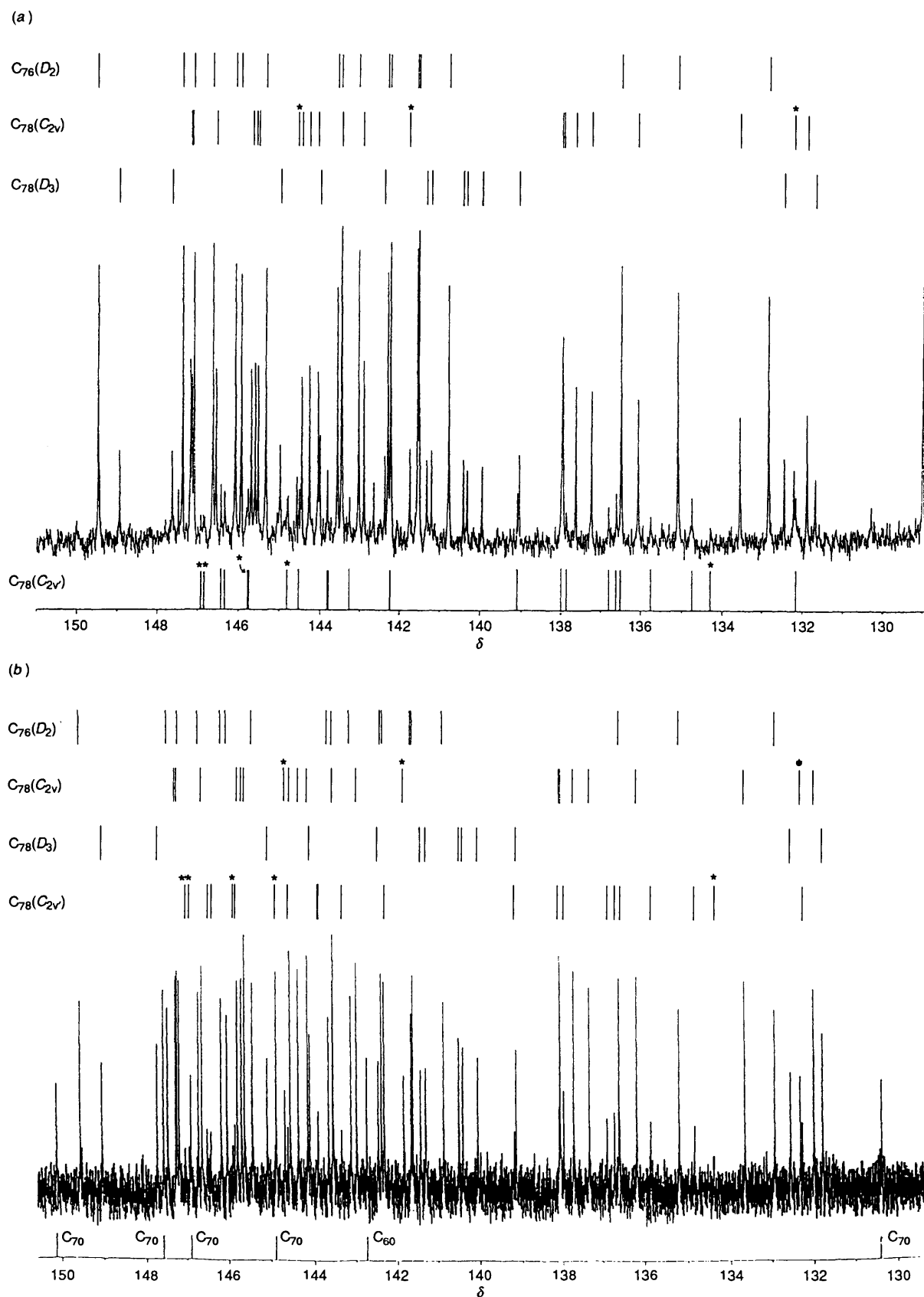C₇₈(D₃)

C₇₈(C₂ᵥ')

150   148   146   144   142   140   138   136   134   132   130

δ

(b)

C₇₆(D₂)

C₇₈(C₂ᵥ)

C₇₈(D₃)

C₇₈(C₂ᵥ')

C₇₀   C₇₀   C₇₀   C₇₀   C₆₀   C₇₀

150   148   146   144   142   140   138   136   134   132   130

δ

Fig. 1 ¹³C NMR spectra for a mixture of C₇₆ and C₇₈: (a) ref. 4; (b) new spectrum. Half intensity peaks are starred.

batch of this material has been obtained from a separate preparation, and the ¹³C NMR spectra for these two batches are shown in Figs. 1(a) and 1(b). All spectra were obtained by using deuteriated chloroform as lock signal, and the resonances

from both data sets agree to ±0.01 ppm. Updated resonance values are given in Table 1, and these supercede those given in the preliminary account,⁴ due to more accurate calibration of the C₆₀ reference.

Table 1 ^{13}C NMR chemical shifts (δ) for C_{76}, C_{78} and C_{84} [a]

| C_{76} (D_2)	C_{78} (C_{2v})	C_{78} (D_3)	C_{78} ($C_{2v'}$)	C_{84} ($D_2 + D_{2d}$)	
149.50	147.21	148.97	146.99[c]	144.04	139.43
147.41	147.18	147.67	146.88[c]	144.02	139.26[c]
147.13	146.57	145.03	146.45	143.92	139.22
147.66	145.72	144.05	146.36	143.41	139.20
146.12	145.63	142.40	145.86[c]	143.24	139.15
145.97	145.56	141.37	145.79	143.22	139.07
145.37	144.63[c]	141.23	144.84[c]	142.33	138.34
143.61	144.49	140.44	144.55	141.99	138.32
143.51	144.30	140.34	143.86	141.57	138.01
143.06	144.09	139.98	143.85	141.02	137.90
142.32	143.49	139.09	143.29	140.77	137.38
142.26	142.91	132.48	142.24	140.44	136.95
141.58	141.78[c]	131.73	139.14	140.04	136.84
141.54	138.01		138.02	139.93	134.92
140.80	137.99		137.90	139.77	134.42
136.53	137.65		136.82	139.72	133.27
135.14[b]	137.28		136.65		
132.87	136.11		136.50		
129.04	133.60		135.79		
	132.25[c]		134.77		
	131.93		134.35[c]		
			132.22		

[a] All peaks relative to C_{60} at 142.68 ppm. [b] The value given for this peak in the preliminary account[1] should have been 135.10, and not 135.01. [c] These peak intensities are approximately half those for the other peaks in the same column.

Table 2 ^{13}C NMR chemical shifts (δ) for minor isomers of C_{84} [a]

148.69	146.10	144.49	141.87	139.39	137.65	135.36
148.46	145.97	144.37	141.80	139.35	137.13	135.30
147.76	145.53	144.28	141.63	139.00	137.01	135.15
147.72	145.50	143.49	141.27	138.76	136.48	134.86
147.54	145.40	142.95	141.19	138.65	136.37	134.59
147.51	145.35	142.93	140.93	138.53	136.26	134.24
147.46	145.06	142.75	140.71	138.49	136.03	134.19
147.38	144.99	142.63	140.00	138.43	135.97	133.72
147.07	144.82	142.56	139.65	138.23	135.85	133.40
146.87	144.71	142.17	139.54	138.14	135.69	132.83
146.53	144.67	141.91	139.49	138.10	135.62	132.60

[a] All peaks relative to C_{60} at 142.68 ppm.

The next yellow fraction consisted of C_{84}, the mass spectra for a partially purified initial batch, and a purer sample from a second preparation are shown in Figs. 2(a) and 2(b), respectively. The mass spectrometric method (DCI heated probe) greatly exaggerates the amount of lower fullerenes present because of their greater volatility. Thus although both C_{76} and C_{78} were indicated to be present in each sample, neither could be detected by ^{13}C NMR. Likewise the peak intensities in Fig. 2(b) would, if taken as a quantitative measure, indicate the amount of C_{60} (say) present to be 29%; in fact the NMR spectrum shows the concentration to be ca. 0.2%. The mass spectrometry also indicated the presence of C_{70} in each sample, but it was detected only in the first [which also contained some $C_{70}H_{12}$, as shown in Fig. 2(b)]. The mass spectra also indicated that C_{82} might be present, but this result may be misleading because C_{82} is the main fragmentation product of C_{84}. (For the same reason the relative proportions of C_{76} and C_{78} in fullerene samples cannot be determined quantitatively by mass spectrometry.) The ^{13}C NMR spectra showed no peaks consistent with the published spectrum for C_{82} (Table 2). Moreover, the retention time of C_{82} is much greater than that for C_{84} (see below), so the latter is unlikely to be contaminated with the former. Nevertheless we may not discount at this stage the possibility that there are two (or more) isomers of C_{82} having very distinct retention times, and that one coelutes with C_{84} and
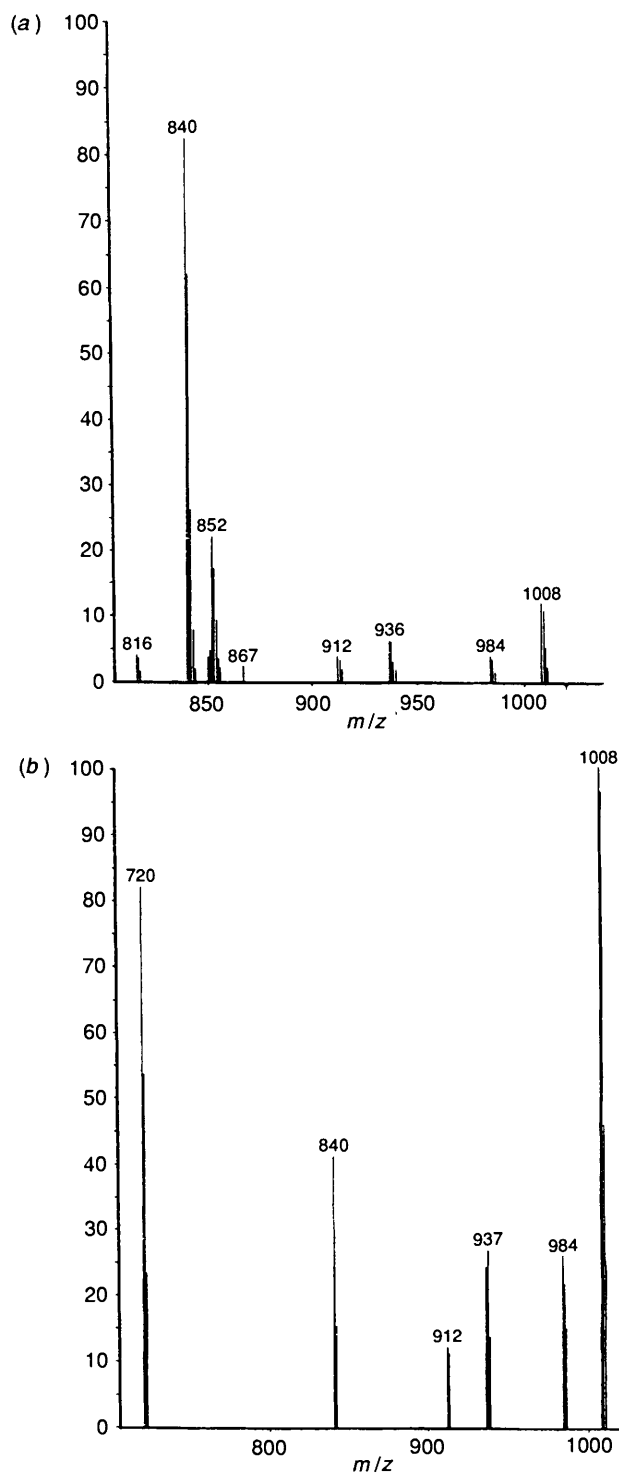
Fig. 2 Mass spectra for samples of C_{84} giving rise to the NMR spectra in Figs. 3(b) and 3(a), respectively. The presence of $C_{70}H_{12}$ is evidence in Fig. 2(a). The peak heights do not reflect intensities (see text).

has a very different ^{13}C NMR spectrum from that published.[3] The ^{13}C NMR spectra for the initial and subsequent samples of C_{84} are shown in Figs. 3(b) and 3(a), respectively.

A third yellow fraction consisted largely of dioctyl phthalate concentrated from the solvents used in processing.

A fourth yellow fraction was separated into two components of which the second was much the larger. Mass spectra [Figs. 4(a), 4(b)] indicated these components to consist respectively of C_{86}–C_{92} and mainly C_{90}/C_{92}, each with traces of C_{84}. The ^{13}C NMR spectra were obtained for each, but the quantities of

(a)

(b)

(c)

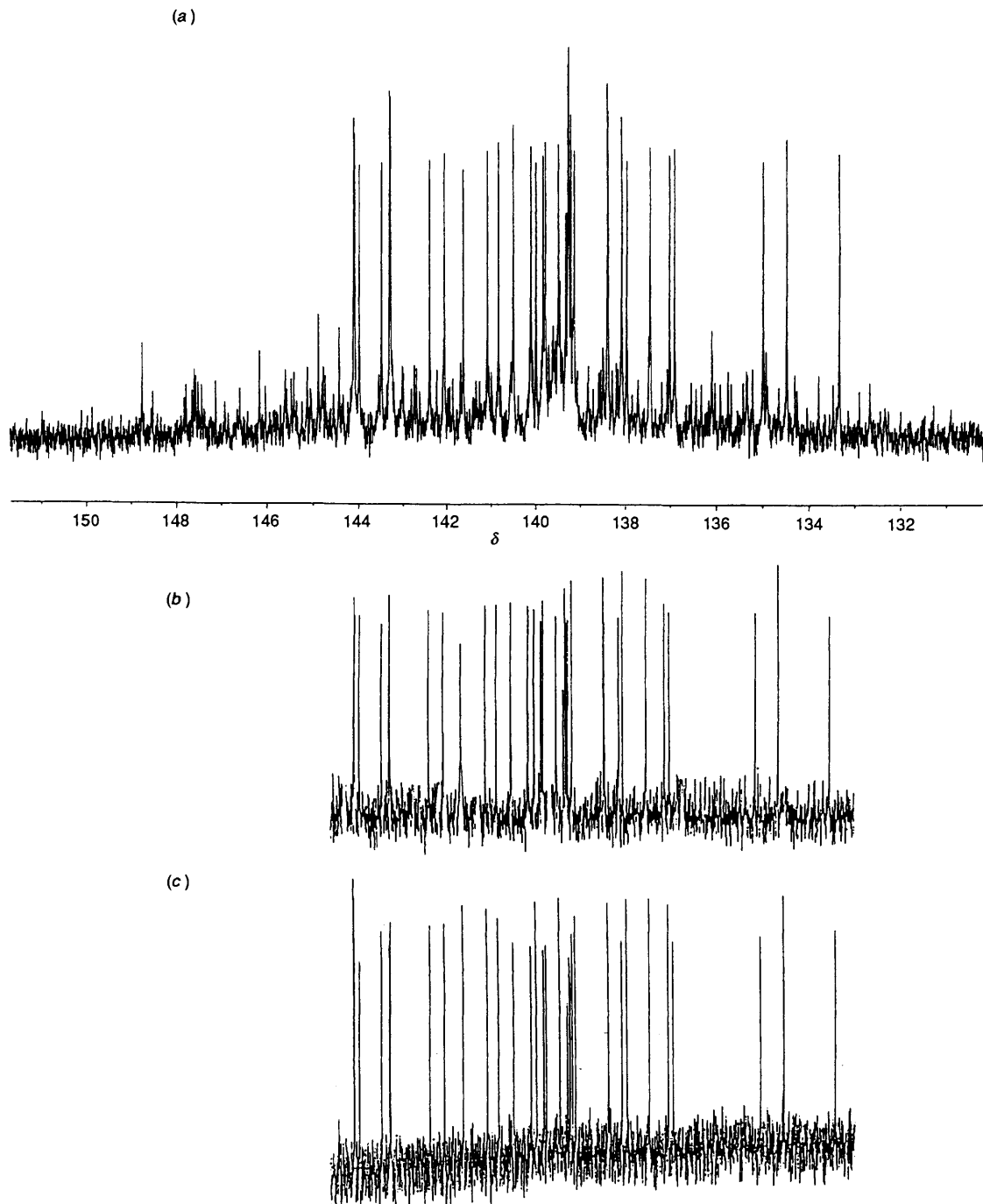**Fig. 3** ^{13}C NMR spectra for C_{84}: (a) new batch; (b) batch described in a preliminary publication;[5] (c) spectrum of Achiba *et al.*[3]

Table 3 ^{13}C NMR chemical shifts (δ) for a mixture of C_{86}, C_{88}, C_{90}, C_{92}[a,b,c]

157.14	154.88	152.39	151.39	145.44	144.53	138.40
156.26	153.63	151.96	150.13	145.10	144.37	134.96
155.29	152.94	151.80	149.46	144.91	141.78	128.63
154.99						

[a] All peaks relative to C_{60} at 142.68 ppm. [b] Only the peaks clearly distinguishable from the baseline are recorded (see text). [c] Peaks due to traces of C_{84} are not included.

Table 4 ^{13}C NMR chemical shifts (δ) for a mixture of C_{90}, C_{92} and C_{94}[a,b,c]

150.04	145.79	144.81	142.16	140.26	136.18	134.62	133.15
147.26	145.58	144.63	141.94	139.57	135.56	134.44	132.05
147.50	145.36	144.34	141.62	138.72	135.44	133.61	131.06
146.49	145.01	142.75	141.10	138.39	135.27	133.46	127.37

[a] All peaks relative to C_{60} at 142.68 ppm. [b] Only the peaks clearly distinguishable from the baseline are recorded (see text). [c] Peaks due to traces of C_{84} are not included.

material were insufficient to obtain peak intensities of sufficient reliability to permit identification of the isomers present. The peaks that were appreciably greater than background and not due to C_{84} are given in Tables 3 and 4, and may be useful for

comparative purposes as larger quantities of these fullerenes become available. The NMR spectrum for the second component fraction (Fig. 5) shows a small number of relatively intense peaks (see Discussion).
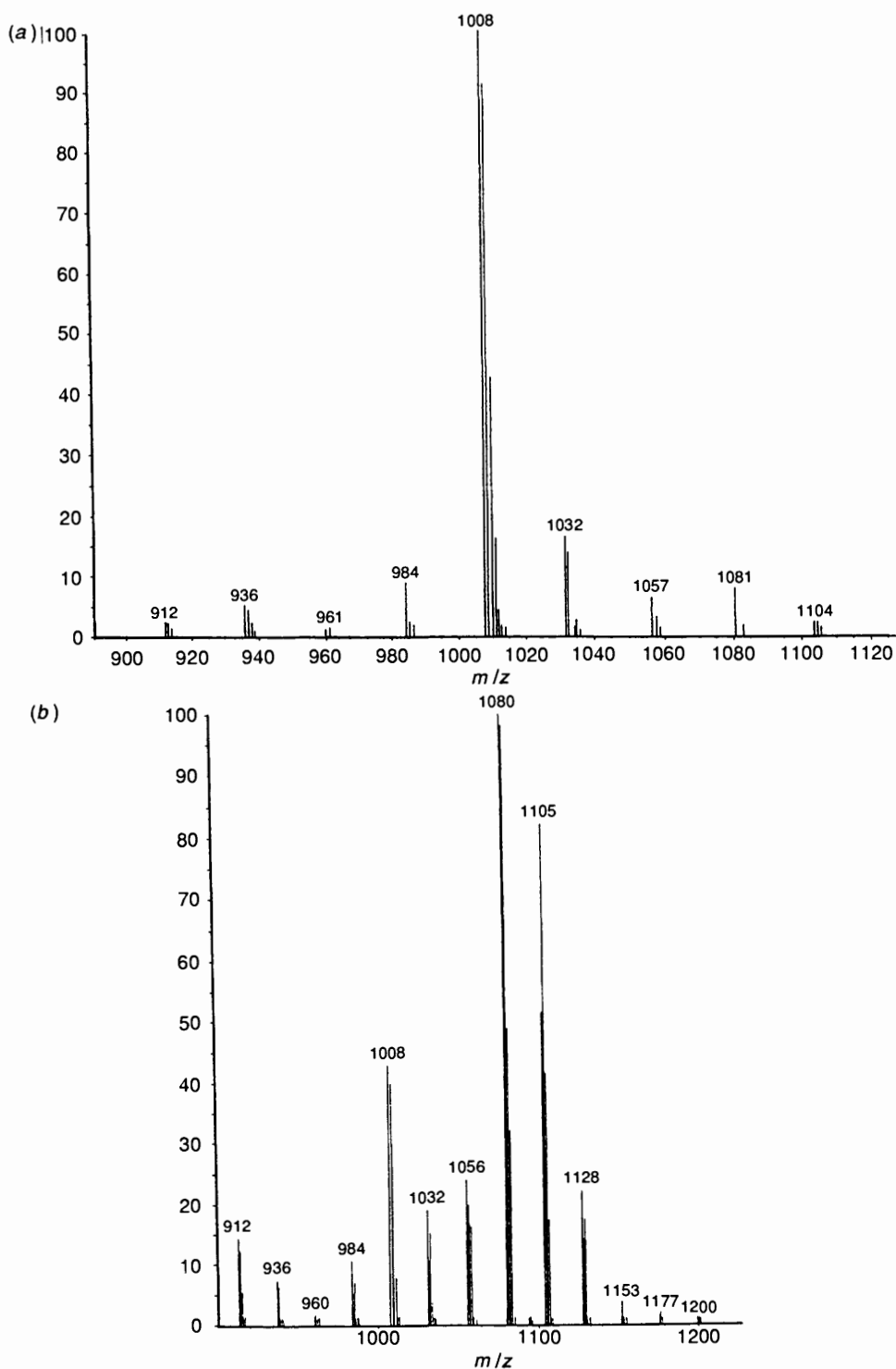
Fig. 4 Mass spectra of C_{84}–C_{92} and mainly C_{90}–C_{94}, respectively

A fifth yellow fraction was separated into five components, mass spectroscopic analysis of which indicated the presence of the following fullerenes: (1) up to C_{102}, especially C_{90-96}, but mainly C_{94}; (2) up to C_{104}, mainly C_{82} and C_{94}; (3) up to C_{108}, mainly C_{82} (Fig. 6); (4, 5) the mass spectrometry signal from these fractions was weak, but showed fullerenes up to C_{96}, with C_{90} the most intense. Note that in Fig. 6, the most intense peaks for fullerenes $> C_{88}$ appear at M + 1, due to the ^{13}C isotope effect.

Discussion

C_{76}.—The first sample [Fig. 1(a)] contained more C_{76} than did the second [Fig. 1(b)]. The chemical shifts for the nineteen peaks (Table 1) lie 0.54 ± 0.015 ppm upfield from those obtained by Diederich et al. (who used deuteriated acetone as the lock signal).[2] Comparison of Figs. 1(a) and (b) reveal that the variations in the peak intensities are fairly random, so that the products of the peak intensities for any given peak from the two spectra are constant to within $\pm 15\%$.

C_{78}.—There have been many calculations of the relative stabilities of the five isolated-pentagon isomers for C_{78} that are possible. Before discussing these it is necessary to clarify the nomenclature used to describe them. In the original paper by Fowler, Batten and Manolopoulos, the D_{3h}, D_{3h}, D_3, C_{2v} and
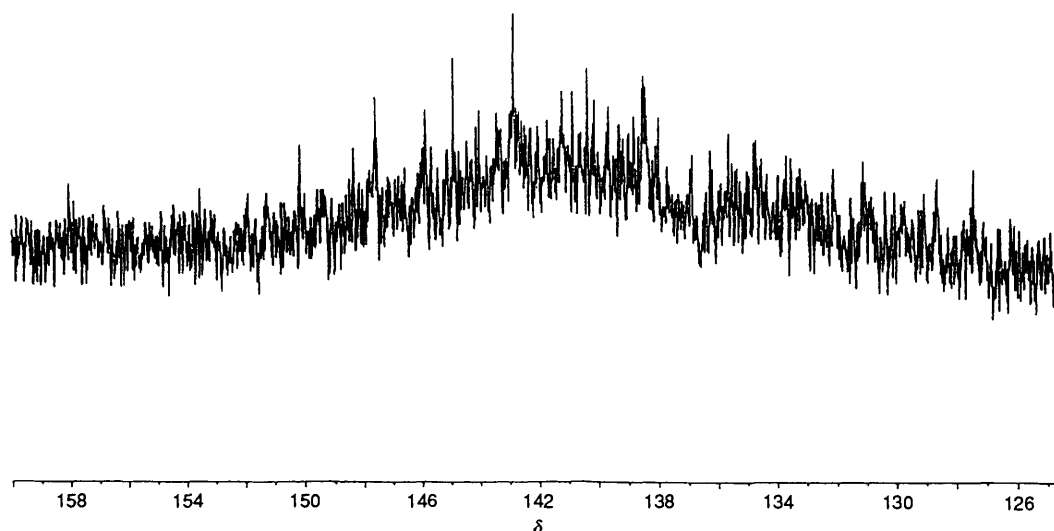
Fig. 5 ^{13}C NMR spectrum of sample giving the mass spectrum in Fig. 4(b)

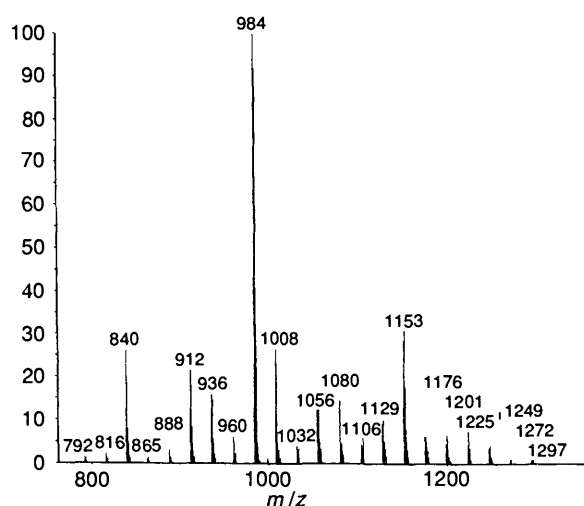**Fig. 6** Mass spectrum for C_{82} (see text)

C_{2v} isomers were numbered 1–5, respectively.[6] Subsequently these were referred to as the D_{3h}, $D_{3h'}$, D_3, C_{2v} and $C_{2v'}$ isomers,[1] the nomenclature used here. (Note that in a recent paper by Wang et al.[7] the D_{3h} isomers were labelled the opposite way around.) The isomers have also been referred to recently as D_{3h}(I), D_{3h}(II), D_3, C_{2v}(II) and C_{2v}(I), respectively.[8]

Both Hückel MO[6] and valence bond calculations[9] predict the stability order: $D_{3h} > C_{2v} > D_3 > C_{2v'} > D_{3h'}$. However, if allowance is made for poorer overlap due to the cage curvature (i.e. a smaller resonance integral β_{CC} is used) then the Hückel calculations predict the order: $C_{2v'} > D_{3h'} > C_{2v} > D_3 > D_{3h}$.[10] Indeed a series of ab initio, MNDO, AM1, MM3, PM3, and SCF calculations all predict the same order except that the $D_{3h'}$ and C_{2v} order is sometimes reversed.[10] The revised Hückel order is also predicted by tight-binding molecular dynamics.[7] A slightly different order: $C_{2v'} > C_{2v} > D_3 > D_{3h'} > D_{3h}$, is predicted by an SCF variant.[8]

In the preliminary communication[4] we reported that our sample of C_{78} contained the C_{2v} and D_3 isomers which had been reported previously.[1] We attributed a further 18 peaks in the ^{13}C NMR spectrum to the $C_{2v'}$ isomer (which requires 22 peaks); the full spectrum was reported by Achiba et al.[3] It is significant that this isomer was the major component in the latter work, a minor component in our work, and absent altogether in the sample studied by Diederich et al.[1] Fig. 1(a)

shows our spectrum of the sample containing the three C_{78} components.

A second significant feature was the absence of a peak for the D_3 isomer, predicted from the work of Diederich et al.,[2] to occur in our spectrum at 134.35 ppm, although we did observe a very small resonance at 134.29 ppm. On the other hand we observed an additional peak of the required intensity (the D_3 isomer should give 13 lines of equal intensity) at 141.21 ppm. Fig. 1(b) shows the ^{13}C NMR spectrum of the new batch of processed material. Significant features of this spectrum, and the comparison with Fig. 1(a), are as follows.

(1) The greater resolution in Fig. 1(b) compared to Fig. 1(a) and the smaller amount of C_{76} present, makes it possible to distinguish all 22 peaks for the C_{2v} isomer.

(2) The proportions of the C_{2v}, D_3 and $C_{2v'}$ isomers in the two batches are similar, viz. 52:29:19% (batch 1) and 52:32:16% (batch 2), respectively. This similarity, despite inevitable differences in processing, indicates that variations in the isomer composition of C_{78} obtained by different groups arise from differences in the arc-discharge method employed. It is possible that differences in temperature and/or helium pressure are responsible for the different isomer yields. However, the conditions in the plasma are so complex that it is unlikely that simple evaluation is possible at this stage. Ultimately it may be possible to optimise conditions for the formation of any particular isomer, and perhaps obtain the other two isomers of C_{78} which have not yet been isolated.[6]

(3) The greater $D_3/C_{2v'}$ ratio in the second batch permits more reliable identification of the peaks due to the D_3 isomer. In the preliminary communication,[4] we reasoned (from comparison of our data with those of Achiba and co-workers) that the 141.23 ppm peak is due to the D_3 isomer, and that the 134.35 ppm peak is one of the five half-intensity peaks for the $C_{2v'}$ isomer. This conclusion is now confirmed by the new results, the intensity for the peak at 141.23 ppm is exactly equal to the average intensity for the other twelve peaks due to the D_3 isomer. The peak at 134.35 ppm has only 27% of the intensity required for the D_3 isomer, but has almost exactly the intensity required for a minor peak of the $C_{2v'}$ isomer.

C_{84}.—Achiba and co-workers[3] described a 32 peak spectrum (31 lines of unit intensity, and 1 line of half intensity) for C_{84}, interpreted in terms of a 2:1 mixture of a D_2 isomer (21 equal intensity lines) and a D_{2d} isomer (10 equal intensity lines, plus 1 line of half intensity). (Recent calculations predict these isomers

to be the most stable ones.[11,12]) The published spectrum of Achiba and co-workers is reproduced in Fig. 3(c).

Given the wide variation in isomer ratios found for C_{78}, one would not *a priori* anticipate obtaining the same spectrum for C_{84} produced under different conditions. Nevertheless, Fig. 3(b) is the spectrum reproduced from our first C_{84} preparation,[5] and comparison with Fig. 3(c) shows a remarkable similarity. [Note that for clarity of presentation, some additional lines due to C_{60}, C_{70} and other minor components were deleted from Fig. 3(b).[5]] A spectrum consisting of 31 lines of approximately equal intensity (the half intensity line was unresolved) has also been reported.[13] Since the same isomer ratios are apparently being produced irrespective of the reaction conditions, this indicates that C_{84} consists largely of a thermodynamic mixture of two isoenergetic isomers. This deduction reduces the possibilities to one specific D_{2d} isomer and one specific D_2 isomer (which can readily interconvert), the involvement of the two enantiomers of the latter being the origin of the respective 1:2 isomer ratio.[5]

To examine this aspect further and to confirm our preliminary result a second purer batch of C_{84} was prepared, the full spectrum being given in Fig. 3(a). Again there is very good reproducibility of the spectrum. Minor variations between Figs. 3(a), (b) and (c) occur in a random way, hence it is not possible at present to associate given lines with any particular isomer. The data from Figs. 3(b) and 3(c) agree to within ± 0.005 ppm for any given resonance, and the values (relative to C_{60} at 142.68 ppm[14]) are given in Table 1.

At least 77 minor peaks are present in the spectrum of C_{84}. These do not correspond to either C_{76}, C_{78}, or the published spectrum for C_{82},[3] and we conclude that they arise from other C_{84} isomers. At present it is not possible to identify the isomers concerned, especially as some lines occur on the shoulders of larger ones, making their intensities somewhat uncertain. The present results will however provide a comparison for subsequent work, and the peak locations are given in Table 3. We note that 11 peaks at 148.69, 146.10, 144.82, 144.37, 141.63, 140.00, 139.54, 139.39, 138.43, 136.03 and 134.86 ppm exhibit substantially enhanced intensities and probably arise from isomers of relatively high symmetry.

Manolopoulos and Fowler have calculated the ^{13}C NMR patterns for all isolated-pentagon isomers of C_{84}.[15] Apart from the D_{2d} isomer, only four others have relatively high symmetries capable of generating an NMR spectrum consisting of few lines. These are a D_{2d} isomer [12 lines, $(3 \times 1) + (9 \times 2)$], D_{3d} [8 lines, $(4 \times 1) + (6 \times 2)$], T_d [4 lines, $(1 \times 1) + (3 \times 2)$], and D_{6h} [5 lines, $(3 \times 1) + (2 \times 2)$]. The calculations that predict the most stable isomers of C_{84} to be the D_2 and D_{2d} ones,[12] also predict high stability for the D_{6h} and D_{3d} isomers (but not for the others). Moreover, each of these latter two isomers is only two Stone-Wales transformations (*via* a C_s isomer)[16] from the particular D_2 isomer known to be present. A 2:1 ratio of the D_{3d} and D_{6h} isomers would produce 11 lines of similar intensity. This offers a reasonable explanation of the data, given the present degree of accuracy.

Also predicted to be stable are the C_s isomer noted above, and also a C_2 isomer. These will generate a 43 line spectrum $[(2 \times 1) + (41 \times 2)]$ and a 42 line spectrum $[42 \times 2]$, respectively. One of these isomers may account for the many other lines in the spectrum; other isomers will generate spectra of *ca.* 20 or 40 lines, so overall the presence of many background lines in our spectrum is not surprising.

C_{90}–C_{94}.—The ^{13}C NMR spectrum for the fraction producing the mass spectrum shown on Fig. 4(b), is shown in Fig. 5. The occurrence of a small number of relatively intense peaks suggests that a high symmetry isomer is present. There appear to be six peaks with greater intensity than the others,

conceivably due to the D_{6h} isomer of C_{90}. This has been prediced to have high stability,[9,17] and should give rise to a six-line spectrum with peak intensities, $(3 \times 1) + (3 \times 2)$.[9]

C_{82}.—The long retention time for this fullerene is surprising. There has only been one other chromatographic separation of C_{82}, and this used CS_2 as the solvent, whereby C_{82} eluted between C_{78} and C_{84}.[18] (The figure shown[18] indicates that the fullerenes eluted in reverse molecular weight order, but this may be a presentation error.) In that study it was noted that a C_{3v} isomer of C_{82} may have been present as a minor batch-dependent product. Moreover, it was implied[18] that a general preparation-dependent formation accounted for the absence of C_{82} in the sample of Diederich and Whetten.[14]

Since the fullerenes have hitherto been found to elute in inverse molecular weight order, the principal C_{82} isomer produced by our equipment evidently has a property that sets it apart from the other fullerenes. We suggest it is the C_{3v} isomer since it will be polar, unlike all other fullerenes isolated to date. (This polarity arises because the molecule is asymmetric along the 3v symmetry axis.) Moreover, the preponderence of this isomer in our material is consistent with the previous indication[3] that the formation is preparation dependent. Given the unexpected elution (after C_{96} etc.), it is possible that some may have been produced, though not isolated, by Diederich and Whetten.[14]

Our results may have important bearing on the propensity for C_{82} to form endohedral complexes,[19] and the belief that the C_{3v} isomer is involved in the formation of $Sc_3@C_{82}$, which, moreover, shows different chromatographic behaviour to $Sc_2@C_{82}$.[20]

Finally we note that the material with longest retention time in these experiments was mainly C_{90}, whereas the bulk of C_{90} had already eluted. This result suggests that a second (more polar) isomer of this fullerene is also present.

$C_{70}H_{12}$.—The mass spectrum of a sample obtained during a preliminary HPLC purification of C_{84} showed a peak at $m/z = 852$. The sample was subjected to further HPLC purification, but as the peak was retained [Fig. 2(a)], the material evidently coelutes with C_{84}.

Since odd-numbered fullerenes cannot exist the material cannot be C_{71}. Moreover, fullerenes fragment by loss of 24 amu (C_2) and 48 amu $(2 \times C_2)$, and do not show $M^+ - 1$, $M^+ - 2$ etc. ions. By contrast the sample showed loss of up to 4 amu. Only $C_{70}H_{12}$ is consistent with this observation, a conclusion confirmed by accurate mass measurement which gave $m/z = 852.0946$, *cf.* 852.0939 calculated (and 852.0000 for C_{71}).

The addition of 12 atoms to a molecule of five-fold symmetry may appear surprising. However it is reasonable to assume that the most stable fullerene derivatives will be those with the highest symmetry and thus the least polar. The interpentagonal bonds in C_{70} calculated to have the highest π-density are those either exocyclic to the pentagonal cap, or parallel to it, the π-bond orders being 0.597 and 0.602, respectively. Thus addition could be expected to occur near the polar caps, and in order to maintain symmetry along the long axis, four hydrogens must be added. However this process will create polarity orthogonal to the long axis, which can be minimised by addition of another eight hydrogens (four at each cap) as shown in Fig. 7(a). All other addition combinations (either 2, 4, 6, 8, hydrogens exocyclic to each cap) will produce a more polar product. [An alternative possibility is that the extra four hydrogens may add as shown in Fig. 7(b).[21]]

The proton NMR of the fraction containing $C_{70}H_{12}$ showed two uncoupled doublets centred at 6.15 and 5.87 ppm (relative intensities 2:1). It is relevant therefore that the proton NMR of $C_{60}H_2$ shows a singlet at 5.93 ppm.[21] The signal appears at this
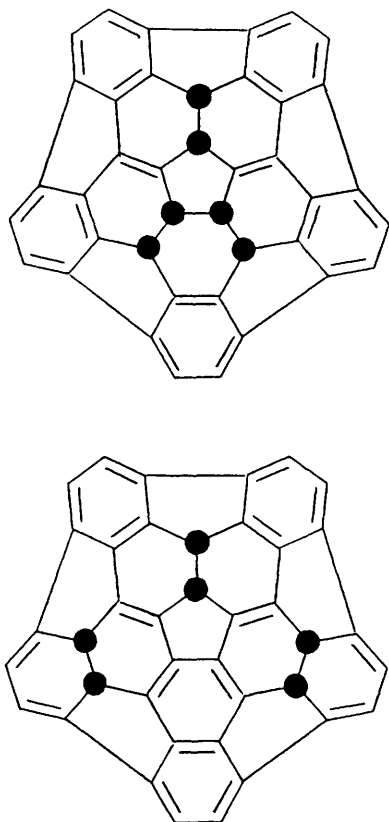
Fig. 7 End cap of C_{70} showing possible sites for hydrogen addition in $C_{70}H_{12}$ (see text)

leading us to the interesting conclusion that C_{70} may dehydrogenate some of the hexane producing a volatile component with a strong UV absorption.

position if the hydrogens are isolated, i.e. adjacent to two sp^2-hybridised carbons. This result tends to support the variant in Fig. 7(b), though there is a difficulty with either interpretation in that although the peak intensities are correct, splitting would be expected. However the expected splitting in cyclohexa-1,4-diene is absent for example, so coupling may be too small to be observed in each case. Some minor peaks were also found between 3.33 and 4.13 ppm.

The origin of $C_{70}H_{12}$ is unclear. The higher fullerenes were recovered from very large volumes of hexane, used as eluent in the isolation of 450 mg of pure (> 99%) C_{70} by HPLC. If the C_{70}-containing hexane solutions were allowed to stand after initial processing, then a large peak (UV detector) with a low retention time appeared. However, collection of these samples and evaporation of the solutions to dryness yielded no residue,

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