# A Mass Spectrometric–NMR Study of Fullerene-78 Isomers

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Three isomers of $C_{78}$ have been detected by ^{13}C NMR spectroscopy; one of the signals ascribed in the literature to the $D_3$ isomer is absent from our spectrum.

Fullerene-78, first isolated by Diederich et al.,[1] is of particular interest because of the five possible isomers conforming to the pentagon isolation rule (PIR);[2,3] two (with $C_{2v}$ and $D_3$ symmetry) have been identified[4] from their ^{13}C NMR spectra. Diederich et al.[4] have pointed out that the five fullerene-78 isomers predicted to be stable by Fowler and Manolopoulos[5] can be divided into two sets: one consisting solely of the $D_3$ isomer, and the other of the remaining four ($D_{3h}$, $C_{2v}$, $C_{2v'}$ and $D_{3h'}$), the latter group being interconvertible by Stone–Wales pyracyclene transformations (SWPT).[6] Diederich et al. also suggested that these other isomers were absent because they had readily converted into the $C_{2v}$ isomer, conceivably the most stable member of the SWPT-linked set. The $D_{3h}$ and $C_{2v}$ isomers are predicted to be particularly susceptible to additions.[7]

The $C_{2v}$ isomer exhibits one group of eighteen lines and another group of three lines (peak height ratio = 2:1),[4] as predicted.[5] Thirteen lines, reported to be of equal intensity, were assigned on the basis of the Fower–Manolopoulos work[5] to the $D_3$ isomer, and the $C_{2v}:D_3$ ratio was estimated to be 5:1.[4] We have reproduced the spectrum of the $C_{2v}$ isomer but have located only twelve of the reported[4] thirteen lines attributed to the $D_3$ species. In addition, we have detected eighteen further lines which we propose belong to a third isomer. The major problem in obtaining an unambiguous assignment lies in the difficulty in chromatographically resol-

ving the various components, in particular separation of the fullerene-78 group from fullerene-76 (^{13}C NMR spectrum, see ref. 8).

The original fullerene separation technique[9] was used. Soxhlet extraction (chloroform and dichloromethane) of soot produced by the carbon-arc procedure,[10,11] followed by concentration and elution of the extract with hexane from neutral alumina columns removed most of the $C_{60}$ and $C_{70}$. The columns were then stripped with carbon tetrachloride to give yellowish solutions, the mass spectra of which revealed the presence of $C_{76}$, $C_{78}$, $C_{82}$, $C_{84}$ and higher fullerenes $\leq C_{102}$ (Fig. 1). The combined solutions were evaporated to dryness and the residue was dissolved in hexane and chromatographed using a Gilson high pressure liquid chromatogram equipped with a 41.4 mm × 25 cm preparative Rainin Dynamax 60 A column (8 μm cyano) operating at 45 bar [elution with hexane (20 l pumped per day); typical injection = 30 cm³: run time = 28 min]. Residual $C_{60}$ and $C_{70}$ eluted initially, followed by three yellow fractions and one red–brown fraction (subsequent fractions, containing higher fullerenes, were combined and concentrated pending reprocessing). The first yellow fraction was rechromatographed twice in order to eliminate the second yellow fraction together with all but traces of $C_{60}$ and $C_{70}$ which were deliberately retained for reference purposes. The EI positive ion mass spectrum (heated probe) showed the first yellow fraction (Fig. 2) to contain $C_{76}$ and $C_{78}$
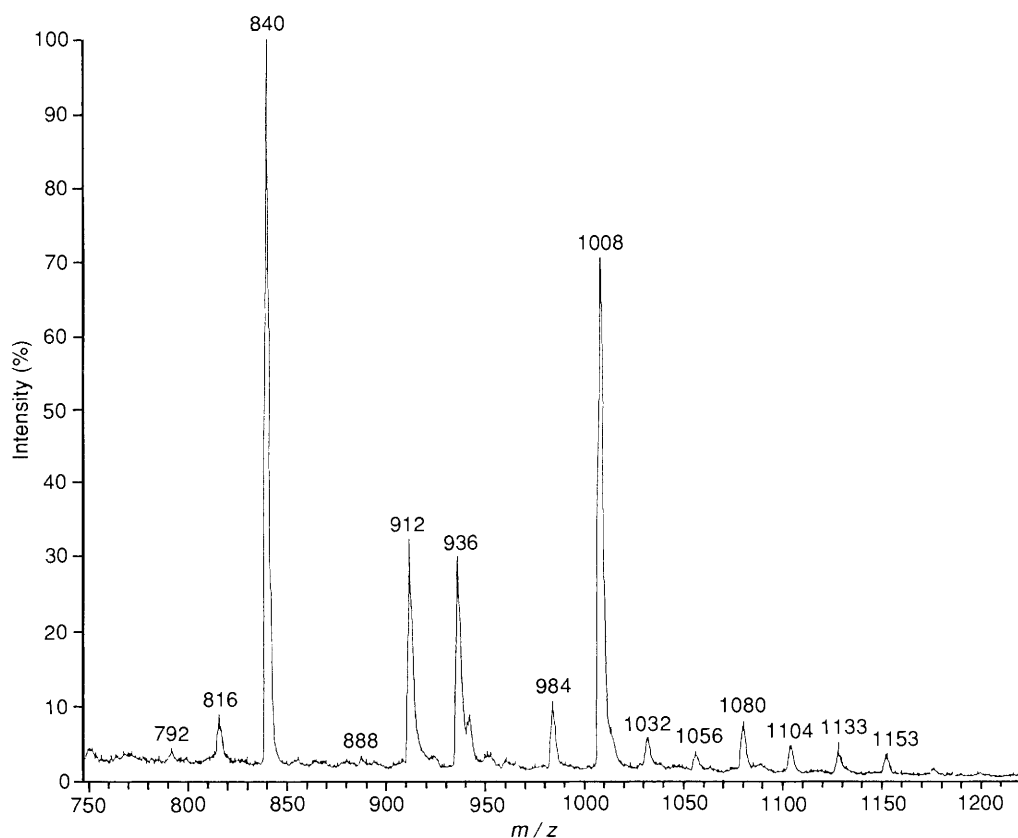


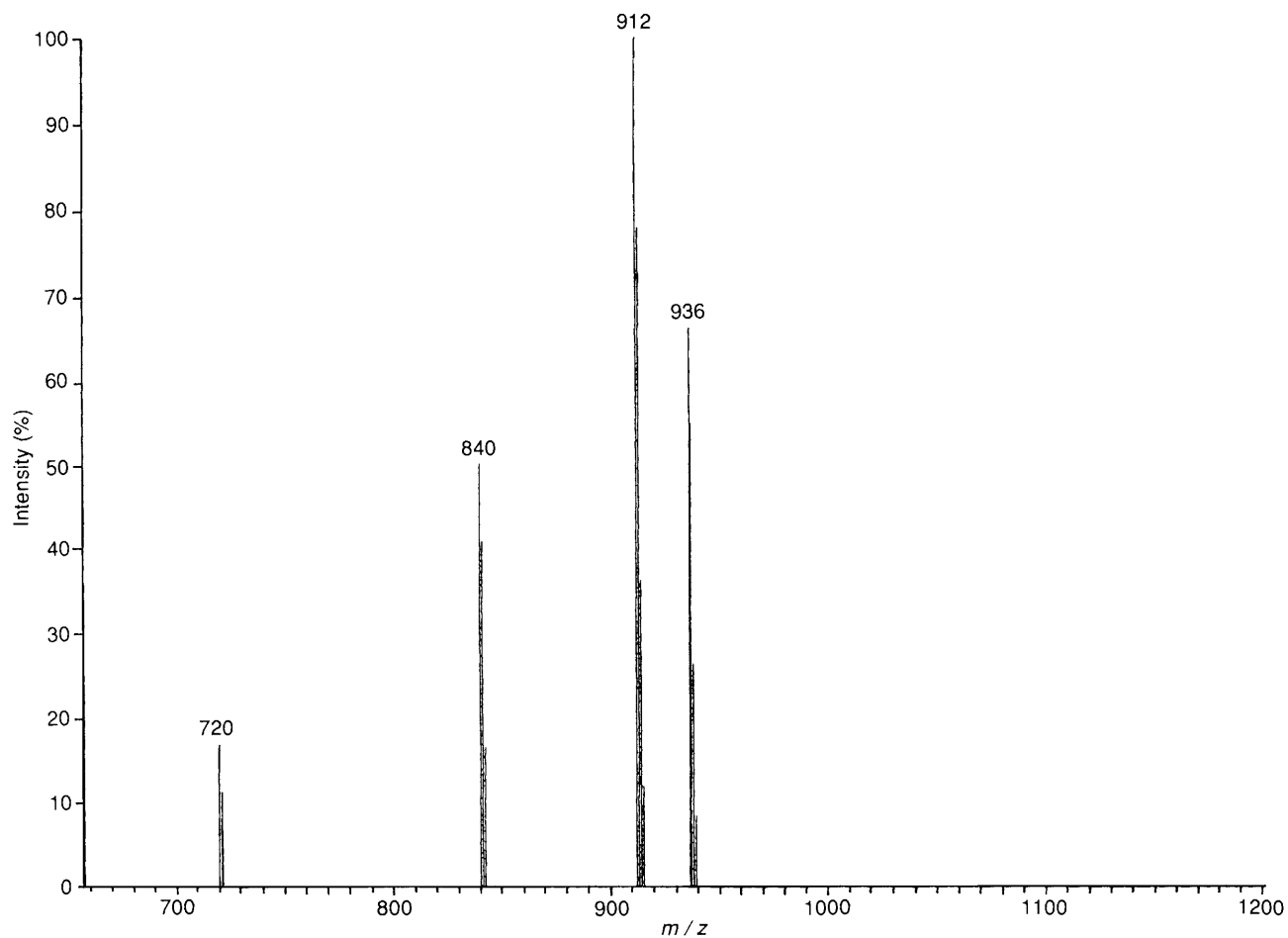Fig. 1 Mass spectrum of soot extract after partial removal of $C_{60}$ and $C_{70}$

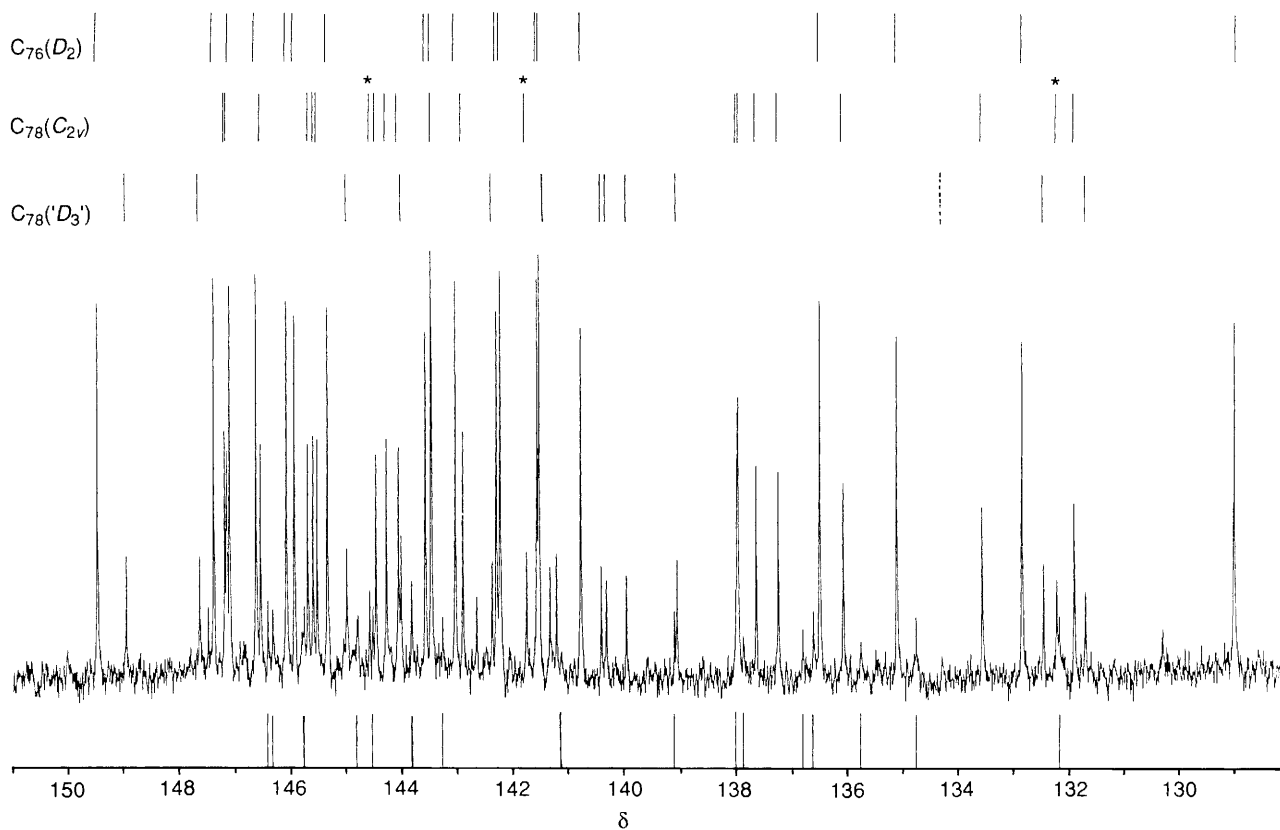**Fig. 2** Mass spectrum of purified $C_{76}/C_{78}$ containing < 1% each of $C_{60}$ and $C_{70}$



**Fig. 3** ^{13}C NMR spectrum of $C_{76}$ and $C_{78}$

**Table 1** $^{13}$C NMR shifts ($\delta$ in ppm)$^a$ for C$_{76}$ and C$_{78}$

| C$_{76}$(D$_2$) | Intensity | C$_{78}$(C$_{2v}$) | Intensity | C$_{78}$(D$_3$) | Intensity | C$_{78}$(C$_{2v'}$) | Intensity |
|---|---|---|---|---|---|---|---|
| 149.46 | 6.6 | 147.18 | 4.33 | 148.94 | 2.14 | 146.41 | 1.31 |
| 147.38 | 7.0 | 147.14 | 4.00 | 147.63 | 2.14 | 146.32 | 1.15 |
| 147.09 | 6.9 | 146.54 | 4.11 | 144.99 | 2.27 | 145.76 | 1.20$^b$ |
| 146.62 | 7.1 | 145.69 | 4.09 | 144.01 | 2.53 | 144.82 | 1.27 |
| 146.08 | 6.7 | 145.60 | 4.24 | 142.37 | 2.03 | 144.52 | 1.35 |
| 145.93 | 6.4 | 145.52 | 4.18 | 141.33 | 1.93 | 143.83 | 1.62$^c$ |
| 145.33 | 6.5 | 144.58 | 1.50 | 140.40 | 1.96 | 143.81 | 1.05$^c$ |
| 143.57 | 6.1 | 144.46 | 3.90 | 140.31 | 1.68 | 143.26 | 1.01 |
| 143.47 | 7.5 | 144.27 | 4.18 | 139.95 | 1.77 | 141.21 | 2.18 |
| 143.03 | 7.0 | 144.06 | 4.03 | 139.05 | 2.05 | 139.10 | 1.14 |
| 142.29 | 6.5 | 143.45 | 4.20$^c$ | 132.45 | 1.98 | 138.00 | 0.80 |
| 142.22 | 7.1 | 142.90 | 4.33 | 131.69 | 1.49 | 137.85 | 0.73 |
| 141.56 | 7.0 | 141.75 | 2.21 | | | 136.79 | 0.92 |
| 141.52 | 7.5 | 137.98 | 4.63$^c$ | | | 136.61 | 1.20 |
| 140.77 | 6.2 | 137.96 | 4.98$^c$ | | | 135.75 | 0.65 |
| 136.49 | 6.6 | 137.63 | 3.85 | | | 134.75 | 1.13 |
| 135.01 | 6.0 | 137.24 | 3.77 | | | 132.18 | 1.13 |
| 132.84 | 5.9 | 136.07 | 3.52 | | | | |
| 129.00 | 6.2 | 133.56 | 3.03 | | | | |
| | | 132.21 | 2.10 | | | | |
| | | 131.89 | 3.06 | | | | |

$^a$ Relative to C$_{60}$ at $\delta$ 142.67. $^b$ Two almost coincident peaks. $^c$ Shoulder.

but no higher fullerenes. [Owing to their higher volatility the amounts of C$_{60}$ and C$_{70}$ in the sample are greatly exaggerated in the mass spectrum. The $^{13}$C NMR spectrum indicates that approximately equal amounts of C$_{76}$ and C$_{78}$ are present. The greater mass spectral intensity of C$_{76}$ is due to the inverse relationship between intensity and volatility (mass-dependent) and, we also suggest, because C$_2$ extrusion from C$_{78}$ should be particularly facile in view of the stability of C$_{76}$.] Resolution of C$_{76}$ and C$_{78}$ was not attempted owing to lack of resources. The UV spectrum exhibited maxima at 316, 317, 358, 376, 408, 432, 469, 526, 638, 710, 752, 768 and 820 nm consistent with data already reported.$^{4,8}$ The $^{13}$C NMR spectrum of the mixture [CS$_2$ solution, added Cr(acac)$_3$ (Hacac = pentane-2,4-dione), CDCl$_3$ internal lock, 190000 scans, Bruker 500 MHz instrument] is shown in Fig. 3 (expanded version, see Fig. 4). The small C$_{60}$ line at $\delta$ 142.67 serves as a reference for the entire spectrum. C$_{70}$ peaks are discernible at 150.05, 147.48, 146.82, 144.78 and 130.29; all of these peaks are within $\pm$0.02 ppm of values previously described.$^9$

The C$_{76}$(D$_2$) (main component; Fig. 3 top) $^{13}$C NMR spectrum consists of 19 lines of approximately equal intensity (Table 1); each line is 0.575 $\pm$ 0.015 ppm upfield from the values previously reported (acetone lock).$^8$ The second row identifies and confirms all the lines reported for C$_{78}$(C$_{2v}$) (starred peaks, half intensity), the lines (Table 1) being 0.44 $\pm$ 0.02 ppm upfield compared to the earlier report (acetone lock).$^4$

The third row corresponds to peaks attributed to C$_{78}$(D$_3$).$^4$ However, only twelve of the thirteen peaks cited (all 0.50 $\pm$ 0.04 ppm upfield, lock not quoted) are present. The peak which, according to ref. 4, should appear at $\delta$ 134.35, is absent. Although there is a very weak feature at $\delta$ 134.29, it is an order of magnitude lower in intensity than that required to fit the proposed D$_3$ structure.$^4$ We conclude from this observation that *either* the proposed structure is incorrect *or* that, more likely, the thirteenth peak lies elsewhere. As the original assignment was made on a sample containing C$_{76}$,$^4$ a possible explanation is that this line is overlapped. (Expansion of our spectrum in the $\delta$ 131.5–132.5 region shows that the D$_3$ peak at $\delta$ 131.69 appears to be a triplet and the peak at $\delta$ 132.5 a doublet, a feature we hope subsequently to investigate further.)

Our NMR spectrum also reveals the presence of at least one further component commensurate with a third fullerene-78 isomer on the basis of mass spectrometry. The eighteen new NMR peaks are identified at the bottom of Fig. 3 and the shifts and intensities are recorded in Table 1 (column 4). The other isomers: C$_{2v'}$, D$_{3h}$ and D$_{3h'}$, should have 22 [17(4C) + 5(2C)], 8[5(12C) + 3(6C)] and 8[5(12C) + 3(6C)] lines respectively.$^5$ On the basis of this circumstantial evidence we tentatively suggest that the new lines probably belong to the C$_{2v'}$ isomer, especially as eighteen is a lower limit for the number of lines in the spectrum. Note that the only other C$_{76}$ isomer allowed by the PIR$^{2,3}$ has $T_d$ symmetry and should exhibit five lines (ratio 1 : 3 : 3 : 6 : 6).$^{12}$

The relative stabilities of the various fullerene isomers pose important questions. Fowler and Manolopoulos have studied the effect of electronic factors using MO theory$^5$ and Taylor$^{13}$ has discussed them from the VB point of view. Diederich *et al.*$^4$ on the other hand have emphasised skeletal strain. It still remains to be seen precisely how important these factors actually are. In this context, the recent observation that corannulene can invert$^{14}$ indicates how limited our understanding is of out-of-plane strain (OOPS) in the context of these novel extended carbon network molecules. It is interesting to note that in the original study$^4$ the C$_{2v}$ : D$_3$ ratio was 5 : 1, whereas in our work the ratio is *ca.* 3 : 1 and a new isomer has been detected. The identification of a third fullerene-78 isomer, coupled with its lack of detection in the original study,$^4$ suggests that interconversion within a SWPT-linked manifold may not be facile. On the other hand, if the noise level in that study$^4$ was such that the third isomer was obscured, a SWPT interconversion may still be facile and our observed fullerene-78 distribution may represent the population at thermal equilibrium. Clearly there are difficulties in advancing detailed mechanistic arguments applicable to these systems, as the materials are produced in carbon arcs operating at high temperatures in excess of 2000–3000 K and in the presence of very high UV fluxes. Under such conditions almost all types of skeletal rearrangements are feasible and the isomer distribution may depend upon conditions associated with diverse fullerene production methods rather than their intrinsic relative stabilities. Although criteria for SWPT transformations, which are thermally forbidden but photochemically allowed, have been set, as yet it is not clear that such processes significantly reduce the plethora of higher fullerene isomers which may be realised in practice.
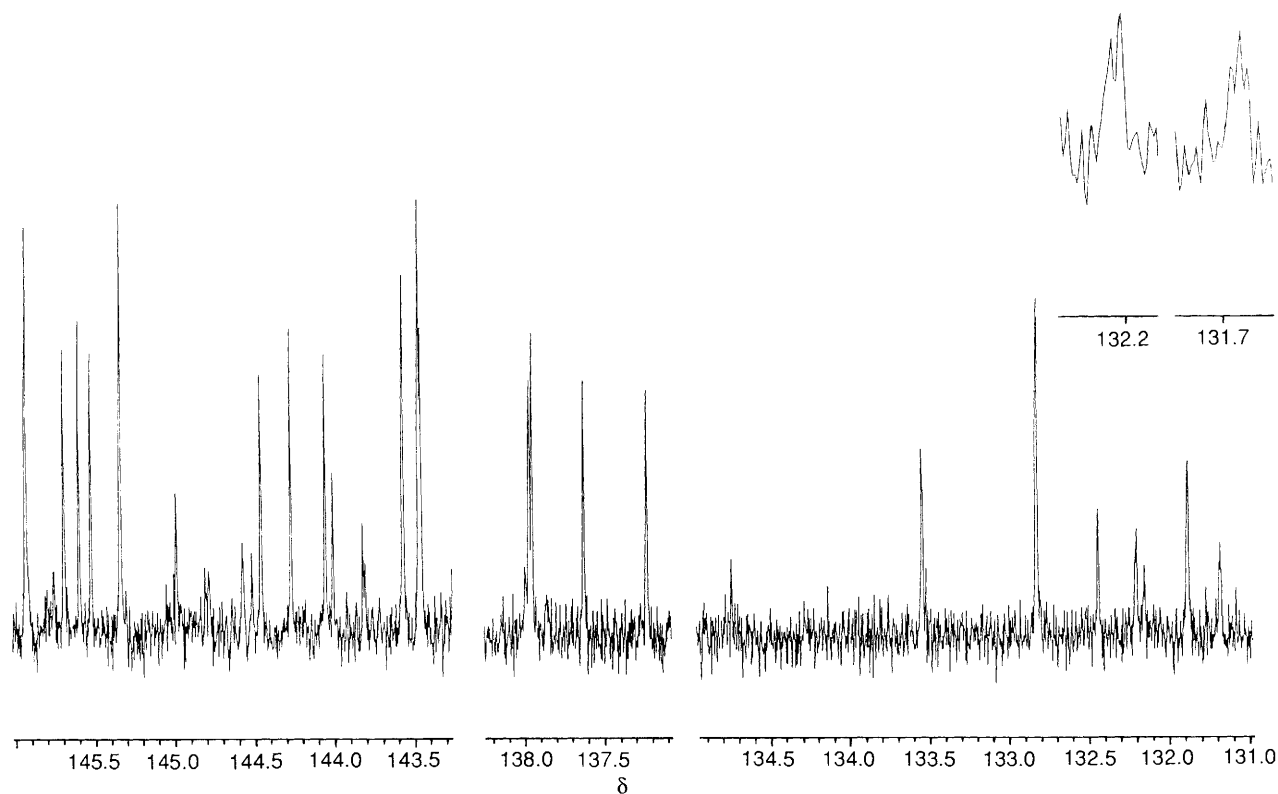
**Fig. 4** Expansion of sections of $^{13}C$ NMR spectrum of $C_{76}$ and $C_{78}$

## Added in proof

Achiba and coworkers[15] have now reported that they also find the $C_{2v'}$ isomer of $C_{78}$, giving 22 peaks, 18 of which agree precisely with those reported here (0.60 ± 0.02 ppm lock shift). Two of the additional peaks should be of half intensity, at δ 146.91 and 146.82, and are just discernible in our spectrum. The other two peaks (at δ 142.22 and 136.48) coincide with two of the $C_{76}$ peaks and so are not discernible. They find the $C_{2v'}$ isomer to be the major one, and from comparison of both spectra, it is possible to deduce that the weak feature noted (above) at δ 134.29 is one of the *minor* $C_{2v'}$ *peaks* whereas the peak at δ 141.21 is the *'missing' one for the* $D_3$ *isomer*. The intensity of this peak (Table 1) also indicates that it belongs to the $D_3$ isomer, rather than the $C_{2v'}$ one.

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