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Isolation, characterization, and chemical reactions of fullerenes

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Abstract Extension of the chromatographic work that led to the first isolation of pure C_{60} and C_{70} has resulted in the isolation and characterisation of C_{76} and three isomers of C_{78}. Comparison with other work indicates the composition ratio of C_{78} to be dependent upon the method of carbon production. Halogenation of C_{60} gives derivatives that have been characterised either by NMR, or by single crystal X-ray diffraction. The halogeno derivatives readily undergo nucleophilic substitution, which provides a route to the formation of many fullerene compounds, but precludes use of the fluoro derivatives as lubricants. In the presence of Friedel-Crafts catalysts, the bromo derivatives substitute into aromatics to give aryl derivatives of C_{60}, especially those containing either 6, 8, 12, or 16 aryl groups per C_{60} molecule. Possible structures for these are compared with those for addition products which have only low eclipsing steric interactions.

My involvement in fullerenes stemmed from work on electrophilic aromatic substitution (especially hydrogen exchange) of novel aromatics and in particular those with distorted benzenoid rings (ref. 1). This led to an interest in determining the reactivity of corannulene and the difficult 16-step synthesis given in the literature (ref. 2) was undertaken, the expected overall yield (0.3%) being sufficient for hydrogen exchange studies. Whilst this work was underway, the evidence for the existence of C_{60} was reported (ref. 3) and this intensified interest in corannulene: if appropriate fully carboannelated derivatives could be synthesised then they might react readily together to give C_{60} ('zip-fastener synthesis'). A higher yield synthetic route to making corannulene would clearly be necessary, and one based on fluoranthene which it was thought might achieve this, was devised. Funding was sought (together with Harry Kroto) for this work, but the referees considered the synthesis to be too speculative. Interestingly, a successful fluoranthene-based synthesis of corannulene has been reported recently by Scott and coworkers (ref. 4).

ISOLATION AND CHARACTERISATION OF PURE C_{60} AND C_{70}

All thoughts of continuing with the C_{60} synthesis were abandoned when we became aware of the success of Kraetschmer and Huffman and their coworkers in showing the presence of C_{60} and C_{70} in soot produced by the arc-discharge of graphite rods in helium (ref. 5). It seemed probable that use of separation techniques commonly used in organic chemistry might lead to successful isolation of pure fullerene. Accordingly I soxhlet extracted (using chloroform) 200 mg of soot that Kroto and Jonathan Hare had accumulated during the preceding months from similar arc-discharge experiments. The brown-black extract was found to be slightly soluble in hexane which suggested that column chromatography might result in separation. A slurry of the extract (ca. 8 mg) with benzene and silica (ca. 1 g), evaporated to dryness, was placed at the top of a 1 cm x 40 cm column, packed with neutral Woelm alumina. The latter was left over from work described in ref. 1, and had fortunately acquired a small water content. (Subsequent work showed anhydrous alumina to be particularly aggressive towards C_{70}.) Elution was carried out with just 500 ml of spectroscopic grade hexane (the total departmental stock - no more could be procured quickly). Astonishingly, a magenta band appeared on the column followed by a pink one, at which point the traffic through my lab-office to see the phenomenon became quite intense. Light-hearted speculations that these bands were C_{60} and C_{70} respectively, proved in the event to be correct as shown by mass spectra obtained by VG instruments (and subsequently in house, Fig.1). The pure fullerenes were obtained for the first time on 22nd August, 1990.

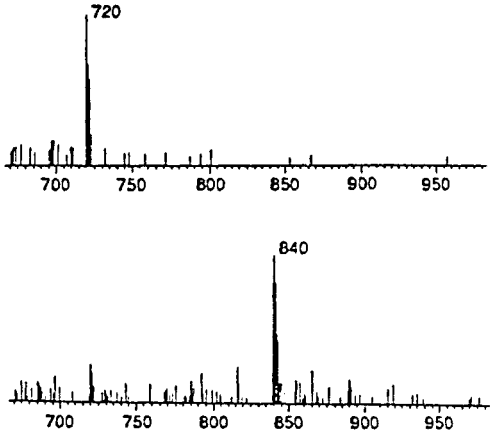

Fig. 1. Mass spectra of C_{60} (above) and C_{70} (below)

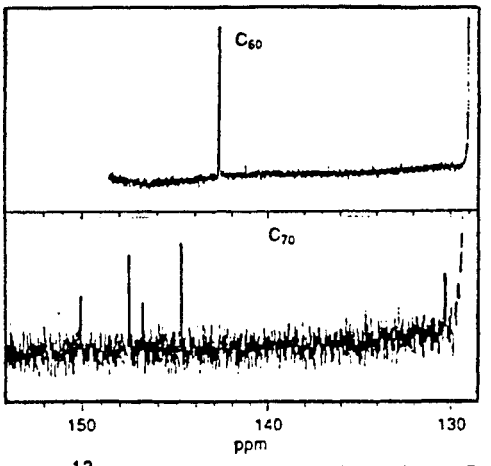

Fig. 2. ^{13}C NMR spectra of C_{60} (above) and C_{70} (below) that proved that the fullerenes were cages

Further extract was then run on a 2 cm x 40cm column (flash chromatography conditions) to provide sufficient material for the critical ^{13}C NMR spectra for C_{60} and C_{70} that together proved the cage structure of the fullerenes (Fig. 2, ref. 6). Significantly, both the initial UV and NMR spectra of C_{60} that had been dissolved in benzene and concentrated to dryness showed the presence of benzene, despite being on the heated rotary evaporator for a considerable time. This was thus the first observation that C_{60} tenaciously retains solvents, a phenomenon evidently due to the excellent packing properties of the spherical molecules (ref. 6).

Preparation of the fullerenes by the Sussex-group has been on a resource-limited small scale, and hexane only (recoverable) is used for elution for the same reason. This latter has fortuitously avoided the difficulty encountered in removal from the fullerenes of toluene (used subsequently in chromatography by other groups, e.g. ref. 7). To avoid the problems of tailing of C_{60} into the C_{70} fraction encountered when scaling up the chromatographic procedure, a concentrated hexane solution of the soot extract is passed down the column, followed by elution with pure hexane. Two passes of this procedure gives C_{70} of 95-97% purity. Further purification is now carried out by preparative HPLC using a 41.4 mm x 25 cm, 8 um cyano column operated at 45 bar, with elution by hexane, and in this way ca. 500 mg of >99% purity C_{70} has been produced.

ISOLATION AND CHARACTERISATION OF HIGHER FULLERENES

Stripping of the columns with chlorinated solvent (after elution of C_{70} with hexane), yielded a greenish-yellow material shown by mass spectrometry to contain C_{76}, C_{78}, and C_{84}. These components were more positively identified by Diederich and coworkers (ref. 8). The fractions from numerous columns were combined and subjected to preparative HPLC, which yielded in sequence three yellow fractions, and a red-brown one. The first yellow fraction was then reprocessed to give ca. 2 mg of material shown by mass spectrometry (EI conditions) to be a mixture of C_{76} and C_{78}, (together with traces of C_{60} and C_{70}). The ^{13}C NMR spectrum of this material (Fig. 3) showed nineteen equal height peaks for D_2-C_{76} in precisely the reported (relative) positions (cf. ref. 8). Likewise the reported (ref. 9) twenty-one peaks for the C_{2v} isomer of C_{78} (three of which are half intensity) were similarly confirmed. However, whilst twelve of the reported (ref. 9) thirteen peaks for the D_3 isomer of C_{78} can be precisely located, the thirteenth is absent, and has been identified at a different position in the spectrum (see below). An additional eighteen lines in the spectrum were attributed to the C_{2v}' isomer of C_{78} (ref. 10), and the full twenty-two line spectrum for this isomer has now been published by Achiba and coworkers (ref. 11); two of the four lines not identified in our spectrum lie under two of the C_{76} peaks at 142.22 and 136.48 ppm, and the other two (minor intensity) peaks at 146.91 and 146.82 ppm are not clearly distinguishable from the baseline. The C_{2v}' isomer is the *major* one in the spectrum of Achiba and coworkers, and from the relative line intensities in the two sets of work it is possible to unambiguously locate the missing line for D_3-C_{78} at 141.21 ppm (ref. 10). The positions of the peaks for C_{76} and each of the three isomers for C_{78} relative to C_{60} at 142.67 ppm ($CDCl_3$ lock signal) are given in Table 1. The occurence of the C_{2v}' isomer as being either major (ref. 11), minor (this work), or absent (ref. 10) suggests a considerable dependence on the arc discharge conditions for its formation. In particular the effect of the UV flux of the arc upon the Stone-Wales electrocyclic rearrangement, which enables interconversion of some of the C_{78} isomers to occur (ref. 10) may be critical; this rearrangement is a four-electron process and is therefore photochemically allowed, but thermally forbidden.

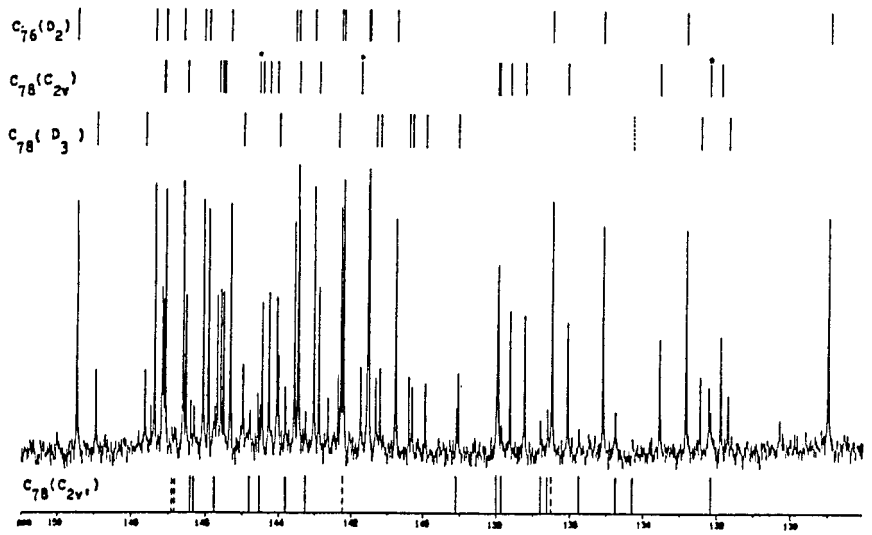

Fig. 3. ^{13}C NMR spectrum of C_{76} and C_{78}. The dotted line in the D_3-C_{78} band indicates the position of a peak reported in the literature. Two pairs of peaks in the $C_{2v'}$-C_{78} spectrum separate at high resolution; four other unresolved peaks occur at positions shown by the dashed lines (see text).

Table 1
^{13}C NMR shifts (ppm) for C_{76} and C_{78} (relative to C_{60} at 142.67 ppm)

$C_{76}(D_2)$	$C_{78}(C_{2v})$	$C_{78}(D_3)$	$C_{78}(C_{2v'})$
149.46	147.18	148.94	146.91**
147.38	147.14	147.63	146.82**
147.09	146.54	144.99	146.41
146.62	145.69	144.01	146.32
146.08	145.60	142.37	145.76*/**
145.93	145.52	141.33	144.82**
145.33	144.58**	141.21	144.52
143.57	144.46	140.40	143.83
143.47	144.27	140.31	143.81
143.03	144.06	139.95	143.26
142.29	143.45	139.05	142.22
142.22	142.90	132.45	139.10
141.56	141.75**	131.69	138.00
141.52	137.98		137.85
140.77	137.96		136.79
136.49	137.63		136.61
135.01	137.24		136.48
132.84	136.07		135.75
129.00	133.56		134.75
	132.21**		134.29**
	131.89		132.18

* Two almost coincident peaks. **Peaks of half intensity.

HPLC processing of the second yellow fraction showed it to contain all thirty-two peaks in the locations and with the intensities reported by Achiba's group (ref. 11). They have attributed this spectrum to a 2:1 mixture of D_2 and D_{2d} isomers of C_{84}, which should give twenty-one and eleven peaks (one of half intensity), respectively. Fig .4 compares the Achiba spectrum with our one (in which all other peaks have been deleted for clarity).The similarity of the spectra, particularly between 133 and 139 ppm is remarkable. Caution with the interpretation of the spectra in terms of two isomers may therefore be necessary since it is unexpected (given the result for C_{78}) that precisely the same isomer mixture would be obtained in both

works. Moreover, similar peak intensities (one peak absent, presumably unresolved) has been reported by Diederich et al. (ref. 12). Our material shows a number of additional peaks (not shown, some intense) which cannot be attributed to either C_{76}, C_{78}, or C_{82}, and is under further investigation. Of considerable interest is the mass spectrum of this material which shows the presence of $C_{70}H_{12}$ which elutes together with C_{84}; the hydrogen may have been abstracted from the hydrocarbon solvent.

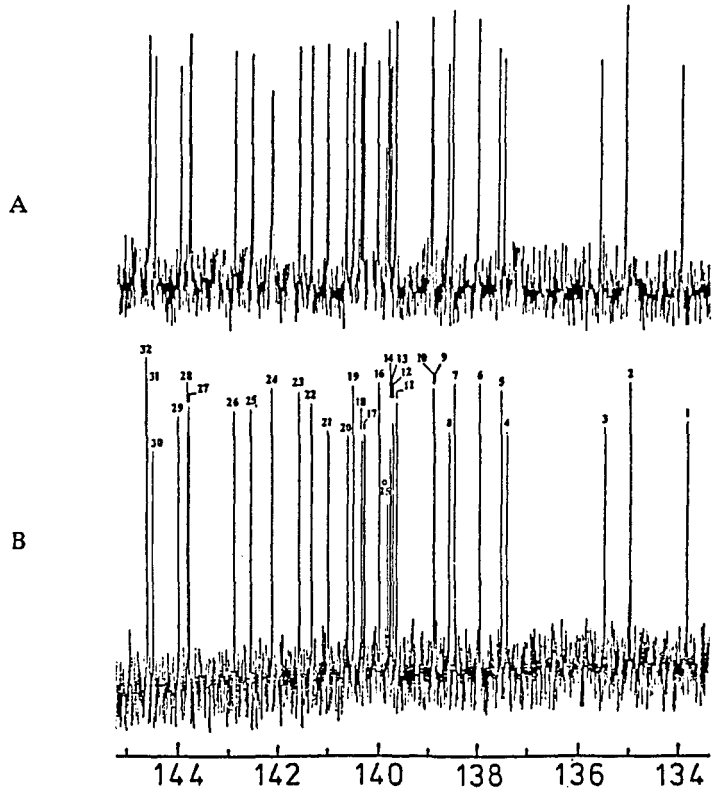

Fig. 4. ^{13}C NMR spectra of C_{84}: A) This work, (with additional peaks deleted for clarity). B) Spectrum given in ref. 11.

FLUORINATION

Fluorination of C60 with fluorine gas produces initially no change in appearance apart from an increase in volume. After a day or so the colour then changes to dark brown, and then to light brown after a further similar interval. It then continues to slowly take up fluorine to give eventually an off-white product (ref. 13). More extensive studies showed that fluorine uptake can continue over a period of weeks. Weight uptake indicates that after 8 days there is an average of 45 fluorines per C_{60} molecule, with fluorine uptake continuing at a rate of approximately one fluorine per day (ref. 14).

The fluorinated material is very soluble in polar solvents and can be separated into two components with chloroform. More soluble material gave a broad IR peak centred at ca. 1148 cm^{-1} (C-F stretch), and a broad peak in the ^{19}F NMR spectrum between ca. -140 and -160 ppm. Less soluble material (itself very soluble in acetone or THF) gave sharp peaks in the IR at 1067 and 1027 cm^{-1}, and a sharp NMR singlet at ca. -150.5 ppm. On allowing an acetone solution of this latter material to slowly evaporate, colourless plates giving a sharp m.p. of 287 °C, and an NMR singlet at ca. -153.9 ppm were isolated: the shift of the NMR singlet was attributed to hydrogen bonding by HF, which is present. FAB mass spectrometry of the chloroform-soluble material showed a continuum of peaks (due to reaction with the matrix), with significant intensities corresponding to $C_{60}F_{42}$ and $C_{60}F_6$; microanalysis indicated the presence of 40-45 fluorines per C_{60} molecules. The material giving the singlet in the NMR was provisionally proposed as being due to $C_{60}F_{60}$. Satisfactory mass spectra and microanalyses could not be obtained with this material, but this behaviour is common for highly fluorinated inorganic materials. Alternative structures containing either six, twelve, eighteen, twenty, or twenty-four fluorines would also give singlets, but these seemed less likely since they should give satisfactory mass spectra and microanalyses (ref. 14).

In attempting to confirm that the peak in the ^{19}F NMR spectrum at ca. -190 ppm was due to HF, I found that the fluorinated material reacted rapidly with sodium bicarbonate due, unexpectedly, to nucleophilic substitution. Moreover, whereas reaction with water is very slow because of the hydrophobic nature of the material, in the presence of a cosolvent such as acetone or THF, reaction is rapid and exothermic; this reaction accounts for the formation of HF observed in the NMR spectra. The reactivity towards a range of nuclophiles has now been determined, and follows the expected order. With many, addition of the nucleophile results in instantaneous reaction, with a substantial fraction of the fluorine being replaced. The rate of fluorine replacement decreases with time which follows from a) the increase in steric hindrance that is likely to result, and b) reduction in electronegativity of the cage as fluorines are replaced. Whilst the reactivity towards nucleophiles rules out the suitability of fluorinated C_{60} as a lubricant, it offers routes to a wide range of derivatives. Moreover, the higher solubility of the fluorinated fullerenes compared to other halogenated fullerenes, makes for homogeneous reaction conditions, with better control over the extent of addition. The disadvantage at present is the slowness of heterogeneous fluorination, and the lack of any control over the positions of fluorination. Nucleophilic substitution in chlorinated C_{60} by methoxy groups has also been reported recently (ref. 15).

Recent experiments on partial fluorination of C_{60} indicate that the reaction product consists of a mixture of unreacted C_{60} and highly fluorinated material. Thus once a given molecule begins to fluorinate, the loss of conjugation causes reaction to progress rapidly to the highly fluorinated stage (ref. 13). Mass spectra under EI conditions of partially fluorinated material shows species up to $C_{60}F_{52}$ present. Particularly interesting however is the presence of many species containing oxygen, and it seems possible that replacement of F by OH is then followed by elimination of HF from adjacent F and OH groups to give epoxide structures. In the mass spectrum, species $C_{60}F_2O$, $C_{60}F_4O$ and $C_{60}F_6O$ are evident (presumably produced as a result of fragmentation) as well as the oxygenated derivatives of $C_{60}F_{34}$, $C_{60}F_{36}$, $C_{60}F_{38}$, $C_{60}F_{40}$, aand $C_{60}F_{42}$ (Fig. 5). Numerous other O/F containing derivatives are evident under other conditions, and there is preliminary evidence that fluorine loss occurs with time, which may or may not be due to hydrolysis. For C_{60} there have been a number of reports of formation of the epoxide, with $C_{60}O$ having now been isolated (ref. 16). Both $C_{60}O$ and $C_{60}O_2$ are prominent in the spectra of the fluorinated material (Fig. 5).

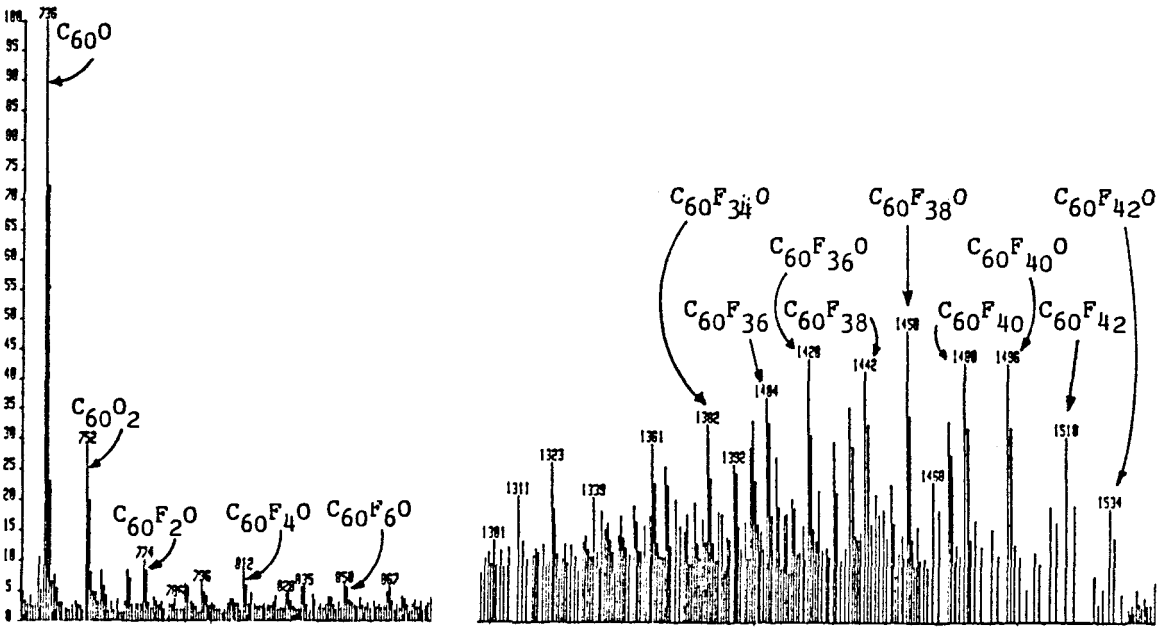

Fig. 5. Mass spectrum of partially fluorinated C_{60}

BROMINATION

Results of bromination (below) suggested that brominated C_{60} acts as a Friedel-Crafts alkylating reagent. Bromine was therefore reacted with C_{60} to see if bromo intermediates could be formed (ref. 17). Neat bromine resulted in fairly rapid formation of yellow microcrystals which analysed for approximately $C_{60}Br_{28}$, and this observation coincided with that in a preliminary report (ref. 18).

In order to produce less highly brominated products, bromination conditions utilising as high a C_{60}:Br_2 ratio as possible were sought. Since C_{60} is more soluble in CS_2 than in any other solvent, and the latter is also a standard solvent for bromination, reaction was carried out in this, initially with a low bromine concentration. No reaction occurred, but on increasing the bromine concentration, dark brown crystals appeared. Single crystal X-ray diffraction of these showed them to be 1,3,6,11,13,18,28,31-octabromofullerene-60 (Fig. 6), with two additional molecules of bromine per fullerene molecule, occluded in the lattice. This material is also obtained from bromination in chloroform.

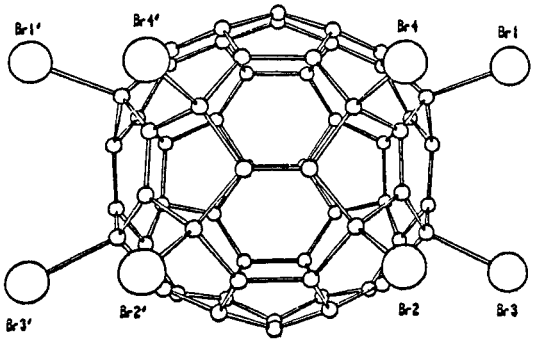

Fig. 6. Structure of $C_{60}Br_8$

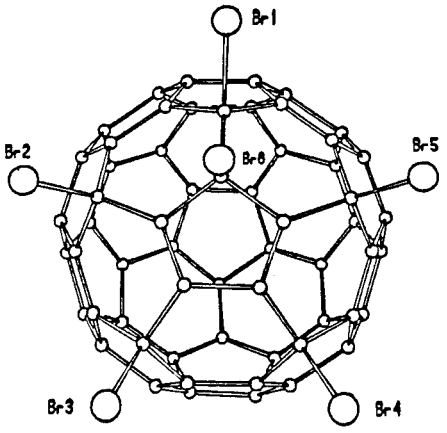

Fig. 7. Structure of $C_{60}Br_6$

Bromination in either benzene or carbon tetrachloride produces magenta plates of 1,6,9,12,15,18-hexabromofullerene-60 (Fig. 7), again containing two molecules of bromine per fullerene molecule, occluded in the lattice; this isomer is fairly soluble in organic solvents. The adjacent bromine atoms in the hexabromo compound introduces strain, shown by one C-Br bond being longer than the other five. Consequently, on gently heating this isomer in either benzene or carbon tetrachloride, it disproportionates to $C_{60}Br_8$ and C_{60} (ref. 17). Formation of $C_{60}Br_8$ in this way may involve a series of three 1,3-allylic bromine shifts initiated by the eclipsing strain (Fig. 8), followed by bromination with either displaced or occluded bromine.

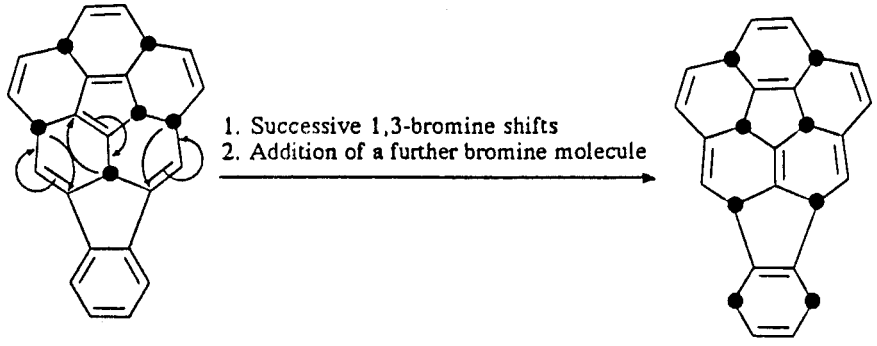

Fig. 8. Possible mechanism for rearrangement of $C_{60}Br_6$ into $C_{60}Br_8$

$C_{60}Br_{28}$ exhibits a very simple IR spectrum indicating a highly symmetrical structure. Since both the Br_6 and Br_8 compounds have two molecules of bromine per fullerene occluded in the lattice, it was proposed that $C_{60}Br_{28}$ consistes of $C_{60}Br_{24}$ with two molecules of bromine occluded in the lattice. On the basis of the structure of the Br_8 compound, the structure was proposed to be that given in Fig. 9)(1,3,6,8,11,13,16,18,21,23,26,28,31,41,44,46,49,51,54,57,60-tetracosabromofullerene-60) (ref. 17). This structure has now been shown to be correct (ref. 19).

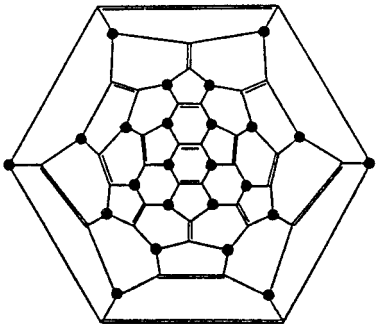

Fig. 9. Schlegel diagram of the structure of $C_{60}Br_{24}$

Each of the bromo derivatives lose bromine on heating in the absence of solvent ($C_{60}Br_{24}$ is the more stable and requires heating at 150 °C during 24 h to eliminate all of the bromine), and this precludes obtaining mass spectra. The higher stability of $C_{60}Br_{24}$ is reasonable given the major bond reorganisation required to regain the C_{60} structure, leading to a transition state of higher energy. Loss of bromine from $C_{60}Br_{24}$ appears to be a cascade process since the IR spectrum indicates that at any time the decomposition product is a mixture of C_{60} and $C_{60}Br_{24}$. Pure C_{70} takes up a similar number of bromine atoms and likewise loses them on heating. The cascade loss of bromine is paralleled by the reverse cascade uptake of fluorine in fluorination, indicative of the high stability of C_{60} relative to that of its addition products.

PHENYLATION

A preliminary report of the attachment of benzene rings to C_{60} (ref. 20) aroused my interest since it seemed possible that a phenyl ring could be attached which, if tritium labelled, would permit measurement of the electronic effect of the fullerene cage as a substituent, via acid-catalysed hydrogen exchange, (and hence its sigma plus value). The experimental conditions (bromine, ferric chloride, benzene and C_{60}) were therefore repeated, but with heating under reflux, and extraction and work up of the products in the normal way. Column chromatography (alumina, hexane) of the product, produced unreacted C_{60} together with a second, more soluble component having a longer retention time. Mass spectrometry (Fig. 10) showed this material to consist of a range of phenylated C_{60}, with $C_{60}Ph_6$ and $C_{60}Ph_8$ especially prominent. Further work showed $C_{60}Ph_{12}$ and $C_{60}Ph_{16}$ to be also present (ref. 21) The formation of the former two compounds parallels the observation in bromination above, and the same pattern of substitution may apply.

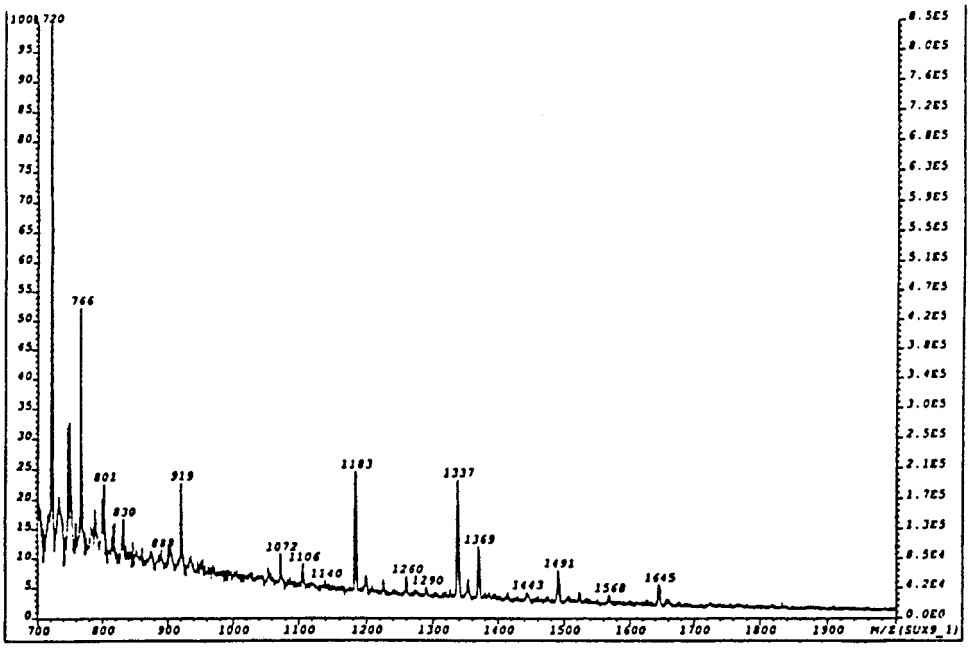

Fig. 10. Mass spectrum of phenylated C_{60}

If this is so then it is becoming evident that at least two addition patterns apply in C_{60}. For the addition of bulky groups such as bromine and phenyl, a pattern which mainly avoids eclipsing interaction is dominent. It appears then that for bromine and other similarly sized groups, that twenty-four groups is the maximum that can be accommodated by the cage. By contrast, groups such as platinum derivatives which do not have eclipsing interactions, add across the high order bonds in an octahedral fashion (ref, 22) and a possible reason for this has been considered (ref. 23). The addition of six diaryl carbon moieties to C60 also suggests that octahedral addition is involved (ref. 24).

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