C_{60}, C_{70}, C_{76}, C_{78} and C_{84}: Numbering, π-Bond Order Calculations and Addition Pattern Considerations

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The increasing number of fullerene derivatives now being produced raises the problem of site identification within a given molecule. Some nomenclature aspects for C_{60}, C_{70}, C_{76}, C_{78} and C_{84}, and problems which arise from this are described. A site location system for each fullerene is proposed. π-Density calculations have been performed for each of these fullerenes in order to predict sites that may be involved in the addition of non-bulky reagents. Possible addition sites for bulky reagents are also identified on the basis that no two groups can be adjacent and symmetrical addition is optimal.

Since September 1990, approximately 1200 papers on the closed-cage sp^2-hybridised carbon molecules (fullerenes), have been described, but only a small proportion (*ca.* 70) refer to chemical reactions and hence derivatives. However, this proportion is now increasing rapidly which makes the problem of devising an agreed nomenclature for derivatives, one that needs urgent resolution. Some difficulties that arise are described here together with possible solutions. The need to present the results of π-density calculations in an understandable way has necessitated addressing this problem at this time.

Numbering System

It is generally recognised that a fully systematic numbering system according to the IUPAC method is sufficiently unwieldly as to be ruled out of consideration. Merely to describe the basic cage for C_{60} takes many lines of print, is error prone,[1] and the corresponding names of derivatives would simply be too difficult to interpret. A more useable alternative could be based upon a clockwise spiral numbering system in which the carbon atoms in a fullerene are numbered consecutively from the cap of its longest axis of symmetry through to the other cap. This does however lead to some difficulties not previously recognised and which are unavoidable, so that for some isomers, some deviation is necessary. Nevertheless this should cause no more difficulty than say the non-systematic numbering in anthracene. Moreover the system is based on Schlegel diagrams which once produced, as here, can be readily copied and modified with the adducts as required.

An alternative system is to identify equivalent carbons in a given fullerene, according to 'layers' as was introduced for C_{70}.[2] However, this is impossible for chiral fullerenes, and in any event cannot be applied without the diagram of the fullerene structure being available, and so seems less advantageous than the proposals in this paper. Numbering according to layers, and difficulties which arise for *e.g.* D_n and T symmetry groups has been described for boron polyhedra.[3] The descriptors introduced for these make it difficult to visualise the molecules concerned. Moreover use of an analogous system based, as in the case of the boron polyhedra, on analysis of three-dimensional representations, appears unacceptable for fullerenes because of the greater complexity of the carbon cages. By contrast the use of Schlegel diagrams is already well established in this field and they are easy to comprehend.

Each of the fullerenes described in the title are considered as follows.

C_{60} (I_h).—There are in fact three ways of numbering the carbon atoms in C_{60} in a spiral fashion. The first numbers from a pentagonal ring (Fig. 1) and was used in the provisional labelling of the points of attachment of bromine in the Br_6, Br_8 and Br_{24} derivatives.[4] All carbons in the pentagonal ring are equivalent so it is immaterial from which point numbering commences, but it should be noted that this is not generally true (see below). Labelling from the pentagonal ring commends itself because of the relationship to C_{70} (D_{6h}), which has pentagonal caps at the end of its symmetry axis. However, since none of the other fullerenes that have been isolated have five-fold symmetry, this may be a less important consideration. Although it is not possible to predict reliably the structures of fullerenes as yet not isolated, nevertheless the larger the fullerene, the lower the statistical probability of five-fold symmetry in the stable isomers, since there are only 12 pentagons whatever the size of the fullerene.

The two alternative numbering systems for C_{60} begin with a hexagonal cap, but here the carbons are non-equivalent in a numbering sense [see Figs. 2(a) and (b)] since the bonds are not identical in the hexagonal ring, those joining the pentagons having a lower bond order. Labelling as in Fig. 2(b) is preferable in that the bond between the pentagonal rings, already shown to be involved in a number of *cis* additions,[5–9] is the 1,2-bond. By contrast the numbering as in Fig. 2(a) means addition occurs across a 2,3- or 1,9-bond, and this latter would also be the case using the system shown in Fig. 1. Moreover, octahedral addition[10] already shown to occur with platinum[8] (and inferred in preliminary reports of a number of other six-fold additions), takes place across the 1,2; 18,36; 22,23; 27,45; 31,32; and 55,60 positions according to the numbering used in Fig. 2(b). This gives lower locants and is thus preferred over the alternatives *viz.* 1,9; 16,17; 21,40; 30,31; 44,45; and 52,60 (Fig. 1) and 2,3; 21,22; 26,27; 31,48; 35,36; 55,56 [Fig. 2(a)].

Using the system given in Fig. 2(b) the bromines in $C_{60}Br_6$[4] would be located in either the 1, 2, 4, 11, 15 and 30, or 1, 2, 5, 10, 21 and 24 positions. The former is preferable because 1,2,4... should take priority over 1,2,5... For $C_{60}Br_8$[4] the locations are the 1, 4, 7, 10, 16, 19, 24 and 36 positions, and for $C_{60}Br_{24}$[4,10] they are the 1, 4, 7, 10, 12, 14, 16, 19, 22, 24, 27, 29, 31, 33, 36, 38, 41, 43, 46, 49, 52, 54, 57 and 60 positions. The locants for $C_{60}Br_6$ are thus lower than those obtained using the system in Fig. 1 (1,6,9 . . .), but for $C_{60}Br_8$ and $C_{60}Br_{24}$ are higher than those obtained using the system in Fig. 1 (1,3,6,8 . . .).[4] This exemplifies the special problems that arise in dealing with fullerene derivatives. The pattern observed with bromine addition is probably general for the addition of bulky reagents,[11] and this is addressed below with regard to the other fullerenes.
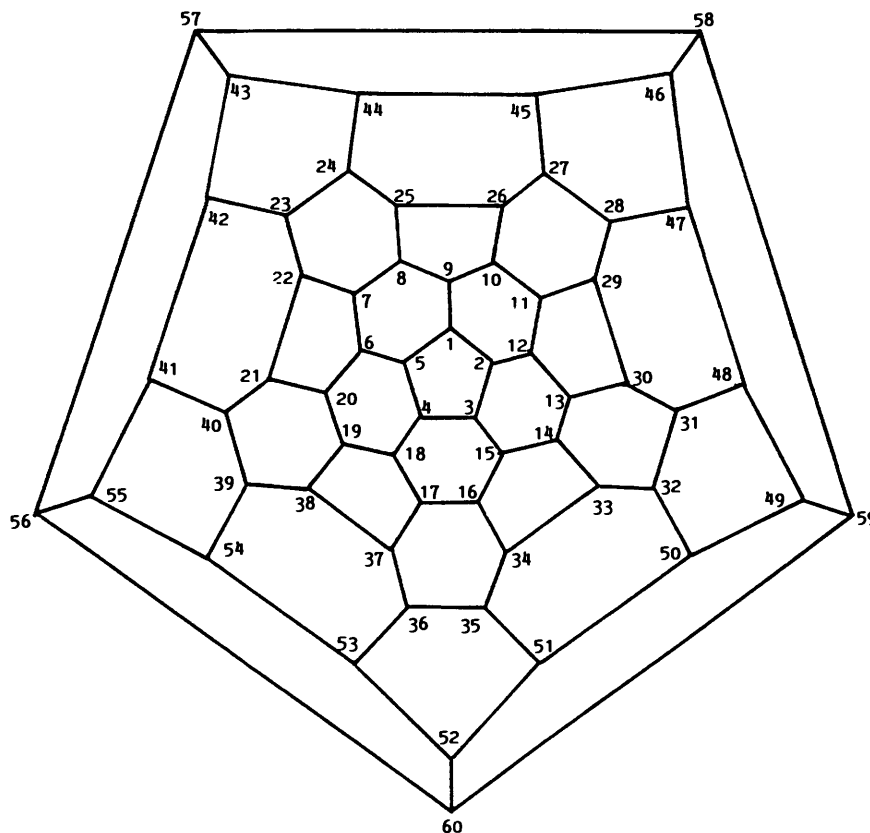
Fig. 1   Numbering for C_{60}, commencing in a pentagon

C_{70} (D_{5h}).—C_{70} presents a particular problem with regard to nomenclature, since it is not possible to number the carbons in a contiguous spiral fashion from one polar cap through to the other. Because of the five-fold symmetry, no other pair of rings on opposite sides of the cage are symmetrical with respect to one another, so no alternative symmetrical numbering system is achievable. The optimum notation would seem to be that given in Fig. 3, in which there are discontinuities between carbons 64 and 65, 68 and 69. Whereas one polar cap has carbons labelled consecutively (1–5) the other does not (62, 63, 66, 67, 70). An alternative that could be considered is to commence labelling around a hexagonal ring adjacent to a pentagonal cap. This method (not shown) makes the numbering more consistent with that for C_{60} [Fig. 2(b) system], and results in discontinuities only between carbons 68 and 69 for the numbering in that system.

C_{76} (D_2).—It is possible to number from one hexagonal cap through to the other hexagonal cap as shown in Fig. 4. *The point of commencement of numbering, and its direction in the hexagonal cap is unique for the particular enantiomer shown.* By commencing at any of the other carbons labelled 2–6 in the central hexagonal ring, it is not possible to label contiguously through to the other cap, hence this cap will not contain carbons 71–76.

C_{78}.—There are five isomers of C_{78} predicted to be of high stability,[12,13] and three have been isolated.[14–16] Numbering systems for all five isomers are here proposed.

D_{3h}. In this (as yet unisolated) isomer, contiguous spiral numbering can be achieved as shown in Fig. 5, the carbons of the opposite cap having the desired numbering 73–78. The same result can be achieved by starting from the equivalent carbons numbered 3 and 5 in the central ring, but not by commencing at carbons 2, 4 or 6.

C_{2v}. This isomer is generally present in C_{78}.[14–16] Numbering

as shown in Fig. 6 is continuous through to the opposite cap, *but the point of commencement in the hexagonal ring is unique.* Commencement at any of points 2–6 fails to produce contiguous numbering.

D_3. This is also generally present in C_{78}.[14–16] Continuous spiral numbering from one cap through to the other is possible as shown in Fig. 7, and also by commencing at the equivalent points (3, 5) in the central hexagon; by contrast this fails if one commences at either of the equivalent positions 2, 4 or 6.

$C_{2v'}$. This can be either the major component of C_{78}, or absent altogether.[14–16] It is possible to number the carbons in this isomer in a consecutive, but not fully symmetrical way, by commencing numbering from either of the positions labelled 1, 3 or 5 in Fig. 8. There is however a difference between these three positions, in that by commencing at position 1 (as shown) or from position 5, only one deviation from the consecutive numbering of the opposite hexagon is necessary. By contrast, commencement from position 3 requires two deviations, hence the recommended method is that shown. Contiguous numbering cannot be achieved by commencing from either of positions 2, 4 or 6.

$D_{3h'}$. This isomer has not been isolated. Contiguous numbering is possible by commencing from either of the equivalent positions 1 (as shown in Fig. 9), 3, or 5, though in each case two departures from the perimeter of the opposite hexagon are necessary. Contiguous numbering fails on beginning at positions 2, 4 or 6.

C_{84}.—Two isomers of C_{84} have been isolated,[14,17] namely the D_{2d} and a chiral D_2 isomer. There are four possible structures for the latter that fit the NMR data, but one isomer is of lower energy than the others and is, moreover, predicted to have similar stability to that of the D_{2d} isomer.[18] The invariance of the relative yields of these isomers with method of production indicates that they are of very similar energy, hence the low energy D_2 isomer is believed to be the one that is formed.[18] The
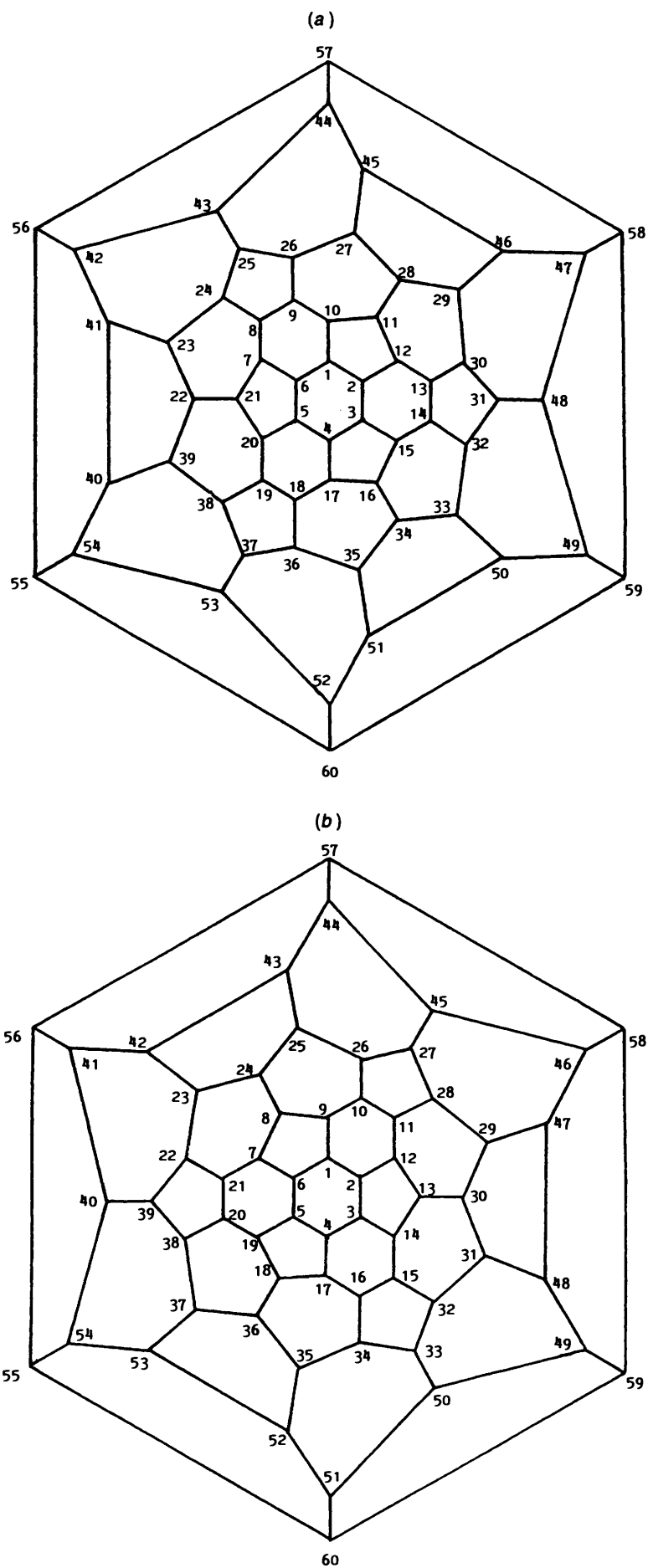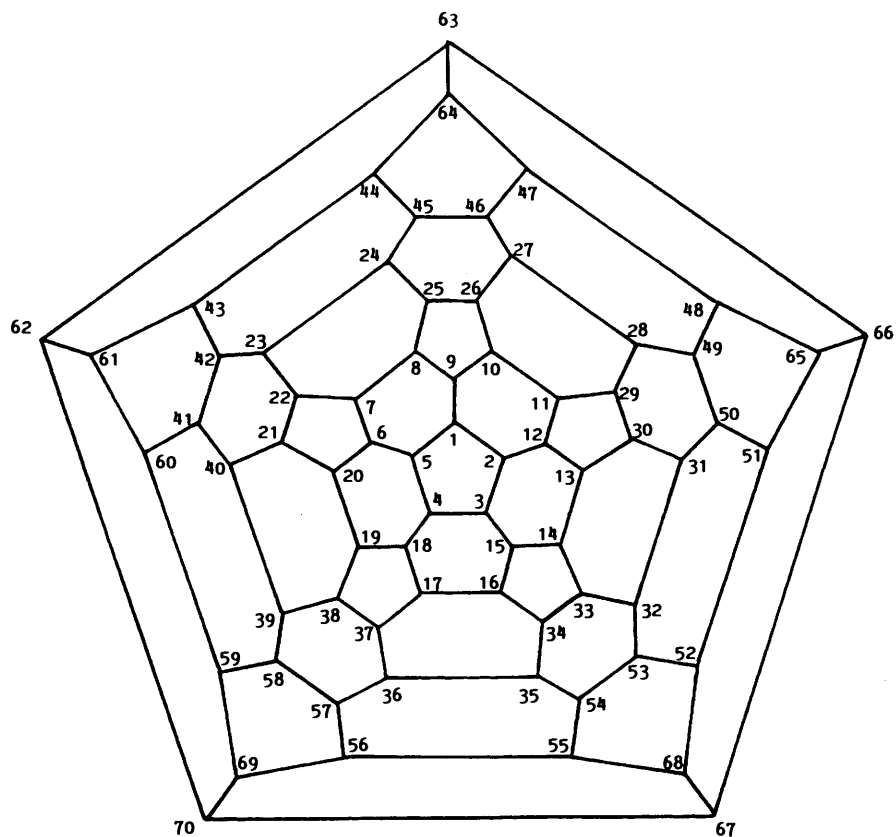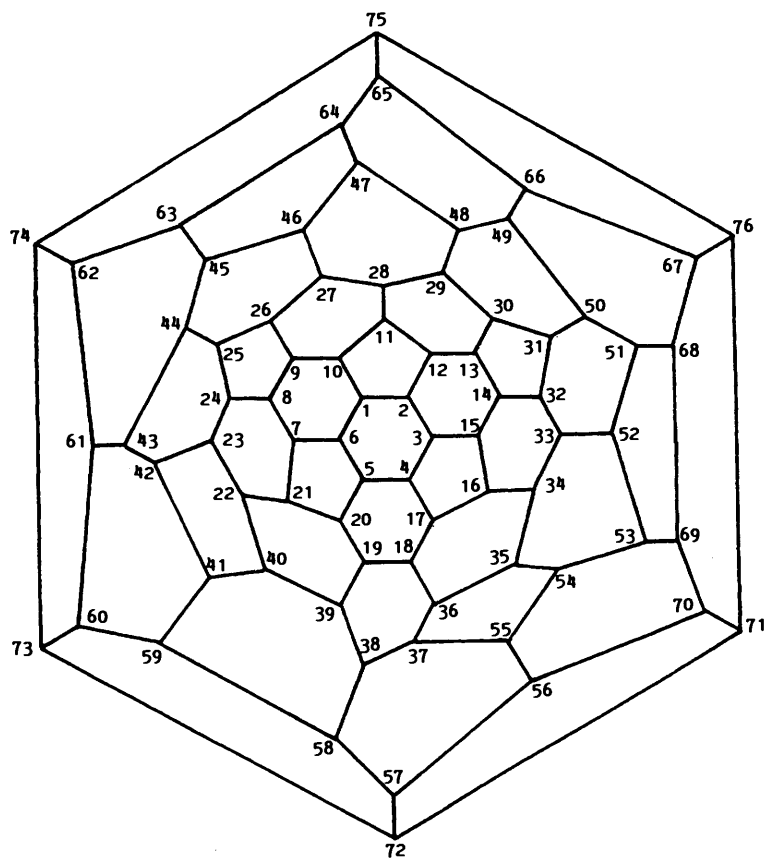
Fig. 2 (*a*) Numbering for C$_{60}$, commencing in a hexagon; (*b*) alternative numbering for C$_{60}$, commencing in a hexagon (recommended method)

Fig. 3 Numbering for C_{70}

Fig. 4 Numbering for C_{76} (D_2)

numbering systems for both this, and the D_{2d} isomer are given below.

D_2. The numbering for one enantiomer is shown in Fig. 10, and is contiguous through to the other cap. Contiguous numbering can be achieved here by commencing at any point in the hexagonal ring, but the recommended start point is as shown in Fig. 10, in order to maintain consistency with the D_{2d} isomer.
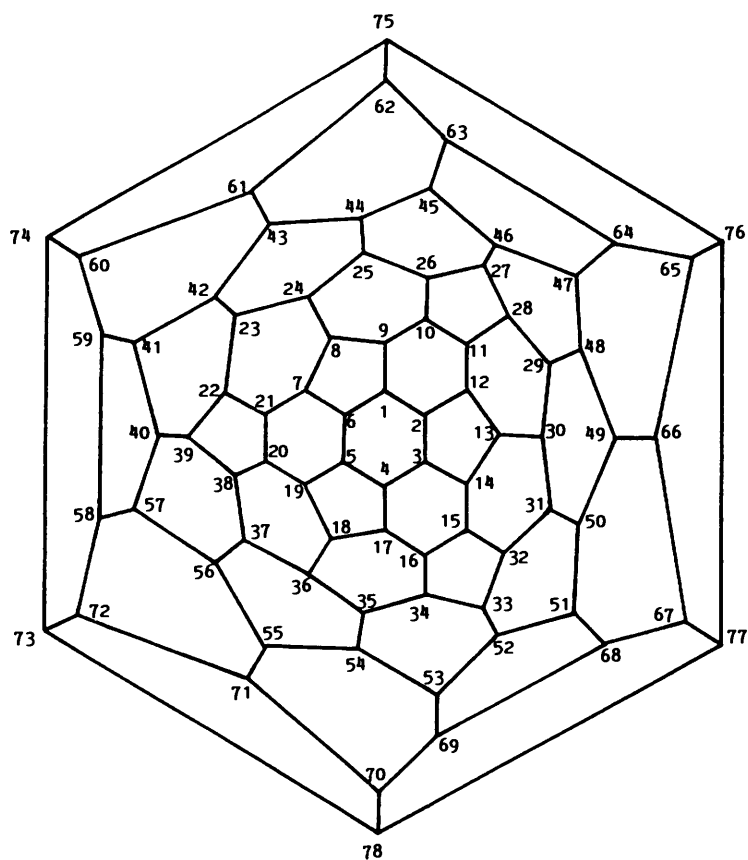
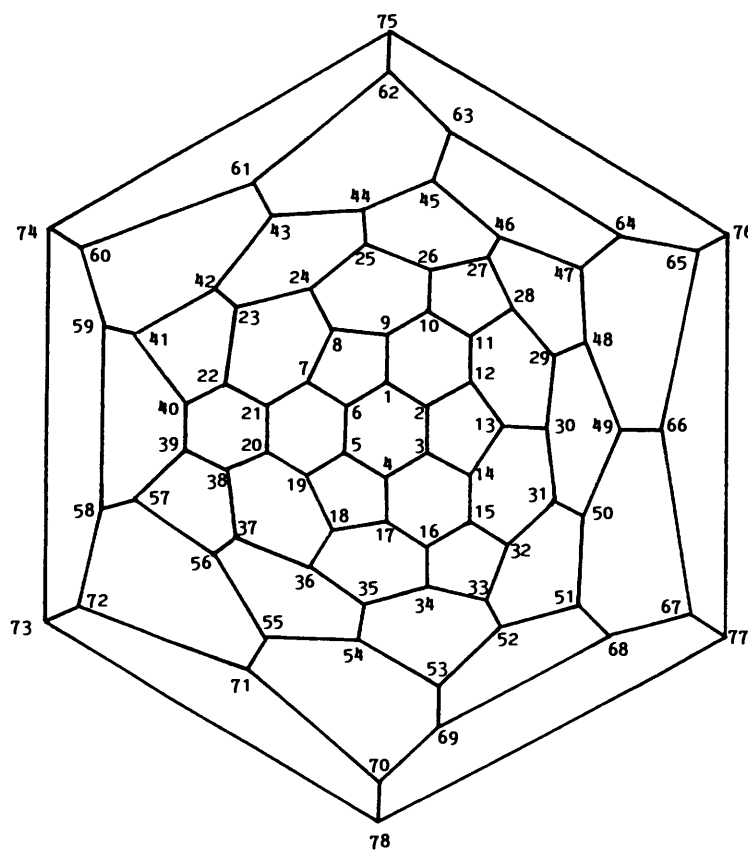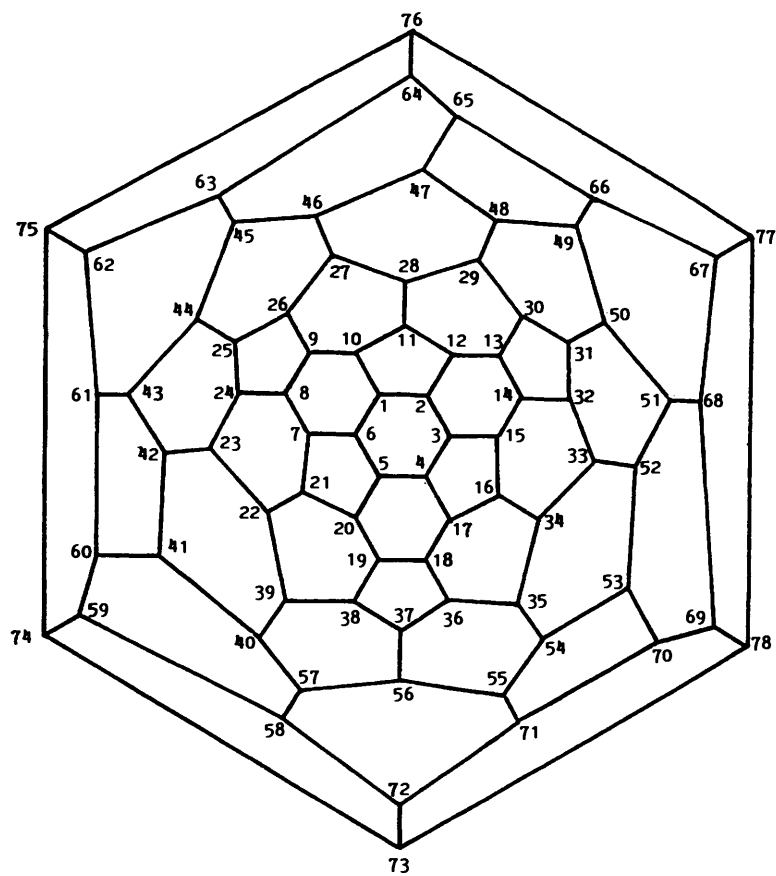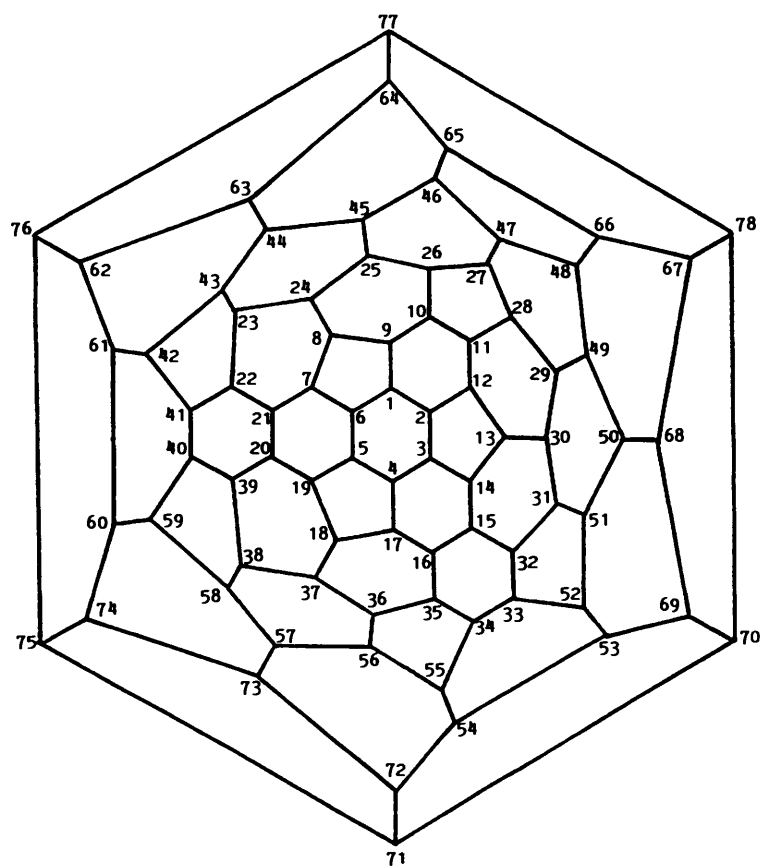**Fig. 5** Numbering for C_{78} (D_{3h})

Fig. 6 Numbering for C_{78} (C_{2v})

D_{2d}. Numbering here resembles the situation for C_{76} in that the method shown (Fig. 11) is unique; starting at any other carbon in the same hexagon fails to give contiguous numbering.

Fig. 7 Numbering for C_{78} (D_3)
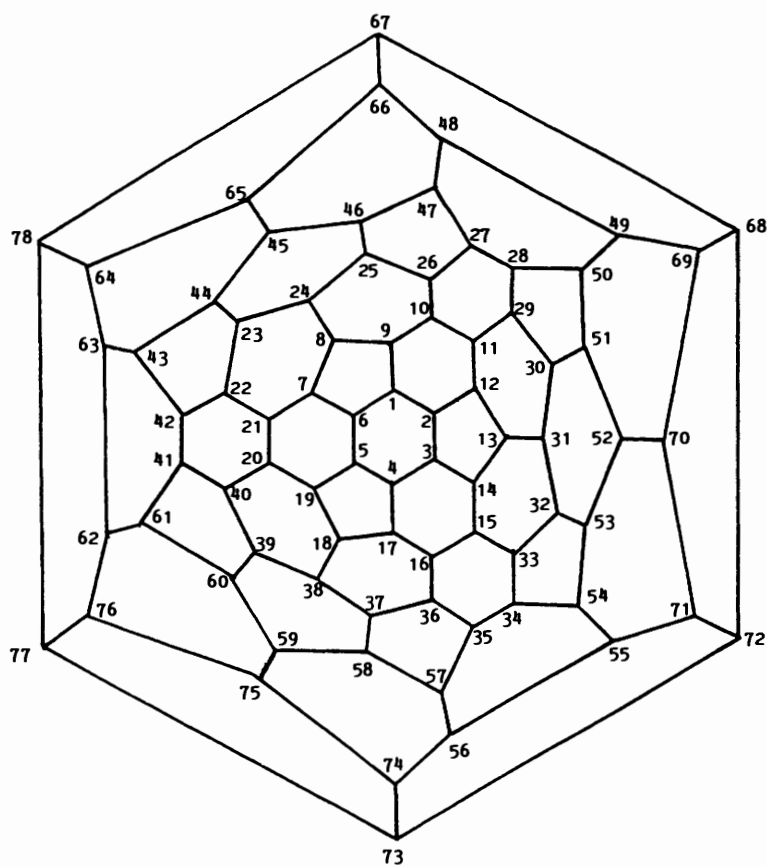

Fig. 8 Numbering for C_{78} (C_{2v})

Fig. 9 Numbering for C_{78} ($D_{3h'}$)
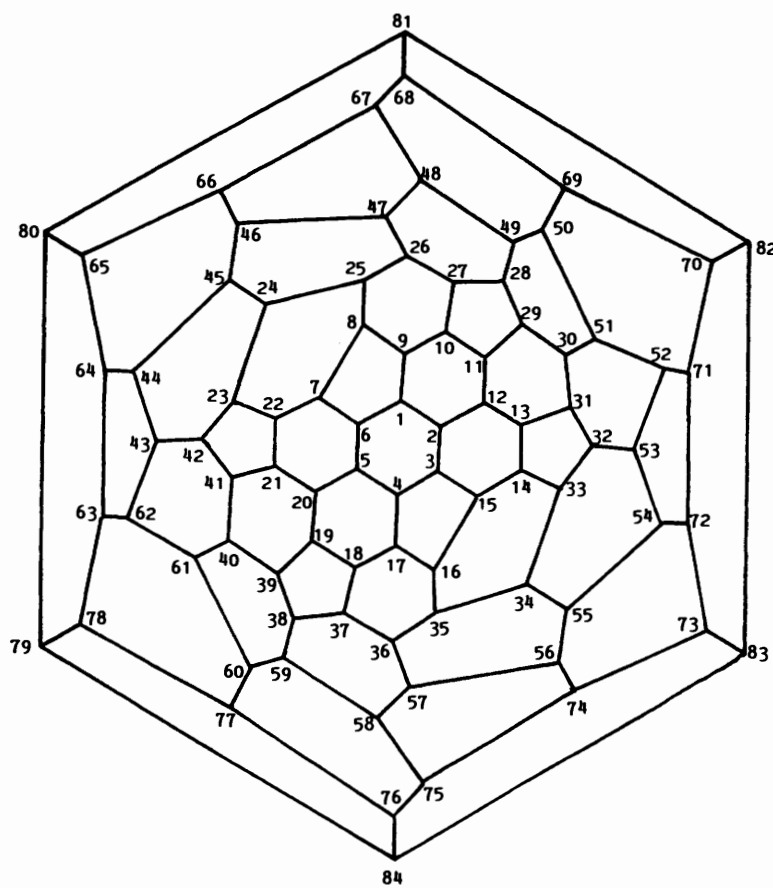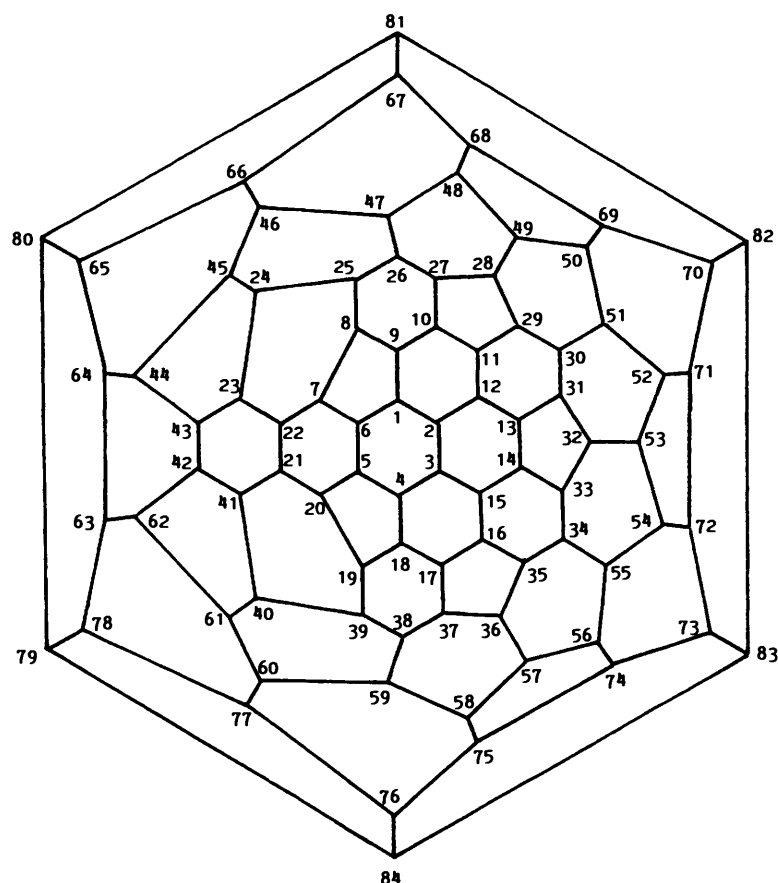

Fig. 10 Numbering for C_{84} (D_2)

Fig. 11   Numbering for C_{84} (D_{2d})

Prediction of Addition Patterns in Higher Fullerenes

Improved methods of chromatographic separation of higher fullerenes will lead to useable amounts of these fullerenes becoming available for reactions. Given the very considerable difficulties associated with fullerene product identification, it is appropriate to try to gain some idea as to the likely reaction sites. We make the assumption that addition will tend to occur so as to preserve symmetry. Two classes of addition reactions may be considered: those which do not give rise to significant eclipsing interactions, carbenes, epoxides, etc, and those involving bulky reagents.[11] For the former category π-densities can be expected to give a good indication of the probable reaction sites. For calculating these we have used the Hückel MO method which although very simple gives remarkably good results for carbocyclic molecules. For example it correctly predicts the positional reactivity orders in many aromatics, e.g. all five positions in phenanthrene, and even all eight positions of hexahelicene (benzo[c]naphtho[1,2-g]phenanthrene).[19] Higher level calculations offer little advantage as indicated by the almost linear correlation of Hückel π-bond orders for C_{70} (there is one small deviation for the equatorial bonds) with either bond lengths or overall bond orders calculated by the ab initio method.[20]

π-Bond order calculations have been performed for each of the above molecules, and are listed in decreasing bond order, in Tables 1–4 where the numbering corresponds to that shown on Figs. 2(b), 3–11. For each fullerene, there are a number of bond sets, with each set containing identical bonds. The bond of each set that has the lowest (first) location number is given in the Tables.

C_{60} and C_{70}.—For C_{60} the π-bond orders are 0.476 and 0.601 (cf. ref. 21), and these predict correctly that addition should

occur across the interpentagonal bonds which have the higher bond order. Data for C_{70} (Table 1) predict addition across either the 1,9- or 7,8-bonds. Iridium preferentially adds across the latter, and this specificity may be due either to steric hindrance from the bulky ligands,[22] or to relief of steric strain which will be greater near the caps in C_{70};[2] strain effects will be more significant in smaller fullerenes.

C_{76}.—For C_{76} there are 114 bonds consisting of 30 non-equivalent sets, each containing either two or four identical bonds. The data (Table 2) show the general trend of the bonds with highest π-density being those exocyclic to the pentagonal rings.[23] Indeed the locations of the bonds of high and low bond order can be accurately predicted merely by drawing the bonds in this way (see refs. 13, 23). Addition is predicted at, or in the vicinity of, the end caps, and may take place somewhat more readily than in C_{60} or C_{70}. This is also indicated by the greater bond fixation (poorer delocalisation), relative to these fullerenes. There are 12 high π-density bonds, and these occur in four sets: (14,15;23,24;53,54;62,63),(4,5;9,10;67,68;72,73),(1,6; 71,76) and (2,3; 74,75). Up to 12-fold addition in two-fold steps can be anticipated.

C_{78}.—Each isomer contains 117 bonds divided into the following numbers of sets (isomer in parentheses): 13 (D_{3h}); 34 (C_{2v}); 20 (D_3); 34 ($C_{2v'}$); 13 ($D_{3h'}$) and the π-densities are given in Table 3. Delocalisation tends to decrease down the Table, and amongst the isomers so far isolated, addition could be expected to take place most readily and stereospecifically for the $C_{2v'}$ isomer. It is notable that the bonds around the equatorial waist of the D_{3h}, C_{2v}, $C_{2v'}$ and $D_{3h'}$ isomers, predicted by a Valence Bond procedure to be susceptible to addition,[24] are all found to be either of high order, or the highest order in these molecules. In general, the bonds of highest density in these molecules are

Table 1 π-Bond orders for C_{70}

| | Bond (Fig. 1) | | | | | | | |
	1,2	1,9	6,7	7,8	7,22	21,22	22,23	23,24
Bond order	0.477	0.597	0.479	0.602	0.469	0.534	0.545	0.489

Table 2 π-Bond orders for C_{76}

Bond	Bond order	Bond	Bond order	Bond	Bond order
14,15	0.608	18,36	0.540	2,12	0.480
4,5	0.603	32,33	0.539	1,10	0.478
1,6	0.603	16,17	0.533	13,14	0.475
2,3	0.598	13,30	0.509	3,15	0.472
29,30	0.578	19,39	0.505	1,2	0.472
11,28	0.576	11,12	0.499	5,20	0.470
12,13	0.574	27,28	0.492	4,17	0.468
16,34	0.548	33,34	0.491	14,32	0.467
17,18	0.547	29,48	0.488	15,16	0.466
35,36	0.545	8,9	0.483	30,31	0.459

Table 3 π-Bond orders for C_{78}

Isomer	Bond	Bond order	Bond	Bond order	Bond	Bond order
D_{3h}	1,2	0.599	23,24	0.498	22,39	0.484
	7,21	0.594	23,42	0.496	1,6	0.481
	27,46	0.587	10,26	0.490	1,9	0.473
	22,23	0.578	7,8	0.487	10,11	0.471
	8,24	0.577				
C_{2v}	39,40	0.617	8,24	0.538	2,3	0.485
	5,6	0.608	7,8	0.537	1,6	0.483
	9,10	0.603	21,22	0.535	27,28	0.483
	1,2	0.594	25,44	0.501	1,9	0.477
	11,12	0.592	26,27	0.500	10,11	0.476
	28,29	0.581	29,30	0.498	2,12	0.474
	25,26	0.578	29,48	0.493	10,26	0.471
	13,30	0.578	24,25	0.493	8,9	0.471
	27,46	0.573	20,21	0.490	22,40	0.462
	22,23	0.556	11,28	0.488	5,19	0.456
	7,21	0.553	12,13	0.487	23,42	0.440
	23,24	0.547				
D_3	7,8	0.610	23,24	0.541	8,9	0.473
	1,6	0.602	9,26	0.510	2,12	0.472
	26,27	0.578	10,11	0.508	1,10	0.470
	9,10	0.575	22,39	0.506	8,24	0.469
	11,28	0.574	22,23	0.492	7,21	0.464
	23,42	0.546	27,46	0.486	25,26	0.456
	24,25	0.542	1,2	0.479		
$C_{2v'}$	33,34	0.614	7,8	0.535	4,5	0.485
	3,4	0.601	36,37	0.533	10,11	0.483
	9,10	0.600	15,32	0.533	1,9	0.480
	25,26	0.584	16,35	0.522	8,9	0.472
	1,2	0.582	18,37	0.517	10,26	0.468
	27,47	0.567	17,18	0.513	34,55	0.464
	16,17	0.564	25,45	0.497	4,17	0.463
	35,36	0.563	26,27	0.495	22,41	0.457
	22,23	0.562	1,6	0.491	3,14	0.455
	14,15	0.555	24,25	0.490	36,56	0.446
	23,24	0.551	15,16	0.488	23,43	0.426
	8,24	0.537				
$D_{3h'}$	27,28	0.627	10,26	0.521	10,11	0.488
	1,2	0.589	8,24	0.517	1,9	0.464
	22,23	0.574	7,8	0.513	22,42	0.450
	7,21	0.564	1,6	0.497	23,44	0.425
	23,24	0.533				

Table 4 π-Bond orders for C_{84}

Isomer	Bond	Bond order	Bond	Bond order	Bond	Bond order
D_2	9,10	0.614	3,4	0.544	25,26	0.487
	32,53	0.604	39,40	0.544	31,32	0.475
	7,22	0.594	26,27	0.540	23,42	0.472
	23,24	0.578	1,2	0.539	10,27	0.468
	8,25	0.577	11,12	0.534	10,11	0.466
	12,13	0.544	13,33	0.530	8,9	0.465
	11,29	0.552	7,8	0.507	1,9	0.463
	2,3	0.549	24,25	0.504	13,14	0.461
	26,47	0.549	14,33	0.497	28,29	0.449
	27,28	0.545	2,12	0.489	3,15	0.449
	30,31	0.545	24,45	0.487		
D_{2d}	32,53	0.624	7,8	0.541	21,22	0.489
	9,10	0.611	11,12	0.540	1,9	0.471
	5,6	0.593	21,41	0.535	8,9	0.466
	1,2	0.572	2,3	0.509	23,43	0.457
	13,31	0.558	1,6	0.507	5,20	0.451
	7,22	0.553	2,12	0.489	13,14	0.435
	12,13	0.548				

located at the polar caps and around the waist, and the region of highest π-density changes from the former to the latter along the above series. The Valence Bond method also correctly predicted that there would not be a particularly high π-density region around the waist of the D_3 isomer.[24]

The specific addition patterns expected are as follows, where the numbers in parentheses indicate the numbers of equivalent bonds.

D_{3h}. Addition across up to 15 bonds 1,2 (6), 7,21 (3), 27,46 (6).

C_{2v}. One bond has significantly higher π-density than the others and gives a symmetrical product, so a single product could be anticipated. Further addition could be expected across the 5,6-bond (2) and 9,10-bond (4) in that order.

D_3. There are 18 interpentagonal bonds in three sets, 7,8 (6), 1,6 (6) and 26,27 (6) and of these the former 12 are of significantly higher order, leading to the expectation of 12-fold addition in two-fold steps (to maintain symmetry).

$C_{2v'}$. The 33,40-bonds (2) have significantly higher π-density than the others, so two-fold addition giving a single symmetrical product is expected here. Subsequent addition should occur across the 3,4-bond (4) and 9,10-bond (4), in two-fold steps to preserve symmetry.

$D_{3h'}$. Three-fold addition across the three equivalent 27,28-bonds is predicted, giving a single symmetrical product.

C_{84}.—For this fullerene there are 126 bonds, and for the two isomers so far isolated, these fall into the following numbers of sets: 32 (D_2); 19 (D_{2d}) (Table 4). Delocalisation is less in the D_{2d} isomer, and indeed, of the fullerenes so far isolated this one is predicted to be the most susceptible to addition, and to have the highest stereospecificity. In both isomers there are three pairs of interpentagonal bonds, and these have the highest π-densities. In the D_2 isomer the highest π-density is found at the cap, followed by that at the equatorial waist. In the D_{2d} isomer the symmetry precludes distinguishing between cap and waist: the 32,53-bond (which has the highest π-density) is identical to the
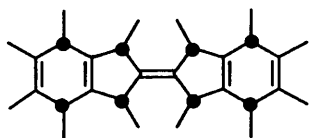
Fig. 12 General disposition of groups (●) in $C_{60}Br_8$, $C_{60}Br_{24}$ (and probably $C_{60}Cl_{24}$ and $C_{60}Me_{24}$)
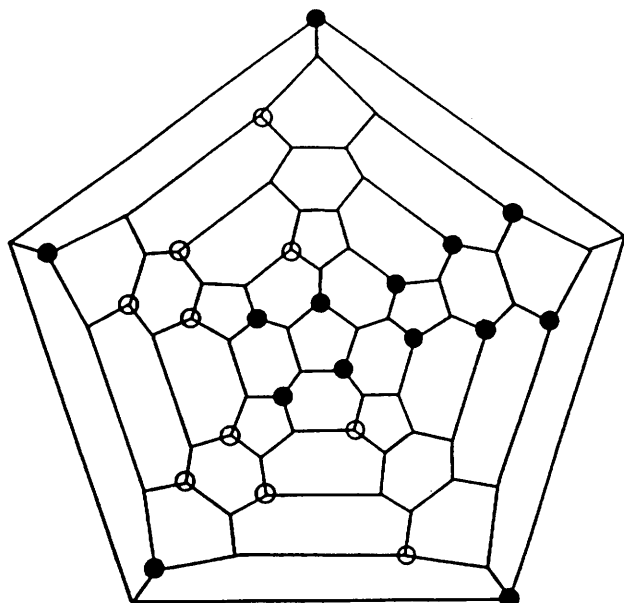

Fig. 13 Proposed disposition of bulky groups in C_{70}: primary (●) and secondary (○) addition sites
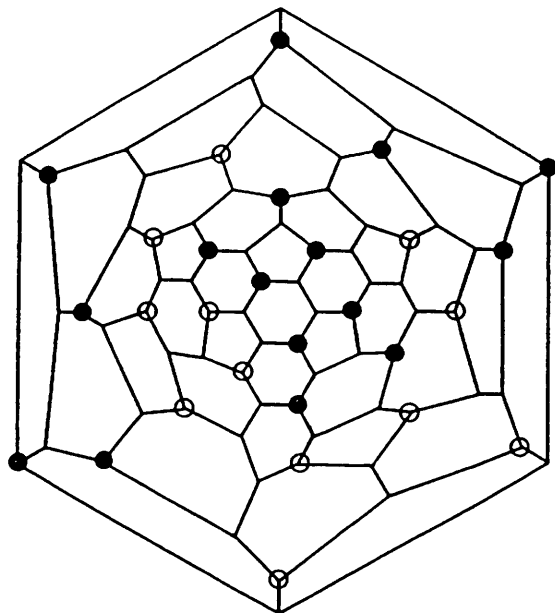

Fig. 14 Proposed disposition of bulky groups in C_{76}: primary (●) and secondary (○) addition sites

42,43-bond, whilst the 5,6– and 28,49–bonds are also identical, as are the 9,10– and 17,18–bonds. It is reasonable to assume that both isomers will readily undergo up to six-fold addition in two-fold steps.

Addition of Bulky Reagents

The π-densities calculated above are inapplicable to prediction of the sites of addition of bulky groups. This is because the fullerene cages are unable to flex sufficiently to relieve eclipsing
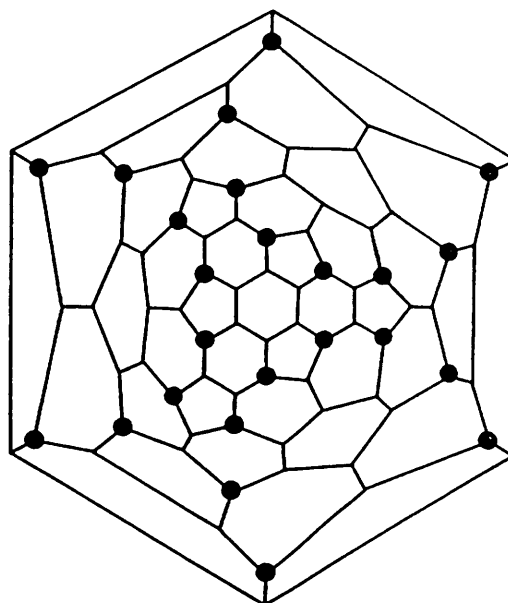

Fig. 15 Proposed disposition of bulky groups in C_{78} (D_{3h})

strain that arises from 1,2-addition.[11] The pattern of addition of bromine, and in particular that found in $C_{60}Br_8$[4] (Fig. 12) is likely to apply generally since it is also found in $C_{60}Br_{24}$[4,10] and almost certainly in $C_{60}Cl_{24}$[25] and $C_{60}Me_{24}$.[26] Features of the pattern are: (a) no groups are adjacent; (b) groups are either 1,3 or 1,4 with respect to each other; (c) the structures are symmetrical; and (d) no radical species are present, i.e. there are no isolated sp^2 carbon atoms.

Applying these conditions permits prediction of addition patterns for the higher fullerenes. The patterns turn out to have significant differences to the extent that formation of adducts and separation followed by elimination may prove to be a viable method for separation of the higher fullerenes. Analysis of each fullerene is as follows:

C_{70}.—A band of 14 groups can be added along the direction of the long axis [Fig. 13 (●)], giving a product symmetrical in two dimensions. It is also possible to add a further ten groups which complete encirclement and branch to either side of this band [Fig. 13 (○)], giving a product again symmetrical in two dimensions. Thus, $C_{70}X_{14}$ and $C_{70}X_{24}$ products are predicted.

C_{76}.—Here 16 groups can be added in two groups of eight to give a symmetrical product [Fig. 14 (●)]. A further ten groups [Fig. 14 (○)] may also be added to give a second symmetrical product. We should expect $C_{76}X_{16}$ and $C_{76}X_{26}$ products here.

C_{78}.—D_{3h}. The three-fold symmetry indicates that 24 groups would add in three bands of eight along the long axis (Fig. 15) to give a product symmetrical in three dimensions. The inter-mediate X_8 and X_{16} products are less symmetrical.

C_{2v}. There are three possibilities here. Addition of either two bands of eight groups along the axis of the molecule [Fig. 16 (●)] or a band of eight groups around the equatorial waist [Fig. 16 (○)], or both together. Anticipated products are thus $C_{78}X_8$, $C_{78}X_{16}$ and $C_{78}X_{24}$.

D_3. It does not appear possible to add groups symmetrically to this isomer in other than the full complement of 30 groups (Fig. 17), giving only $C_{78}X_{30}$. Of all the fullerenes described in this paper, this one is able to accommodate the greatest number of adducts. The resultant structure comes closest to having the perfectly symmetrical arrangement found in $C_{60}X_{24}$.

$C_{2v'}$. The situation here might at first sight be assumed to be the converse of that appertaining to the C_{2v} isomer, i.e. a band of
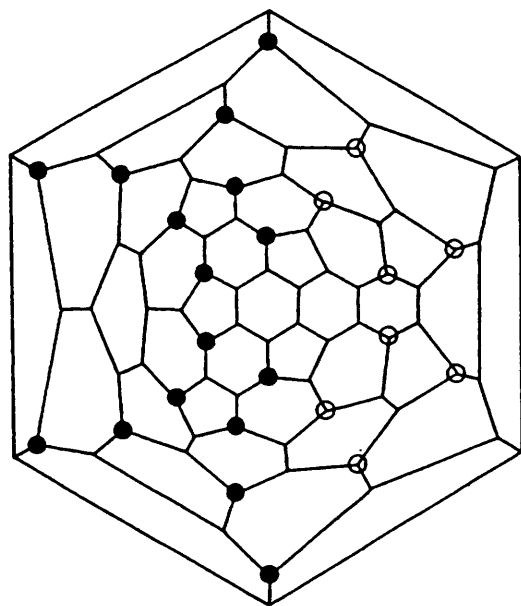
Fig. 16 Proposed disposition of bulky groups in C_{78} (C_{2v}): primary (●) and secondary (○) addition sites
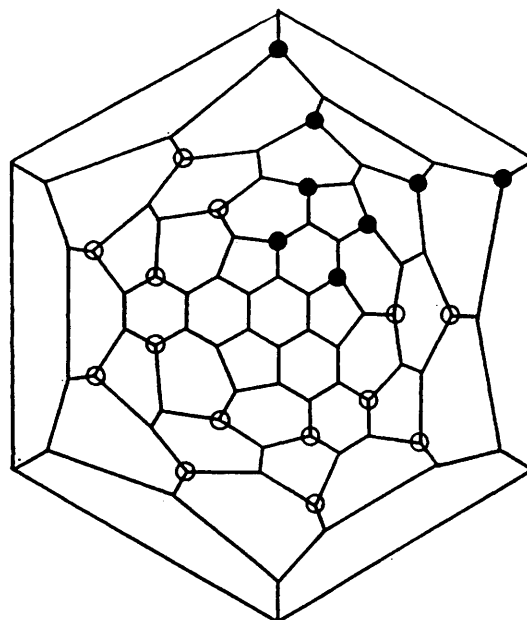

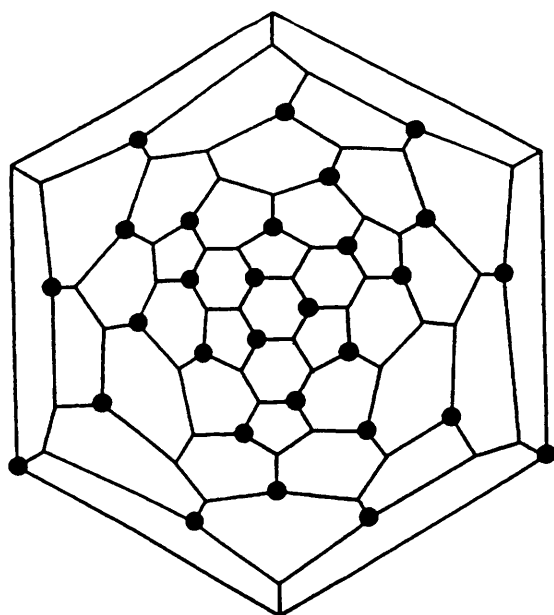Fig. 18 Proposed disposition of bulky groups in C_{78} (C_{2v}·): mutually exclusive addition sites (●, ○)

Fig. 17 Proposed disposition of bulky groups in C_{78} (D_3)

Fig. 19 Proposed disposition of bulky groups in C_{78} D_{3h}·): all the sites ● can only be occupied if the sites ○ are also occupied (see Text)

Fig. 20 Proposed disposition of bulky groups in the vicinity of pentagons on opposite sides of a hexagon (see Text)

eight groups aligned along the long axis [Fig. 18 (●)], and an equatorial band of, in this case, 14 groups [Fig. 18 (○)]. However there is one major difference which is that it is not possible to have both these possibilities because a diradical results. Thus, for this isomer, we expect only $C_{78}X_8$ and $C_{78}X_{14}$. The lower extent of addition here may facilitate separation of this isomer *via* addition–elimination.

D_{3h}·. Addition here cannot consist solely of the anticipated equatorial band of 18 added groups [Fig. 19 (●)], because this also creates a diradical due to the isolation of an odd number (25) of carbons at each cap. This may be overcome either by the addition of a further six groups at the positions shown in Fig. 19 (○), or by having eight or 14 groups around the equatorial waist. Predicted derivatives are therefore $C_{78}X_8$, $C_{78}X_{14}$ and $C_{78}X_{24}$.

C_{84}.—The isomers here differ in being the first fullerenes to have some pentagons in *para* arrangements. As well as addition taking place according to the pattern given in Fig. 12, some
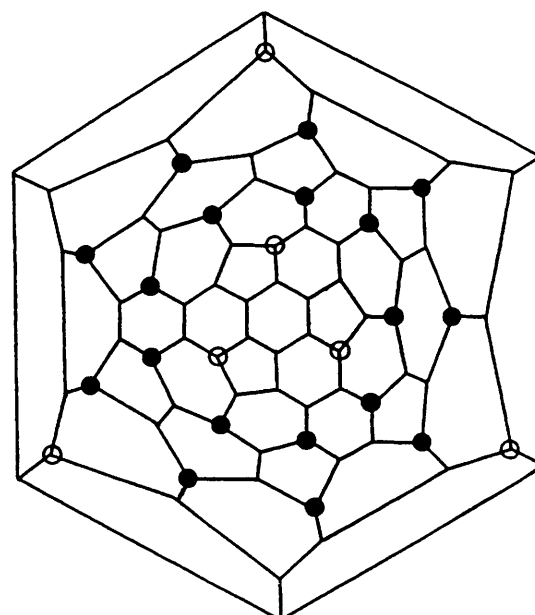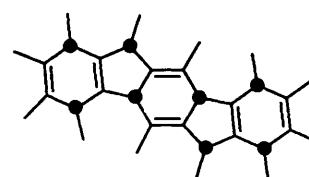
further addition according to the pattern shown in Fig. 20 may also be possible.

D_2. Symmetrical addition of 16 groups [Fig. 21 (●)] may be accompanied by a secondary symmetrical addition of a further 12 groups [Fig. 21 (○)]. Thus, the expected products here will be $C_{84}X_{16}$ and $C_{84}X_{28}$.

D_{2d}. Although the pattern is different here, the overall conclusion is the same as for the D_2 isomer, *i.e.* addition of 16
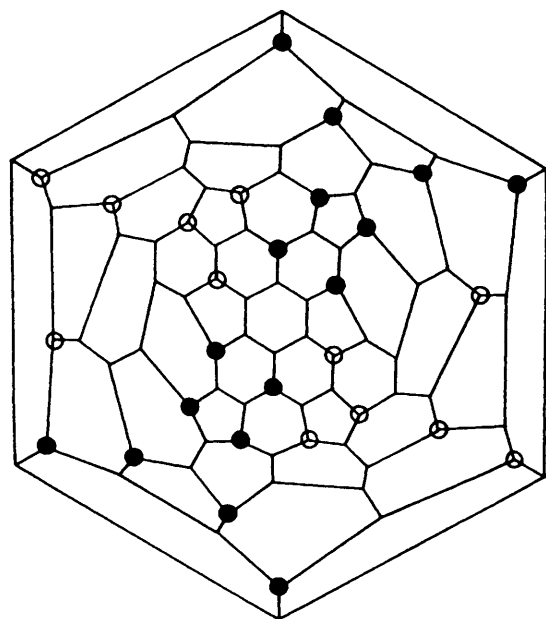
Fig. 21 Proposed disposition of bulky groups in C_{84} (D_2): primary (●) and secondary (○) addition sites
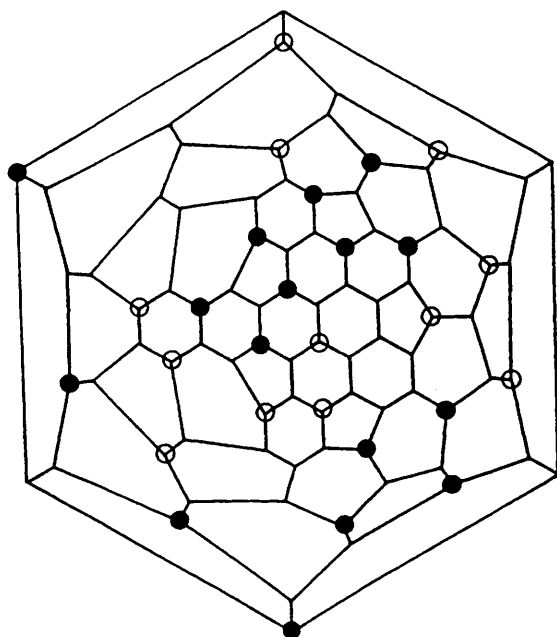

Fig. 22 Proposed disposition of bulky groups in C_{84} (D_{2d}): primary (●) and secondary (○) addition sites

groups in a symmetrical way [Fig. 22 (●)] followed by a secondary addition of a further 12 groups [Fig. 22 (○)].

Acknowledgement

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