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Stereochemical patterns formed by addition to fullerene C_{60}

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Abstract

A combined theoretical and experimental approach is used to recognize the sterochemical patterns which emerge when X_2 (X = H, halogen, etc.) is added to C_{60} to form $C_{60}X_n$, and the patterns formed by rings which incorporate carbon atoms of the fullerene, $C_{60}(ring)_n$. Addition to form $C_{60}X_2$ occurs either at an edge linking two hexagonal faces on C_{60}, or across the *para*-positions of one of the hexagonal faces. Further addition occurs to produce potentially a very great number of isomers, but in some cases at least the pattern emerging is relatively simple. An important feature is the tendency of hexagonal faces with low degrees of addition, for example C_6H_2 or C_6Br, to add further groups to form C_6H_4 or C_6Br_2 for example. This feature results in the production of chains, formed by the edge sharing of these hexagonal faces, which progressively increase in length as the extent of addition increases. Particularly stable structures are formed if these chains eliminate the chain ends to form cyclic structures. Examples include the skew pentagonal pyramids in $C_{60}X_6$, $C_{60}X_{12}$ and $C_{60}X_{18}$, the crowns in $C_{60}X_{18}$ and $C_{60}X_{36}$, and the rhombicuboctahedral pattern in $C_{60}X_{24}$. The ring compounds $C_{60}(ring)_{1-6}$, formed by additions to hex–hex edges, have rings occupying octahedral sites about the C_{60}.

Keywords: Stereochemical patterns; Fullerene halides; Molecular structure; Fullerene hydrides

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1. Introduction

This review is dedicated to Professor Dr. Kees Vrieze on the occasion of the 25th anniversary of his appointment to the Chair of Inorganic Chemistry at the University of Amsterdam.

Kees, Barry Lever, the Editor of this journal, and one of us (DLK) shared a laboratory at University College London in the early 1960s when we were, to quote one of Kees's expressions "all bright-eyed and bushy tailed". Our friendship included some collaborative work on metal–metal bonded clusters, and this review is the most recent example of a continuing interest in chemistry, clusters and geometry.

There are two important questions which need to be answered concerning any molecule, including C_{60}. The first is: "What are the reactions?" Research in this area is developing rapidly and the reader is referred to a 1993 review by Taylor and Walton [1] and a 1994 monograph by Hirsch [2]. The second important question is: "Where are the reactions occurring?" This question is of particular interest when several groups are attached to the initial molecule. All chemists are aware of the dominant importance of such questions of isomerism and the fact that disubstituted benzenes may exist as *ortho*, *meta* and *para* isomers, and that trisubstituted benzenes also exist as three isomers, and the *cis* and *trans* isomerism in disubstituted octahedral metal complexes, and the *mer* and *fac* isomerism in trisubstituted complexes.

Consequently, it may come as a shock when one starts to consider the isomerism possible in C_{60} (Fig. 1). The number of geometric isomers possible for $C_{60}X_2$ is 23, and 15 of these will exist as a pair of optical isomers. The number of isomers increases rapidly as the number of X groups in $C_{60}X_n$ increases, as shown in Table 1, even for the simple case when all X groups are the same [3]. These very large numbers immediately suggest that mixtures of a very large number of isomers will be observed, reminiscent of the difficulty of describing a unique structure for soil molecules such as humic acid, or for polymers such as polypropylene, or for biological molecules such as DNA. Nevertheless, there is no doubt that, at least in some cases, it is possible to obtain single well-defined isomers of $C_{60}X_n$.

This review is concerned with the still sparse experimental data on the structure of fullerene adducts, together with an appropriate theoretical framework in which the patterns of addition can be understood. In creating the theoretical framework it is necessary to calculate the stabilities of many hundreds or even thousands of isomers. It is also necessary not to impose any preconceived ideas of symmetry upon the molecule. The most appropriate theoretical technique is a semi-empirical quantum-mechanical method and all results quoted here, unless otherwise stated, were obtained using the AM1 Hamiltonian and the program MOPAC 6.0.

An important result from calculations of this type carried out on C_{60} show that there is a much greater electron density in those carbon–carbon bonds along the polyhedral edges between two hexagonal faces (the hex–hex edges) than in those bonds along the polyhedral edges between a pentagonal face and a hexagonal face (the pent–hex edges) (Fig. 1). The theoretical method described above yields bond orders of 1.49 for the hex–hex edges and 1.10 for the pent–hex edges. In many

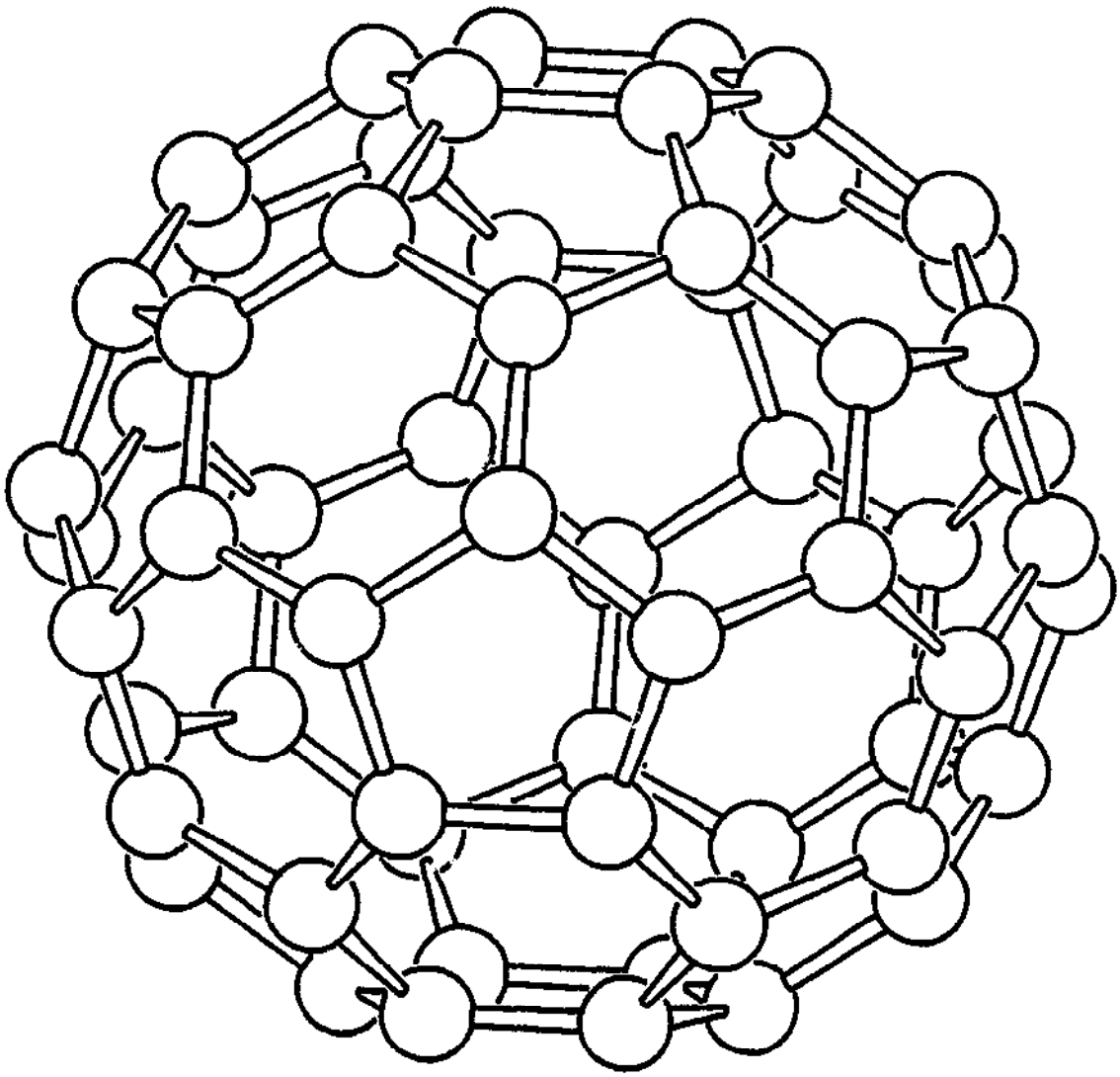
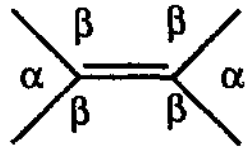


Fig. 1. The truncated icosahedral structure of C_{60}.

Table 1
Number of geometric isomers for $C_{60}X_n$

$C_{60}X_n$	Number
$n=2$	23
$n=4$	4 190
$n=6$	418 470
$n=8$	21 330 558
$n=10$	628 330 629
$n=12$	11 661 527 055
$n=20$	34 932 048 763 560
$n=30$	985 538 239 868 528

reactions C_{60} behaves as an olefin [1,2]. The preference of the double bonds for the hex–hex edges can be rationalized in terms of valence-shell electron-pair repulsion theory [4]. Consider the double bond



The angle α is expected to be less than β because of the increased electron density in the double bond compared with the single bonds, so that the double bond is expected to project towards a pentagon (bond angle, 108°) rather than a hexagon (bond angle, 120°).

2. Addition to hex–hex edges

2.1. *Molecules of the first series*

2.1.1. $C_{60}X_2$

There are 23 possible isomers for $C_{60}H_2$. Calculations using the AM1 Hamiltonian show that the heats of formation range from 931.2 to 990.5 kcal mol^{-1} [5]. The most stable isomer is that formed by simple addition of H_2 onto one of the localized double bonds on a hex–hex edge (Fig. 2). These two carbon atoms are lifted out of the spherical C_{60} surface by 0.29 Å and have a normal tetrahedral stereochemistry (C–C–C = 110.2°; H–C–C = 108.7°). The remainder of the fullerene structure is relatively unchanged, with the 29 hex–hex edges having bond orders of 1.47–1.50 and the 60 pent–hex single bonds having bond orders of 0.97–1.14.

The second most stable isomer of $C_{60}H_2$ is formed by the addition of H_2 across the *para* positions of a C_6 ring. This isomer is 4.4 kcal mol^{-1} less stable than the hex–hex isomer. The third most stable isomer is 16.1 kcal mol^{-1} less stable than the hex–hex isomer.

The relative stabilities of the hex–hex and *para*-C_6H_2 isomers is a balance between steric and electronic effects. There is significant H—H repulsion in the hex–hex C_2H_2 isomer as the rigidity of the C_{60} cage results in the two C—H bonds being held in the unfavourable eclipsed arrangement. On the other hand, the *para* addition forms a C_6H_2 ring with a quinone arrangement of double bonds, one of which must lie on a pent–hex edge, which is unfavourable. Indeed, there is a direct correlation between stability and the number P of double bonds on pent–hex edges, as indicated, for example, for the eight most stable isomers of $C_{60}H_2$ (Fig. 3).

Calculations at the Hartree–Fock level using 3–21G and 6–31G* basis sets confirm the order of stability of these isomers, with a somewhat larger difference of 7.6–7.8 kcal mol^{-1} between the hex–hex and *para*-C_6H_2 isomers [6].

For the more general case of $C_{60}X_2$ molecules, the unfavourable X–X repulsion

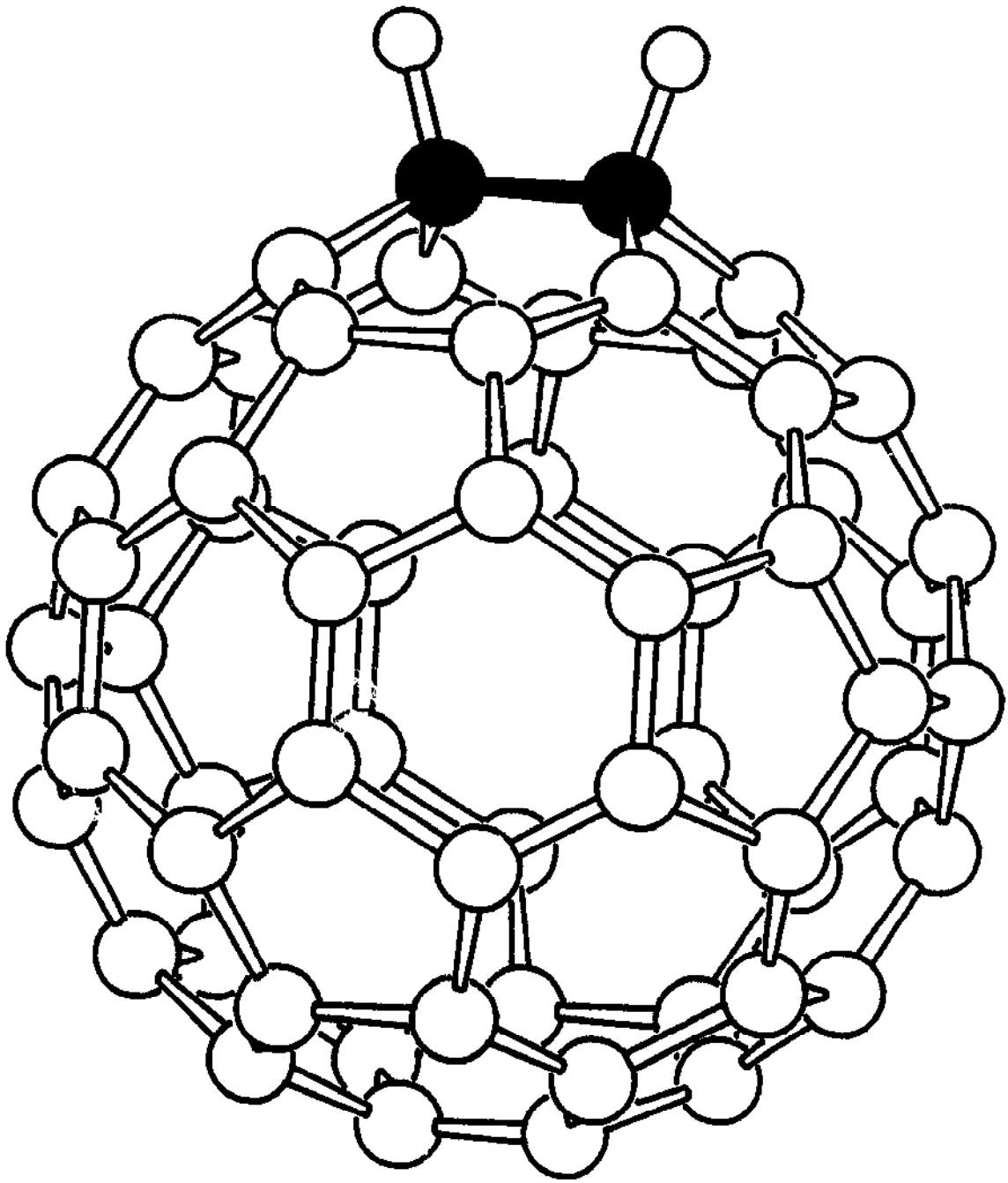
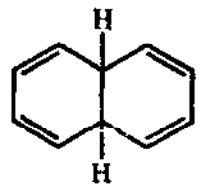


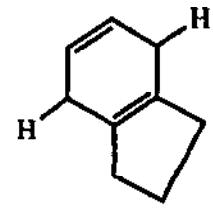
Fig. 2. Structure of $C_{60}H_2$. For clarity, the HC–CH carbon atoms and bond are shaded. A pair of hydrogen atoms are attached to the carbon atoms, forming a hex–hex edge.

present for large groups such as Br and Me destabilize the hex–hex isomer so that it becomes comparable in stability to the *para*-C_6X_2 isomer (Table 2) [7–9].

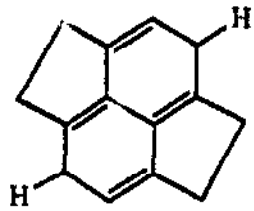
These general expectations are confirmed by experiment. $C_{60}H_2$ has been prepared by the reaction of C_{60} with $BH_3 \cdot THF$ [10] or $(C_5H_5)_2Zr(H)Cl$ [11] followed by hydrolysis, or even by zinc–acid reduction [12]. Only the hex–hex isomer has been found.



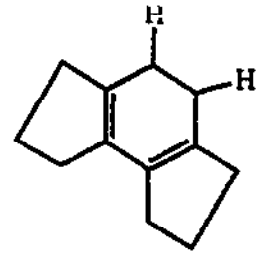
$P = 0$
$\Delta H_f^\circ = 931.2$



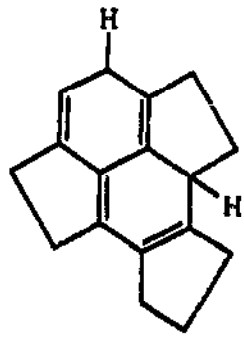
$P = 1$
$\Delta H_f^\circ = 935.6$



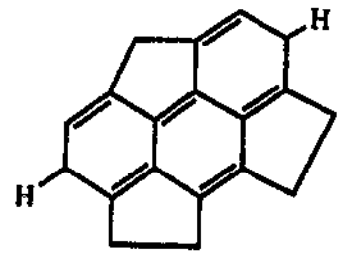
$P = 2$
$\Delta H_f^\circ = 947.3$



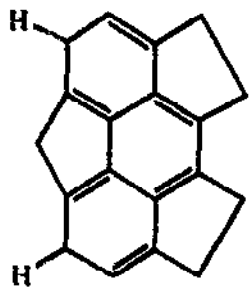
$P = 2$
$\Delta H_f^\circ = 950.0$



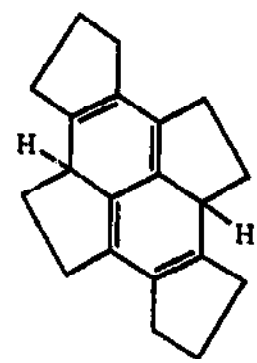
$P = 3$
$\Delta H_f^\circ = 956.2$



$P = 3$
$\Delta H_f^\circ = 957.6$



$P = 4$
$\Delta H_f^\circ = 964.5$



$P = 4$
$\Delta H_f^\circ = 964.6$

Table 2
Heats of formation, for two isomers of $C_{60}X_2$

	Heat of formation (kcal mol^{-1})		B-A (kcal mol^{-1})
	Hex–hex isomer (A)	*para*-C_6X_2 isomer (B)	
$C_{60}H_2$	931.2	935.6	4.4
$C_{60}F_2$	864.8	869.0	4.2
$C_{60}Br_2$	960.7	959.5	−1.2
$C_{60}Me_2$	930.9	930.7	−0.3

There are a number of molecules of the type $C_{60}(H)(X)$ [13,14]. The addition of lithium alkyls or Grignard reagents to C_{60} followed by hydrolysis forms $C_{60}(H)(R)$, where R = Me, Et, Pr, Bu. Only the hex–hex isomer was obtained in each case. Even in the case of the bulky $SnBu_3$ group, only the hex–hex isomer of $C_{60}(H)(SnBu_3)$ was obtained. Amines (R_2NH) readily react with C_{60} to form $C_{60}(H)(NR_2)$ where the H and NR_2 groups are again attached to the two carbon atoms of a hex–hex edge [15]. However, the addition of very bulky azacrown ethers, such as $HN(C_8H_{16}O_3)$, to C_{60} to form $C_{60}(H)[N(C_8H_{16}O_3)]$ yielded two isomers, believed to be the hex–hex and *para*-C_6X_2 isomers [16].

Greater steric interactions will occur in $C_{60}X_2$ if neither group is H. Electrochemical reduction of C_{60} to C_{60}^{2-} in benzonitrile followed by the addition of a large excess of methyl iodide forms $C_{60}(Me)_2$. Two isomers were isolated, which are believed to be the hex–hex and *para*-C_6X_2 isomers [17].

A number of examples of the addition of rings to hex–hex edges are discussed in the next section.

2.1.2. $C_{60}X_4$ to $C_{60}X_{12}$

The number of possible geometric isomers increases rapidly as the number of groups attached to C_{60} increases from 23 isomers for $C_{60}X_2$ to 1.2×10^{10} for $C_{60}X_{12}$ (Table 1). It clearly becomes impossible to consider each isomer separately. The problem can be considerably simplified to a first approximation by making two assumptions.

(1) Successive addition of pairs of atoms always occurs on a hex–hex edge, as observed for $C_{60}H_2$ and $C_{60}(H)(X)$. Even if this assumption is not completely justified, it is a reasonable starting point. Even if the results are of questionable value for $C_{60}X_n$, they will be useful in predicting the stereochemical consequences of adding a number of rings to the hex–hex edges of C_{60} in those cases where the steric requirements of the ring prohibit the formation of *para*-C_6X_2 addition. This assump-

Fig. 3. Localization of double and single bonds in $C_{60}H_2$ to form six-membered quinone-type rings in the immediate vicinity of the hydrogen atoms. Those pentagonal faces containing double bonds are also shown. The remainder of each structure is unaltered, with double bonds along the hex–hex edges and single bonds along the pent–hex edges, as in C_{60}. *P* is the number of bonds along pent–hex edges. Values of ΔH_f° are in kcal mol^{-1}.

tion at least has the virtue of reducing the number of possible isomers to a manageable size (eight for $C_{60}X_4$, 46 for $C_{60}X_6$ and 262 for $C_{60}X_8$), but the numbers again become too large for the higher homologues: 1.3×10^3 for $C_{60}H_{10}$, 5.1×10^3 for $C_{60}X_{12}$, 2.5×10^5 for $C_{60}X_{20}$ and 1.3×10^6 for $C_{60}X_{30}$ (cf. Table 1).

(2) The positions of all X atoms in $C_{60}X_n$ do not change when further addition takes place to form $C_{60}X_{n+2}$. The validity of this assumption probably depends upon experimental conditions. It appears to be valid for $C_{60}H_n$ at low temperatures, but it is not valid for cases such as $C_{60}Br_n$, which readily and reversibly lose bromine.

The application of these two assumptions leads to the first series of molecules. Discarding assumption 2 is discussed in Section 2.2, and discarding Assumption 1 is discussed in Section 3.

The addition of hydrogen to $C_{60}H_2$ can form eight possible isomers of $C_{60}H_4$, with pairs of hydrogen atoms occupying hex–hex edges. The AM1 calculations [5] show that the most stable isomer is the one in which the vectors joining the centre of the molecule to the midpoints of the two HC–CH edges form an angle of 90°. However, this result is of marginal significance as the heats of formation of the first five isomers are all within 0.5 kcal mol^{-1} of the most stable isomer, and all eight isomers lie within 3.5 kcal mol^{-1} of each other. Calculations at the Hartree–Fock level using 3–21G and 6–31G* basis sets predict that the most stable isomer is the one containing a C_6H_4 ring [18]. Experimentally, it is found that the reduction of $C_{60}H_2$ with $BH_3 \cdot THF$ yields a complex mixture of six products, of which the one containing the $C_{60}H_4$ ring is the most stable [18].

The AM1 calculations [5] for $C_{60}H_6$ again predict that the most stable isomer is the one in which the vectors from the centre of the molecule to the midpoints of the three HC–CH edges are mutually at right angles to each other. The structure can be conveniently described as a *facial* arrangement of three C_2H_2 moieties on the three vertices of an octahedron centred on the centre of the molecule. Again, the result is of marginal significance as there are eight other isomers with values of the heat of formation within 1.0 kcal mol^{-1} of that for the most stable isomer.

This pattern of hydrogenation continues to $C_{60}H_8$ and $C_{60}H_{10}$ and culminates at $C_{60}H_{12}$ in which there is an octahedral arrangement of six C_2H_2 (Fig. 4). This rather beautiful molecule has T_h symmetry and has only three types of carbon atom, those that are attached to hydrogen atoms and two types that are hydrogen free.

Structurally characterized molecules $C_{60}X_6$ to $C_{60}X_{12}$, in which pairs of X atoms are attached to pairs of carbon atoms forming hex–hex edges, are not known. However, an extensive chemistry involving the double bond on the hex–hex edge with a variety of reagents, including organometallic fragments, dienes, diamines and cyclopropane units, is known.

One of the very early structures of C_{60} derivatives to be determined was that of $C_{60}[Pt(PEt_3)_2]_6$ in which a double bond on a hex–hex edge behaves as an alkene, donating a pair of electrons to the metal atom forming a three-membered C_2Pt ring. Each metal atom occupies the site of a pair of hydrogen atoms in Fig. 4, with the six metal atoms forming a large octahedron about the C_{60} [19].

Likewise, the reaction of C_{60} with diethylbromomalonate forms $C_{60}[C(COOEt)_2]_6$ in which there is an octahedral arrangement of six cyclopropane groups [20].

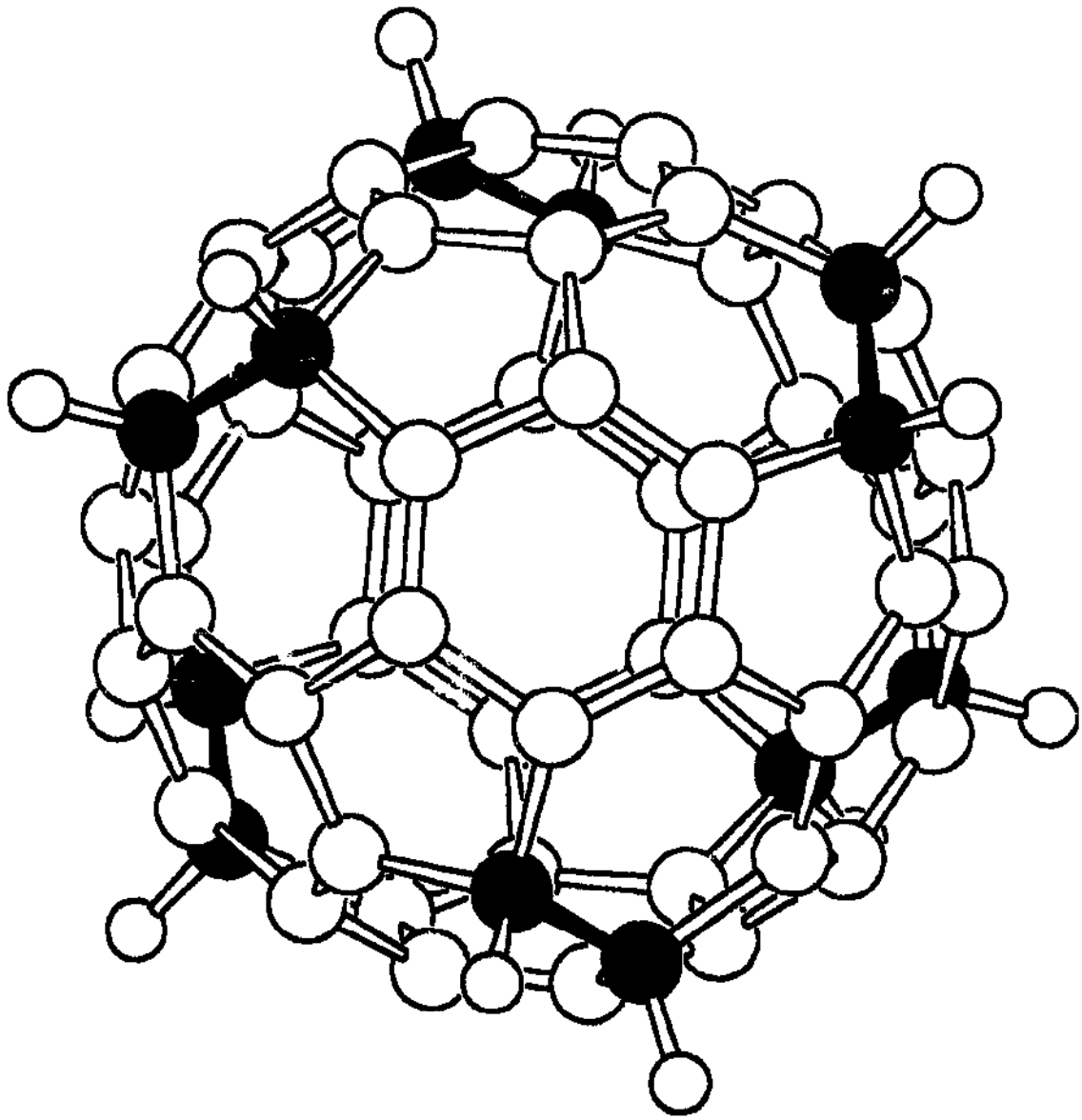
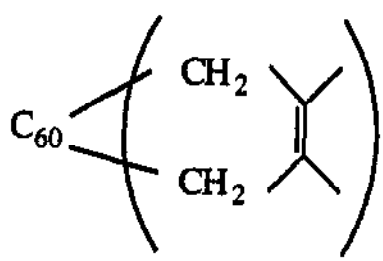


Fig. 4. Structure of $C_{60}H_{12}$ (first series). For clarity, the HC–CH carbon atoms and bonds are shaded. Six pairs of hydrogen atoms are attached to the hex–hex edges, with the midpoints forming a regular octahedron.

More recent examples [21] include the addition of six 2,3-dimethyl-1,3-butadiene molecules to a set of six mutually octahedral hex–hex edges of C_{60} to form



The addition of two, three, four or five ring systems to C_{60} is more complex and may lead to mixtures of isomers, which is consistent with the calculations described above for the simple hydrides. For example, diamines such as $HN(CH_2CH_2)_2NH$ form $C_{60}[N(CH_2CH_2)_2N]$ with loss of hydrogen. In the case of the bisadduct $C_{60}[N(CH_2CH_2)_2N]_2$ six different isomers were isolated, confirming the energetic similarity of a number of isomers [15].

In $C_{60}[O_2OsO_2(NC_5H_4Bu)_2]_2$, in which each osmium atom is connected to a hex–hex edge via two bridging oxygen atoms, five isomers were isolated, including the *cis* and *trans* octahedral isomers [22]. In the case of $C_{60}[Ir(CO)Cl(PMe_2Ph)_2]_2$, in which each iridium atom is attached to a hex–hex edge, the two metal atoms are as far apart as possible [23]. The observation of this *trans* isomer can be attributed to the much greater bulk of this organometallic group.

The 9,10 positions of anthracene add onto hex–hex edges of C_{60} to form C_{60} (anthracene) and C_{60} (anthracene)$_2$. The appearance of only three ^1H NMR and thirteen ^{13}C NMR signals indicates D_{2h} symmetry, i.e. the anthracene molecules are on opposite hex–hex edges to give the *trans* octahedral structure [24].

A series of compounds of the type $C_{60}(CR_2)_n$, where $n=1$ to 6, are known. Experimental [25–27] and theoretical [28–30] studies show that addition can take place in two ways.

(a) The carbon atom can add onto the double bond of the hex–hex edge, converting it into a single bond with the formation of a cyclopropane ring.

(b) The carbon atom can add onto the pent–hex edge, breaking this carbon–carbon single bond with the creation of a six-membered ring and a seven-membered ring.

A particularly interesting series of reactions occur on the reaction of diethylbromomalonate and base to C_{60} to form $C_{60}[C(COOEt)_2]$ with a cyclopropane ring as in (a) above [20]. Addition of a second group forms $C_{60}[C(COOEt)_2]_2$; seven different isomers were isolated, again showing the energetic similarity of a number of isomers for this degree of addition. The isomer obtained in highest yield was the *cis* octahedral isomer. Addition of a third cyclopropane ring to this *cis* octahedral isomer forms $C_{60}[C(COOEt)_2]_3$; only the *fac* octahedral isomer was obtained, which corresponds to the most stable isomer of $C_{60}H_6$ in this first series. Likewise, addition of further groups only forms the isomers of $C_{60}[C(COOEt)_2]_4$ and $C_{60}[C(COOEt)_2]_5$, as expected from the calculations for $C_{60}H_8$ and $C_{60}H_{10}$. The completion of the octahedral $C_{60}[C(COOEt)_2]_6$ has been referred to above.

2.1.3. $C_{60}X_{14}$ to $C_{60}X_{36}$

Further addition of hydrogen to the hex–hex edges of $C_{60}H_{12}$ necessarily eliminates the possibility of well-separated HC–CH groups. All unhydrogenated hex–hex edges of the T_h structure of $C_{60}H_{12}$ are identical, all belonging to bare C_6 rings. There are eight such rings, one lying on each octahedral face of the octahedron of HC–CH groups. Therefore only a single isomer of $C_{60}H_{14}$ is possible. It should be noted that this structure contains a C_6H_4 ring [31].

The most favourable position for the addition of a further pair of hydrogen atoms to form $C_{60}H_{16}$ is adjacent to the pair that were added when forming $C_{60}H_{14}$ from

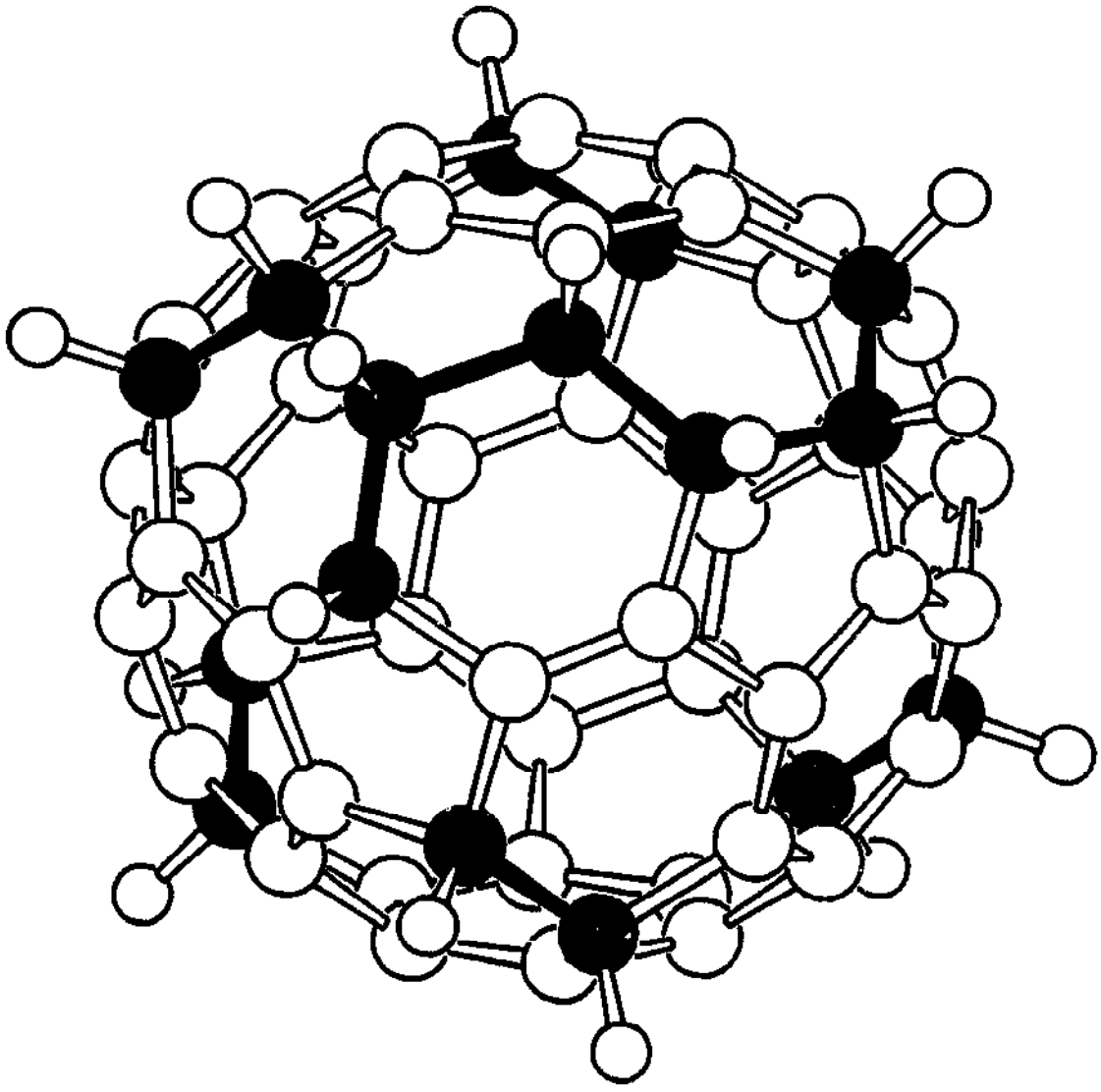


Fig. 5. Structure of $C_{60}H_{16}$ (first series). For clarity, the HC–CH carbon atoms and bonds are shaded. The molecule is drawn in the same orientation as for $C_{60}H_{12}$ (Fig. 4).

$C_{60}H_{12}$ [31]. The structure is shown in Fig. 5 and contains a number of interesting features. Firstly, it contains three linked C_6H_4 rings, the linkage occurring by the sharing of common HC–CH edges. Secondly, there is branched aliphatic string of eight CH groups winding over the structure.

This progressive growth of a chain of edge-shared C_6H_4 rings, or the progressive growth of the aliphatic $(CH)_n$ string, continues with the addition of further pairs of hydrogen atoms to hex–hex edges [31]. This process culminates at $C_{60}H_{24}$ [31] (Fig. 6) in which there are nine C_6H_4 rings linked in a circle. The aliphatic string $C_{18}H_{18}$ forms a continuous crown sitting on top of the C_{60}. This crown includes three of the six HC–CH groups present in $C_{60}H_{12}$. The structure has C_3 symmetry, with the three-fold axis passing through an unhydrogenated C_6 ring at the centre of the crown. This C_6 ring is isolated from the other bare carbon atoms by the aliphatic

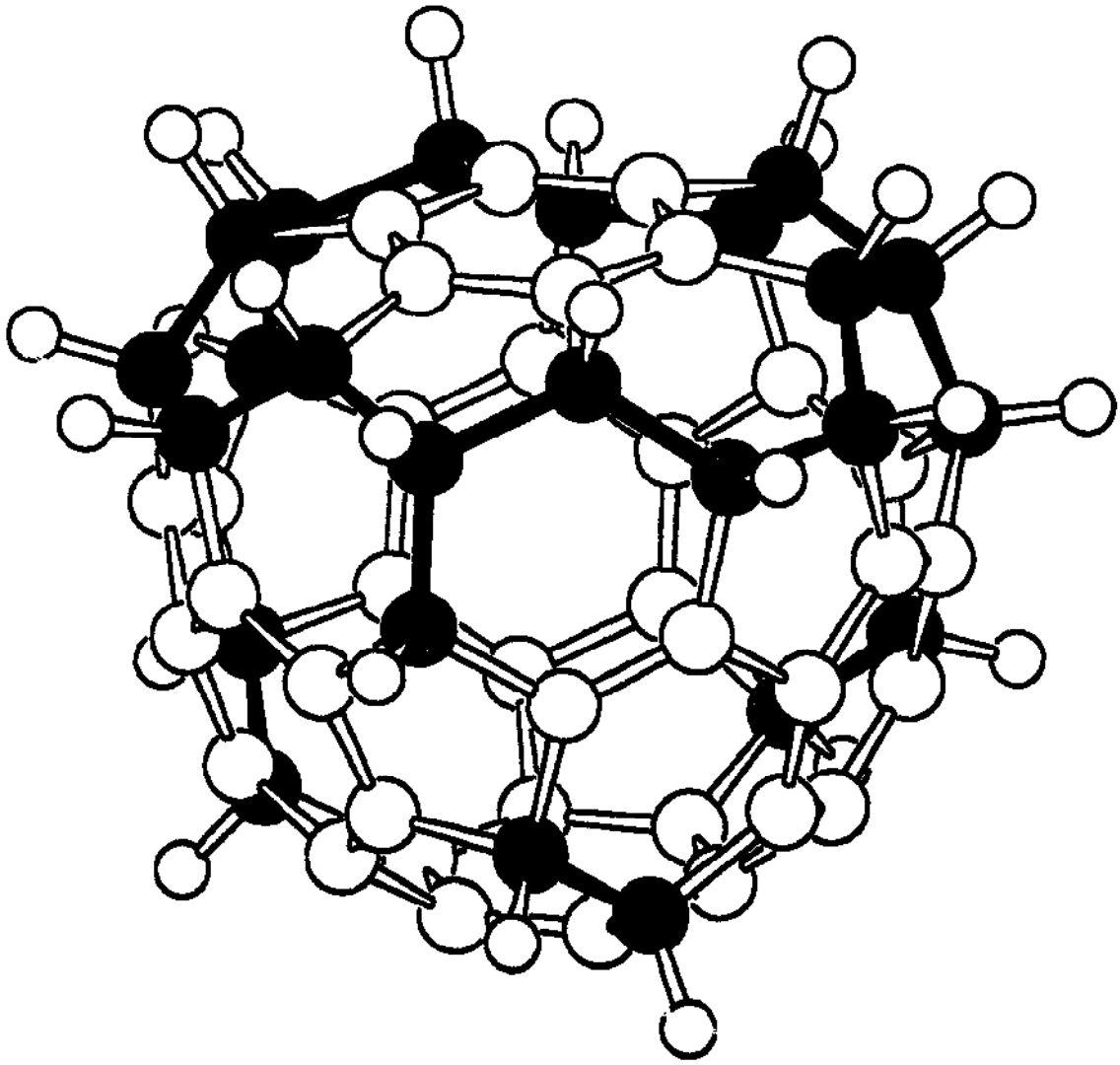


Fig. 6. Structure of $C_{60}H_{24}$ (first series). For clarity, the HC–CH carbon atoms and bonds are shaded. The molecule is drawn in the same orientation as for $C_{60}H_{12}$ (Fig. 4) and $C_{60}H_{16}$ (Fig. 5).

$C_{18}H_{18}$ crown, and the bonds radiating out from the C_6 are relatively coplanar with the C_6 ring because the tetrahedral carbon atoms of the crown are lifted out from the spherical fullerene surface. A chemically interesting consequence is that the bonding in this central C_6 ring is relatively delocalized with alternate bond orders of 1.28 and 1.48, compared with 1.10 and 1.49 for the C_6 rings in C_{60}.

Further addition of pairs of hydrogen atoms to hex–hex edges [32] results in the commencement of a second string of CH groups, growing from one of the three remaining HC=CH edges of $C_{60}H_{12}$. The growth of this second string is complete at $C_{60}H_{32}$, which is viewed down the two-fold axis in Fig. 7. The structure consists of two $C_{18}H_{18}$ crowns fused together by sharing a string of six CH groups, with each crown having an isolated bare C_6 ring at its centre. There is also one remaining isolated HC–CH group.

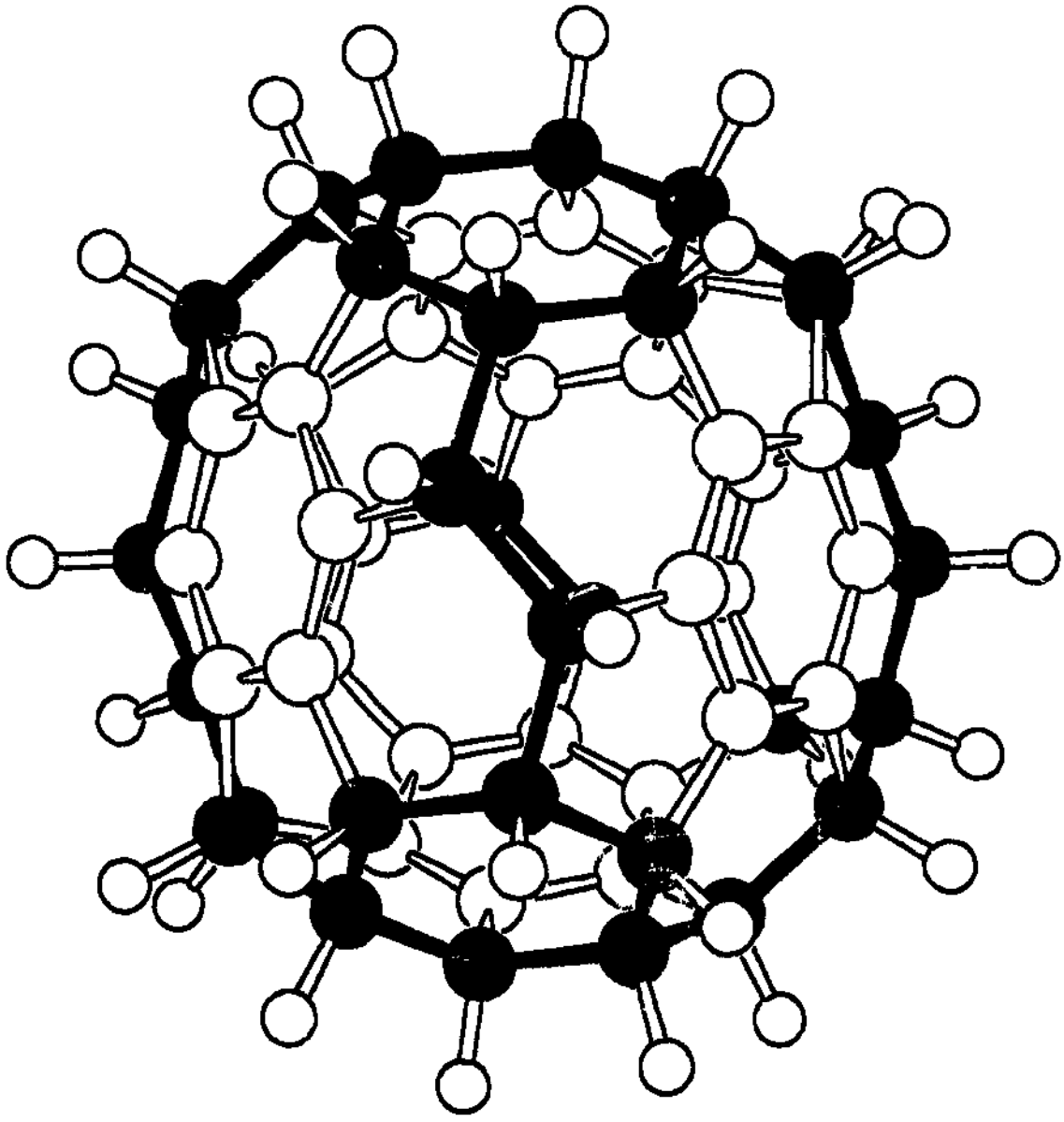


Fig. 7. Structure of $C_{60}H_{32}$ (first series) viewed down the two-fold axis. For clarity, the HC–CH carbon atoms and bonds are shaded.

Further hydrogenation links this last HC–CH group into the string structure. The structure of $C_{60}H_{36}$ is shown in Fig. 8 [32]. This aesthetically beautiful molecule consists of four $C_{18}H_{18}$ crowns fused together. The tetrahedral, rather than the spherical, shape of the molecule is clearly shown in Fig. 8. The vertices of the tetrahedron are formed by four C_6H_6 groups, whereas the flat faces are formed by four bare C_6 groups. The four C_6H_6 rings are linked together by six HC–CH groups lying approximately along the tetrahedral edges. The edges of the C_6H_6 and C_6 rings are twisted by about 10° relative to the tetrahedral edges so that there are no mirror planes in the molecule, with the overall symmetry being T. It should be noted that

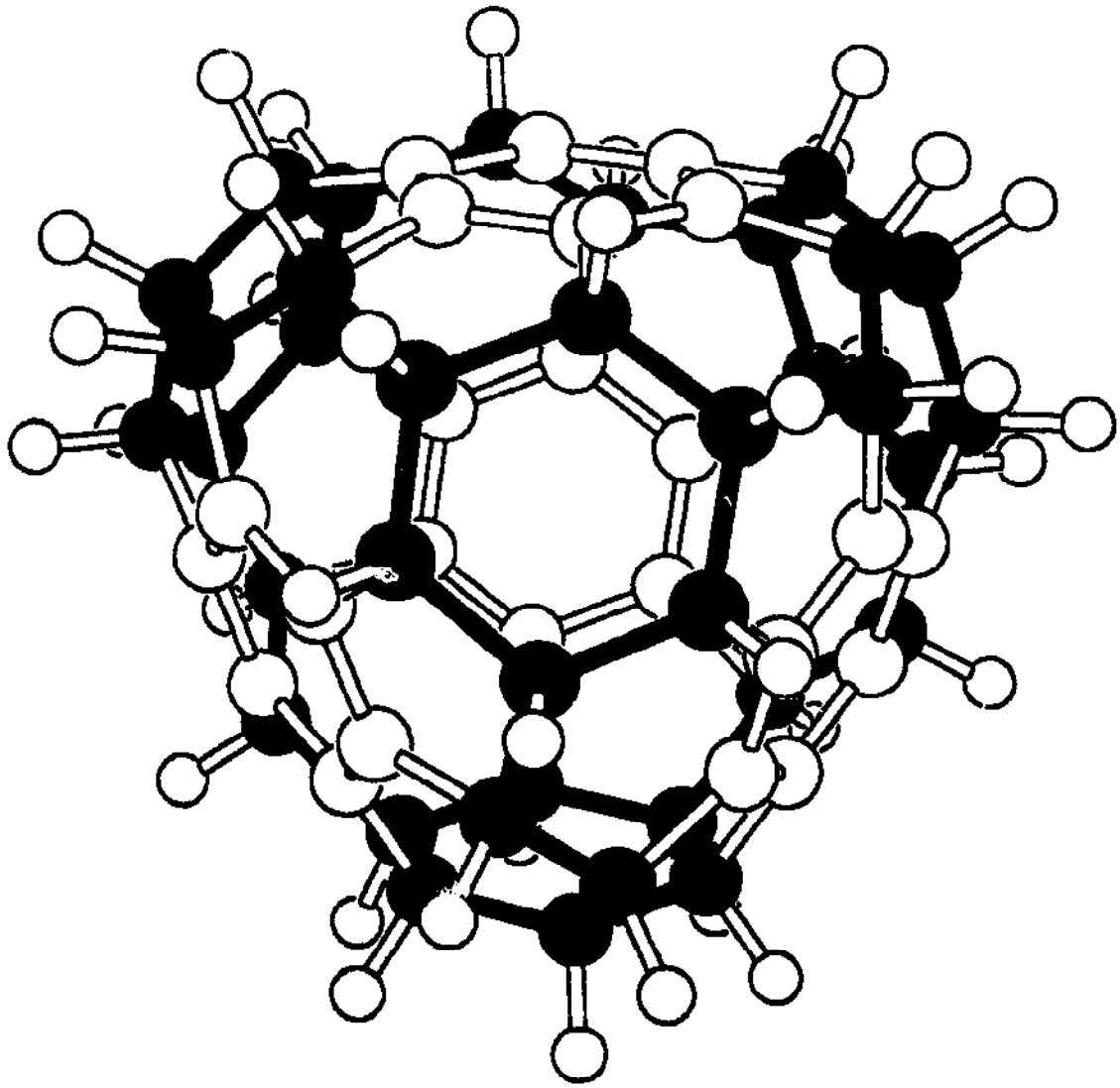


Fig. 8. Structure of $C_{60}H_{36}$ (first series) viewed down the three-fold axis. For clarity, the HC–CH carbon atoms and bonds are shaded.

this tetrahedral structure of symmetry T is not the same as the tetrahedral structure of symmetry T_h proposed by a number of workers which has twelve localized double bonds on pent–hex edges and is less stable than the T structure.

$C_{60}H_{36}$ is discussed in more detail at the end of the next section.

2.2. *Structures arising from rearrangement of X atoms*

The theoretical framework used in Section 2.1 leading to the first series of fullerene hydrides was based on two assumptions.

(a) Pairs of hydrogen atoms add onto hex–hex edges.

(b) When each pair of hydrogen atoms adds onto a fullerene hydride, those atoms already attached to carbon atoms remain attached to those carbon atoms. This

assumption about the non-lability of X atoms probably depends upon the experimental conditions as well as the nature of X.

The consequences of discarding this second assumption are examined in this section. This discarding increases enormously the number of possible isomers and there are far too many for them to be considered individually. Two general methods have been used to further our understanding:

(a) an intuitive approach;

(b) a more analytical approach.

One success of the intuitive approach is based on the observation of the particularly stable structure of $C_{60}H_{24}$ in the first series of molecules, which consists of a $C_{18}H_{18}$ crown and three isolated HC–CH groups (Fig. 6). The question then arises as to whether the crown structure is stable in the absence of the three HC–CH groups. It turns out that this is the case [31], as the crown structure of $C_{60}H_{18}$ with C_3 symmetry shown in Fig. 9 is 1.5 kcal mol^{-1} more stable than the first-series structure of $C_{60}H_{18}$.

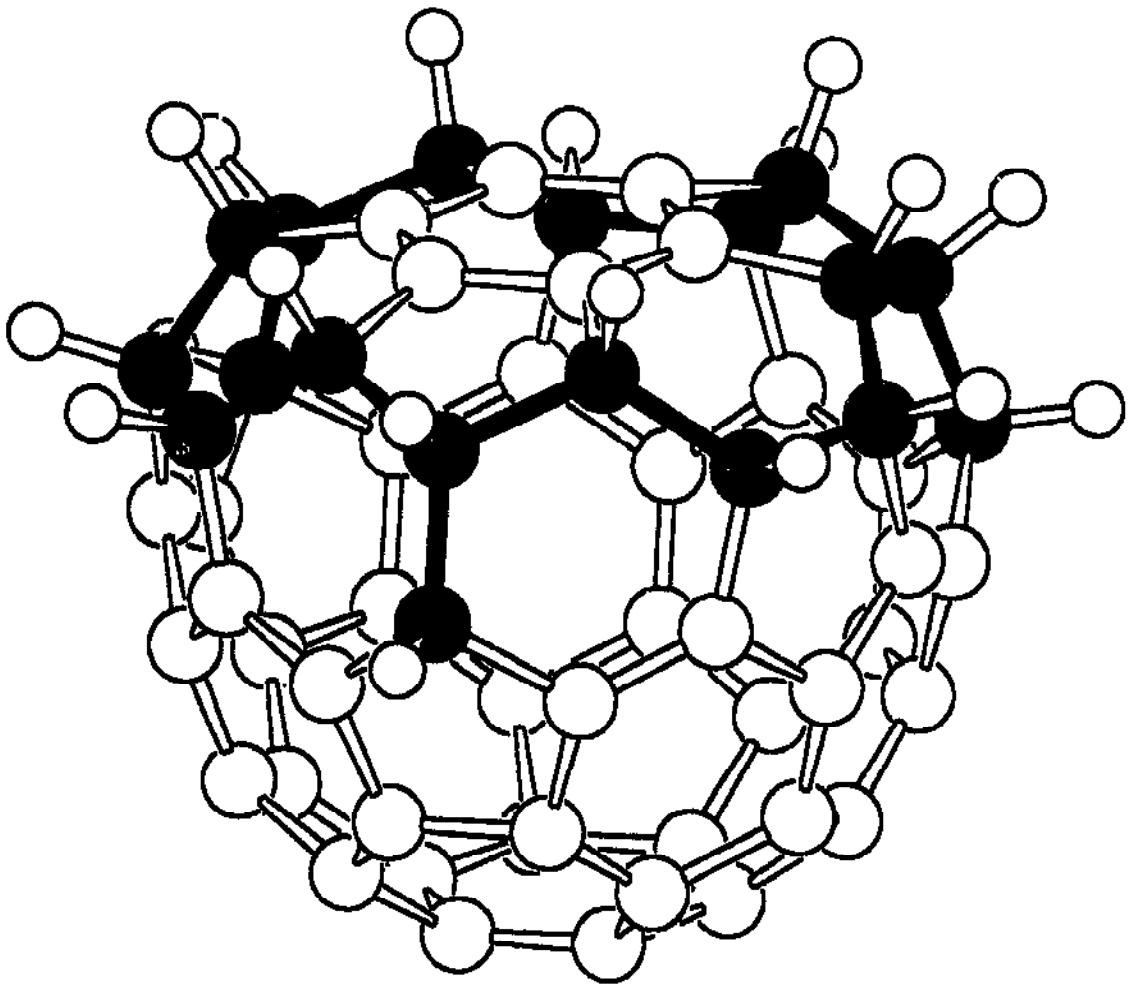


Fig. 9. Structure of $C_{60}H_{18}$ (second series) containing all CH groups linked into a crown. For clarity, the HC–CH carbon atoms and bonds are shaded.

A second series of structures based on this crown structure of $C_{60}H_{18}$ can be obtained by adding successive pairs of hydrogen atoms to hex–hex edges. In this way structures of $C_{60}H_{20}$, $C_{60}H_{22}$, $C_{60}H_{24}$ and $C_{60}H_{26}$, which are more stable than the corresponding structures of the first series, can be generated [31,32].

It is also possible to arrange two $C_{18}H_{18}$ crowns on the surface of C_{60}, as shown in Fig. 10 [32]. A three-fold axis passes through the C_6 rings at the centres of the crowns at the top and bottom of the figure. The two crowns are separated by six C=C groups related to each other by three vertical mirror planes and three horizontal two-fold axes, with the overall symmetry being D_{3d}. This double-crown structure is slightly more stable (0.8 kcal mol^{-1}) than the fused quadruple-crown structure of the first series. A third series of structures can be based on this double-crown structure as before.

The relative energies of the first, second and third series structures for $C_{60}H_n$ are shown in Fig. 11, plotted as $(\Delta H_f^\circ + 18n)$ against n. Extensive searches based on

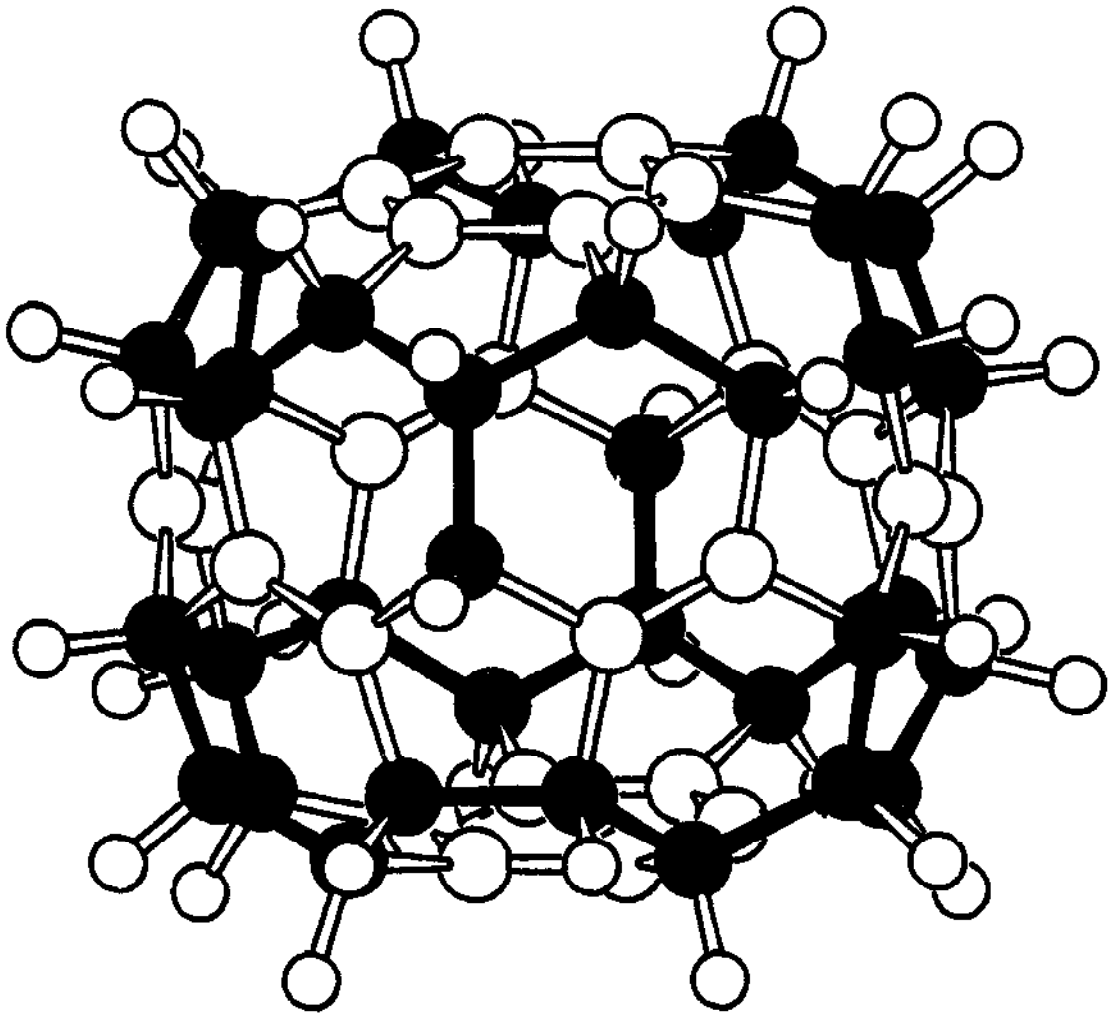


Fig. 10. Structure of $C_{60}H_{36}$ (third series) containing two $C_{18}H_{18}$ crowns. For clarity, the HC–CH carbon atoms and bonds are shaded.

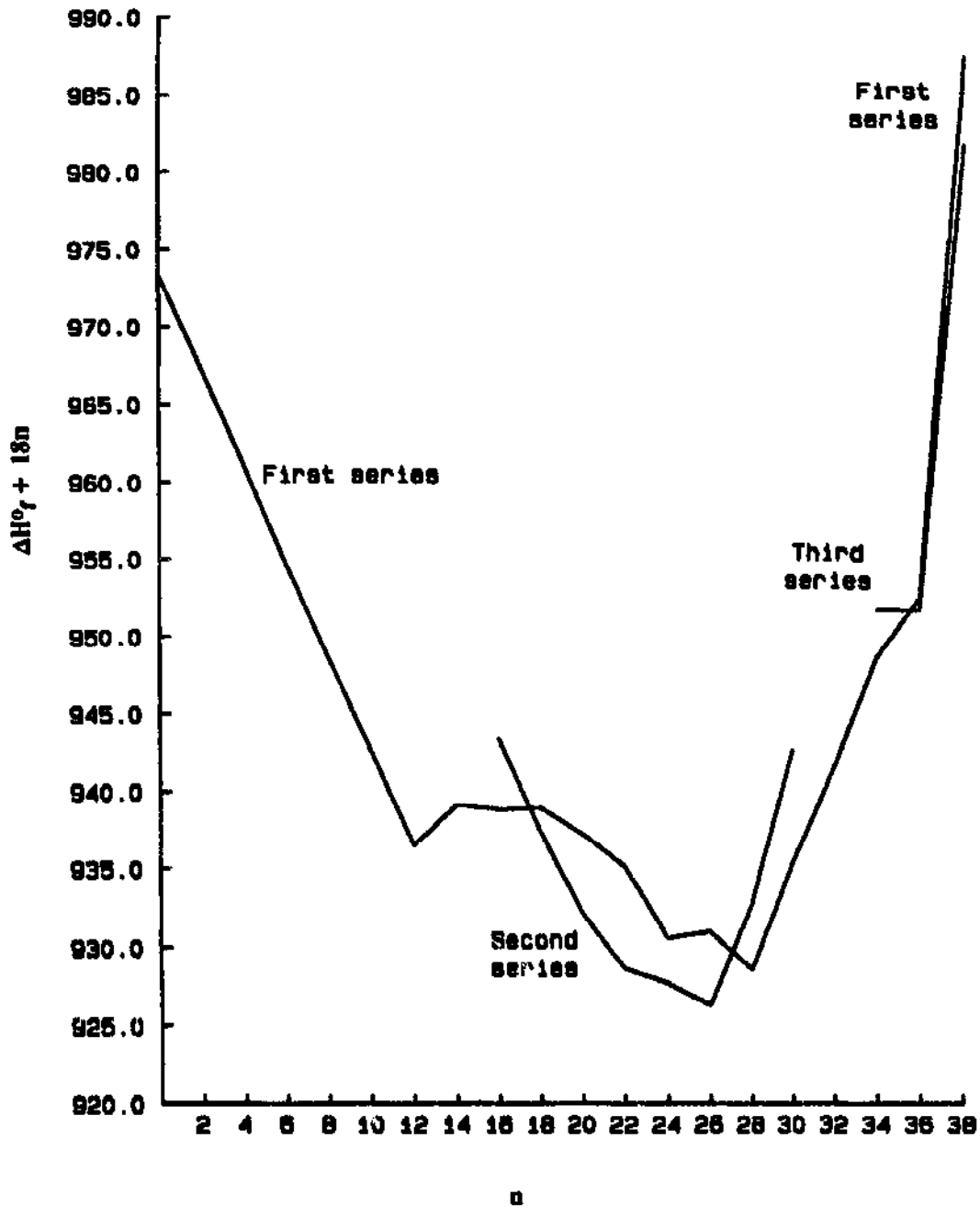


Fig. 11. Heats of formation of $C_{60}H_n$, in which pairs of hydrogen atoms add to hex–hex edges, plotted as $(\Delta H_f^\circ + 18n)$ (kcal mol^{-1}) against n.

further intuitive ideas on the addition of H_2 to hex–hex edges, or based on the many structures which have been proposed in the literature, have failed to reveal any structures that are more stable than those in the first, second and third series described above.

The more analytical approach to the search for stable structures is based on an extensive series of calculations which have been carried out on one of the key

molecules in this area, $C_{60}H_{36}$. The heats of formation of all 63 possible isomers of $C_{60}H_{36}$ formed by successive addition to hex–hex edges and which contain a three-fold axis have been calculated [33]. This group includes both the fused quadruple-crown structure of T symmetry in the first series, and the two-crown structure of D_{3d} symmetry in the third series. These two structures remain the most stable, and are over 26 kcal mol^{-1} more stable than any of the other 61. A listing of all isomers in order of increasing ΔH_f° reveals the qualitative information that the least stable structures have the hydrogen atoms grouped together, leaving large patches of bare carbon atoms. A detailed statistical analysis in terms of the number of each of the 12 types of polyhedral face, C_6H_x and C_5H_x, which may be present shows that the presence of C_6H_4 and/or C_6 faces are particularly stable, as are 1,2,3-C_5H_3, 1,2-C_5H_2 and C_5 faces, whereas C_6H_6 and C_5H_5 rings are particularly destabilizing. In broad terms, this result is consistent with the trend noted above, namely the importance of structures containing linked C_6H_4 rings. An extension of the statistical analysis shows that the stability is further enhanced by the edge-sharing of C_6 and 1,2,3-C_5H_3 rings. This combination of features is precisely that which occurs in the $C_{18}H_{18}$ crowns.

There are a very limited number of ways in which C_6H_4 rings can be linked together around central C_6 rings. All these have been investigated [33]. Only one is more stable than the best of the structures described above. This is the D_{5d} structure of $C_{60}H_{20}$ (Fig. 12), which is a mere 0.5 kcal mol^{-1} more stable than second-series structure of $C_{60}H_{20}$ consisting of a $C_{18}H_{18}$ crown and an isolated HC–CH group.

As commented above, the molecule $C_{60}H_{36}$ is of particular importance. It appears to be the end-product of several methods of reduction, including a large excess of dihydroanthracene at 350°C [34] and hydrogen at 7 MPa and 400°C in the presence of methyl iodide [35]. The structures favoured by theory are the quadruple fused crown structure of the first series of symmetry T, and the two-crown structure of the third series of symmetry D_{3d}. The latter may be more stable, but the calculated difference of 0.8 kcal mol^{-1} is of marginal significance. The solid state ^{13}C NMR of the compound formed by direct hydrogenation [35] shows two lines of equal intensity due to the bare carbon atoms, and four lines of intensity 2:1:2:1 due to CH. This is not consistent with the tetrahedral T structure where there is only one type of bare carbon atom and two types of CH in the ratio 2:1. However, the NMR is consistent with the D_{3d} structure and also with a different structure, also of D_{3d} symmetry, proposed by the authors of the study [35] (or possibly with a mixture of isomers).

3. Addition to *para* positions of C_6 rings

3.1. *Fullerene bromides*

It was shown in Section 2.1.1 that the two preferred structures of $C_{60}X_2$ are those in which the two X groups are on (a) a hex–hex edge or (b) the *para* positions of the C_6X_2 ring. For $C_{60}X_2$ there is a preference for the first mode of addition for

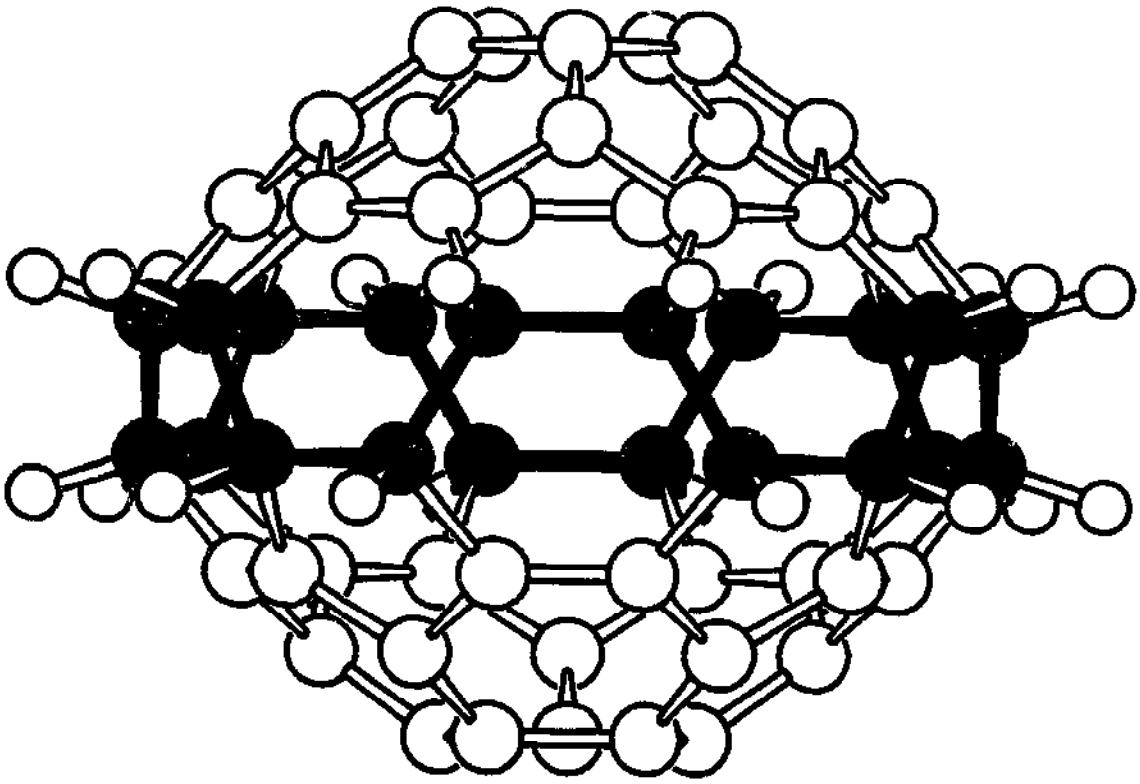


Fig. 12. D_{5d} structure of $C_{60}H_{20}$. For clarity, the HC–CH carbon atoms and bonds are shaded.

hydrogen and fluorine, but for larger groups such as bromine and methyl there is a preference for the second mode of addition.

The assumption made in Section 2 was that the preference for hydrogenation at a hex–hex edge remained for subsequent hydrogenations up to $C_{60}H_{36}$. This assumption is tested in this section. It is also necessary to consider more broadly the bromination pattern in view of the observed structure of $C_{60}Br_6$ which contains *para*-C_6Br_2 and 2,3,5-C_6Br_3 rings, the structure of $C_{60}Br_8$ which contains *para*-C_6Br_2 and *meta*-C_6Br_2 rings, and the structure of $C_{60}Br_{24}$ which contains *para*-C_6Br_2 and 1,3,5-C_6Br_3 rings [36,37].

The abandonment of this assumption results in an enormous increase in the number of possible isomers. However, considerable guidance can be obtained from experimental structures and by carrying out extensive searches involving hundreds or even thousands of isomers using simple and rapid molecular orbital methods. The most extensive set of calculations has been carried out on the bromides.

Calculations [8] for $C_{60}Br_2$ reveal that, compared with $C_{60}H_2$, two of the 23 possible isomers are significantly destabilized. One of these has the two bromine atoms on a hex–hex edge and the other has the two bromine atoms on a pent–hex edge, with the destabilization amounting to approximately 6 kcal mol^{-1} and 3 kcal mol^{-1} respectively. This instability is simply attributed to close Br···Br distances of 3.11 Å and 3.16 Å respectively, which also results in slight increases of about 0.01 Å in the C–Br bond length.

In the case of $C_{60}Br_4$, there are 46 possible isomers based on two lots of hex–hex addition, or one hex–hex plus one *para*-C_6Br_2 addition, or two lots of *para*-C_6Br_2 addition [8]. Three isomers of $C_{60}Br_4$ are substantially more stable than all other isomers and are shown in Fig. 13.

A statistical treatment of the calculated heats of formation reveals that, in addition to the expected instability associated with *para*-C_6Br_2 addition, there is increased stability associated with 2,3,5-C_6Br_3 rings (where 2,3 is the hex–hex edge), *meta* or 1,3-C_6Br_2 rings and C_6 rings. The observation that stability is associated with C_6, C_6Br_2 and C_6Br_3 rings, but not with C_6Br rings, means that for further bromination it is preferable to add a bromine atom onto existing C_6Br or C_6Br_2 rings rather than C_6 rings. This implies that bromination will occur through the formation of strings based on the edge-sharing of C_6Br_2 and C_6Br_3 hexagons. The number of string ends, i.e. C_6Br rings, can be minimized by minimizing the number of strings or by forming the strings into loops with no ends, or lassos with one end.

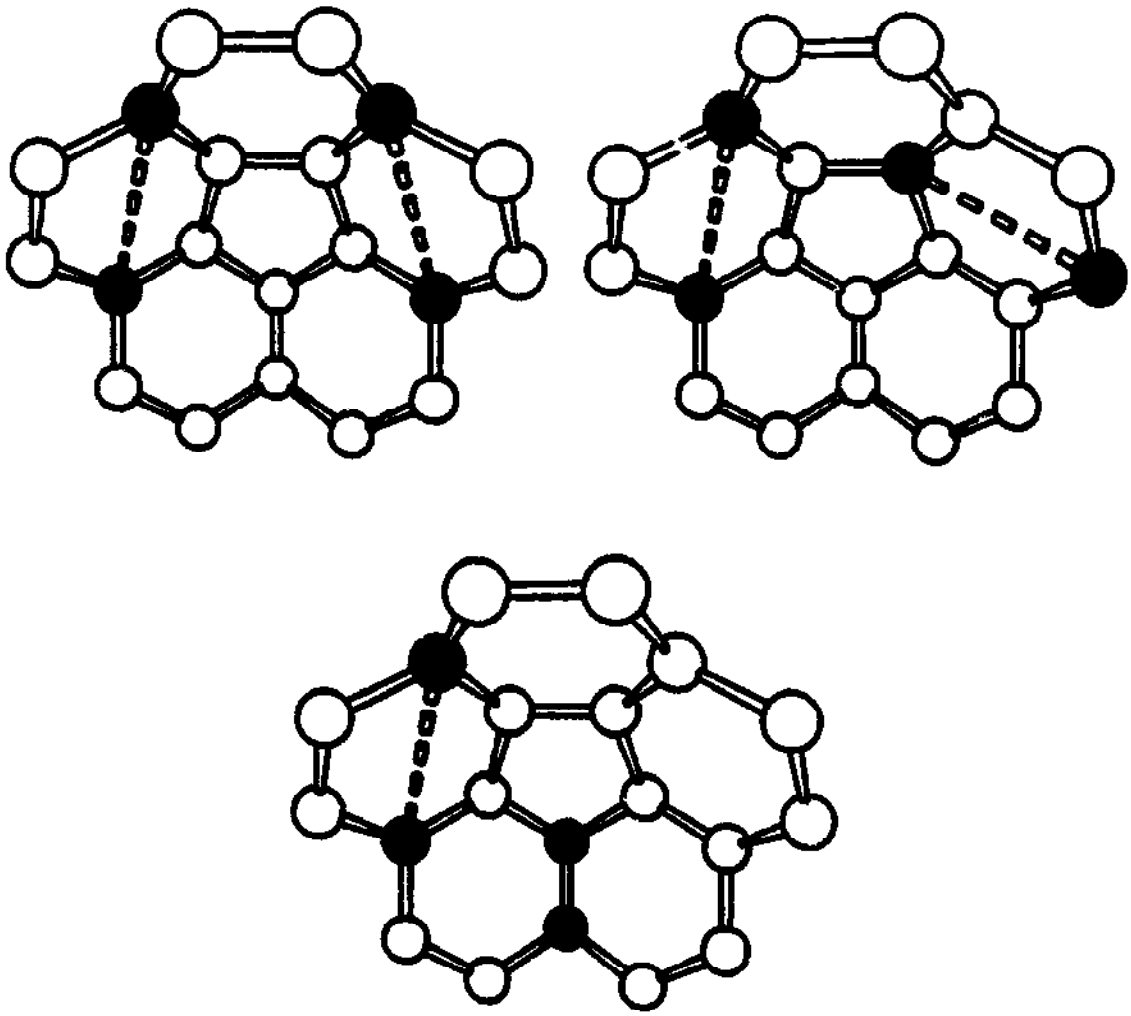


Fig. 13. The arrangement of bromine atoms in the three most stable isomers of $C_{60}Br_4$. Bromine atoms are attached to the shaded carbon atoms. The broken lines connect *para* pairs of bromine atoms.

It is not possible to continue the string of *para*-C_6Br_2 rings on the surface of C_{60} beyond $C_{60}Br_4$, and for $C_{60}Br_6$ it is necessary to include *meta*-C_6Br_2 or C_6Br_3 rings, or to commence a new string. The four isomers calculated to be the most stable are shown in Fig. 14.

The most stable structure of $C_{60}Br_6$ contains a skew pentagonal pyramidal arrangement of six bromine atoms and is also shown in Fig. 15. Five of the bromine atoms form a pentagonal plane and are arranged at the *para* positions of five edge-shared C_6Br_2 rings grouped around a C_5 pentagon. The sixth bromine atom is attached to one of the five equivalent carbon atoms of this pentagon to give a skew pentagonal pyramidal arrangement. There are three *para*-C_6Br_2 rings and two 2,3,5-C_6Br_3 rings.

This skew pentagonal pyramidal structure is observed experimentally in

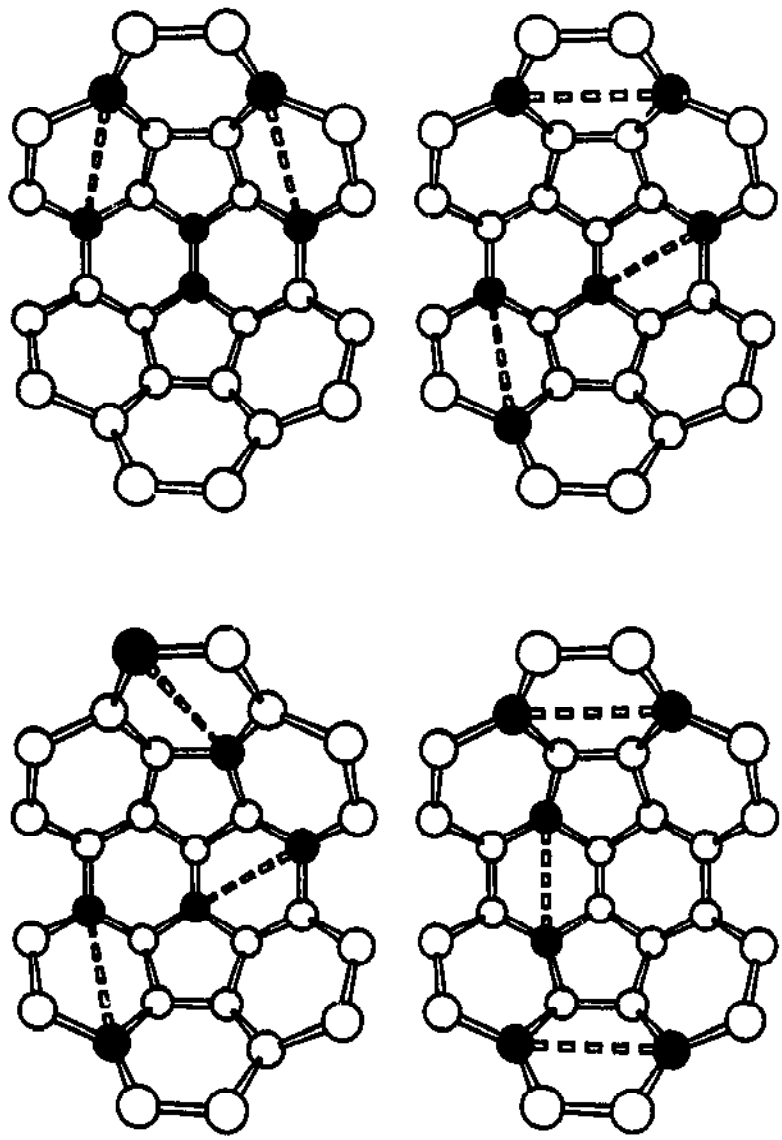


Fig. 14. The arrangement of bromine atoms in the four most stable isomers of $C_{60}Br_6$. Bromine atoms are attached to the shaded carbon atoms. The broken lines connect *para* pairs of bromine atoms.

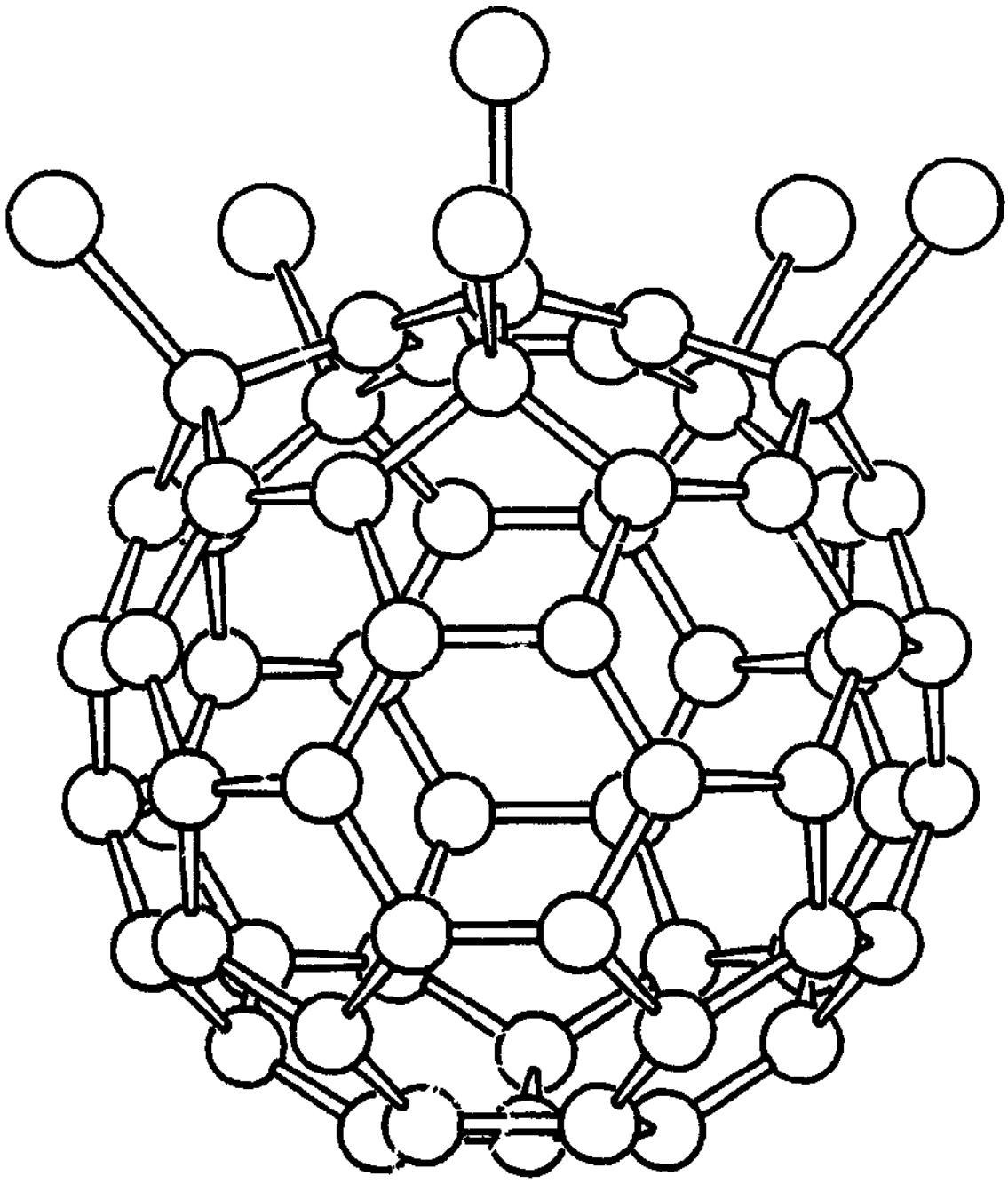


Fig. 15. The skew pentagonal pyramidal arrangement of bromine atoms in the most stable structure of $C_{60}Br_6$.

$C_{60}Br_6 \cdot Br_2 \cdot CCl_4$ and $C_{60}Br_6 \cdot 2Br_2$ [36,37]. The reaction between C_{60} and iodine monochloride in benzene at room temperature forms $C_{60}Cl_6$ which, from NMR evidence, also has the skew pentagonal pyramidal structure [38]. It is also relevant to note that benzyl radicals add to C_{60} forming $Bz_nC_{60}^{\bullet}$ [39]. The $Bz_5C_{60}^{\bullet}$ radical is relatively stable and was identified by ESR spectroscopy as having five benzyl

groups attached to the *para* positions of five connected C_6 rings as in $C_{60}Br_6$, with the radical electron delocalized over the central pentagonal ring.

The other three structures in Fig. 14 contain strings of C_6Br_2 hexagons, but with the intervention of *meta*-C_6Br_2 between some of the pairs of *para*-C_6Br_2. The second most stable isomer in Fig. 14 contains one *meta* link (i.e. *para–para–para–meta–para*), whereas the next two isomers contain two *meta* links (*para–meta–para–meta–para*). Note that all three isomers contain unfavourable string ends.

A further molecule of bromine cannot readily add onto the completed skew pentagonal pyramidal structure of $C_{60}Br_6$, so either it adds onto the *para* positions of a C_6 ring far removed from the skew pentagonal pyramid in the most stable structure or it continues the string pattern in the other isomers of $C_{60}Br_6$. This can occur in a variety of ways, the two most stable being (*para–para–para–meta–para–meta–para*) and (*para–para–para–meta–para–para–para*). The experimental structure of $C_{60}Br_8 \cdot 2Br_2$ [36,37] (*para–meta–para–meta–para–meta–para–*) is related to this motif, but this structure has no string ends (Fig. 16). According to calculations, this experimental structure is 3.1 kcal mol^{-1} less stable than the most stable string

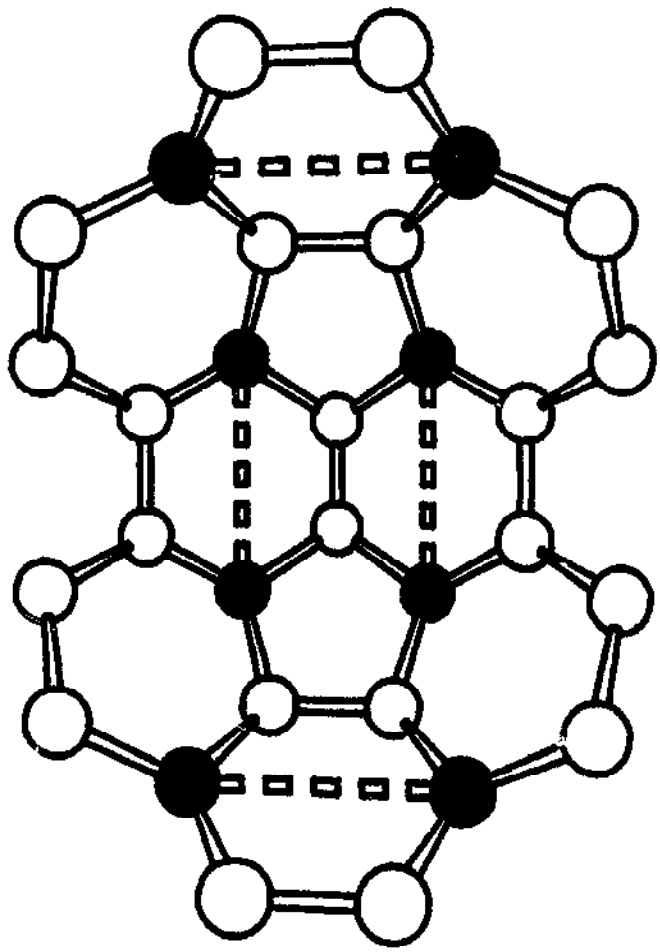


Fig. 16. The experimental structure of $C_{60}Br_8$. Bromine atoms are connected to the shaded carbon atoms. The broken lines connect *para* pairs of bromine atoms.

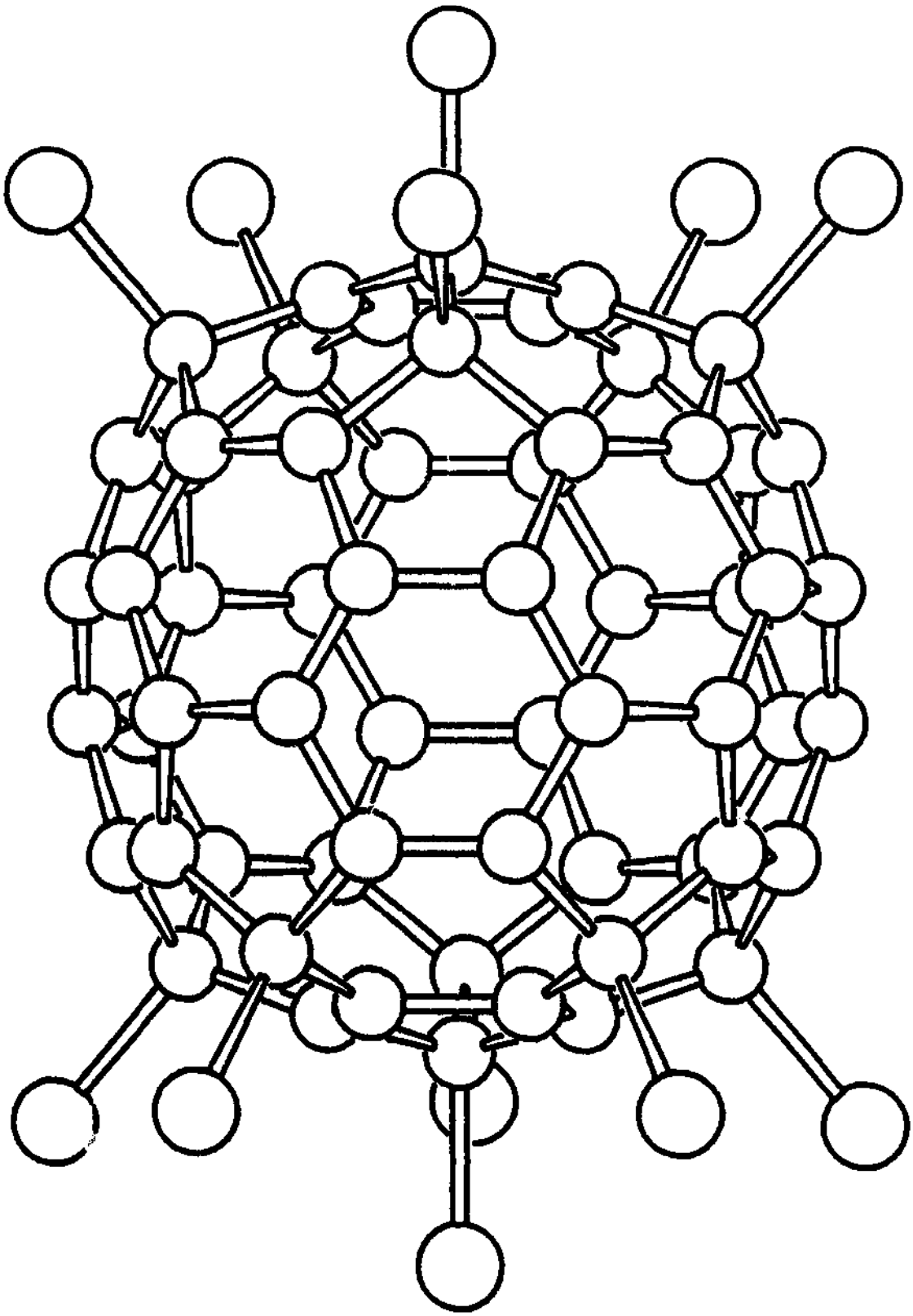


Fig. 17. The double skew pentagonal pyramidal structure of $C_{60}Br_{12}$ (C_{2h} symmetry).

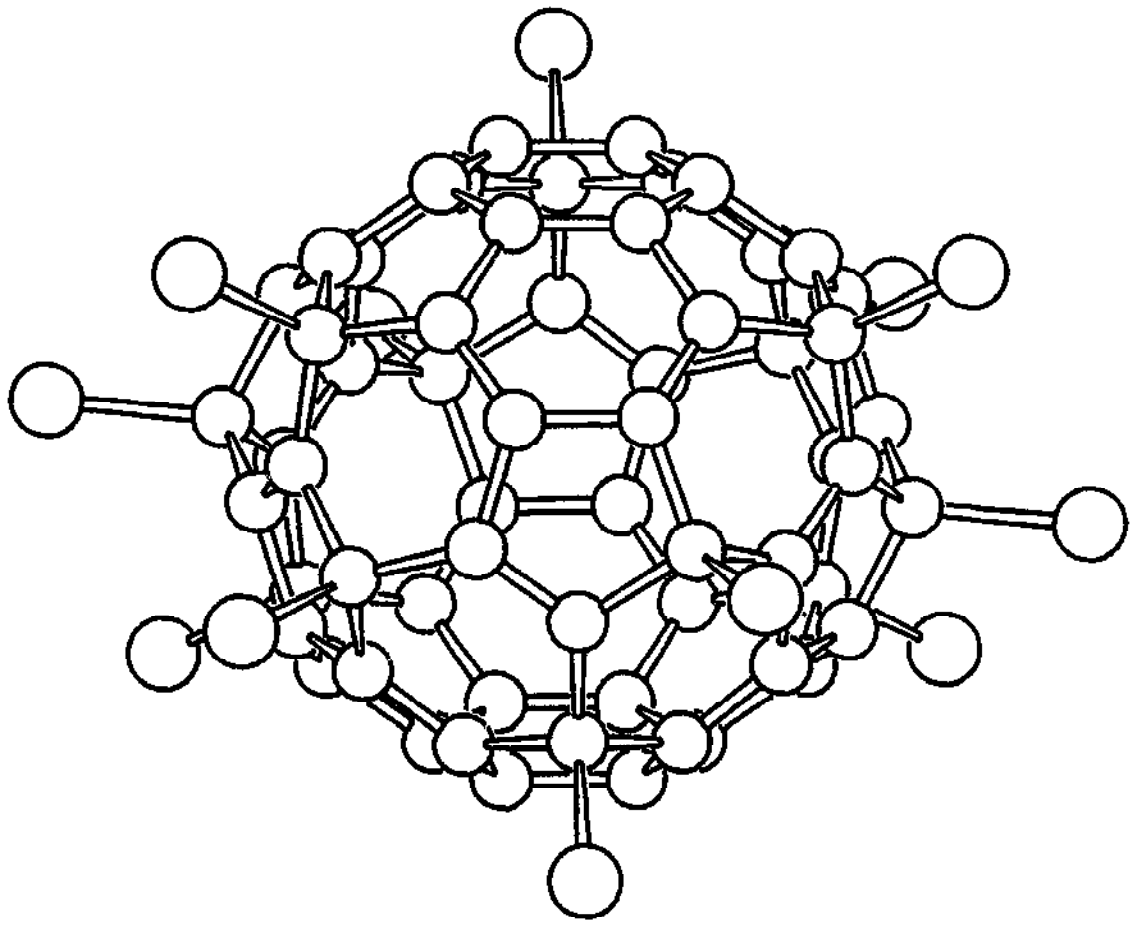


Fig. 18. The alternating *para meta* string structure of $C_{60}Br_{12}$ (S_6 symmetry).

structure, but additional stability may be due to $C_{60}Br_8 \cdots Br_2$ interactions which are estimated to contribute approximately 4 kcal mol^{-1} for each Br_2.

The same general motifs are seen on further bromination to $C_{60}Br_{10}$ and $C_{60}Br_{12}$ [8]. There are two important structures for $C_{60}Br_{12}$. The first is the most stable of the 12 possible isomers containing two Br_6 skew pentagonal pyramids (Fig. 17). The second important structure is the string (*para–meta–para–meta–para–meta–para–meta–para–meta–para*) which joins ends to form a loop of S_6 symmetry (Fig. 18).

Calculations show that further bromination [40] is dominated by two features.

(a) The structure of $C_{60}Br_{18}$ containing three Br_6 skew pentagonal pyramids (Fig. 19). Additional structures are obtained by adding pairs of bromine atoms to the double skew pentagonal pyramid structure of $C_{60}Br_{12}$, or by adding or removing pairs of bromine atoms from the triple skew pentagonal pyramid structure of $C_{60}Br_{18}$.

(b) Branched string structures based on the S_6 loop in the string structure of $C_{60}Br_{12}$. Branching occurs at the *meta*- or 1,3-C_6Br_2 rings, converting them into 1,3,5-C_6Br_3 rings. This branch then grows with alternating *para–meta* links as before until it rejoins the S_6 loop. Ultimately, at $C_{60}Br_{24}$, this polycyclic pattern of strings

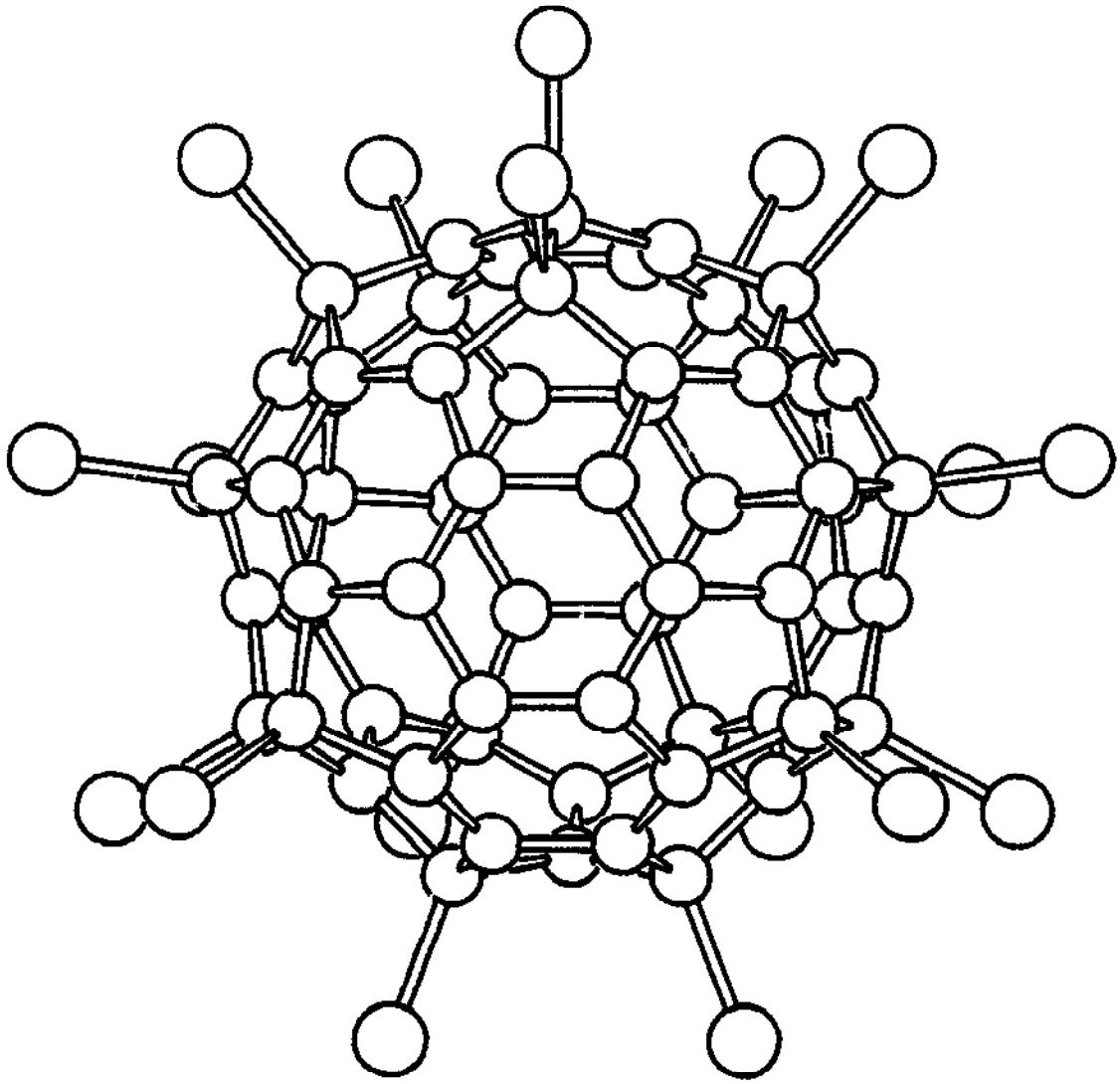


Fig. 19. The triple skew pentagonal pyramidal structure of $C_{60}Br_{18}$ (C_{3v} symmetry).

covers the entire surface, when there are 12 *para*-C_6Br_2 rings and eight 1,3,5-C_6Br_3 rings. Alternatively, this structure can be considered to be a rhombicuboctahedral arrangement of 24 bromine atoms outside a truncated icosahedral arrangement of 60 carbon atoms (Fig. 20). This rhombicuboctahedral arrangement is the known experimental structure of $C_{60}Br_{24}$ [36,37].

The addition of bromine to a carbon atom lifts it out of the spherical C_{60} surface by approximately 0.25 Å and the adjacent carbon atoms are depressed under the surface by approximately 0.06 Å. The particular stability of the *para*-C_6Br_2 and 1,3,5-C_6Br_3 rings is related to their favourable conformations, which are shallow boats in *para*-C_6Br_2 and shallow chairs in 1,3,5-C_6Br_3.

The relative stabilities of structures based on skew pentagonal pyramids and structures based on Br–Br strings are shown in Fig. 21. Within the sequence of string structures, $C_{60}Br_{12}$ and $C_{60}Br_{24}$ are particularly stable and are the only two molecules

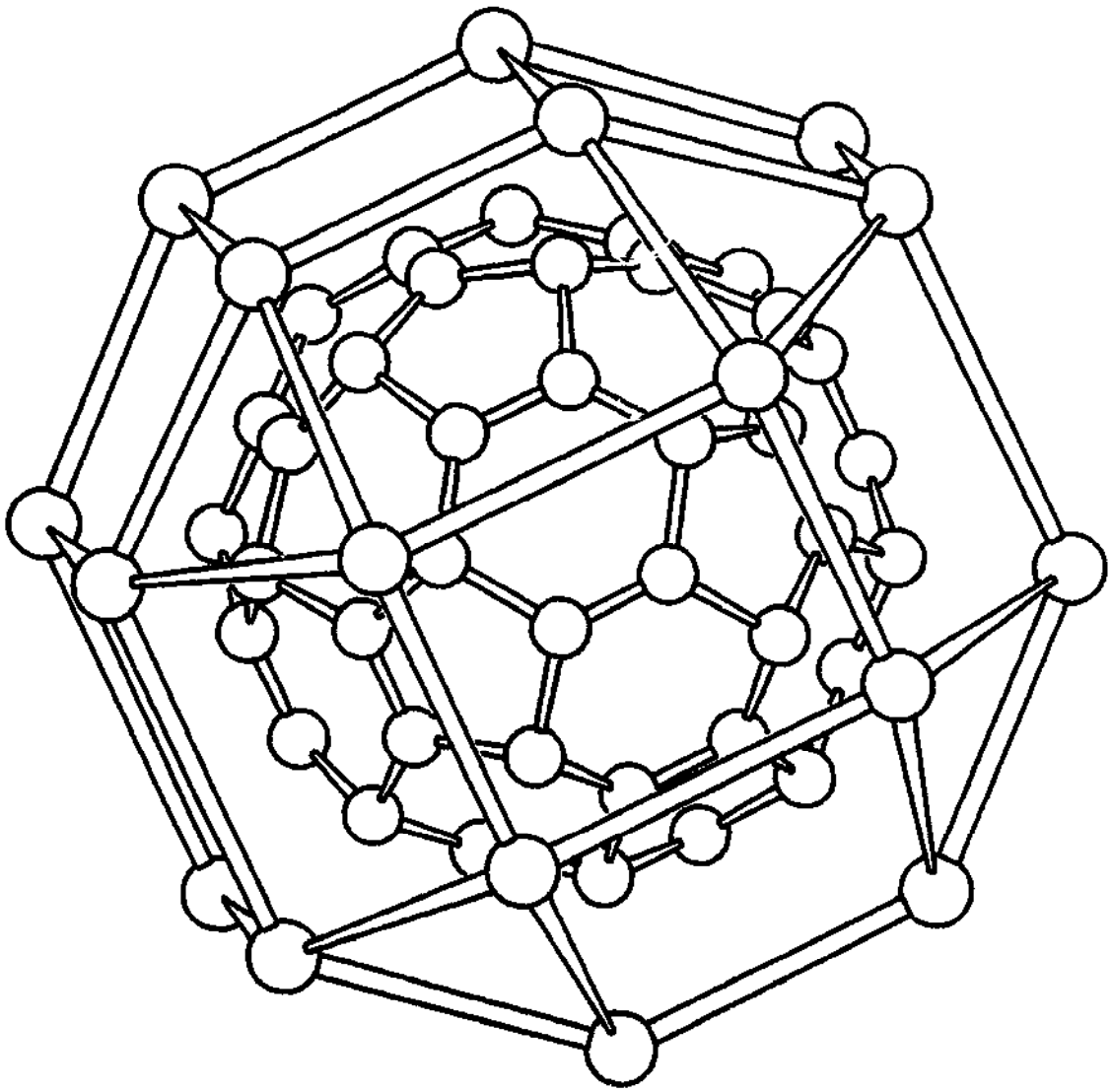


Fig. 20. The structure of $C_{60}Br_{24}$ showing a rhombicuboctahedral arrangement of 24 bromine atoms outside a truncated icosahedral arrangement of 60 carbon atoms.

in this sequence that are stable with respect to disproportionation. A more erratic sequence of values for ΔH_f° is observed for the skew pentagonal pyramidal isomers that are particularly stable at $C_{60}Br_6$, $C_{60}Br_{12}$ and $C_{60}Br_{18}$ which are the only molecules in this sequence that are stable with respect to disproportionation.

3.2. *Fullerene hydrides*

It was shown in Section 3.1 that particularly stable structures containing one, two or three skew pentagonal pyramids are found for $C_{60}Br_6$, $C_{60}Br_{12}$ and $C_{60}Br_{18}$. In an analogous fashion, the corresponding structures for $C_{60}H_6$, $C_{60}H_{12}$ and $C_{60}H_{18}$ are also particularly stable, as are molecules obtained by removing pairs of hydrogen atoms from, or adding pairs of hydrogen atoms to, these basic structures [41].

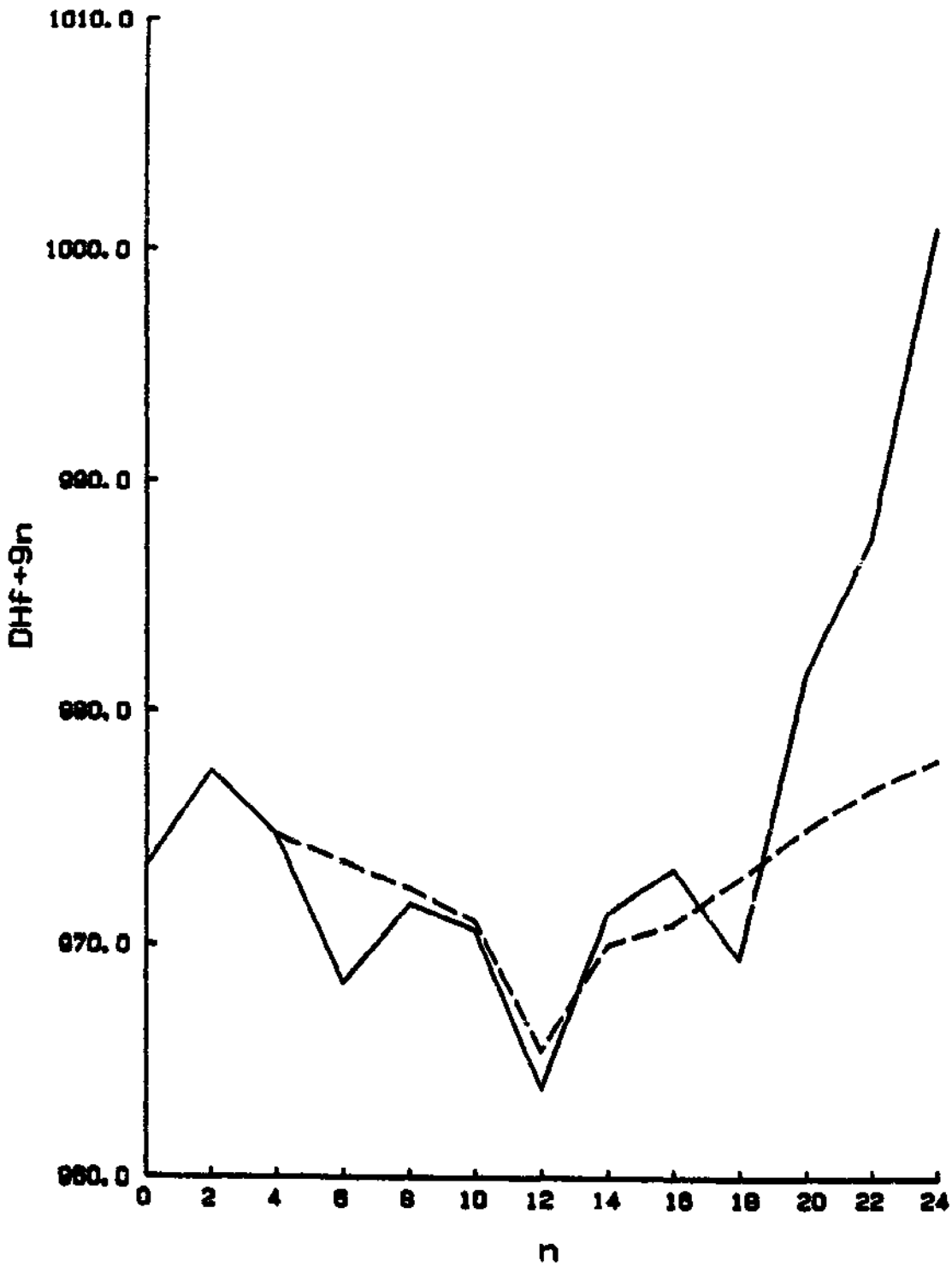


Fig. 21. Heats of formation of C_mBr_n, plotted as $(\Delta H_f^\circ + 9n)$ (kcal mol^{-1}) against n: —— skew pentagonal pyramid structures; - - -, string/rhombicuboctahedral structures.

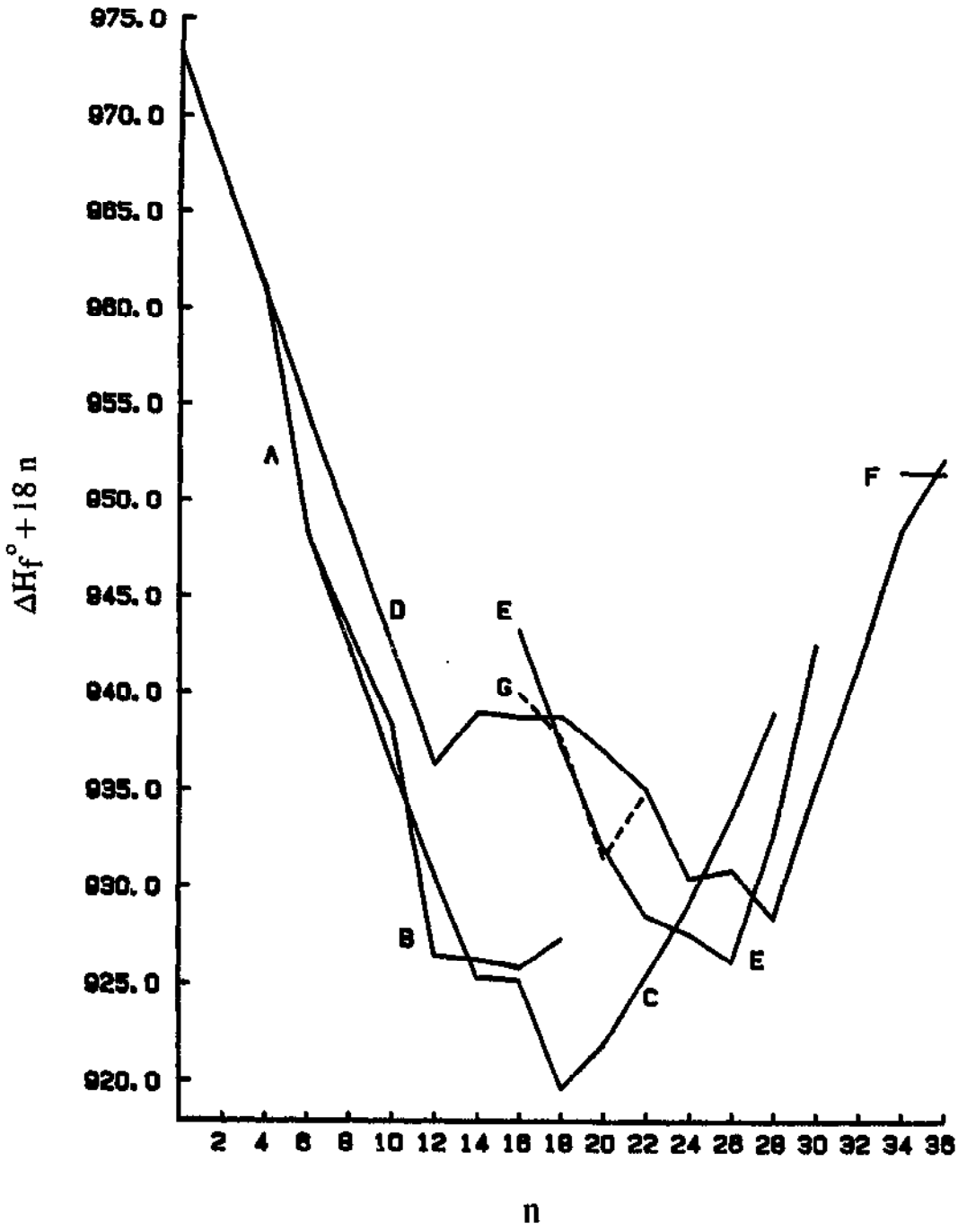


Fig. 22. Heats of formation of $C_{60}H_n$, plotted as $(\Delta H_f^\circ + 18n)$ (kcal mol^{-1}) against n: (A) single skew pentagonal pyramidal series; (B) double skew pentagonal pyramid series; (C) triple skew pentagonal pyramid series; (D) first series; (E) second series; (F) third series; (G) D_{5d}-$C_{60}H_{20}$ series.

The relative energies of the fullerene hydrides obtained in the first series (Section 2.1), the second and third series (Section 2.2), the $D_{5d}C_{60}H_{20}$ series (Section 2.2) and the three skew pentagonal pyramid series (this section) are shown in Fig. 22. The only molecules which are stable with respect to disproportionation

are the single skew pentagonal pyramidal $C_{60}H_6$, the double skew pentagonal pyramidal $C_{60}H_{12}$, the triple skew pentagonal pyramidal $C_{60}H_{18}$, $C_{60}H_{26}$ based on the $C_{18}H_{18}$ crown of $C_{60}H_{18}$, $C_{60}H_{28}$ based on the structure of $C_{60}H_{24}$, which also contains a $C_{18}H_{18}$ crown, and the double-crown structure of $C_{60}H_{36}$.

3.3. *Fullerene fluorides*

The fluorination of solid C_{60} has led to a variety of ill-defined products. However, the direct fluorination of solid C_{60} mixed with a large excess of sodium fluoride at 250 °C followed by extraction with $CFCl_3$ yielded predominantly two isomers of $C_{60}F_{48}$ [42]. The ^{19}F NMR showed eight sets of six equivalent fluorine atoms implying some symmetry element in addition to C_3, i.e. D_3 or S_6. COSY experiments allowed structural assignment. The most abundant geometric isomer, consisting of two optical isomers, is of D_3 symmetry and has six well-separated double bonds. The minor isomer of S_6 symmetry is closely related and can be considered as the *meso* isomer.

Molecular orbital calculations of all 94 isomers of $C_{60}F_{48}$ [43] with at least a C_3 axis reveal that the two isomers found above are indeed the most stable, with the most stable D_3 isomer (Fig. 23) being only 0.06 kcal mol^{-1} lower in energy than the S_6 isomer (Fig. 24). The next most stable isomer is 18.1 kcal mol^{-1} higher in energy. An analysis of all 94 isomers reveals that the most stable isomers have the six double bonds along pent–hex edges in a distorted octahedral arrangment with the maximum possible separation between them. The most stable isomer has three $(CF)_4$ and nine $(CF)_3$ bridges linking the double bonds along the 12 octahedral edges, whereas the second most stable isomer has 12 $(CF)_3$ bridges. The next two isomers have some $(CF)_2$ bridges. The existence of double bonds along pent–hex edges shows that the structures result from six *para*-C_6F_2 additions and 18 hex–hex additions. The next group of isomers have some double bonds on pent–hex edges and some on hex–hex edges, and the least stable have all double bonds on hex–hex edges. The most unstable isomers belong to the last group and also have no bridging CF groups between the double bonds, i.e. they are all conjugated to each other in the same part of the molecule.

4. Concluding remarks

A prodigously large number of isomers are possible for compounds of the type $C_{60}X_n$, and undoubtedly complex mixtures are obtained for some X and for some values of n and for some methods of synthesis. However, it is also clear that well-defined isomers may be obtained under the appropriate conditions.

The available experimental data, combined with the calculations of the stabilities of many hundreds or even thousands of structures, creates a framework in which the patterns of addition can be understood.

One feature which emerges from this work is the growth of edge-sharing C_6X_n rings across the structure. This growth can be related to the conformation of these rings, for example the shallow boat conformation of *para*-C_6Br_2 rings, the inverted

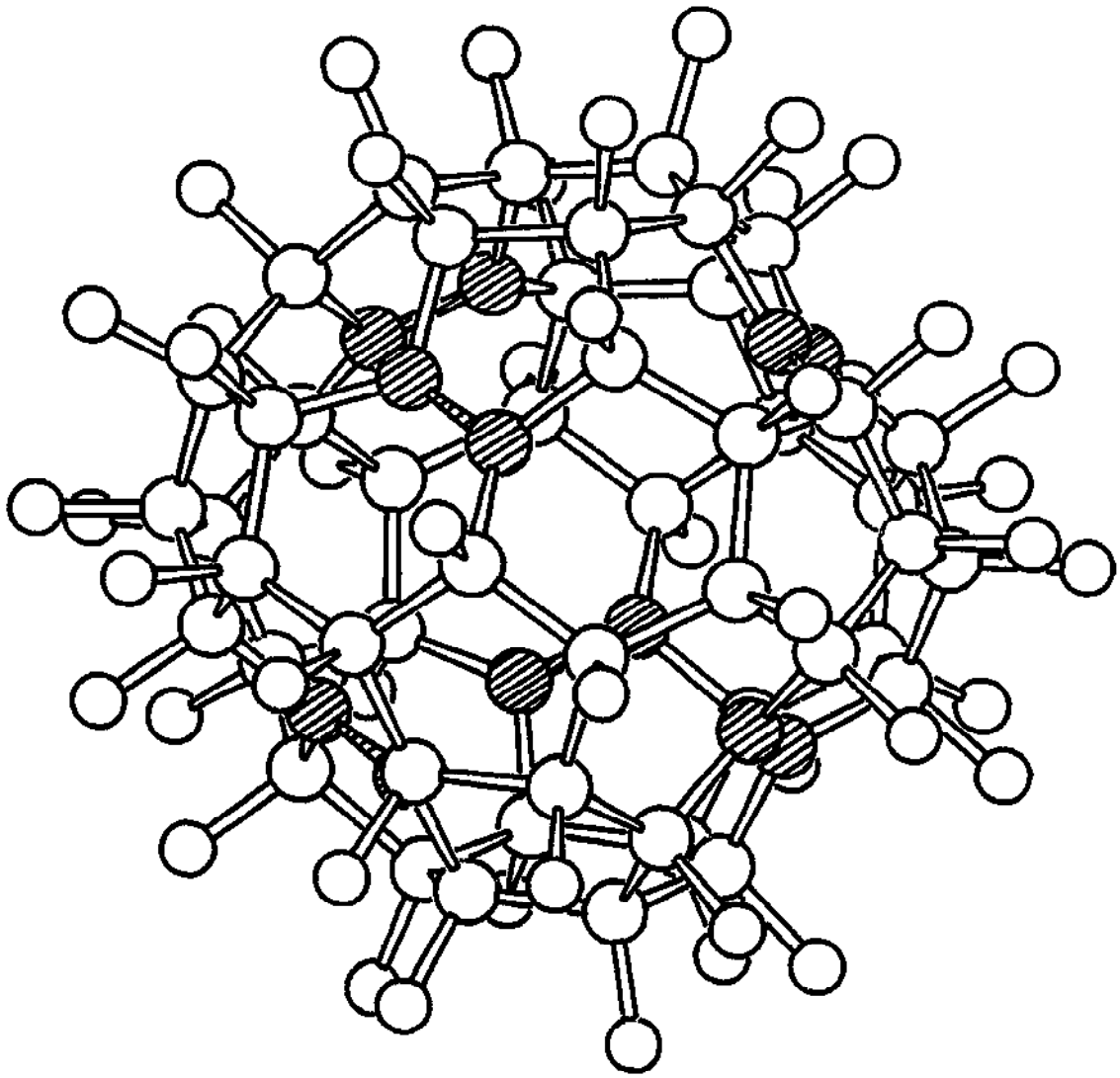


Fig. 23. The D_3 isomer of $C_{60}F_{48}$. The three-fold axis is from the top to the bottom of the figure. For clarity, the C=C carbon atoms and bonds are hatched.

boat of C_6H_4 rings or the shallow chairs of C_6Br_3 rings. These non-planar conformations arise as a result of the tetrahedrally coordinated carbon atoms being lifted out of the spherical surface created by the remaining trigonally coordinated carbon atoms. To take the boat conformation of the *para*-C_6Br_2 ring in $C_{60}Br_2$ as an example, this ring shares edges with two neighbouring C_6Br rings, each of which will be in a half-boat conformation. It appears that these half-boats are predisposed to add further bromine atoms to complete the puckering of these rings, so that there is a rippling effect as these non-planar rings spread across the structure. Similarly, for the inverted boat conformation of the C_6H_4 rings in the fullerene hydrides, the half-boat conformation of the attached C_6H_2 rings preferentially adds further hydrogen atoms.

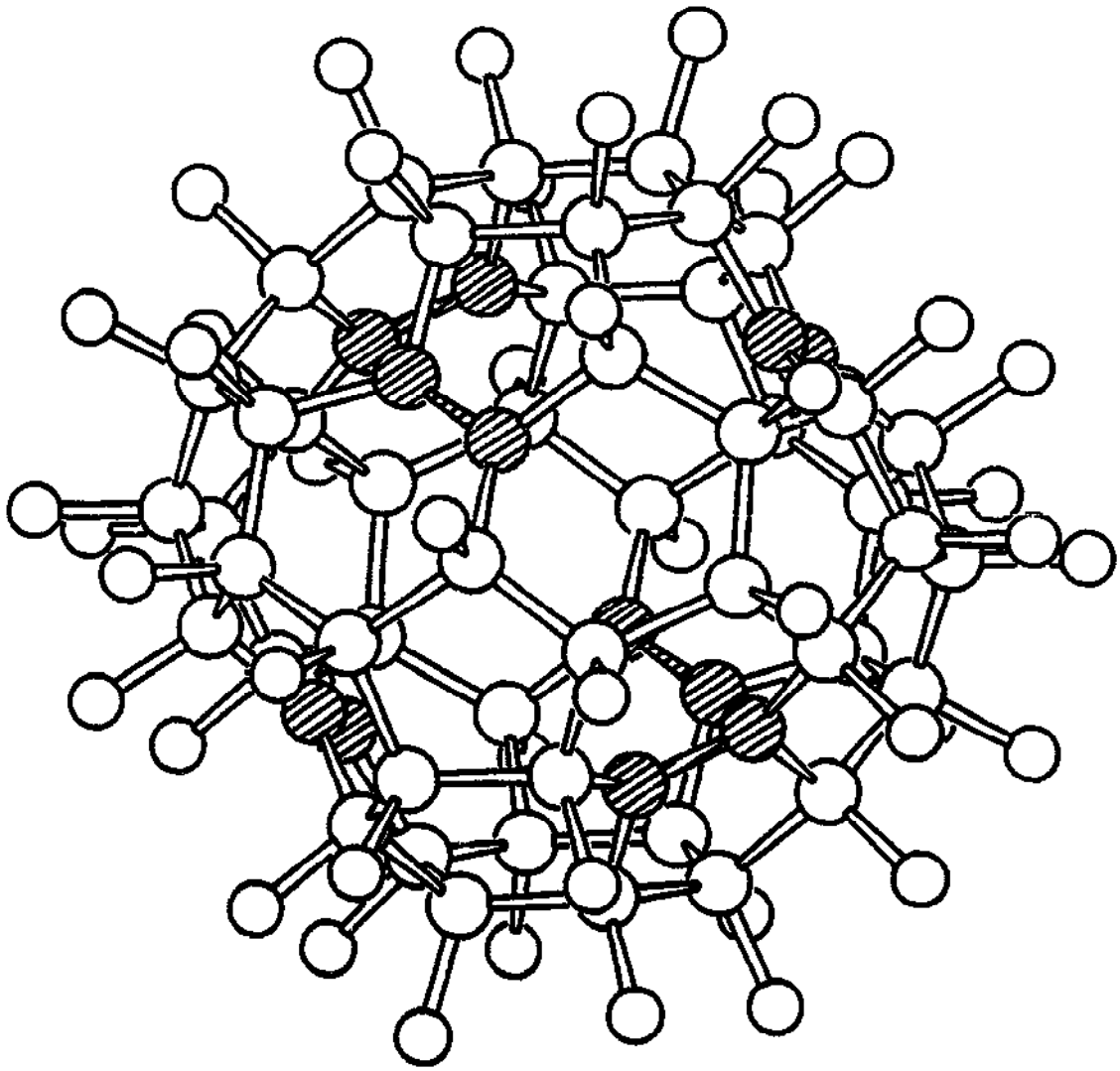


Fig. 24. The S_6 isomer of $C_{60}F_{48}$. The three-fold axis is from the top to the bottom of the figure. For clarity, the C=C carbon atoms and bonds are hatched.

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