Figure 8.5   Three representations of the structure of C_{60}. (a) normal "ball-and-stick" model; (b) the polyhedron derived by truncating the 12 vertices of an icosahedron to form 12 symmetrically separated pentagonal faces; (c) a conventional bonding model.

8.2.4 Fullerenes

One of the most exciting and challenging developments in recent chemistry has been the synthesis and characterization of many new, soluble, *molecular* modifications of carbon. As a result, the number of identified allotropes of this element has increased enormously and their intriguing chemistry is gradually being elucidated. The new allotopes form an extensive series of polyhedral cluster molecules, C_n (n even), comprising fused pentagonal and hexagonal rings of C atoms. The first member to be characterized was C_{60} which features 12 pentagons separated by 20 fused hexagons as shown in Fig. 8.5. It has full icosahedral symmetry (p. 141) and was given the name buckminsterfullerene in honour of the architect R. Buckminster Fuller whose buildings popularized the geodesic dome, which uses the same tectonic principle. Other fullerenes which have been isolated and characterized include C_{70}, C_{76} (chiral), C_{78} (3 isomers), C_{84} (3 isomers), C_{90} and C_{94}, but there is mass spectrometric evidence for all even C_n from C_{30} to $C_{>600}$, (m.wt. 7206.6).

The fullerene story began in September 1985 when a group lead by H. W. Kroto (Sussex, UK) and R. E. Smalley (Rice, Texas) laser-blasted graphite at $T > 10^4\,°C$ and showed mass spectrometrically that the product contained a series of molecules with even numbers of atoms from C_{44} to C_{90}.[14] Concentrations of the individual molecules varied with conditions but the peak for C_{60} was always by far the strongest, followed by C_{70}. This experiment showed the existence of new molecular forms of carbon but was not a bulk preparation. However, in a brilliant flash of insight it was conjectured that the stability of C_{60} might result from the football-like "spherical" structure of a truncated icosahedron, the most symmetrical of all possible structures in 3-dimensional space (Nobel Prize, 1996, see p. 270).

Three years later two astrophysicists, W. Krätschmer (Heidelberg, Germany) and D. R. Huffman (Tucson, Arizona), remembered an unusual and unexpected UV spectrum they had obtained in 1983 from soot obtained by striking an arc between graphite electrodes at about 3500°C under a low pressure of helium gas. They re-examined the material mass-spectrometrically and found it contained high concentrations of C_{60} and C_{70} which were soluble in aromatic hydrocarbon solvents such as benzene and toluene.[15] Here was a stunningly simple preparation of fullerenes in bulk, although separation of individual members proved to

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[14] H. W. KROTO, J. R. HEATH, S. C. O'BRIEN and R. E. SMALLEY, *Nature* **318**, 162–4 (1985).

[15] W. KRÄTSCHMER, L. D. LAMB, K. FOSTIROPOULOS and D. R. HUFFMAN, *Nature* **347**, 354–8 (1990).

be more difficult. Pure C_{60} and C_{70} were obtained for the first time on 22 August 1990 by chromatographic separation (alumina, hexane).[16] The process can easily be scaled up using multi-rod apparatus to give about 20 g/day of soot containing up to 10% of fullerenes; this can be extracted with toluene to yield about 15 g/week of mixed fullerenes which can be further separated if required. Commercial availability has also assisted progress, typical prices (1994) being £150/g for C_{60} (99.9%) and £2000/g for C_{70} (98%).

Other routes to C_{60} and C_{70} are being developed, e.g. (*i*) heating naphthalene vapour ($C_{10}H_8$) in argon at about 1000°C followed by extraction with CS_2; (*ii*) burning soot in a benzene/oxygen flame at about 1500°C with argon as a diluent. C_{60} and C_{70} have also been detected in several naturally occurring minerals, e.g. in carbon-rich semi-anthracite deposits from the Yarrabee mine in Queensland, Australia;[17a] in shungite, a highly metamorphosed meta-anthracite from Shunga, Karelia, Russia;[17b] and in a Colorado, USA fulgurite (a glassy mineral which can be formed when lightning strikes the ground).[17c] Most recently, significant finds of naturally occurring fullerenes have been made in Sudbury (Canada) and New Zealand.[17d]

The purified fullerenes have very attractive colours. Thin films of C_{60} are mustard-coloured (dark brown in bulk) and solutions in aromatic hydrocarbons are a beautiful magenta. Thin films of C_{70} are reddish brown (greyish black in bulk) and solutions are port-wine red. C_{76}, C_{78} and C_{84} are yellow.[16]
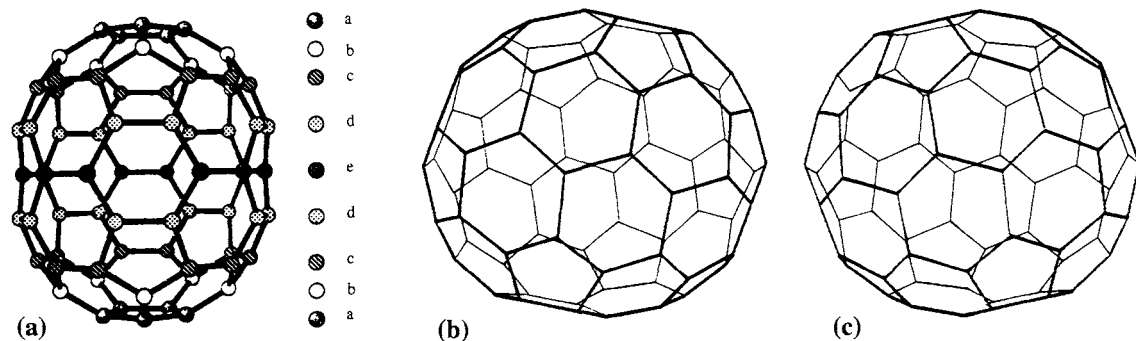
Structure of the fullerenes

The structural motif of the fullerenes is a sequence of polyhedral clusters, C_n, each with 12 pentagonal faces and ($\frac{1}{2}n - 10$) hexagonal faces. C_{60} itself has 20 hexagonal faces and, significantly, is the first member for which all 12 pentagonal faces are non-adjacent. Smaller homologues have increasing numbers of contiguous pentagonal faces; e.g. C_{32} is expected to have only 6 hexagonal faces. As can be seen from Fig. 8.5, all C atoms in C_{60} are structurally identical and, consistent with this, only one signal is observed in the ^{13}C nmr spectrum (at 142.68 ppm). However, there are two geometrically distinct types of C–C bond: those at an edge shared between two fused hexagons, and those at an edge between a hexagon and a pentagon.

By contrast, C_{70} has 25 hexagonal faces and D_{5h} symmetry (Fig. 8.6a) with 5 types of C atom (a, b, c, d, e) and 8 types of C–C bond. Five ^{13}C nmr signals are therefore expected, with intensities in the ratio 10:10:20:20:10, and these are observed in the range 150.77–130.28 ppm.[16] Again, a ^{13}C nmr study of chromatographically isolated of C_{76} showed it to have 28 hexagonal faces and a fascinating chiral structure of D_2 symmetry, consisting of a spiralling double helical arrangement of edge-sharing pentagons and hexagons (Fig. 8.6b and c) uniquely consistent with the observed 19 ^{13}C nmr signals in the range 150.03–129.56 ppm, and each of equal intensity (19 × 4 = 76).[18]

The total potential number of geometric isomers increases enormously with increase in cluster size, being, for example, three for C_{30}, 40 for C_{40}, 271 for C_{50} and no fewer than 1812 for C_{60}.[19] However, the number becomes much more manageable if one considers only those isomers that have no contiguous pentagons. The theoretical justifications for this

16 R. TAYLOR, J. P. HARE, A. K. ABDUL-SADA and H. W. KROTO, *J. Chem. Soc., Chem. Commun.*, 1423–5 (1990).
R. TAYLOR (and 12 others), *Pure Appl. Chem.* **65**, 135–42 (1993).

17a M. A. WILSON, L. S .K. PANG and A. M. VASSALLO, *Nature* **355**, 117–8 (1992).

17b P. R. BUSEK, S. J. TSIPURSKI and R. HETTICH, *Science* **257**, 215–17 (1992).

17c T. K. DALT, P. R. BUSECK, P. W. WILLIAMS and C. F. LEWIS, *Science* **259**, 1599–601 (1993).

17d R. DAGANI, *Chem. & Eng. News*, Aug. 1, 1994, pp. 4,5. See also L. BECKER, R. J. POREDA and J. L. BADA, *Science* **272**, 249–52 (1996).

18 R. ETTL, I. CHAO, F. DIEDERICH and R. L. WHETTEN, *Nature* **353**, 149–53 (1991). D. E. MANOLOPOULOS, *J. Chem. Soc., Faraday Trans.*, **87**, 2861–2 (1991).

19 D. E. MANOLOPOULOS and P. W. FOWLER, *J. Chem. Phys.* **96**, 7603–14 (1991).

Figure 8.6 (a) The D_{5h} structure of C_{70} with the 5-fold rotation axis vertical; the five sets of geometrically distinct C atoms are labelled a-e (see text). (b), (c) Line drawings of the two enantiomers of C_{76} viewed along the short C_2 rotation axis and illustrating the chiral D_2 symmetry of the molecule.

restriction would be (a) that isomers with fused pentagons are expected to have greater σ-bonding strain energy and (b) that, since two fused pentagons have an 8-cycle around their periphery, there would be a further Hückel antiaromatic destabilizing effect on the overall π electron system. In fact, in the range C_{20}–C_{70} this restriction of isolated pentagons eliminates all structures except the observed $C_{60}(I_h)$ and $C_{70}(D_{5h})$. From mass-spectrometric evidence other oligomers clearly exist, though not yet in isolable concentrations. Above C_{70} the number of distinct geometric isomers (i) with isolated pentagons increases rather rapidly with n as indicated below:[19]

n	72	74	76	78	80	82	84	86
i	1	1	2	5	7	9	24	19

n	88	90	92	94	96	98	100
i	35	46	86	134	187	259	450

Numerous other fullerenes have been isolated by the same techniques and their structures elucidated by ^{13}C nmr spectroscopy, e.g. C_{76} (see above); C_{78} [3 isomers: $C_{2v}\{18(4C) + 3(2C)$ nmr lines$\}$, $D_3\{13(6C)\}$ and $C_{2v}\{17(4C) + 5(2C)\}$]; C_{82} [3 isomers: $C_2\{41(2C)\}$, $C_{2v}\{17(4C) + 7(2C)\}$ and $C_{3v}\{12(6C) + 3(3C) + 1(1C)\}$]; and C_{84} [2 isomers: $D_2\{21(4C)\}$ and $D_{2d}\{10(8C)$

+ 1(4C)$\}$].[20] A copiously illustrated atlas of fullerenes elaborating and enumerating the numbers and structures of all possible fullerenes and fullerene isomers C_n as a function of n up to high n has recently been published.[20a]
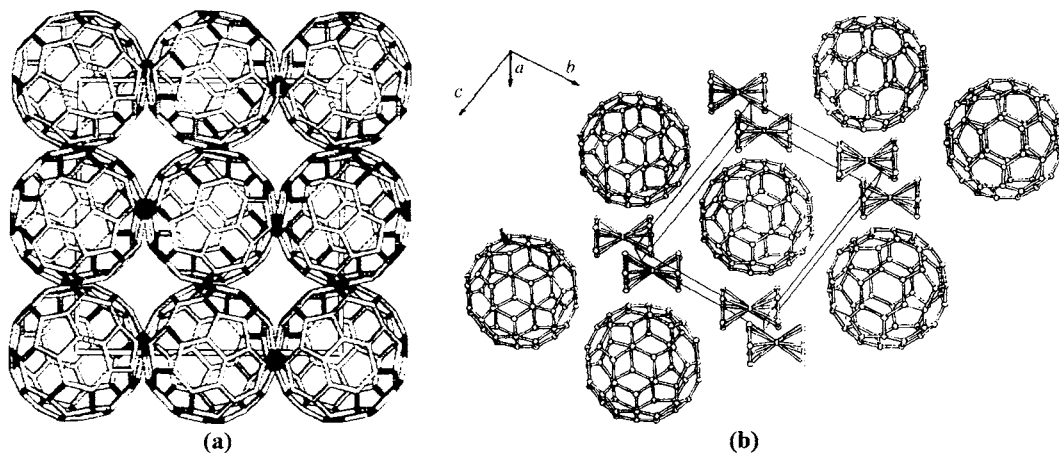
Except for C_{60},[†] lack of sufficient quantities of pure material has prevented more detailed structural characterization of the fullerenes by X-ray diffraction analysis, and even for C_{60} problems of orientational disorder of the quasi-spherical molecules in the lattice have exacerbated the situation. At room temperature C_{60} crystallizes in a face-centred cubic lattice ($Fm\overline{3}$) but below 249 K the molecules become orientationally ordered and a simple cubic lattice ($Pa\overline{3}$) results. A neutron diffraction analysis of the ordered phase at 5 K led to the structure shown in Fig. 8.7a;[21] this reveals that the ordering results from the fact that

[20] F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, I. Chao and M. M. Alvarez, *Science* **254**, 1768–70 (1991). R. Taylor, G. J. Langley, T. J. S. Dennis, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1043–6 (1992). K. Kikuchi, Y. Achiba (and eight others) *Nature* **357**, 142–5 (1992).

[20a] P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon Press, Oxford, 1995, 392 pp.

[†] Gram amounts of purified C_{70} can now also be obtained by column chromatography (see *J. Am. Chem. Soc.* **116**, 6939 (1994)) and are available commercially.

[21] W. I. F. David, R. M. Ibberson, J. C. Mathewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor and D. R. M. Walton, *Nature* **353**, 147–9 (1992).

Figure 8.7 (a) The low-temperature, ordered, simple cubic arrangement of C_{60} molecules as revealed by neutron diffraction at 5 K; above 249 K the molecules become orientationally disordered and the lattice becomes fcc. (b) The packing arrangement for $[C_{60}(ferrocene)_2]$ in the bc plane.

the electron-rich short bonds *between* pentagons (139.1 ± 1.8 pm)are positioned directly above the electron-poor pentagon face-centres of adjacent C_{60} units. The bonds *within* a given pentagon are somewhat longer (145.5 ± 1.2 pm).

The structures of the black crystalline benzene solvate $C_{60}.4C_6H_6$,[22] the black charge-transfer complex with bis(ethylenedithio)tetrathiafulvene, $[C_{60}(BEDT-TTF)_2]$,[23] and the black ferrocene adduct $[C_{60}\{Fe(Cp)_2\}_2]$ (Fig. 8.7b)[24] have also been solved and all feature the packing of C_{60} clusters.

Other molecular allotropes of carbon

Quite apart from the fullerene cluster molecules, numerous other molecular allotropes of carbon, C_n, have been discovered in the gases formed by the laser vaporization/supersonic expansion of graphite. The products are detected by mass spectrometry after separation into identifiable series by gas-ion chromatography.[25] The technique suggests that linear oligomers exist from $n = 3-10$ and an overlapping series of monocyclic planar ring isomers from $n = 7-36$. Planar bicyclic rings appear for $n = 21-44$ and yet other series of condensed rings occur in the ranges $n = 37-54$ and $55-61$. Three-dimensional fused ring clusters form a series with $n = 28-35$, and the fullerenes from $C_{30}-C_{70}$ were seen as a quite distinct series. For each value of n from $29-41$ there are at least three isomers: e.g. C_{32}^+ comprises 23% monocyclic ring, 71% bicyclic ring, 2.4% open 3D cluster and 3.2% fullerene. The structural assignments are tentative.

Chemistry of the fullerenes

The tremendous burst of excitement which attended the initial isolation in 1990 of weighable amounts of separated fullerenes has been followed by an unparalleled and sustained surge of activity as chemists throughout the world rushed to investigate the chemical reactivity of these novel molecular forms of carbon.

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[22] M. F. MEIDINE, P. B. HITCHCOCK, H. W. KROTO, R. TAYLOR and D. R. M. WALTON, *J. Chem. Soc., Chem. Commun.*, 1534–7 (1992).

[23] A. IZUOKA, T. TACHIKAWA, T. SUGAWARA, Y. SUZUKI, M. KONO, Y. SAITO and H. SINOHARA, *J. Chem. Soc., Chem. Commun.*, 1472–3 (1992).

[24] J. D. CRANE, P. B. HITCHCOCK, H. W. KROTO, R. TAYLOR and D. R. M. WALTON, *J. Chem. Soc., Chem. Commun.*, 1764–5 (1992).
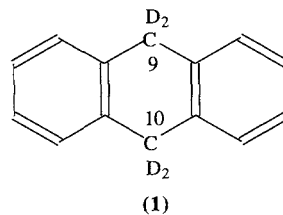
[25] G. VON HELDEN, M.-T. HSU, P. R. KEMPER and M. T. BOWERS, *J. Chem. Phys.* **95**, 3835–7 (1991).

Considerable attention has been paid to possible mechanisms of formation[26,27] since a firm understanding of this aspect could lead to the development of more effective synthetic routes to the individual fullerenes. It is also known that, when thin films of C_{60} and C_{70} are laser-vaporized into a rapid stream of an inert gas, individual molecules of C_{60} or C_{70} can themselves coalesce to form stable larger fullerenes such as C_{120} or C_{140}, and higher multiples. Even more dramatically, when a sample of C_{60} is subjected to a pressure of 20 GPa (i.e. 200 kbar), it apparently immediately transforms into polycrystalline diamond.

Most solvents will only dissolve a few mg/l of the fullerenes. Solubility in benzene, toluene or CS_2 is somewhat higher but even so the acquisition of ^{13}C nmr data is still a lengthy and tedious business. By far the best solvents to date for C_{60} at 25°C are *o*-dichlorobenzene (25 mg cm^{-3}), 1-methylnaphthalene (33 mg cm^{-3}) and 1-Br-2-Me-naphthalene (35 mg cm^{-3}).[28] Colours in a range of some 30 solvents are variously pink, magenta, magenta-brown, brown-yellow, brown-green and brown, no doubt reflecting the varying interaction of the solute with the solvent (cf. I_2, p. 807).

Hydrogenation — One of the first chemical reactions of C_{60} to be studied was its Birch reduction. In a typical procedure, Li metal was added under an argon atmosphere to a suspension of C_{60} in liquid NH_3/thf, followed after 30 min by addition of Bu^{t}OH. Initially the off-white product was thought to be $C_{60}H_{36}$ but subsequent work using a variety of techniques[29] has shown that the product at low temperatures is a mixture of polyhydrofullerenes ranging from $C_{60}H_{18}$ to $C_{60}H_{36}$ with $C_{60}H_{32}$ being the predominant species. This mixture is thermally labile and in the mass spectrometer probe (>250°C) $C_{60}H_{36}$ predominates, consistent with a molecule in which the 12 isolated pentagons of the C_{60} cluster each retain one double bond, i.e. $[(C_2)_{12}(CH)_{36}]$. A cleaner route to pure, white $C_{60}H_{36}$ is by using a 120-fold molar excess of 9,10-dihydroanthracene (1) as a H-transfer reagent at 350°C for 30 min. Prolonging the reaction time to 24 h produces $C_{60}H_{18}$ as a second product and the method has the added advantage that it permits the ready synthesis of $C_{60}D_{36}$, by use of 9,9',10,10'[D_4]dihydroanthracene.[30]

(1)

Oxidation reactions — Direct fluorination of solid C_{60} with F_2 gas at 70° proceeds slowly in a stepwise manner *via* several coloured partially fluorinated materials to give, after a period of several days, the colourless fully fluorinated product $C_{60}F_{60}$.[31] Rapid fluorination under more forcing conditions (F_2 gas/UV irradiation/250°) yields $C_{60}F_{48}$ as the main product, plus an intractable mixture of other fluorides $C_{60}F_{2n}$ including some hyperfluorinated materials ($2n > 60$) which would require the opening of some skeletal C–C bonds.[32] $C_{60}F_{48}$ itself has over 20 million possible isomers but, astonishingly, the high-yield synthesis of just one of these has recently been achieved by heating a mixture of C_{60} and NaF under F_2 at 275° for several days.[33] Actually a racemic mixture of the two

[26] R. F. CURL, *Phil. Trans. Roy. Soc.* **343**, 119–32 (1993).

[27] H. SCHWARZ, *Angew. Chem. Int. Edn. Engl.* **32**, 1412–5 (1993). R. M. BAUM, *Chem. & Eng. News*, May 17, 32–4 (1993) and references cited therein.

[28] W. A. SCRIVENS and J. M. TOUR, *J. Chem. Soc., Chem. Commun.*, 1207–9 (1993).

[29] M. R. BANKS (and 14 others), *J. Chem. Soc., Chem. Commun.*, 1149–52 (1993).

[30] C. RÜCHARDT (and 8 others), *Angew. Chem. Int. Edn. Engl.* **32**, 584–6 (1993).

[31] J. H. HOLLOWAY (and 8 others), *J. Chem. Soc., Chem. Commun.*, 966–9 (1991).

[32] A. A. TUINMAN, A. A. GAKH, J. L. ADCOCK and R. N. COMPTON, *J. Am. Chem. Soc.* **115**, 5885–6 (1993).

[33] A. A. GAKH, A. A. TUINMAN J. L. ADCOCK, R. A. SACHLEBEN and R. N. COMPTON, *J. Am. Chem. Soc.* **116**, 819–20 (1994).
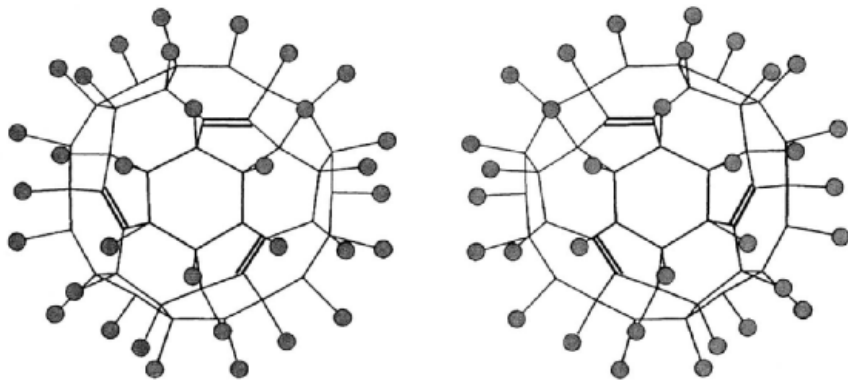
Figure 8.8 The enantiomeric pair of isomers of $C_{60}F_{48}$.[33]

chiral enantiomers shown in Fig. 8.8 is obtained. Shorter reaction times give complex mixtures of $C_{60}F_{46}$ and $C_{60}F_{48}$ isomers.

Direct chlorination of C_{60} with Cl_2 gas at 250–400°C led to an intractable pale orange mixture of polychlorinated species having on average about 24 Cl atoms per cluster molecule, but milder conditions using Cl_2 at various temperatures in a range of chloro organic solvents produced no detectable reaction.[34] By contrast, treatment of C_{60} with an excess of ICl in benzene or toluene at room temperature gave a quantitative yield of deep orange $C_{60}Cl_6$[35] which is isostructural with $C_{60}Br_6$ (see below).

Bromination of C_{60} in solution gives $C_{60}Br_6$ (magenta plates) and $C_{60}Br_8$ (dark brown prisms). The former has a structure involving one monobrominated pentagon with a long C–Br bond (203 pm) itself adjacent to five other monobrominated pentagons (C–Br 196 pm) as shown in Fig. 8.9a. It disproportionates on being warmed to give C_{60} and $C_{60}Br_8$ which has a C_{2v} structure with pairs of Br atoms arranged *meta* on four 6-membered rings (Fig. 8.9b).[36]

Bromination with liquid Br_2 yields the somewhat more stable $C_{60}Br_{24}$ which has T_h symmetry (Fig. 8.9c) with 12 hexagons disubstituted *para* and in pairs with boat conformation but mutually *meta* on the other 8 hexagons which have the chair conformation. The structure has 18 C=C arranged one per pentagon (12) and one at each 6:6 bond (6).[37] All three bromides can be completely dehalogenated on strong heating, as can the polychlorides. Iodine appears not to add directly to C_{60} but forms an intercalation product.

Fullerene epoxide, $C_{60}O$, is formed by the UV irradiation of an oxygenated benzene solution of C_{60}.[38] The O atom bridges a 6:6 bond of the closed fullerene structure. The same compound is also formed as one of the products of the reaction of C_{60} with dimethyldioxirane, $Me_2\overline{COO}$ (see later).[39]

Fullerols, $C_{60}(OH)_n$ ($n = 24–26$), can be synthesized directly by aerobic oxidation of a benzene solution of C_{60} using an aqueous solution of NaOH containing a few drops of Bu_4NOH as the most efficient catalyst: the deep violet benzene solution rapidly decolorizes and a brown sludge precipitates; further reaction with more water over a period of 10 h gives a clear red-brown solution from which the

[34] G. A. OLAH, I. BUSCI, C. LAMBERT, R. ANISFELD, N. J. TRIVEDI, D. K. SENSHARMA and G. K. S. PRAKASH, *J. Am. Chem. Soc.* **113**, 9385–7 (1991).
[35] P. R. BIRKETT, A. G. AVENT, A. D. DARWISH, H. W. KROTO, R. TAYLOR and D. R. M. WALTON, *J. Chem. Soc., Chem. Commun.*, 1230–2 (1993).
[36] P. R. BIRKETT, P. B. HITCHCOCK, H. W. KROTO, R. TAYLOR and D. R. M. WALTON, *Nature* **357**, 479–81 (1992).

[37] F. N. TEBBE (and 8 others), *Science* **256**, 822–5 (1992).
[38] K. M. CREEGAN (and 10 others), *J. Am. Chem. Soc.* **114**, 1103–5 (1992).
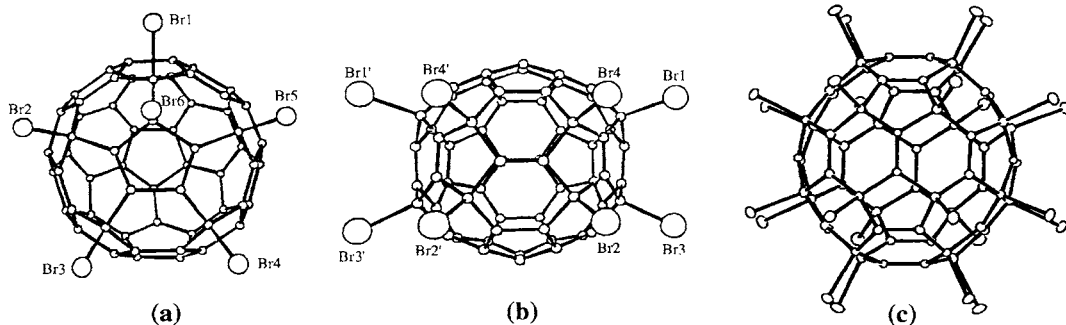[39] Y. ELEMES (and 6 others), *Angew. Chem. Int. Edn. Engl.* **31**, 351–3 (1992).

Figure 8.9   Structures of (a) $C_{60}Br_6$; (b) $C_{60}Br_8$; (c) $C_{60}Br_{24}$.

brown solid product is obtained by vacuum evaporation.[40] Hydroboration of C_{60} followed by treatment either with glacial acetic acid or aqueous $NaOH/H_2O_2$ affords another route to water-soluble fullerols, suggesting that C–H bonds on the fullerene cluster are readily oxidized to C–OH groups.[41]

Reduction of fullerenes to fullerides — Reversible electrochemical reduction of C_{60} in anhydrous dimethylformamide/toluene mixtures at low temperatures leads to the air-sensitive coloured anions $C_{60}{}^{n-}$, ($n = 1$–6). The successive mid-point reduction potentials, $E_{1/2}$, at $-60°C$ are -0.82, -1.26, -1.82, -2.33, -2.89 and -3.34 V, respectively.[42] Liquid NH_3 solutions can also be used.[43] C_{60} is thus a very strong oxidizing agent, its first reduction potential being at least 1 V more positive than those of polycyclic aromatic hydrocarbons. C_{70} can also be reversibly reduced and various ions up to $C_{70}{}^{6-}$ have been detected.

Chemical reduction by alkali metals leads to solid fullerides which are sometimes solvated.

Thus, fullerides M_nC_{60} are known for $n = 1$ when M = Rb, Cs and for $n = 2, 3, 4$ and 6 when M = Na, K, Rb and Cs. An important alternative route treats C_{60} in toluene with a solution of $Na[Mn(\eta^5\text{-}C_5Me_5)_2]$ in thf to give an 80% yield of the dark-purple, air- and moisture-sensitive crystalline solvate $NaC_{60} \cdot 5thf$.[44]

Interest in the unsolvated compounds M_nC_{60} increased dramatically when several were found to be good electrical conductors. C_{60} films when doped with alkali metal vapour become organic metals, some of which show superconductivity at low temperatures. For example, K_3C_{60}, prepared from stoichiometric amounts of solid C_{60} and potassium vapour, has T_c 19.3 K: it has an fcc structure derived from that of C_{60} itself by incorporating K ions into all the octahedral and tetrahedral interstices of the host lattice as shown in Fig. 8.10.[45] Rb_3C_{60} has an even higher superconducting critical temperature, $T_c \sim 28$ K. It seems that, when electrons are added to C_{60} from an alkali metal, they enter a conduction band composed of the triply degenerate t_{1u} π orbitals of the individual C_{60} molecules. Maximum conductivity is observed when this band is half-filled (at $C_{60}{}^{3-}$) after which the conductivity gradually decreases until the composition M_6C_{60} when it is full, consistent

[40] J. Li, A. Takeuchi, M. Ozawa, X. Li, K. Saigo and K. Kitazawa, *J. Chem. Soc., Chem. Commun.*, 1784–5 (1993) and references cited therein.
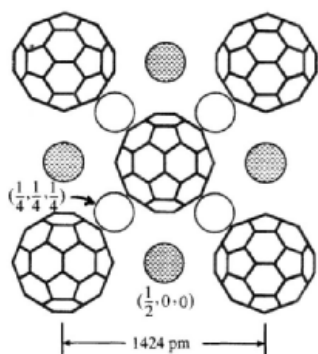
[41] N. S. Schneider, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 463–4 (1994).

[42] Y. Oshawa and T. Saji, *J. Chem. Soc., Chem. Commun.*, 781–2 (1992).

[43] W. K. Fullagar, I. R. Gentle, G. A. Heath and J. W. White, *J. Chem. Soc., Chem. Commun.*, 525–7 (1993).

[44] R. H. Douthwaite, A. R. Brough and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 267–8 (1994).

[45] P. W. Stephens (and 7 others), *Nature* **351**, 632–4 (1991). See also H. H. Wang (and 13 others), *Inorg. Chem.* **30**, 2838–9 (1991).
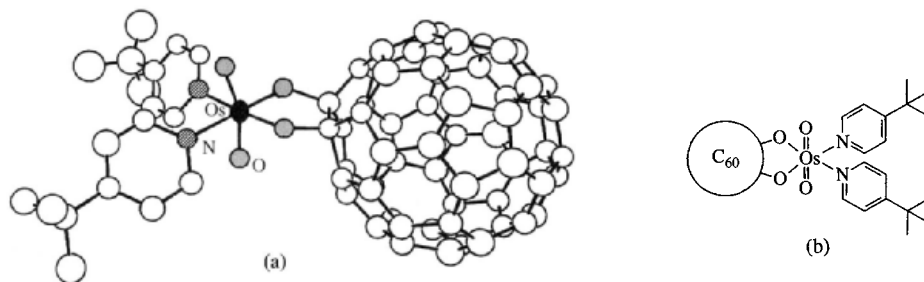
Figure 8.10   The fcc structure of K_3C_{60}, showing potassium ions occupying the tetrahedral (○) and octahedral (◉) sites. The shortest K–K distance is 617 pm (much larger than in metallic K) and the diameter of C_{60}^{3-} is 708 pm.

with the observation that K_6C_{60} (bcc lattice) is an insulator.[46]

Addition reactions — The fullerenes C_{60} and C_{70} react as electron-poor olefins with fairly localized double bonds. Addition occurs preferentially at a double bond common to two annelated 6-membered rings (a 6:6 bond) and a second addition, when it occurs is generally in the opposite hemisphere. The first characterizable mono adduct was $[C_{60}OsO_4(NC_5H_4Bu^t)_2]$, formed by reacting C_{60} with an excess of OsO_4 in 4-butylpyridine. The structure is shown in

Fig. 8.11 and was, in fact, the first definitive X-ray structural determination of a fullerene derivative.[47]

Other addition reactions are shown in the scheme.[48] Thus, C_{60} reacts as an olefin towards $[Pt^0(PPh_3)_2]$ to give the η^2 adduct $[Pt(\eta^2-C_{60})(PPh_3)_2]$. Indeed six M^0 centres can simultaneously be coordinated by a single fullerene cluster to give $[C_{60}\{M(PEt_3)_2\}_6]$, (M = Ni, Pd, Pt), with the 6M arranged octahedrally about the $(\eta^2)_6-C_{60}$ core.[49] Likewise, reaction of C_{60} with $[Ir(CO)Cl(PMe_2Ph)_2]$ provides two conformational isomers of $[(\eta^2,\eta^2-C_{60})-\{Ir(CO)Cl(PMe_2Ph)_2\}_2]$ in both of which the Ir atoms are ligated by 6:6 double bonds at diametrically opposite sides of the fullerene. Similarly,[50] C_{70} reacts with $[Ir(CO)Cl(PPh_3)_2]$ in benzene solution to give brown crystals of $[Ir(\eta^2-C_{70})(CO)Cl(PPh_3)_2]$, ligation occurring from a 6:6 double bond near one of the poles (i.e. an a–b bond in Fig. 8.6), and the bis-adduct $[(\eta^2,\eta^2-C_{70}\{Ir(CO)Cl(PPh_3)_2\}_2]$ involves a–b bonds at opposite poles. Very recently, in addition to η^2 dihapto and

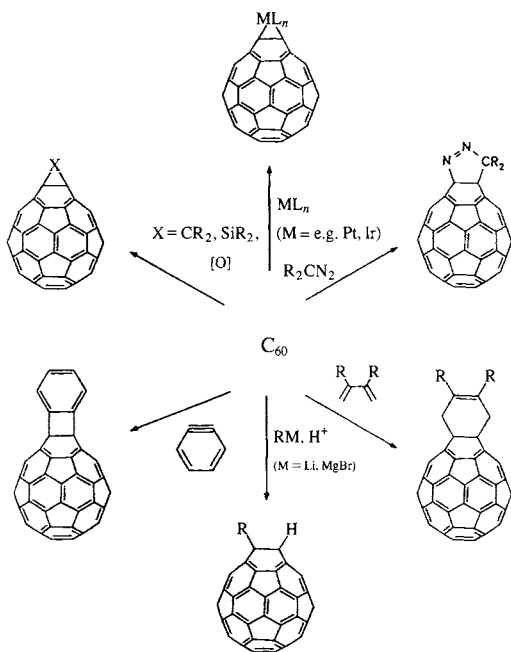[46] R. C. HADDON, *Pure Appl. Chem.* **65**, 11–15 (1993) and refs. cited therein.

[47] J. M. HAWKINS, A. MEYER, T. LEWIS, S. LOREN and F. J. HOLLANDER, *Science* **252**, 312–4 (1991).

[48] A. HIRSCH, *Angew. Chem. Int. Edn. Engl.* **32**, 1138–41 (1993) and references cited therein.

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Figure 8.11   (a) Structure of $C_{60}OsO_4(NC_5H_4Bu^t)_2$ as determined by X-ray diffraction analysis.[47]
(b) A schematic representation of the structure.

Scheme   Syntheses of exohedral fullerene derivatives. For clarity only the front sides of the fullerenes are shown.[48]

η^2,η^2 tetrahapto ligation of C_{60}, an example of η^2,η^2,η^2 hexahapto coordination has been identified in the red crystalline complex $[Ru_3[\mu_3-\eta^2,\eta^2,\eta^2-C_{60})(CO)_9]$, formed by heating C_{60} with $Ru_3(CO)_{12}$ in n-hexane, the three C=C bonds from one hexagonal face displacing one CO from each Ru atom in the cluster.[50a][50b] Extensive cluster opening can also occur, as in the cobalt(I) cyclopentadienyl adduct of the purple C_{60}/butadiene fulleroid, $[Co(\eta^5-C_5H_5)(\eta^2,\eta^2-C_{60}C_4H_4)]$, which features an unprecedented fifteen-membered "trimethano[15]annulene" opening within the C_{60} framework.

Returning now to the reactions in the scheme it can be seen that carbenes and silenes

yield the derivatives $C_{60}CR_2$ and $C_{60}SiR_2$. The structurally related epoxide $C_{60}O$ has already been mentioned (p. 284). Benzyne yields a $[2+2]$ adduct as shown, since the $[4+2]$ adduct would require the formation of an energetically unfavourable 5:6 double bond. Nucleophilic reactions with Grignard reagents and Li alkyls yield intermediates which, after protonolysis, afford 1,9-C_{60}RH derivatives, whereas hydroboration (not shown) yields $C_{60}H(BH_2)$ which on protonolysis gives the parent 1,9-dihydrofullerene, $C_{60}H_2$. Diels–Alder reactions give highly regiospecific addition products which can be isolated in high yield. By contrast, diphenyldiazomethane and related diazoalkanes and diazoacetates give substituted dihydropyrazole intermediates (via a $[3+2]$ cycloaddition reaction) which then lose N_2 to form the thermally stable final products; these may be *opened* π homoaromatic structures bridged at either a 5:6 or a 6:6 ring junction (Fig. 8.12a,b), or a *closed* σ homoaromatic fullerene bridged at a 6:6 ring junction (Fig. 8.12c). In the special case of diazomethane, $C_{60}(CH_2N_2)$ is formed as a thermally unstable brown solution in toluene; this loses N_2 when heated under reflux and $C_{61}H_2$ can be isolated as a dark powder from the now purple solution.[51] Structure type a (Fig. 8.12) in which the CH_2 group bridges an opened 5:6 junction is assigned on the basis of spectroscopic evidence. The opened azafulleroids C_{60}NR (Fig. 8.12d) can be
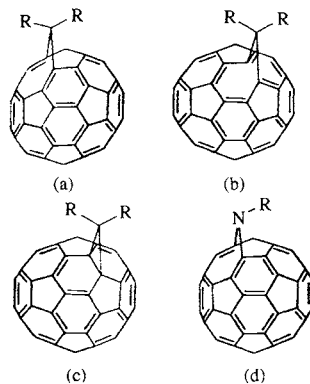
50a H.-F. Hsu and J. R. Shapley, *J. Am. Chem. Soc.* **118**, 9192–3 (1996).
50b M.-J. Arce, A. L. Viado, Y.-Z. An, S. I. Khan and Y. Rubin, *J. Am. Chem. Soc.* **118**, 3775–6 (1996).
51 T. Suzuki, Q. C. Li, K. C. Khemani and F. Wudl, *J. Am. Chem. Soc.* **114**, 7301–2 (1992).

Figure 8.12   Structures (a), (b), (c) and (d); see text.

obtained from C_{60} and organic azides, RN_3, by [3 + 2] cycloaddition and subsequent loss of N_2.

Heteroatom fullerene-type clusters — The possibility of incorporation of hetero atoms into C_n clusters has excited the attention of both theoreticians and experimentalists since the earliest days of fullerene chemistry, particularly in view of the known stability and ubiquity of organic heterocycles. The structural relationship between C_{60} and β-rhombohedral boron has already been alluded to (p. 142).

Laser vaporization of a composite pressed disc of graphite and BN using He as carrier gas, followed by mass spectrometric analysis, gave a range of clusters with even numbers of atoms from less than 50 to well above 72:[52] the peak with 60 atoms was the most abundant and, in a typical run, was shown to be a mixture of clusters: C_{60} (22%), $C_{59}B$ (21%), $C_{58}B_2$ (24%), $C_{57}B_3$ (18%), $C_{56}B_4$ (9%), $C_{55}B_5$ (4%) and $C_{54}B_6$ (2%). Brief exposure of this mixture of 60-atom clusters to NH_3 at 1 μtorr for 2 s led, typically, to the formation of $C_{60-x}\{B.NH_3\}_x$ ($x = 0-4$).

Preliminary experiments with contact-arc vaporization of graphite in a stream of He containing N_2 or NH_3 yielded nitrogen-containing products tentatively assigned to species such as $C_{70}N_2$ and $C_{59}N_x$ ($x = 2, 4, 6$) of as yet undetermined structure.

The possibility of the isoelectronic replacement of pairs of C atoms by contiguous BN groups (p. 207) in fullerenes is particularly intriguing, e.g. $C_{58}BN$, $C_{60-2x}(BN)_x$. Because each fullerene, C_n, contains 12 pentagonal faces, the limit of such substitution of C_2 by alternating BN would seem to be at $C_{12}B_{24}N_{24}$, since there is a structural frustration at the odd (fifth) C atom of each pentagon.[54]

Encapsulation of metal atoms by fullerene clusters — It is readily apparent that there is sufficient space inside fullerene clusters to accommodate several other atoms: the trick has been in learning how to synthesize such species. When a composite rod of graphite/La_2O_3 was vaporized at 1200°C in argon and the resulting "soot" extracted with pyridine, the products included not only C_{60} and C_{70} but also LaC_{60}, LaC_{70}, LaC_{74} and LaC_{82}.[55] Photo fragmentation by laser irradiation can then strip off C atoms pairwise to "shrink wrap" the metal with ever smaller clusters down to about LaC_{44}. In each of these compounds the La is encapsulated by C_n, i.e. it is an *endo* compound, in contradistinction to the alkali metal fullerides discussed on p. 285. The accepted symbolism for this novel type of compound is $[La@C_{60}]$ etc., and esr shows that the correct electronic formulation is $[La^{3+}@C_{60}{}^{3-}]$. The smallest endohedral metallafullerene so far is $[U@C_{28}]$.[56] It is notable that C_{28} would have its 12 pentagons as 4 sets of 3, plus 4 hexagons, all arranged tetrahedrally to give T_d symmetry. MO calculations suggest that neutral C_{28} lacks $4e^-$ to fill completely its bonding MOs and these are supplied by M in $[M^{4+}@C_{28}{}^{4-}]$, (M = U, Ti, Zr, Hf).

The first dimetalla analogue to be characterized was $[La_2@C_{60}]$, and mixed metal and trimetalla compounds are also known, e.g. $[YLa@C_{80}]$[57] and $[Sc_3@C_{82}]$.[58] Other known compounds include the monometalla species $[M@C_{82}]$ for M = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho and Er,[59] the dimetalla compounds $[Ce_2@C_{80}]$, $[Tb_2@C_{80}]$, $[Sc_2@C_{82}]$, $[Y_2@C_{82}]$, $[La_2@C_{82}]$ and $[Sc_2@C_{84}]$, and the trimetalla species $[La_3@C_{106}]$ and $[La_3@C_{112}]$. The products

[52] T. Guo, C. Jin and R. E. Smalley, *J. Phys. Chem.* **95**, 4948–50 (1991).

[53] T. Pradeep, V. Vijayakrishnan, A. K. Santra and C. N. R. Rao, *J. Phys. Chem.* **95**, 10564–5 (1991).

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[56] R. E. Smalley (and 9 others), *Science* **257**, 1661–4 (1992).

[57] M. M. Ross, H. H. Nelson, J. H. Callahan and S. W. McElvaney, *J. Phys. Chem.* **96**, 5231–4 (1992).

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[59] E. G. Gillan, C. Yeretzian, K. S. Min, M. M. Alvarez, R. L. Whetten and R. B. Kaner, *J. Phys. Chem.* **96**, 6869–71 (1992).

obtained depend sensitively on the relative concentrations of metal oxide and carbon in the electrode material.[59] Note also that only metals from the left-hand side of the periodic table have so far been encapsulated and there are no substantiated examples with $M = Fe$, Cu, Ag, Au, etc.

Some recent books and general reviews on the preparation, properties and chemical reactions of the fullerenes and their derivatives are in ref. 60.

The endohedral metallofullerenes just described (and the alkali metal fullerides described on p. 285) are all formally examples of metal carbides, M_xC_y, but they have entirely different structure motifs and properties from the classical metal carbides and the more recently discovered metallacarbohedrenes (metcars) on the one hand (both to be considered in Section 8.4) and the graphite intercalation compounds to be discussed in Section 8.3. Before that, however, we must complete this present section on the various forms of the element carbon by describing and comparing the chemical properties of the two most familiar forms of the element, diamond and graphite.
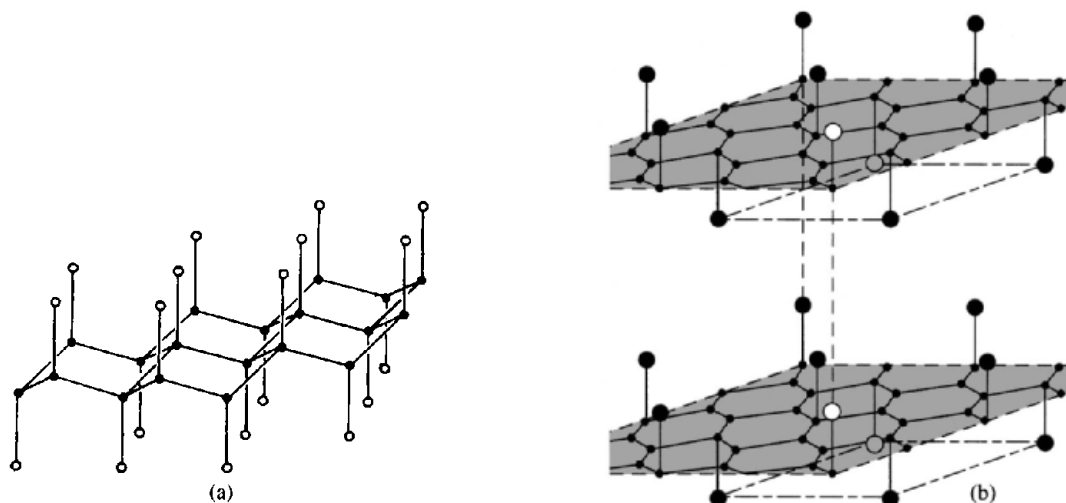
8.2.5 Chemical properties of carbon

Carbon in the form of diamond is extremely unreactive at room temperature. Graphite, although thermodynamically more stable than diamond under normal conditions, tends to react more readily due to its more vulnerable layer structure. For example, it is oxidized by hot concentrated HNO_3 to mellitic acid, $C_6(CO_2H)_6$, in which planar-hexagonal C_{12} units are preserved. Graphite reacts with a suspension of $KClO_4$ in a 1:2 mixture (by volume) of conc HNO_3/H_2SO_4 to give "graphite oxide" an unstable, pale lemon-coloured product of variable stoichiometry and structure. Similar products can be prepared by anodic oxidation of graphite or by reaction with $NaNO_3/KMnO_4/conc\ H_2SO_4$. Graphite oxide decomposes slowly at 70°C, and at 200° it undergoes a spectacular deflagration with the formation of CO, CO_2, H_2O and soot. Infrared and X-ray evidence suggest that the structure-motif is a puckered hexagonal network of C_6 rings predominantly in the "chair" conformation but with a few remaining $C=C$ bonds; in addition there are terminal and bridging O atoms and pendant OH groups; keto-enol tautomerism is implied and the empirical formula can be represented as $C_6O_x(OH)_y$ with $x \sim 1.0$–1.7 and $y \sim 2.25$–1.7.

Graphite reacts with an atmosphere of F_2 at temperatures between 400–500°C to give "graphite monofluoride" CF_x ($x \sim 0.68$–0.99). The reaction is catalysed by HF and can then occur at much lower temperatures (leading, on occasion, to the destruction of graphite electrodes during the preparation of F_2 by the electrolysis of KF/HF melts, p. 797). At $\sim$600° the reaction proceeds with explosive violence to give a mixture of CF_4, C_2F_6, and C_5F_{12}. The colour of CF_x depends on the reaction temperature and on the fluorine content, becoming progressively lighter from black ($x \sim 0.7$) to grey ($x \sim 0.8$), silver ($x \sim 0.9$) and transparent white ($x > 0.98$).[61] The structure has not been definitely established but the idealized layer lattice shown in Fig. 8.13a accounts for the observed interplanar spacings, infrared data, colour, and lack of electrical conductivity ($\rho > 3000\ ohm\ cm$). CF is very unreactive, but when heated slowly between

60 J. BAGGOTT, *Perfect Symmetry* (the discovery of buckminsterfullerene), Oxford University Press, Oxford, 1994, 300 pp. H. ALDERSLEY-WILLIAMS, *The Most Beautiful Molecule*, Aurum Press, London, 1995, 340 pp. T. BRAUN, A. SCHUBERT, H. MACZELKA and L. VASVÁRI, *Fullerene Research 1985–1993* (A computer-generated cross-indexed bibliography of the Journal literature), World Scientific Singapore, 1995, 480 pp. R. TAYLOR, *The Chemistry of the Fullerenes* (vol. 4 in *Advanced Series in Fullerenes*), World Scientific, Singapore, 1995, 260 pp. T. BRAUN (ed.) *Fullerene Science and Technology*, [now a regular Journal, vol. 3 (1995)], Marcel Dekker, New York, 1995. W. E. BILLUPS, and W. E. CIUFOLINI (eds.) *Buckminsterfullerenes*, VCH, New York, 1993, 308 pp. H. W. KROTO, J. E. FISCHER and D. E. COX (eds.), *The Fullerenes*, Pergamon Press, Oxford, 1993. 318 pp.

61 Y. KITA, N. WATANABE and Y. FUJII, *J. Am. Chem. Soc.* **101**, 3832–41 (1979) and refs cited therein. See also H. TOUHARA, K. KADONO, Y. FUJII and N. WATANABE, *Z. anorg. allg. Chem.* **544**, 7–20 (1987) for structure of $(C_2F)_n$.

Figure 8.13 (a) Idealized structure of CF showing puckered layer lattice of fused C_6 rings in "chair" conformation and axial F atoms. The spacing between successive C layers is $\sim$817 pm (cf. graphite 335.4 pm) and the density 2.43 g cm^{-3}. (b) Proposed structure for C_4F showing retention of the planar graphite sheets but with regularly spaced F atoms above and below each layer.The spacing between successive C layers is $\sim$534 pm and the density is 2.077 g cm^{-3}.

600–1000° it gradually liberates fluorocarbons, C_nF_{2n+2}.

When gaseous mixtures of F_2/HF are allowed to react with finely powdered graphite at room temperature an inert bluish-black compound with a velvety appearance is formed with a composition which varies in the range C_4F to $C_{3.57}F$. The in-plane C–C distance remains as in graphite but the interlayer spacing increases to 534–550 pm depending on the F content. The infrared and X-ray data are best interpreted in terms of the structure shown in Fig. 8.13b. The electrical conductivity, though less than that of graphite, is still appreciable, the resistivity being $\sim$2–4 ohm cm. Other chemical and electrochemical routes to C_xF ($x < 2$) and $C_{14}F(HF)_y$ have also been explored.[62]

At high temperatures, C reacts with many elements including H (in the presence of a finely

divided Ni catalyst), F (but not the other halogens), O, S, Si (p. 334), B (p. 149) and many metals (p. 297). It is an active reducing agent and reacts readily with many oxides to liberate the element or form a carbide. These reactions, which reflect the high enthalpy of formation of CO and CO_2, are of great industrial importance (p. 307).

Carbon is known with all coordination numbers from 0 to 8 though compounds in which it is 3- or 4-coordinate are the most numerous. Some typical examples are summarized in the Panel (p. 291). Particular mention should also be made of hypercoordinate "non-classical" carbonium ions such as 5-coordinate CH_5^+, square pyramidal $C_5H_5^+$ (cf. the isoelectronic cluster B_5H_9, p. 154), pentagonal pyramidal $C_6Me_6^{2+}$ (cf. iso-electronic B_6H_{10}, p. 154) and the bicyclic cation 2-norbornyl, $C_7H_{11}^+$.[63]

[62] R. HAGIWARA, M. LERNER and N. BARTLETT, *J. Chem. Soc., Chem. Commun.*, 573–4 (1989); H. TAKENAKA, M. KAWAGUCHI, M. LERNER and N. BARTLETT, *J. Chem. Soc., Chem. Commun.*, 1431–2 (1987).

[63] G. A. OLAH, *J. Am. Chem. Soc.* **94**, 808–20 (1972); G. A. OLAH, G. K. S. PRAKASH, R. E. WILLIAMS, L. D. FIELD and K. WADE, *Hypercarbon Chemistry*, Wiley, New York, 1987, 311 pp.

Coordination Numbers of Carbon

CN	Examples	Comments
0	C atoms	High-temp, low-press, gas phase
1	CO	Stable gas
	CH• (carbynes)	Reactive free-radical intermediates
2 (linear)	CO_2, CS_2	Stable gas, liquid
	HCN, HC≡CH, NCO^-, NCS^-	The ions are isoelectronic with CO_2 and COS respectively
	$M(CO)_n$	Terminal M–CO groups sometimes <180°
	RP≡C≡PR (R = 2,4,6-$Bu_3^tC_6H_2$)	Angle PCP 172.6°[63]
2 (bent)	$Ph_3P:C:PPh_3$	A bis(ylide) with angle PCP 130.1° (and 143.8°)[64]
	$:CH_2$, $:CX_2$ (carbenes)	Reactive intermediates with 1 lone-pair and 1 vacant orbital; (carbenes are bent for X = H, F, OH, OMe, NH_2, but linear if X is less electronegative, e.g. BH_2, BeH, Li)[65]
	•CH_2•, •CPh_2• (methylenes)	Reactive intermediates with 2 unpaired electrons
3 (planar)	COXY (X = H, hal, OH, O^- R, Ar)	Stable oxohalides, carbonates, carboxylic acids, aldehydes, ketones, etc.
	$[C(N≡PCl_3)_3]^+[SbCl_6]^-$	Colourless crystals prepared from $[C(N_3)_3]^+ + PCl_3$[66]
	$M_m(CO)_n$	Metal carbonyl clusters with bridging CO groups M–C(O)–M
	$[PhC(OMe)M(CO)_5]$	Stable metal — carbene complexes, e.g. M = Cr, W
	CH_3^+ (carbonium ions)	Unstable reaction intermediates with 1 vacant orbital[67]
3 (pyramidal)	CH_3^-, CPh_3^- (carbanions), RMgX	Unstable reaction intermediates with 1 lone pair of electrons
	$Ph_3C^•$, $R_3C^•$ (free radicals)	Paramagnetic species of varying stability
3 (T-shaped)	$[Ta(≡CHCMe_3)_2(2,4,6,-Me_3C_6H_2)(PMe_3)_2]$	The unique H is equatorial and angle Ta≡C–CMe_3 is 169°[68]
4 (tetrahedral)	CX_4, etc.	4-coord covalent compds such as CF_4, C_2H_6, CHXYZ, etc.
	$M_m(CO)_n$	Metal carbonyl clusters with triply bridging CO groups (p. 928)
4 (see-saw, C_{2v})	$[Fe_4C(CO)_{13}]$	The μ_4-carbido C caps Fe_4 "butterfly"[69]
5	Al_2Me_6	Alkyl-bridged organometallics involving 3c–2e, bonds (pp. 259, etc.)
	$C_2B_4H_6$, etc.	Several stable carboranes (p. 183)
	$[(\eta^5-C_5H_5)NiRu_3(CO)_9CCHBu^t]$	The C atom bonds to CHBu^t and to M_4 "butterfly"[70]
	$[Os_5C(CO)_{13}HL_2]$	The μ_5-carbido C bonds to all 5 Os[71]
	$[C\{AuPPh_3\}_5]^+BF_4^-$	trigonal bipyramidal cation[72]
6	$C_2B_{10}H_{12}$, etc.	Several stable carboranes (p. 185)
	$[C(AuPPh_3)_6]^{2+}[BF_3(OMe)]_2^-$	octahedral dication[73]
7	$(LiMe)_4$ crystals	See structure, p. 104
8	Be_2C (antifluorite),	See structure, p. 118
	$[Co_8C(CO)_{18}]^{2-}$	See structure, p. 1142

[64] A. T. VINCENT and P. J. WHEATLEY, *J. Chem. Soc., Dalton Trans.*, 617–22 (1972). G. E. HARDY, J. I. ZINK, W. C. KASKA and J. C. BALDWIN, *J. Am. Chem. Soc.* **100**, 8001–2 (1978). see also E. FLUCK, B. NEUMÜLLER, R. BRAUN, G. HECKMANN, A. SIMON and H. BORRMANN, *Z. anorg. allg. Chem.* **567**, 23–38 (1988) and the many references cited therein.

[65] W. W. SCHOELLER, *J. Chem. Soc., Chem. Commun.*, 124–5 (1980).

[66] U. MÜLLER, I. LORENZ, and F. SCHMOCK, *Angew. Chem. Int. Edn. Engl.* **18**, 693–4 (1979).

[67] Note, however, that an X-ray structure analysis of the stable, crystalline carbocation 3,5,7-trimethyladamantyl showed the 3-coordinate C(1) atom as a considerably flattened pyramid 21 pm above the plane of the 3 adjacent C atoms and with bond angles 120°, 118° and 116° ($\Sigma = 354°$). T. LAUBE, *Angew. Chem. Int. Edn. Engl.* **25**, 349–51 (1986).

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[70] E. SAPPA, A. TIRIPICCHIO and M. T. CAMELLINI, *J. Chem. Soc., Chem. Commun.*, 154 (1979).

[71] J. M. FERNANDEZ, B. F. G. JOHNSON, J. LEWIS and P. RAITHBY, *J. Chem. Soc., Dalton Trans.*, 2250–7 (1981).

[72] F. SCHERBAUM, A. GROHMANN, G. MÜLLER and H. SCHMIDBAUR, *Angew. Chem. Int. Edn. Engl.* **28**, 463–5 (1989).

[73] F. SCHERBAUM, A. GROHMANN, B. HÜBER, C. KRÜGER and H. SCHMIDBAUR, *Angew. Chem. Int. Edn. Engl.* **27**, 1544–6 (1988).
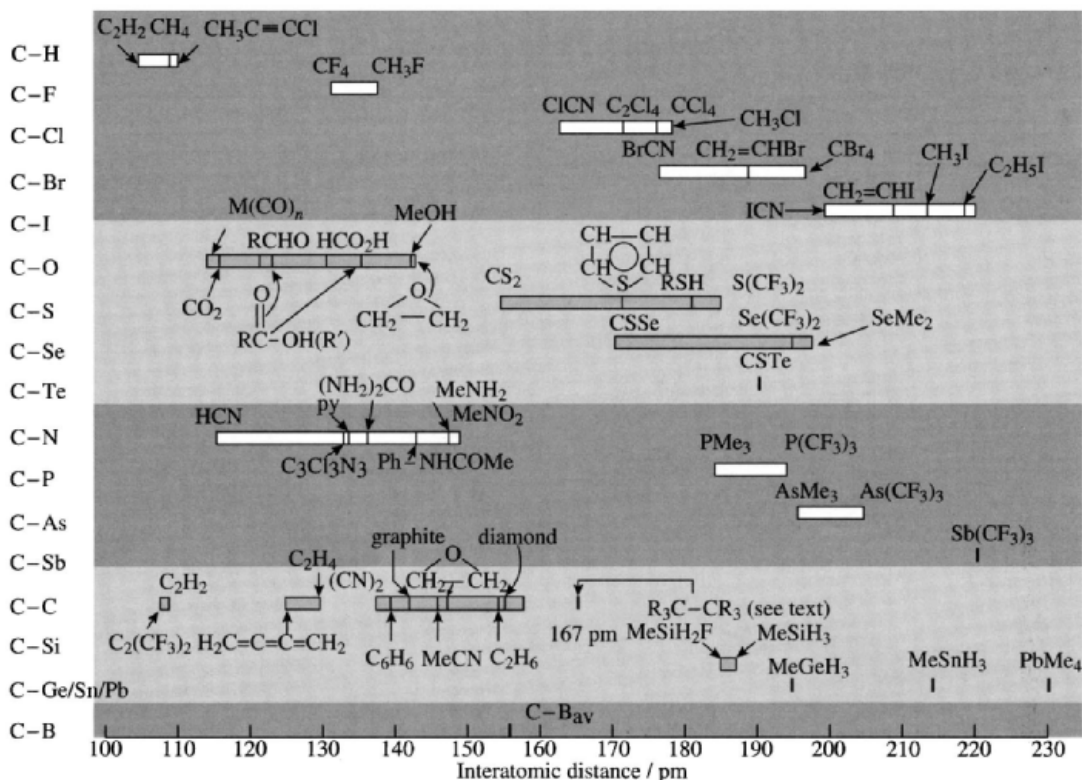
Figure 8.14   Some interatomic distances involving carbon.

Interatomic distances vary with the type of bond and the nature of the other atoms or groups attached to the bonded atoms. For example, the formally single-bonded C–C distance varies from 146 pm in Me–CN to 163.8 pm in $Bu_2^nPhC–CPhBu_2^n$ [74] and 167 pm in 3,5-Bu_2^t-$C_6H_3)_2C–C(C_6H_3$-3,5-$Bu_2^t)_3$ and $(CF_3)_2(4$-$FC_6H_4)C–C(C_6H_4$-4-F)$(CF_3)_2$. [75] Some typical examples are in Fig. 8.14. Note that because of the breadth of some of these ranges the interatomic distance between quite different pairs of atoms can be identical. For example, the value 133 pm includes C–F, C–O, C–N and C–C; likewise the value of 185 pm includes C–Br, C–S, C–Se, C–P and C–Si. The conventional

classification into single, double and triple bonds is adopted for simplicity, but bonding is frequently more subtle and more extended than these localized descriptions imply. Bond energies are listed on p. 374, where they are compared with those for other elements of Group 14. It should perhaps be emphasized that interatomic distances are experimentally observable, whereas bond orders depend on theoretical models and the estimation of bond energies in polyatomic molecules depends additionally on various assumptions as to how the total energy is apportioned. Nevertheless, taken together, the data indicate that an increase in the order of a bond between 2 atoms is accompanied both by a decrease in bond length and by an increase in bond energy. Similarly, for a given bond order between C and a series of other elements (e.g. C–X), the bond energy increases as the bond length decreases.

[74] W. LITTKE and U. DRÜCK, *Angew Chem. Int. Edn. Engl.* **18**, 406–7 (1979).
[75] B. KAHR, D. VAN EUGEN and K. MISLOW, *J. Am. Chem. Soc.* **108**, 8305–7 (1986), and references cited therein.