

# CHAPTER 1

## INTRODUCTION



### 1.1 The fullerenes : The molecular allotropes of carbon

A molecule containing an even number of carbon atoms arranges in a closed hollow cage. The fullerenes were discovered as a consequence of astrophysically motivated chemical physics experiments that were interpreted by using geodesic architectural concepts. Fullerenes chemistry, a new field that appears to hold much promise for materials development and other applied areas, was born from pure fundamental science.

In 1985, fifteen year after it was conceived theoretically, the molecule buckminsterfullerene ( $C_{60}$  or fullerene-60) was discovered [1]. Fullerene-60 (Fig. 1.1) is the archetypal member of the fullerenes, a set of hollow, closed-cage molecules consisting purely of carbon. Some representative structures are shown in Fig. 1.2. The fullerenes can be considered, after graphite and diamond, to be the third well-defined allotrope of carbon. Microscopic amounts of various fullerenes were first isolated in 1990, and since then they have been studied intensively. It has been discovered that members of this new class of spheroidal aromatic organic molecules have numerous novel physical and chemical properties. The fullerenes promise to have synthetic, pharmaceutical, and industrial applications [2]-[4]. Already, derivatives have been found to exhibit fascinating electrical and magnetic behavior, in particular superconductivity [5]-[6] and ferromagnetism [6].

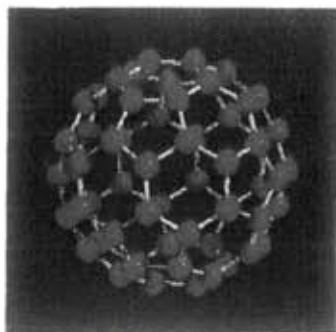


Figure 1.1 Structure of fullerene-60 ( $C_{60}$ ).

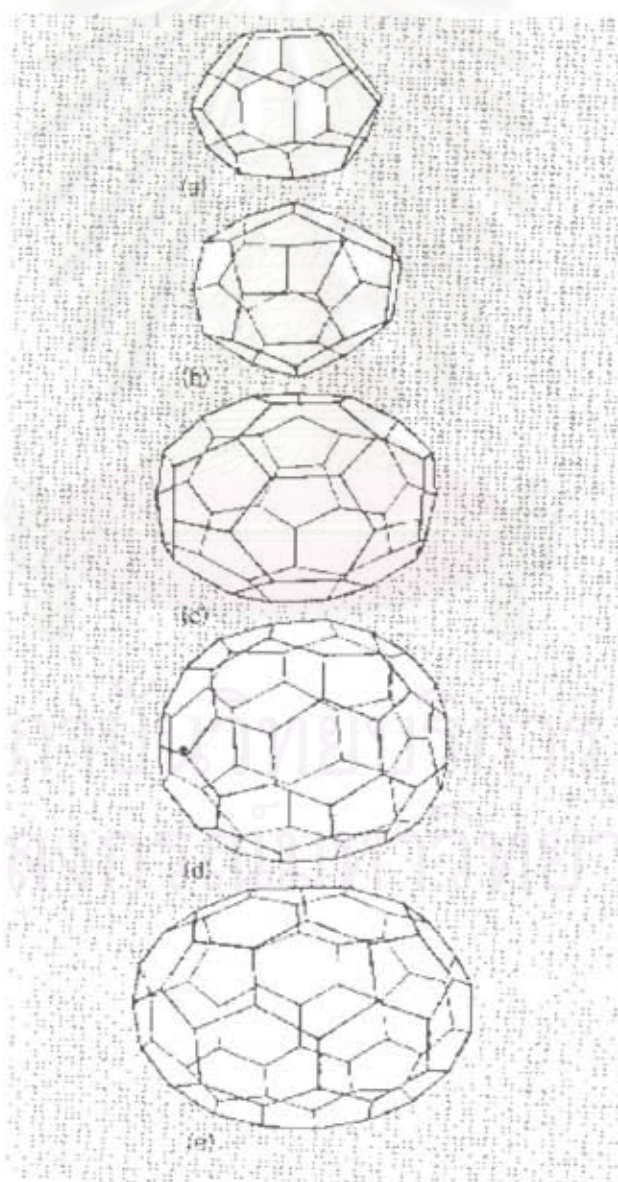
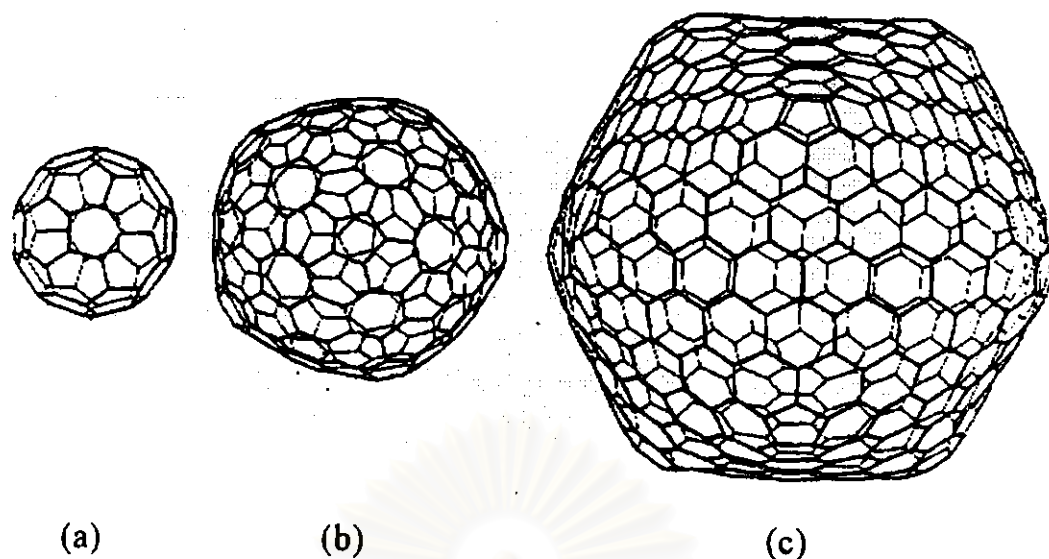


Figure 1.2 The family of fullerenes (a)  $C_{28}$ , (b)  $C_{32}$ , (c)  $C_{50}$ , (d)  $C_{60}$  and (e)  $C_{70}$ .

**Structures:** In a fullerene molecule an even number of carbon atoms are arrayed over the surface of a closed hollow cage. Each atom is trigonally linked to its three neighbors by bonds that delineate a polyhedral network consisting of 12 pentagons and  $n$  hexagons (such structures conform to *Euler's theorem* for polyhedrons in that  $n$  may be any number other than one, including zero). All 60 atoms in fullerene-60 are equivalent and lie on the surface of a sphere distributed with the symmetry of a truncated icosahedron. The 12 pentagons are isolated and interspersed symmetrically among 20 linked hexagons; that is, the symmetry is that of a modern soccerball. The molecule was named after R. Buckminster Fuller, the inventor of geodesic domes, which conform the same underlying structural formula. Three of the four valence electrons of each carbon atom are involved in the  $sp^2$  sigma-bonding skeleton, and the fourth  $p$  electron is one of the 60 involved in a pi-delocalized molecular-orbital electron sea that covers the outside (exo) and inside (endo) surface of the molecule. The resulting cloud of pi-electron density is similar to that which covers the surface of graphite; indeed, the molecule can be considered a round form of graphite. The smallest member of the family, fullerene-20, is dodecahedrane, whose fully hydrogenated analog ( $C_{20}H_{20}$ , dodecahedrane) has been created by rational synthesis (production of a compound by using a sequence of chemical reaction steps strategically chosen for the purpose). Several members of the family have now been isolated, in particular  $C_{70}$ ,  $C_{76}$ , and  $C_{84}$ . Giant fullerenes with at least 600 atoms also seem to form, and appear to have interesting polyhedral shapes. The highly symmetric icosahedral species  $C_{60}$ ,  $C_{240}$ , and  $C_{540}$  are shown in Fig. 1.3.



**Figure 1.3** Comparison of the structure of fullerene-60 with those of two giant fullerenes (a) C<sub>60</sub>, (b) C<sub>240</sub> and (c) C<sub>540</sub>.

**Discovery and preparation :** In 1985 laboratory experiments were initiated that aimed to simulate the physicochemical conditions in a cool red giant star by using a pulsed laser focused on a graphite target to generate a plasma expanded supersonically and cooled, the carbon atoms aggregated in the vapor phase. An exceptionally strong signal was detected for the C<sub>60</sub><sup>-</sup> ion by mass spectrometry [7], [8]. The signal for C<sub>70</sub><sup>+</sup> was also prominent. It was proposed that these observations indicated that the C<sub>60</sub> and C<sub>70</sub> species were long lived, and that on the basis of geodesic and chemical arguments. This unexpected stability was commensurate with closed-cage fullerene structures.

Subsequent experiment and theory yielded significant support for the cage proposal. For instance, the formation of endohedral metallofullerene complexes, in which a metal atom is encapsulated in the cage, was demonstrated. Fullerenes with nonabutting pentagons should be especially stable (the isolated pentagon rule), a conclusion that readily explained the observation that both C<sub>60</sub> and C<sub>70</sub> are prominent. Although there was initially

some skepticism about the fullerene proposal, a great deal of supporting data was subsequently amassed.

In 1990 the dust produced by a carbon arc struck under argon was found to contain around 10% fullerenes, which could be extracted by using solvents or by sublimation. Individual fullerenes were found to be separable by standard chromatographic techniques. The structures of fullerenes-60 and -70 have been confirmed unequivocally by X-ray [1], nuclear magnetic resonance (NMR) [9], and other spectroscopic measurements [9], [10]. The simplicity of the preparative procedure has enabled the chemistry and physics of the fullerenes to advance very rapidly. It has also been found that a benzene/oxygen combustion flame can be adjusted so that the resulting soot contains up to 4% fullerenes. The implications for a more detailed understanding of soot formation are interesting.

**Properties :** In benzene solution, fullerene-60 is magenta and fullerene-70 is red. Fullerene-60 forms translucent magenta face-centered cubic (fcc) crystals that sublime [11]. The ionization energy is 7.61 eV [12] and the electron affinity is 2.6-2.8 eV [12]. The strongest absorption bands lie at 213, 257, and 329 nanometers [9]. Studies with NMR spectroscopy yield a chemical shift of 142.7 ppm [9]; this result is commensurate with an aromatic system. Other NMR measurements indicate that the molecule is rotating in the lattice even at very low temperatures [13]-[16].

Fullerene-60 behaves as a soft electrophile, a molecule that readily accepts electrons during a primary reaction step. It can accept three electrons readily and perhaps even more. The molecule can be multiply hydrogenated, methylated, ammoniated, and fluorinated. It forms exohedral complexes in which an atom (or group) is attached to the outside of the cage, as well as endohedral complexes in which an atom [for example, lanthanum (La), potassium (K), or calcium (Ca)] is trapped inside the cage. Exohedral transition-

metal complexes with ligands containing osmium and potassium has been made. Evidence for oxygen addition compounds such as  $C_{60}O$  and  $C_{70}O$ , has also been reported [17], [18]. A stable endohedral metallofullerene,  $La@C_{82}$ , has been isolated. Fullerene-60 appears to catalyze the formation of singlet oxygen in the presence of light. This ability may be related to the observation that under certain conditions solutions of fullerene-60 decompose in the presence of oxygen and light.

The possible hazards associated in working with fullerene-60 have not yet been determined. However, common sense and the compound's ability to catalyze formation of singlet oxygen suggest that some care should be exercised when working with it until more is known about possible toxicity.

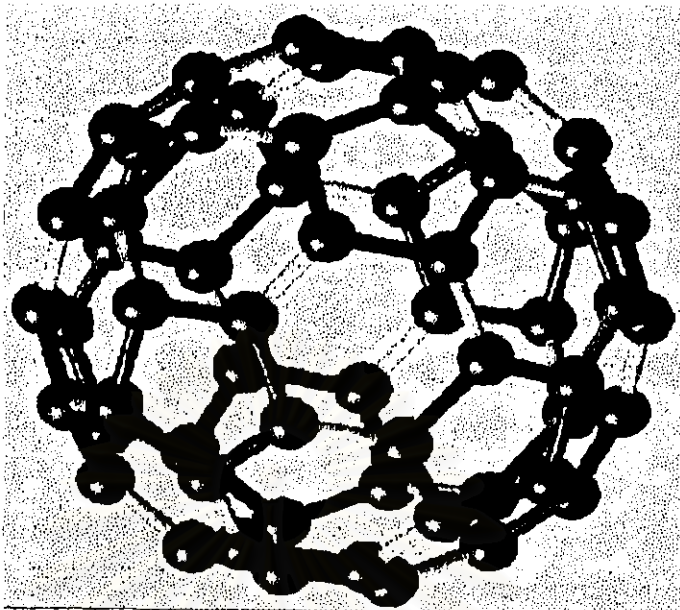
Metal-doped crystals such as  $K_3C_{60}$  have been found to be isotropically superconducting at 30 K (-406 °F), and charge-transfer complexes have been found to be ferromagnetic [19].

**Applications :** The properties of fullerene materials that have been determined suggest that there is likely to be a wide range of areas in which the fullerenes or their derivatives will have used. The facility for acceptance and release of electrons suggests a possible role as a charge carrier in batteries. The properties of graphite suggest that lubricative as well as tensile and other mechanical properties of the fullerenes are worthy of investigation. Liquid solutions exhibit excellent properties of optical harmonic generation. The high temperature at which superconducting behavior is observed is particularly exciting. This observation suggest possible applications in microelectronics devices, as does the detection of ferromagnetism in other fullerene derivatives.

## 1.2 Buckminsterfullerene : C<sub>60</sub>

C<sub>60</sub> has the soccer ball structure of a truncated icosahedron, a polyhedron having sixty vertices, ninety bonds, twelve pentagonal faces (five-membered rings) and twenty hexagonal faces (six-membered rings). This structure places each carbon atom in an identical molecular environment. Each atom is  $sp^2$  bonded to three of its neighbors, leaving a sea of sixty  $\pi$  electrons to produce many resonance structures. The name buckminsterfullerene was chosen after the architect R. Buckminster Fuller, whose geodesic dome provided a guide to the hollow cage structure hypothesis. The general name, fullerene, has been adopted for all similar hollow shell carbon molecules C<sub>n</sub> closed by twelve five-membered rings. The term buckyball is often used more colloquially.

The structure of fullerene-60-I<sub>h</sub> was shown in Fig. 1.4. Two features of this C<sub>60</sub> structure are of special significance: (i) all the twelve pentagons are isolated by hexagons and (ii) the bonds at the junctions of two hexagons (6-6 bonds : double bonds) are shorter than the bonds at the junctions of a hexagon and a pentagon (6-5 bonds : single bonds). From the X-ray data [20] the length of single bond (red stick) and double bond (yellow stick) are 1.467 Å and 1.355 Å, respectively. The interior diameter of ball is about 7 Å. The fullerene-60-I<sub>h</sub> is the only C<sub>60</sub> isomer and the same time the possible fullerene, which obeys the "isolated pentagon rule" (IPR) [21], [22]. The IPR predicts fullerene structures with all the pentagons isolated by hexagons to be stabilized against structures with adjacent pentagons. Solid C<sub>60</sub> forms a face-centered-cubic (fcc) structure at room temperature [23]. The density in the solid state is 1.68 g.cm<sup>-3</sup> [24]. Four equivalent molecules are contained in a cube with edge length  $a = 14.198$  Å, at the origin and face centers. Due to weak intermolecular interactions the spherical molecules in this "plastic crystal" almost freely rotate at room temperature.



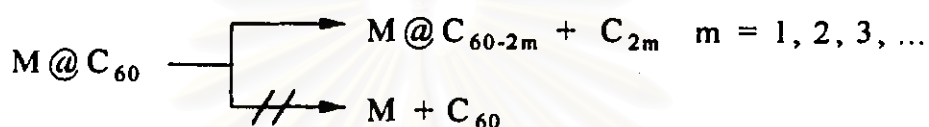
**Figure 1.4** The structure of fullerene-60- $I_h$  ( $C_{60}$ ).

### **1.3 Complexation of buckminsterfullerene**

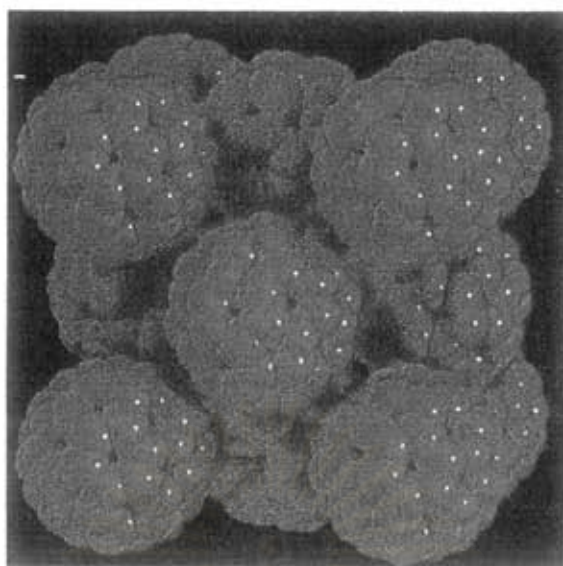
The hollow spherical structure of  $C_{60}$  and the diameter of the cage is about 7 Å. This makes it possible to trap atoms inside the cage. Within one week after the initial discovery of  $C_{60}$ , evidence for an endohedral lanthanum complex of  $C_{60}$  was detected [25]. The encapsulated compound of  $C_{60}$  and La was accomplished by the laser vaporization of a graphite disk, soaked in  $LaCl_3$  solution. Now there are many methods for encapsulation particles in  $C_{60}$  such as high-energy collisions method [26], injected-ion drift-tube technique [27], and arc or resistive heating method [28]. It has been proposed that endohedral fullerenes containing small polar molecule could be assembled into useful ferroelectric materials [29], [30]. To facilitate the discussion of these complexes, a special symbolism and nomenclature was introduced [28]. Thereby the symbol @ is used to indicate the atoms in the interior of the



fullerene. All atoms, that are listed to the left of the @ symbol are located inside the cage and all atoms to the right are a part of the cage structure, which includes heterofullerenes for example  $C_{59}B$ . A  $C_{60}$ -caged metal species is then written as  $M@C_{60}$ , expressed as “metal at  $C_{60}$ ”. For the interesting method of encapsulation is the high energy collision method. The particles attack at the surface of the  $C_{60}$  cage cause the loosing successively  $C_2$  fragments without cracking the cluster or loosing the incorporated metal called “shrink wrap” process [31]



Carbon-60 molecules form a face-centered-cubic solid (Fig. 1.5). In this lattice, there is plenty of space to intercalate other atoms or small molecules in between the bucky balls (this *fcc* structure has three available sites per  $C_{60}$ , one “octahedral” and two “tetrahedral”). When alkali metal atoms are put into this structure they donate their 1 valence electron to a neighboring  $C_{60}$  molecule.  $C_{60}$  has a free electronic band which can hold up to six more electrons. The first stable structure is  $MC_{60}$  - one alkali atom in each “octahedral” site. Further doping produces  $M_3C_{60}$  - now the  $C_{60}$  molecules have their electronic band exactly half full so this is a metal and in fact it becomes superconducting at 30 K for rubidium, 20 K for potassium, and various mixtures can produce other superconducting transition temperatures. Next is  $M_4C_{60}$  - the lattice must not be expanded to include more than three intercalated atoms, and become body-centered-tetragonal (*bct*). The structure can be expanded once more, to body-centered-cubic (*bcc*), and now 6 atoms will fit in. This is the highest alkali doped fullerene,  $M_6C_{60}$ , which now has a full electronic band and is therefore an insulator.



**Figure 1.5** The face-centered-cubic (*fcc*) lattice of  $C_{60}$ .

#### **1.4 Reasons for understanding this study**

Why the Li- $C_{60}$  system is chosen for study? Due to the closed hollow cage structure of  $C_{60}$  with quite big diameter and a large space between  $C_{60}$  in *fcc* lattice, several types of the complexes between  $C_{60}$  and alkali metals both endohedral and exohedral forms can be consequently formed. The endohedral complexes behave ferroelectric. For the exohedral types, their properties are varying from being conductors to insulators depending strongly on the Li: $C_{60}$  ratio. The M- $C_{60}$  complexes, where M are Na, K and Cs, have been widely synthesized and their properties have been intensively elucidated [5], [19], [32]-[37]. Complexes between  $C_{60}$  and Li was rarely studied [38], [39]. It should be noted that  $K_3C_{60}$  [5] complex is superconductor whereas  $M_nC_{60}$  complexes are insulators; whereby M are Li, Na and Cs and  $n = 1, 2, 3, \dots, 6$  [6], [40]. However, alloy metal fullerides of Na or Li are superconductors [35]. Relation between superconductivity of the complexes and transition temperatures ( $T_c$ ) and lattice parameters ( $a_0$ ) was summarized in Table 1.1.

**Table 1.1** Transition temperatures ( $T_c$ ) and lattice parameters ( $a_0$ ) of *fcc*  $M_3C_{60}$  superconductors, where atomic radii of Li, Na, K, Rb and Cs are 1.520, 1.537, 2.272, 2.475 and 2.654 Å, respectively.

Material	$T_c$ (K)	$a_0$ (Å)
$C_{60}$	-	14.198
$K_3C_{60}$	19	14.240
$Rb_3C_{60}$	29	14.384
$Li_2CsC_{60}$	12	14.120
$Na_2KC_{60}$	2.5	14.025
$Na_2RbC_{60}$	2.5	14.028
$Na_2CsC_{60}$	12	14.134
$RbCs_2C_{60}$	33	14.555
$Rb_2CsC_{60}$	31	14.431
$KRb_2C_{60}$	27	14.323
$K_2CsC_{60}$	24	14.292
$K_2RbC_{60}$	23	14.243

It is interesting to note that the  $M_3C_{60}$  complexes with the medium-sized alkali metal atoms such as K and Rb are superconductors. Unfortunately, data related to superconductivity of  $Li_3C_{60}$  is not available in which case, if available, would be very useful to understand the conductivity properties of the metal- $C_{60}$  of the alkali series. Accordingly, the present work is aimed to provide new results of conductivity and other interesting properties of the exohedral complex of Li and  $C_{60}$ .

The collision process of metal and  $C_{60}$  to form  $M@C_{60}$  is also of great interest because these information are useful for the synthesis of the endohedral complexes. Several methods have been introduced to study such process, i.e.

high-energy collisions method [26], injected-ion drift-tube technique [27] and arc or resistive heating method [28]. Therefore, it is interesting to investigate the collision process of Li and  $C_{60}$ , especially the kinetic energy required to break the potential wall.

When a metal atom forms complex with  $C_{60}$ , the metal atom releases its electron to the  $C_{60}$ . This charge transfer determines the stability and electronic properties, i.e. dipole moment, of the complex. In this work, the charge transfer will be investigated both qualitatively, in terms of stability and dipole moment of the complex, and quantitatively, in term of localized charge distribution.

To eliminate possible confusion in the notation of symbol that represents the complex, “Li- $C_{60}$ ” is utilized to denote both endohedral and exohedral complex, which are represented usually by  $Li@C_{60}$  and  $LiC_{60}$ , respectively.



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**Objectives of this study :**

- 1) To develop the potential energy surface for the Li-C<sub>60</sub> system.
- 2) To approximate the threshold kinetic energy for firing Li to penetrate the surface of C<sub>60</sub> cage to form the endohedral Li@C<sub>60</sub> complex.
- 3) To investigate the relationship between dipole moment and stabilization energy of the Li-C<sub>60</sub> complexes.
- 4) To analyze the electron transfer between the two monomers.
- 5) To investigate the changes of the geometrical parameters and electronic structures of the Li<sub>n</sub>C<sub>60</sub> complexes in order to approximate the conductivity of the complexes.

All properties mentioned above, i.e. stabilization energy, electron density, dipole moment, electronic structure, conductivity and the threshold collision energy between Li and C<sub>60</sub> are computed via *ab initio* calculations.

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