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COMPUTATIONAL STUDY OF RELATIVE STABILITIES OF $C_{60}(I_h)$ AND $C_{70}(D_{5h})$ GAS-PHASE CLUSTERS *

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ABSTRACT

Structures, energetics, vibrations, and thermodynamics of the title species were evaluated within the AM1 semiempirical method. Whereas this method also indicates that $C_{70}(D_{5h})$ is the more abundant component of an equilibrium gas-phase mixture than the $C_{60}(I_h)$ cluster, the possible effect of pressure on the relative stability of C_{60} vs. C_{70} species was pointed out. A comparison with MMP2 and MNDO results is also made.

INTRODUCTION

Quite recently Smalley and co-workers [1,2] studied the mass spectra of carbon clusters C_n ($n \approx 40$–90) resulting from the laser vaporization of graphite, and found two stable peaks at carbon number 60 (more intense) and 70. They suggested that C_{60} has a truncated icosahedral structure (I_h point group of symmetry) † while C_{70} has an egg-shaped structure (see Fig. 1). These papers were immediately followed by a series of experimental [4–7] as well as theoretical [8–14] studies. The experimental observations [1,2,4–7] gave a new impetus to the long-standing theoretical interest in C_n clusters [15–21]. Researchers are also interested by applied high technology, for example, regarding the vaporization of protecting carbonaceous heat shields

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† Schulman et al. [3] have suggested the use of the symbol I_i instead of the widespread I_h.

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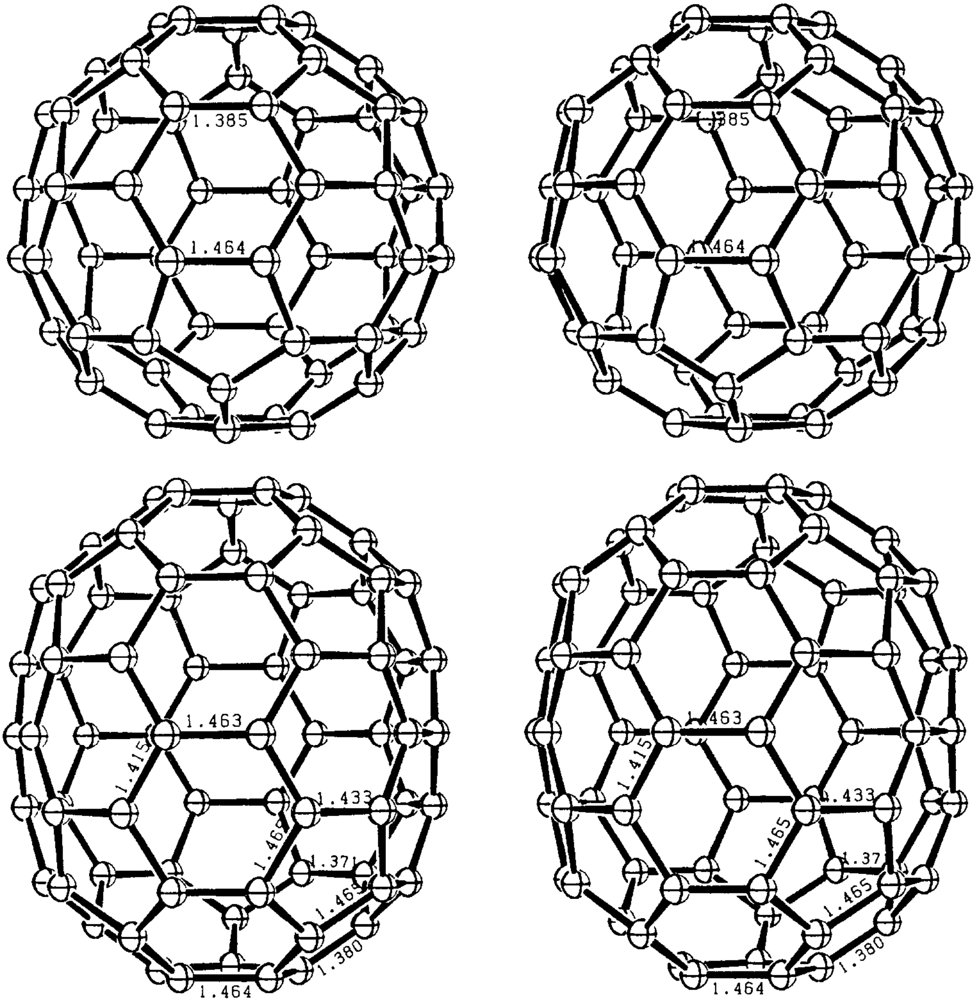

Fig. 1. Stereoscopic views of AM1 structures of $C_{60}(I_h)$ (top) and $C_{70}(D_{5h})$ (bottom) clusters; the bond lengths are given in 10^{-10} m. The two bond lengths of 1.465×10^{-10} m in C_{70} are not identical, being 1.4652 (the upper) and 1.4646×10^{-10} m (the lower). The bond angles in $C_{60}(I_h)$ are exactly 108 (five-membered ring) or 120 ° (six-membered ring), while in $C_{70}(D_{5h})$ they range between 107.8 and 108.0 ° (five-membered ring), or between 117.6 and 120.5 ° (six-membered ring).

for space reentry vehicles, (see ref. 18). So far the most comprehensive theoretical study of the C_{60}/C_{70} system was by Newton and Stanton [11] (using the MNDO approach), who proved that C_{60} possessing I_h symmetry and C_{70} with D_{5h} symmetry are local energy minima. They also observed that in terms of the heat of formation per carbon atom, $\Delta H^{\ominus}_{f,298}/n$, the latter structure was favored by 4.2 kJ mol^{-1} $atom^{-1}$. In order to explain the disagreement with experimental observations [1], kinetic factors or the influence of mass-spectrometric detection method were invoked [11].

The MNDO method was recently improved to AM1 [22], which exhibits a better agreement with observed data (containing, amongst others, naphthalene and cubane) for several molecular characteristics (including one test for vibrational frequencies [23]). We applied this latest version of the semiempirical quantum-chemical method to $C_{60}(I_h)$ and $C_{70}(D_{5h})$, treating their relative stability in a thermodynamically consistent way (employing the MOPAC program package [24] implementation [25]).

COMPARISON OF MNDO AND AM1 MOLECULAR PARAMETERS

Geometrical features of both optimized species (Fig. 1) are in a qualitative sense essentially the same in the MNDO and AM1 approaches. Quantitatively, bond-length ranges are slightly lower in AM1 than those reported for the MNDO method [11], while $\Delta H^{\ominus}_{f,298}$ and ionization potentials are higher for both species for AM1 than those found [11] for MNDO (Table 1). Vibrational frequencies are available for MNDO [11] for $C_{60}(I_h)$ only, and their ranges are again higher for AM1 evaluations. Nevertheless, in terms of the heat of formation per carbon atom the $C_{70}(D_{5h})$ structure remains favored, now by 3.8 kJ mol^{-1} atom^{-1}.

The clusters have never been studied by molecular mechanics. Thus, Table 1 contains MMP2 data, in which the $C_{60}(I_h)$ species is favored (by 0.7 kJ mol^{-1} atom^{-1}). It indicates that a deeper molecular–mechanical study of C_n aggregates will be worthwhile.

Several remarkable features are demonstrated by C_{60} and C_{70} aggregates, both from the experimental and theoretical points of view. Let us mention that $C_{70}(D_{5h})$ is, to our knowledge, the largest system for which vibrational analysis has been carried out on a quantum-chemical basis. It should also be noted that in AM1 treatment $C_{70}(D_{5h})$ exhibits considerably poorer convergency properties, both at SCF and geometry optimization levels, than the $C_{60}(I_h)$ structure. The values of symmetry number are important: for $C_{60}(I_h)$ it reads 60 and belongs to the same (highest ever described) level as dodecahedrane and $B_{12}H_{12}^{2-}$. (For example, cubane possesses a symmetry number of 24, only.)

EQUILIBRIUM BETWEEN $C_{60}(I_h)$ AND $C_{70}(D_{5h})$

In order to evaluate relative stabilities between C_{60} and C_{70}, thermodynamic functions of the following hypothetical equilibrium

$$C_{60}(I_h;\ g) \rightleftharpoons 6/7C_{70}(D_{5h};\ g) \qquad (1)$$

(where g refers to the gas phase) were calculated based on the results of AM1 treatment of both components, using the conventional rigid-rotor and

TABLE 1

Comparison of MNDO and AM1 molecular parameters of $C_{60}(I_h)$ and $C_{70}(D_{5h})$

Species	$\Delta H^{\ominus}_{f,298}$(kJ mol^{-1})			I.P.[a] (eV)		Equilibrium bond length[b] (10^{-10} m)						Vibrational frequency (cm^{-1})			
	MMP2	MNDO	AM1	MNDO	AM1	MMP2		MNDO		AM1		MNDO		AM1	
						Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
$C_{60}(I_h)$	1197	3637	4072	9.1	9.6	1.393	1.444	1.400	1.474	1.385	1.464	186[c]	1217[c]	284	1816
$C_{70}(D_{5h})$	1443	3954[c]	4485	8.7[c]	9.1	1.388	1.443	1.39[c]	1.49[c]	1.380	1.465			237	1862

[a] Ionization potential. [b] $C_{60}(I_h)$ has only two kinds of bond. [c] Taken from ref. 11.

TABLE 2

AM1 standard [a] changes of basic thermodynamic functions, $\Delta X^{\ominus}_{298}$ [b], for reaction (1) at room temperature

$\Delta H^{\ominus}_{298}$ (kJ mol^{-1})	$\Delta S^{\ominus}_{298}$ (J K^{-1} mol^{-1})	$\Delta G^{\ominus}_{298}$ (kJ mol^{-1})	K_p [c] (atm$^{-1/7}$)
-228 [d]	-15.0	-224	1.74×10^{39}

[a] Standard state, an ideal gas at 1 atm = 101 325 Pa pressure. [b] $X = H$ (enthalpy), S (entropy), or G (Gibbs free energy). [c] Equilibrium constant of reaction (1). [d] MMP2 value reads 40 kJ mol^{-1}.

TABLE 3

Pressure dependence of equilibrium relative populations [a] of $C_{60}(I_h)$ and $C_{70}(D_{5h})$ at room temperature

p_0 (atm)	x_{60} (%)	x_{70} (%)
10^{-2}	1.11×10^{-37}	100.0
10^{-10}	1.54×10^{-36}	100.0
10^{-20}	4.14×10^{-35}	100.0
10^{-40}	2.98×10^{-32}	100.0

[a] Mole fractions x_i in %: $x_i = p_i/p_0 \times 100$ (i = 60 or 70).

harmonic-oscillator model. Table 2 presents the results, including the equilibrium constant expressed in partial pressure terms *

$$K_p = p_{70}^{6/7}/p_{60} \qquad (2)$$

Initially it was expected that the inclusion of entropic effects might reverse the enthalpic advantage of C_{70} over C_{60} as reported by Newton and Stanton [11]. However, the $C_{70}(D_{5h})$ structure is still favored by 3.7 kJ mol^{-1} atom^{-1} on the Gibbs free energy per atom scale, $\Delta G^{\ominus}_{f,298}/n$. This is a result of the rather complex interplay of individual entropic contributions (for example, there are 22 and 27 vibrational frequencies below an arbitrary threshold of 500 cm^{-1} in the vibrational spectrum of $C_{60}(I_h)$ and $C_{70}(D_{5h})$, respectively).

Nevertheless, owing to the stoichiometry of reaction (1), populations of the reactant and product are pressure dependent, and thus the equilibrium constant in eqn. (2) alone generally cannot give a final answer on the relative stabilities. In order to follow the relative populations of both species it is convenient to introduce the total pressure p_0 of the carbon vapor. If p_0 is approximated ** by the sum of p_{60} and p_{70}, equilibrium populations of

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* p_{60} and p_{70} denote the partial pressures of $C_{60}(I_h)$ and $C_{70}(D_{5h})$ species, respectively.

** Clearly the p_0 values cannot straightforwardly be induced from the observed data [1], because of the presence of the helium carrying gas.

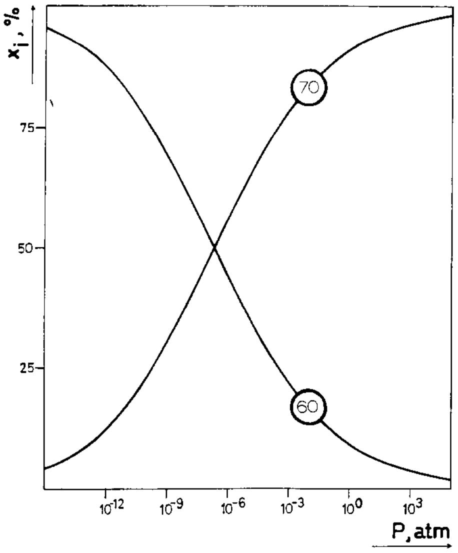

Fig. 2. An illustrative example of a possible pronounced pressure dependence of relative equilibrium gas-phase populations (mole fractions, x_i, in %) of $C_{60}(I_h)$ (60), and $C_{70}(D_{5h})$ (70), for a hypothetical choice of K_p of 10 $\mathrm{atm}^{-1/7}$ (for the specification of standard state, see Table 2).

both structures follow from the solution of the equation

$$K_p p_{60} = (p_0 - p_{60})^{6/7} \tag{3}$$

Table 3 presents the relative equilibrium populations, showing that at any pressure p_0 which we considered the C_{70} population was overwhelmingly predominant.

However, let us stress finally that the relation $K_p > 1\ \mathrm{atm}^{-1/7}$ * does not necessarily imply that C_{70} is more stable throughout the whole of a conceivable pressure p_0 region. The stability interplay can be considerably pressure-dependent as is illustrated in Fig. 2 for a hypothetical choice of K_p at 10 $\mathrm{atm}^{-1/7}$ *. In spite of K_p being larger than the corresponding unit, the population of C_{70} becomes negligible at very low pressures.

CONCLUDING REMARKS

This AM1 study changes nothing in the existing disagreement [11] between theory and experiment regarding relative populations of C_{60} and C_{70}

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* For related standard-state specification see Table 2.

clusters. The study points out a need to include entropy, temperature and pressure effects, for thermodynamically consistent reasoning on stability. From that point of view it seems desirable to elucidate the rather complex and difficult question of temperature and pressure conditions and of reaching the intercluster equilibrium [1]. Moreover, in our study the role of other clusters, beyond the magical two, was ignored as well as of other possible isomers of both the structures studied (see refs. 11, 13, 14 and 18). The isomerism cannot be distinguished in mass-spectrometry observations but should be important for the reasoning on stability. However, an exhaustive study of this type (yielding both a complete list of isomers and a final proof of the supposed stabilomers (see ref. 26)) is still beyond the possibilities of quantum-chemical calculations, and thus molecular mechanics search seems more suited for the purpose, particularly when being supported by graph-theoretical reasoning. Studies along these lines are in progress in our laboratories.

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