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On the relative stabilities of dodecahedron-shaped and bowl-shaped structures of C_{20}

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Abstract

Purely carbonaceous aggregates, C_{20}, were studied by the AM1 quantum-chemical method. In addition to one dodecahedron-shaped structure possessing C_1 symmetry, another three-dimensional species was revealed, namely a bowl-shaped structure of C_{5v} symmmetry. The temperature dependence of the relative stabilities of both structures is evaluated, showing that the fullerenic species prevails in the temperature region studied. However, at very high temperatures, a relative-stability interchange is predicted. In view of the absence of any symmetry in the dodecahedron-shaped structure, the species is treated both as an equimolar mixture of two enantiomers and as one pure optical form. The effects of the enantiomerism on the overall properties of C_{20} are briefly discussed.

INTRODUCTION

A new class of molecules, fullerenes, has recently been established [1,2] as being a purely carbonaceous species C_n with $n \geq 20$, possessing a polyhedral shape built from five- and six-membered rings. At first, research concentrated on the already recognized C_{60} and C_{70} aggregates [3–6]. Quite recently, other fullerenes have also been observed [7,8]. Computations based on quantum chemical methods have followed [9–13] the experimental developments and descriptions of some key structural, spectral and energetic features of some selected fullerenes have been presented. It has been pointed out [13–15] that fullerene isomerism can become a significant phenomenon during fullerene synthesis.

This report deals with the smallest member of the fullerene family, C_{20}, and compares its thermodynamic stability with another plausible structure built from carbon rings that are not, however, closed into a cage. The

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thermodynamic treatment is based on the results obtained using the AM1 quantum-chemical method [16].

THE C_{20} SPATIAL STRUCTURES

Topological reasoning [1,2] can prove that any fullerene always contains exactly $f_5 = 12$ five-membered rings, and the number of six-membered rings f_6 varies with the number of carbon atoms m

$$f_6 = m/2 - 10 \tag{1}$$

Hence, the smallest fullerene, C_{20}, is built from just 12 pentagons (and no hexagons). Such a structure is known [17] from the hydrocarbon dodecahe-

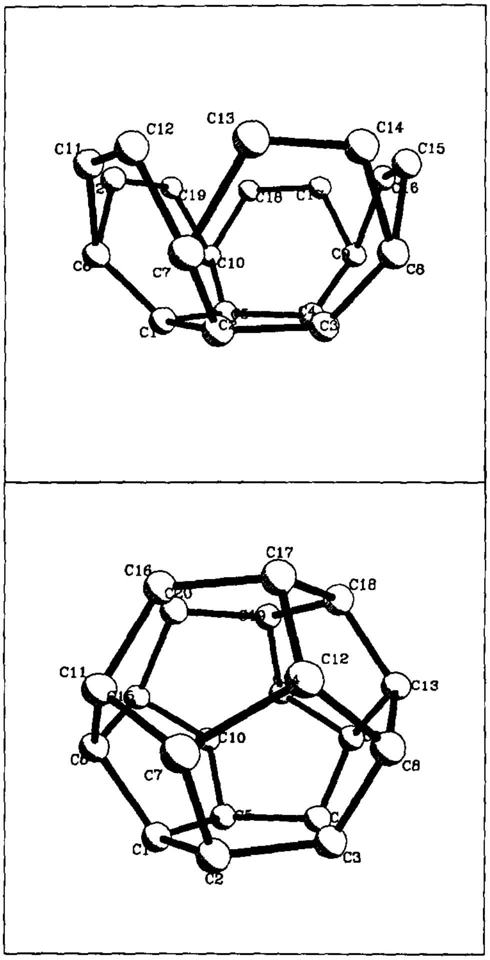

Fig. 1. Schemes of the AM1 structures of the C_1 dodecahedron-shaped (bottom) and C_{5v} bowl-shaped (top) C_{20}.

TABLE 1

Relative AM1 potential energy terms ΔE for the C_1 dodecahedron-shaped [a] and C_{5v} bowl-shaped structures [b] of C_{20}

Species	ΔE (kJ mol^{-1})
C_1	0.0
C_{5v}	208.68

[a] The energetics is the same for (+) or (−) species as well as for their equimolar mixture.
[b] See Fig. 1.

drane, to be derived from the polyhedron dodecahedron (I_h point group of symmetry). However, in our calculations with the AM1 quantum-chemical method [16], the local energy minimum of the dodecahedron shape (Fig. 1) exhibited C_1 symmetry, i.e. no symmetry element is present. This means that all the five-membered rings in the framework are somewhat distorted, apparently in order to compensate for the steric tension originating in the five-membered ring junctions.

There is another non-planar (though not fullerenic) structure which can be considered in connection with C_{20}: the structure related to the hydrocarbon corannulene [18]. The latter structure is composed of one five-membered and five six-membered rings arranged in a bowl-like shape. Indeed, AM1 geometry optimization revealed that there is a local energy minimum for C_{20}, possessing C_{5v} symmetry (Fig. 1). The bowl-shaped structure is higher in energy by about 210 kJ mol^{-1} than the dodecahedron C_1 form (Table 1).

Although there can be several minimum-energy structures of C_{20}, the two three-dimensional species still represent an interesting system. In view of the stability interchanges found in other carbon-aggregate systems [13–15], this limited C_{20} set should also be submitted to thermodynamic stability evaluation. In fact, the temperature of the relative-stability interchange between two isomers should be independent of the presence of other species in the reaction mixture, i.e. this result for the two-membered mixture can be transferred to more general multi-isomer equilibrium mixtures.

THERMODYNAMIC STABILITY EVALUATION

In an n-membered equilibrium isomeric set at a non-zero temperature, all its members are present, in principle, although their relative populations can vary considerably with temperature. This sensitivity in the isomeric composition has recently been documented for diverse cluster systems [19–23]. Let us introduce mole fractions w_i of the components of the isomeric equilibrium mixture. In terms of the ground-state energies $\Delta H_{0,i}^{\ominus}$

(i.e. the standard enthalpies at 0 K) and the isomeric partition functions q_i, the mole fractions are given by [22,23]

$$w_i = \frac{q_i \exp[-\Delta H_{0,i}^{\ominus}/(RT)]}{\sum_{j=1}^{n} q_j \exp[-\Delta H_{0,j}^{\ominus}/(RT)]} \tag{2}$$

where R stands for the gas constant and T for the temperature. The partition functions q_i are determined from the AM1 calculations using the rigid-rotor and harmonic-oscillator approximation [22].

There is no symmetry element present in the C_1 dodecahedron-shaped structure. Although there is no asymmetric carbon atom in the conventional sense (i.e. a carbon atom with four different substituents) present in the structure, the structure possesses chirality, i.e. it is not superimposable upon its mirror image. In this more general approach to chirality, it is not the asymmetric carbon atom but the dissymmetry of a structure as a whole that is important (dissymmetry, however, is most frequently caused by the asymmetric carbon atom). Dissymmetry indicates that there is no reflection symmetry, which is the case in only the C_n and D_n point groups of symmetry. In particular, the C_1 dodecahedron species forms a pair of enantiomers ((+), (−) optical isomers). We can distinguish two situations: (i) an equilibrium mixture of one of the C_1 enantiomers (either (+) or (−)) with the C_{5v} isomer; and (ii) an equilibrium mixture of both C_1 optical isomers with the bowl-shaped species. Formally, we can introduce into eqn. (2) the chirality partition functions $q_\chi = 1$ or $q_\chi = 2$ for situations (i) or (ii), respectively.

One can distinguish two classes of thermodynamic terms for an isomeric mixture: overall, many-component thermodynamic terms $\Delta X_T^{\ominus}$ and partial, one-component terms $\Delta X_i^{\ominus}$. It is convenient to study the isomerism effects by means of so-called isomerism contributions [22,23] to thermodynamic terms δX_1

$$\delta X_1 = \Delta X_T^{\ominus} - \Delta X_1^{\ominus} \tag{3}$$

The most stable species (at the low-temperature limit) is chosen as the reference structure and labelled by $i = 1$. If we deal with a ground-state species composed of two enantiomers, there are two conventions that can be followed. Here, we shall use in the $q_\chi = 2$ case, the equimolar enantiomeric mixture as the reference standard (i.e. we consider the enantiomeric effects but we do not treat the optical isomers as the individual components of the isomeric mixture). In this article we shall study the isomeric effects on heat capacity at constant pressure ($X = C_p$); for the respective formulae see ref. 23. The heat capacity case is particularly interesting because the full (relaxation) term $\delta C_{p,1}$ can exhibit a distinct temperature maximum, which can even be conserved in the overall standard heat capacity term $C_p^\ominus$.

RESULTS AND DISCUSSION

Table 2 presents the temperature development of the equilibrium mole fractions w_i in the mixture of the C_1 and C_{5v} isomers of C_{20}. Both situations ($q_\chi = 1$ or 2) are considered. The C_1 species prevails, even at the highest temperature considered. For low $w_{C_{5v}}$ values, the C_{5v} populations in its equilibrium mixture with just one C_1 enantiomer are about twice as high as in the three-membered mixture. This is a natural consequence of the form of eqn. (2).

From a purely thermodynamic point of view, we can investigate the relative stability proportions at still higher temperatures (laser heating can actually create even higher temperatures than those used in the first small carbon-cluster observations [24]). It turns out (see Table 3) that in such an extremely high temperature region, there is a relative-stability interchange. Beyond the temperature threshold, the C_{5v} species becomes more populated than one or both enantiomers. The crossing temperature is naturally lower for two-membered than for three-membered mixtures and the difference is quite large. In the high temperature region, we can observe temperature maxima in the isomerism contribution to heat capacity $\delta C_{p,1}$ or in the relative enhancement $\delta C_{p,1}/C_p^\ominus$ of the overall standard $C_p^\ominus$ term.

The results in Table 3 are interesting from a general thermodynamic point of view – optimizing a fullerene synthesis is still a considerably more complex kinetic problem. Moreover, C_{20} itself is apparently quite an unstable fullerenic system. However, there is another fullerenic system [13] (C_{50}) for which the enantiomeric effects can be shown at considerably lower temperatures. The C_{50} system is composed of (at least) three minimum-energy structures of D_{5h}, D_3 and C_{2v} symmetries. The D_{5h} structure

TABLE 2

Equilibrium mole fractions w_i (%) for the C_1 dodecahedron-shaped [a] and C_{5v} bowl-shaped structures of C_{20} at selected temperatures

T (K)	$q_\chi = 1$		$q_\chi = 2$	
	w_{C_1}	$w_{C_{5v}}$	w_{C_1}	$w_{C_{5v}}$
1000	100.0	6×10^{-8}	100.0	3×10^{-8}
2000	99.98	0.02	99.99	9×10^{-3}
3000	98.83	1.17	99.41	0.59
4000	91.20	8.80	95.40	4.60

[a] The C_1 species is treated either as just one of the (+), (−) isomers ($q_\chi = 1$) or as their equimolar mixture ($q_\chi = 2$).

TABLE 3

Specification of some distinguished points [a] in the temperature interplay of the C_1 and C_{5v} isomers of C_{20}

Type [a]	q_X [b]	T (K)	w_{C_1} [c] (%)	$w_{C_{5v}}$ [c] (%)	$\delta C_{p,1}$ [d] (J K^{-1} mol^{-1})	$C_p^\ominus$ (J K^{-1} mol^{-1})	$\delta C_{p,1}/C_p^\ominus$ (%)
Crossing	1	6366	50.0	50.0	32.4	512	6.3
	2	7720	50.0	50.0	22.0	503	4.4
$\delta C_{p,1}$ maximum	1	5203	70.7	29.3	40.2	519	7.8
	2	5883	73.4	26.6	29.6	509	5.8
$\delta C_{p,1}/C_p^\ominus$ maximum	1	5197	70.9	29.1	40.2	519	7.8
	2	5876	73.5	26.5	29.6	509	5.8

[a] That is, the point of two-isomer equimolarity (crossing), the maximum in the isomerism contribution to heat capacity $\delta C_{p,1}$ and the maximum in the relative enhancement $\delta C_{p,1}/C_p^\ominus$ of the $C_p^\ominus$ term by isomeric interplay.

[b] The C_1 species is treated either as just one of the (+), (−) isomers (the upper line) or as their equimolar mixture (the lower line).

[c] The mole fraction of the species in the equilibrium isomeric mixture.

[d] Isomerism contribution to heat capacity related to the species more stable in the low temperature region, i.e. to the C_1 isomer(s).

TABLE 4

Enantiomeric effects on some distinguished points [a] in temperature interplay of the D_{5h}, D_3 and C_{2v} isomers of C_{50}

Type [a]	q_X [b]	T (K)	$w_{D_{5h}}$ [c] (%)	w_{D_3} [c] (%)	$w_{C_{2v}}$ [c] (%)	$\delta C_{p,1}$ [d] (J K^{-1} mol^{-1})	$C_p^\ominus$ (J K^{-1} mol^{-1})	$\delta C_{p,1}/C_p^\ominus$ (%)
Crossing	1	1390	50.0	50.0	8×10^{-57}	24.9	1135	2.2
	2	1146	50.0	50.0	1×10^{-69}	34.3	1095	3.1
$\delta C_{p,1}$ maximum	1	1110	69.3	30.7	1×10^{-71}	29.9	1082	2.8
	2	970	66.7	33.3	1×10^{-82}	38.9	1044	3.7
$\delta C_{p,1}/C_p^\ominus$ maximum	1	1070	72.5	27.5	1×10^{-74}	29.7	1069	2.8
	2	932	70.5	29.5	5×10^{-86}	38.6	1029	3.8

[a] That is, the point of two-isomer equimolarity (crossing), the maximum in the isomerism contribution to heat capacity $\delta C_{p,1}$ and the maximum in the relative enhancement $\delta C_{p,1}/C_p^\ominus$ of the $C_p^\ominus$ term by isomeric interplay.

[b] The D_3 species is treated either as just one of the (+), (−) isomers (the upper line) or as their equimolar mixture (the lower line).

[c] The mole fraction of the species in the equilibrium isomeric mixture.

[d] Isomerism contribution to heat capacity related to the species most stable in the low temperature region, i.e. to the D_{5h} isomer.

has the lowest heat of formation, being followed after 30 and 1600 kJ mol^{-1} by the D_3 and C_{2v} isomers [13]. Incidentally, the second structure belongs to the dissymmetric D_3 point group of symmetry which ensures that the structure cannot be superimposed on its mirror image. Thus, two enantiomers are again present. Table 4 compares the results [13] for $q_\chi = 1$ with the $q_\chi = 2$ case. It turns out that the inclusion of the other D_3 enantiomer decreases considerably the three distinguished temperatures of the isomeric interplay. This is a consequence of the fact that the dissymmetric D_3 species is not the ground-state structure in the C_{50} system.

It is to be expected that isomerism including optical isomerism will quite frequently be associated with fullerenic systems. A recent observation [25] has, in fact, provided clear experimental evidence that isomerism is present throughout carbon clusters. However, our finding optical isomerism in the C_1 species is based on the semi-empirical AM1 quantum-chemical treatment, i.e. on a method of an approximate nature. Thus, it would certainly be useful to study the C_{20} fullerene structure at a non-empirical level as well, in order to avoid a methodical artifact.

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