

Mg@C₇₂ MNDO/d evaluation of the isomeric composition

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Temperature development of the relative stabilities of isomers of Mg@C₇₂ (which has not yet been isolated) is computed using the recently introduced MNDO/d method. Four isomers originally considered for the Ca@C₇₂ case are treated: one isolated-pentagon-rule (IPR) structure, two structures with a pair of adjacent pentagons, and one cage with a heptagon. The IPR structure comes as the lowest in MNDO/d potential energy, being rather closely followed by the two structures with a pentagon–pentagon pair. On the other hand, the structure with a heptagon is located too high in potential energy to be of any experimental significance. The entropy contributions are evaluated by the MNDO/d-based partition functions so that the relative concentrations can be treated accordingly. The computations suggest that if Mg@C₇₂ is isolated, it should be a mixture of either two or three isomers. The prediction depends on temperature pre-history. If preparation takes place at temperatures of approximately 1000 K, two isomers should be produced. If temperatures are increased to approximately 2000 K, there will already be three isomers with significant relative concentrations. The study supplies a further interesting example of the profound role of enthalpy–entropy interplay in stabilities of isomeric fullerene structures. © 2001 by Elsevier Science Inc.

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INTRODUCTION

There has been research interest^{1–3} in C₇₂ and Ca@C₇₂, but of the two species only Ca@C₇₂ has been isolated so far.² C₇₂ has a large⁴ HMO HOMO–LUMO gap (larger than that of C₇₀), though we still do not have enough experience in using the gaps as stability measures. Nevertheless, C₇₄ with a considerably smaller HMO HOMO–LUMO gap has recently been produced electrochemically.⁵ C₇₂ has only one⁴ isolated-pentagon-rule (IPR) structure. However, it has been established^{1,2} that non-IPR structures should be significant for both C₇₂ and Ca@C₇₂. Four selected Ca@C₇₂ structures¹ were computed: the IPR structure (**a**), two non-IPR structures each with one pair of connected pentagons (**b**, **c**), and finally a structure with one heptagon (**d**).

It has been known^{6–9} that the composition of isomeric fullerene mixtures cannot always be understood in terms of computed potential energies only. Sometimes a structure that is not the lowest in potential energy is actually the most abundant. Such events could be explained^{6–9} after addition of the entropy effects, as in other isomeric systems.¹⁰ Interestingly enough, the treatment has never been applied to a set of isomeric endohedral fullerenes. This report fills the gap and computes temperature dependencies of the relative concentrations of the four isomers (**a–d**) of a model system Mg@C₇₂. In other words, this study predicts what should be expected once the

system is really isolated. Such predictions have always been a part of fullerene research, even from its very early days.^{10–16}

CALCULATIONS

The computations are performed with a new parametrization of the MNDO method designed by Thiel and Voityuk¹⁷ and known as MNDO/d, or MNDO with d orbitals. MNDO/d provides significant improvements over established semiempirical quantum-chemical methods.^{18–23} For example, the mean absolute error in the MNDO/d heats of formation in a set of 575 molecules amounts to 5.4 kcal/mol. The MNDO/d parameters are available for Mg but not for Ca.¹⁷ This factor selects Mg@C₇₂ as the target of our model study. In fact, Mg belongs to a subset of atoms in MNDO/d with new parameters but with an s,p rather than an s,p,d basis. The MNDO/d calculations were performed with the method implementation in the AMPAC program package.²⁴

Geometry optimizations were carried out with the analytical first derivatives of energy. The geometry optimizations were performed in Cartesian coordinates with no symmetry constraints. In the MNDO/d optimized geometries, harmonic vibrational analysis was carried out by numerical differentiation of the analytical energy gradient. The vibrational analysis distinguishes between local minima, transition states, and higher saddle points. Moreover, it predicts vibrational spectra and the calculated vibrational frequencies are applied in construction of partition functions.

Symmetry of the optimized structures was determined by a new procedure,²⁵ which treats precision of the computed coordinates as a variable parameter, ϵ . For example, the candidates for C₂ axes are either lines connecting any two nuclei or perpendicular bisectors of the distance between any two nuclei of the same kind. Similarly, the inversion center, C₂ axes with $n > 2$, S_n and S_{2n} axes, and planes of symmetry are searched. For each symmetry operation considered, coordinates of the interrelated atoms before and after the symmetry operation are checked with respect to ϵ . If the coordinates are identical within the accuracy ϵ (i.e., the largest difference is smaller than ϵ) a symmetry element is found at the accuracy level ϵ . In any case, the symmetry operations found have to create one of the known point groups of symmetry. This flexible approach actually produces a sequence of symmetries and the relevant group is selected according to the supposed accuracy of the computed coordinates.

Relative concentrations (mole fractions) x_i of the four isomers of Mg@C₇₂ were computed using their partition functions constructed within the rigid-rotor and harmonic-oscillator approximation. The semiempirical quantum-chemical methods are parametrized for room temperature, i.e., they produce the conventional heats of formation at room temperature $\Delta H_{f,298}^o$ (or the related relative terms $\Delta H_{f,298,rel}^o$). Thus, they should be converted to the heats of formation at the absolute zero temperature $\Delta H_{f,0}^o$. Moreover, the vibrational zero-point energy should be extracted so that the relative potential energies $\Delta E_{pot,rel}$ finally result from the

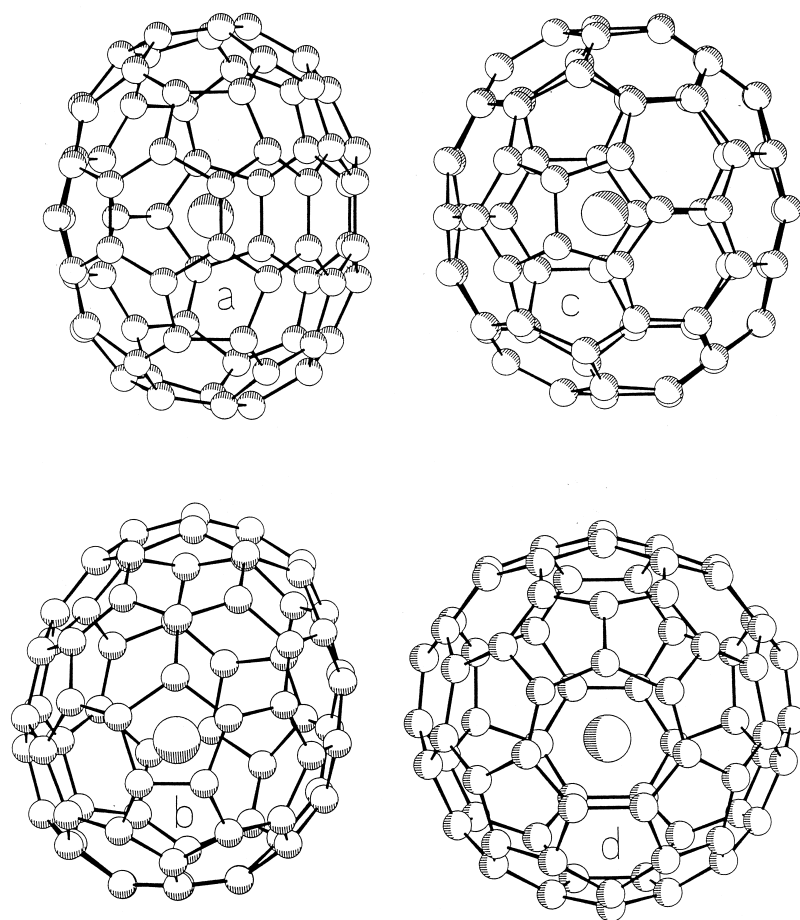


Figure 1. The MNDO/d optimized structures of four isomers of Mg@C₇₂.

Table 1. Survey of the MNDO/d computed energetics^a and structures^b of four isomers^c of Mg@C₇₂

Species ^c	Group	$\Delta H_{f,298,rel}^o$ kJ/mol	$\Delta E_{pot,rel}$ kJ/mol	A cm ⁻¹	B cm ⁻¹	C cm ⁻¹
a	C _s	0.0	0.0	0.001628	0.002027	0.002027
b	C ₁	49.95	53.07	0.001701	0.001907	0.002061
c	C ₁	6.80	11.19	0.001818	0.001879	0.001964
d	C _s	176.89	180.65	0.001737	0.001853	0.002061

^a The relative heat of formation at room temperature $\Delta H_{f,298,rel}^o$ or the relative potential energy $\Delta E_{pot,rel}$.

^b Rotational constants A, B, C.

^c See Figure 1.

treatment. The vibrational frequencies were not scaled, as it has been known that such scaling is not important for relative concentrations at higher temperatures.²⁶

Chirality contribution into entropy are also considered—for an enantiomeric pair, its partition function has to be doubled (if we assume the presence of both optical isomers, which seems justified for the conditions of fullerene synthesis). There is no asymmetric carbon atom in the conventional sense in the fullerene cages (as they contain three-coordinated carbon atoms only). Nevertheless, some of the structures are still chiral, i.e., they are not superimposable upon their mirror image. This structural dissymmetry can readily be recognized from the point group of symmetry as the presence of no reflection symmetry, i.e., the absence of rotation-reflection axes S_n : only the C₂, D_n, T, O, and I groups allow for chirality.

RESULTS AND DISCUSSION

Figure 1 shows the MNDO/d-optimized structures of the four isomers of Mg@C₇₂ (**a–d**). According to our flexible symmetry evaluation, their point groups of symmetry are (from **a** to **d**, see Table 1): C_s, C₁, C₁, and C_s. They are lower than the symmetries of the corresponding Ca@C₇₂ species.¹ Three factors can contribute to this: different metal atom, different computational method, and the flexible method for symmetry extraction. In particular, this

last factor should be stressed as fullerene cages are relatively large and the conventional symmetry searchers are not particularly adjusted to them.

Table 1 presents the MNDO/d relative energetics and rotational constants. In both scales, $\Delta H_{f,298,rel}^o$ and $\Delta E_{pot,rel}$, the IPR species **a** comes as the lowest energy structure (the ground-state isomer). However, there are nonnegligible differences between the both scales. The two non-IPR species with one pentagon–pentagon pair are relatively low-energy lying, the **c** species being lower in both scales. The structure with heptagon is on the other hand located quite high. However, we are not particularly concerned with potential energies, they are just intermediate terms in our connections. Our true target are the Gibbs free energies as the relevant stability measures.

Thus, Figure 2 shows the MNDO/d-computed relative concentrations of the four isomers of Mg@C₇₂ (using molar fractions x_i in %). The relative concentration of the isomer lowest in potential energy, **a**, steadily decreases. The species second lowest in energy, **c**, exhibits an interesting course with a maximum temperature. With temperatures of approximately 1000 K, the **a** and **c** structures are close to equimolarity. However, at temperatures around and greater than 2000 K, the species third in potential energy, **b**, exhibits significant relative concentrations. The **d** structure is negligible throughout.

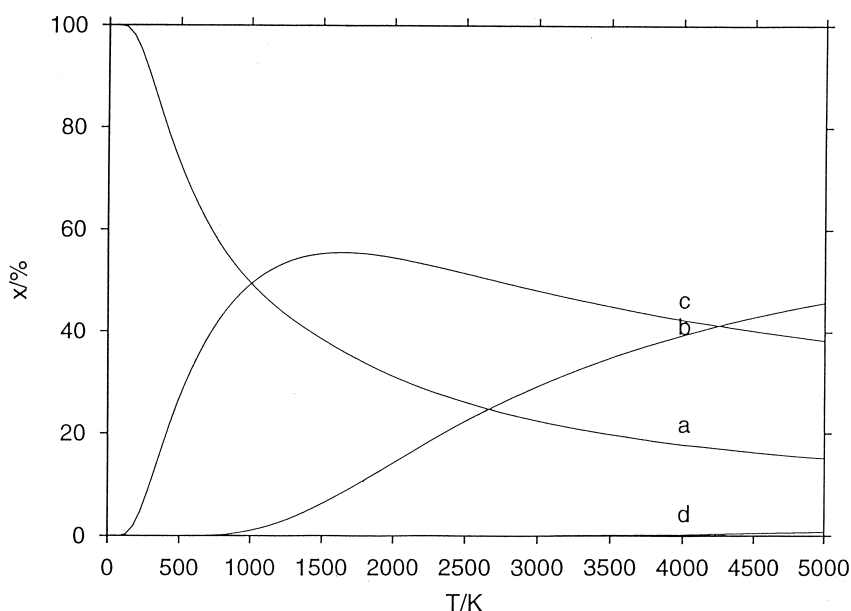


Figure 2. The MNDO/d computed relative concentrations of the four isomers of Mg@C₇₂ from Figure 1.

Overall, the computations suggest that if $\text{Mg}@C_{72}$ is isolated, it should be a mixture of either two or three isomers. The prediction depends on temperature prehistory. If preparation (at present still hypothetical) takes place at temperatures of approximately 1000 K, two isomers should be produced. If temperatures are increased to approximately 2000 K, there will already be three isomers with significant relative concentrations: two non-IPR structures and one IPR structure. Hence, this study supplies a further interesting example of the profound role of enthalpy–entropy interplay for relative stabilities of isomeric fullerene structures. However, other structures should be tested in Gibbs function terms, as a strong entropy stabilization may occur²⁷ for isomers placed relatively high in potential energy. Moreover, the separation energetics should be checked at higher levels of theory. The motion of the endohedral atom is too complicated to be described as a harmonic oscillator (though a nonanharmonic approach is still difficult).²⁸ Finally, the treatment presupposes interisomeric thermodynamic equilibrium, an important presumption that is impossible to verify experimentally at present.

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