A Comparative Study of C\textsubscript{60}, Si\textsubscript{60}, and Ge\textsubscript{60}

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ABSTRACT

Relative stabilities of the fullerene structures C\textsubscript{60}, Si\textsubscript{60}, and Ge\textsubscript{60} are studied by means of semiempirical quantum-chemical methods. It is suggested that atomization energies rather than heats of formation should be used for the purpose at this level of description. In the former terms Si\textsubscript{60} and Ge\textsubscript{60} are located higher than the fullerene itself by about 4100 and 6500 kcal/mol, respectively. A poor SCF convergence is reported for both fullerene analogues. While Si\textsubscript{60} still exhibits the exact I\textsubscript{h} symmetry, the Ge\textsubscript{60} cage shows some distortion from the highly symmetric form though the fullerene topology is present. Mass effects create a considerably narrow vibrational spectrum for Si\textsubscript{60} and especially Ge\textsubscript{60}. A related computation on B\textsubscript{60} suggests a better energy position comparing to Si\textsubscript{60}.

INTRODUCTION

Soon after the establishment of the C\textsubscript{60} research itself\textsuperscript{1–3}, silicon aggregates have become\textsuperscript{4–16} a natural subject of study, too, and indeed, there are

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mass-spectrometric evidences\textsuperscript{10,17} of large charged silicon and even germanium clusters. This computational study treats the relative stabilities of the three key species, C\textsubscript{60}, Si\textsubscript{60}, and Ge\textsubscript{60}, in a systematic way.

**CALCULATIONS**

The computations were performed with the standard parametrizations of the MNDO and AM1 semiempirical quantum-chemical methods\textsuperscript{18,19}, namely with their versions implemented in the Gaussian 92\textsuperscript{20} and MOPAC 5.0\textsuperscript{21} program packages. The geometry optimizations were carried out using the analytical energy gradient within the smallest possible set of internal coordinates, or in the Cartesian coordinates. Cases of poor SCF convergence were treated by the quadratic convergence SCF method\textsuperscript{22}. In the geometry optima found, harmonic vibrational analysis was carried out in order to check the stationary-point type and to generate its vibrational spectrum. The vibrational analysis was carried out in Cartesian coordinates by means of a numerical differentiation of the analytical energy gradient.

**RESULTS AND DISCUSSION**

In fullerene computations three methods from the MNDO family\textsuperscript{23,24} (MNDO, AM1, PM3) have so far been applied. There is still not enough experience gained to decide which of the three methods should be preferred in fullerene computations. For example, with the relative stabilities of the
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$C_{78}$ aggregates\textsuperscript{25} the results are quite close, however, a direct comparison with observed values is still not possible. The MNDO heat of formation of $C_{60}(g)$ is closer\textsuperscript{26–28} to experiment than the AM1 value (though both methods overestimate the term substantially). On the other hand, in the group of general organics\textsuperscript{24} with Si (and halogens) performances of AM1 and PM3 are about the same, and somewhat better than that of the MNDO method.

There is a shortage of thermochemical data\textsuperscript{29,30} for the $X_n\ (X = C, Si, Ge)$ aggregates - only triad available concerns the gas-phase dimers. Even if one takes the observed values for granted, there is a problem that while in experiment one deals with a mixture of several low-lying states, the computations concern the ground state only. For example, the ground state\textsuperscript{3,29} of $C_2$ is a singlet located only about 2.0 kcal/mol below a triplet state. The ground states of $Si_2$ and $Ge_2$ are however triplets\textsuperscript{4,31}. Dewar et al.\textsuperscript{32} reported a better performance of AM1 over PM3 with the heat of formation of the $C_2$ species (treated in fact as an open shell). This remains true if we recompute the term for the singlet state $C_2$, and the AM1 value is now rather close to the experiment\textsuperscript{29,30} (calculated 216 vs. observed 200 kcal/mol). Similarly, we can find a good performance of the AM1 method with the $Si_2$ (calculated 126 vs. observed\textsuperscript{30} 142 kcal/mol) and the MNDO method (Ge parameters not included in the AM1 version applied) with the $Ge_2$ species (calculated 131 vs. observed\textsuperscript{30} 113 kcal/mol). For the two triplet species the unrestricted
Table 1
Key structural and vibrational molecular parameters of C$_{60}$, Si$_{60}$, and Ge$_{60}$

<table>
<thead>
<tr>
<th>Species</th>
<th>$A$, $B$, $C^a$ (GHz)</th>
<th>$X$-$X_{\text{min}}^b$ (Å)</th>
<th>$X$-$X_{\text{max}}^b$ (Å)</th>
<th>$\omega_{\text{min}}^c$ (cm$^{-1}$)</th>
<th>$\omega_{\text{max}}^c$ (cm$^{-1}$)</th>
<th>$i^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$, AM1</td>
<td>0.0832</td>
<td>1.385</td>
<td>1.464</td>
<td>284</td>
<td>1816</td>
<td>0</td>
</tr>
<tr>
<td>Si$_{60}$, AM1</td>
<td>0.0149</td>
<td>2.092</td>
<td>2.297</td>
<td>61</td>
<td>439</td>
<td>0</td>
</tr>
<tr>
<td>Ge$_{60}$, MNDO</td>
<td>0.00543</td>
<td>2.229</td>
<td>2.474</td>
<td>29</td>
<td>345</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.00543</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00537</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

$^a$ Rotational constants.

$^b$ The two X-X bonds (X = C, Si), or the shortest and longest Ge-Ge bond.

$^c$ The lowest or highest harmonic vibrational frequency.

$^d$ The Hessian index.

Hartree-Fock values are mentioned, the open-shell restricted Hartree-Fock values are somewhat higher.

In view of the above fragmentary comparisons between the theory and experiment, and with respect to the parametrizations available in the program packages$^{20,21}$, we deal here with the AM1 results for C$_{60}$ and Si$_{60}$, and the MNDO results for Ge$_{60}$. Table 1 surveys the computed parameters. Similar to C$_{60}$, the Si$_{60}$ cage also possesses the high $I_h$ symmetry and it is indeed a local energy minimum. It is known$^{33,34}$ that the AM1 computed C$_{60}$ parameters are quite close to the MNDO terms and to the experimental
values. The Si-Si bond distances are of course considerably longer than the C-C ones, and vibrational frequencies are substantially lowered. The trends remain when going from Si$_{60}$ to Ge$_{60}$.

A poor SCF convergence was encountered in both Si$_{60}$ and Ge$_{60}$ cases. While in the former case the problem could be solved by the quadratic convergence SCF method$^{22}$, this approach did not help with the latter species. In fact, it turned out to be virtually impossible to optimize the $I_h$ symmetry Ge$_{60}$ species owing to the lack of SCF convergence. Therefore the high symmetry was relaxed and the complete set of Cartesian coordinates was optimized (instead of the sole two internal coordinates). In this way a local
energy minimum was reached for the Ge$_{60}$ species, too. Although it still possesses the topology of a truncated icosahedron (Fig. 1), there however are more than two degrees of freedom as an inspection of the bond distances reveals (and this should not be caused by a mere numerical inaccuracy). It could be viewed in the terms of a (pseudo) Jahn-Teller distortion (indeed, the LUMO-HOMO gap is rather small in the first iteration). However, it is also possible that an $I_h$ symmetry local minimum simply does not exist for Ge$_{60}$. Even if it exists (and could not be found owing to the SCF convergence problems), the energy separation from the reported distorted (near $I_h$) structure cannot be large. After all, the distortion from the $I_h$ symmetry may not be immediately apparent from Fig. 1.

Once heats of formation are available, a qualitative reasoning on the relative stabilities of the X$_{60}$ ($X = C, Si, Ge$) aggregates can be done, though it will be only a simple thermodynamic treatment even neglecting the entropy term. Heats of formation presented in Table 2 seem relatively close for C$_{60}$ and Si$_{60}$. The choice of the thermodynamic reference state is the same for C, Si, and Ge, i.e., the related solid phase. Hence, the calculated heats of formation, $\Delta H_f^o$, refer to the processes:

$$60X(s) = X_{60}(g).$$  \hfill (1)

However, the evaporation heat, i.e., the enthalpy change for the transformation:

$$X(s) = X(g)$$  \hfill (2)
Formation and atomization heats\textsuperscript{a} (kcal/mol) of C\textsubscript{60}, Si\textsubscript{60}, and Ge\textsubscript{60}

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_f^{o,298.15}$</th>
<th>$\Delta H_{at,298.15}^{o}$</th>
<th>$\Delta H_{at,298.15,rel}^{o}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{60}, AM1</td>
<td>973.3</td>
<td>-9280</td>
<td>0</td>
</tr>
<tr>
<td>Si\textsubscript{60}, AM1</td>
<td>1296</td>
<td>-5207</td>
<td>4073</td>
</tr>
<tr>
<td>Ge\textsubscript{60}, MNDO</td>
<td>2543</td>
<td>-2827</td>
<td>6453</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The formation and atomization heat is denoted by the index $f$ and $at$, respectively, both types of terms refer to the room temperature.

is then contained in the calculated values. The evaporation heats (which are adopted in the semiempirical methods at their available experimental values) are considerably varied\textsuperscript{35}: 171, 108, and 89 kcal/mol for $X=$C, Si, and Ge, respectively (especially so if multiplied by a numerical factor of 60). In a real experimental situation the monoatomic gas is created first and nucleation processes go on after that. The reaction mixture is then cooled down. It is therefore more appropriate to evaluate relative thermodynamic stabilities from atomization energies or heats, $\Delta H_{at,298.15}^{o}$, i.e., the reaction heats for processes with all the components in the gas phase (the atomization heats are to be negative for a bound species in the convention):

$$60X(g) = X_{60}(g),$$

(3)
and the related values are reported in Table 2. In the new terms, the picture is quite changed. The difference between Si$_{60}$ and C$_{60}$ in $\Delta H^0_{st,298.15}$ is by one order of magnitude larger than in $\Delta H^0_{f,298.15}$. The related separation between Ge$_{60}$ and Si$_{60}$ in the new terms is about two times larger. It suggests that, thermodynamically, creation of C$_{60}$ is favored over Si$_{60}$ or even Ge$_{60}$. It however does not take into account kinetic barriers. Clearly enough, a kinetic stabilization is still not excluded for the latter two species.

There is a fourth related species, B$_{60}$, our MNDO computations of which resemble the Ge$_{60}$ case. SCF convergence is poor, even if geometry is distorted from the $I_h$ symmetry (however, HOMO/LUMO is degenerated in the first iteration, i.e., the Jahn-Teller case as in$^{36}$ $I_h$ C$_{20}$). Moreover, the distortion of geometry is really progressive with a tendency towards creation of typical triangular faces$^{37}$ (however, the vibrational analysis could not be performed owing to the SCF convergence problems). In the above scale of the atomization heats $\Delta H^0_{st,298.15}$ the B$_{60}$ system is according to our MNDO calculations placed somewhere in the middle between C$_{60}$ and Si$_{60}$.

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REFERENCES AND NOTES


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