MNDO computations of the 6/6 and 5/6 structures of C\textsubscript{60}S

Zdeněk Slanina*,†, Shyi-Long Lee

Department of Chemistry, National Chung-Cheng University, Ming-Hsiung, Chia-Yi 621, Taiwan

Received 8 November 1994; accepted 14 January 1995

Abstract

Bridging with an S atom across the two different C–C bonds in C\textsubscript{60} is treated by the MNDO method. The C\textsubscript{2v} (6/6) closed isomer is located 41 kJ mol\textsuperscript{-1} below the C\textsubscript{s} (5/6) open structure (i.e. the reverse order of that computed for C\textsubscript{60}O). An ab initio computation in the 3-21G basis set yields the same isomeric stability order. However, at elevated temperatures a coexistence of both isomers is predicted for the equilibrium conditions, not very different from 1 : 1. Other possible structures are also discussed.

1. Introduction

Several sulfur containing fullerene species have been observed [1–5], mostly with a high sulfur content. Although there has been no report on the simplest derivative C\textsubscript{60}S, the compound is of clear interest as an analog of the relatively well studied C\textsubscript{60}O [6–16]. This paper presents the first computational results for C\textsubscript{60}S, which have been obtained at the MNDO semiempirical quantum-chemical level.

2. Computations

The standard version of the MNDO semiempirical quantum-chemical method [17–19] has been employed, utilizing implementations in the SPARTAN 3.0 (Iris/Silicon Graphics XZ4000 workstation) [20], GAUSSIAN 92 [21], and MOPAC 5.0 [22] program packages. The geometry optimization was carried out using the analytical energy gradient. In the geometry optimum found, harmonic vibrational analysis was performed in order to check the stationary-point type and to supply its vibrational spectrum. The vibrational analysis dealt with numerical differentiation of the analytical energy gradient (the numerical differentiation step size was 0.01 Å). Although singlet electronic states have mostly been considered, some computations were performed for related triplet electronic states, using the unrestricted open-shell treatment. In order to check the MNDO results, an ab initio SCF computation with the standard 3-21G basis set [21] has been performed in the MNDO optimized geometries (HF/3-21G).

3. Results and discussion

There are two different, obvious places in C\textsubscript{60} for
a group insertion: bridging across the C–C bond between two six-membered rings (6/6), or bridging across the C–C bond between five- and six-membered rings (5/6) of the cage (Fig. 1). Symmetry of the original C$_{60}$ cage is reduced considerably to C$_{2v}$ (6/6) and C$_{s}$ (5/6). However, in principle, two types of structures could still be considered for each symmetry; the critical C–C bond (which is bridged over) either remains or is broken (closed or open species). With the C$_{60}$O system [12,14] the 5/6 structure has been computed as open but the 6/6 species as closed, and no other isomers could be discovered on the potential hypersurface. A similar picture has been reported for the C$_{60}$CH$_2$ system [23,24].

The situation in C$_{60}$S is, however, different. Table 1 surveys molecular parameters for the 6/6 (closed) and 5/6 (open) C$_{60}$S structures computed at the MNDO level. There is a striking difference with respect to the C$_{60}$O case; the 6/6 structure

![Fig. 1. The MNDO optimized 6/6 (C$_{2v}$, left) and 5/6 (C$_{s}$) C$_{60}$S structures.](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>6/6 (C$_{2v}$)</th>
<th>5/6 (C$_{s}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational constants (GHz)</td>
<td>0.0821, 0.0718, 0.0714</td>
<td>0.0820, 0.0724, 0.0709</td>
</tr>
<tr>
<td>C–S$^a$ (Å)</td>
<td>1.729</td>
<td>1.695</td>
</tr>
<tr>
<td>C–C$^b$ (Å)</td>
<td>1.594</td>
<td>2.296</td>
</tr>
<tr>
<td>Energy difference C$<em>i$ – C$</em>{2v}$ (kJ mol$^{-1}$)</td>
<td>(298.15 K)</td>
<td>38.51</td>
</tr>
<tr>
<td></td>
<td>(0 K)</td>
<td>40.45</td>
</tr>
<tr>
<td>HF/3-21G$^c$</td>
<td></td>
<td>122.7</td>
</tr>
</tbody>
</table>

$^a$ Distance of the S atom from each of the two adjacent carbons (Fig. 1).
$^b$ Distance between the two carbons closest to the S atom (Fig. 1).
$^c$ Computed in the MNDO geometries.
represents the ground state of \( \text{C}_{60}\)S (while for \( \text{C}_{60}\)O the computed ground state exhibits the 5/6 pattern [12,14]). The computed energy separation between both isomers is similar for \( \text{C}_{60}\)O and \( \text{C}_{60}\)S (but of course differs in sign). The physical meaning of the computed MNDO energy deserves comment. Strictly speaking, the MNDO energy, owing to parametrization, corresponds to room temperature rather than to absolute zero, and it is in fact an enthalpy term. Using the computed vibrational frequencies we can reduce the values to the zero temperature and even extract the zero-point contribution from the latter term, thus arriving at the pure potential energy terms \( \Delta E \). However, there is no appreciable difference between the isomer energy separation derived from the heats of formation at room temperature (\( \Delta H_{298.15}^{\circ} \)) and from the sole potential energy term. At this point we performed ab initio SCF computations in the 3-21G basis set in the MNDO optimized geometries. The results confirm (Table 1) the 6/6 structure as the ground state. In fact the HF/3-21G separation energy is larger that the MNDO one, but it is plausible to expect an overestimation in the term with the basis set [23].

The 5/6 isomer exhibits a clear fullerene inflation as its bridged C–C bond is elongated to 2.30 Å. The C–C bond in the 6/6 isomer is still present though it is longer than the 6/6 bond in the original MNDO \( \text{C}_{60} \) cage [25] (1.40 Å), so that we can speak of a clear single bond. However, the C–S bonds are rather close in both computed structures. The differences in the rotational constants are not negligible and could serve as a spectroscopic proof.

Vibrational spectroscopy is, however, a more common tool in fullerene research and therefore Table 2 presents the computed vibrational frequencies with a higher IR intensity (above a threshold of 1 km mol\(^{-1}\)). First of all, it is important to note that for both isomers all the 177 computed frequencies are real, and not imaginary, so that we indeed deal with two local energy minima. Although the \( C_5 \) spectrum exhibits more such lines of higher intensity, there is frequently an overlap in the real spectrum. Two frequencies with the highest intensity are quite close in both isomers, indeed (1625, 1627 cm\(^{-1}\) and 1629, 1631 cm\(^{-1}\) in the (6/6) and (5/6) cases respectively). However, the intense frequency of 875 cm\(^{-1}\) in the 6/6 case does not have a clear counterpart in the 5/6 isomer. Moreover, the 5/6 structure possesses an intense frequency at 1545 cm\(^{-1}\) which should not be an active region for the more symmetric isomer. Hence, IR spectra could allow for a proof of both isomers even in their mixture. No attempt was made to scale down the computed frequencies, though they are expected to be somewhat overestimated.

The computed MNDO potential energy gap of the isomers is close to 40 kJ mol\(^{-1}\) (Table 1). Hence, at elevated temperatures an isomeric coexistence can be expected. The isomer relative populations were evaluated in terms of the partition functions of the rigid-rotor and harmonic-oscillator quality [26] in a wide temperature interval, using the MNDO computed structural, vibrational and energy data. Table 3 reports temperature evolution

### Table 2

<table>
<thead>
<tr>
<th>MNDO higher IR intensity harmonic vibrational modes(^a) of the ( \text{C}_{60})S structures</th>
<th>( \omega_{\text{cm}}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/6 (( C_5 ))</td>
<td></td>
</tr>
<tr>
<td>433/A(_{1}/1)</td>
<td>574/ /5</td>
</tr>
<tr>
<td>583/B(_{1}/2)</td>
<td>602/B(_{2}/3)</td>
</tr>
<tr>
<td>724/B(_{2}/2)</td>
<td>751/A(_{1}/1)</td>
</tr>
<tr>
<td>875/A(_{1}/22)</td>
<td>921/ /3</td>
</tr>
<tr>
<td>1337/B(_{1}/6)</td>
<td>1345/B(_{2}/1)</td>
</tr>
<tr>
<td>1356/A(_{1}/18)</td>
<td>1386/B(_{1}/3)</td>
</tr>
<tr>
<td>1616/A(_{1}/10)</td>
<td>1625/B(_{2}/31)</td>
</tr>
<tr>
<td>1659/A(_{1}/8)</td>
<td></td>
</tr>
<tr>
<td>5/6 (( C_5 ))</td>
<td></td>
</tr>
<tr>
<td>338/A(_{1}/1)</td>
<td>389/A(_{1}/1)</td>
</tr>
<tr>
<td>508/A(_{1}/4)</td>
<td>558/A(_{1}/1)</td>
</tr>
<tr>
<td>587/A(_{1}/1)</td>
<td>588/A(_{1}/3)</td>
</tr>
<tr>
<td>660/A(_{1}/8)</td>
<td>687/A(_{1}/3)</td>
</tr>
<tr>
<td>729/A(_{1}/1)</td>
<td>756/A(_{1}/1)</td>
</tr>
<tr>
<td>860/A(_{1}/1)</td>
<td>865/A(_{1}/1)</td>
</tr>
<tr>
<td>1111/A(_{1}/2)</td>
<td>1202/A(_{1}/4)</td>
</tr>
<tr>
<td>1324/A(_{1}/2)</td>
<td>1339/A(_{1}/3)</td>
</tr>
<tr>
<td>1353/A(_{1}/5)</td>
<td>1355/A(_{1}/12)</td>
</tr>
<tr>
<td>1354/A(_{1}/7)</td>
<td>1571/A(_{1}/1)</td>
</tr>
<tr>
<td>1632/A(_{1}/32)</td>
<td>1658/A(_{1}/4)</td>
</tr>
</tbody>
</table>

\(^a\) For modes with an IR intensity greater than 1 km mol\(^{-1}\), the harmonic vibrational frequency \( \omega \) is followed by the mode symmetry (if it could be assigned unambiguously) and its IR intensity in km mol\(^{-1}\).
of the relative concentrations of the (6/6) and (5/6) isomers. The ground state structure, of course, prevails at low temperatures; however, at higher temperatures the concentrations approach one another. In fact, at a very high temperature (over 4700 K) the computations finally show a relative stability interchange after crossing the equimolarity point. This is another example in the fullerene field that the potential energy difference $\Delta E$ between two (or more) isomers is not sufficient information and rotational–vibrational motions (i.e. entropy factors) can create a different stability order at higher temperatures. Although, the rigid-rotor and harmonic-oscillator approximations can be a rather rough approach for higher temperatures it is still the only treatment applicable with respect to the amount of information available on the potential hypersurface. Moreover, for the special case of the interisomeric equilibrium an ample cancellation can be expected, including, for example, even an effect of frequency scaling. Overall, our computations suggest the possibility of an isomeric mixture rather than a single structure, at least for some temperature histories of the samples in future experiments. The isomeric interplay can also enhance the heat capacity; the highest enhancement was computed at about 1730 K, though it only had the modest value of 8 J K$^{-1}$ mol$^{-1}$.

Triplet electronic states were also studied for both structural types, but computations were conclusive only for the 6/6 pattern. The resulting structure was again closed with a slightly shorter bridged C–C bond (1.575 Å). This triplet state is in fact located below the singlet 6/6 isomer; however, we deal here with two different approaches, restricted and unrestricted. The restricted open-shell Hartree–Fock approach would be more suitable for the energy comparisons; however, it did not converge.

Furthermore, it is not possible to locate a stationary point of the 6/6 type with the bridged C–C bond considerably elongated, i.e. an open species (in contrast to the above described closed 6/6 structure). However, after some effort a closed 5/6 isomer was found, though it was higher in energy. The last mentioned structure is located about 41 kJ mol$^{-1}$ ($\Delta H_{298.15}^{2}$ scale) above the open 5/6 species, described above. The critical C–C bond is now computed at 1.641 Å, and the C–S bonds at 1.734 Å. There is no imaginary frequency in the computed vibrational spectrum, and thus we deal with a third local energy minimum. There is a significant change in charge distribution so that the closed 5/6 species is less polar compared to the open one. It should be realized that an inclusion of this third isomer in the thermodynamic treatment would somewhat scale down the values in Table 3 but it would not change their ratio. The HF/3-21G treatment of the open and closed 5/6 structures in the MNDO optimized geometries shows smaller separation energy, placing the closed 5/6 structure 22 kJ mol$^{-1}$ below the open 5/6 one.

There is still another structural type which needs to be mentioned. The S atom can be placed inside the cage, i.e. the S@C$_{60}$ case according to the suggested nomenclature [27]. We could optimize the geometry for the $I_h$ symmetry, i.e. the sulfur atom exactly in the cage center, though an adsorption from inside of the cage is also likely. The central location is placed some 555 kJ mol$^{-1}$ above the 6/6 ground state. The introduction of the sulfur atom brings almost no elongation of the sphere diameter. Optimization for the related triplet state did not converge (though it is clear it should be lower in energy, but again we would meet the restricted/unrestricted treatment inconsistency).

There has not yet been enough experience with predictions of fullerene stability. It is well known that the heat of formation per carbon atom decreases systematically (and does not exhibit a clear minimum for 60 carbons). Hence we deal
with a complex thermodynamic and kinetic stability control. It is thus difficult to relate stabilities of the C_{60}S species to C_{60}O or to C_{60}. The HOMO–LUMO gap is relatively low, 1.6 kcal mol\(^{-1}\) and 1.4 kcal mol\(^{-1}\) for the 6/6 and 5/6 C_{60}S respectively, which may indicate a lower stability. However, a more sophisticated approach to the absolute stability problem would require evaluations of equilibrium or even rate constants and solution of the related thermodynamic or kinetic schemes. This clearly goes beyond the presently possible computational frame in fullerene research.

Acknowledgments

Acknowledgment is made to the National Science Council, Taiwan, for support, and to the National Center for High-Performance Computing in Hsinchu for computer time on the Convex C3840. Last but not least, the referee comments are also highly appreciated.

References