The Structure of the Cyclopentathiazenium Cation ($S_5N_5^+$) – a MNDO Investigation

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Geometry Optimization, Heats of Formation

The total energies, heats of formation ($\Delta H_f$), bond lengths and bond angles of four isomers of $S_5N_5^+$ (1) have been calculated using the MNDO method. The heart shaped and azulene like structures 1e and 1f have been found to be the most stable isomers with about equal energies.

Recently we investigated [1] the structural possibilities for the ten-membered ring of the cyclopentathiazenium cation ($S_5N_5^+$, 1) using the Extended Hückel (EH) method [2]. In these calculations we started with a regular ten-membered ring ($D_{sh}$) by assuming equal bond lengths and angles and varied bond angles only. This led us to compute the energies of the isomers 1a to 1f shown below. It was found that the two species of lowest energy were those with the heart shaped structure, 1e, and the azulene like structure, 1f, whose structural parameters have been reported recently from X-ray investigations [3, 4]. To our surprise the energy difference calculated between both isomers (1e and 1f) was found to be 2 eV, a difference rather large for two conformational isomers occurring in Nature. Together with the relatively large temperature factors found for the centers (NSN) around the tip of the heart in 1e the reliability of the structural results has been questioned [1, 5].

Since EH results derived for cations are at most qualitative in character [6], we have carried out SCF calculations on 1 using the MNDO method [7] which has been proven to be quite reliable in predicting structural properties of sulfur-nitrogen species [8].

To calculate the total energies and heats of formation of 1a to 1f we started with an assumed ideal geometry (S–N = 1.56 Å) and the angles reported in [1]. Varying all bond lengths and angles with respect to the total energy around the area corresponding to 1a-1f of the potential surface of $S_5N_5^+$ leads to four local minima. The geometrical parameters of the corresponding structures are shown in Fig. 1, the energies and heats of formation ($\Delta H_f$) are given in Table I. Selfconsistency could only be achieved for structures corresponding to the formulae 1a and 1d-1f.

Fig. 1. Geometrical parameters for 1a and 1d-1f according to a MNDO calculation.
Table I. Total energies and heats of formation ($\Delta H_f$) of 1a and 1d–1f.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Total energy (eV)</th>
<th>$\Delta H_f$ (kcal/mol)</th>
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<tbody>
<tr>
<td>la</td>
<td>−2209.87</td>
<td>442.96</td>
</tr>
<tr>
<td>ld</td>
<td>−2208.96</td>
<td>463.96</td>
</tr>
<tr>
<td>le</td>
<td>−2210.24</td>
<td>434.38</td>
</tr>
<tr>
<td>lf</td>
<td>−2210.23</td>
<td>434.67</td>
</tr>
</tbody>
</table>

A comparison of the $\Delta H_f$ values of 1a and 1d–1f shows essentially equal energies for le and lf. As anticipated the $\Delta H_f$ values computed for 1a and 1d are much larger. The bond lengths and bond angles calculated for le and lf are reasonably close to the experimental ones [3, 4]. Even the S–N–S bond angles of 177° around the tip of the heart of 1e found [3] are reproduced in the calculations.

These calculations suggest that the two isomeric structures for $S_5N_5^+$, namely 1e and 1f reported in the literature are existent and not due to any errors. What remains to be solved is the question concerning the relatively high temperature factors reported for the atoms around the tip of the heart in 1e.

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