THE \textit{AB INITIO} CALCULATED MOLECULAR STRUCTURES, FORCE FIELDS AND VIBRATIONAL FREQUENCIES OF SOME ORGANIC AZIDES

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ABSTRACT

Double zeta basis molecular orbital calculations were carried out on the hydrazoic acid and azidomethane molecules. The molecular structures were optimized by the gradient method and the force fields were obtained by numerical differentiation of the gradient vector. The computed harmonic force fields and vibrational frequencies were compared with experimental values.

INTRODUCTION

Vapour phase structural data on organic azides \(R-N_2\) is rare due to their explosive nature, but it now seems well established that the azido group of the covalent azides has a slightly bent structure, with a shorter terminal \(N\equiv N\) distance (ref.1,2) and a \textit{trans} configuration around the middle \(N-N\) bond.

While the isoelectronic isocyanato group prefers an \textit{eclipsed} position with respect to single bonds, electron diffraction measurements on azidotrifluoromethane, \(\text{CF}_3\text{N}_3\), (ref.3) and a series of azides recently studied in our laboratory (ref.1), show that the azido group generally prefers a \textit{staggered} position. Although azidomethane, \(\text{CH}_3\text{N}_3\), has been studied by both electron diffraction (ref.4,5) and microwave spectroscopy (ref.6), the available data did not prove sufficient to determine whether the azido group is linear, nor has the orientation of the methyl group been unambiguously determined.

Hydrazoic acid, \(\text{HN}_3\), has been studied extensively by microwave spectroscopy and the structure has been reported (ref.7).

CALCULATIONS

\textit{Ab initio} Hartree-Fock calculations were carried out in order to investigate the molecular structures and properties of \(\text{HN}_3\) and \(\text{CH}_3\text{N}_3\). The calculations were performed with a gradient version of
the program MOLECULE (ref.8,9) and a double zeta basis set was employed, contracted from 7s3p primitive sets for C and N (ref.10) and from a 4s set for H (ref.11). The geometry relaxation was continued until all cartesian forces on the atomic coordinates were less than 0.001 atomic units (hartree/bohr).

The force constants were calculated by numerical differentiation of the gradient vector in a number of distorted geometries. The bond lengths were displaced ±2.5 pm and the angles ±2 degrees from their equilibrium values.

Molecular force fields, including anharmonic terms, were also obtained by a least squares fitting of a potential energy expansion to the \( \text{a}\text{b}\text{i}\text{m}\text{t}\text{t}\text{a} \) calculated gradients in a number of points on the potential energy surface, and these results will be the subject of a later paper (ref.2).

The computed geometries are shown in Figs. 1 and 2, the \text{e}\text{t}\text{a}\text{g}\text{g}\text{e}\text{d} form of CH\(_3\)N\(_3\) being the more stable. A complete geometry optimization of the \text{e}\text{l}\text{i}\text{s}\text{p}\text{e}\text{d} form was also carried out and the energy difference was found to be 3.7 kJ/mol. The harmonic force field of HN\(_3\) is shown in Table 1 and the corresponding force field of CH\(_3\)N\(_3\) is given in Table 3. The methyl group force constants have been omitted for the sake of brevity.

Tables 2 and 4 contain the harmonic vibrational frequencies calculated from the force fields of HN\(_3\) and CH\(_3\)N\(_3\), respectively. The experimental frequencies of HN\(_3\) (ref.12) and CH\(_3\)N\(_3\) (ref.13) are included for comparison.

DISCUSSION

\text{H}\text{y}\text{d}\text{r}\text{a}\text{z}\text{o}\text{i}\text{c} \text{a}\text{c}\text{i}\text{d}

The calculated geometric structure of HN\(_3\) shows a satisfactory agreement with the structure determined experimentally (ref.7), although CI level calculations (ref.14), employing a larger basis set, give an even better agreement. The diagonal force constants are known to be overestimated in Hartree-Fock calculations and this is reflected in the frequency values given in Table 2. The difference between the observed and calculated vibrational frequencies is also due to the neglect of anharmonicity and it has been shown that the inclusion of cubic and quartic terms using a second order perturbation treatment, essentially halves the difference between the calculated and observed values (ref.15).
Fig. 1. The \textit{ab initio} molecular structure of hydrazoic acid, HN$_3$. Computed energy: -163.583218 hartree. Bond lengths in picometers and angles in degrees.

\begin{table}
\centering
\caption{The \textit{ab initio} harmonic force field$^a$ of hydrazoic acid, HN$_3$.}
\begin{tabular}{ccccccc}
\hline
\hline
N=N & 22.500 & 2.362 & -0.136 & -0.056 & -0.058 & \\
N=N & 7.238 & 6.745 & -0.025 & 0.267 & 1.171 & 0.338 \\
N=H & 6.745 & 6.745 & 6.745 & 0.792 & 0.089 & \\
N=H & 6.745 & 6.745 & 6.745 & 0.792 & 0.089 & \\
N=N torsion & & & & & & 0.018 \\
\hline
\end{tabular}
\end{table}

$^a$Units: Stretch and stretch/stretch, mdyn/Å; stretch/bend, mdyn/Å/Å; bend and bend/bend, mdyn·Å/Å$^2$.

\begin{table}
\centering
\caption{The \textit{ab initio} harmonic frequencies (cm$^{-1}$) of hydrazoic acid, HN$_3$.}
\begin{tabular}{ccc}
\hline
 & Observed$^a$ & Calculated & P.E.D.$^b$ \\
\hline
$\nu_1$ & 3497 & 3488 & 99 N-H \\
$\nu_2$ & 2140 & 2330 & 997 N=N \\
A$'$ $\nu_3$ & 1265 & 1465 & 81 N=N-H \\
$\nu_4$ & 1157 & 1026 & 116 N=N + 35 N=H \\
$\nu_5$ & 527 & 599 & 99 N=N-N \\
A$''$ $\nu_6$ & 587 & 683 & 100 N=N torsion \\
\hline
\end{tabular}
\end{table}

$^a$Ref. 12. $^b$Potential energy distribution: PED($I,J$) = 100·F($I,J$)·L($I,J$)$^2/\lambda(J)$; terms below 10 neglected.
Azidomethane

The calculations on CH$_3$N$_3$ showed the staggered conformer depicted in Fig. 2 to be the more stable, whereas the experimental investigations of CH$_3$N$_3$ (ref.4-6) have so far not led to an unambiguous determination of the molecular structure. Thus, the present results can best be compared to the combined microwave and electron diffraction study of azidotridifluoromethane, CF$_3$N$_3$ (ref.3).

**TABLE 3**

The *ab initio* harmonic force field$^a$ of azidomethane, CH$_3$N$_3$.

<table>
<thead>
<tr>
<th></th>
<th>N=N</th>
<th>N-C</th>
<th>N≡N=N</th>
<th>N=N-C</th>
<th>N=N torsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>N≡N</td>
<td>21.840</td>
<td>2.420</td>
<td>-0.147</td>
<td>-0.097</td>
<td>-0.134</td>
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<tr>
<td>N≡N-N</td>
<td>7.660</td>
<td>0.230</td>
<td>0.303</td>
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<td>N=N-C</td>
<td>4.506</td>
<td></td>
<td>-0.003</td>
<td>0.719</td>
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</tr>
<tr>
<td>N≡N</td>
<td></td>
<td>0.792</td>
<td>0.139</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N=N torsion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.367</td>
</tr>
</tbody>
</table>

$^a$Units, see Table 1.

![Molecular structure of azidomethane](image)

**Fig. 2.** The *ab initio* molecular structure of azidomethane. Computed energies: -202.567219 hartree (staggered) and -202.565796 hartree (eclipsed). Bond lengths in picometers and angles in degrees.
<table>
<thead>
<tr>
<th>Observed&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Calculated</th>
<th>P.E.D.&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
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<td>ν&lt;sub&gt;1&lt;/sub&gt;</td>
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<td>3357</td>
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<tr>
<td>ν&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2893</td>
<td>3188</td>
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<tr>
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<td>2106</td>
<td>2288</td>
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<td>1661</td>
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<tr>
<td>ν&lt;sub&gt;5&lt;/sub&gt;</td>
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<td>1602</td>
</tr>
<tr>
<td>A&lt;sup&gt;+&lt;/sup&gt; ν&lt;sub&gt;6&lt;/sub&gt;</td>
<td>1272</td>
<td>1205</td>
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<td>1254</td>
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<td>890</td>
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<td>666</td>
<td>746</td>
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<tr>
<td>ν&lt;sub&gt;10&lt;/sub&gt;</td>
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<td>291</td>
</tr>
<tr>
<td>A&lt;sup&gt;+&lt;/sup&gt; ν&lt;sub&gt;11&lt;/sub&gt;</td>
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<td>712</td>
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<tr>
<td>ν&lt;sub&gt;15&lt;/sub&gt;</td>
<td>126</td>
<td>135</td>
</tr>
</tbody>
</table>

<sup>a</sup>Ref. 13. <sup>b</sup>See Table 2.

The calculations showed the azido group of CH<sub>3</sub>N<sub>3</sub> to be trans planar and the methyl group to be tilted away from the C-N bond by 4.2 degrees, which is in excellent agreement with the experimental results on CF<sub>3</sub>N<sub>3</sub> (ref.3). Indeed, all the quantum chemical calculations on the organic, covalent azides, to be published later (ref.2), as well as recent electron diffraction results (ref.1), show the azido group to prefer the trans planar configuration with an NNN angle of 172-174 degrees.

Rotation of the methyl group 8 degrees away from the staggered position resulted in a significantly higher energy and, as a consequence, the intermediate methyl position suggested earlier (ref.5), was rejected.

Although the calculated frequencies were found to differ somewhat from the observed values, it is apparent from Table 5 that the observed frequency shifts between NN<sub>3</sub> and CH<sub>3</sub>N<sub>3</sub> are reproduced fairly well by the calculations. The largest discrepancy was found for the N=N stretching mode and this is believed to be due to the fact that this particular vibration mixes considerably with the various vibrational modes of the substituent group. The present results also showed the stretching modes of the azido group to be highly anharmonic, but this will be discussed in more detail elsewhere (ref.2).
TABLE 5

Group Frequencies of HN₃ and CH₃N₃.

<table>
<thead>
<tr>
<th>Description</th>
<th>Observed frequencies</th>
<th>Calculated shift</th>
<th>$\Delta_{\text{calc.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HN₃</td>
<td>CH₃N₃</td>
<td>$\Delta_{\text{obs.}}$</td>
</tr>
<tr>
<td>N=N stretch</td>
<td>2140</td>
<td>2106</td>
<td>34</td>
</tr>
<tr>
<td>N=N stretch</td>
<td>1151</td>
<td>1272</td>
<td>-121</td>
</tr>
<tr>
<td>N=N bend</td>
<td>527</td>
<td>666</td>
<td>-139</td>
</tr>
<tr>
<td>N=N torsion</td>
<td>587</td>
<td>560</td>
<td>27</td>
</tr>
</tbody>
</table>

$\Delta = \text{obs.}(\text{HN}_3) - \text{obs.}(\text{CH}_3\text{N}_3)$

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REFERENCES

2 C.E. Sjøgren and C.J. Nielsen, to be published.