An ab Initio SCF Study on the Stability and Structure of H$_2$CN$^+ \cdot n$N$_2$ Clusters

Tae-Kyu Ha
Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, CH-8092 Zurich, Switzerland

Minh Tho Nguyen
Department of Chemistry, University of Leuven, B-3030 Heverlee, Belgium

Z. Naturforsch. 38a, 855–858 (1983); received April 18, 1983

The clustering energies and geometries of the H$_2$CN$^+ \cdot n$N$_2$ ($n = 1$, 2 and 3) species have been determined by ab initio SCF calculations with the 4-31G basis set. The calculated clustering energies are in good agreement with the experimentally estimated heats of formation of the corresponding clusters. The stability of various conformers has been studied in terms of localized orbitals and charge distributions.

1. Introduction

Evidence of complex chemical processes arising in the atmosphere of Titan, the largest satellite of Saturn, is of considerable interest, since these processes might be similar to the formation of prebiotic molecules in the primitive earth's atmosphere. It has been established that a dense atmosphere around Titan is mainly composed of N$_2$ with some CH$_4$ and other minor compounds including hydrocarbons and organic nitrogen molecules and that the clustering reaction of the dihydrogen cyanide cation, H$_2$CN$^+$ and molecular nitrogen (N$_2$) plays a major role in the formation of various organic molecules [1].

Recently, Speller et al. [2] have observed the H$_2$CN$^+ \cdot N_2$ cluster ion in a simulated laboratory mass spectrometric experiment. In the following study [3], these authors also reported the results of laboratory measurements of equilibrium constants for the clustering of N$_2$ with H$_2$CN$^+$ leading to H$_2$CN$^+ \cdot n$N$_2$ ($n = 1$–6) formation, H$_2$CN$^+ + n$N$_2$ → H$_2$CN$^+ \cdot n$N$_2$. The experimental heat of formation of the H$_2$CN$^+ \cdot n$N$_2$ cluster has been estimated from the equilibrium constant as 7.6 ($n = 1$), 5.1 ($n = 2$) and 3.2 ($n = 3$) kcal/mol respectively.

In a recent theoretical study [4], we have reported an ab initio calculation of the formation and structure of H$_2$CN$^+ \cdot N_2$ and showed that the calculated clustering energy of 8.9 or 6.5 kcal/mol in two levels of approximation is in good agreement with the experimental heat of formation. Furthermore, the structures of two stable reaction products and the reaction pathway of the ion-molecular reaction, H$_2$CN$^+ + N_2$ have been reported in detail.

In the present theoretical study we extend our investigation to the H$_2$CN$^+ \cdot n$N$_2$ species ($n = 2$ and 3) and report the results of ab initio SCF studies on the favourable structures and clustering energies of these species. The clustering mechanisms and relative stabilities are analyzed in detail in terms of localized orbitals and charge distributions.

2. Calculation

Ab initio SCF calculations have been performed employing the split-valence 4-31G basis set [5]. A systematic geometry optimization of the H$_2$CN$^+ \cdot n$N$_2$ ($n = 1$, 2, 3) species and some fragments (N$_2$, H$_2$CN$^+$, HN$_2$, HCN and HNC) has been carried out by the force gradient method with an analytical gradient [6] as implemented in the Monstergauss program [7]. The localized molecular orbitals were obtained by the method of Foster-Boys [8] using the Boyloc program [9].

3. Results and Discussion

Various structures of the H$_2$CN$^+ \cdot n$N$_2$ ($n = 1$, 2 and 3) clusters and some of their fragments (H$_2$CN$^+$, N$_2$, HN$_2$, HCN and HNC), optimized with the split-valence 4-31G basis set, are shown in

Reprint requests to PD Dr. T.-K. Ha, Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zürich, Schweiz.
The total SCF energies and the relative energies of the H$_2$CN$^+ \cdot n$N$_2$ species with respect to the H$_2$CN$^+ \cdot (n-1)$N$_2$ species, calculated for these optimized geometries are summarized in Table 1. The clustering energies are compared with the experimentally estimated heats of formation of the corresponding species.

In a previous theoretical study [4], we showed that the interstellar H$_2$CN$^+ \cdot$N$_2$ species might exist as a stable species in either two collinear conformations, HCNH$^+ \cdot$N$_2$ and N$_2 \cdot$HCNH$^+$, the former being more stable than the latter. The calculated energy difference between the more stable complex, HCNH$^+ \cdot$N$_2$ and its fragment was found to agree well with the estimated heat of formation of 7.65 kcal/mol from the laboratory experiment.

Fig. 1. Optimized (4-31G) geometries of considered species. Distances in Å and angles in degrees. Values in parentheses are the calculated dipole moment in Debye units.

Fig. 2. Gross atomic charges and overlap populations (in parentheses) of the H$_2$CN$^+$ and H$_2$CN$^+ \cdot n$N$_2$ ($n = 1, 2$ and 3) species.
Table 1. Total and relative energies of the HCNH\(^+\) \(\cdot\) \(n\)N\(_2\) clusters and comparison with experiment.

<table>
<thead>
<tr>
<th>(n)</th>
<th>Species*</th>
<th>(E_T) (a.u.)</th>
<th>(\Delta E_{n-1,b}) (kcal/mol)</th>
<th>(\Delta H_{n-1,c}^0) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>HC(N+) (1)</td>
<td>(-93.02235)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>N(_2) (2)</td>
<td>(-108.75424)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>HC(N+) (\cdot) N(_2) (3)</td>
<td>(-201.79084)</td>
<td>(-8.94)</td>
<td>(-7.65)</td>
</tr>
<tr>
<td></td>
<td>HC(N+) (\cdot) HC(N+) (4)</td>
<td>(-201.78805)</td>
<td>(-7.19)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>N(_2) (\cdot) HC(N+) (\cdot) N(_2) (5)</td>
<td>(-310.55581)</td>
<td>(-6.73)</td>
<td>(-5.10)</td>
</tr>
<tr>
<td></td>
<td>(N(_2)) (\cdot) HC(N+) (\cdot) N(_2) (6)</td>
<td>(-310.55047)</td>
<td>(-3.38)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>HC(N+) (\cdot) (N(_2)) (\cdot) N(_2) (7)</td>
<td>(-310.54841)</td>
<td>(-2.09)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>HC(N+) (\cdot) (N(_2)) (8)</td>
<td>(-310.54847)</td>
<td>(-2.12)</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>N(_2) (\cdot) (N(_2)) (\cdot) HC(N+) (\cdot) N(_2) (9)</td>
<td>(-419.31487)</td>
<td>(-3.02)</td>
<td>(-3.2)</td>
</tr>
<tr>
<td></td>
<td>N(_2) (\cdot) HC(N+) (\cdot) (N(_2)) (\cdot) N(_2) (10)</td>
<td>(-419.31339)</td>
<td>(-2.09)</td>
<td>-</td>
</tr>
</tbody>
</table>

\(\Delta E_{n-1,a} = E_T(\text{HC\(N+\)} \(\cdot\) n\text{N}_2) - E_T(\text{HC\(N+\)} \(\cdot\) (n - 1)\text{N}_2) - E_T(\text{N}_2)\).

* Experimental values of [3].

For the \(n = 2\) species, we have obtained four stable conformations ((5), (6), (7) and (8) of Fig. 1), among which the N\(_2\) \(\cdot\) HC\(N+\) \(\cdot\) N\(_2\) conformer is shown to be unequivocally the most stable one. The calculated clustering energy (\(\Delta E_{n-1,a}\)) of 6.73 kcal/mol is found to be in good agreement with the experimental heat of formation of 5.10 kcal/mol. The clustering energies of the other three conformers are calculated to be less than half of that of the N\(_2\) \(\cdot\) HC\(N+\) \(\cdot\) N\(_2\) conformer.

The two conformers of the \(n = 3\) species ((9) and (10) of Fig. 1) have almost the same clustering energy, the difference being less than 1 kcal/mol, and the calculated clustering energy of 3.02 kcal/mol for the more stable one (see (9)) is in excellent agreement with the experimental heat of formation of 3.2 kcal/mol. The calculated dipole moments are also listed in Figure 1. It is worthwhile to note that the most stable conformer for each \(n\) has the largest dipole moment. For example, the calculated dipole moment of 7.80 Debye of the most stable N\(_2\) \(\cdot\) HC\(N+\) \(\cdot\) N\(_2\) conformer for \(n = 2\) is found to be much larger than those of other conformers.

In order to have an idea about the stability of the two stable conformers of the H\(_2\)CN\(+\) \(\cdot\) N\(_2\) complex, we have independently calculated the reaction paths of the following reactions:

\[
\text{H} - \text{C} \equiv \text{N}^+ - \text{H} \rightarrow \text{H} - \text{C} \equiv \text{N} + \text{H} - \text{N} \equiv \text{N}^+ \tag{3}
\]

Table 2. Positions and sizes of charge centroids of the lone pair LMO for molecular nitrogen (N\(\equiv\)N) in different species.

<table>
<thead>
<tr>
<th>Species*</th>
<th>(r(\text{Å}))</th>
<th>(\Delta r(\text{Å}))</th>
<th>(q(%))</th>
<th>(\langle r^2 \rangle^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n = 0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) N(\equiv)N (\cdot) x</td>
<td>0.345</td>
<td>0.0</td>
<td>-</td>
<td>1.350</td>
</tr>
<tr>
<td>(n = 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3) x (\cdot) N(_1) (\equiv) N</td>
<td>0.384</td>
<td>0.039</td>
<td>20.3</td>
<td>1.420</td>
</tr>
<tr>
<td>(4) N(_1) (\cdot) x</td>
<td>0.377</td>
<td>0.032</td>
<td>18.2</td>
<td>1.407</td>
</tr>
<tr>
<td>(n = 2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5) N(_2) (\cdot) x</td>
<td>0.376</td>
<td>0.031</td>
<td>18.1</td>
<td>1.406</td>
</tr>
<tr>
<td>x (\cdot) N(_2)</td>
<td>0.382</td>
<td>0.037</td>
<td>20.0</td>
<td>1.408</td>
</tr>
<tr>
<td>(6) N(_2) (\cdot) x</td>
<td>0.365</td>
<td>0.020</td>
<td>13.9</td>
<td>1.310</td>
</tr>
<tr>
<td>x (\cdot) N(_2)</td>
<td>0.382</td>
<td>0.037</td>
<td>19.9</td>
<td>1.409</td>
</tr>
<tr>
<td>(7) N(_2) (\cdot) x</td>
<td>0.358</td>
<td>0.013</td>
<td>12.7</td>
<td>1.381</td>
</tr>
<tr>
<td>x (\cdot) N(_2)</td>
<td>0.379</td>
<td>0.034</td>
<td>18.9</td>
<td>1.408</td>
</tr>
<tr>
<td>(n = 3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9) x (\cdot) N(_3) (\equiv) N</td>
<td>0.381</td>
<td>0.036</td>
<td>19.9</td>
<td>1.408</td>
</tr>
<tr>
<td>N(_3) (\cdot) x</td>
<td>0.375</td>
<td>0.030</td>
<td>18.0</td>
<td>1.404</td>
</tr>
<tr>
<td>N(_3) (\cdot) N(_3)</td>
<td>0.362</td>
<td>0.017</td>
<td>12.3</td>
<td>1.387</td>
</tr>
<tr>
<td>(10) x (\cdot) N(_3)</td>
<td>0.381</td>
<td>0.035</td>
<td>19.8</td>
<td>1.407</td>
</tr>
<tr>
<td>N(_3) (\cdot) x</td>
<td>0.376</td>
<td>0.031</td>
<td>18.1</td>
<td>1.405</td>
</tr>
<tr>
<td>N(_3) (\cdot) N(_3)</td>
<td>0.357</td>
<td>0.012</td>
<td>11.9</td>
<td>1.380</td>
</tr>
</tbody>
</table>

* Values in parentheses are the numberings of molecules whose geometrical parameters are given in Figure 1.

\(r\) is the distance between charge centroid and terminal nitrogen.

\(\Delta r\) is the elongation of \(r\) with respect to free N\(\equiv\)N.

\(g = r/d(\text{N} \ldots \text{H})\) is the ratio of \(r\) and the intermolecular distance \(d(\text{N} \ldots \text{H})\).

\(\langle r^2 \rangle^{1/2}\) is the second moment of the lone pair orbital.
and
\[ N=N \ldots H-C=N+H \rightarrow N=N-H^+ + C=N-H . \]
(4) \hspace{1cm} (11) \hspace{1cm} (13)
Both reactions are found to be endothermic and proceed without energy barrier. From Table 1, the 
\( H-C=N \ldots N=N \) complex is calculated to be 
70.8 kcal/mol more stable than its fragments HCN and HNN\(^+\) and that the complex
\[ N=N \ldots H-C=N+H \]
is more stable than its fragments HNN\(^+\) and HNC by 76.1 kcal/mol. This indicates that molecules such
as HCN and HNC could not be obtained from the
direct dissociation of the \( H_2CN^+ \cdot N_2 \) complex.
In order to study the change in the charge distribution of the \( N_2 \) molecule to the clustering, a
localized molecular orbital (LMO) analysis has been
carried out. In Table 2, the positions and sizes of
charge centroids of the lone pair LMO for \( N_2 \) in
different species are summarized. The second
moment \( \langle r^2 \rangle \) measures the extent of the electronic
dispersion around the LMO charge centroid. As to
the free nitrogen molecule, the H-bonded \( N=N \)
exhibits significant changes both in the position and
extent of the charge centroid of the lone pair LMO.
The most significant change is found in the \( N_1 \) posi-
tion (cf. Fig. 1) in all cases, since the \( N_1 \ldots H \)
distance is also shown to be shorter than other
\( N \ldots H \) distances, and the ordering of these changes is
found to be \( N_1 > N_2 > N_3 \). It is also worthwhile
to note that the most stable conformer for each \( n \)
has the largest change in the position and in the
second moment. This result also shows that the
formation of the complex needs an elongation of the
lone pair of molecular nitrogen and that this elonga-
tion is the largest for \( n = 2 \) (0.031–0.037 Å) and
becomes smaller for \( n = 3 \) (0.017 Å). Thus, the
linear structure of the \( n = 2 \) species turns out to be
the most important species for the formation of
higher complexes. It seems that this species might
serve as a skeleton from which a variety of higher
order complexes could be formed.
The calculated gross atomic charges and overlap
populations for the \( H_2CN^+ \cdot nN_2 \) \((n = 1, 2 \) and 3) complexes are summarized in Figure 2. Compared
to the \( H_2CN^+ \) species, the gross atomic charges on
both C and N become larger in the \( H_2CN^+ \cdot nN_2 \) complexes. It is also of interest to note that the
terminal N atom in all complexes is slightly posi-
tively charged. The electron transfer from \( N_2 \) to
\( H_2CN^+ \) is calculated to be 0.05 \((n = 1), 0.08 \)
\((n = 2)\) and 0.09 \((n = 3)\), respectively, and it shows that the
electron transfer in the most stable conformer for
each species is slightly larger than those in the less
stable conformers.
The electron population analysis also clearly re-
lects the polarity and large dipole moment of the
\( H_2CN^+ \cdot nN_2 \) species. The dipole moment of the
reacting \( H_2CN^+ \) species was previously shown to be
very small: 0.62 [10] and 0.57 Debyes [11] from SCF
calculations and 0.71 [10] and 0.23 Debyes [11] from
configuration interaction (CI) calculations. Thus,
the intensity of the rotational spectra is expected to
be very weak, making the experimental detection
extremely difficult. On the other hand, the very
large dipole moment \((\sim 7.8 \text{ Debye})\) of the weakly
bonded \( H_2CN^+ \cdot nN_2 \) complexes calculated in the
present study indicates that these species are rela-
tively easily detectable by spectroscopical means.
In conclusion, the present ab initio study shows
that the interstellar species \( H_2CN^+ \cdot nN_2 \) might exist
as stable species in either two collinear conforma-
tions \((n = 1)\), in four \((n = 2)\) or two \((n = 3)\) different
conformations. The calculated energy difference
between the complex, \( H_2CN^+ \cdot nN_2 \) and its
fragments, \( H_2CN^+ \) and \( nN_2 \), agrees well with the
estimated heat of formation obtained from simu-
lated laboratory experiments. The present detailed
theoretical study on the structure and electronic
properties may serve as a guide for an unambiguous
identification of this important interstellar species.

Whitten, J. Dubach, and K. Santhanam, Nature
in press (1983), personal communication.
Phys. 56, 2257 (1972).
[6] H. B. Schlegel, Ph. D. Thesis, Queen’s University,
Kingston, Canada 1975.
Monstergauss program, University of Toronto,
Canada 1981.
240, L171 (1980).
61, 396 (1979).