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A possible role for triplet $\text{H}_2\text{CN}^+$ isomers in the formation of HCN and HNC in interstellar clouds

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The structures and energies of the lowest triplet states of four isomers of $\text{H}_2\text{CN}^+$ have been determined by self-consistent field and configuration interaction calculations. When both hydrogen atoms are attached to the nitrogen atom, $\text{H}_2\text{NC}^+$, the molecule has its lowest triplet state energy, which is 97.2 kcal mol$^{-1}$ above the energy of the linear singlet ground state. The structure has $C_s$ symmetry, with an HCN bond angle of 116.8° and bond lengths of 1.099 Å (H-N) and 1.268 Å (N-C). Other isomers investigated include the $\text{H}_2\text{CN}^+$ isomer at 104.7, the cis-\text{HCNH}$^+$ isomer at 105.3, and the trans-\text{HCNH}$^+$ isomer at 113.6 kcal mol$^{-1}$. The $\text{H}_2\text{CN}^+$ isomer has an unusual “carbonium nitrene” structure, with a C-N bond length of 1.398 Å. It is suggested that the triplet $\text{H}_2\text{NC}^+$ isomer may play a role in determining the relative yields of HCN and HNC from the reaction of $\text{C}^+$ and $\text{NH}_3$. Specifically, a triplet path is postulated in which $\text{C}^+$ and $\text{NH}_3$ yield the triplet $\text{H}_2\text{NC}^+$ isomer, which then yields the singlet $\text{H}_2\text{NC}^+$ isomer by phosphorescent emission. Because this emission removes a large amount of energy, the singlet $\text{H}_2\text{NC}^+$ isomer may have insufficient energy to isomerize to the linear singlet ground state. Subsequent dissociative recombination would yield the HNC isomer exclusively.

INTRODUCTION

While the dihydrogen cyanide cation $\text{H}_2\text{CN}^+$ has not been detected in interstellar space thus far, it is commonly postulated as the immediate precursor to hydrogen cyanide HCN and hydrogen isocyanide HNC, both of which have been found in significant quantities in interstellar clouds. The structures and energies of the lowest singlet states of three isomers of $\text{H}_2\text{CN}^+$ have previously been calculated by the techniques of molecular quantum mechanics, but nothing is known of the triplet states. Due to their possible importance in the solution of various problems associated with the formation of HCN and HNC, as well as their intrinsic importance, particularly in comparison to the triplet states of the isoelectronic molecule acetylene, we have calculated the structures and energies of the lowest triplet states of four isomers of $\text{H}_2\text{CN}^+$.

THEORETICAL APPROACH

Our first investigations were of the restricted self-consistent-field$^3$ type using the standard contracted double zeta (DZ) Gaussian basis set of Fink and Goddard,$^3$ and Dunning.$^3$ It is designated C (9s5p/4s2p), N (9s5p/4s2p), H (4s/2s). Variation of bond lengths and bond angles to find the optimum geometry of the lowest triplet state of each isomer was greatly assisted by the Pulay gradient technique$^4$ in a form developed for open-shell calculations. To determine the orbital occupancy having the lowest energy for each isomer, the initial calculations were made in $C_2v$ symmetry, where it is not necessary to specify a particular symmetry pattern for the singly and doubly occupied orbitals. After identifying the symmetries of the various occupied orbitals, subsequent calculations were made in $C_2v$ or $C_{3v}$ symmetry. At the optimum geometries, forces in Cartesian coordinates were all less than 0.3 mhartree/bohr.

Once the optimum geometry was determined, it was fixed and additional computations were made at three higher levels of theory. First, the SCF function was extended by configuration interaction (DZ + CI), including all single and double excitations, and with the two occupied orbitals of lowest energy (core MO) and the two virtual orbitals of highest energy (core complements) frozen. Next, a more comprehensive SCF calculation (DZ + P) was carried out with the addition of polarization functions (a set of three p-type functions for each hydrogen atom and a set of five d-type functions each for carbon and nitrogen). This basis set is designated C (9s5p1d/4s2p1d), N (9s5p1d/4s2p1d), H (4s1p/3s1p). The orbital exponents of these polarization functions were 1.0 for the p orbitals on hydrogen, and 0.75 for the d orbitals on carbon and nitrogen. Finally, the double zeta plus polarization SCF function was extended by configuration interaction (DZ + P + CI) including all single and double excitations. Again, the two occupied orbitals of lowest energy and the two virtual orbitals of highest energy were frozen. In these largest calculations the total number of configurations for the two isomers with $C_2$ symmetry was greater than 4505 ($\text{CNH}_3$) and 4488 ($\text{H}_2\text{CN}^+$), and 8878 for the two isomers with $C_3$ symmetry. All CI calculations were performed with the graphical unitary group approach (GUGA) programs.$^5$

RESULTS

Orbital energies

The four isomers studied were $\text{CNH}_3^+$, $\text{H}_2\text{CN}^+$, cis-\text{HCNH}$^+$, and trans-\text{HCNH}$^+$. Table I lists the electronic configuration of the lowest triplet state of each isomer. When all structures are viewed in $C_2$ symmetry, it may be seen that the $\text{H}_2\text{CN}^+$ isomer involves a different excitation than the other three isomers. However, the different excitations for the $\text{CNH}_3^+$ and $\text{H}_2\text{CN}^+$ isomers

TABLE I. Electronic configurations and excitations from the ground state for the lowest triplet states of four isomers of $H_2CN^+$.  

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Symmetry</th>
<th>Electronic configuration</th>
<th>Excitation</th>
<th>Excitation in $C_2$ symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CNH_2^+$</td>
<td>$C_{2v}$</td>
<td>$1a^1 2a^1 3a^1 4a^1 5a^1 2b_2$</td>
<td>$5a_1 - 2b_2$</td>
<td>$6a' - 7a'$</td>
</tr>
<tr>
<td>$H_2CN^+$</td>
<td>$C_{2v}$</td>
<td>$1b^2 2b_2 3b_2 4b_2 5b_2$</td>
<td>$1b_1 - 2b_2$</td>
<td>$1a'' - 7a'$</td>
</tr>
<tr>
<td>cis-$HCNH^+$</td>
<td>$C_s$</td>
<td>$1a^1 2a^1 3a^1 4a^1 5a^1 6a^1 7a^1 8a^1$</td>
<td>$6a' - 7a'$</td>
<td>$6a' - 7a'$</td>
</tr>
<tr>
<td>trans-$HCNH^+$</td>
<td>$C_s$</td>
<td>$1a^1 2a^1 3a^1 4a^1 5a^1 6a^1 7a^1 8a^1$</td>
<td>$6a' - 7a'$</td>
<td>$6a' - 7a'$</td>
</tr>
</tbody>
</table>

are consistent with the different patterns of orbital energies in the corresponding lowest singlet states (see Fig. 1). For singlet $CNH_2^+$ the highest occupied orbital is $5a_1$, and the excitation in the triplet is from $5a_1$ to $2b_2$. For singlet $H_2CN^+$ the highest occupied orbital is $1b_1$, and the excitation in the triplet state is from $1b_1$ to $2b_2$. (For each isomer the $2b_2$ orbital is the lowest virtual orbital of the singlet state.)

Table II lists the orbital energies of the various singlet and triplet states, obtained with the DZ basis. As found for the triplet states of acetylene, the singly occupied orbitals of both the cis and trans isomers are well separated in energy. Figure 2 shows a comparison of the cis and trans orbital energies of the two molecules.

Structures

The bond lengths and bond angles of the triplet states are shown in Fig. 3. All are stable to distortion from a planar geometry. Also, the $CNH_2^+$ and $H_2CN^+$ isomers are stable to in-plane distortions from $C_2v$ symmetry.

Three isomers have C-N bond lengths in the range 1.27–1.29 Å, only slightly longer than the lengths of 1.23–1.26 Å previously found for the singlet $CNH_2^+$ and $H_2CN^+$ isomers. We interpret these bond lengths as indicating essentially double-bond character in all cases. (The sum of the double-bond radii is 1.29 Å.) For the $H_2CN^+$ triplet the C–N bond length is substantially longer (1.39 Å), which we interpret as indicating largely single-bond character. (The sum of the single-bond radii, corrected for electronegativity difference, is 1.47 Å. On using the Pauling relation between bond length and bond order, modified to fit a single-bond length of 1.47 Å and a double-bond length of 1.29 Å, a bond order of 1.32 is obtained for the C–N bond of the $H_2CN^+$ triplet.)

The reason why excitation from the singlet to the triplet weakens the C–N bond in the $H_2CN^+$ isomer is that excitation occurs from the bonding $1b_1$ orbital. (The singly occupied $1b_1$ orbital retains some of its bonding character, and this accounts for the fact that the C–N bond order in the triplet is somewhat larger than one.) By contrast, excitation in the $CNH_2^+$ isomer occurs from the nonbonding $5a_1$ orbital, leaving the C–N double bond intact.

The Lewis structures corresponding to the above interpretation are also shown in Fig. 3. If these structures correctly represent the main features of the electr...
TABLE II. Orbital energies of the lowest singlet and triplet states of the HNCN molecule, obtained with the DZ basis. (Geometries of the singlet states are listed in Ref. 14.) The top half of the table lists the first four orbitals for each isomer; the bottom half lists the other occupied orbitals. For the triplet states, the last two orbitals are singly occupied.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>State</th>
<th>Orbital energies (in hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear HCNH*</td>
<td>Singlet</td>
<td>1\sigma - 15.9578 1\sigma - 11.6789 2\sigma - 1.6234 2\sigma - 1.1887</td>
</tr>
<tr>
<td></td>
<td>Triplet</td>
<td>1\alpha - 15.9578 2\alpha - 11.6853 3\alpha - 1.5612 4\alpha - 1.1712</td>
</tr>
<tr>
<td>cis-HCNH*</td>
<td>Triplet</td>
<td>1\alpha - 15.9677 2\alpha - 11.6637 3\alpha - 1.5548 4\alpha - 1.1865</td>
</tr>
<tr>
<td>trans-HCNH*</td>
<td>Triplet</td>
<td>1\alpha - 15.9471 2\alpha - 11.7402 3\alpha - 1.6373 4\alpha - 1.1841</td>
</tr>
<tr>
<td>CNH2</td>
<td>Singlet</td>
<td>1\beta - 15.9414 2\beta - 11.6933 3\beta - 1.5894 4\beta - 1.1403</td>
</tr>
<tr>
<td></td>
<td>Triplet</td>
<td>1\alpha - 16.0645 2\alpha - 11.6326 3\alpha - 1.6232 4\alpha - 1.1384</td>
</tr>
<tr>
<td>H2CN</td>
<td>Singlet</td>
<td>1\alpha - 15.9754 2\alpha - 11.7059 3\alpha - 1.5078 4\alpha - 1.1694</td>
</tr>
<tr>
<td></td>
<td>Triplet</td>
<td>3\alpha - 1.0768 1\beta - 0.8543</td>
</tr>
<tr>
<td>cis-HCN</td>
<td>Triplet</td>
<td>5\alpha - 1.0328 1\alpha' - 0.8180 6\alpha' - 0.9785 7\alpha' - 0.7816</td>
</tr>
<tr>
<td>trans-HCN</td>
<td>Triplet</td>
<td>6\alpha - 1.0564 1\alpha' - 0.8170 5\alpha' - 1.0187 4\alpha' - 0.7551</td>
</tr>
<tr>
<td>CNH2</td>
<td>Singlet</td>
<td>1\beta - 1.0030 1\beta - 0.8475 5\beta - 0.8181</td>
</tr>
<tr>
<td></td>
<td>Triplet</td>
<td>1\alpha - 1.0394 1\beta - 0.8173 3\alpha - 1.0046 2\beta - 0.7674</td>
</tr>
<tr>
<td>H2CN</td>
<td>Singlet</td>
<td>1\beta - 0.9904 5\alpha - 0.9280 1\beta - 0.8548</td>
</tr>
<tr>
<td></td>
<td>Triplet</td>
<td>1\beta - 0.9945 5\alpha - 0.8658 1\alpha - 0.8613 2\beta - 0.8521</td>
</tr>
</tbody>
</table>

Electronic structures of these molecules, then the two unpaired electrons are both localized on the carbon atom in the CNH2 isomer, and are both localized on the nitrogen atom in the H2CN isomer. For cis- and trans-HCNH* there is one unpaired electron on each heavy atom.

The coefficients of the various atomic orbitals which make up the singly occupied molecular orbitals allow one to assess where the unpaired electrons are localized. For the CNH2 isomer, the largest coefficient in each singly occupied MO belongs to a carbon AO (specifically, \(p_x\) or \(p_y\)), while the reverse is true for the H2CN* isomer—the largest coefficient in each singly occupied MO belongs to a nitrogen AO (specifically, \(p_x\) or \(p_y\)). For both cis- and trans-HCNH*, a carbon AO (\(p_x\)) has the largest coefficient for one singly occupied MO, and a nitrogen AO (\(p_y\)) has the largest coefficient for the other singly occupied MO. (The C–N axis is designated \(z\), and the \(x\) axis is perpendicular to the molecular plane.) All of these results are consistent with the Lewis structures shown in Fig. 3.

The structure found for the triplet H2CN* isomer is particularly intriguing, as it is regarded as a “carbonyl nitrene.” To have both a carbonyl ion structure and a nitrene structure in the same small molecule is certainly unusual and perhaps unique.

It should be noted that, in both the cis and trans isomers, the HNC bond angles are substantially larger than the HCN bond angles, more so in the trans than in the cis isomer. (The differences are 13.6° in the cis and 19.4° in the trans isomer.) A possible explanation is discussed below under Mulliken populations.

Comparison of cis- and trans-HCNH* with the lowest triplet states of acetylene\(^{19}\) shows that the bond angles at the carbon atoms are about the same in the two molecules. Thus, in the cis isomers the bond angles at the carbon atoms are 127.0° (HCNH*) and 127.8° (HCCH); in the trans isomers the bond angles at the carbon atoms are 126.8° (HCNH*) and 130.7° (HCCH).

Total energies

The energy of the lowest triplet state of each isomer (relative to the energy of the linear singlet ground state) is listed in Table III for each of the four levels of theory. Although the energies do not differ greatly, at each level of theory the CNH2 isomer has the lowest energy and the trans-HCNH* isomer has the highest energy. The H2CN* isomer is second lowest at all levels but DZ + CI, and for the DZ + P level it has practically the same energy as the CNH2* isomer.

The fact that the CNH2* isomer is lower in energy than either of the HCNH* structures stands in contrast to the relative energies of the singlet states, where the linear HCNH* lies well below both the CNH2* and the H2CN* isomers.

TABLE III. Energies of the lowest triplet states of four isomers of H2CN*, relative to the energy of the linear singlet ground state.\(^{13}\) Energies are in kcal mol\(^{-1}\).

<table>
<thead>
<tr>
<th>Isomer</th>
<th>DZ</th>
<th>DZ + CI</th>
<th>DZ + P</th>
<th>DZ + P + CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNH2</td>
<td>78.3</td>
<td>93.0</td>
<td>77.5</td>
<td>97.2</td>
</tr>
<tr>
<td>H2CN*</td>
<td>78.2</td>
<td>111.4</td>
<td>77.7</td>
<td>104.7</td>
</tr>
<tr>
<td>cis-HCNH*</td>
<td>82.6</td>
<td>105.6</td>
<td>94.2</td>
<td>105.3</td>
</tr>
<tr>
<td>trans-HCNH*</td>
<td>86.9</td>
<td>113.2</td>
<td>91.8</td>
<td>113.6</td>
</tr>
</tbody>
</table>

\(^{13}\)Absolute energies of the linear singlet ground state are \(-93.12904\), \(-93.32082\), \(-93.17576\), and \(-93.41399\) hartree at the four levels of theory, respectively.
As found for the triplet states of the isoelectronic acetylene molecule, the lowest cis structure has a lower energy than the lowest trans structure. However, the energies of both the cis and trans triplets are substantially higher (compared to the linear singlet ground state) for HCNH⁺ than for HCCH. The cis-HCNH⁺ isomer lies at 105.3 kcal mol⁻¹ compared to 79.1 kcal mol⁻¹ for the lowest cis-HCCH isomer; trans-HCNH⁺ lies at 113.6 kcal mol⁻¹ compared to 87.2 kcal mol⁻¹ for the lowest trans-HCCH isomer (where all energies are from DZ + P + CI calculations). Another comparison of interest between the two molecules is found in the close competition (less than 1 kcal at the DZ + P + CI level) at the different levels of theory between the energies of triplet H₂CN⁺ and triplet cis-HCNH⁺, which resembles that of triplet vinylidene and triplet cis-acetylene.¹⁹

Table IV lists the correlation energies for each isomer at both the DZ + CI level and the DZ + P + CI level. Three isomers have very similar correlation energies, but those of the H₂CN⁺ isomer are significantly smaller. These results indicate that the H₂CN⁺ isomer is better described by a single configuration SCF wave function than are the other isomers. The most obvious reason for this situation is the relatively large size of the H₂CN⁺ isomer, caused by its long C-N bond. (As the size of a molecule increases, its correlation energy decreases toward the sum of the atomic correlation energies.)

<table>
<thead>
<tr>
<th>Isomer</th>
<th>DZ + CI</th>
<th>DZ + P + CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNH₂⁺</td>
<td>99.9</td>
<td>147.4</td>
</tr>
<tr>
<td>H₂CN⁺</td>
<td>87.1</td>
<td>140.1</td>
</tr>
<tr>
<td>cis-HCNH⁺</td>
<td>97.3</td>
<td>140.1</td>
</tr>
<tr>
<td>trans-HCNH⁺</td>
<td>96.7</td>
<td>145.4</td>
</tr>
</tbody>
</table>

*¹DZ + CI energy – DZ energy.
*²DZ + P + CI energy – DZ + P energy.
Mulliken populations

Figure 4 shows the net atomic charges resulting from the Mulliken populations of the triplet states and the linear singlet ground state. These charges show little resemblance to the formal charges of Fig. 3. For each structure a hydrogen atom has a net charge of about +0.3 when bonded to carbon, and about +0.4 when bonded to nitrogen. The carbon and nitrogen atoms exhibit somewhat greater variations in net charge. They have their most positive values when in the terminal position of an \( H_2XY^+ \) structure, and their most negative (or least positive) values when in the central position of the same structure. It appears that differences in electronegativity between the different atoms are largely responsible for the different net charges.

Although the concept of population analysis is not very precise, the results of population analyses are often helpful in providing at least a qualitative understanding of problems of molecular structure, and such is the case here. For both the cis and trans isomers the atoms bonded to nitrogen have substantial positive net atomic charges; repulsion between these charges would be expected to lead to relatively large CNH bond angles. On the other hand, the atoms bonded to carbon have charges of opposite sign (the charge on one atom, i.e., nitrogen, being very close to zero), and therefore the HCN bond angles would be expected to be somewhat smaller. While it is not suggested that net atomic charge is the only factor that influences bond angles, these arguments offer a qualitative explanation for the observation that the HNC bond angles are in fact substantially larger than the HCN bond angles, as noted above in the section on Structures.

ASTROPHYSICAL IMPLICATIONS

Thermochemistry

To assist in visualizing the energy changes involved in various paths for the formation of HCN or HNC by way of an \( H_2CN^+ \) intermediate, some of the different structures and their energies are shown in Fig. 5. It may be seen that one has a series of exothermic pathways lead-
ing from \( C^+ + \text{NH}_3 \) through the various isomers of the dihydrogen cyanide cation to HCN or HNC. The most commonly postulated pathway is the sequence

\[
\text{(1)} \quad C^+ + \text{NH}_3 \rightarrow \text{H}_2\text{CN}^- + \text{H}, \\
\text{(2)} \quad \text{H}_2\text{CN}^- + e^- \rightarrow \text{H} + \text{HCN} \quad \text{(or \ HNC)}.
\]

Other reactions which can lead to formation of \( \text{H}_2\text{CN}^- \) are

\[
\text{(3)} \quad \text{N}^+ + \text{CH}_3 \rightarrow \text{H}_2\text{CN}^- + \text{H}, \\
\text{(4)} \quad \text{CH}_3^+ + \text{N} \rightarrow \text{H}_2\text{CN}^- + \text{H}.
\]

Reaction (4) is known to have a much smaller rate constant than Reaction (1). Besides Reaction (2), another reaction which converts \( \text{H}_2\text{CN}^- \) to HCN or HNC is deprotonation by bases such as \( \text{NH}_3 \):

\[
\text{(5)} \quad \text{H}_2\text{CN}^- + \text{B} \rightarrow \text{B}^- + \text{HCN} \quad \text{(or \ HNC)}.
\]

Other reactions which compete with Reaction (2) include

\[
\text{(6)} \quad \text{H}_2\text{CN}^- + e^- \rightarrow \text{CN} + 2\text{H}, \\
\text{(7)} \quad \text{H}_2\text{CN}^- + e^- \rightarrow \text{CH} + \text{H}_3, \\
\text{(8)} \quad \text{H}_2\text{CN}^- + e^- \rightarrow \text{CH} + \text{NH}.
\]

If Reaction (1) or (3) forms \( \text{H}_2\text{CN}^- \) in a triplet state, one would expect it to have the \( \text{H}_2\text{NC}^- \) structure. In Reaction (1) two hydrogen atoms should remain bonded to nitrogen, yielding the \( \text{H}_2\text{NC}^- \) isomer directly. In Reaction (3) two hydrogen atoms should remain bonded to carbon, yielding the \( \text{H}_2\text{CN}^- \) isomer; because of the exothermicity of Reaction (3) (~103 kcal to form this triplet) isomerization to the lowest triplet state of structure \( \text{H}_2\text{NC}^- \) is likely to occur, even if as for triplet vinylidene rather large barriers exist to 1, 2 hydrogen shifts. The molecule should remain in this structure until either (a) the forbidden transition to the singlet \( \text{H}_2\text{NC}^- \) isomer occurs, or (b) the molecule reacts with an electron or a base [Reaction (2) or Reactions (5)–(8)]. Because of the much higher energies of both \( \text{H} + \text{CN}^- \) and \( \text{H} + \text{HCN}^- \), there appears to be no possibility of either molecular or radical dissociation of triplet \( \text{H}_2\text{NC}^- \) analogous to the dissociation of triplet formaldehyde unless the \( \text{H}_2\text{CN}^- \) is formed by Reaction (3) and retains most of the energy change of Reaction (3) in its vibrational modes.

For the singlet isomers, the linear structure has the lowest energy. The \( \text{H}_2\text{NC}^- \) singlet isomer can react directly with an electron or a base [Reactions (2) and (5)] or else it can first isomerize to the linear structure. This point will be discussed further in the next section. (The \( \text{H}_2\text{CN}^- \) isomer is apparently not represented by a minimum on the DZ + P SCF potential energy surface, and it has therefore been omitted from Fig. 5.)

If the linear singlet ground state of \( \text{H}_2\text{CN}^- \) is formed, either directly by Reaction (1), (3), or (4), or indirectly via another state of \( \text{H}_2\text{CN}^- \), it should eventually react with an electron or a base and form HCN or HNC [Reactions (2) and (5)] or other products [Reactions (6)–(8)]. Although Reaction (8) is slightly endothermic for the linear singlet ground state, the \( \text{H}_2\text{CN}^- \) ion should initially possess considerable vibrational energy from the large exothermicity of the reactions leading to its formation. If this energy has not been entirely removed by collisional deactivation, then Reaction (8) may occur.

Once HCN (or HNC) has been formed, \( \text{H}_2\text{NC}^- \) can be regenerated by reactions such as

\[
\text{(9)} \quad \text{HNC} + \text{H}_2 \rightarrow \text{H}_2\text{CN}^- + \text{H}_2, \\
\text{(10)} \quad \text{HCN} + \text{HCO}^- \rightarrow \text{H}_2\text{CN}^- + \text{CO}.
\]

Other reactions to be considered are the direct formation of \( \text{HCN}^- \) (or \( \text{HNC}^- \)) followed by electron capture from an atom or molecule having a lower ionization potential:

\[
\text{(11)} \quad \text{C}^+ + \text{NH}_3 \rightarrow \text{H}_2 + \text{HCN}^- \quad \text{(or \ HNC)}, \\
\text{(12)} \quad \text{N}^+ + \text{CH}_3 \rightarrow \text{H}_2 + \text{HCN}^- \quad \text{(or \ HNC)}, \\
\text{(13)} \quad \text{CH}_3^+ + \text{N} \rightarrow \text{H}_2 + \text{HCN}^- \quad \text{(or \ HNC)}, \\
\text{(14)} \quad \text{HCN}^- \quad \text{(or \ HNC)} + \text{X} + \text{X}^+ \rightarrow \text{HCN} \quad \text{(or \ HNC)}.
\]

Reaction (11) has a much smaller rate constant than Reaction (1).

**Relative abundances of HCN and HNC**

One of the many strange features of the chemistry of interstellar clouds is the fact that the abundances of HCN and HNC are of the same order of magnitude, in spite of the fact that the energy of HNC lies ~0.63 eV or ~14.5 kcal mol\(^{-1}\) above the energy of HCN. In some clouds the HNC abundance is significantly greater than that of HCN. Clearly, these two molecular species are very far indeed from equilibrium, for the equilibrium constant for the reaction

\[
\text{HCN} \rightleftharpoons \text{HNC}
\]

has been estimated to be about \( 10^{30} \) at 100 K. Furthermore, a recent study indicates that in a comparison of two interstellar cloud types, the ratio [HNC]/[HCN] is actually higher in the type of cloud which is regarded as more chemically evolved.

To explain the relatively high abundance of HNC, it has been suggested that when the linear singlet ground state undergoes Reaction (2), the CH and NH bonds rupture with about the same probability, leading to the production of approximately equal amounts of HCN and HNC. A recent statistical study of Reaction (2) supports this hypothesis. However, this explanation does not seem to encompass those interstellar clouds where the [HNC]/[HCN] ratio is substantially larger than one.

A possible route to the production of HNC without simultaneously forming HCN was suggested by Brown. If only one N–H bond ruptures in Reaction (1), then the \( \text{H}_2\text{NC}^- \) isomer will be produced exclusively, and when this isomer undergoes Reaction (2) one would expect that only HNC would be formed. A difficulty with this suggestion is the large amount of energy released in Reaction (1). When this is taken into account along with the relative ease with which the singlet \( \text{H}_2\text{NC}^- \) isomerizes to the linear ground state (the energy barrier is ~29.6 kcal mol\(^{-1}\)), it seems likely that the singlet \( \text{H}_2\text{NC}^- \) would...
have sufficient excitation energy to isomerize to the linear ground state.

These arguments do not rule out the possibility that a triplet H$_2$NC$^\cdot$ isomer might play the role envisioned by Brown, and in fact this was one of the main reasons for the present investigation. [Formation of a triplet state of H$_2$NC$^\cdot$ by Reaction (1) is, of course, spin allowed.] Since the triplet H$_2$NC$^\cdot$ isomer is indeed the lowest energy state for the triplet manifold, it appears that the triplet path would lead to HNC exclusively, provided that Reaction (2) or (5) occurs prior to the forbidden transition to the singlet manifold. Unfortunately for this hypothesis, the average lifetime of an H$_2$CN$^*$ molecule before the occurrence of Reaction (2) has been estimated at about 300 years!$^{19}$ It seems extremely unlikely that the average lifetime of the triplet could be nearly this long. However, the phosphorescence of triplet H$_2$NC$^\cdot$ might provide sufficient radiative dissipation of excitation energy to cool off the molecule to the point where the singlet H$_2$NC$^\cdot$ isomer would have insufficient energy to isomerize to the linear singlet ground state. It would then remain in this structure until the occurrence of Reaction (2) or (5), producing HNC without any HCN (see Fig. 6). The HNC would, of course, be accompanied by CN, CH, and NH from Reactions (6)–(8). Whether a particular C$^\cdot$ ion and NH$_3$ molecule react via the triplet or singlet path is presumably dictated by statistical considerations. (One should also consider infrared chemiluminescence by triplet H$_2$NC$^\cdot$, which might remove substantial amounts of vibrational excitation energy prior to phosphorescence. In the present state of knowledge it appears to be difficult to estimate the relative importance of this process.)

Will phosphorescence of triplet H$_2$NC$^\cdot$ remove sufficient energy to prevent isomerization of the singlet H$_2$NC$^\cdot$ isomer to the linear singlet ground state? The answer to this question depends on the energy distribution in the products of Reaction (1). One way to estimate the energy distribution is by looking at studies of reactions of molecules of a similar degree of complexity. Such a study is the investigation by Farrar and Lee$^{18}$ of the reaction

\[ \text{F} + \text{C}_2\text{H}_4 \rightarrow \text{H} + \text{C}_2\text{H}_2\text{F} \]

They found that about 50% of the exothermicity of the reaction went into the relative translational kinetic energies of the products, with a rather broad distribution. Comparing this reaction with Reaction (1), we note two differences. They affect the relative proportions of translational kinetic energy in opposite directions, so that their effects tend to cancel. (a) Reaction (1) is much more exothermic than the F + C$_2$H$_4$ reaction, for which the exothermicity is only ~14 kcal. With a larger exothermicity, the energy distribution of the products should more nearly approximate a classical equipartition, and therefore Reaction (1) might have a smaller fraction of energy going into translation. (b) Because H$_2$NC$^\cdot$ has one less heavy atom than C$_2$H$_2$F, H$_2$NC$^\cdot$ should have a smaller proportion of vibrational energy, and Reaction (1) should yield products having a larger proportion of translational kinetic energy.

Another approach to the energy distribution (which, in light of Farrar and Lee's results, may be wrong) is to assume a statistical distribution of the reaction energy among the different degrees of freedom. This could be done precisely if one determined the vibrational frequencies of triplet H$_2$NC$^\cdot$, or assumed that they are similar to those of another molecule (formaldehyde, for example). Two crude calculations are as follows: (a) Assume that the quantum vibrational distributions are roughly represented by classical vibrational distributions for all atoms but hydrogen. In this case we have only the C–N stretch, with two squared terms in the energy. There are also three terms for relative rotational energy and three terms for relative translational energy. Under equipartition of energy, there is then $\frac{1}{3}$ = 37.5% of the total energy in translation. Also, most of the rotational energy should be unavailable for transfer to vibrational modes because of conservation of angular momentum. (The moments of inertia do not appear to change much in going from singlet H$_2$NC$^\cdot$ to the transition state.) So perhaps close to $\frac{1}{3}$ is 75% of the total energy is unavailable for transfer to vibrational modes. (However, note that Farrar and Lee found <5% of the total energy in rotational excitation.) (b) To consider an extreme case, suppose that all six vibrational modes are excited classically. Then there are $(2 \times 6) + 3 + 3 = 18$ fully excited squared terms of which $\frac{1}{18} = 16.7\%$ is translational energy and $\frac{3}{3} = 18.7\%$ is rotational energy. Let us now consider the energy changes in these reactions. They are

\[ \text{C}^\cdot + \text{NH}_3 \rightarrow \text{H}_2\text{NC}^\cdot(7) + \text{H}, \quad \Delta E = -46.6 \text{ kcal} \]
\[ \Delta E = -51.2 \text{ kcal} \]
\[ \text{H}_2\text{NC}^\cdot(7) + \text{H} \]
\[ \Delta E = -46.0 \text{ kcal (barrier = 29.6 kcal)} \]
\[ \text{HCNH}^\cdot(5) + \text{H} \]

...
To prevent isomerization to the linear singlet ground state by the triplet path, more than 46.6 - 29.6 = 17.0 kcal or >36.5% of the energy of the first reaction must go into translational energy plus unavailable rotational energy, assuming that 51.8 kcal are emitted as light. (Because singlet and triplet H₂NC⁺ isomers have very similar structures, the phosphorescence energy should be about equal to the difference in energy between the minima of the two potential surfaces.) To prevent isomerization by the strictly singlet path more than 97.8 - 28.6 = 68.2 kcal or >69.7% of the reaction energy must go into translational energy plus unavailable rotational energy.

If one uses the proton affinity of HCN from Ref. 29, then ΔH°° of H₂CN⁺ is 228.5 kcal at 298 K or 227.9 kcal at 0 K. This reduces the exothermicity of Reaction (2) by 3.5 kcal, and the fraction of the reaction energy which must go into translational energy plus unavailable rotational energy to prevent isomerization becomes 31.3% for the triplet path, and 68.6% for the singlet path.)

The above analysis leads us to conclude that a large majority of molecules following the triplet path will not have sufficient energy to isomerize, and therefore the triplet path will yield HNC as the major product. On the other hand, a large majority of molecules following the singlet path will have sufficient energy to isomerize to the linear singlet ground state, and therefore the singlet path will yield both HCN and HNC in approximately equal amounts.

As a final point it is of interest that whereas triplet states usually are important to the extent that they are low in energy, in this system the triplet state is important because it is high in energy, enabling phosphorescence to remove a large part of the excitation energy of the molecule.

Deuterium isotope effect

Another remarkable feature of the chemistry of interstellar clouds is the very large deuterium enrichment of HCN and HNC. Whereas an overall [D]/[H] ratio of 1.8 × 10⁻⁵ characterizes a large part of the galaxy, ⁴¹,⁴² in certain sources HCN is enriched 10⁰-fold in deuterium. ⁴³ Enrichment of HNC is even larger ⁴⁰,⁴⁴; excluding sources near the galactic center, the ratio [DNC]/[HCN] varies from 0.04 to 1.3, corresponding to enrichment by factors in the range from 2000- to 70,000-fold.

These isotope effects have been often explained on the basis of equilibrium considerations, where differences in zero-point energies can lead to very substantial isotopic enrichment. However, it has been pointed out ⁴⁵,⁴⁶ that it is impossible to reconcile the assumption of equilibrium for reactions involving HNC with the fact that such equilibrium would convert practically all HNC to the more stable isomer HCN. The equilibrium hypothesis is also at variance with observations of the effect of source temperature on isotopic composition of HCN. ⁴⁶

Consideration of possible mechanisms ⁶ for deuterium enrichment of HCN and HNC has been hampered by lack of information on the ratio [NH₂D]/[NH₃], which of course affects the deuterium content of HCN and HNC formed by Reactions (1) and (2). However, a recent study ⁴⁵ indicates that this ratio is very large, of the order of unity, such that [NH₂D]/[NH₃] ≈ [DNC]/[HCN]. It is thus possible that the deuterium enrichment in Reactions (1) and (2) is relatively small, occurring mainly by the breaking of N–H bonds (in preference to the breaking of N–D bonds) as suggested by Brown. ⁸

Rather than a mechanism for deuterium enrichment of either HNC or HCN, what seems to be needed is a mechanism for the deuterium depletion of the HCN isomer, which appears to have a deuterium content much lower than that of HNC. The most obvious candidate is the following. Because of its relative instability, all observed HNC must be relatively new. (It includes, of course, not only HNC formed directly by Reactions (1)-(4), but also HNC formed by the recycling of HCN and HNC through Reactions (9), (10), and (2).) As it ages, it undergoes isomerization by reactions such as

\[ \text{HCN} + H^- + H^+ + \text{HCN} \]  (16)

Thus, the deuterium content of existing HNC is identical to that of nascent HNC from Reaction (2). On the other hand, HCN, being the stable isomer, will equilibrate its deuterium content with that of the pool of hydrogen, and the ratio [DNC]/[HCN] will decrease toward the equilibrium value.

As a final point, we wish to note a possible mechanism for isotopic enrichment which we have not seen discussed in connection with the chemistry of interstellar clouds, namely, isotopic differences in branching reactions. When there are two or more channels for the products of two reacting species, then there exists the possibility of relatively large isotopic variations in the relative rates of the different channels. For example, the reaction between an electron and the H₂NC⁺ isomer leads to several possible products [Reactions (2) and (6)-(8)]. The relative amounts of the different products should depend on the vibrational–rotational density of states for the products of each channel, ⁸ and this density should be sensitive to the deuterium content of the H₂NC⁺ isomer.

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APPENDIX

Standard heats of formation used to construct Fig. 5 are listed below; all data are in kcal mol⁻¹ and refer to the hypothetical ideal gas at 0 K; H₂CN⁺ refers to the linear singlet ground state of structure HCNH⁺: C, 429.14; CH, 141.2; CH₂, 55.62; CH₃, 262.60; CN, 103.2; CN⁺, 428.6; HCN, 32.39; HCN⁺, 353.2; HNC, 47.0; H₂CN⁺, 224.4; H⁺, 51.634; H**, 365.236; H, 355.727; N, 112.5; N⁺, 447.6; NH, 90.15; NH₂, -9.30.

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