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A possible role for triplet H_2CN^+ 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 H_2CN^+ have been determined by self-consistent field and configuration interaction calculations. When both hydrogen atoms are attached to the nitrogen atom, H_2NC^+, 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_{2v} symmetry, with an HCH bond angle of 116.8°, and bond lengths of 1.009 Å (H–N) and 1.268 Å (N–C). Other isomers investigated include the H_2CN^+ isomer at 104.7, the *cis*-HCNH$^+$ isomer at 105.3, and the *trans*-HCNH$^+$ isomer at 113.6 kcal mol^{-1}. The H_2CN^+ isomer has an unusual "carbonium nitrene" structure, with a C–N bond length of 1.398 Å. It is suggested that the triplet H_2NC^+ isomer may play a role in determining the relative yields of HCN and HNC from the reaction of C^+ and NH_3. Specifically, a triplet path is postulated in which C^+ and NH_3 yield the triplet H_2NC^+ isomer, which then yields the singlet H_2NC^+ isomer by phosphorescent emission. Because this emission removes a large amount of energy, the singlet H_2NC^+ 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 H_2CN^+ 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.[1–12] The structures and energies of the lowest singlet states of three isomers of H_2CN^+ have previously been calculated by the techniques of molecular quantum mechanics,[3,13,14] 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,[15–20] we have calculated the structures and energies of the lowest triplet states of four isomers of H_2CN^+.

THEORETICAL APPROACH

Our first investigations were of the restricted self-consistent-field type[21] using the standard contracted double zeta (DZ) Gaussian basis set of Huzinaga[22] and Dunning.[23] 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[24] in a form developed for open-shell calculations.[25] To determine the orbital occupancy having the lowest energy for each isomer, the initial calculations were made in C_1 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_s or C_{2v} 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 $(4s1p/2s1p)$. 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_{2v} symmetry was 4505 (CNH_2^+) and 4488 (H_2CN^+), and 8878 for the two isomers with C_s symmetry. All CI calculations were performed with the graphical unitary group approach (GUGA) programs.[26]

RESULTS

Orbital energies

The four isomers studied were CNH_2^+, H_2CN^+, *cis*-HCNH$^+$, and *trans*-HCNH$^+$. Table I lists the electronic configuration of the lowest triplet state of each isomer. When all structures are viewed in C_s symmetry, it may be seen that the H_2CN^+ isomer involves a different excitation than the other three isomers. However, the different excitations for the CNH_2^+ and H_2CN^+ isomers

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

Isomer	Symmetry	Electronic configuration	Excitation	Excitation in C_s symmetry
CNH_2^+	C_{2v}	$1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_1^2 5a_1^2 1b_1^2 2b_2$	$5a_1 \rightarrow 2b_2$	$6a' \rightarrow 7a'$
H_2CN^+	C_{2v}	$1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_2^2 5a_1^2 1b_1 2b_2$	$1b_1 \rightarrow 2b_2$	$1a'' \rightarrow 7a'$
cis-HCNH$^+$	C_s	$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a' 1a''^2 7a'$	$6a' \rightarrow 7a'$	$6a' \rightarrow 7a'$
$trans$-HCNH$^+$	C_s	$1a'^2 2a'^2 3a'^2 4a'^2 5a' 6a'^2 1a''^2 7a'$	$6a' \rightarrow 7a'$	$6a' \rightarrow 7a'$

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,[20] 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.[14] We interpret these bond lengths as indicating essentially double-bond character in all cases. (The sum of the double-bond radii[27(a)] is 1.29 Å.) For the H_2CN^+ triplet the C–N bond length is substantially longer (1.398 Å), which we interpret as indicating largely single-bond character. (The sum of the single-bond radii, corrected for electronegativity difference,[27(a)] is 1.47 Å. On using the Pauling relation between bond length and bond order,[27(b)] 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 elec-

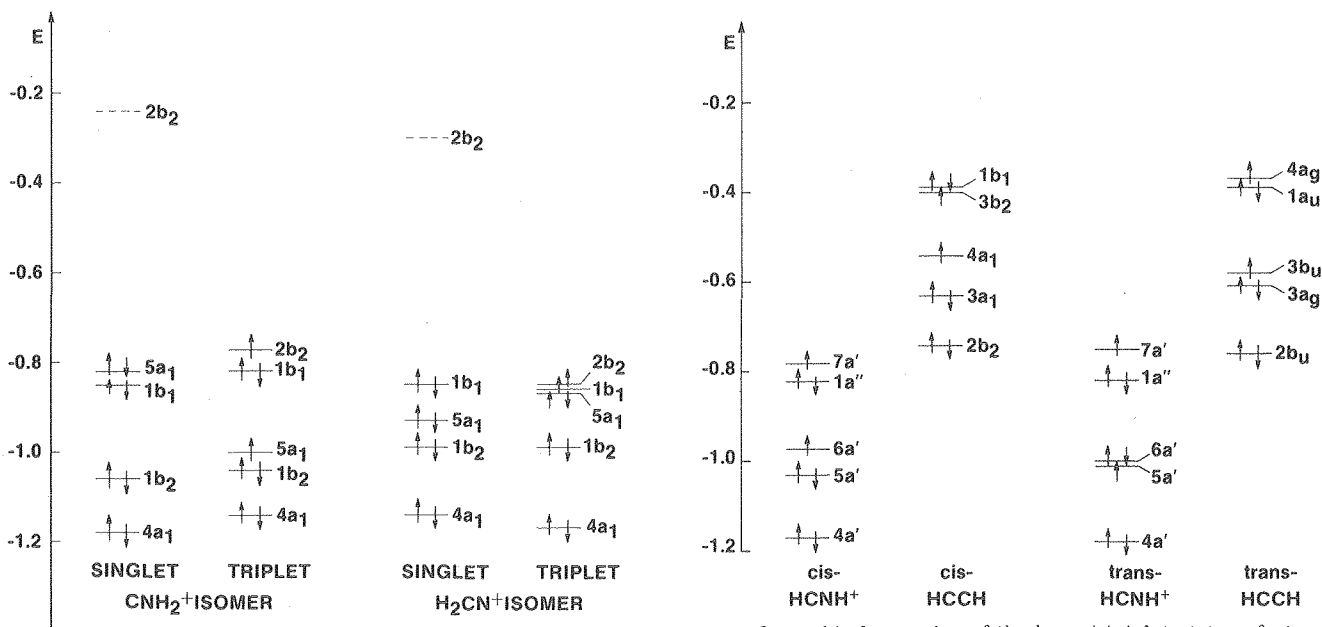FIG. 1. Orbital energies of the lowest singlet and triplet states of CNH_2^+ and H_2CN^+ isomers from a DZ basis.

FIG. 2. Orbital energies of the lowest triplet states of cis- and $trans$-acetylene and dihydrogen cyanide cation from a DZ + P basis.

TABLE II. Orbital energies of the lowest singlet and triplet states of the H_2CN^+ 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.

Isomer	State	Orbital energies (in hartree)			
Linear HCNH$^+$	Singlet	$1\sigma_g - 15.9578$	$1\sigma_u - 11.6789$	$2\sigma_g - 1.6224$	$2\sigma_u - 1.1887$
cis-HCNH$^+$	Triplet	$1a' - 15.9732$	$2a' - 11.6853$	$3a' - 1.5612$	$4a' - 1.1712$
trans-HCNH$^+$	Triplet	$1a' - 15.9677$	$2a' - 11.6837$	$3a' - 1.5548$	$4a' - 1.1865$
CNH$_2^+$	Singlet	$1a_1 - 15.9471$	$2a_1 - 11.7402$	$3a_1 - 1.6373$	$4a_1 - 1.1841$
CNH$_2^+$	Triplet	$1a_1 - 15.9414$	$2a_1 - 11.6933$	$3a_1 - 1.5894$	$4a_1 - 1.1403$
H$_2$CN$^+$	Singlet	$1a_1 - 16.0645$	$2a_1 - 11.6526$	$3a_1 - 1.6232$	$4a_1 - 1.1384$
H$_2$CN$^+$	Triplet	$1a_1 - 15.9754$	$2a_1 - 11.7059$	$3a_1 - 1.5078$	$4a_1 - 1.1694$
Linear HCNH$^+$	Singlet	$3\sigma_g - 1.0768$	$1\pi_u - 0.8543$		
cis-HCNH$^+$	Triplet	$5a' - 1.0328$	$1a'' - 0.8186$	$6a' - 0.9785'$	$7a' - 0.7816$
trans-HCNH$^+$	Triplet	$6a' - 1.0054$	$1a'' - 0.8170$	$5a' - 1.0187$	$7a' - 0.7551$
CNH$_2^+$	Singlet	$1b_2 - 1.0620$	$1b_1 - 0.8475$	$5a_1 - 0.8181$	
CNH$_2^+$	Triplet	$1b_2 - 1.0394$	$1b_1 - 0.8173$	$5a_1 - 1.0046$	$2b_2 - 0.7674$
H$_2$CN$^+$	Singlet	$1b_2 - 0.9904$	$5a_1 - 0.9280$	$1b_1 - 0.8548$	
H$_2$CN$^+$	Triplet	$1b_2 - 0.9945$	$5a_1 - 0.8658$	$1b_1 - 0.8613$	$2b_2 - 0.8521$

tronic structures of these molecules, then the two unpaired electrons are both localized on the carbon atom in the CNH$_2^+$ isomer, and are both localized on the nitrogen atom in the H$_2$CN$^+$ 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 CNH$_2^+$ isomer, the largest coefficient in each singly occupied MO belongs to a carbon AO (specifically, p_x or p_z), while the reverse is true for the H$_2$CN$^+$ 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_x) has the largest coefficient for the other singly occupied MO. (The C—N axis is designated z, and the y 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 H$_2$CN$^+$ isomer is particularly intriguing, as it may be regarded as a "carbonium nitrene." To have both a carbonium 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[20] 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 CNH$_2^+$ isomer has the lowest energy and the trans-HCNH$^+$ isomer has the highest energy. The H$_2$CN$^+$ isomer is second lowest at all levels but DZ + CI, and for the DZ + P level it has practically the same energy as the CNH$_2^+$ isomer.

The fact that the CNH$_2^+$ 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 CNH$_2^+$ and the H$_2$CN$^+$ isomers.

TABLE III. Energies of the lowest triplet states of four isomers of H_2CN^+, relative to the energy of the linear singlet ground state.[a] Energies are in kcal mol^{-1}.

Isomer	DZ	DZ + CI	DZ + P	DZ + P + CI
CNH$_2^+$	73.3	93.6	77.5	97.2
H$_2$CN$^+$	78.2	111.4	77.7	104.7
cis-HCNH$^+$	82.5	105.5	84.2	105.3
trans-HCNH$^+$	89.6	113.2	91.8	113.6

[a]Absolute energies of the linear singlet ground state are -93.12904, -93.32082, -93.17575, and -93.44209 hartree at the four levels of theory, respectively.
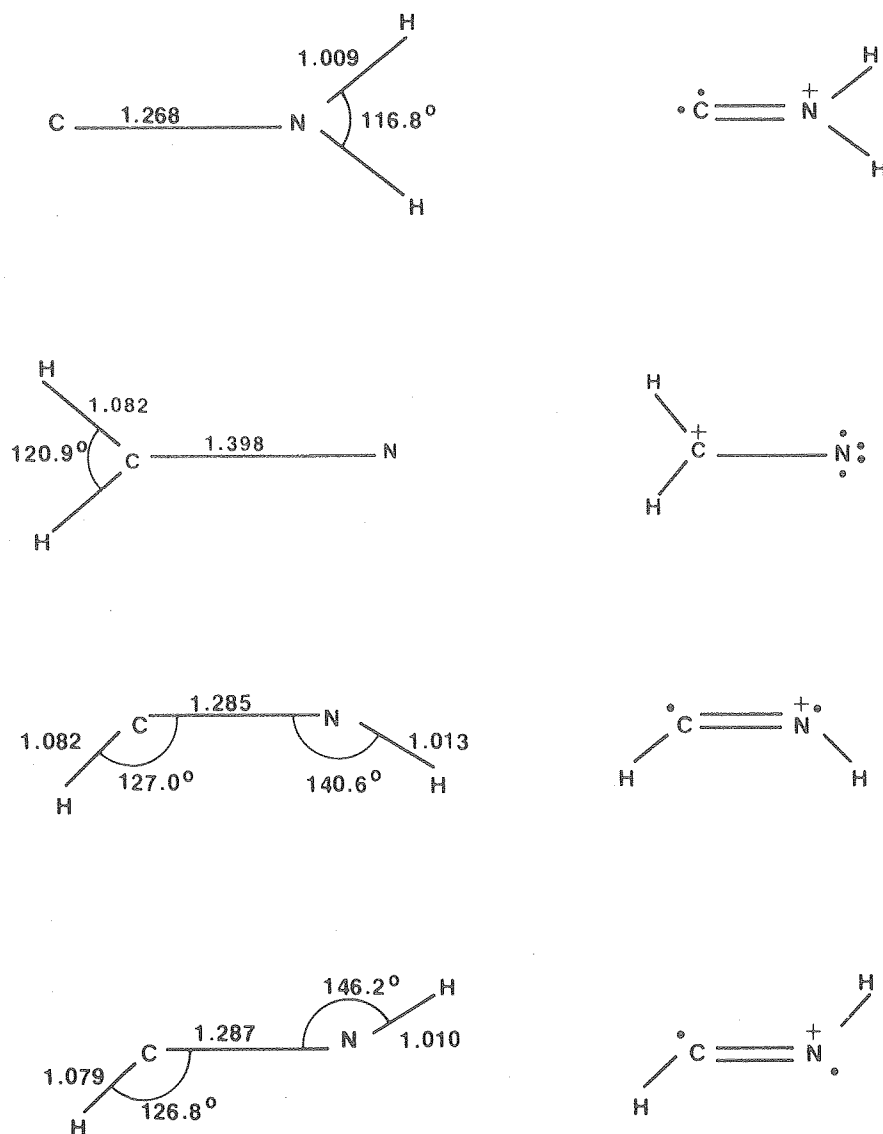
FIG. 3. Bond lengths and bond angles of the lowest triplet states for four isomers of H_2CN^+, from DZ SCF calculations, and the corresponding Lewis structures. Bond lengths are in Å.

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.[20] 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 H_2CN^+ 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 H_2CN^+ isomer are significantly smaller. These results indicate that the H_2CN^+ 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 H_2CN^+ 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 IV. Correlation energies (in kcal mol^{-1}) of the lowest triplet states of four isomers of H_2CN^+.

Isomer	DZ + CI[a]	DZ + P + CI[b]
CNH_2^+	99.9	147.4
H_2CN^+	87.1	140.1
cis-HCNH[+]	97.3	146.1
trans-HCNH[+]	96.7	145.4

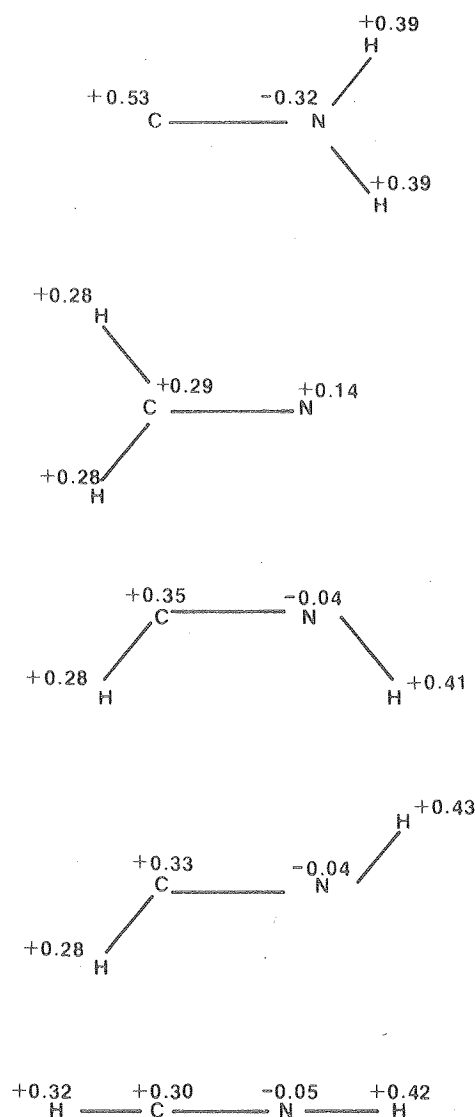[a]DZ + CI energy − DZ energy.
[b]DZ + P + CI energy − DZ + P energy.

FIG. 4. Net atomic charges from Mulliken populations of the triplet states and linear singlet ground state based on DZ + P SCF calculations.

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-
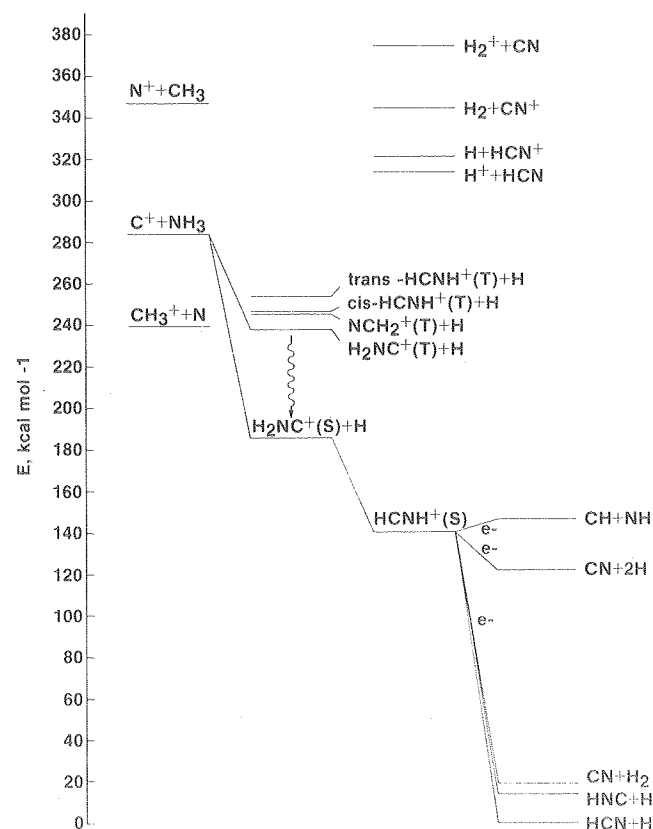
FIG. 5. Relative energies (in kcal mol^{-1}) of the H_2CN^+ system and related molecules. Data for H_2CN^+ in its linear singlet ground state [denoted HCNH$^+$(S)] are from Ref. 28 (see also Refs. 29–31). At 298 K, ΔH_f^0 of $H_2CN^+(g)$ is 225.0 kcal mol^{-1}; correction to 0 K assuming that $H_{298 K}^0 - H_{0 K}^0$ of H_2CN^+ is the same as that of acetylene decreases this value to 224.4 kcal mol^{-1}. Data for the singlet H_2NC^+ isomer are from Ref. 14; for the triplet states (T) of H_2CN^+ from this work; for HNC from Ref. 32; ionization potentials of C and N from Moore[33]; ionization potentials of H_2, HCN, and CH_3 from Herzberg[34]; other data from JANAF tables.[35] The various thermochemical data are summarized in the Appendix.

ing from $C^+ + NH_3$ through the various isomers of the dihydrogen cyanide cation to HCN or HNC. The most commonly postulated pathway[1-12] is the sequence
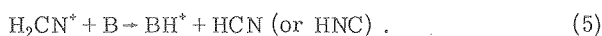
$$C^+ + NH_3 \rightarrow H_2CN^+ + H , \tag{1}$$

$$H_2CN^+ + e^- \rightarrow H + HCN \text{ (or HNC)} . \tag{2}$$

Other reactions which can lead to formation of H_2CN^+ are[8]

$$N^+ + CH_3 \rightarrow H_2CN^+ + H , \tag{3}$$

$$CH_3^+ + N \rightarrow H_2CN^+ + H . \tag{4}$$

Reaction (4) is known to have a much smaller rate constant than Reaction (1).[5,36]

Besides Reaction (2), another reaction which converts H_2CN^+ to HCN or HNC is deprotonation by bases such as NH_3,[5]:

$$H_2CN^+ + B \rightarrow BH^+ + HCN \text{ (or HNC)} . \tag{5}$$

Other reactions which compete with Reaction (2) include[9]

$$H_2CN^+ + e^- \rightarrow CN + 2H , \tag{6}$$

$$H_2CN^+ + e^- \rightarrow CN + H_2 , \tag{7}$$

$$H_2CN^+ + e^- \rightarrow CH + NH . \tag{8}$$

If Reaction (1) or (3) forms H_2CN^+ in a triplet state, one would expect it to have the H_2NC^+ structure. [In Reaction (1) two hydrogen atoms should remain bonded to nitrogen, yielding the H_2NC^+ isomer directly. In Reaction (3) two hydrogen atoms should remain bonded to carbon, yielding the H_2CN^+ isomer; because of the exothermicity of Reaction (3) (~ 103 kcal to form this triplet) isomerization to the lowest triplet state of structure H_2NC^+ is likely to occur, even if as for triplet vinylidene[19] 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 H_2NC^+ 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 $H_2 + CN^+$ and $H + HCN^+$, there appears to be no possibility of either molecular or radical dissociation of triplet H_2NC^+ analogous to the dissociation of triplet formaldehyde[37] unless the H_2CN^+ 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 H_2NC^+ singlet isomer can react directly with an electron or a base [Reactions (2) and (5)–(8)], or else it can first isomerize to the linear structure. This point will be discussed further in the next section. (The H_2CN^+ isomer is apparently not represented by a minimum on the DZ + P SCF potential energy surface,[14] and it has therefore been omitted from Fig. 5.)
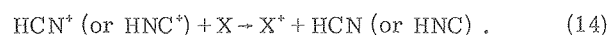
If the linear singlet ground state of H_2CN^+ is formed, either directly by Reaction (1), (3), or (4), or indirectly via another state of H_2CN^+, it should eventually react with an electron or a base and form HCN or HNC [Reactions (2) and (5)] or other products [Reactions (6)–(8)]. Although Reaction (8) is slightly endothermic for the lin-

ear singlet ground state, the H_2CN^+ 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, H_2NC^+ can be regenerated by reactions such as[5]

$$HCN + H_3^+ \rightarrow H_2CN^+ + H_2 , \tag{9}$$

$$HCN + HCO^+ \rightarrow H_2CN^+ + CO . \tag{10}$$

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

$$C^+ + NH_3 \rightarrow H_2 + HCN^+ \text{ (or } HNC^+) , \tag{11}$$

$$N^+ + CH_3 \rightarrow H_2 + HCN^+ \text{ (or } HNC^+) , \tag{12}$$

$$CH_3^+ + N \rightarrow H_2 + HCN^+ \text{ (or } HNC^+) , \tag{13}$$

$$HCN^+ \text{ (or } HNC^+) + X \rightarrow X^+ + HCN \text{ (or HNC)} . \tag{14}$$

Reaction (11) has a much smaller rate constant than Reaction (1).[5]

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.[32] 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

$$HCN \rightleftharpoons HNC \tag{15}$$

has been estimated to be about 10^{-30} at 100 K.[8] 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.[38]

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.[9] 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.[8] If only one N–H bond ruptures in Reaction (1), then the H_2NC^+ 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 H_2NC^+ isomerizes to the linear ground state (the energy barrier[14] is ~ 29.6 kcal mol^{-1}), it seems likely that the singlet H_2NC^+ would

$$C^+ + NH_3 \longrightarrow H_2NC^+(T) + H$$

$$H_2NC^+(S) + h\nu$$

$$\downarrow e^-$$

$$HNC + H$$

TRIPLET PATH

$$C^+ + NH_3 \longrightarrow H_2NC^+(S) + H$$

$$\downarrow$$
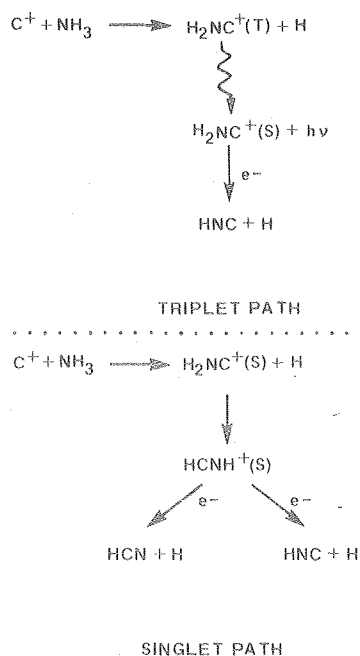
$$HCNH^+(S)$$

$$HCN + H \qquad HNC + H$$

SINGLET PATH

FIG. 6. Proposed triplet path (upper diagram) and singlet path (lower diagram) for the reaction of C^+ and NH_2.

have sufficient excitation energy to isomerize to the linear ground state.

These arguments do not rule out the possibility that a triplet H_2NC^+ 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_2NC^+ by Reaction (1) is, of course, spin allowed.] Since the triplet H_2NC^+ 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_2CN^+ molecule before the occurrence of Reaction (2) has been estimated at about 300 years![39] It seems extremely unlikely that the average lifetime of the triplet could be nearly this long. However, the phosphorescence of triplet H_2NC^+ might provide sufficient radiative dissipation of excitation energy to cool off the molecule to the point where the singlet H_2NC^+ 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^+ 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_2NC^+, 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_2NC^+ remove sufficient energy to prevent isomerization of the singlet H_2NC^+ isomer to the linear singlet ground state? The
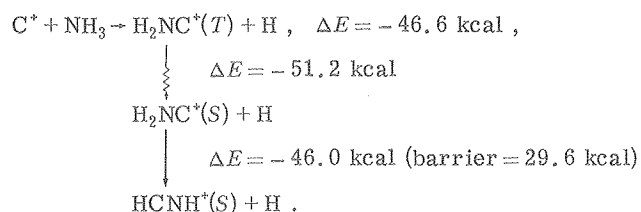
answer to this question depends on the energy distribution in the products of Reaction (1). One way to estimate the energy distribution is by looking at studies of reactions of molecules of a similar degree of complexity. Such a study is the investigation by Farrar and Lee[40] of the reaction

$$F + C_2H_4 \rightarrow H + C_2H_3F \quad .$$
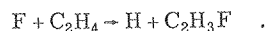
They found that about 50% of the exothermicity of the reaction went into the relative translational kinetic energies of the products, with a rather broad distribution. Comparing this reaction with Reaction (1), we note two differences. They affect the relative proportions of translational kinetic energy in opposite directions, so that their effects tend to cancel. (a) Reaction (1) is much more exothermic than the $F + C_2H_4$ 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_2NC^+ has one less heavy atom than C_2H_3F, H_2NC^+ 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_2NC^+, 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 $\frac{3}{8} = 37.5\%$ 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_2NC^+ to the transition state.) So perhaps close to $\frac{6}{8} = 75\%$ of the total energy is unavailable for transfer to vibrational modes. (However, note that Farrar and Lee found $\leqslant 5\%$ 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 $\frac{3}{18} = 16.7\%$ is translational energy and $\frac{3}{18} = 16.7\%$ is rotational energy.

Let us now consider the energy changes in these reactions. They are

$$C^+ + NH_3 \rightarrow H_2NC^+(T) + H, \quad \Delta E = -46.6 \text{ kcal},$$

$$\Delta E = -51.2 \text{ kcal}$$

$$H_2NC^+(S) + H$$

$$\Delta E = -46.0 \text{ kcal (barrier} = 29.6 \text{ kcal)}$$

$$HCNH^+(S) + H \quad .$$

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 51.2 kcal are emitted as light. (Because singlet and triplet H_2NC^+ 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 $97.8 - 29.6 = 68.2$ 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_f° of H_2CN^+ 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 $\times 10^{-5}$ characterizes a large part of the galaxy,[41,42] in certain sources HCN is enriched 100-fold in deuterium.[42] Enrichment of HNC is even larger[43,44]; excluding sources near the galactic center, the ratio $[DNC]/[HNC]$ 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[8,43] that it is impossible to reconcile the assumption of equilibria for reactions involving HNC with the fact that such equilibria 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.[42]

Consideration of possible mechanisms[8] for deuterium enrichment of HCN and HNC has been hampered by lack of information on the ratio $[NH_2D]/[NH_3]$, 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 $[NH_2D]/[NH_3] \simeq [DNC]/[HNC]$. 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

$$ HNC + H^+ \rightarrow H^+ + HCN . \tag{16} $$

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 $[DCN]/[HCN]$ 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 H_2NC^+ 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,[9] and this density should be sensitive to the deuterium content of the H_2NC^+ isomer.

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; H_2CN^+ refers to the linear singlet ground state of structure HCNH$^+$: C^+, 429.14; CH, 141.2; CH_3, 35.62; CH_3^+, 262.60; CN, 103.2; CN^+, 428.6; HCN, 32.39; HCN^+, 353.2; HNC, 47.0; H_2CN^+, 224.4; H, 51.634; H^+, 365.236; H_2^+, 355.727; N, 112.5; N^+, 447.6; NH, 90.15; NH_3, −9.30.

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