An ab Initio SCF Study on the Stability and Structure of $H_2CN^+ \cdot nN_2$ Clusters

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The clustering energies and geometries of the $H_2CN^+ \cdot nN_2$ ($n = 1$, 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_2CN^+ 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 $H_2CN^+ \cdot N_2$ cluster ion in a simulated laboratory mass spectroscopic 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_2CN^+ leading to $H_2CN^+ \cdot nN_2$ ($n = 1-6$) formation, $H_2CN^+ + nN_2 \rightarrow H_2CN^+ \cdot nN_2$. The experimental heat of formation of the $H_2CN^+ \cdot nN_2$ 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 $H_2CN^+ \cdot N_2$ 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, $H_2CN^+ + N_2$ have been reported in detail.

In the present theoretical study we extend our investigation to the $H_2CN^+ \cdot nN_2$ 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 $H_2CN^+ \cdot nN_2$ ($n = 1$, 2, 3) species and some fragments (N_2, H_2CN^+, 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 $H_2CN^+ \cdot nN_2$ ($n = 1$, 2 and 3) clusters and some of their fragments (H_2CN^+, N_2, HN_2, HCN and HNC), optimized with the split-valence 4-31G basis set, are shown in

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Figure 1. The total SCF energies and the relative energies of the $H_2CN^+ \cdot nN_2$ species with respect to the $H_2CN^+ \cdot (n-1)N_2$ 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 $H_2CN^+ \cdot N_2$ species might exist as a stable species in either two collinear conformations, $HCNH^+ \ldots N_2$ and $N_2 \ldots HCNH^+$, the former being more stable than the latter. The calculated energy difference between the more stable complex, $HCNH^+ \ldots N_2$ and its fragment was found to agree well with the estimated heat of formation of 7.65 kcal/mol from the laboratory experiment.

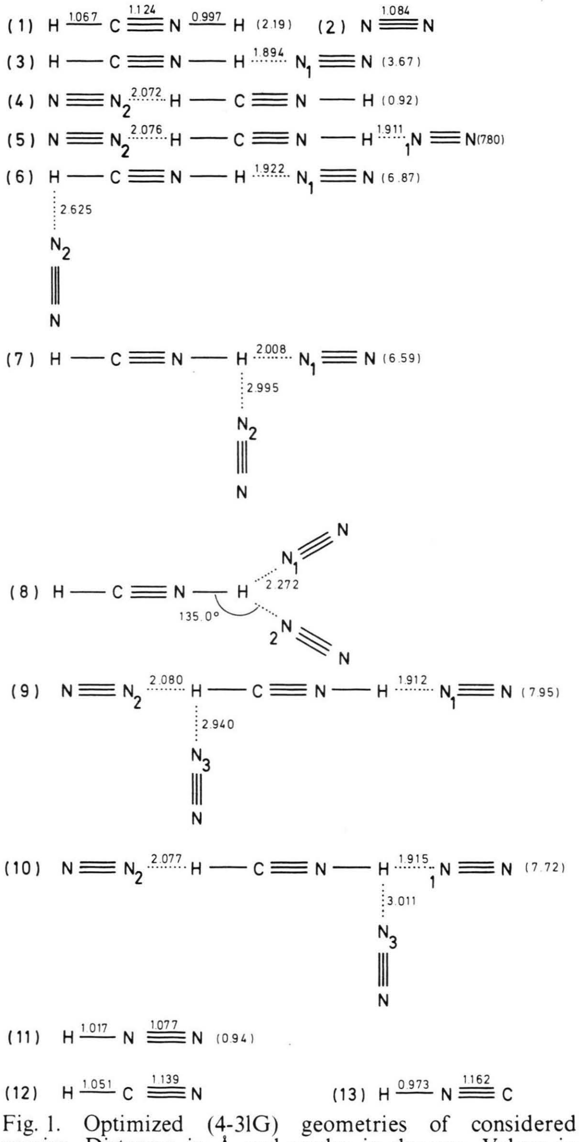

Fig. 1. Optimized (4-31G) geometries of considered species. Distances in Å and angles in degrees. Values in parentheses are the calculated dipole moment in Debye units.

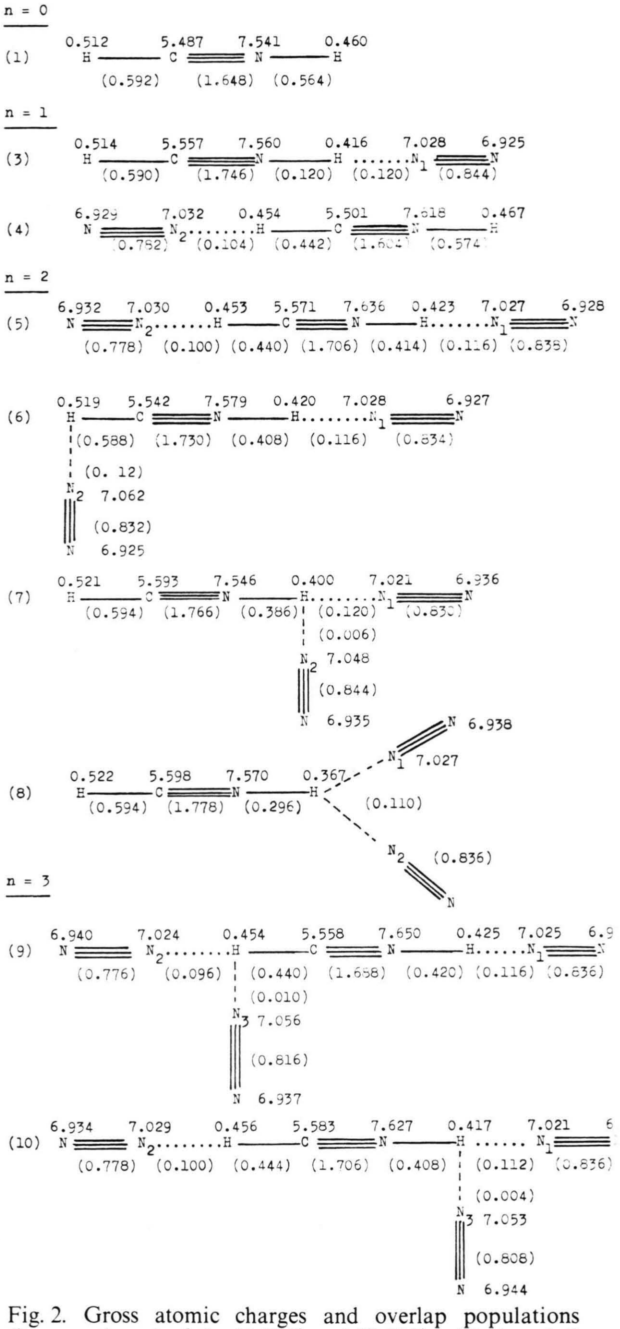

Fig. 2. Gross atomic charges and overlap populations (in parentheses) of the H_2CN^+ and $H_2CN^+ \cdot nN_2$ ($n = 1$, 2 and 3) species.

Table 1. Total and relative energies of the $HCNH^+ \cdot nN_2$ clusters and comparison with experiment.

n	Species[a]	E_T (a.u.)	$\Delta E_{n-1,n}$[b] (kcal/mol)	$\Delta H^0_{n-1,n}$[c] (kcal/mol)
0	$HCNH^+$ (1)	− 93.02235	−	−
	N_2 (2)	−108.75424	−	−
1	$HCNH^+ \ldots N_2$ (3)	−201.79084	−8.94	−7.65
	$N_2 \ldots HCNH^+$ (4)	−201.78805	−7.19	
2	$N_2 \ldots HCNH^+ \ldots N_2$ (5)	−310.55581	−6.73	−5.10
	$(N_2) \ldots HCNH^+ \ldots N_2$ (6)	−310.55047	−3.38	
	$HCNH^+ \ldots (N_2) \ldots N_2$ (7)	−310.54841	−2.09	
	$HCNH^+ \ldots (N_2)_2$ (8)	−310.54847	−2.12	
3	$N_2 \ldots (N_2) \ldots HCNH^+ \ldots N_2$ (9)	−419.31487	−3.02	−3.2
	$N_2 \ldots HCNH^+ \ldots (N_2) \ldots N_2$ (10)	−419.31339	−2.09	

[a] Values in parentheses are the numbering of molecules whose geometrical parameters are given in Figure 1.
[b] $\Delta E_{n-1,n} = E_T(HCNH^+ \cdot nN_2) - E_T(HCNH^+ \cdot (n-1)N_2) - E_T(N_2)$.
[c] 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 $N_2 \ldots HCNH^+ \ldots N_2$ conformer is shown to be unequivocally the most stable one. The calculated clustering energy ($\Delta E_{n-1,n}$) 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 $N_2 \ldots HCNH^+ \ldots N_2$ 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 $N_2 \ldots HCNH^+ \ldots N_2$ 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 $H_2CN^+ \cdot N_2$ complex, we have independently calculated the reaction paths of the following reactions:

$$\underset{(3)}{H{-}C{\equiv}N^+{-}H \ldots N{=}N} \rightarrow \underset{(12)}{H{-}C{\equiv}N} + \underset{(11)}{H{-}N{\equiv}N^+}$$

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

Species[a]	r(Å)[b]	Δr(Å)[c]	q(%)[d]	$\lvert\langle r^2\rangle\rvert^{1/2}$[e]
$n = 0$				
(2) $N{\equiv}N \ldots x$	0.345	0.0	−	1.350
$n = 1$				
(3) $x \ldots N_1{\equiv}N$	0.384	0.039	20.3	1.420
(4) $N{=}N_2 \ldots x$	0.377	0.032	18.2	1.407
$n = 2$				
(5) $N{\equiv}N_2 \ldots x$	0.376	0.031	18.1	1.406
$x \ldots N_1{\equiv}N$	0.382	0.037	20.0	1.408
(6) $N{\equiv}N_2 \ldots x$	0.365	0.020	13.9	1.310
$x \ldots N_1{\equiv}N$	0.382	0.037	19.9	1.409
(7) $N{\equiv}N_2 \ldots x$	0.358	0.013	12.7	1.381
$x \ldots N_1{\equiv}N$	0.379	0.034	18.9	1.408
$n = 3$				
(9) $x \ldots N_1{\equiv}N$	0.381	0.036	19.9	1.408
$N{\equiv}N_2 \ldots x$	0.375	0.030	18.0	1.404
$N{\equiv}N_3 \ldots x$	0.362	0.017	12.3	1.387
(10) $x \ldots N_1{\equiv}N$	0.381	0.035	19.8	1.407
$N{\equiv}N_2 \ldots x$	0.376	0.031	18.1	1.405
$N{\equiv}N_3 \ldots x$	0.357	0.012	11.9	1.380

[a] Values in parentheses are the numberings of molecules whose geometrical parameters are given in Figure 1. The centroids of the lone pair electrons are denoted by x.
[b] r is the distance between charge centroid and terminal nitrogen.
[c] Δr is the elongation of r with respect to free N≡N.
[d] $q = r/d(N \ldots H)$ is the ratio of r and the intermolecular distance $d(N \ldots H)$.
[e] $\langle r^2\rangle$ is the second moment of the lone pair orbital.

and

$$\underset{(4)}{N{\equiv}N\ldots H{-}C{\equiv}N^+{-}H} \rightarrow \underset{(11)}{N{\equiv}N{-}H^+} + \underset{(13)}{C{=}N{-}H}\,.$$

Both reactions are found to be endothermic and proceed without energy barrier. From Table 1, the $H{-}C{\equiv}N^+{-}H\ldots N{\equiv}N$ complex is calculated to be 70.8 kcal/mol more stable than its fragments HCN and HNN^+ and that the complex

$$N{\equiv}N\ldots H{-}C{\equiv}N^+{-}H$$

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 $N{\equiv}N$ 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 position (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 elongation 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 positively 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 reflects 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 (~ 7.8 Debye) of the weakly bonded $H_2CN^+ \cdot nN_2$ complexes calculated in the present study indicates that these species are relatively 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 conformations ($n = 1$), 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 simulated 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.

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