

A theoretical study for the reaction of vinyl cyanide $C_2H_3CN(X^1A')$ with the ground state carbon atom $C(^3P)$ in cold molecular clouds

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The reaction of the ground state atomic carbon, $C(^3P)$, with simple unsaturated nitrile, $C_2H_3CN(X^1A')$ (vinyl cyanide), is investigated theoretically to explore the probable routes for the formation of carbon–nitrogen-bearing species in extraterrestrial environments particularly of ultralow temperature. Five collision complexes without entrance barrier as a result of the carbon atom addition to the π systems of C_2H_3CN are characterized. The B3YLP/6–311G(d,p) level of theory is utilized in obtaining the optimized geometries, harmonic frequencies, and energies of the intermediates, transition states, and products along the isomerization and dissociation pathways of each collision complex. Subsequently, with the facilitation of computed RRKM rate constants at collision energy of 0–10 kcal/mol, the most probable paths for each collision complexes are determined, of which the CCSD(T)/6–311G(d,p) energies are calculated. The major products predicted are exclusively due to the hydrogen atom dissociations, while the products of H_2 , CN, and CH_2 decompositions are found negligible. Among many possible H-elimination products, cyano propargyl (**p4**) and 3-cyano propargyl (**p5**) are the most probable, in which **p5** can be formed via two intermediates, cyano allene (**i8**) and cyano vinylmethylene (**i6**), while **p4** is yielded from **i8**. The study suggests this class of reaction is an important route to the synthesis of unsaturated nitriles at the temperature as low as 10 K, and the results are valuable for future chemical models of interstellar clouds. © 2005 American Institute of Physics. [DOI: 10.1063/1.1846672]

I. INTRODUCTION

The significance of the neutral–neutral reactions in the astronomical environments such as interstellar clouds has been recognized only fairly recently compared with the ion–molecule reactions.^{1,2} It can be attributed to the conception that while it is barrierless along the entrance channel of the ion–molecule reaction which results in a near gas-kinetics rate, the often present barrier slows down the neutral–neutral reaction in general. In the interstellar clouds, where the density is low and the temperature in the range of 10–50 K, the reaction is required to be almost barrierless to occur. Nevertheless, the measured absolute rate constants of the reactions such as the ground state carbon atom $C(^3P)$ with unsaturated hydrocarbons, and the CN radical with various hydrocarbons at both room^{3–11} and ultralow^{12–14} temperatures are surprisingly of gas-kinetics magnitude, an indication these reactions are barrierless and capable of competing effectively with the ion–molecule reactions at low temperature. The laboratory findings have prompted Herbst and co-workers^{2,15} to include more neutral–neutral reactions in the chemical model that intends to explain and predict the abundances of species in

the interstellar clouds. Intriguingly the incorporation is found to influence the predicted abundances greatly, which confirms the essential role of the neutral–neutral reactions and at the same time signifies potentially more varieties should be considered. However, the lack of enough studied neutral–neutral reactions related to the interstellar chemistry hinders the development of an accurate model: the rate investigations are very often based on the consumption of reactants without the elucidation of reaction paths and products so that many reactions integrated in the model are speculative. The situation in parts triggers recent surge of investigations on the neutral–neutral reactions.

The reactions of carbon atom are particularly important in the synthesis and growth of complex hydrocarbon molecules. Studies^{16–29} of prototype $C(^3P)$ +unsaturated hydrocarbon reactions with crossed-beam experiments, or with combined *ab initio* calculations and crossed-beam experiments, make possible the reaction path scrutinization and the product observation. Together these results and the rate measurements based on $C(^3P)$ consumption provide a clearer picture of reaction mechanism and dynamics to reassert the $C(^3P)$ +unsaturated hydrocarbon reactions in the reaction networks of interstellar clouds.

Among the detected interstellar molecules and species in

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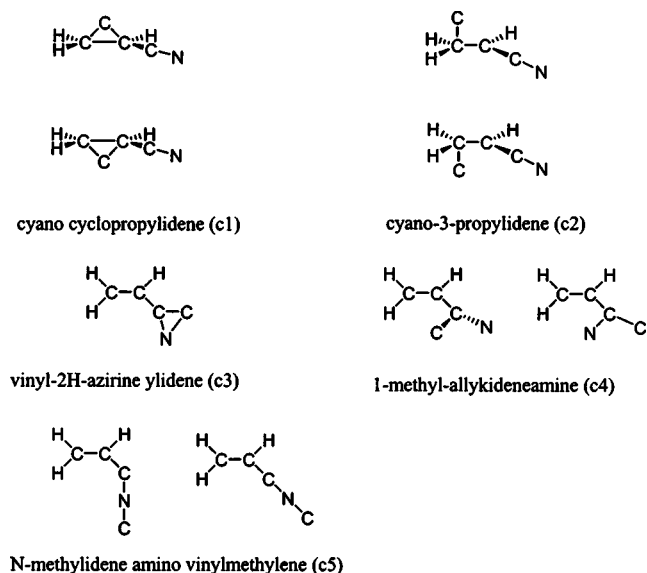


FIG. 1. The schematic diagram for the five collision complexes of $C(^3P) + C_2H_3CN(X^1A')$ reaction.

the atmospheres of planets and moons, nitriles are of particular interest as nitrogen-bearing species with strong relevance to the formation of biological molecules.³⁰ The significance of the rapid reactions of the CN radical with unsaturated hydrocarbons is well recognized in combustion chemistry, they are also implicated³¹ as a probable route to the nitrile formation and thus intensively investigated.^{32–40} $C(^3P) + \text{unsaturated nitrile}$ reaction would appear to be a logical and probable alternative to the $CN + \text{unsaturated hydrocarbon}$ reaction for the synthesis of nitriles. Indeed, in their chemical model of interstellar clouds, Herbst *et al.*¹⁵ incorporate the reaction of $C + HC_3N(\text{acetylene nitrile}) \rightarrow C_4N + H$, the feasibility of which is attributable to being analogous to the $C + \text{unsaturated hydrocarbon}$ reaction. Previous works indicate the reactions of $C(^3P) + \text{unsaturated hydrocarbon}$ are initiated by the carbon atom addition to the π system. Presumably through the addition to the carbon–carbon multiple-bond or the triple-bond of the cyano group resulting in multiple collision complexes, the carbon atom, abundant in the interstellar clouds, is expected to react rapidly with unsaturated nitriles, leading to versatile molecules of one more carbon unit including nitriles. However, the details concerning the reaction paths, products and the dynamics of the $C(^3P) + \text{unsaturated nitrile}$ reaction have not been examined. Theoretical study is especially of great value in elucidating reaction mechanism of which the intermediates, transition states and products that define reaction paths can be characterized, when generally speaking only reactant consumptions or product formations are observed in experiments. The vinyl cyanide (C_2H_3CN), or cyano ethylene, is an excellent prototype to investigate, considering that it is the simplest alkene nitrile and its existence in cold molecular clouds has been confirmed by the observation^{41,42} of rotational transitions. The aim of the current theoretical investigation is to identify the reaction paths with no entrance barrier, which are relevant to ultralow temperature environments of the interstellar

clouds, to calculate rate constants for the elementary steps, and to assess the product abundance for the reaction of $C(^3P)$ with $C_2H_3CN(X^1A')$.

II. THEORETICAL METHODS

A. *Ab initio* electronic structure calculations

Assuming the reaction proceeds adiabatically, channels of the $C(^3P) + C_2H_3CN(X^1A')$ reaction on the adiabatic triplet ground-state potential-energy surface of C_4H_3N are explored. The paths with energy below the reactants are emphasized since they are most likely to dominate in collision-induced reaction at ultralow temperature. The geometries and harmonic frequencies of intermediates, transition states, and products, which characterize the reaction pathways are obtained at the level of the hybrid density functional theory, B3LYP (Ref. 43)/6-311G(*d,p*). For the pathways identified as most probable, the corresponding coupled cluster⁴⁴ CCSD(T)/6-311G(*d,p*) energies with B3LYP/6-311G(*d,p*) zero-point energy corrections are calculated. The GAUSSIAN98 program⁴⁵ is utilized in the electronic structure calculations.

B. The RRKM rate constants

The rate constants of the elementary steps in the reaction mechanisms derived from the most probable paths are computed at collision energies, 0.0, 0.03, 0.15, 2, 5, and 10 kcal/mol, which are approximately equivalent to the average kinetic energy of an ideal gas molecule at temperatures of 0, 10, 50, 671, 1678, and 3355 K, respectively. If the rate of the energy equilibration among degrees of freedom in the molecule is faster than the reaction rate, the rate constant can be characterized statistically, and if the reaction is completed with single collision as in interstellar clouds and in crossed-beam experiments the energy is constant through out the course of the reaction. Under these circumstances the rate constant is appropriately described by the RRKM theory.

Briefly, in an unimolecular reaction $A^* \xrightarrow{k} A^\ddagger \rightarrow P$, where A^* is the energized reactant, $A^\ddagger$ the transition state, and P the products. The rate constant $k(E)$ is expressed as

$$k(E) = \frac{\sigma W^\ddagger(E - E^\ddagger)}{h \rho(E)},$$

where σ is the symmetry factor, $W^\ddagger$ the number of states of the transition state, and ρ the density of states of the reactant. In this work, the saddle-point method^{46,47} is applied to evaluate the number of states and the density of states, and the molecule is viewed as a collection of harmonic oscillators, of which the harmonic frequencies and energies are obtained in Sec. II A.

III. RESULTS AND DISCUSSION

A. Collision complexes

The collisions between carbon atom and vinyl cyanide may initially result in six collision complexes due to the carbon addition to the π systems. Namely, with the carbon–carbon double bond, $C(^3P)$ could form a three-member ring,

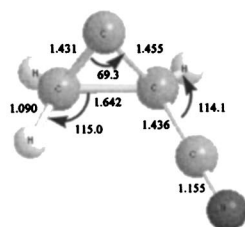
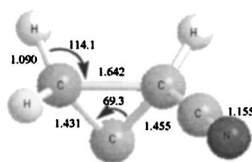
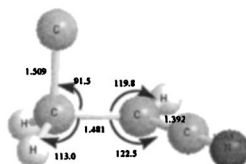
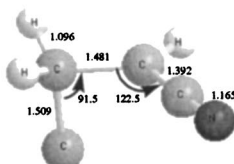
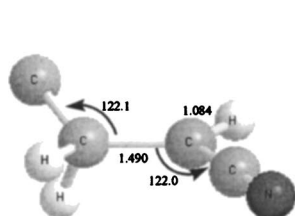
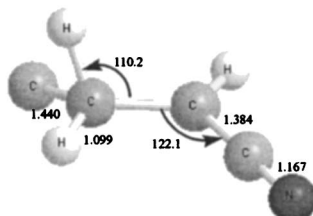
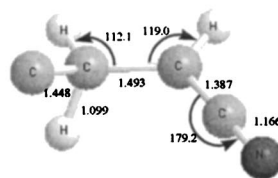
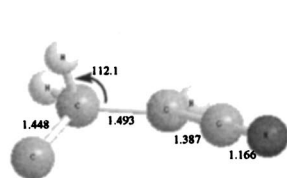
(a) c1 (cyano cyclopropylidene, C_1)**ap****bp****(b) c2 (cyano-3-propylidene, C_1)****ap****bp****trans****cis**

FIG. 2. The B3LYP/6-311G(*d,p*) optimized geometries of the conformers for the five collision complexes of $C(^3P) + C_2H_3CN(X^1A')$ reaction, in which the point group is in parentheses, lengths in angstrom, and the angles in degree.

or add to each of the end carbons, and likewise with the cyano group. All are located in the present work, except for the one resulting from carbon atom addition to the more substituted carbon of the double bond. Previous investigations (e.g., Ref. 48 and references therein) have indicated that in general, the radical attacks to the substituted olefins proceeds regioselectively, the attack on the less substituted carbon occurs more commonly. The schematic diagrams of these five collision complexes, cyano cyclopropylidene (**c1**), cyano-3-propylidene (**c2**), vinyl-2H-azirine ylidene (**c3**), 1-methyl-allylideneamine (**c4**), and *N*-methylidene amino vinylmethylene (**c5**), are depicted in Fig. 1; the B3LYP/6-311G(*d,p*) optimized geometries of their conformers are illustrated in Fig. 2. As anticipated, energy barrier is not found on the entrances of $C(^3P) + C_2H_3CN(X^1A')$ leading to these collision complexes. The energies of the complexes are predicted to be well below the reactants as seen in Table S I

(EPAPS).⁴⁹ Consequently, once the complexes are formed, the excess energy allows isomerization and at times decomposition to readily take place.

Since apparently only one of the five collision complexes would be formed for a single carbon–vinyl cyanide collision, the reaction channels of **c1**–**c5** are followed separately to make the seemingly complicated paths tractable. The optimized geometries of intermediates, dissociation products, and transition states obtained at B3LYP/6-311G(*d,p*) level of theory are displayed in Figs. 3 and 4, and s1 (EPAPS),⁴⁹ respectively. The reaction pathways characterized by the B3LYP/6-311G(*d,p*) calculation for collision complexes **c1**–**c5** are revealed in Figs. 5–9, respectively, in which possible immediate paths of each collision complex are identified and only the channels of the intermediates on energetically favored paths are pursued further. The most probable paths of the **c1**–**c5** collision complexes are subsequently determined with the facilitation of the RRKM rate

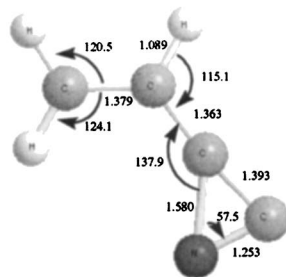
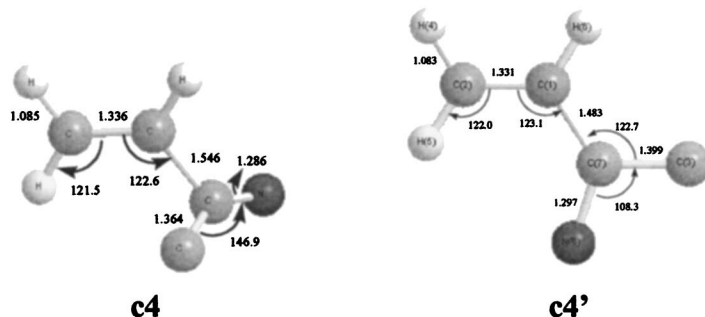
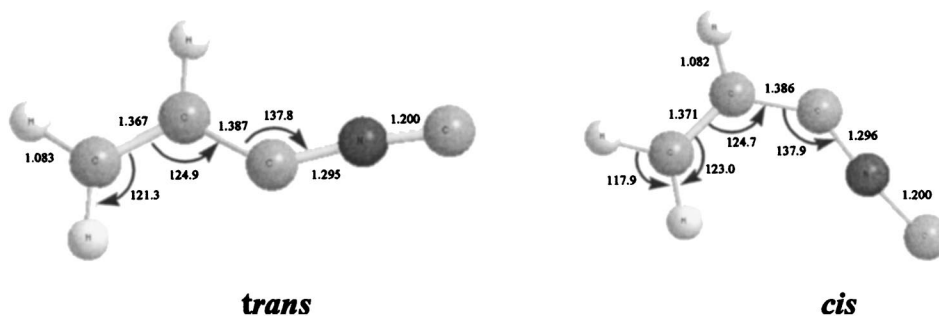
(c) c3 (vinyl-2*H*-azirine ylidene, C_s)**(d) c4 (1-methyl-allylideneamine, C_1)**

FIG. 2. (Continued).

(e) c5 (*N*-methylidene amino vinylmethylene, C_s)

constant calculations as shown in Figs. 10–14, respectively, which are constructed according to the CCSD(T)/6-311G(*d,p*) energies with B3LYP/6-311G(*d,p*) zero-point energy corrections. The reaction mechanisms derived from the most probable paths of the collision complexes are illustrated in Fig. 15. The computed energies of species in figures are listed in Table S1 (EPAPS); Table I exhibits the rate constants at collision energies, 0.0, 0.03, 0.15, 2.0, 5.0, and 10.0 kcal/mol.

B. Reaction paths of cyano cyclopropylidene ($c1$)

The predicted paths of the $c1$ complex are unveiled in Fig. 5, in which the energies relative to the reactants are obtained at the B3LYP/6-311G(*d,p*) level with zero-point energy corrections. In principle, it would appear there are four possible 1,2-hydrogen migrations leading $c1$ to cycloprop-1-enecarbonitrile ($i7$), cycloprop-2-enecarbonitrile ($i11$), but-2-ynenitrile ($i13$), and but-3-ynenitrile ($i14$), where the formation of the latter two is also accompanied by ring-opening. The transition states to $i7$ and $i11$ are located, while the search for those to $i13$ and $i14$ is not successful.

Ring-opening reactions bring $c1$ to $c2$ and *cis*-, *trans*-cyano allene ($i8$). Hydrogen atom dissociation is found energetically feasible for $c1$ to yield 3-cyano cyclopropenyl ($p1$) and 2-cyano cyclopropenyl ($p2$), where the transition states are located at -3.7 and -2.6 kcal/mol, respectively. The loss of molecular hydrogen results in $p16 + H_2$ and $p17 + H_2$ of computed energies, 7.1 and -21.0 kcal/mol, respectively, where the latter is notably lower than the -4.9 and -5.5 kcal/mol of H-loss products, $p1$ and $p2$. The energy of product $p15 + CN$ as a result of CN decomposition is calculated to be relatively higher at 16.9 kcal/mol above the reactants.

It is clear from Fig. 5 that the ring opening to $i8$ is the dominant minimum-energy path of $c1$ with a barrier of only 7.5 kcal/mol, considering the next lowest hindrance is a distant 24.2 kcal/mol for the rearrangement to $c2$. It is known⁵⁰ that the singlet ground state allene (C_3H_4) is of D_{2d} symmetry with twisted geometry while the triplet allene (C_3H_4) is of planar and bent structure in C_{2v} symmetry. These results are also consistent with the present triplet substituted allene, cyano allene, $i8$, as in Fig. 3. Our calculation indicates that $i8$ is planar and the *cis*- $i8$ is only less favored energetically by 0.24 kcal/mol than the *trans*. Both isomers are more stable

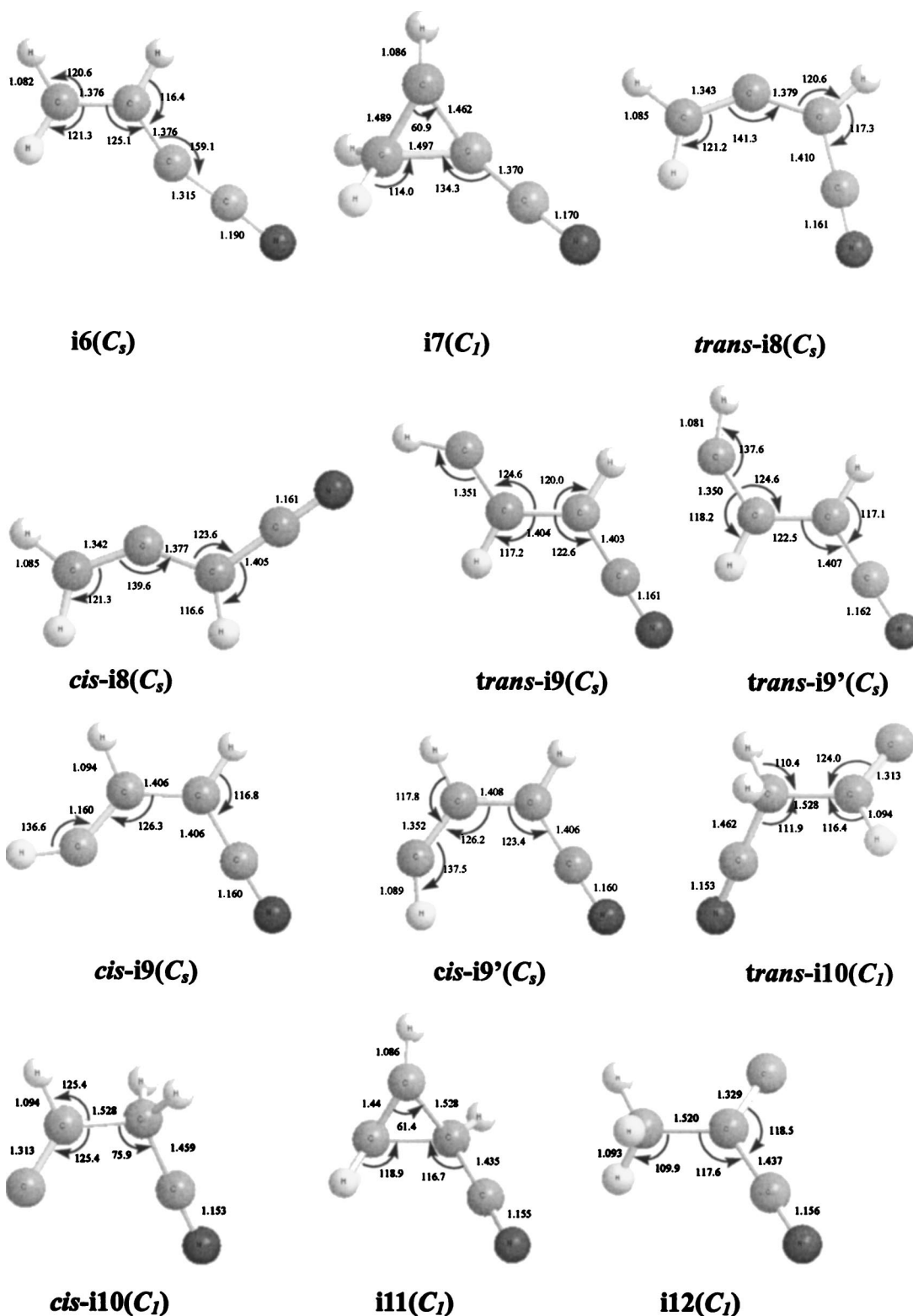


FIG. 3. The B3LYP/6-311G(*d,p*) optimized geometries of the intermediates for $C(^3P) + C_2H_3CN(X^1A')$ reaction on the adiabatic triplet ground state potential energy surface of C_4H_3N , in which the point group is in parentheses, the lengths in angstrom, and the angles in degree.

than **c1** by around 39 kcal/mol; it costs approximately 4 kcal/mol for the mutual conversion to occur.

The 1,2- and 1,3-hydrogen shift, atomic hydrogen dissociation, and ring-closing channels of **i8** are calculated to be lower in energy than the reactants. **i8** could convert to cyano vinylmethylene (**i6**) by overcoming 58.4 and 45.8 kcal/mol

of 1,2-hydrogen migration for the *trans* and *cis*, respectively, or by a stepwise mechanism through a 1,3-hydrogen shift yielding *trans* and *cis* but-2-ynenitrile (**i13**) with however a higher activation energy of about 64 kcal/mol. The structure of **i6** is similar to *cis-i8*, which may explain the transition state of *trans*- is 12.4 kcal/mol higher than *cis*-**tsi6i8**. De-

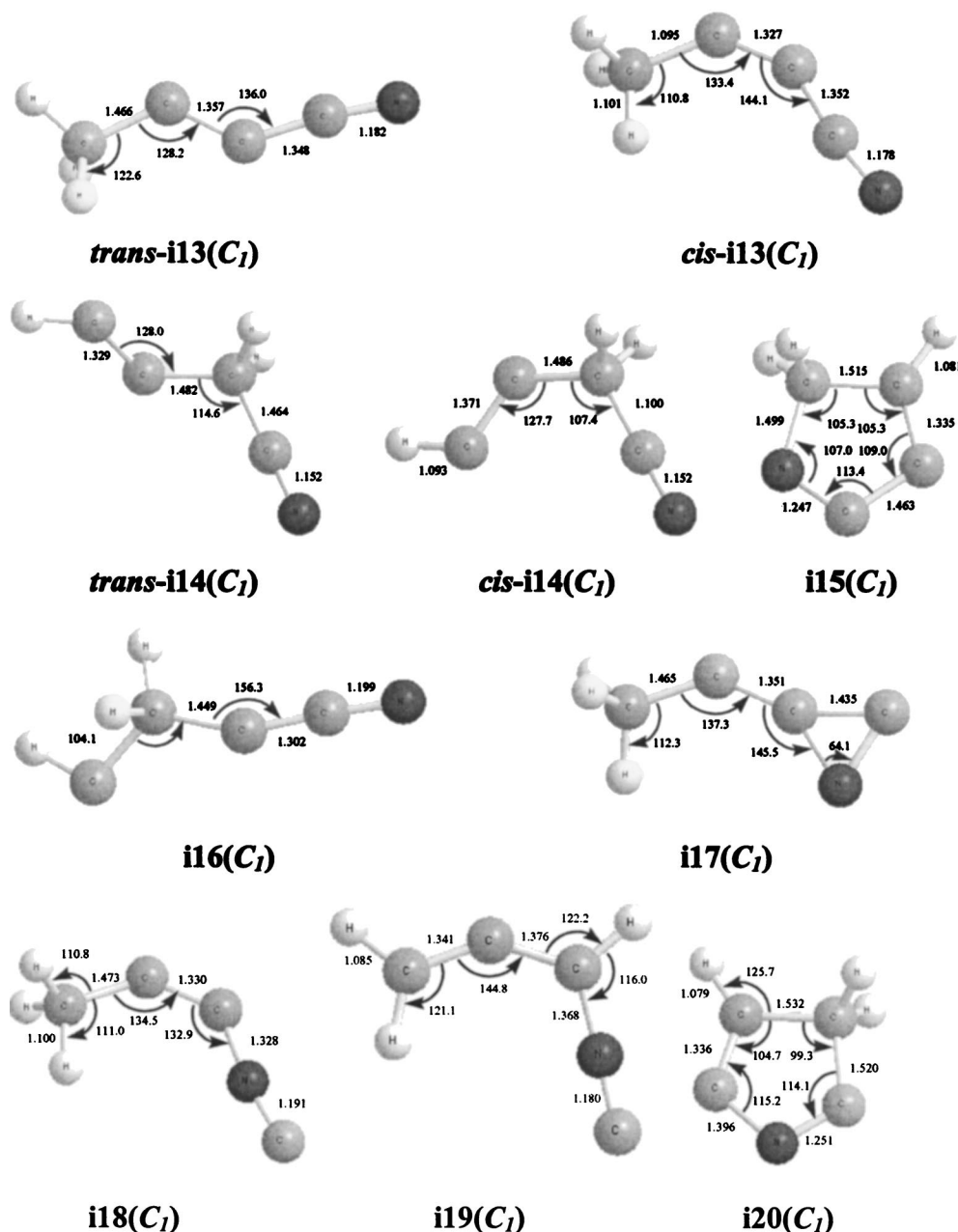


FIG. 3. (Continued).

manding 70 and 48.8 kcal/mol for the barriers, 1,3- and 1,2-hydrogen shift from the methylene group of **i8** could result in but-3-ynenitrile (**i14**) and 2-cyano vinylmethylene (**i9**), respectively, both of C_s symmetry. Release of a methylene hydrogen-atom produces cyano propargyl (**p4**), while C–H bond breaking at the CH group generates 3-cyano propargyl (**p5**); both are of the lowest barriers around 43 kcal/mol among all possible paths of **i8**. Although the molecular hydrogen elimination products **p18**+H₂ of **i8** is predicted of energy lower than the reactants by 23.5 kcal/mol, it is still much higher than the atomic hydrogen products. The well recognized astrochemically important species, propargyl (**p20**) radical is found probable products of **i8** with the energy being –27.7 kcal/mol via a direct dissociation of the cyano radical.

It appears there are five energetically more favored channels with comparable barriers for **i8**, where the transition

states are located in the range of –42 to –49 kcal/mol. In the order of decreasing barrier, these are the paths to **i9**, **c1**, **i6**, **p4**, and **p5**.

In addition to the three-member ring-closure reaction that consumes 53.8 kcal/mol in activation energy to give **i7**, **i6** could undergo five-member ring-closing with a barrier of 62.0 kcal/mol to generate the 2H-pyrrole-5-yl radical (**i15**). **i6** is also capable of isomerizing to **i8** and **i13** by 1,2-hydrogen migration, and the 1,3-H shifting to **i9**. The C–H bond rupture of the CH group leading to **p5** that costs the least barrier of 49.1 kcal/mol appears to be the most likely faith of **i6**, while the 1-cyano-1-propene-1-yl-3-ylidene (**p7**) as a result of the ejection of a hydrogen atom from the methylene would only be a minor product considering its location at a much higher 13.8 kcal/mol.

The intermediate **i9** has four conformations: in two of them, the heavy atoms are in *trans* position and in the other

(a)

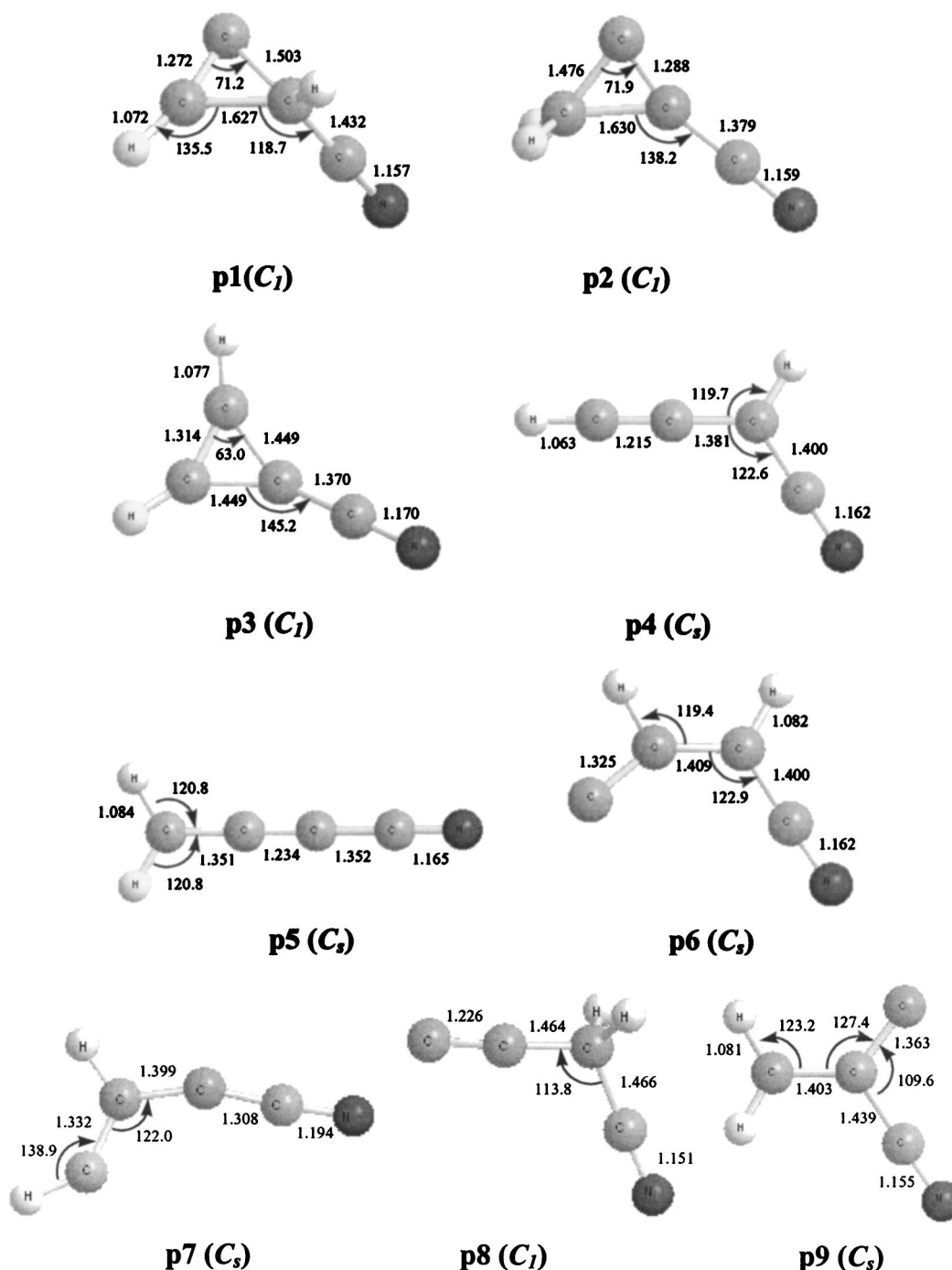


FIG. 4. The B3LYP/6-311G(*d,p*) optimized geometries of dissociation products for $C(^3P) + C_2H_3CN(X^1A')$ reaction, in which the point group is in parentheses, the lengths in angstrom, and the angles in degree: (a) the hydrogen atom dissociation products, C_4H_2N , in doublet ground states; (b) the CN dissociation products, C_3H_3 , in doublet ground states; (c) the hydrogen molecule dissociation products, C_4HN , in singlet ground states; (d) the CH_2 dissociation product in singlet ground state.

two, *cis*, denoted as *trans-i9*, *trans-i9'*, *cis-i9*, and *cis-i9'*. Their energies are -91.0, -90.3, -89.9, -89.8 kcal/mol relative to the reactants, respectively. The conversions of *trans-i9'* $\Rightarrow$ *trans-i9* and *cis-i9'* $\Rightarrow$ *cis-i9* are made possible by in-plane swinging of the H on terminal carbon; the activation energies are close to 3 kcal/mol. The transition states of *cis* and *trans* conversion are lying at -75.9 and -76.4 kcal/mol for *cis-i9'* $\Rightarrow$ *trans-i9'* and *cis-i9* $\Rightarrow$ *trans-i9*, respectively.

Four more isomers resulting from the 1,2-hydrogen shift in **i9** are characterized: one of **c2** conformers, **i8**, but-3-ynenitrile (**i14**), and **i16**, among which **i8** is the least hindered with the transition states found at -42 kcal/mol for both *trans* and *cis* forms. Intermediate **i11** can be formed through ring-closure in **i9**; however, the transition state for *trans-i9* $\Rightarrow$ **i11** is located at a relatively high energy of -36.6 kcal/mol. H-decomposition of **i9** generates **p4**,

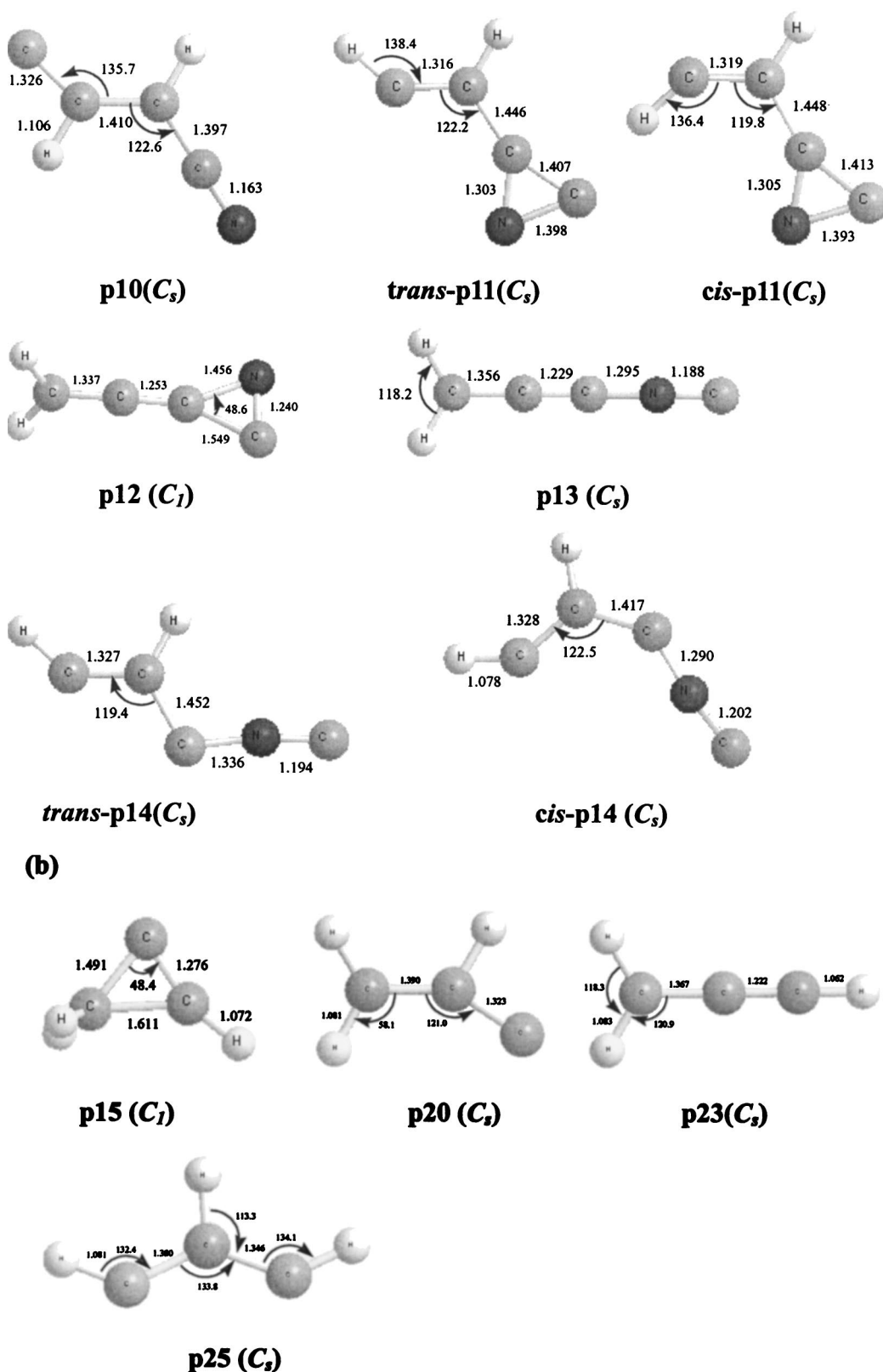


FIG. 4. (Continued).

1-cyano-2-propene-1-yl-3-ylidene (*cis*) (**p6**), and 1-cyano-1-propene-1-yl-3-ylidene (**p7**). The much higher energies of -2.6 and 13.8 kcal/mol for the latter two easily make **p4** + H of -50.7 kcal/mol the most likely products. The min-

imum energy path of **i9** is the conversion to the most stable intermediate **i6** by 1,3-hydrogen shift that requires 43.0 kcal/mol for the activation energy, of which the hydrogen dissociation product seems overwhelmingly **p5**.

(c)

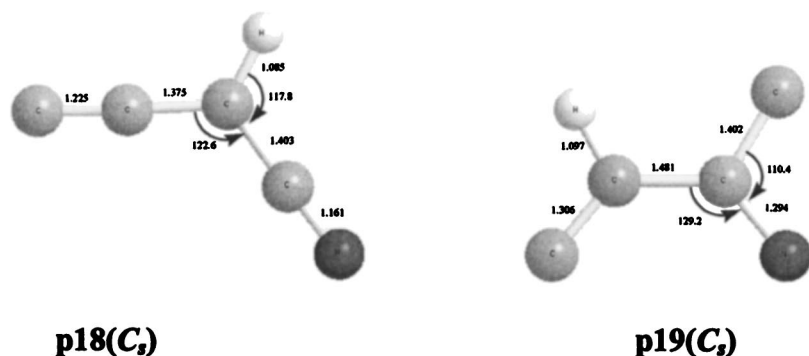
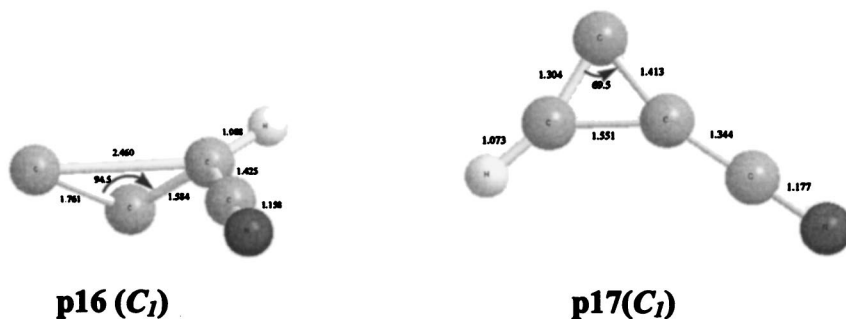
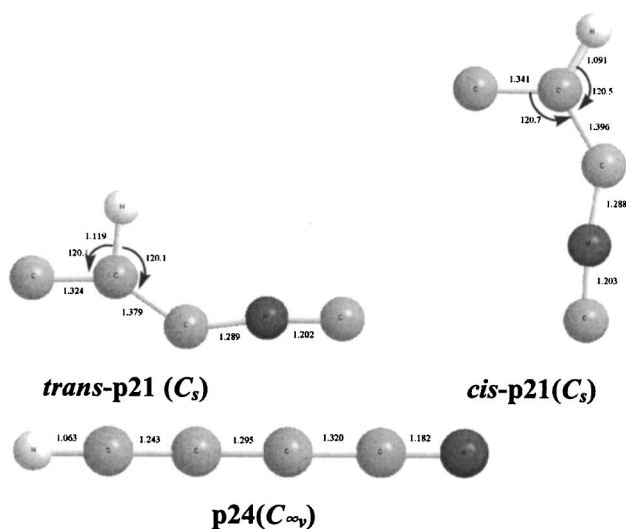
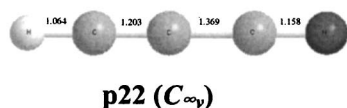


FIG. 4. (Continued).



(d)



C. Reaction paths of cyano-3-propylidene (c2)

Six conformation isomers of **c2** as a result of the relative orientations of two end groups respective to the original carbon-carbon double bond by an increment of 60° are identified; their optimized geometries are depicted in Fig. 2. The collision complex **c2** would appear to be the ones denoted as “ap” and “bp” of which the carbon atom is perpendicularly above and below the C₂H₃CN molecular plane, respectively.

As seen in Fig. 6, the transition states for carbon migration, 1,3-hydrogen shift, and hydrogen decomposition that lead to **c4**, **i16**, **p6**, and 1-cyano-2-propene-1-yl-3-ylidene (*trans*) **p10**, are found with activation energies of 8.4, 16.1, 29.4, and 28.6 kcal/mol, respectively. Though the first two channels are well below the energy of the reactants, they become insignificant compared with the cyclization reaction yielding **c1**, of which the B3LYP/6-

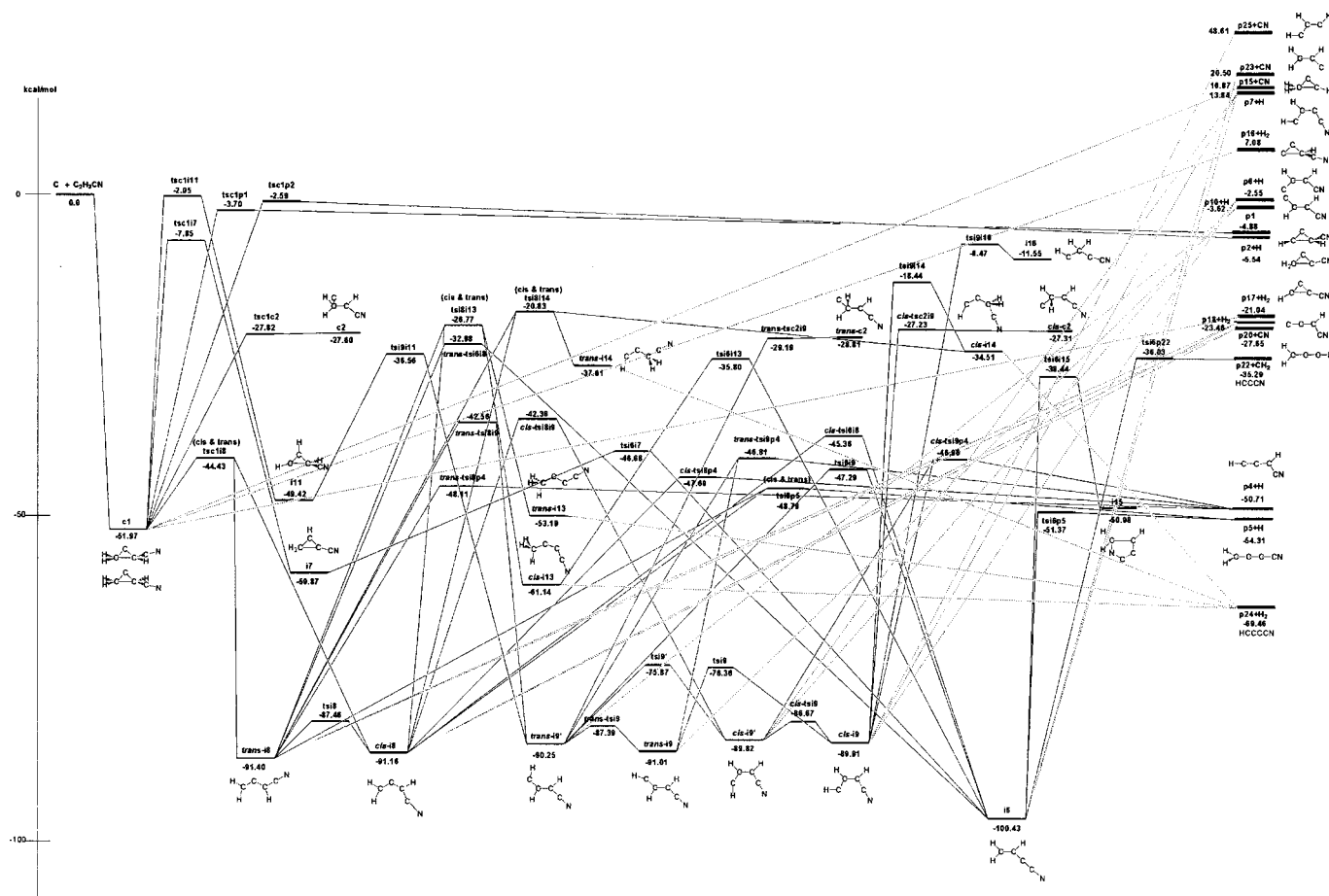


FIG. 5. The reaction paths of the collision complex, **c1**, in which the energies in kcal/mol relative to the reactants, $C(^3P) + C_2H_3CN(X^1A')$, are computed with the B3LYP/6-311G(*d,p*) level of theory with zero-point energy corrections at the B3LYP/6-311G(*d,p*) optimized geometries as shown in Figs. 2–4 and s1 (EPAPS). Note the attempts are not made to locate the transition states for those paths in dotted lines.

311G(*d,p*) energy with zero-point energy correction gives a negative barrier of -0.22 kcal/mol, an indication of almost being barrierless. Thus, despite characterized as a species located at an energy minimum on the potential energy surface, kinetically **c2** appears extremely unstable as it inevitably cyclizes to **c1** instantly.

D. Reaction paths of cyclic vinyl-2H-azirine ylide (**c3**)

Figure 7 clearly demonstrates that for **c3**, the ring-opening reactions are the only channels below the energy of reactants and make accessible three isomers. Among them, **c5** can be formed by the carbon–carbon bond rupture, **c4'** and **i6** are the consequences of two different C–N bond breakings, respectively.

Notably, the path leading to **i6** has the lowest hindrance of 4.1 kcal/mol for **c3**, which makes **i6** the most likely intermediate following **c3**. Even if **c3** chooses the next competitive route overcoming a barrier of 5.4 kcal/mol to **c5**, which would still leak back to **c3** as discussed below and eventually yield **i6**. As discussed previously, **i6** would prefer the production of **p5**. Nevertheless, a much less probable path of **c4'** could take **c3** to **c2** that immediately leads to the ringed **c1** triggering the paths in Fig. 5.

The H-migration of **c3** gives the cyclic isomer, CH_3C-

(cyclo-CNC) (**i17**). Although **i17** is computed to be bound by 25.7 kcal/mol, the barrier is 56.4 kcal/mol or equivalently the transition state is obtained at 9.0 kcal/mol above the reactants, which makes **c3** hydrogen migration difficult to proceed at low temperature. Through H-loss, **c3** can presumably reach two different doublet products: $HC=CH-(cyclo-CNC)$ (**p11**) of *cis*- and *trans*-isomers, and $H_2C=C-(cyclo-CNC)$ (**p12**), however, of 30.8, 31.5, and 5.4 kcal/mol higher than the reactants, respectively.

E. Reaction paths of 1-methyl-allylideneamine (**c4**)

The conversion of the less stable **c4'** to **c4**, of which the skeletal four carbon atoms are in *trans* and *cis* arrangement, respectively, can be achieved through the rotation of the terminal CCN group; the hindrance is 1.5 kcal/mol and 3.5 kcal/mol vice versa as seen in Fig. 8. The migration of the terminal carbon and formation of a ring bring **c4** and **c4'** to three other collision complexes, **c2**, **c5**, and **c3**, of barriers, 1.4, 7.8, and 7.0 kcal/mol. With the least hindrance, 1,3 carbon migration takes **c4** to **c2**, which would form a ring to become **c1** whose final products are **p4** and **p5** as discussed in Sec. III A. The CCN ring closure turns **c4** to **c3** that gives product **p5** via **i6**. The carbon migration to the nitrogen atom

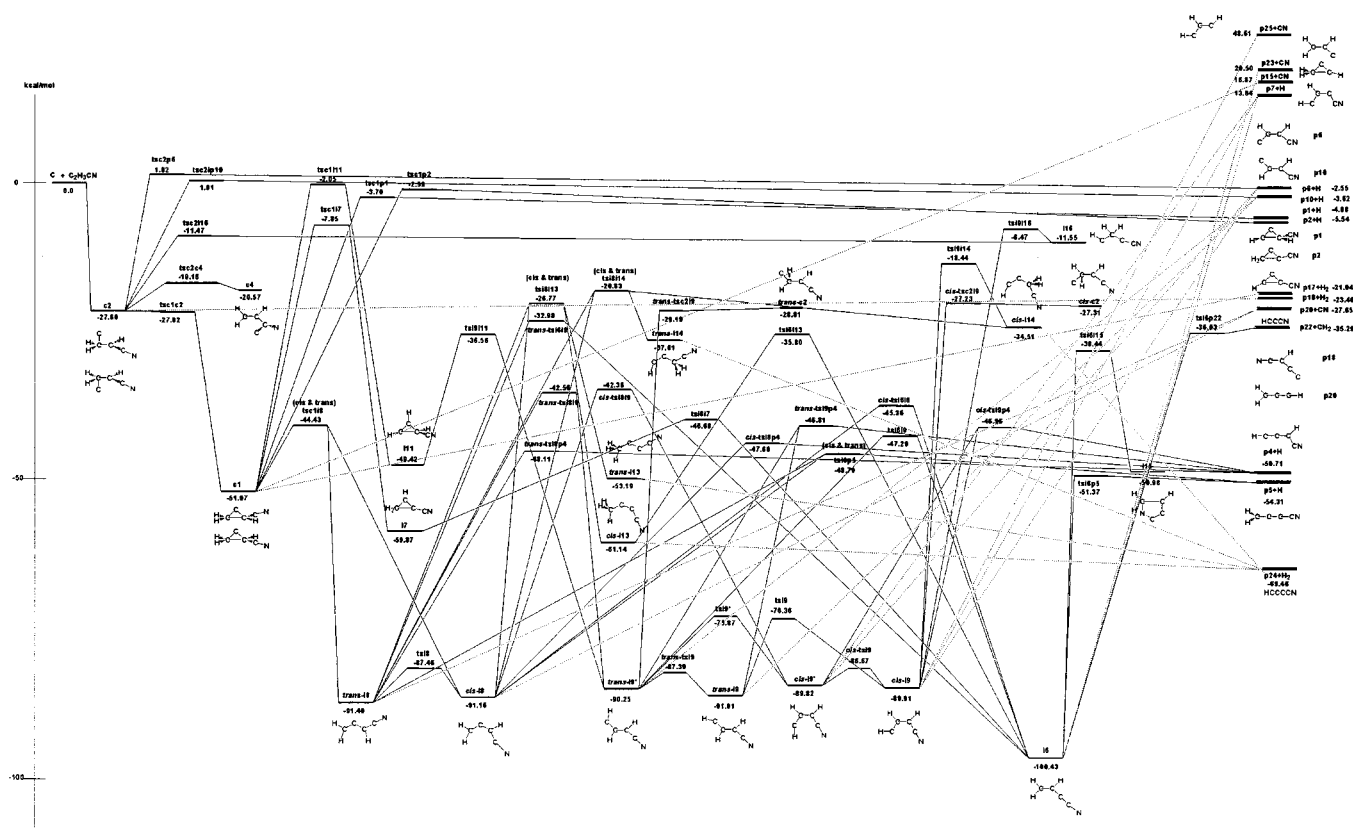


FIG. 6. The reaction paths of the collision complex, **c2**, in which the energies in kcal/mol relative to the reactants, $C(^3P) + C_2H_3CN(X^1A')$, are computed with B3LYP/6-311G(*d,p*) level of theory with zero-point energy corrections at the B3LYP/6-311G(*d,p*) optimized geometries as shown in Figs. 2–4 and s1 (EPAPS). Note the attempts are not made to locate the transition states for those paths in dotted lines.

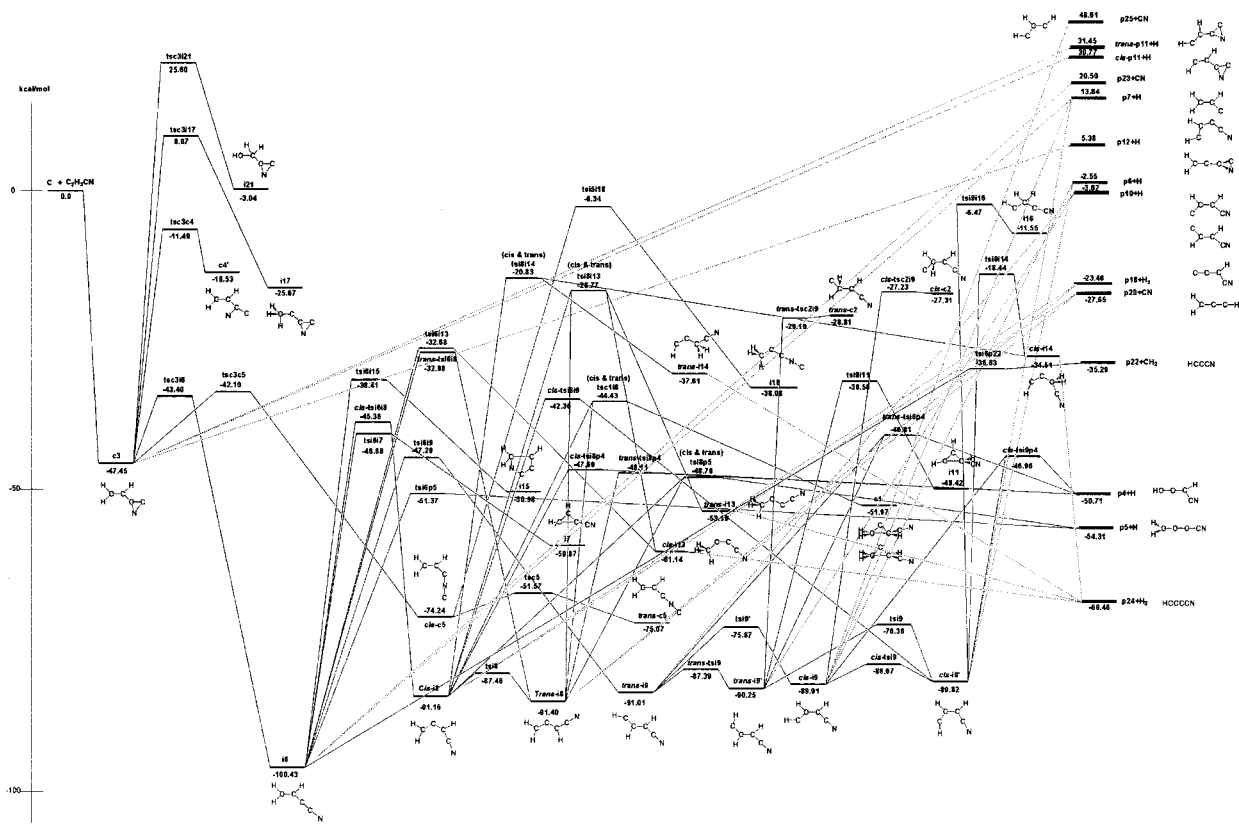


FIG. 7. The reaction paths of the collision complex, **c3**, in which the energies in kcal/mol relative to the reactants, $C(^3P) + C_2H_3CN(X^1A')$, are computed with the B3LYP/6-311G(*d,p*) level of theory with zero-point energy corrections at the B3LYP/6-311G(*d,p*) optimized geometries as shown in Figs. 2–4 and s1 (EPAPS). Note the attempts are not made to locate the transition states for those paths in dotted lines.

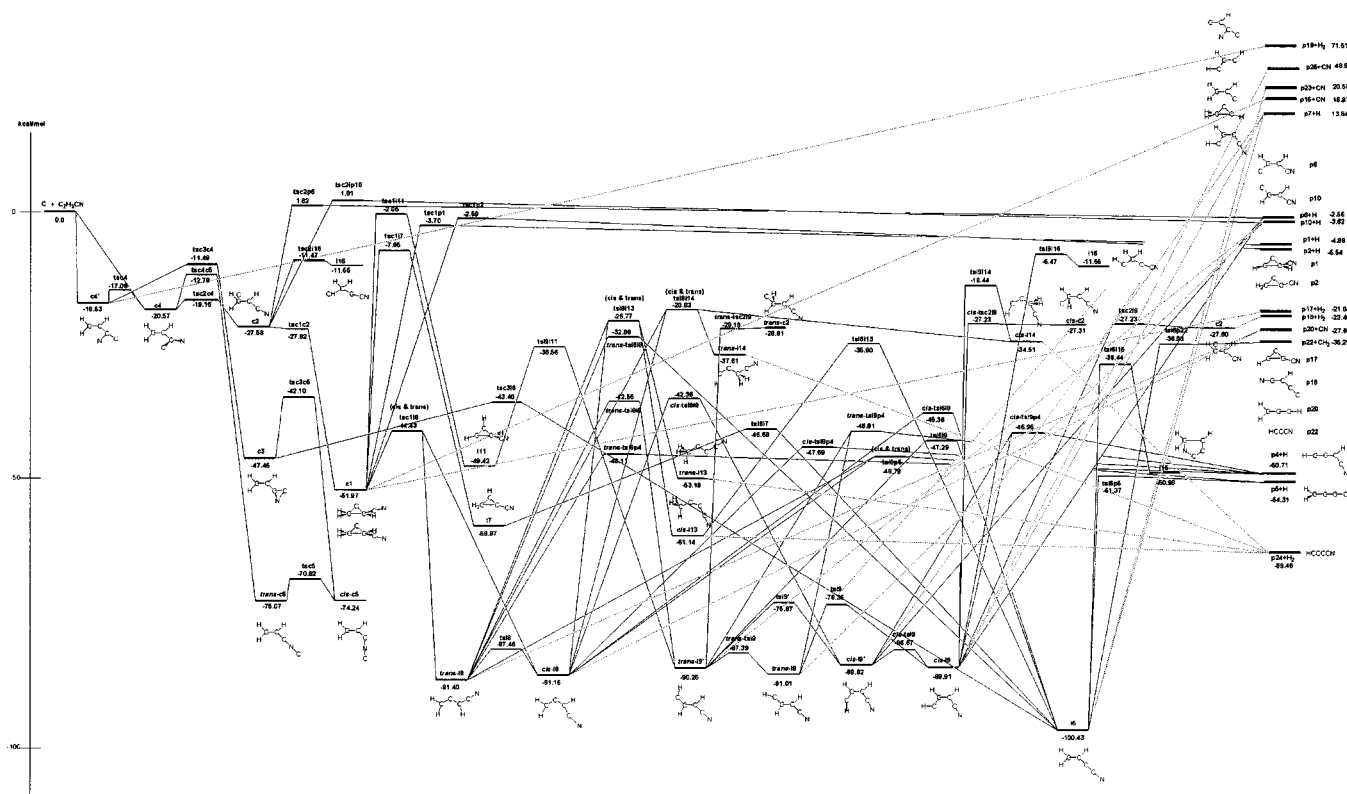


FIG. 8. The reaction paths of the collision complex, **c4**, in which the energies in kcal/mol relative to the reactants, $C(^3P) + C_2H_3CN(X^1A')$, are computed with B3LYP/6-311G(*d,p*) level of theory with zero-point energy corrections at the B3LYP/6-311G(*d,p*) optimized geometries as shown in Figs. 2–4 and s1 (EPAPS). Note the attempts are not made to locate the transition states for those paths in dotted lines.

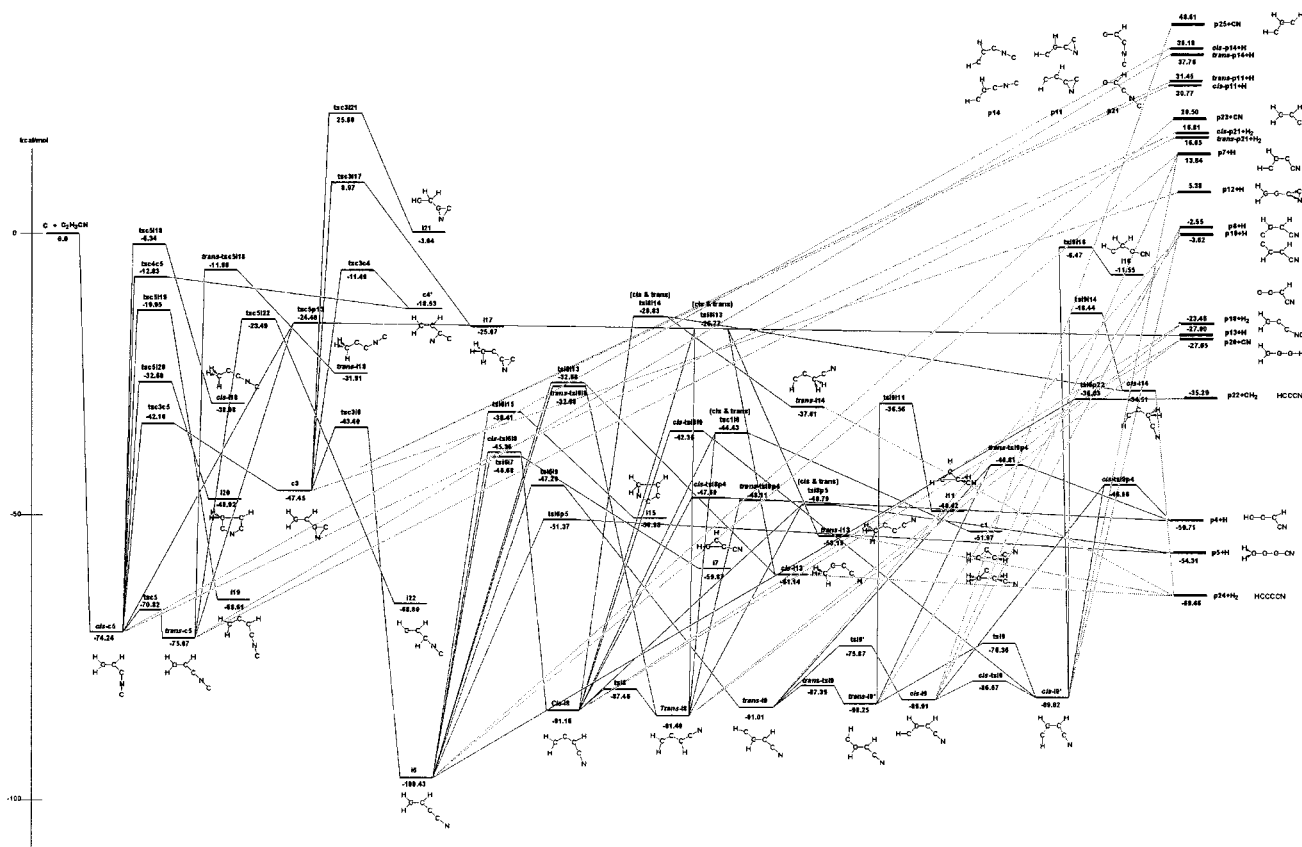
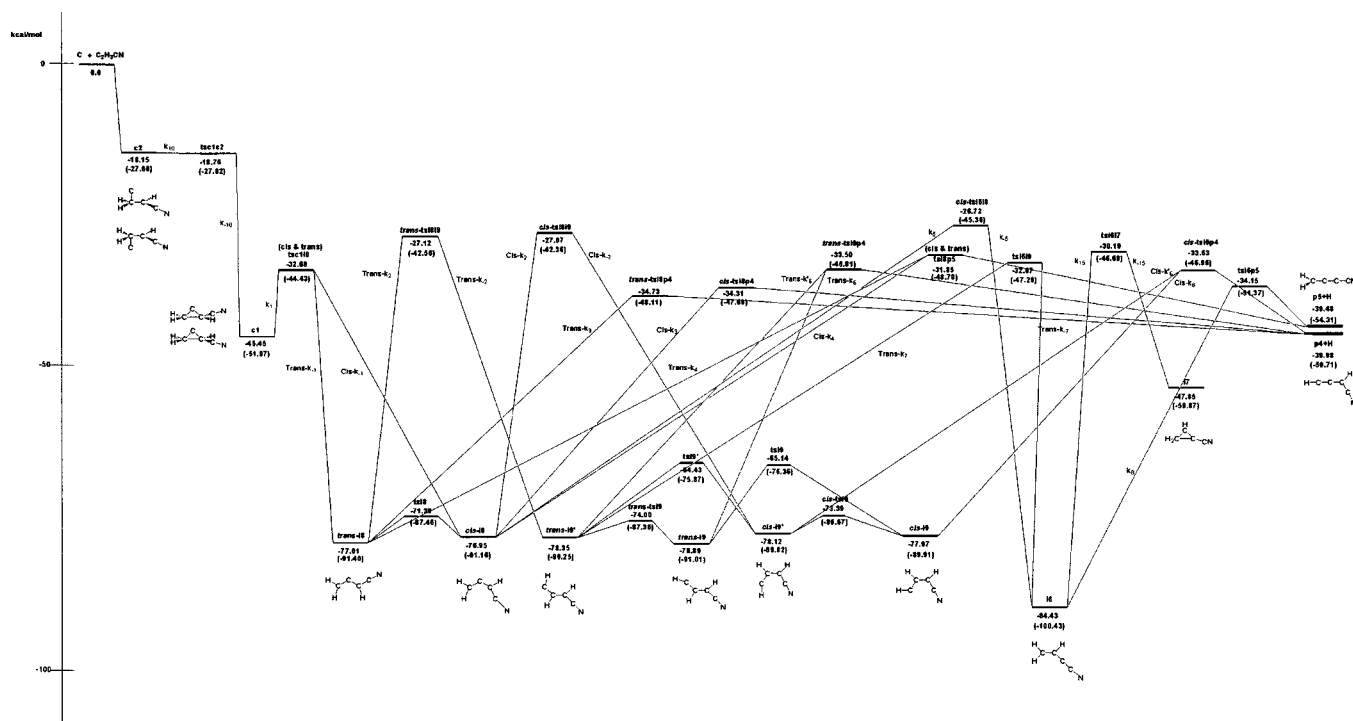
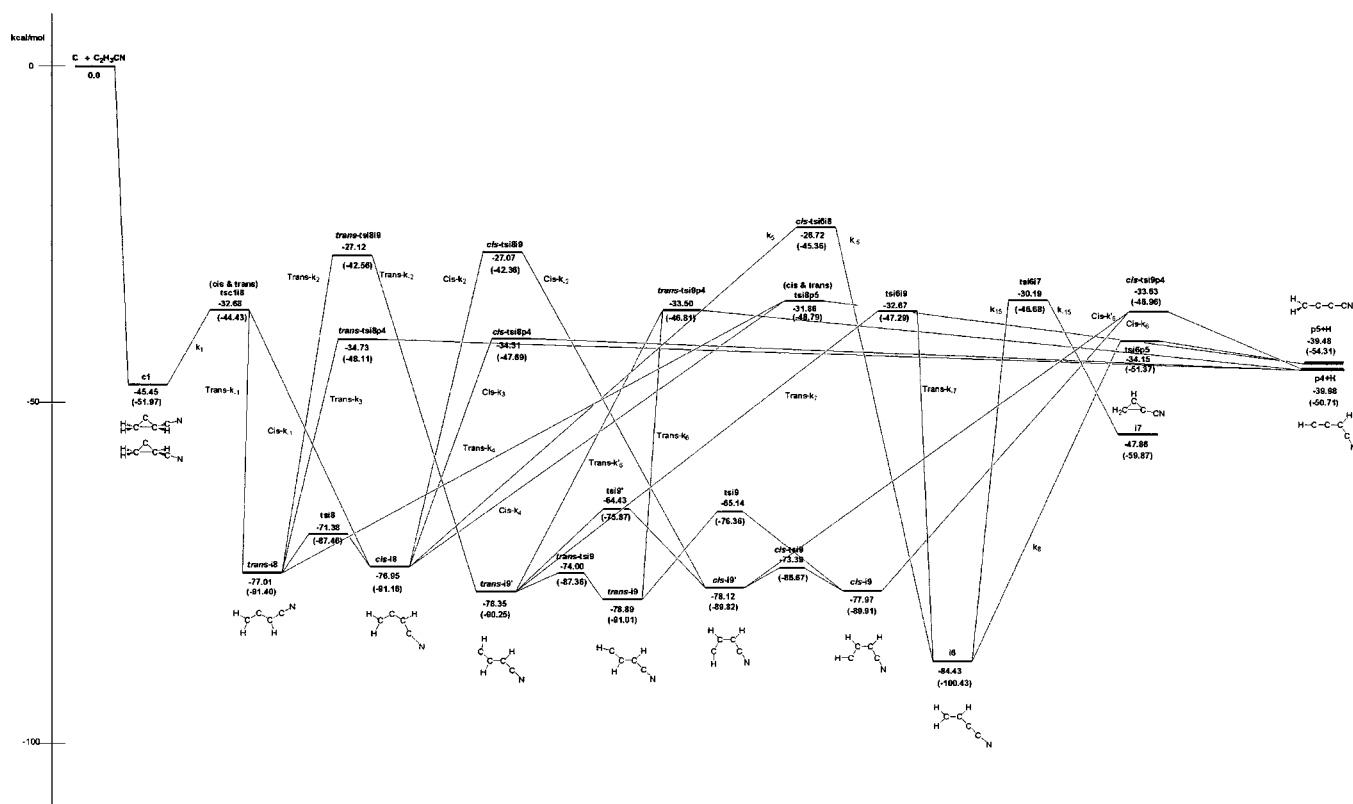


FIG. 9. The reaction paths of the collision complex, **c5**, in which the energies in kcal/mol relative to the reactants, $C(^3P) + C_2H_3CN(X^1A')$, are computed with the B3LYP/6-311G(*d,p*) level of theory with zero-point energy corrections at the B3LYP/6-311G(*d,p*) optimized geometries as shown in Figs. 2–4 and s1 (EPAPS). Note the attempts are not made to locate the transition states for those paths in dotted lines.



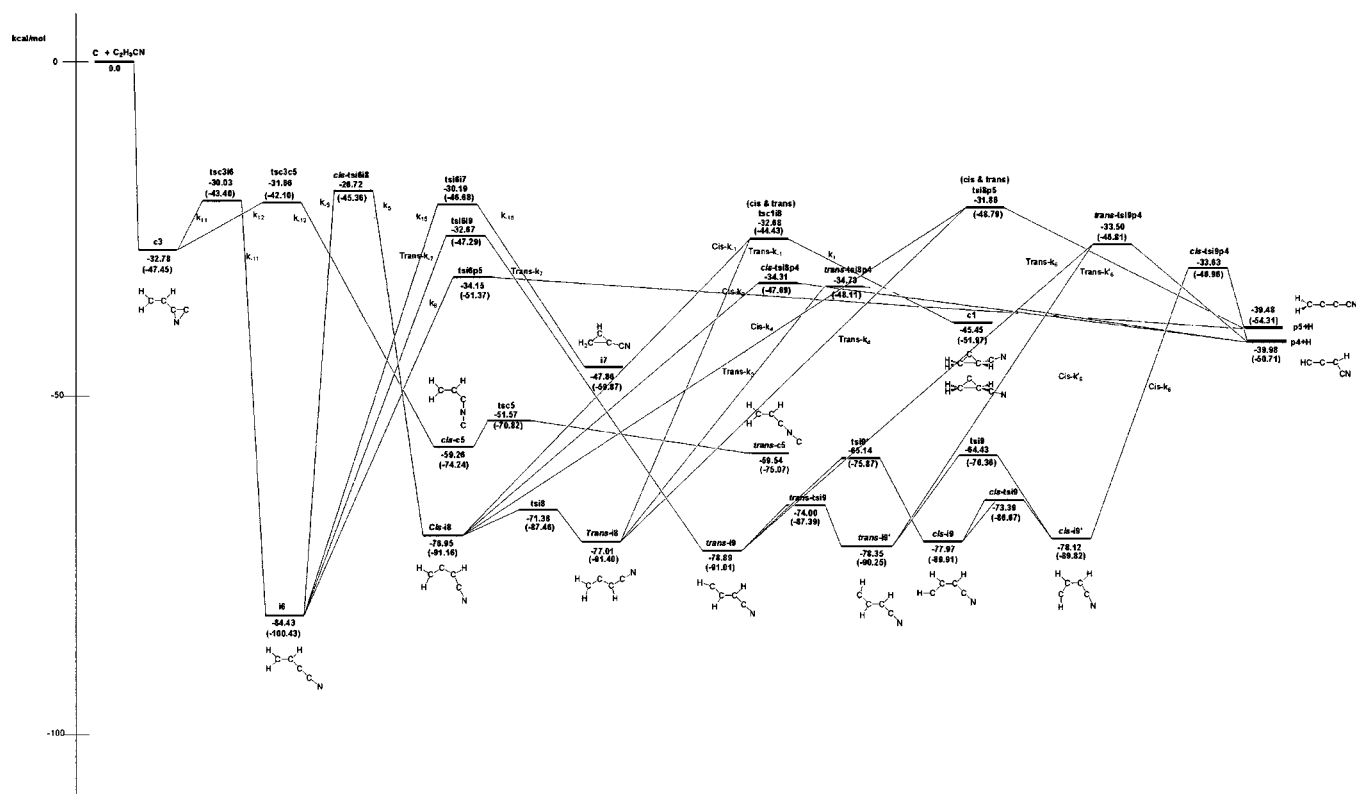


FIG. 12. The most probable paths of the collision complex, c_3 , in which the energies in kcal/mol relative to the reactants, $C(^3P) + C_2H_3CN(X^1A')$, are computed with CCSD(T)/6-311G(d,p) level of theory with B3LYP/6-311G(d,p) zero-point energy corrections at the B3LYP/6-311G(d,p) optimized geometries as shown in Figs. 2–4 and s1 (EPAPS), the energies in parentheses are the B3LYP/6-311G(d,p) energies as in Fig. 7.

results in c_5 , which favors the route to c_3 and subsequently to the products, $p_5 + H$.

The attempts to locate the isomers due to the hydrogen migration and hydrogen dissociation products of c_4 are not successful, which seems to demonstrate that the addition of a carbon atom to the cyano triple bond is not able to sustain a stable H-migrated intermediate and H-loss product.

F. Reaction paths of *N*-methylidene amino vinylmethylene (c_5)

The transformation of *cis*- c_5 to *trans*- c_5 requires 3.4 kcal/mol. Figure 9 reveals for c_5 , the 1,2- and 1,3-hydrogen shift, C-migration, ring-closure, and H-dissociation channels are open. The 1,2 hydrogen shift could lead to

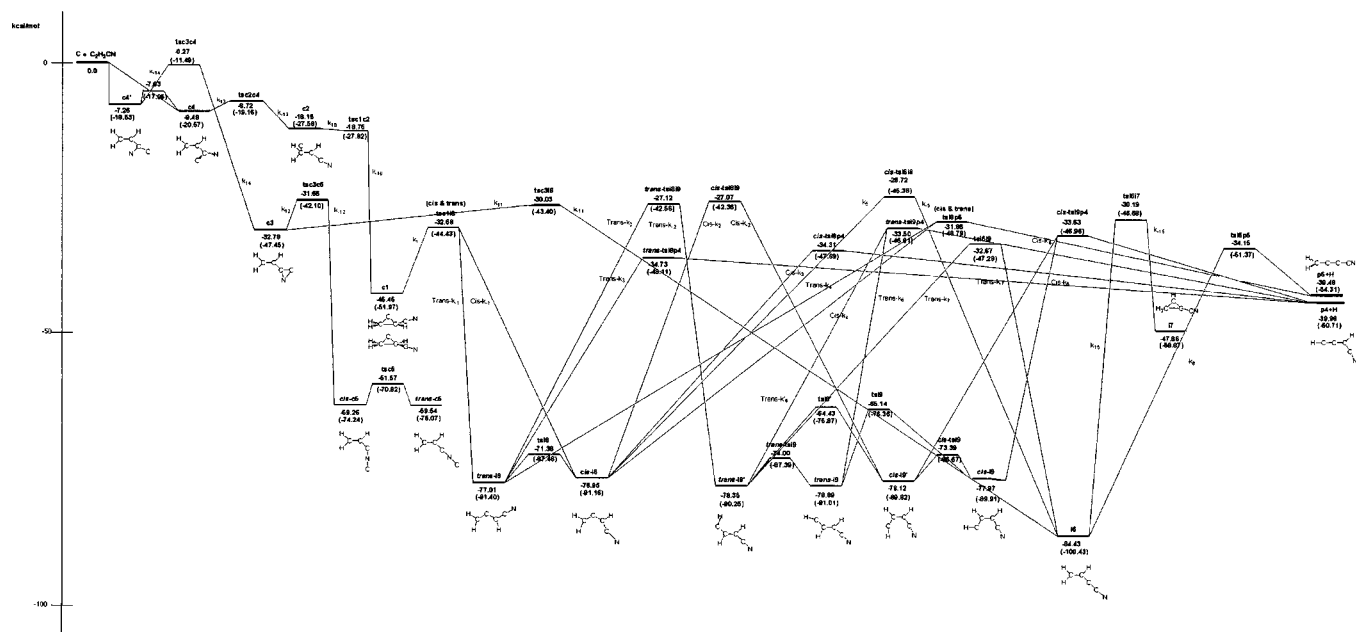


FIG. 13. The most probable paths of the collision complex, c_4 , in which the energies in kcal/mol relative to the reactants, $C(^3P) + C_2H_3CN(X^1A')$, are computed with the CCSD(T)/6-311G(d,p) level of theory with B3LYP/6-311G(d,p) zero-point energy corrections at the B3LYP/6-311G(d,p) optimized geometries as shown in Figs. 2–4 and s1 (EPAPS), the energies in parentheses are the B3LYP/6-311G(d,p) energies as in Fig. 8.

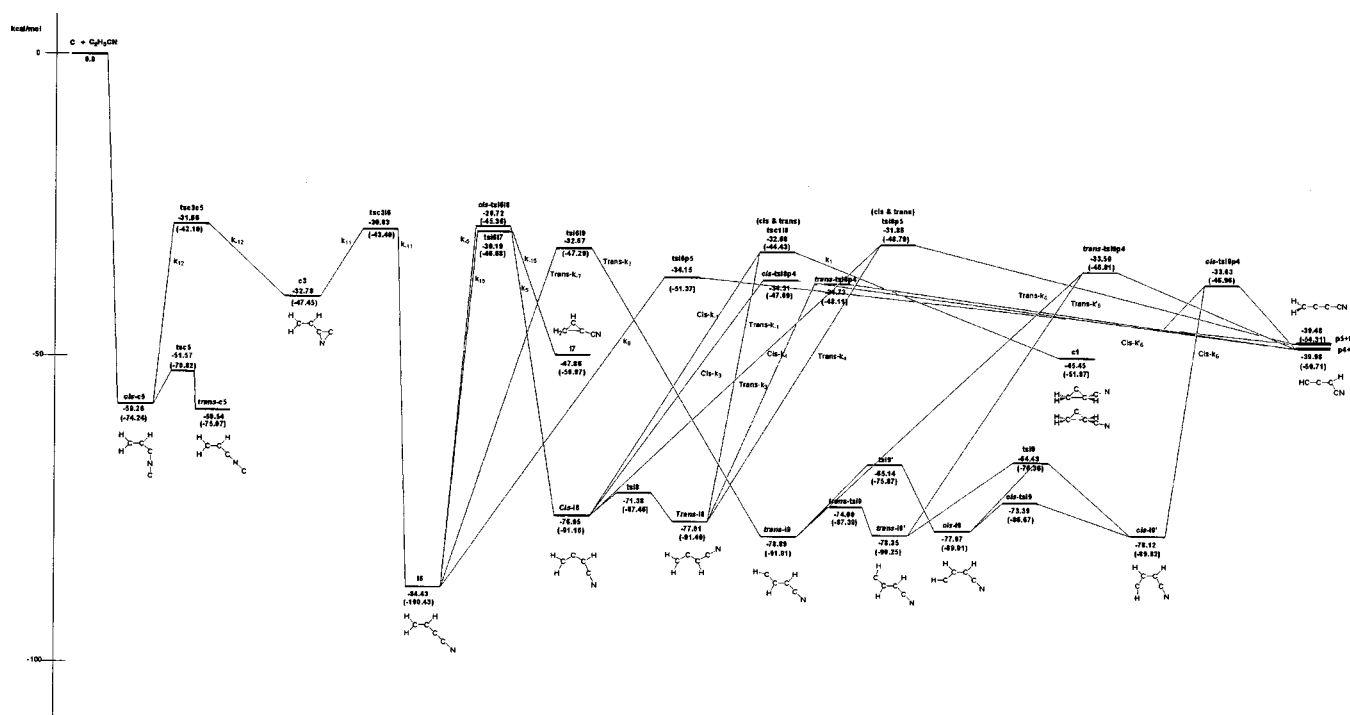


FIG. 14. The most probable paths of the collision complex, **c5**, in which the energies in kcal/mol relative to the reactants, $C(^3P) + C_2H_3CN(X^1A')$, are computed with the CCSD(T)/6-311G(*d,p*) level of theory with B3LYP/6-311G(*d,p*) zero-point energy corrections at the B3LYP/6-311G(*d,p*) optimized geometries as shown in Figs. 2–4 and s1 (EPAPS), the energies in parentheses are the B3LYP/6-311G(*d,p*) energies as in Fig. 9.

CH_3-CCNC (**i18**) and $CH_2=C=C(CNC)H$ (**i19**); 1,3-hydrogen shift from the methylene gives **i22**; the conversion to **c4** is achieved through the migration of carbon; the ring-closing reaction yields the three-member ringed **c3** and a five-member ringed $H_2C-CH=C-N=C$ (**i20**). With a lowest activation energy of 32.1 kcal/mol for *cis*-**c5**, the conversion to **c3** subsequently generates the products of **p5** + H as described earlier. The rupture of a H atom from the CH_2 and CH of **c5** gives CH_2CCNC (**p13**) and $CH=CH(CNC)$ (*cis*- and *trans*-**p14**), respectively. While the former is found at energy of -27.0 kcal/mol, the latter is above the reactant by appreciable amounts of 39.2 and 37.8 kcal/mol for *cis* and *trans*, respectively, which are too high to be significant. The products of H_2 dissociation, *cis*- and *trans*-**p21** are calculated at energies of 16.8 and 16.7 kcal/mol, respectively.

G. The most probable paths of cyano cyclopropylidene (**c1**)

The paths of energy below -42 kcal/mol in Fig. 5 are included in the most probable paths for **c1** as illustrated in Fig. 10, where the energies are obtained at the level of CCSD(T)/6-311G(*d,p*) with B3LYP/6-311G(*d,p*) zero-point energy corrections. Figure 15(a) depicts the reaction mechanism of **c1** thus inferred, including the corresponding rate constants.

As seen in Table I, it is sensible only the path to **i8** is included for **c1** since the rate constant k_{-10} of the next least-hindered route, which yields **c2**, lags behind by two orders of magnitude than k_1 (**c1** → **i8**). In Fig. 15(a), there are five competitive channels of comparable energy hindrances for the consumption of **i8**. The corresponding rate constants are

in the order of $k_3 > k_4 > k_2 > k_5 > k_{-1}$, which notably is not entirely in accord with the order of the computed activation energy. With the advantages of lowest barrier and symmetry factor being 2, k_3 (**i8** → **p4** + H) is around five times larger than k_4 (**i8** → **p5** + H); interestingly, despite the fact that the corresponding activation energy is the second lowest, k_{-1} (**i8** → **c1**) is predicted being the least probable owing to a relatively tight transition state. Being one tenth of k_4 , k_2 and k_5 appear distant three and four, which makes **i8** → **i6** negligible compared with the direct dissociations of hydrogen atom. Hence, both via an allene **i8**, the products resulting from complex **c1** can be deduced as predominately **p4** + H and **p5** + H with approximately 5:1 ratio.

H. The most probable paths of cyano-3-propylidene (**c2**)

The instability of **c2** toward the cyclization to **c1** makes this path the most probable while others are difficulty to compete. The most probable channels of **c2** are presented in Fig. 11, which are essentially of **c1**'s as discussed in Sec. III G. Figure 15(b) illustrates **c2** reaction mechanisms and the corresponding rate constants, in which the attempt is not made to calculate the k_{10} of **c2** → **c1**.

I. The most probable paths of cyclic vinyl-2H-azirine ylidene (**c3**)

As seen in Fig. 7, with the third lowest barrier of **c3** being 36.0 kcal/mol for ring-opening to **c4'**, the most probable paths are logically the ring-opening to **i6** and **c5**, in which the activation energies are of the much lower 4.1 and 5.4 kcal/mol, respectively. The most probable paths are plot-

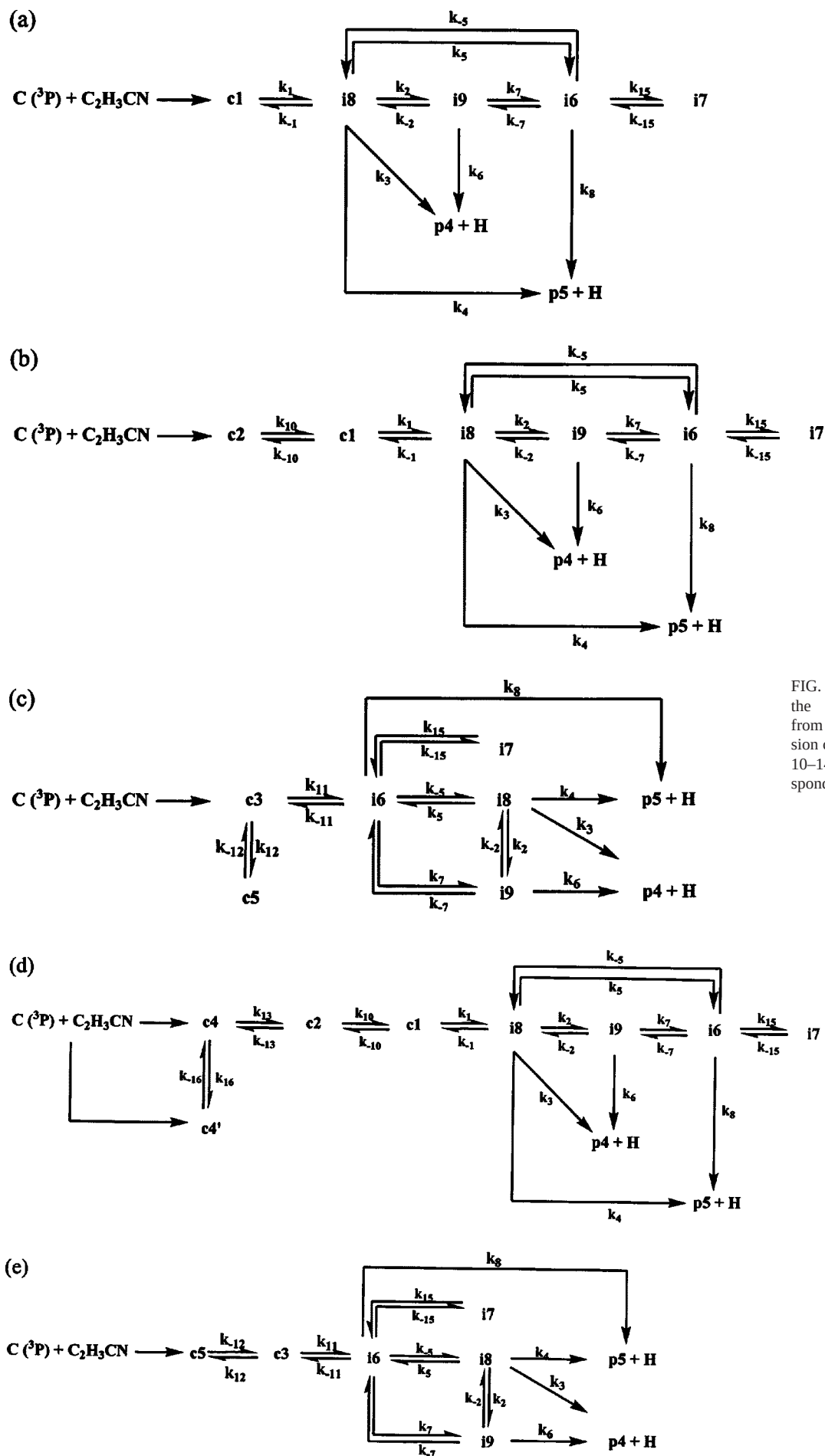


FIG. 15. The schematic diagrams for the reaction mechanisms deduced from the most probable paths of collision complexes c1–c5 as seen in Figs. 10–14, in which the k 's are the corresponding rate constants.

TABLE I. The RRKM rate constants (s^{-1}) computed with CCSD(T)/6-311G(*d,p*) energies and B3LYP/6-311G(*d,p*) harmonic frequencies at collision energies of 0.0, 0.03, 0.15, 2.0, 5.0, and 10.0 kcal/mol.

	0.0	0.03	0.15	2.0	5.0	10.0
<i>trans</i> - k_1 (<i>trans</i> - c1 → i8)	1.02×10^{12}	1.02×10^{12}	1.03×10^{12}	1.16×10^{12}	1.38×10^{12}	1.77×10^{12}
<i>cis</i> - k_1 (<i>cis</i> - c1 → i8)	1.02×10^{12}	1.02×10^{12}	1.03×10^{12}	1.16×10^{12}	1.38×10^{12}	1.77×10^{12}
<i>trans</i> - k_{-1} (<i>trans</i> - i8 → c1)	6.36×10^8	6.38×10^8	6.49×10^8	8.31×10^8	1.21×10^9	2.10×10^9
<i>cis</i> - k_{-1} (<i>cis</i> - i8 → c1)	4.72×10^8	4.74×10^8	4.81×10^8	6.16×10^8	8.94×10^8	1.55×10^9
<i>trans</i> - k_2 (<i>trans</i> - i8 → i9)	9.33×10^8	9.38×10^8	9.60×10^8	1.36×10^9	2.28×10^9	4.86×10^9
<i>cis</i> - k_2 (<i>cis</i> - i8 → i9)	1.06×10^9	1.06×10^9	1.07×10^9	1.55×10^9	2.60×10^9	5.55×10^9
<i>trans</i> - k_{-2} (<i>trans</i> - i9 → i8)	9.29×10^8	9.38×10^8	9.60×10^8	1.36×10^9	2.29×10^9	4.95×10^9
<i>cis</i> - k_{-2} (<i>cis</i> - i9 → i8)	1.06×10^9	1.07×10^9	1.09×10^9	1.61×10^9	2.72×10^9	5.86×10^9
<i>trans</i> - k_3 (<i>trans</i> - i8 → p4)	6.10×10^{10}	6.13×10^{10}	6.24×10^{10}	8.14×10^{10}	1.22×10^{11}	2.21×10^{11}
<i>cis</i> - k_3 (<i>cis</i> - i8 → p4)	6.19×10^{10}	6.22×10^{10}	6.33×10^{10}	8.31×10^{10}	1.25×10^{11}	2.29×10^{11}
<i>trans</i> - k_4 (<i>trans</i> - i8 → p5)	9.30×10^9	9.35×10^9	9.53×10^9	1.28×10^{10}	2.01×10^{10}	3.90×10^{10}
<i>cis</i> - k_4 (<i>cis</i> - i8 → p5)	1.25×10^{10}	1.26×10^{10}	1.29×10^{10}	1.73×10^{10}	2.72×10^{10}	5.27×10^{10}
k_5 (i8 → i6)	7.27×10^8	7.31×10^8	7.48×10^8	1.06×10^9	1.78×10^9	3.82×10^9
k_{-5} (i6 → i8)	1.13×10^8	1.13×10^8	1.16×10^8	1.68×10^8	2.90×10^8	6.47×10^8
<i>trans</i> - k_6 (<i>trans</i> - i9 → p4)	3.05×10^{10}	3.06×10^{10}	3.12×10^{10}	4.16×10^{10}	6.42×10^{10}	1.22×10^{11}
<i>trans</i> - k'_6 (<i>trans</i> - i9' → p4)	3.29×10^{10}	3.31×10^{10}	3.37×10^{10}	4.50×10^{10}	6.92×10^{10}	1.31×10^{11}
<i>cis</i> - k_6 (<i>cis</i> - i9 → p4)	3.59×10^{10}	3.61×10^{10}	3.68×10^{10}	4.88×10^{10}	7.47×10^{10}	1.41×10^{11}
<i>cis</i> - k'_6 (<i>cis</i> - i9' → p4)	3.64×10^{10}	3.66×10^{10}	3.73×10^{10}	4.95×10^{10}	7.58×10^{10}	1.43×10^{11}
<i>trans</i> - k_7 (<i>trans</i> - i9 → i6)	9.65×10^8	6.69×10^8	9.86×10^8	1.29×10^9	1.93×10^9	3.50×10^9
<i>trans</i> - k_{-7} (<i>trans</i> - i6 → i9)	2.19×10^8	2.20×10^8	2.24×10^8	2.96×10^8	4.52×10^8	8.46×10^8
k_8 (i6 → p5)	8.72×10^9	8.77×10^9	8.94×10^9	1.20×10^{10}	1.86×10^{10}	3.57×10^{10}
k_9 (c5 → i20)	4.94×10^7	4.97×10^7	5.09×10^7	7.22×10^7	1.21×10^8	2.51×10^8
k_{-9} (i20 → c5)	7.52×10^{10}	7.55×10^{10}	7.68×10^{10}	9.87×10^{10}	1.42×10^{11}	2.37×10^{11}
k_{10} (c2 → c1)	...	...	...	...	...	...
k_{-10} (c1 → c2)	1.17×10^{10}	1.18×10^{10}	1.21×10^{10}	1.70×10^{10}	2.79×10^{10}	5.56×10^{10}
k_{11} (c3 → i6)	6.21×10^{12}	6.21×10^{12}	6.23×10^{12}	6.47×10^{12}	6.83×10^{12}	7.37×10^{12}
k_{-11} (i6 → c3)	1.72×10^8	1.73×10^8	1.76×10^8	2.39×10^8	3.75×10^8	7.33×10^8
k_{12} (c3 → c5)	4.43×10^{12}	4.43×10^{12}	4.43×10^{12}	4.49×10^{12}	4.58×10^{12}	4.72×10^{12}
k_{-12} (c5 → c3)	1.77×10^{10}	1.77×10^{10}	1.80×10^{10}	2.19×10^{10}	2.95×10^{10}	4.55×10^{10}
k_{13} (c4 → c2)	8.65×10^{11}	8.66×10^{11}	8.68×10^{11}	8.96×10^{11}	9.31×10^{11}	9.72×10^{11}
k_{13} (c2 → c4)	1.28×10^{10}	1.28×10^{10}	1.31×10^{10}	1.79×10^{10}	2.67×10^{10}	4.33×10^{10}

TABLE I. (Continued.)

	0.0	0.03	0.15	2.0	5.0	10.0
k_{14} (c3 → c4')	4.98×10^4	5.31×10^4	6.80×10^4	7.42×10^5	6.60×10^6	6.29×10^7
k_{-14} (c4' → c3)	2.73×10^9	2.88×10^9	3.51×10^9	1.94×10^{10}	7.03×10^{10}	2.14×10^{11}
k_{15} (i7 → i6)	1.03×10^8	1.03×10^8	1.06×10^8	1.42×10^8	2.21×10^8	4.27×10^8
k_{-15} (i6 → i7)	2.74×10^{11}	2.75×10^{11}	2.78×10^{11}	3.25×10^{11}	4.11×10^{11}	5.76×10^{11}
k_{16} (c4 → c4')	7.71×10^{11}	7.74×10^{11}	7.84×10^{11}	9.35×10^{11}	1.15×10^{12}	1.46×10^{12}
k_{-16} (c4' → c4)	3.37×10^{12}	3.77×10^{12}	3.79×10^{12}	3.95×10^{12}	4.15×10^{12}	4.38×10^{12}
k_{17} (c4 → c5)	3.40×10^{10}	3.46×10^{10}	3.67×10^{10}	7.71×10^{10}	1.69×10^{11}	3.73×10^{11}
k_{-17} (c5 → c4)	7.74×10^3	7.96×10^3	8.88×10^3	3.87×10^4	2.34×10^5	2.01×10^6

ted in Fig. 12; the choice is reinforced by the rate constant calculations that disclose at 0.0 collision energy, the k_{14} (**c3**→**c4'**) being eight orders of magnitude slower than k_{11} (**c3**→**i6**) and k_{12} (**c3**→**c5**). Consistent with the **tsc3c5** being 1.3 kcal/mol higher than **tsc3i6** as seen in Fig. 12, the predicted corresponding rate constants k_{11} and k_{12} are $6.21 \times 10^{12} \text{ s}^{-1}$ and $4.43 \times 10^{12} \text{ s}^{-1}$ at 0.0 collision energy, which suggests the route to **i6** is more competitive only by a factor close to 1.5. However, the fact that the intermediate **c5** would most likely undergo ring-closing back to **c3** makes **i6** the predominate intermediate which dictates the outcome of the **c3** paths. Figure 15(c) shows the most probable paths and the corresponding rate constants of **c3**.

The rate constants for the **i6** consumption are in the order of $k_8 > k_{-7} > k_{-11} > k_{-5} > k_{15}$, which is different from the order of activation energy, $E_{a8} < E_{a-7} < E_{a15} < E_{a-11} < E_{a-5}$. Note that the k_8 for **i6**→**p5**+H is predicted larger than others by at least 40 times, which implies **i6** preferably dissociates to 3-cyano propargyl (**p5**)+H while other pathways are almost negligible. Consequently, the most probable reaction path leads **c3** to **p5**+H via the intermediate **i6**.

J. The most probable paths of 1-methyl-allylideneamine (**c4**)

The minimum energy path as a consequence of 1,3 carbon shift to produce **c2** is easily identified as the most probable channel of **c4**, particularly when the corresponding rate constant k_{13} of $8.65 \times 10^{11} \text{ s}^{-1}$ at 0.0 collision energy is compared with the next two probable k_{-14} (**c4'**→**c3**) and k_{17} (**c4**→**c5**) of 2.73×10^9 and $3.40 \times 10^{10} \text{ s}^{-1}$, respectively. Ultimately, the channels of **c1** are followed to yield the products of **p5**+H and **p4**+H as described in Sec. III G. The mechanism is shown in Figs. 15(d) and 13.

K. The most probable paths of *N*-methylidene amino vinylmethylene (**c5**)

Since the rate constant k_9 of the next probable route **c5**→**i20** is a mere $1/10^5$ of k_{12} (**c5**→**c3**) at low collision energies, including only the minimum energy path of **c5**, the

favorable mechanism would proceed through the transition state **tsc3c5** to **c3** that eventually yields **p5** and H as discussed in Sec. III I. The schematic diagram of the most probable paths for **c5** is depicted in Figs. 15(e) and 14.

L. The dissociation products of the **C**+**C₂H₃CN** reaction

The species emerging from dissociations and of energies below the reactants include various products of H (**p1**,**p2**,**p4**,**p5**,**p6**,**p10**), H₂ (**p17**,**p18**,**p24**), CN (**p20**), and C₂H (**p22**) decompositions. In spite of the fact that the cyano propargylene (**p24**)+H₂ are of the lowest energy among the products studied in this work, the propargyl radical (**p20**) is the only CN decomposition product of which the energy is bound by the reactants, and the cyano acetylene (**p22**) appear quite energetically accessible, the detection of these species are expected to be highly unlikely for the reaction of C(³P)+C₂H₃CN(X¹A'). As analyzed in Secs. III G–III K, the elimination of a hydrogen atom remains the exclusive dissociation process included in the most probable paths, where the two substituted propargyl radicals, **p4** and **p5**, are the only products been predicted. It is worth noting that likewise, in the reaction of C(³P)+C₂H₄ only the hydrogen dissociation product of the propargyl radical are predicted⁵¹ to be probable.

Three out of the five collision complexes, **c1**, **c2**, and **c4**, which arise from the carbon addition to the carbon–carbon double bond for the first two and to the carbon of the cyano group for the latter, all give rise to **p4** and **p5** with a ratio close to 5:1 through the ring-opening of **c1** to intermediate cyano allene (**i8**), the immediate predecessor of the final products. Both born of carbon addition to the cyano group, collision complexes **c3** and **c5**, via **c3** ring-opening to the energetically most stable intermediate cyano vinylmethylene (**i6**), produce solely **p5**. It can be inferred simply that while **p5** could be generated from both cyano allene (**i8**) and cyano vinylmethylene (**i6**), the formation of **p4** is due to the decomposition of **i8**.

IV. CONCLUSION

The reaction of a ground state atomic carbon, $C(^3P)$, with a simple unsaturated nitrile, $C_2H_3CN(X^1A')$ (vinyl cyanide) is investigated theoretically to explore the probable routes to the formation of carbon–nitrogen-bearing species in extraterrestrial environments. For the $C(^3P) + C_2H_3CN(X^1A')$ reaction occurring in the environments of ultralow temperature such as interstellar medium, special attention is paid to the channels of energy below the colliding reactants. With the combination of *ab initio* electronic structure calculations and statistics based RRKM theory, the most probable reaction paths and most important products are identified.

With *ab initio* electronic structure calculations, the portions of potential energy surface relevant to the $C(^3P) + C_2H_3CN(X^1A')$ reaction have been characterized by tracking the reaction pathways of the five collision complexes, of which the formation is found barrierless and a result of the carbon-atom addition to the π systems of the C_2H_3CN molecule. They are cyano cyclopropylidene (**c1**), cyano-3-propylidene (**c2**), vinyl-2H-azirine ylidene (**c3**), 1-methylallylideneamine (**c4**), and *N*-methylidene amino vinylmethylene (**c5**). The B3YLP/6-311G(*d,p*) level of theory is utilized in obtaining the optimized geometries, harmonic frequencies, and energies (with zero-point energy corrections) of the intermediates, transition states, and products along the isomerization and dissociation pathways of the collision complexes, including 1,2- and 1,3-hydrogen shift, carbon migration, ring-closure, ring-opening, *cis*–*trans* transformation, and the hydrogen atom, hydrogen molecule, cyano radical, and C_2H decompositions. With the facilitation of computed RRKM rate constants, the most probable paths for each collision complexes are determined, which are comprised mainly of energetically advantageous channels. The CCSD(T)/6-311G(*d,p*) energies with B3YLP/6-311G(*d,p*) zero-point energy corrections are further acquired for the species along the most probable paths at their B3YLP/6-311G(*d,p*) optimized geometries. For each elementary step in the reaction mechanism composed of the most probable paths, the rate constant is calculated according to the RRKM theory for the collision energy in the range of 0–10 kcal/mol. The likely products are identified and the estimation of their yields is provided through the predicted rate constants.

The chained nitriles, cyano propargyl (**p4**) and 3-cyano propargyl (**p5**), resulting from the atomic hydrogen dissociation appear to be the most probable products for the titled reaction. The collision complexes, **c1**, **c2**, and **c4**, are to yield both **p4** and **p5** with 5:1 ratio via decomposition of intermediate cyano allene (**i8**). **p5** is found to be the exclusive dissociation product for collision complexes, **c3** and **c5**, by way of the most stable cyano vinylmethylene (**i6**). The amounts of the products due to H_2 , CN, and C_2H dissociations are expected to be negligible even though the pathways are found energetically accessible. Notably, the most energetically stable product, cyano propargylene (**p24**), as a result of H_2 elimination is not among the most probable products.

For the titled reaction, this study establishes a detailed picture of the products and short-lived intermediates, identifies the paths below the energy of the separated reactants, and predicts the most likely products. In particular, the most probable products of $C(^3P) + C_2H_3CN(X^1A')$, the simplest alkene nitrile, imply an explicit identification of the C vs H atom exchange pathways under single-collision condition, which can be viewed as a one-step mechanism to build up nitrogen-bearing hydrocarbon radicals, similar to the reactions of $C(^3P)$ and unsaturated hydrocarbons. It suggests this class of reaction is an important route to the synthesis of unsaturated nitriles at the temperature as low as 10 K, and the results of the current investigation should be incorporated in future chemical models of interstellar clouds.

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- ¹E. Herbst, *Annu. Rev. Phys. Chem.* **46**, 27 (1995).
- ²R. P. A. Bettens, H.-H. Lee, and E. Herbst, *Astrophys. J.* **443**, 664 (1995).
- ³N. Haider and D. Husain, *Z. Phys. Chem. (Munich)* **176**, 133 (1992).
- ⁴N. Haider and D. Husain, *J. Chem. Soc., Faraday Trans.* **89**, 7 (1993).
- ⁵N. Haider and D. Husain, *J. Photochem. Photobiol., B* **70**, 119 (1993).
- ⁶N. Haider and D. Husain, *Combust. Flame* **93**, 327 (1993).
- ⁷D. C. Clary, N. Haider, D. Husain, and M. Kabir, *Astrophys. J.* **422**, 416 (1994).
- ⁸D. Husain and A. X. Ioannou, *J. Chem. Soc., Faraday Trans.* **93**, 3620 (1997).
- ⁹D. A. Lichtin and M. C. Lin, *Chem. Phys.* **96**, 473 (1985).
- ¹⁰D. L. Yang, T. Yu, N. S. Wang, and M. C. Lin, *Chem. Phys.* **160**, 317 (1992).
- ¹¹K. Seki, M. Yagi, M. He, J. B. Halpern, and H. Okabe, *Chem. Phys. Lett.* **258**, 657 (1996).
- ¹²I. R. Sims, J.-L. Queffelec, D. Travers, B. R. Rowe, L. B. Herbert, J. Karthäuser, and I. W. M. Smith, *Chem. Phys. Lett.* **211**, 461 (1993).
- ¹³D. Chastaing, P. L. James, I. R. Sims, and I. W. M. Smith, *Phys. Chem. Chem. Phys.* **1**, 2247 (1999).
- ¹⁴I. W. M. Smith and B. Rowe, *Acc. Chem. Res.* **33**, 261 (2000).
- ¹⁵E. Herbst, H.-H. Lee, D. A. Howe, and T. J. Millar, *Mon. Not. R. Astron. Soc.* **268**, 335 (1994).
- ¹⁶R. I. Kaiser, Y. T. Lee, and A. G. Suits, *J. Chem. Phys.* **103**, 10395 (1995).
- ¹⁷R. I. Kaiser, Y. T. Lee, and A. G. Suits, *J. Chem. Phys.* **105**, 8705 (1996).
- ¹⁸R. I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y. T. Lee, and A. G. Suits, *Science* **274**, 1508 (1996).
- ¹⁹R. I. Kaiser, D. Stranges, Y. T. Lee, and A. G. Suits, *J. Chem. Phys.* **105**, 8721 (1996).
- ²⁰R. I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y. T. Lee, and A. G. Suits, *J. Chem. Phys.* **106**, 1729 (1997).
- ²¹R. I. Kaiser, D. Stranges, H. M. Bevssek, Y. T. Lee, and A. G. Suits, *J. Chem. Phys.* **106**, 4945 (1997).
- ²²R. I. Kaiser, D. Stranges, Y. T. Lee, and A. G. Suits, *Astrophys. J.* **477**, 982 (1997).
- ²³R. I. Kaiser, A. M. Mebel, A. H. H. Chang, S. H. Lin, and Y. T. Lee, *J. Chem. Phys.* **110**, 10330 (1999).
- ²⁴R. I. Kaiser, I. Hahndorf, L. C. L. Huang, Y. T. Lee, H. F. Bettinger, P. V. Schleyer, H. F. Schaefer, and P. R. Schreiner, *J. Chem. Phys.* **110**, 6091 (1999).
- ²⁵I. Hahndorf, H. Y. Lee, A. M. Mebel, S. H. Lin, Y. T. Lee, and R. I. Kaiser, *J. Chem. Phys.* **113**, 9622 (2000).
- ²⁶B. Balucani, H. Y. Lee, A. M. Mebel, Y. T. Lee, and R. I. Kaiser, *J. Chem. Phys.* **115**, 5107 (2001).
- ²⁷R. I. Kaiser, A. M. Mebel, and Y. T. Lee, *J. Chem. Phys.* **114**, 231 (2001).
- ²⁸R. I. Kaiser, T. L. Nguyen, A. M. Mebel, and Y. T. Lee, *J. Chem. Phys.* **116**, 1318 (2002).
- ²⁹I. Hahndorf, Y. T. Lee, R. I. Kaiser, L. Vereecken, J. Peeters, H. F. Bettinger, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **116**, 3248 (2002).
- ³⁰R. I. Kaiser and N. Balucani, *Acc. Chem. Res.* **34**, 699 (2001).

- ³¹E. Herbst and C. M. Leung, *Astron. Astrophys.* **233**, 177 (1990).
- ³²K. Fukuzawa and Y. Osamura, *Astrophys. J.* **489**, 113 (1997).
- ³³K. Fukuzawa, Y. Osamura, and H. F. Schaefer, *Astrophys. J.* **505**, 278 (1998).
- ³⁴L. C. L. Huang, N. Balucani, Y. T. Lee, R. I. Kaiser, and Y. Osamura, *J. Chem. Phys.* **111**, 2857 (1999).
- ³⁵N. Balucani, O. Asvany, A. H. H. Chang, S. H. Lin, Y. T. Lee, R. I. Kaiser, H. F. Bettinger, P. v. R. Schleyer, and H. F. Schaefer, *J. Chem. Phys.* **111**, 7472 (1999).
- ³⁶N. Balucani, O. Asvany, A. H. H. Chang, S. H. Lin, Y. T. Lee, R. I. Kaiser, H. F. Bettinger, P. v. R. Schleyer, and H. F. Schaefer, *J. Chem. Phys.* **111**, 7457 (1999).
- ³⁷N. Balucani, O. Asvany, A. H. H. Chang, S. H. Lin, Y. T. Lee, R. I. Kaiser, and Y. Osamura, *J. Chem. Phys.* **113**, 8643 (2000).
- ³⁸L. C. L. Huang, A. H. H. Chang, O. Asvany, N. Balucani, S. H. Lin, Y. T. Lee, R. I. Kaiser, and Y. Osamura, *J. Chem. Phys.* **113**, 8656 (2000).
- ³⁹N. Balucani, O. Asvany, L. C. L. Huang, Y. T. Lee, R. I. Kaiser, Y. Osamura, and H. F. Bettinger, *Astrophys. J.* **545**, 892 (2000).
- ⁴⁰N. Balucani, O. Asvany, Y. T. Lee, R. I. Kaiser, and Y. Osamura, *J. Phys. Chem. A* **106**, 4301 (2002).
- ⁴¹F. F. Gardner and G. Winnewisser, *Astrophys. J.* **195**, L127 (1975).
- ⁴²H. E. Matthews and T. J. Sears, *Astrophys. J.* **272**, 149 (1983).
- ⁴³(a) A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993); (b) **96**, 2155 (1992); (c) **97**, 9173 (1992); (d) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ⁴⁴(a) G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982); (b) C. Hampel, K. A. Peterson, and H.-J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992); (c) P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1994); (d) M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.* **227**, 321 (1994).
- ⁴⁵M. J. Frisch *et al.*, GAUSSIAN 98, Revision A.5 (Gaussian, Inc., Pittsburgh, Pennsylvania, 1998).
- ⁴⁶H. Eyring, S. H. Lin, and S. M. Lin, *Basic Chemical Kinetics* (Wiley, New York, 1980).
- ⁴⁷A. H. H. Chang, A. M. Mebel, X.-M. Yang, S. H. Lin, and Y. T. Lee, *J. Chem. Phys.* **109**, 2748 (1998).
- ⁴⁸S. S. Shaik and E. Canadell, *J. Am. Chem. Soc.* **112**, 1446 (1990).
- ⁴⁹See EPAPS Document No. E-JCPSA6-122-306506 for the illustrations of Table sI and Figure sI. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory/epaps. See the EPAPS homepage for more information.
- ⁵⁰N. Honjou, J. Pacansky, and M. Yoshimine, *J. Am. Chem. Soc.* **107**, 5332 (1985).
- ⁵¹T. N. Le, H. Y. Lee, A. M. Mebel, and R. I. Kaiser, *J. Phys. Chem.* **105**, 1847 (2001).