

THE FORMATION OF INTERSTELLAR C₂N ISOMERS IN CIRCUMSTELLAR ENVELOPES OF CARBON STARS: AN AB INITIO STUDY

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Received 2001 May 25; accepted 2001 September 13

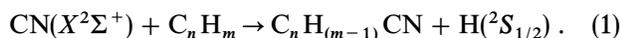
ABSTRACT

The reaction of carbon atoms in their 3P_j electronic ground state with hydrogen cyanide, HCN ($X^1\Sigma^+$), is explored computationally to investigate the formation of hitherto undetected C₂N isomers in the interstellar medium via a neutral-neutral reaction. Our ab initio calculations expose that the reaction has no entrance barrier and proceeds on the triplet surface via addition of the carbon atom to the π -bond, yielding a cyclic HC₂N intermediate. This complex either decomposes to cyclic C₂N plus atomic hydrogen or rearranges via ring opening to the HCNC or HCCN isomers. These molecules can fragment via atomic hydrogen ejection to the linear CCN ($^2\Pi$) and CNC ($^2\Pi_g$) radicals. The formation of all three C₂N isomers proceeds without any exit barrier, but the reactions to form CNC, CCN, and *c*-C₂N are found to be strongly endothermic by 52.7, 59.0, and 99.6 kJ mol⁻¹, respectively. Based on these investigations, the neutral-neutral reaction of atomic carbon with hydrogen cyanide cannot synthesize C₂N isomers in cold molecular clouds, where average translation temperatures of the reactants are only 10–15 K. However, the physical conditions in circumstellar envelopes of, for example, IRC + 10216, differ strongly; close to the photosphere of the central star, temperatures can reach 4000 K, and the elevated velocity of both reactants in the long tail of the Maxwell-Boltzmann distribution can overcome the reaction endothermicity to form at least the linear CNC and CCN isomers. Therefore, these environments represent ideal targets to search for hitherto undetected CNC ($^2\Pi$) and CNC ($^2\Pi_g$) via either infrared or microwave spectroscopy.

Subject headings: astrochemistry — ISM: molecules — molecular processes

1. INTRODUCTION

Exploring the formation of nitrogen-bearing molecules in extraterrestrial environments represents an ideal tool for understanding the chemical history and development of interstellar clouds, circumstellar envelopes of dying carbon stars, and star-forming regions. In particular, the formation of chemically homologous cyanopolyynes [H-(C≡C)_n-CN; $n = 1-5$; Bettens & Herbst 1997; Cernicharo, Guelin, & Kahane 2000; Broten et al. 1984; Bell et al. 1997, 1998] and their radicals [(C≡C)_n-CN; $n = 0-2$; Ohishi & Kaifu 1998; Cernicharo et al. 2000; Guelin, Neinger, & Cernicharo 1998] as observed in the circumstellar envelope of IRC + 10216 have been studied comprehensively in the last years, theoretically in astrochemical models (Cherchneff & Glassgold 1993; Millar & Herbst 1994; Doty & Leung 1998; Ruffe et al. 1997; Millar, Macdonald, & Gibb 1997; Woon & Herbst 1997; des Forets, Flower, & Herbst 1991; Suzuki et al. 1992) and in laboratory experiments (Smith & Rowe 2000; Smith, Sims, & Rowe 1997; Kaiser et al. 1998; Balucani et al. 2000). These studies yielded compelling evidence that neutral-neutral reactions of cyano radicals, CN($X^2\Sigma^+$), with unsaturated hydrocarbons yield nitriles in the interstellar medium via an initial addition of the cyano radical to the carbon-carbon double or triple bond, followed preferentially by atomic hydrogen elimination:

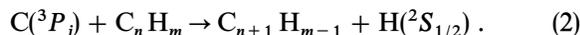


The homologous row H_nC₂N ($n = 0-3$), comprising C₂N (cyanomethylidene), HC₂N (cyanomethylene), H₂C₂N

(cyanomethyl), and H₃C₂N (methylcyanide), represents a particular problem in astrochemistry. Whereas methylcyanide, cyanomethyl, and cyanomethylene have all been observed in the circumstellar shell of the carbon star IRC + 10216, in hot cores (H₃CCN; Olmi et al. 1996), and toward the cold molecular cloud TMC-1 (HC₂N; Irvine et al. 1988), no C₂N isomer has been detected in the interstellar medium so far. Quite surprisingly, the formation of C₂N molecules in extraterrestrial environments has not yet been investigated either experimentally or theoretically in chemical models, although these isomers could represent crucial tracers of physical and chemical conditions where they were formed.

What might be a possible formation mechanism of these C₂N isomers? During the last years, crossed molecular beam experiments of carbon atoms in their C(3P_j) electronic ground state with astrophysically important unsaturated hydrocarbons such as acetylene (C₂H₂), ethylene (C₂H₄), allene (H₂CCCH₂), methylacetylene (CH₃CCH), benzene (C₆H₆), propargyl radicals (C₃H₃), and C₄H₆ isomers demonstrated explicitly that neutral-neutral reactions can synthesize complex, carbon-bearing molecules in cold molecular clouds, as well as in outflow of carbon-rich asymptotic giant branch (AGB) stars (Kaiser et al. 1995, 1996a, 1996b, 1996c, 1997a, 1997b, 1997c, 1998, 1999a, 1999b, 1999c; Ochsenfeld et al. 1997; Huang et al. 2000; Mebel, Kaiser, & Lee 2000; Balucani et al. 2001; Hahndorf et al. 2000). These reactions proceed mainly via an initial collision complex and are dominated by a carbon versus atomic hydrogen exchange pathway to form cyclic and linear hydrocarbon radicals via the generalized reaction

scheme



Since the $C(^3P_j)/C_2H_2$ system was found to reproduce the relative abundances of cyclic and linear C_3H isomers in the cold molecular cloud TMC-1 and in the circumstellar envelope of the carbon star IRC+10216, it is worthwhile to investigate whether the reaction of interstellar carbon atoms with hydrogen cyanide, $HCN(^1\Sigma^+)$, could form the missing C_2N isomers via a similar exchange pathway,



Atomic carbon is ubiquitous in the interstellar medium and has been detected in circumstellar envelopes of evolved stars IRC+10216 and α Ori (Keene et al. 1993; van der Veen, Huggins, & Matthews 1998), in molecular clouds Orion A (Ikeda et al. 1999) and TMC-1 (Flower et al. 1994; Schilke et al. 1995; Maezawa 1999), and toward the proto-planetary nebulae CRL 618 and CRL 2688 (Young 1997). The hydrogen cyanide molecule is isoelectronic with acetylene and has been identified, for example, in the circumstellar envelope of IRC+10216 via *Infrared Space Observatory* (ISO) SWS surveys (Schilke, Mehringer, & Menten 2000; Cernicharo et al. 2000). Therefore, the reaction of atomic carbon with hydrogen cyanide might form C_2N isomers in those regions where both reactants exist. This hypothesis is tested here theoretically, employing electronic structure calculations on the astrophysically important reaction of atomic carbon with hydrogen cyanide.

2. THEORETICAL METHODS

The geometries of the reactants, products, intermediates, and transition states were optimized using the hybrid density functional B3LYP method, i.e., Becke's three-parameter nonlocal exchange functional (Becke 1992) with the nonlocal correlation functional of Lee, Yang, & Parr (1988) and the 6-311G** basis set (Krishnan, Frisch, & Pople 1980). Vibrational frequencies, calculated at the B3LYP/6-311G** level, were used for characterization of stationary points and zero-point energy (ZPE) correction. The stationary points were positively identified for minimum or transition state. In order to obtain more reliable energies, we used the coupled-cluster CCSD(T) method with single, double, and perturbative treatment of triple excitations (Purvis & Bartlett 1982) in conjunction with the correlation-consistent polarized valence triple- and quadruple- ζ basis sets cc-pVTZ and cc-pVQZ (Dunning 1989). The B3LYP/6-311G** optimized geometries were used for the single-point coupled cluster calculations without reoptimization at the CCSD(T)/cc-pVTZ or CCSD(T)/cc-pVQZ levels. For various isomers of C_2N , a comparison of the B3LYP/6-311G** and CCSD(T)/TZ2P (Martin et al. 1994) structures showed that they are very close (see Fig. 2). The GAUSSIAN 98 (Frisch et al. 1998) and MOLPRO 98 (Werner & Knowles 1998)¹ programs were used for the potential energy surface computations.

3. RESULTS

The computations indicate that the carbon atom $C(^3P_j)$ adds to the π -orbital of the $C\equiv N$ triple bond of hydrogen

cyanide without entrance barrier, to yield a three-membered ring intermediate, $c\text{-HC}_2\text{N}$; cf. Figures 1 and 2. According to the CCSD(T)/cc-pVTZ calculations, this complex is bound by $135.6 \text{ kJ mol}^{-1}$ with respect to the reactants, and has a 3A electronic ground state. The carbon-carbon bond is 1.435 \AA long, thus ranging between a C—C single bond in ethane (1.526 \AA) and a C=C double bond in ethylene (1.339 \AA). The newly formed carbon-nitrogen bond is very long (1.563 \AA) and can be best described as a C—N single bond. The original carbon-nitrogen triple bond in hydrogen cyanide extends slightly from 1.1532 to 1.239 \AA . We would like to stress that no reaction pathway from the separated reactants via addition to terminal nitrogen atom or insertion into the H—C bond to form HCNC or HCCN, respectively, could be located. Therefore, $c\text{-HC}_2\text{N}$ represents the initial collision complex in the neutral-neutral reaction of ground-state atomic carbon with hydrogen cyanide.

The $c\text{-HC}_2\text{N}$ intermediate either decomposes via atomic hydrogen loss without exit barrier to the cyclic $c\text{-C}_2\text{N}$ isomer (C_{2v} point group; 2A_1 electronic state), or the ring opens. The cyclic reaction product shows a long C—C bond of 1.585 \AA (1.6081 \AA at the CCSD(T)/TZ2P level of theory; Martin et al. 1994), which is slightly longer by $0.06\text{--}0.08 \text{ \AA}$ than the carbon-carbon single bond in the ethane molecule. On the other hand, the carbon-nitrogen bond is very short (1.302 \AA). This short bond distance can be explained in terms of two classical resonance structures, as shown in Figure 3.

A ring opening of $c\text{-HC}_2\text{N}$ can form triplet isocyanocarbene (HCNC) and cyanocarbene (HCCN) via barriers of only 18.2 and 21.8 kJ mol^{-1} , respectively. The transition states to ring opening thus lie 117.4 and $113.8 \text{ kcal mol}^{-1}$ lower in energy than the reactants, $C(^3P_j) + HCN$; i.e., the barriers are considerably below the entrance energy. Both intermediates are bent (C_s point group) and have a $^3A''$ electronic state. The computed bent

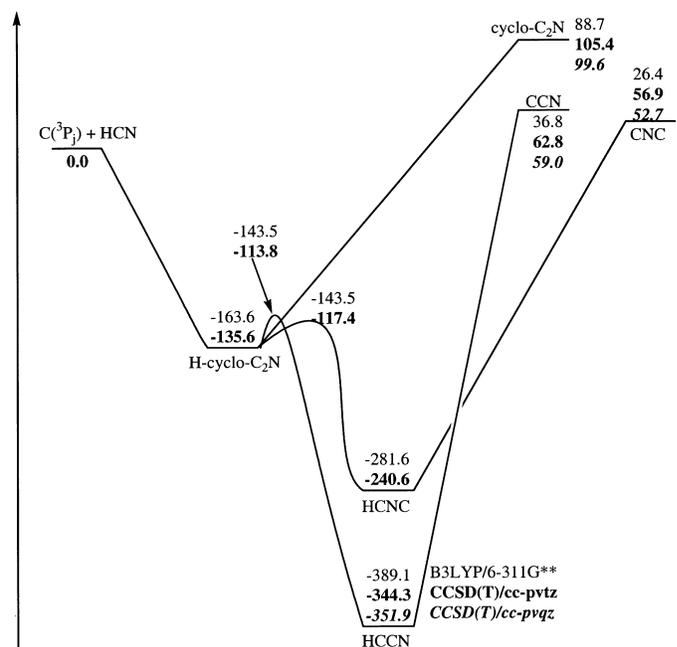


FIG. 1.—Schematic potential energy surface of the reaction of atomic carbon $C(^3P_j)$ with hydrogen cyanide HCN; calculations are indicated at three levels of theory.

¹ MOLPRO User's Manual (Werner & Knowles 1998) is also available at <http://www.tc.bham.ac.uk/molpro>.

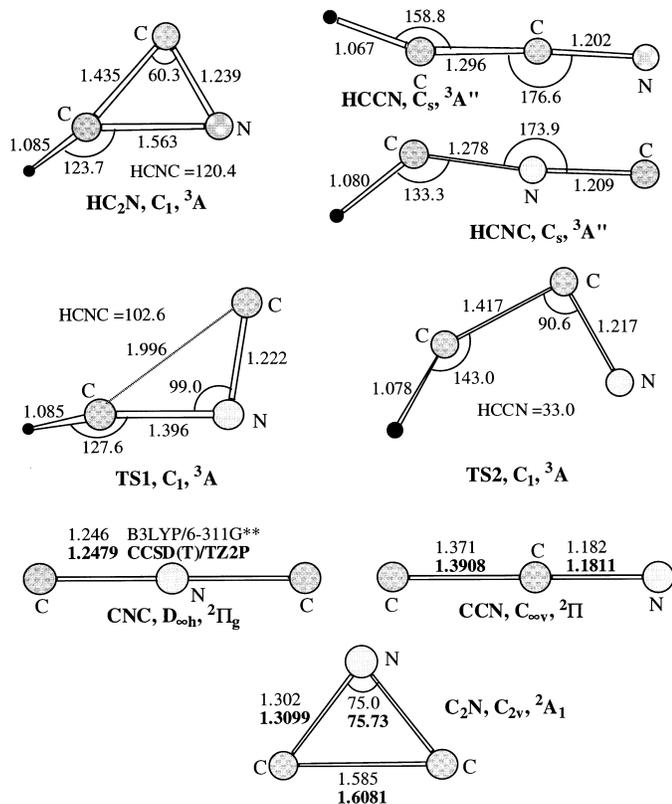


FIG. 2.—B3LYP/6-311G** optimized geometries of intermediates, transition states, and products involved in the reaction of atomic carbon with hydrogen cyanide, together with their point groups and electronic wave functions. Important bond distances are given in angstroms, bond angles in degrees. Bold numbers show CCSD(T)/TZ2P optimized geometric parameters for the C_2N isomers (Martin et al. 1994).

HCCN geometry agrees with earlier theoretical (Goldberg, Fiedler, & Schwarz 1995; Seidel & Schaefer 1992) and experimental (McCarthy et al. 1995) investigations; the linear carbene-like $H-C=C=N$ structure was found to be a transition state located only 9 kJ mol^{-1} (Seidel & Schaefer 1992) and 3 kJ mol^{-1} (McCarthy et al. 1995) above the C_s minimum. Our calculations show that the $C\equiv N$ moiety is well noticeable in both isomers, and conjugation with the second carbon atom increases the carbon-nitrogen triple bond length to 1.209 and 1.202 Å, compared to 1.1532 Å in hydrogen cyanide. Both isomers reside in deep potential energy wells of $240.6 \text{ kJ mol}^{-1}$ (HCNC) and $344.3 \text{ kJ mol}^{-1}$ (HCCN) at the CCSD(T)/cc-pVTZ level of theory. When the larger cc-pVQZ basis set is used to calculate HCCN, the well depth slightly increases to $351.9 \text{ kJ mol}^{-1}$. Analogously to triplet HCN/HNC, the cyano isomer HCCN is more stable by about 104 kJ

mol^{-1} than the HCNC structure. This data is in strong agreement with a recent investigation of Goldberg et al. (1995), yielding a similar value of 108 kJ mol^{-1} . A common reaction pathway of HCCN and HCNC is the barrierless atomic hydrogen loss to form linear $CNC(^2\Pi_g)$ and $CCN(^2\Pi)$, respectively. The computed geometries of the linear C_2N isomers depict short carbon-nitrogen distances (1.246 and 1.182 Å) as well as a longer carbon-carbon bond (1.371 Å). Therefore, the CNC structure is best described as two carbon-nitrogen double bonds with the unpaired electron delocalized in the π molecular orbital; the geometry of the energetically less stable CCN product suggests a contribution of two resonance structures $C=C=N$ and $C-C\equiv N$, i.e., a carbon-carbon distance ranging between a single and double bond and a slightly elongated carbon-nitrogen bond compared to the hydrogen cyanide reactant. The computed geometry of the CNC isomer is in excellent agreement with an experimental data of the carbon-nitrogen bond length of 1.245 Å (Merer & Travis 1996). Likewise, our bond distances of the CCN product are close to the recent results of Pd & Chandra (2001), i.e., 1.4045 and 1.1889 Å at the full-valence CASSCF level. For all three C_2N isomers, our B3LYP/6-311G** bond distances are very similar to the most reliable CCSD(T)/TZ2P data by Martin et al. (1994), with an average absolute deviation of only 0.01 Å.

Regarding a possible future search for interstellar C_2N isomers, it is further very interesting to compare the computed vibrational frequencies with experimental data. So far, only data of the CCN structure has been obtained experimentally as 1923 cm^{-1} (ν_1), 325 cm^{-1} (ν_2), and 1051 cm^{-1} (ν_3) (Brazier, O'Brien, & Bernath 1987; Oliphant et al. 1990). These frequencies are reasonably close to ours (2017.9 , 401.7 , and 1077.5 cm^{-1}) and previously calculated ones, e.g., 1970 , 328 , and 996 cm^{-1} (Pd & Chandra 2001; Hakuta et al. 1983; Gillett & Brown 1994; Gabriel, Reinsch, & Rosmus 1994; Martin et al. 1994; Allen et al. 2000). Table 1 compiles the vibrational frequencies of all C_2N isomers investigated in the present study.

Last but not least, we investigated the overall energetics of the reaction to form C_2N isomers in the interstellar medium. At the highest level of theory [CCSD(T)/cc-pVQZ with ZPE], the overall reactions to form $CNC(^2\Pi_g)$, $CCN(^2\Pi)$, and $c-C_2N(^2A_1)$ from the separated reactants was found to be strongly endothermic by 52.7, 59.0, and 99.6 kJ mol^{-1} , respectively. This result correlates nicely with previous CCSD(T) and MRD-CI calculations with smaller basis sets, illustrating that the $CNC(^2\Pi_g)$ isomer is thermodynamically more stable than $CCN(^2\Pi)$ by 3.1 kJ mol^{-1} (Martin et al. 1994) and 0.7 kJ mol^{-1} (Pd & Chandra 2001), and the $c-C_2N(^2A_1)$ isomer lies 50.7 kJ mol^{-1} above $CNC(^2\Pi_g)$ (Martin et al. 1994).

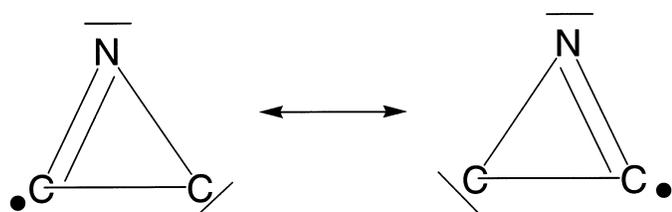


FIG. 3.—Classical resonance structures of the $c-C_2N$ isomer

TABLE 1

CALCULATED VIBRATIONAL FREQUENCIES OF C_2N ISOMERS

Isomer	Vibration Frequencies (cm^{-1})
CCN ($X^2\Pi$)	2017.9 (111.0), 1077.5 (71.5), 401.7 (16.3)
CNC ($X^2\Pi_g$)	1502.1 (48.4), 1298 (0.0), 318.5 (7.6)
$c-C_2N$ (X^2A_1)	1612.8 (39.6), 898.7 (31.5), 662.1 (0.4)

NOTE.—Infrared intensities in km mol^{-1} are given in parentheses.

It should also be noted that the other reaction product channels are much more endothermic than the carbon/hydrogen exchange, by 192.7, 193.1, and 336.0 kJ mol⁻¹ for N(⁴S) + C₂H(X²Σ⁺), CH(X²Π) + CN(X²Σ⁺), and NH(X³Σ) + C₂(X¹Σ_g⁺), respectively.

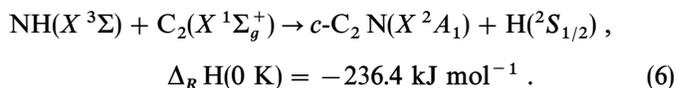
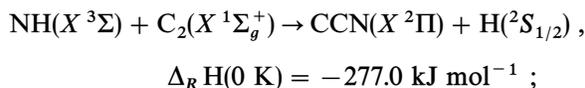
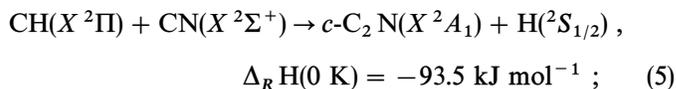
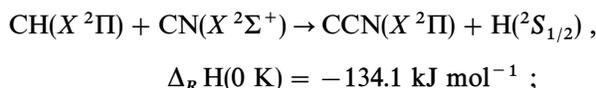
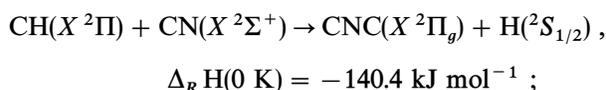
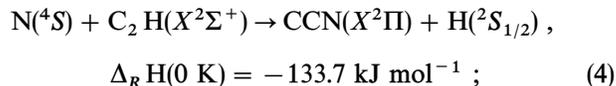
4. DISCUSSION AND ASTROPHYSICAL IMPLICATIONS

Our investigations demonstrated explicitly that the reaction of atomic carbon with hydrogen cyanide can form three C₂N isomers, i.e., CCN(X²Π), CNC(X²Π_g), and *c*-C₂N(X²A₁). But although the addition of atomic carbon to hydrogen cyanide has no entrance barrier and all isomerization barriers of the initial *c*-HC₂N addition complex range below the energy of the separated reactants, the overall reactions to C₂N isomers are strongly endothermic by at least 52.7 kJ mol⁻¹ to form the thermodynamically most stable CNC structure. These energetics impose considerable constraints on the formation of C₂N molecules in the interstellar medium. First, a synthesis of these doublet radicals via the neutral-neutral reaction of atomic carbon with hydrogen cyanide in cold molecular clouds can be safely ruled out. Although both reactants have been observed in the dark molecular clouds TMC-1 and OMC-1, the averaged translational temperatures of C(³P_j) and HCN of only 10–15 K cannot compensate for a reaction endothermicity of even 52.7 kJ mol⁻¹. Recall that typical temperatures in cold clouds correspond approximately to an average translation energy of about 0.1 kJ mol⁻¹. Since the HC₂N intermediates cannot be stabilized by collisions and do not have sufficient energy to give the products, they decompose back to the reactants, C(³P_j) + HCN. However, the physical conditions in carbon-rich, circumstellar envelopes differ strongly from those of cold interstellar environments. Spectroscopic investigations suggest that close to the atmosphere of the central star, temperatures can reach up to 4000 K, and the elevated velocity of both reactants in the long tail of the Maxwell-Boltzmann distribution might overcome the reaction endothermicity to form at least the linear CNC and CCN isomers. Based on the potential energy surface involved, CNC is expected to be slightly more abundant than CCN. First, the barrier of ring-opening in the *c*-HC₂N intermediate to HCNC (the precursor to CNC) is a little lower, by 3.6 kJ mol⁻¹, than the corresponding barrier to form HCCN, the precursor to yield CCN. Second, the reaction to synthesize CNC is less endothermic by 6.3 kJ mol⁻¹ compared to CCN. Both effects should be reflected in a slightly enhanced abundance of CNC compared to CCN. The cyclic *c*-C₂N isomer is expected to be only a minor reaction product. These findings are in strong contrast to the isoelectronic C(³P_j)/C₂H₂ system studied earlier (Kaiser et al. 1995, 1996b, 1997a, 1997b, 1999a; Ochsenfeld et al. 1997). The reactions to both the *c*-C₃H and *l*-C₃H isomers were found to be slightly exothermic by -8.6 and -1.5 kJ mol⁻¹, respectively. These discrepancies underline that a careful investigation of potential energy surfaces even of isoelectronic systems is of crucial importance to draw meaningful, astrochemically relevant conclusions on important chemical problems.

Based on the C(³P_j)/HCN potential energy surface, future astronomical surveys for the hitherto undetected C₂N isomer can be guided carefully. First, prospective searches should focus on the detection of the CNC and CCN structures, rather than the *c*-C₂N isomer. Second, circumstellar

envelopes of carbon-rich AGB stars, such as of IRC+10216, should be investigated preferentially, since the energetics inhibit a synthesis of any C₂N isomer in cold molecular clouds. The CCN isomer has only a small dipole moment of 0.1328 D, and a search via microwave spectroscopy might be extremely challenging. Since further CNC depicts no pure rotational spectrum, a detection of both linear isomers in the infrared regime might be advisable; cf. Table 1 and § 3 for theoretically predicted and experimentally obtained vibrational frequencies.

Finally, we would like to discuss possible alternative synthetic routes to interstellar C₂N isomers via neutral-neutral reactions, i.e., binary collisions of two open-shell reactants in the following reactions:



The reaction energies shown above were obtained from our CCSD(T)/cc-pVQZ+ZPE (B3LYP/6-311G**) calculations. All reactants in reactions (4)–(6) are ubiquitous in the interstellar medium. For example, both the cyano CN(X²Σ⁺) and the ethynyl C₂H(X²Σ⁺) radicals have been observed in interstellar clouds such as the Taurus Molecular Cloud 1 (TMC-1), the Orion Molecular Cloud (OMC-1), and the outflow of old, dying carbon stars such as IRC+10126 (Cherchneff & Barker 1992a; Cherchneff, Barker, & Tielens 1991; Tucker, Kunter, & Thaddeus 1974; Cernicharo et al. 2000). Transitions of C₂(X¹Σ_g⁺) were observed toward warm carbon stars such as IRC+10126 (Yorka 1983) and post-AGB stars such as HD 56126 (Crawford & Barlow 2000). Atomic nitrogen, for example, is expected to react with the ethynyl radical without entrance barrier to form the triplet HCCN intermediate, which decomposes in a strongly exothermic reaction (reaction [4]) to the CCN(X²Π) isomer plus atomic hydrogen. Likewise, both cyano and methyldene radicals can react without barrier to either singlet/triplet HCCN and/or HCNC complexes fragmenting to CCN(X²Π) and CNC(X²Π_g) radicals, respectively (reaction [5]). Alternatively, methyldene can add to the carbon-nitrogen triple bond to form a three-membered ring intermediate, which loses a hydrogen atom, giving *c*-C₂N(X²A₁). Finally, NH(X³Σ) could react with the dicarbon molecule via either cyclic *c*-NHC₂ or a HNCC intermediate; both can decompose via an H loss to

form *c*-C₂N(*X*²A₁) or CCN(*X*²Π). These possibilities have to be investigated further in detail. Most importantly, however, reactions (4) and (5) most likely have no entrance barrier and are strongly exothermic, thus representing potential pathways to C₂N isomers even in cold molecular clouds.

A. M. M. is indebted the National Science Council, ROC (grant NSC 90-2113-M-001-068) for support. R. I. K. acknowledges support from The University of York, Department of Chemistry, UK. This work was performed within the International Astrophysics Network.

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