

Energy Landscape, and Structural and Spectroscopic Characterization of Diazirine and Its Cyclic Isomers

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ABSTRACT

Identifying new nitrogenated hydrocarbon molecules in the interstellar medium (ISM) is challenging due to the lack of comprehensive spectroscopic data from experiments. In this computational work, we focus on investigating the structures, relative energies, spectroscopic constants, and energy landscape of the cyclic isomers of diazirine ($c\text{-CH}_2\text{N}_2$) using *ab initio* quantum chemical methods. Density functional theory (DFT) methods and coupled cluster theory with singles and doubles including perturbative triples [CCSD(T)] and CCSD(T) with the explicitly correlated F12b correction [CCSD(T)-F12b] were employed for this purpose along with large correlation consistent cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets. Harmonic vibrational frequencies, infrared vibrational intensities, rotational constants, and dipole moments are reported. Anharmonic vibrational fundamentals along with centrifugal distortion constants, and vibration-rotation interaction constants are also reported for all the cyclic isomers. The energies computed with the CCSD(T) and CCSD(T)-F12b methods were extrapolated to the one-particle complete basis set (CBS) limit following a three-point formula. At the CCSD(T)-F12b/CBS level of theory the 3,3*H*-diazirine ($c\text{-CH}_2\text{N}_2$) is the lowest energy cyclic isomer followed by 1,3*H*-diazirine, (E)-1,2*H*-Diazirine, and (Z)-1,2*H*-diazirine which are 20.1, 47.8, and 51.3 kcal mol⁻¹ above the 3,3*H*-Diazirine, respectively. Accurate structures and spectroscopic constants that are reported here could be useful for future identification of these cyclic nitrogenated organic molecules in the interstellar medium or circumstellar disks.

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I. INTRODUCTION

Pure carbon containing cyclic molecules as well as nitrogenated organics have been identified in the interstellar medium (ISM) via telescopic observation. Large organic molecules with nitrogen containing rings have been extracted from meteoritic samples and have been proven to be of extraterrestrial origin.¹⁻² A variety of organic molecules are observed in astrophysical environments; yet many more simple molecules have yet to be identified.³ Interstellar clouds are well-known to be a reservoir of molecules with unusual structures,⁴ some of these molecules are nitrogenous. Although, nitrogenous hetero-cyclic organics form the basis of many biomolecules, no nitrogen containing cyclic molecule in which nitrogen is part of the cyclic structure has ever been detected in the gas phase ISM despite numerous observational and theoretical studies.⁵⁻¹⁴ Non-cyclic nitrogen-containing molecules such as methyl cyanide, methyl isocyanide and etheneimine have been detected.^{3, 15-18} Some linear isomers of diazomethane (CH_2N_2) have been identified in the interstellar medium although diazomethane itself has not been identified thus far.^{16-17, 19} Azirines ($\text{C}_2\text{H}_3\text{N}$) are cyclic molecules isomeric with methyl cyanide which has been observed in many astronomical environments.⁸ Cyclic diazirines ($\text{c-H}_2\text{NCN}$) are isomeric with cyanamide, NH_2CN , which has been detected in the interstellar medium;²⁰ isomeric with diazomethane (CH_2N_2); and isoelectronic with methyl cyanide (CH_3CN).

Diazomethane is a versatile reactant that produces alcohol or carboxylic acid in solution depending on the $p\text{H}$. Diazirine can form reactive carbenes by thermolysis or photolysis making it a favorable molecule to study.²¹ Cyclic diazirine has been synthesized in the gas phase,²²⁻²⁴ and its transformation to diazomethane has been reported both in the gas phase and in a matrix.²⁵ Diazirine can be formed via cyclization of diazomethane or its other linear isomers. In the gas phase, diazirines can be formed straightforwardly by the bimolecular association reactions of NH and HCN , and CH_2 with N_2 . Ogilvie²⁶⁻²⁸ and other authors indicated that cyclic diazirine can be formed by the dissociation-recombination or by the rearrangement of diazomethane in a matrix. Photodissociation of diazomethane reversibly produces diazirine, although excitation of diazirine to its first excited electronic state may dissociate it to carbene and nitrogen.²⁹ The photoionization and dissociation processes via electronic excitation to the first two excited states lead to CH and N_2H^+ , and CH_2^+ and N_2 .³⁰

While vibrational and rotational spectral properties are well known for cyanamide, this is not the case for all the cyclic diazirines.³¹⁻³² While the 3,3H-diazirine has been synthesized and its microwave and infrared (IR) spectra are recorded, those for the other three cyclic isomers are not well known. The ground state rotational constants and molecular geometry 3,3H-diazirine were measured by microwave spectroscopy by Pierce et al.²⁷ Gas and matrix phase microwave spectra were also reported by Ogilvie.²⁶ The purpose of this work is to investigate the structural, energetic and rovibrational spectroscopic characterization of all the low-lying cyclic isomers of diazirine using high-level *ab initio* quantum chemical methods. Recent identification of benzonitrile in the gas phase indicates that nitrogen containing cyclic molecules do exist in the ISM.⁶ Nevertheless, no molecules have been identified in the gas phase interstellar medium thus far that contain a nitrogen atom in the ring of an organic molecule.

II. METHODS

Molecular geometries of the isomers were computed using coupled cluster theory with singles and doubles with perturbative triples [CCSD(T)] and the CCSD(T)-F12b method, which includes explicit correlation, with the correlation consistent cc-pVTZ, and cc-pVQZ basis sets. The CCSD(T)-F12b method shall be referred to as CCSD(T)-F12 from hereon. Harmonic vibrational frequencies were calculated using the cc-pVTZ, cc-pVQZ basis sets in conjunction with CCSD(T). Density Functional Theory (DFT) using the hybrid B3LYP functional with cc-pVTZ were employed for initial geometry optimizations, harmonic frequency calculations, and double harmonic intensity computations. All DFT computations were performed using the Q-Chem 5.0³³ quantum chemistry package. All coupled cluster calculations were done using the MOLPRO 2015 package.³⁴ The energies were further extrapolated to the complete basis set limit by a three-point extrapolation formula. using energies obtained with CCSD(T)//cc-pVTZ, cc-pVQZ, and cc-pV5Z at the CCSD(T)/cc-pVQZ geometry. The same extrapolation to the complete basis set limit was performed using the CCSD(T)-F12 method as well. Anharmonic vibrational fundamentals and rovibrational anharmonic constants were calculated using the well-established second-order vibrational perturbation theory (VPT2) including resonances.³⁵ The anharmonic vibrational frequencies and related spectroscopic constants were computed at the CCSD(T)/cc-pVTZ level of theory. Quartic force fields (QFF) at this level of theory are known to produce

anharmonic vibrational fundamentals that are within about ~ 10 wavenumbers of the experimental fundamentals. Our own tests show that the vibrational fundamentals are usually close to the experimental vibrational fundamentals for small molecules.³⁵ The SURF and POLY programs, available within the MOLPRO 2015 package, were used for the VPT2 anharmonic analysis. For analyzing these geometries, the molecular visualization and analysis program Visual Molecular Dynamics (VMD) was used.³⁶

III. RESULTS AND DISCUSSION

For this study we investigated four cyclic isomers of diazirine ($c\text{-CH}_2\text{N}_2$). Out of the cyclic isomers, 3,3*H*-diazirine (3*H*-diazirine) (Figure 1) is lowest in energy followed by 1,3*H*-diazirine (1*H*-diazirine), (E)-1,2*H*-diazirine ((E)-3-diaziridinylidene), and (Z)-1,2*H*-diazirine ((Z)-3-diaziridinylidene). The relative energies and dipole moments of the isomers are given in Table 1. Molecular geometries were fully optimized, and vibrational frequencies were calculated for the four cyclic isomers given in Figure 1. There are small and expected differences in the relative energies of the isomers between the different methods, but the relative energy ordering of the isomers remains consistent as 3,3*H*-diazirine < 1,3*H*-diazirine < (E)-1,2*H*-diazirine < (Z)-1,2*H*-diazirine. A three-point extrapolation of the energies calculated at CCSD(T)/cc-pVTZ, cc-pVQZ, and cc-pV5Z level based on the geometries obtained at the CCSD(T)/cc-pVQZ level of theory improves the estimated relative energies of the isomers.³⁷⁻³⁹ At the CCSD(T)/CBS level, as indeed at the CCSD(T)-F12/CBS, after correcting for zero-point vibrational energy, the three cyclic isomers 1,3*H*-diazirine, (E)-1,2*H*-diazirine, and (Z)-1,2*H*-diazirine are 20.1, 47.8, and 51.3 kcal mol⁻¹ above 3,3*H*-diazirine, respectively. Relative energies calculated using the CCSD(T)-F12/cc-pVQZ-F12 level of theory (i.e., use of the cc-pVQZ-F12 basis set) does not improve the relative energies any further. Although exact estimates of the uncertainties associated with the relative energies of the isomers are not possible in absence of experimental heats of formation or computationally calculated energies at the full-CI limit with a large basis set, the relative energies reported here extrapolated to the complete basis set limit may have uncertainties of 0.2–0.5 kcal mol⁻¹ as pointed out elsewhere.⁴⁰ Although prescriptions exist about the estimates of uncertainties, without some benchmark calculations on similar systems it is impossible to put a number value for the uncertainty intervals.⁴¹⁻⁴² The inclusion of the explicitly correlated F12 corrections to

CCSD(T) does not alter the relative energies any further, suggesting that they are already converged to near their actual values. At the CCSD(T)/cc-pVTZ level the lowest cyclic isomer 3,3H-diazirine is 8.6 kcal/mol above the linear diazomethane (including the zero-point energies), a zwitterionic versatile reactant used in organic synthesis of a wide variety of organics including acids and cyclic molecules. Diazomethane is known to supply a CH₂ group leaving behind a very stable N₂ in reactions with unsaturated hydrocarbons. The dissociation limit to form ¹CH₂ and N₂ from the lowest cyclic isomer 3,3H-diazirine is 24.5 kcal mol⁻¹ according our calculations as seen in Figure 2. Xu and Lin found this dissociation limit to be 25.5 kcal mol⁻¹ at a slightly lower CCSD(T)/6-311+G(3df,2p) level of theory.⁴³ The dissociation energy due to breaking of two C-N bonds is partially compensated by the formation of a N-N bond in the product N₂. This means that the second-lowest cyclic isomer 1,3H-diazirine is still lower than the dissociation limit on the singlet surface. The transition state between 3,3H-diazirine and 1,3H-diazirine is, however, above the dissociation limit. The other two isomers are above the dissociation limit. These three isomers, therefore, are unlikely to form via a direct hydrogen migration from the lowest cyclic isomer, although many other formation mechanisms may exist. The dissociation to ground state triplet methylene is 14.7 kcal mol⁻¹ above the 3,3H-diazirine.

3,3H-Diazirine. The lowest energy cyclic isomer, 3,3H-diazirine, (C_{2v}, ¹A₁) is shown in Figure 1. Two hydrogen atoms are attached to the carbon atom in a tetrahedral-type arrangement. This cyclic isomer is structurally most closely related with diazomethane. There is a slightly shortened double bond between the two nitrogen atoms and a single bond between the carbon and nitrogen atoms on both sides. The bond angles and bond lengths at the CCSD(T)/cc-pVQZ level are <HCN 117.1°, <HCH 119.8°, <NCN 49.1°, H-C 1.079 Å, C-N 1.480 Å, and N-N 1.230 Å. Structural parameters of 3,3H-diazirine using different methods and basis sets are shown in Figure 1. 3,3H-diazirine has a large dipole moment of 1.95 Debye (calculated at the CCSD(T)/cc-pVQZ level of theory) making it a suitable candidate for detection via pure rotational spectroscopy, or via rovibrational spectroscopy. The cartesian coordinates and x, y, z components of the dipole moment (along with harmonic and anharmonic vibrational fundamentals, overtones, and combination bands) are included in the supplementary information available online. 3,3H-diazirine is not only the lowest energy cyclic isomer but is also flanked by the transition barrier of 110 kcal mol⁻¹ for its conversion to other cyclic structures, which is the tallest on the singlet potential energy surface as shown in

Figure 2. Association of methylene and nitrogen molecule releases 174 kcal mol⁻¹ of energy, as shown in Figure 2. These significant barriers likely makes the cyclic isomer 3,3H-diazirine stable towards isomerization or dissociation.

Harmonic vibrational frequencies, calculated with the B3LYP/cc-pVTZ level of theory (together with double harmonic IR intensities), and the CCSD(T) level with the cc-pVTZ and cc-pVQZ basis sets, are presented in Table 2. Two large intensity modes are seen, one around 1006 cm⁻¹, and the other around 1658 cm⁻¹ due to the symmetric combination CN stretching mode. In Table 3 we report the vibrationally averaged geometry, harmonic and fundamental vibrational frequencies, vibration-rotation interaction constants, centrifugal distortion constants and zero-point vibrational energies of 3,3H-diazirine. The largest anharmonicities are seen in the two CH stretching modes: -134.9 cm⁻¹ (*a₁*) and -147.3 cm⁻¹ (*b₁*) respectively. The stretching modes involving the three heavy elements are relatively less anharmonic, varying by -26.3, -39.9 and -19.4 cm⁻¹. Anharmonic VPT2 corrections for the other modes fall between -14 and -40 cm⁻¹. Vibrational fundamentals calculated in this work compare very well with the experimental vibrational frequencies of gas phase diazirine obtained by Ettinger.⁴⁴ The *v*₈ vibrational frequency observed by Ettinger at 3020 cm⁻¹ is only 0.4 cm⁻¹ above the vibrational fundamental calculated by VPT2 here. The two stretching fundamentals at 964.7 and 989.9 cm⁻¹ are only 2.3 and 1.1 cm⁻¹ from the experimentally obtained frequencies.⁴⁴ Calculated *a₁* symmetry stretching fundamentals are only 2.2 and 0.4 cm⁻¹ from the *v*₂ and *v*₃ experimental vibrational frequencies at 1626 and 1458 cm⁻¹, respectively. Our calculated rotational constants *A*₀ 40696, *B*₀ 23726, and *C*₀ 16731 MHz as reported in Table 3 compare very well with the experimental rotational constants obtained by pure rotation spectroscopy, *A*₀ 40956.72, *B*₀ 23667.76, and *C*₀ 16726.26.²⁷ The molecular geometrical parameters obtained by Pierce et al.²⁷ are in very good agreement with the ones calculated here as well. The calculated rotational constants tend to do (comparatively) the worst for the *A* constant, while *B* and *C* are usually much better, as pointed out by Gardner et al.⁴⁵ for CCSD(T) data in their recent paper. Fundamental vibrational frequencies together with double harmonic intensities were plotted for the four cyclic isomers in Figure 3 with a full width half maximum of 10 cm⁻¹.

1,3H-Diazirine. The second-lowest energy cyclic isomer is 1,3H-diazirine (*C*₁ symmetry), which is 20.1 kcal mol⁻¹ above 3,3H-Diazirine at the CCSD(T)-F12/CBS level of theory. This isomer has a cyclic arrangement with two nitrogen atoms and a carbon in the ring, and one hydrogen is

connected to a carbon atom, and the other to a nitrogen atom. At the CCSD(T)/cc-pVQZ level the bond angles and bond lengths are $\langle\text{HNN}\ 103.1^\circ$, $\langle\text{HNC}\ 107.1^\circ$, $\langle\text{NCH}\ 141.5^\circ$, H-N 1.023 Å, N-N 1.696 Å, N-C (hydrogen attached) 1.413 Å, C-H 1.079 Å, and N-C 1.245 Å. The H-N bond is a slightly elongated single bond, whereas the N-C (hydrogen attached) and C-H bonds are slightly shorter single bonds because of their hybridization state. The N-C with the free nitrogen is a strong double bond. 1,3*H*-diazirine has a large dipole moment of 3.29 Debye – see Table 1. The two transition states, one between 3,3*H*-diazirine and 1,3*H*-diazirine, and one between (E)-1,2*H*-diazirine and 1,3*H*-diazirine are presented in Figure 2. These transition states are essentially the ones in which the hydrogen atom moves from the carbon to nitrogen. The transition state between 1,3*H*-Diazirine and (E)-1,2*H*-Diazirine is 83.3 kcal mol⁻¹ above the 3,3*H*-diazirine minimum at the CCSD(T)/cc-pVTZ level; the hydrogen migration transition barrier is 61.6 kcal/mol. 1,3*H*-Diazirine is rather well-protected by large transition barriers from hydrogen migration leading to either 3,3*H*-diazirine or 1,2*H*-diazirine. Each transition state was confirmed by carrying out an intrinsic reaction coordinate (IRC) calculation, and optimization and frequency calculations.

The harmonic vibrational frequencies of 1,3-*H*-diazirine were determined using the B3LYP, and CCSD(T) methods and are given in Table 2. The CN and CC stretching modes appearing at 972, 1024 and 1192 cm⁻¹ have three of the largest IR intensities due to them deforming the dipole derivatives the most. A vibrational frequency at 790 cm⁻¹ also has a somewhat large IR intensity. In Table 4 we report the vibrationally averaged geometry, harmonic and fundamental vibrational frequencies, vibration-rotation interaction constants, centrifugal distortion constants, and zero-point vibrational energies of 1,3*H*-diazirine calculated using the CCSD(T)/cc-pVTZ level of theory. The largest anharmonicity of -185.1 cm⁻¹ is observed for the NH stretching mode appearing at 3204.2 cm⁻¹. The CH stretching mode appearing at 3100.5 cm⁻¹ also exhibits a large anharmonicity of -138.6 cm⁻¹. The C-N triple bond stretching mode shows a modest anharmonicity of -34.5 cm⁻¹.

(E)-1,2*H*-Diazirine. (E)-1,2*H*-diazirine is 47.8 kcal mol⁻¹ above 3,3*H*-diazirine at the CCSD(T)/cc-pVQZ level of theory, making it the third lowest in energy of the cyclic isomers. The structure of this isomer consists of two nitrogen atoms and the carbon in a cyclic arrangement with one hydrogen coming off each nitrogen. The hydrogen atoms are pointing in opposite directions making it an E isomer with a C₂ point group symmetry. The Z-isomer discussed in the next section

is slightly higher up in energy due to the repulsion of the lone-pair electron cloud of the nitrogen atoms. As for the bond lengths, there are slightly elongated NH single bonds between the two nitrogen atoms and the hydrogen atoms. The two bonds between the carbon atom and the two nitrogen atoms are intermediate between a single and double bond. There is an elongated single bond between the two nitrogen atoms at the base of the molecule. At the CCSD(T)/cc-pVQZ level of theory the bond angles and bond lengths specifically are $\langle\text{HNC}\rangle 114.5^\circ$, $\langle\text{NCN}\rangle 66.0^\circ$, H-N 1.015 Å, N-C 1.386 Å, and N-N 1.510 Å. The dipole moment and rotational constants calculated at the CCSD(T)/cc-pVQZ level of theory is 1.41 Debye. The transition state between 1,3*H*-diazirine and (E)-1,2*H*-diazirine is 83.3 kcal mol⁻¹ above 3,3*H*-diazirine at the CCSD(T)/cc-pVTZ level – see Figure 2. This transition state is essentially the one in which the hydrogen atom moves from the carbon to the open nitrogen. The reverse barrier to go from (E)-1,2*H*-diazirine to 1,3*H*-Diazirine is 35.5 kcal mol⁻¹. All the local minima are flanked by significant barriers to transition to another isomer, easily making them stable on the singlet potential energy surface, except for the barrier between (E)-1,2*H*-diazirine and (Z)-1,2*H*-diazirine, discussed below.

Harmonic vibrational frequencies calculated using the B3LYP/cc-pVTZ and CCSD(T) with cc-pVTZ and cc-pVQZ basis sets are provided in Table 2. The CNN bending mode at 501 cm⁻¹ changes the dipole derivative significantly making it the most intense mode of all the vibrational modes among the isomers. The double harmonic intensity calculated using B3LYP/cc-pVTZ is 229 km/mol. The second most intense mode is the CN stretching mode appearing at 915 cm⁻¹ with a calculated intensity of 171 km/mol. Anharmonic vibrational fundamentals and vibration-rotation interaction constants for 1,2*H*-diazirine are given in Table 5. The two NH stretching modes show a large anharmonicity of about -184.1 cm⁻¹. Unfortunately, to the best of our knowledge there are no experimental data for us to compare the accuracy of the fundamental modes. The CC stretching mode does not exhibit much of an anharmonicity, -12.3 cm⁻¹. The bending fundamentals anharmonicities lie somewhere between -30 - 80 cm⁻¹.

(Z)-1,2*H*-Diazirine. The highest lying cyclic isomer is (Z)-1,2*H*-diazirine sitting 51.3 kcal mol⁻¹ above 3,3*H*-diazirine at the CCSD(T)/CBS level of theory. This isomer has a three-membered cyclic arrangement made up of two nitrogen atoms and a carbon atom. The two hydrogen atoms, attached to each nitrogen atom, are oriented in the same direction giving it a C_s symmetry. The bond angles and bond lengths are $\langle\text{HNC}\rangle 108.5^\circ$, $\langle\text{NCN}\rangle 66.0^\circ$, H-N 1.022 Å, N-C 1.398 Å, and N-

N 1.512 Å at the CCSD(T)/cc-pVQZ level of theory. This indicates that there is a slightly elongated single bond between the nitrogen atoms and the hydrogen atoms. The bonds between the carbon atom and nitrogen atoms are intermediate between a single and double bond distance. There is a longer single bond between the two nitrogen atoms at the base of the molecule. The E and Z isomers are only separated by 3.5 kcal mol⁻¹, and the transition barrier is a shallow 7.5 kcal mol⁻¹ to go from E- to Z-1,2*H*-diazirines. The transition state is a structure where one of the hydrogen atoms moves closer to the plane defined by the heavy atoms and is only 4.0 kcal mol⁻¹ above the latter.

The harmonic vibrational frequencies for (Z)-1,2*H*-diazirine can be found in Table 2. Harmonic vibrational frequencies with the above-mentioned levels of theory (Table 2) indicate that the CN stretching mode at 990 cm⁻¹, and the CNN bending mode at 415 cm⁻¹ possess large IR intensities. Anharmonic vibrational fundamentals and vibration-rotation interaction constants, and accurate geometrical parameters for (Z)-1,2*H*-diazirine are given in Table 6. The NH stretching modes 3250.3 cm⁻¹ (a') and at 3234.4 cm⁻¹ (a'') show large anharmonicities, around -188.4 cm⁻¹. Among the CN stretching modes the antisymmetric combination at 1172.5 cm⁻¹ shows a large anharmonicity of -108.4 cm⁻¹, while the symmetric combination exhibits an anharmonicity of -51.5 cm⁻¹, about half the value of the antisymmetric combination. Other modes show small anharmonicities.

IV. CONCLUSIONS

The four lowest energy cyclic isomers of diazirine, *c*-H₂CN₂, and the transition states connecting them were characterized using density functional theory and *ab initio* coupled cluster quantum chemistry methods with large correlation consistent basis sets. Out of the four cyclic isomers, 3,3*H*-diazirine is the lowest energy isomer followed by 1,3*H*-diazirine, (E)-1,2*H*-diazirine, and (Z)-1,2*H*-diazirine which are 20.1, 47.8, and 51.3 kcal mol⁻¹ higher in energy, respectively, at the CCSD(T)-F12/CBS level of theory. 3,3*H*-diazirine and 1,3*H*-diazirine are flanked by large barriers for their conversion to other isomers, while the (E)-1,2*H*-diazirine, and (Z)-1,2*H*-diazirine isomers are subject to interconversion at low temperature. Geometrical parameters, rotational, harmonic, and anharmonic spectroscopic constants are reported. Computed rotational constants presented here indicate a high degree of similarity with previous experimental results obtained for the lowest energy cyclic isomer (3,3*H*-diazirine) by Pierce.²⁷ The vibrational

fundamentals obtained by Ettinger⁴⁴ compare very well with the vibrational fundamentals reported here – for the CH stretching region they differ by less than 1 cm^{-1} , and in the heavy-atom stretching vibration they differ by up to 2.5 cm^{-1} . This is already excellent agreement for a simple VPT2 anharmonic analysis of vibrational fundamentals using the CCSD(T)/cc-pVTZ method. These spectroscopic results, both rotational and vibrational, for 3,3*H*-diazirine gives us confidence in the accuracy of the results for the other three cyclic isomers for which no direct experimental results are available yet. It is hoped that these structural and spectroscopic results will be useful for future laboratory experimental and possible astronomical identification of the cyclic isomers of diazirine, a nitrogenated cyclic molecule.

V. SUPPORTING INFORMATION

Supporting information file is available in electronic form with atomic coordinates, dipole moment components, harmonic frequencies, anharmonic fundamentals, overtones, and combination bands

VI. ACKNOWLEDGMENTS

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FIGURES

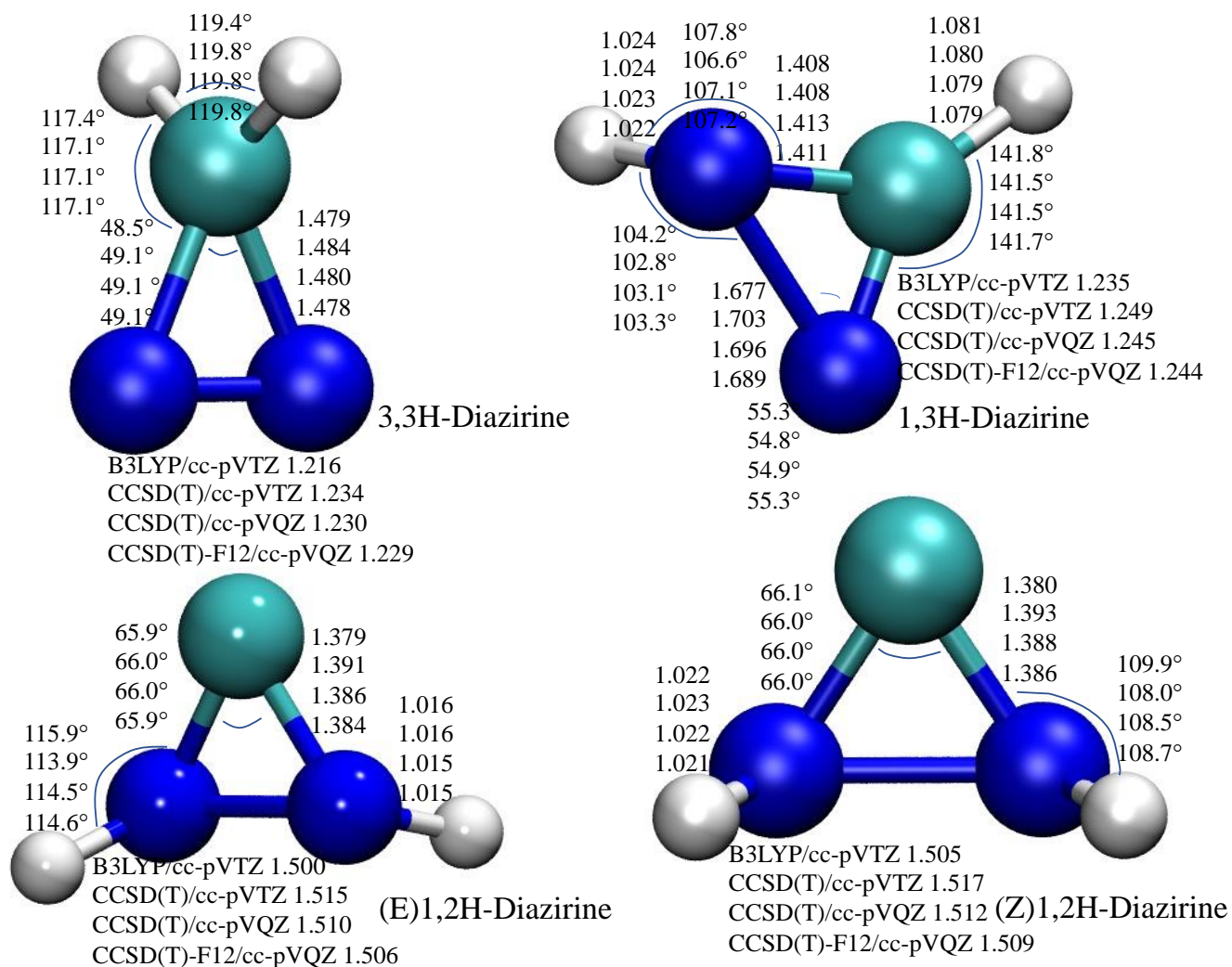


Figure 1. The equilibrium geometries of 3,3*H*-Diazirine (C_{2v}), 1,3*H*-Diazirine (C_1), (*E*)-1,2*H*-Diazirine (C_2) and (*Z*)-1,2*H*-Diazirine (C_s) are presented here using the B3LYP/cc-pVTZ, and CCSD(T)/cc-pVTZ/cc-pVQZ levels of theory.

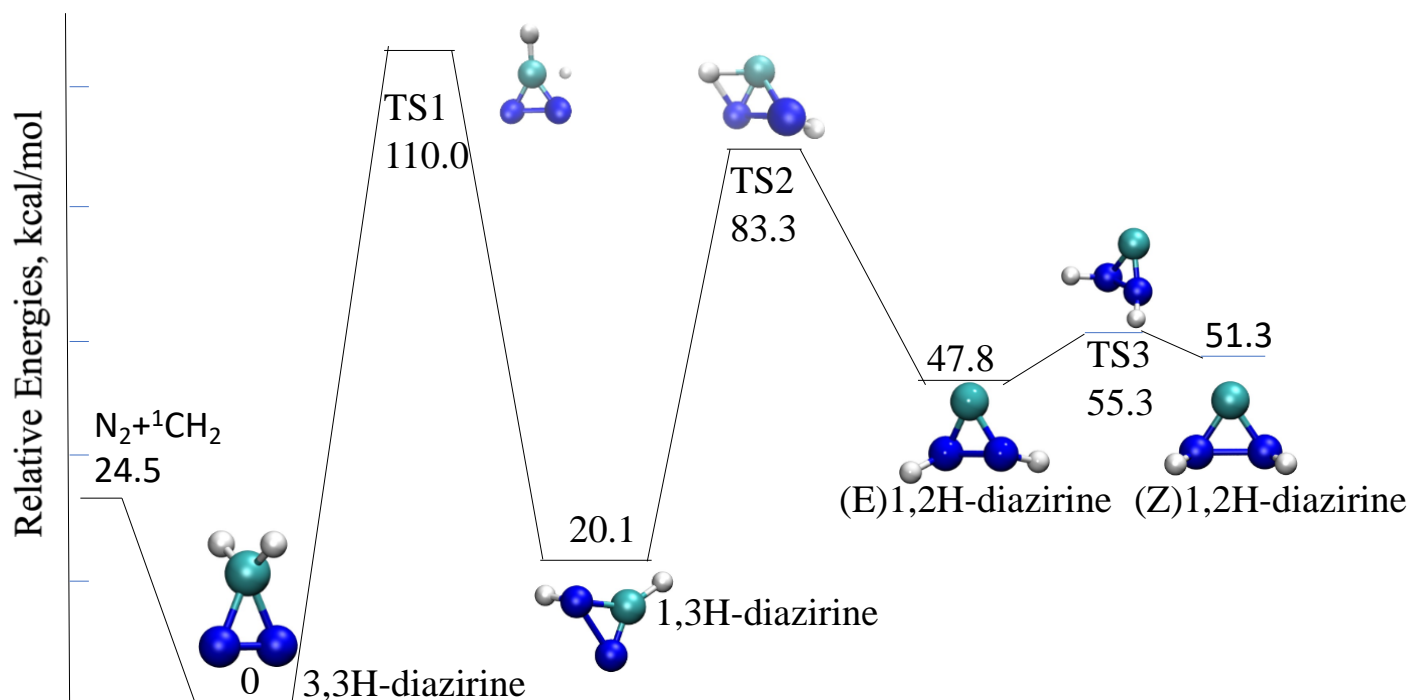


Figure 2. A diagram of cyclic isomers of 3,3H-diazirine and the transition states between the isomers are presented here using the CCSD(T)-F12/CBS level of theory. The dissociation limit to $N_2 + CH_2$ is also shown.

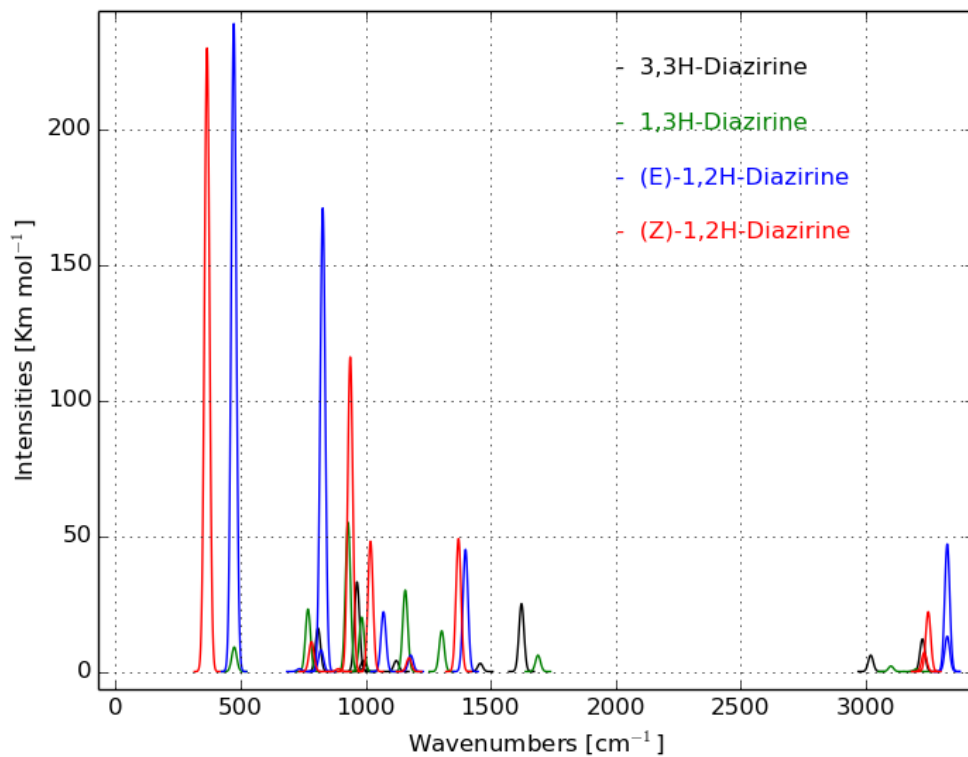


Figure 3. Simulated stick IR spectrum for 3,3H-Diazirine, 1,3H-Diazirine, (E)-1,2H-Diazirine and (Z)-1,2H-Diazirine using the Fundamental vibrational frequencies (cm^{-1}) together with double harmonic intensities ($kmol^{-1}$).

Table 1. Relative energies (in kcal mol⁻¹) of 3,3*H*-diazirine, and its cyclic isomers, 1,3*H*-diazirine, (E)-1,2*H*-diazirine, and (Z)-1,2*H*-diazirine computed at the B3LYP/cc-pVTZ level of theory and at the CCSD(T) and CCSD(T)-F12 levels with cc-pVTZ, cc-pVQZ, and extrapolated to the complete basis set limit. Energies are corrected for zero-point vibrational energy; dipole moments (Debye) calculated at the CCSD(T)/cc-pVQZ level of theory are also given.

Isomer	B3LYP/cc-pVTZ	CCSD(T)/cc-pVTZ	CCSD(T)/cc-pVQZ	CCSD(T)/CBS	CCSD(T)-F12/cc-pVTZ	CCSD(T)-F12/cc-pVQZ	CCSD(T)-F12/CBS	Dipole Moment
3, 3 <i>H</i> -Diazirine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.95
1, 3 <i>H</i> -Diazirine	20.5	21.1	20.3	20.1	20.9	20.3	20.1	3.29
(E)-1,2 <i>H</i> -Diazirine	46.1	49.5	48.1	47.7	48.6	48.0	47.8	1.41
(Z)-1,2 <i>H</i> -Diazirine	49.5	52.4	51.7	51.3	52.1	51.6	51.3	1.50

Table 2. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in km/mol units, in parenthesis) determined with the B3LYP method in conjunction with the cc-pVTZ basis set and the CCSD(T) method in conjunction with the cc-pVTZ, and cc-pVQZ basis sets.

Isomer	Sym	B3LYP/cc- pVTZ	CCSD(T)/cc -pVTZ	CCSD(T)/cc- pVQZ
3,3 <i>H</i> -Diazirine	$\omega_8(\text{a}_1)$	3130 (6.4)	3154	3154
	$\omega_7(\text{a}_1)$	1732 (24.5)	1650	1658
C_{2v}	$\omega_6(\text{a}_1)$	1499 (3.0)	1498	1496
	$\omega_4(\text{a}_1)$	1026 (4.4)	1026	1031
	$\omega_9(\text{b}_1)$	3245 (11.7)	3274	3275
	$\omega_5(\text{b}_1)$	1146 (3.6)	1142	1142
	$\omega_2(\text{a}_2)$	988 (0.0)	989	991
	$\omega_3(\text{b}_2)$	1001 (33.2)	1005	1006
	$\omega_1(\text{b}_2)$	830 (15.9)	835	837
<hr/>				
1,3 <i>H</i> -Diazirine	$\omega_9(\text{a})$	3366 (1.4)	3389	3401
	$\omega_8(\text{a})$	3204 (1.7)	3239	3241
C_1	$\omega_7(\text{a})$	1790 (6.0)	1723	1732
	$\omega_6(\text{a})$	1356 (14.7)	1344	1344
	$\omega_5(\text{a})$	1181 (30.3)	1192	1192
	$\omega_4(\text{a})$	1040 (19.6)	1021	1024
	$\omega_3(\text{a})$	968 (54.7)	969	972
	$\omega_2(\text{a})$	819 (22.9)	784	790
	$\omega_1(\text{a})$	552 (8.7)	490	490
<hr/>				
(E)-1,2 <i>H</i> -Diazirine	$\omega_9(\text{a})$	3475 (12.6)	3509	3513
	$\omega_7(\text{a})$	1435 (45.4)	1411	1417
C_2	$\omega_6(\text{a})$	1236 (5.8)	1236	1236
	$\omega_4(\text{a})$	928 (171.1)	910	915
	$\omega_2(\text{a})$	830 (0.4)	793	798
	$\omega_8(\text{b})$	3474 (47.3)	3508	3512
	$\omega_5(\text{b})$	1130 (22.4)	1123	1126
	$\omega_3(\text{b})$	879 (7.7)	868	874
	$\omega_1(\text{b})$	494 (298.5)	503	501
<hr/>				
(Z)-1,2 <i>H</i> -Diazirine	$\omega_5(\text{a}')$	3410 (21.7)	3439	3447
	$\omega_4(\text{a}')$	1395 (49.1)	1368	1375
C_s	$\omega_3(\text{a}')$	1031 (48.0)	1029	1031
	$\omega_2(\text{a}')$	1007 (115.8)	989	990
	$\omega_1(\text{a}')$	810 (10.6)	792	796
	$\omega_9(\text{a}'')$	3392 (7.2)	3421	3429
	$\omega_8(\text{a}'')$	1276 (5.1)	1281	1280
	$\omega_7(\text{a}'')$	939 (0.3)	924	928
	$\omega_6(\text{a}'')$	407 (229.9)	420	415

Table 3. Anharmonic spectroscopic constants of 3,3H-diazirine calculated by the application of VPT2 with CCSD(T)/cc-pVTZ (bond distances are expressed in Å and rotational constants in MHz), see text for details.

Diazirine	R_{CN}	θ_{CNN} 65.4°							
	1.4837	R_{NN} 1.2338							
	R_{CH}	θ_{NCN} 49.1°	A_0 40696			B_0 23726		C_0 16731	
	1.0792	θ_{HCN} 117.2°							
	Harmonic cm ⁻¹	Fundamental cm ⁻¹ VPT2	Vib-Rot constants (MHz)			Centrifugal Distortion Constants (MHz)			
			α^a	α^b	α^c				
ν_1 (a ₁)	3154.5	3019.6	114.4	23.50	4.317	τ_{aaaa}	-0.446	D_J	0.029
ν_2 (a ₁)	1650.1	1623.8	322.8	-18.86	31.54	τ_{bbbb}	-0.195	D_{JK}	0.079
ν_3 (a ₁)	1498.3	1458.4	-92.6	66.40	-26.59	τ_{cccc}	-0.049	D_K	-0.0026
ν_4 (a ₁)	1026.1	989.9	22.5	200.2	-9.294	τ_{aabb}	-0.052	R_5	-0.028
ν_5 (b ₁)	3273.8	3126.5	108.5	-0.989	3.687	τ_{aacc}	-0.052	R_6	-0.0007
ν_6 (b ₁)	1141.7	1122.3	-496.9	29.26	-120.4	τ_{bbcc}	-0.084	d_j	0.0091
ν_7 (a ₂)	989.2	989.2	145.2	1.559	178.4				
ν_8 (b ₂)	1005.1	964.7	372.9	123.5	103.2				
ν_9 (b ₂)	834.9	809.3	-170.5	139.3	201.6				
ZPE	7189.5								

Table 4. Anharmonic spectroscopic constants of 1,3H-diazirine calculated by the application of VPT2 with CCSD(T)/cc-pVTZ (bond distances are expressed in Å and rotational constants in MHz), see text for details.

	R_{CN}	θ_{CNN} 46.12°							
	1.4129	R_{NN} 1.6953							
	R_{CH}	θ_{NCN} 78.98°	A_0 39810			B_0 29929		C_0 14865	
	1.0795	θ_{HCN} 139.40°							
	Harmonic cm ⁻¹	Fundamental cm ⁻¹ VPT2	Vib-Rot constants (MHz)			Centrifugal Distortion Constants (MHz)			
			α^a	α^b	α^c				
ν_9 (a)	3389.3	3204.2	164.6	-10.1	-9.5	τ_{aaaa}	-0.804	D_J	0.061
ν_8 (a)	3239.1	3100.5	110.5	93.3	56.7	τ_{bbbb}	-0.473	D_{JK}	-0.027
ν_7 (a)	1723.0	1688.5	234.6	7.0	34.7	τ_{cccc}	-0.066	D_K	0.167
ν_6 (a)	1344.3	1304.1	-167.2	112.3	1.8	τ_{aabb}	-0.378	R_5	-0.017
ν_5 (a)	1191.8	1157.6	111.6	-129.2	6.8	τ_{aacc}	-0.065	R_6	-0.003
ν_4 (a)	1020.8	983.7	-65.7	170.8	94.2	τ_{bbcc}	-0.163	D_j	0.025
ν_3 (a)	968.4	928.6	29.2	8.1	51.8				
ν_2 (a)	784.3	766.8	89.7	144.2	-7.4				
ν_1 (a)	490.3	474.3	-435.7	184.0	135.0				
ZPE	6972.63								

Table 5. Anharmonic spectroscopic constants of (E)1,2*H*-dizirine calculated by the application of VPT2 with CCSD(T)/cc-pVTZ (bond distances are expressed in Å and rotational constants in MHz), see text for details.

R_{CN}	θ_{CNN}	57.0°						
1.3913	R_{NN}	1.5155						
R_{CH}	θ_{NCN}	66.0°						
1.0165	θ_{HNC}	113.9°	A_0	36906	B_0	25092	C_0	16365
Harmonic cm ⁻¹	Fundamental cm ⁻¹ VPT2	Vib-Rot constants (MHz)			Centrifugal Distortion Constants (MHz)			
		α^a	α^b	α^c				
$\nu_9 (a)$	3508.8	3326.4	128.3	41.2	10.5	τ_{aaaa}	-0.607 D_J	0.045
$\nu_7 (a)$	1410.9	1398.7	107.1	85.2	56.4	τ_{bbbb}	-0.341 D_{JK}	-0.153
$\nu_6 (a)$	1236.0	1179.8	-111.9	103.9	-68.2	τ_{cccc}	-0.052 D_K	0.046
$\nu_4 (a)$	910.2	828.0	73.0	44.1	39.8	τ_{aabb}	-0.165 R_5	-0.043
$\nu_2 (a)$	792.9	735.0	-112.8	300.2	93.5	τ_{aacc}	-0.043 R_6	-0.228
$\nu_8 (b)$	3507.7	3326.3	119.1	48.3	11.5	τ_{bbcc}	-0.103 D_j	0.181
$\nu_5 (b)$	1123.0	1071.2	-100.4	67.7	53.9			
$\nu_3 (b)$	868.3	821.0	-249.8	150.3	75.1			
$\nu_1 (b)$	503.7	472.3	273.4	-101.6	182.5			
ZPE	6817.9							

Table 6. Anharmonic spectroscopic constants of (Z)1,2*H*-diazirine calculated by the application of VPT2 with CCSD(T)/cc-pVTZ (bond distances are expressed in Å and rotational constants in MHz), see text for details.

R_{CN}	θ_{CNN}	57.0°						
1.3928	R_{NN}	1.5168						
R_{CH}	θ_{NCN}	66.0°						
1.0232	θ_{HCN}	108.0°	A_0	37695	B_0	24469	C_0	16305
Harmonic cm ⁻¹	Fundam ental cm ⁻¹ VPT2	Vib-Rot constants (MHz)			Centrifugal Distortion Constants (MHz)			
		α^a	α^b	α^c				
$\nu_9 (a')$	3438.7	3250.3	104.1	60.2	14.4	τ_{aaaa}	-0.071 D_J	0.004
$\nu_7 (a')$	1367.8	1371.4	208.9	47.9	59.8	τ_{bbbb}	-0.032 D_{JK}	0.021
$\nu_5 (a')$	1029.9	1018.7	-89.4	51.3	-140.0	τ_{cccc}	-0.005 D_K	-0.008
$\nu_4 (a')$	989.1	937.6	-25.7	97.0	25.1	τ_{aabb}	-0.019 R_5	-0.006
$\nu_2 (a')$	792.1	782.6	-243.6	230.2	148.9	τ_{aacc}	-0.004 R_6	-0.0002
$\nu_8 (a'')$	3420.6	3234.4	116.1	55.3	12.2	τ_{bbcc}	-0.010 D_j	0.002
$\nu_6 (a'')$	1280.9	1172.5	-165.3	100.3	-27.3			
$\nu_3 (a'')$	923.9	890.9	92.9	18.5	178.3			
$\nu_1 (a'')$	420.6	364.6	405.5	-182.0	158.1			
ZPE	6718.0							

REFERENCES

1. Sandford, S. A.; Bera, P. P.; Materese, C. A.; Nuevo, M.; Lee, T. J., Photosynthesis and Photostability of Nucleobases in Prebiotic and Extraterrestrial Ices. *Topics Curr. Chem.* **2014**, *356*, 123-164.
2. Sandford, S. A.; Nuevo, M.; Bera, P. P.; Lee, T. J., Prebiotic Astrochemistry and the Formation of Molecules of astrobiological Interest in Interstellar Clouds and Protostellar Disks. *Chem. Rev.* **2020**, *120* (11), 4616-4659.
3. Tennyson, J., Perspective: Accurate ro-vibrational calculations on small molecules. *J. Chem. Phys.* **2016**, *145*, 120901.
4. Thiel, V.; Belloche, A.; Menten, K. M.; Garrod, R. T.; Muller, H. S. P., Complex organic molecules in diffuse clouds along the line of sight to Sgr B2. *A&A* **2017**, *605*, L6.
5. Kuan, Y. J., et al., A search for Interstellar Pyrimidine. *Mon. Not. R. Astron. Soc.* **2003**, *345*, 650-656.
6. McGuire, B. A., et al., Detection of The Aromatic Molecule Benzonitrile (c-C₆H₅CN) in The Interstellar Medium. *Science* **2018**, *359* (6372), 202-205.
7. Hamid, A., et al., Evidence for the formation of pyrimidine cations from the sequential reactions of hydrogen cyanide with the acetylene radical cation. *J. Phys. Chem. Lett.* **2014**, *5*, 3392-3398.
8. Kokkila-Schumacher, S. I. L.; Bera, P. P.; Lee, T. J., Characterization of the Aziriny Cation and Its Isomers. *J. Phys. Chem. A* **2016**, *120*, 1275-1282.
9. Bera, P. P.; Nuevo, M.; Milam, S. N.; Sandford, S. A.; Lee, T. J., Mechanism for the Abiotic Synthesis of Uracil via UV Induced Oxidation of Pyrimidine in Astrophysical Condition. *J. Chem. Phys.* **2010**, *133*, 104303.
10. Bera, P. P.; Lee, T. J.; Schaefer, H. F., Are Isomers of Vinyl Cyanide Ion Missing Links for Interstellar Pyrimidine Formation? *J. Chem. Phys.* **2009**, *131*, 074303-074311.
11. Bera, P. P.; Head-Gordon, M.; Lee, T. J., Initiating Molecular Growth in the Interstellar Medium via Dimeric Complexes of Observed Ions and Molecules. *Astron. Astrophys.* **2011**, *535*, A74-1-A74-12.
12. Dickerson, C. E.; Bera, P. P.; Lee, T. J., Characterization of Azirine and Its Structural Isomers. *J. Phys. Chem. A* **2018**, *122*, 8898-8904.
13. Bera, P. P.; Huang, X.; Lee, T. J., Highly Accurate quartic force field and Ro-Vibrational Spectroscopic Constants for the Aziriny Cation (C₂H₂N⁺) and Its Isomers. *J. Phys. Chem. A* **2020**, *124*, 362-370.
14. Hendrix, J.; Bera, P. P.; Lee, T. J.; Head-Gordon, M., Cation, anion, and radical isomers of C₄H₄N: computational characterization and implication for astrophysical and planetary environments. *J. Phys. Chem. A* **2020**, *124*, 2011-2013.
15. Lovas, F. J.; Hollis, J. M.; Remijan, A. J.; Jewell, P. R., Detection of Ketenimine (CH₂CNH) in Sagittarius B2(N) Hot Cores. *Astrophys. J.* **2006**, *645*, L137-L140.
16. Liu, Y.; Guan, P.; Wang, Y.; Liu, L.; Cao, J., Mechanistic Insights into Decomposition of 2H-Azirines: Electronic Structure Calculations and Dynamics Simulations. *J. Phys. Chem. A* **2015**, *119*, 67-78.
17. Solomon, P. M.; Jefferts, K. B.; Penzias, A. A.; Wilson, R. W., Wilson, R. W., Detection of Millimeter Emission Lines from Interstellar Methyl Cyanide. *Astrophys. J.* **1971**, *168*, L107-L110.
18. Remijan, A. J.; Hollis, J. M.; Lovas, F. J.; Plusquellic, D. F.; Jewell, P. R., Interstellar Isomers: The Importance of Bonding Energy Differences. *Astrophys. J.* **2005**, *632*, 333-339.
19. Remijan, A. J.; Wyrowski, F.; Friedel, D. N.; Meier, D. S.; Snyder, L. E., A Survey of Large Molecules Toward the Proto-Planetary Nebula CRL 618. *Astrophys. J.* **2005**, *626-244*, 233-244.
20. Mathews, H. E.; Sear, T. J., Interstellar molecular line searches at 1.5 centimeters. *Astrophys. J.* **1986**, *300*, 766.
21. Albu, T. V., et al., Dynamics of 1,2-hydrogen migration in carbenes and ring expansion in cyclopropylcarbenes. *J. Phys. Chem. A* **2002**, *106*, 5323-5338.
22. Graham, W. H., *J. Am. Chem. Soc.* **1962**, *84*, 1063.
23. Schmitz, E.; Ohme, R., Synthesis of Azirines and Diazirine *Chem. Ber. Recl.* **1961**, *94*, 2166.
24. Paulsen, S. R., Synthesis of Diazirines. *Angew. Chem. Int. Ed.* **1962**, *72*, 781.
25. Amrich, M. J.; Bell, J. A., *J. Am. Chem. Soc.* **1964**, *86*, 292.

26. Ogilvie, J. F., A Spectroscopic Study of the Photodecomposition of Diazomethane. *Photochemistry and Photobiology* **1969**, *9*, 65-89.
27. Pierce, L.; Dobyns, V., *J. Am. Chem. Soc.* **1962**, *84*, 2651.
28. Moore, C. B.; Pimentel, G. C., *J. Chem. Phys.* **1964**, *41*.
29. Procacci, B.; Roy, S. S.; Norcott, P.; Turner, N.; Duckett, S. B., Unlocking a Diazirine Long-Lived Nuclear Singlet State via Photochemistry: NMR Detection and Lifetime of an Unstabilized Diazo Compound. *J. Am. Chem. Soc.* **2018**, *140*, 16855-16864.
30. Fedorov, I.; Koziol, L.; Mollner, A. K.; Krylov, A. I.; Reisler, H., Multiphoton Ionization and Dissociation of Diazirine: A Theoretical and Experimental Study. *J. Phys. Chem. A* **2009**, *113*, 7412-7421.
31. Puzzarini, C., A theoretical study of the CH₂N isomers: Molecular structure and energetics. *Int J. Quant. Chem.* **2010**, *110* (2483-2494).
32. Tordini, F., et al., Theoretical study of hydration of cyanamide and carbodiimide. *J. Phys. Chem. A* **2003**, *107* (1188-1196).
33. Shao, Y., et al., Advances in Molecular Quantum Chemistry Contained in the Q-Chem 4 Program Package. *Mol. Phys.* **2015**, *113* (2), 184-215.
34. Werner, H.-J., et al., MOLPRO. Version 2015.1, a package of ab initio programs, <http://www.molpro.net>.
35. Fortenberry, R. C.; Lee, T. J., Computational Vibrational Spectroscopy for the Detection of Molecules in Space. *Annual Reports in Comp. Chem.* **2019**, *15*, 173.
36. Humphrey, W.; Dalke, A.; Schulten, K., VMD - Visual Molecular Dynamics. *J. Molecular Graphics* **1996**, *14*, 33-38.
37. Helgaker, T.; Klopper, W.; Koch, H.; Noga, J., Basis set convergence of correlated calculations of water. *J. Chem. Phys.* **1997**, *106* (9639).
38. Martin, J. M. L.; Lee, T. J., The atomization energy and proton affinity of NH₃. An ab initio study. *J. Chem. Phys.* **1996**, *258*, 136.
39. Huang, X.; Lee, T. J., Accurate ab initio Quartic Force Fields for NH₂- and CCH-, and Rovibrational Spectroscopic Constants for their Isotopologues. *J. Chem. Phys.* **2009**, *131*, 104301.
40. Csaszar, A. G.; Allen, W. D.; Schaefer, H. F., In pursuit of the ab initio limit for conformational energy prototypes *J. Chem. Phys.* **1998**, *108*, 9751.
41. Ruscic, B.; Bross, D. H., Thermochemistry. *Computer aided chemical engineering* **2019**, *45*, 3-114.
42. Ruscic, B., Uncertainty quantification in thermochemistry, benchmarking electronic structure computations, and active thermochemical tables. *Int. J. Quantum. Chem.* **2014**, *114*, 1097-1101.
43. Xu, S.; Lin, M. C., Ab Initio chemical kinetics for singlet CH₂ reaction with N₂ and the related decomposition of diazomethane. *J. Phys. Chem. A* **2010**, *114*, 5195-5204.
44. Ettinger, R., Infrared Spectrum of Diazirine. *J. Chem. Phys.* **1964**, *40*, 1693-1699.
45. Gardner, M. B.; Westbrook, B. R.; Fortenberry, R. C.; Lee, T. J., Highly-Accurate Quartic Force Fields for the Prediction of Anharmonic Rotational Constants and Fundamental Vibrational Frequencies. *Spectrochim. Acta* **2021**, *248*, 119184.