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Research Paper

# On the possibility of electronically excited states in stable amine anions: Dicyanoamine, cyanoethynylamine, and diethynylamine

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A B S T R A C T

Of the dicyanomine anion ($NCNCN^-$), cyanoethynylamine anion ($NCNC_2H^-$), and diethynylamine anion ($HC_2NC_2H^-$), only the mixed, $C_s$ $NCNC_2H^-$ anion has are large enough dipole moment to support an electronically excited state at 3.0323 eV. This quantum chemical study shows that this value lies 0.0051 eV below the electron binding energy (eBE) and may have correlation to early-onset diffuse interstellar bands. None of these three anions possess further valence excited electronic states beyond the singlet ground states, and triplet excited states are all beyond their respective eBEs.

## 1. Introduction

Anions are significant for various chemical applications spanning everything from solar energy harvesting to astrophysical observations (Boschloo and Hagfeldt, 2009; Castellani et al., 2019; Hendricks et al., 1998; Sidorkin et al., 2020; Skurski, 2001). However, they represent significant challenges for laboratory experimentation making them well-suited for quantum chemical analysis. Fermi and Teller theoretically explored binding of excess electrons to form anions and found that the strength of the dipole moment is key (Fermi and Teller, 1947). The dipole moment of the corresponding neutral should be greater than 1.625 D to possess a dipole bound state (Fermi and Teller, 1947), but in reality the dipole moment should be larger than this likely at $> 2$ D (Crawford, 1977; Gutowski et al., 1996; Gutsev and Adamowicz, 1995; Jordan, 1976; Jordan and Wang, 2003; Mittleman and Myerscough, 1966; O.Crawford and Dalgarno, 1967; Turner, 1977; Turner and Fox, 1966). The neutral dipole moment strength relates proportionally with the anion electron binding energy (eBE) (Compton et al., 1996). The greater the dipole moment and, consequently, the eBE, the more likely a dipole bound state will be present (Coulson and Walmsley, 1967; Fortenberry and Crawford, 2011; Mittleman and Myerscough, 1966; Turner and Fox, 1966).

$CH_2CN^-$ and $CH_2CHO^-$ are known to have excitations below the eBE that also appear in the visible region. These states are classified as dipole bound excited states (Gutsev and Adamowicz, 1995; Lykke et al., 1987; Mullin et al., 1993; 0000) beyond the ground, valence state of the anion. Sarre even noticed that a $1\ ^1B_1 \leftarrow \tilde{X}\ ^1A'$ excitation of $CH_2CN^-$ at 8037.78 Å coincides with an astronomical absorption feature at 8037.8 $\pm$ 0.15 Å. He theorized that dipole bound transitions of anions are possible carriers of the diffuse interstellar bands (DIBs) (Sarre, 2000). The DIBs are omnipresent absorption lines spread throughout the visible spectrum that went unidentified for nearly a century (Foing and Ehrenfreund, 1994; Maier, 1994; Sarre, 2000). Finally, in 2015, two lines of $C_{60}^+$ were linked with the DIBs (Campbell et al., 2015). Currently, four peaks for $C_{60}^+$ have been identified in the near-infrared range and correlated to the DIBs (Cordiner et al., 2019), but there are hundreds of remaining unattributed peaks across the entire spectrum. The highest density of DIBs are for wavelengths longer than the green.

The excitation energy of anions is typically lower than neutral and cation species since the additional electron has a much lower eBE than the ionization potential of uncharged species.(Fortenberry, 2015) The longer wavelength transitions of anions may therefore be useful for identifing other aborption peaks in the longer-wavelength DIBs where they are more common. Furthermore, most anions typically only have one electronic transition (most often dipole bound if at all) giving few, if any, other excited states (Czekner et al., 2018; Simons, 2008). The long wavelengths and solitary absorptions make anions plausible candidates as carriers of the DIBs (Sarre, 2000).

Anions are already known appear in astrochemical environments ranging from interstellar clouds to planetary atmospheres (Agúndez et al., 2010; Aoki, 2000; Brnken et al., 2007; Cernicharo et al., 2007; 2008; Kawaguchi et al., 1995; Lepp and Dalgarno, 1988; McCarthy et al., 2006; Millar et al., 2000; Ross et al., 2008; Schild et al., 1974; Snow, 1975; Terzieva and Herbst, 2000; Thaddeus et al., 2008; Tulej et al., 1998). The first genuine interstellar anion, $C_6H^-$, was detected in the interstellar medium (ISM) in 2006. Since then, $C_3N^-$, $CN^-$, $C_4H^-$, $C_8H^-$, and $C_5N^-$ are all indexed in various astronomical sources using rotational spectroscopy (Agúndez et al., 2010; Brnken et al., 2007; Cernicharo et al., 2007; 2008; Cordiner et al., 2011; Remijan et al., 2007; Thaddeus et al., 2008). A low upper limit of $C_2H^-$ has been

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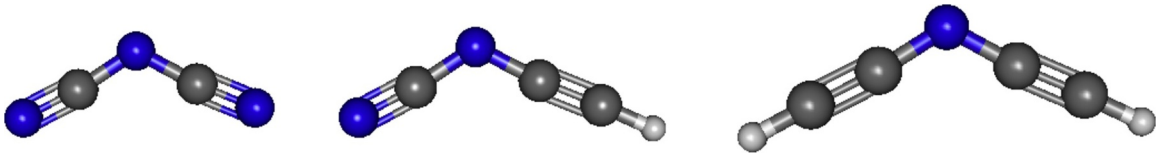

**Fig. 1.** The optimized geometries of the amine anions examined.

determined in the carbon-rich star IRC+10216 (Cernicharo et al., 2008), but its detection has yet to be reported. Other anions have been hypothesized to exist in the ISM like $C_3P^-$ or $CCOH^-$ (Fortenberry and Lee, 2015; Fortenberry and Lukemire, 2015), but no new anions have been detected in a decade.

Radiative electron attachment is believed to form these anions through a dipole bound pathway if the dipole moment is large enough (Carelli et al., 2014; Douguet et al., 2015; Khamesian et al., 2016; McLaughlin et al., 2012). The strongest support for the formation of anions through such a dipole bound pathway is observed in the $C_{2n}H$ radicals and their corresponding anions. The ground state for $C_4H$ is $^2\Sigma^+$ with $^2\Pi$ excited state lying in near degeneracy (Fortenberry et al., 2010; Hoshina et al., 1998; McCarthy et al., 1995; Shen et al., 1990; Taylor et al., 1998; van Hemert and van Dishoeck, 2008; Woon, 1995; Yamamoto et al., 1987). The dipole moment of the $^2\Sigma^+$ state is $\sim$ 0.8 D but shifts to $\sim$ 4.0 D in the $^2\Pi$ state (Agúndez et al., 2008; Maier, 1998; Pino et al., 2002). Hence, the $C_4H$ ground state dipole moment is large enough to possess a dipole-bound state, and the $C_4H$ has to be excited by some currently undetermined amount, possibly in the range of 100 $cm^{-1}$, into the $^2\Pi$ state before a dipole-bound state of the anion can exist. The $A\ ^2\Pi \leftarrow \tilde{X}\ ^2\Sigma^+$ excitation energy in the $C_4H$ radical is small but in the ISM, this is large enough to favor the ground state population notably. The result is that $C_4H^-$ is far less abundant in space than $C_4H$. Conversely, $C_6H^-$ is more abundant in space both its neutral radical (Agúndez et al., 2008). The dipole bound formation pathway clarifies this observation succinctly (Agúndez et al., 2008; Fosse et al., 2001; McGuire et al., 2013; Pety et al., 2012; Turner et al., 2000).

Differently, during the portion of the *Voyager* missions exploring Saturn, Titan was determined to possess an atmosphere containing a variety of hydrocarbons and nitrogen-based molecules (Coates et al., 2007a; Hanel et al., 1981; Kunde et al., 1981; López-Puertas et al., 2013; Maguire et al., 1981; Molina-Cuberos et al., 2002; Samuelson et al., 1981; Yung, 1987; Yung et al., 2020). More than 25 years later, the *Cassini* mission detected heavy anions in Titan's atmosphere ranging in mass from 10 to 200 amu. Peaks shown on the *Cassini* plasma spectrometer are likely related to the anions: $CN^-$ (Bradforth et al., 1993), $NCN^-$ (Clifford et al., 1997), $C_3H^-$(Aoki et al., 1996), high order nitriles, and potentially even polycylic aromatic hydrocarbons (PAHs) (Moustefaoui et al., 1998). Consequently, anions may aid in the production of PAHs in planetary atmospheres (Coates et al., 2007b). Anions found in Titan's atmosphere are believed to form also through radiative electron attachment much like they may in interstellar or circumstellar space (Carelli et al., 2014; Dobrijevic et al., 2014; Hébrard et al., 2013; Herbst and Osamura, 2008; J.C. Loison et al., 2015; Vuitton et al., 2011; 2007), but further observation is necessary to confirm such chemistry. Such anions in the mid range of *Cassini*'s anion mass detection have been proposed to exist in Titan's atmosphere, and one of these is the dicyanoamine anion ($NCNCN^-$) (Dubois et al., 2019) an extension of the $m/z = -40$ assignment to $NCN^-$ (Clifford et al., 1997).

Further interest in $NCNCN^-$ and its corresponding neutral can be traced back to before the 20th century when there was an emphasis on understanding peptide and polypeptide synthesis(Beilstein and Geuther, 1858). In the time since, $NCNCN^-$ has been theorized as an important precursor in the prebiotic chemial evolution on the pathway in the formation of peptides (Schimpl et al., 1965). The dicyanoamine anion is surprisingly stable with an experimental eBE of 4.134 $\pm$ 0.010 eV (Nichols et al., 2016) giving the anion the capability to avoid photodetachment in solution as well as in the gas phase. (Dubois et al., 2019; Nichols et al., 2016; Somogyi et al., 2012). Consequently, this anion may likely survive for long lifetimes in places such as the planetary atmosphere of Titan or in the ISM. However, no electronic spectrum of $NCNCN^-$ has been reported in the literature. Additionally, the ethynyl functional group ( - $C_2H$) is isoelectronic with cyano, and $HC_2NC_2H^-$ or the mixed $NCNC_2H^-$ have yet to be examined for their electronic properties, dipole-bound or otherwise. All three of these amine anions will be examined here and their structures are visually depicted in Fig. 1. The present study will provide insights into the electronic structure of these anions in order to clarify any potential chemical role they may have in Titan's atmosphere or in the ISM beyond.

## 2. Computational methods

The three different amines analyzed are $NCNCN^-$, $NCNC_2H^-$, and $HC_2NC_2H^-$. Geometry optimizations on the neutral radicals, closed-shell anions, and triplet states of the anions are computed with CCSD (T)-F12b/cc-pVTZ-F12 (Adler et al., 2007; Bischoff et al., 2009; Knizia et al., 2009; Khn et al., 2008) in MOLPRO 2015.1 (Werner et al., 2015). The relative energies and radical dipole moments are computed from each of these optimized geometries. This includes radical dipole moments computed from the optimized anion geometries. The triplet state energies are compared with the singlet energies to determine the ground state of the anions, as well.

The optimized geometries of the neutral radical and closed-shell singlet anions are both used for vertically excited state calculations for singlet anion excited states. These are done with equation of motion couple cluster theory at the singles and doubles level (EOM-CCSD) (Krylov, 2008; Shavitt and Bartlett, 2009; Stanton, 1993). The anion excitation energies determined from both the optimized radical and anion geometries are compared in order to gauge behavior from either emission or absorption. The anion reference geometry represents absorption, and the radical signifies emission. Emission is represented by the radical form receiving an additional electron in the dipole bound excited state and giving off energy as it falls to the ground valence state. In the case of the absorption, the closed-shell anion starts at the valence ground state and is excited into the dipole bound excited state.

In order to model either version of dipole bound behavior, additional diffuse functions are added onto the aug-cc-pVDZ basis set (Dunning, 1989; Kendall et al., 1992) to describe the diffuseness of the dipole bound orbitals. These are localized on dummy atoms placed at either the center-of-mass (COM) or center-of-charge (COC) in order to determine if the latter is truly necessary to quantify eBEs and electronically excited state of anions more precisely. The COC is represented by placing the dummy atom at the positive end of the neutral radical dipole moment computed at the respective reference geometry. Conversely, the COM places the dummy atom at the COM which is also the origin coordinate of the amine anion. Past work (Morgan and Fortenberry, 2015; Theis et al., 2015) shows that dipole bound excited states need at minimum an augmented basis set with four, highly diffuse *s*-type basis functions labeled as "+4s" located on this dummy atom. In order to increase the accuracy of the dipole bound excited state energies computed, the basis set is augmented with six *s*-type "+6s", six *p*-type "+6p", and two *d*-type"+2d" highly diffuse basis functions constructed in an even-tempered fashion in line with previous work.

**Table 1**
Energies of singlet & triplet radical.

| | Singlet-Triplet (eV) Energy Gap | eBE (eV) | | Dipole Moment (D) | |
|---|---|---|---|---|---|
| | | Radical Geom | Anion Geom | Radical Geom | Anion Geom |
| NCNCN | 5.5283 | 4.0281 | 4.0321 | 0.903 | 0.937 |
| $NCNC_2H$ | 4.3420 | 2.9849 | 3.0374 | 4.084 | 3.941 |
| $HC_2NC_2H$ | 3.1411 | 2.1724 | 2.1901 | 1.464 | 1.544 |

(Bassett and Fortenberry, 2017)

The eBEs are computed using the CFOUR (Stanton et al., 0000) computational package with the equation of motion ionization potential (EOMIP) formalism at CCSD level with the aug-cc-pVDZ basis set. The radicals do not exhibit as much diffuse character as the dipole-bound anions thus not requiring the "+6s6p2d" functions here. The accuracy behind these eBE computations is shown with the molecule $CH_2CN^-$. The eBE of $CH_2CN^-$ is 1.524 eV using EOMIP/aug-cc-pVDZ, which is within 0.02 eV of the experimental eBE value at 1.543 eV. (Cordiner and Sarre, 2007; Fortenberry and Crawford, 2011; Gutsev and Adamowicz, 1995; Lykke et al., 1987; Morgan and Fortenberry, 2015)

## 3. Results and discussion

### 3.1. Structures and dipole moments

Energy comparisons of the singlet and triplet optimized geometries are given in Table 1. The singlets are the lowest energy states in all three cases examined here with separations of at least 3 eV for each of the anions. The greatest difference is for the $NCNCN^-$ singlet-triplet energy gap with a distinction between spin states of 5.2583 eV. The $NCNC_2H$ anion is in the middle of the three with a value of 4.3420 eV. Lastly, The closest deviation between the lowest-energy singlet and triplet states is with the $HC_2NC_2H$ geometry at 3.1411 eV. These results show that stronger electron-withdrawing groups on the amine anion seem to produce a larger separation between the singlet and triplet states.

The $NCNCN^-$ and $HC_2NC_2H^-$ structures are both of $C_{2v}$ symmetry while the $NCNC_2H$ mixed form is planar, $C_s$. The $CNCNC_2H$ radical has a dipole moment of 4.0846 D, and the radical dipole moment when utilizing the anion optimized geometry for this single-point computation is 3.941 D (Table 1). Such values are large enough to possess dipole bound states, but they showcase that slight changes to the reference geometry can affect the physical observables. The dipole moments for the $C_{2v}$ structures are along the principle axis of rotation (through the central N atom) limiting their possible strength due to the structure of the molecule. However, $CNCNC_2H$ is asymmetrical with respect to rotation, and the dipole stretches across the molecule from the ethynyl group to the more electronegative cyano group inducing a significant charge separation not present in the other two structures. The dipole moments of the NCNCN and $HC_2NC_2H$ radicals are likely too small to support dipole bound excited states. However, they will still be computed in this work in order to show that the current approach is capable of conclusively describing whether or not a dipole bound excited state exists. Regardless, any dipole bound states for this set of anions should be excited states since the ground states of these three anions are valence singlets similar to $CH_2CN^-$ and $CH_2CHO^-$.

The dipole moment is shown to correlate weakly if at all with the eBE for these molecules as shown in Table 1. The strongest dipole moment is in the $NCNC_2H$ radical which also has the second-highest eBE for the set (2.9849 eV). Strangely, the smallest dipole moment in NCNCN at 0.9031 D has the highest eBE (4.0321 eV) in the corresponding anion. This likely results from the local dipoles and stabilities of the cyano groups in $NCNCN^-$ that are weakened in the presence of the ethynyl groups. Consequently, more than global dipole forces affect the eBEs and stabilities of valence state anions. Finally, the experimental eBE of 4.134 ± 0.010 eV for $NCNCN^-$ is within 0.1 eV of that computed here (Nichols et al., 2016).

### 3.2. Electronically excited states

The central nitrogen atom on each of these closed-shell amine anions possesses two lone pairs much like oxygen in water. The antisymmetric out-of-plane lone pair orbital can be thought of as the highest occupied molecular orbital (HOMO) on each of these systems and is of $b_1$ symmetry in the $C_{2v}$ structures and $a''$ symmetry for $C_s$ $NCNC_2H^-$. The lowest-unoccupied molecular orbital (LUMO) is the highly-diffuse *s*-type dipole bound orbital. These are shown for $NCNC_2H^-$ in Fig. 2. The antisymmetric lone-pair of the HOMO mixes with the out-of-plane *p* orbitals on the terminal nitrogen atoms in the cyano group(s) or, equivalently, the outermost carbon in the ethynyl group(s). The LUMO in Fig. 2 clearly is residing over the positive end of the dipole moment (the COC) for this example.

The experimental eBE of $NCNCN^-$ is known at 4.134 ± 0.010 eV (Nichols et al., 2016) and is used as a test for the computational approach utilized here. The computed 4.0281 eV radical geometry eBE is close to this value. Thus the fact that the lowest state ($1^1B_1$) has an excitation energy of 4.0377 eV tells clearly that no dipole-bound state can exist. Additionally, the COM excitation energy for the $1\,^1B_1$ state of $NCNCN^-$ is lower than that for the COC. This behavior is consistent for all of the higher energy states reported herein, as well. The reason for this behavior is that the higher energy COC excitation appears to be an artifact of the computation. The HOMO is destabilized slightly by the presence of the additional diffuse orbitals at the COC and less so at the COM. Such behavior is only present in $NCNCN^-$ in the current set of anionic amines (Table 2).

Differently from the dicyano structure, $NCNC_2H^-$ actually exhibits

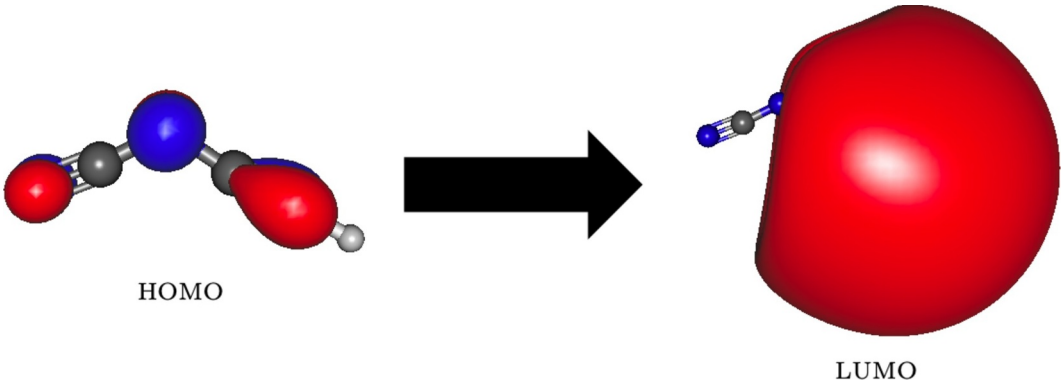


**Fig. 2.** Visual depiction of the $1\,^1A'' \leftarrow \tilde{X}\,^1A'$ dipole bound excitation in $NCNC_2H^-$.

**Table 2**
Electronically Excited States of Dicyanoamine anion ($NCNCN^-$).

| Basis Location | Reference Geometry | $2\ ^1A_1$ | $3\ ^1A_1$ | $1\ ^1B_1$ | $2\ ^1B_1$ | $2\ ^1B_2$ | $3\ ^1B_2$ | $1\ ^1A_2$ | $2\ ^1A_2$ |
|---|---|---|---|---|---|---|---|---|---|
| COC | anion | 4.0492 | 4.0793 | 4.0417 | 4.0444 | 5.3082 | 5.3404 | 4.0495 | 4.0818 |
| COM | anion | 4.0467 | 4.0769 | 4.0392 | 4.0419 | 5.3065 | 5.3388 | 4.0470 | 4.0793 |
| COC | radical | 4.0452 | 4.0752 | 4.0377 | 4.0404 | 5.2522 | 5.2844 | 4.0455 | 4.0778 |
| COM | radical | 4.0429 | 4.0730 | 4.0354 | 4.0381 | 5.2506 | 5.2829 | 4.0432 | 4.0755 |

**Table 3**
Electronically Excited States of Cyano-Ethynylamine Anion ($NCNC_2H^-$).

| Basis Location | Reference Geometry | $2\ ^1A'$ | $3\ ^1A'$ | $1\ ^1A''$ | $2\ ^1A''$ |
|---|---|---|---|---|---|
| COC | anion | 3.0489 | 3.0794 | 3.0323 | 3.0418 |
| COM | anion | 3.0556 | 3.0866 | 3.0400 | 3.0485 |
| COC | radical | 2.9969 | 3.0274 | 2.9780 | 2.9898 |
| COM | radical | 3.0029 | 3.0339 | 2.9853 | 2.9958 |

an electronically excited state. The excitation energies of $C_s$ $NCNC_2H^-$ are enumerated in Table 3. The lowest energy excited state is the $1\ ^1A''$. It falls at 2.9780 eV for the radical geometry, 0.0069 eV below the corresponding eBE; the anion geometry difference is 0.0051 eV again with the $1\ ^1A''$ state below the eBE. Hence, in both emission and absorption, the $1\ ^1A''$ excited state sits below the eBE giving clear dipole-bound behavior in conjunction with the large $\sim 4$ D dipole moment. This $1\ ^1A'' \leftarrow \tilde{X}\ ^1A'$ transition is shown in Fig. 2. The excitation is out of the π valence space of $NCNC_2H^-$ into the Rydberg/dipole bound *s*-type LUMO. This diffuse, virtual orbital is shown at different angles in Fig. 3. The COC excitation energy is smaller than the COM in this case since these additional diffuse orbitals do not destabilize the HOMO. The difference between emission and absorption for this state is determined here to be 0.0452 eV resulting from the slight shifts in the radical and anion geometries. Lastly, all of the other excitations are above the eBE signifying that there is only one excited state for the $NCNC_2H$ amine: the $1\ ^1A''$ dipole bound state.

Like with the dicyano amine, $HC_2NC_2H$ does not appear to possess any electronically excited states. Table 4 contains all of the excited state data for $C_{2v}$ $HC_2NC_2H$. The lowest energy state for both absorption and emission is, again, the $1\ ^1B_1$ state. The anion reference geometry has the COC excitation energy into this state at 2.1934 eV, and the radical is 2.1760 eV. Unfortunately, the eBE for the anion is 2.1901 eV, and the radical is 2.1724 eV. Hence, both the anion and radical dipole bound excited state energies are above the eBE by 0.0033 eV and 0.0036 eV. Such is consistent with the insufficiency of the dipole moments to allow for dipole bound excited states of this anion since the neutral radical dipole moment of the anion geometry is 1.464 D and the radical geometry is 1.544 D. The placement of the dummy atom at the COC exhibits lower energy excited states then its COM counterpart, but the lack of a dipole bound state renders this point moot.

### 3.3. Conclusions & astrophysical implications

The $NCNC_2H^-$ amine anion studied here has a dipole-bound excited state at 3.0323 eV (408.9 nm) in absorption. This is actually into the UV beyond most of the DIBs, but there could be correlation with either the 406.6 nm or 417.7 nm features at the onset of these unknown bands (Fan et al., 2019; Jenniskens P., 1994). The oscillator strength of the $1\ ^1A'' \leftarrow \tilde{X}\ ^1A'$ transition in this anion is $1\times 10^{-3}$. Such a small value casts doubt on the applicability of $NCNC_2H^-$ to be a carrier of either of these DIBs, but this value is not prohibitively small. Furthermore, this dipole bound feature would not correlate with any of the other DIBs like

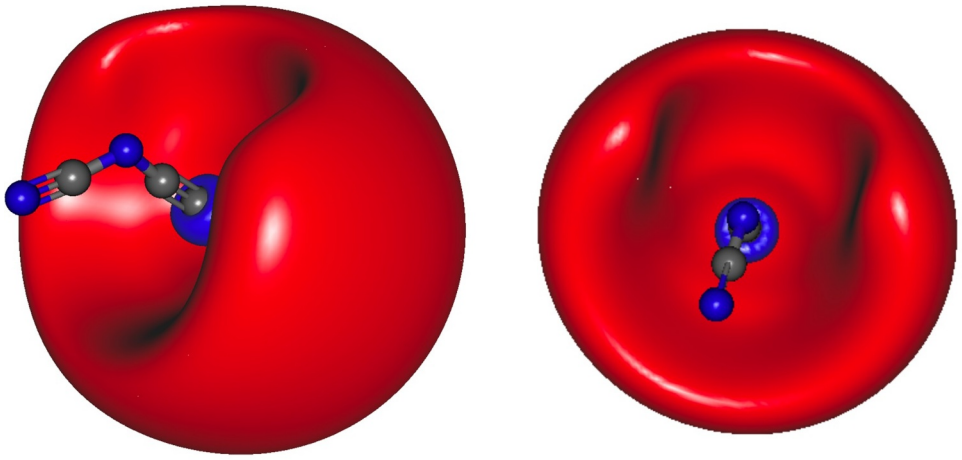

**Fig. 3.** Further depictions of the dipole bound LUMO in $NCNC_2H^-$ from different orientations.

**Table 4**
Electronically Excited States of Diethynylamine anion ($HC_2NC_2H^-$) .

| Basis Location | Reference Geometry | $2\ ^1A_1$ | $3\ ^1A_1$ | $1\ ^1B_1$ | $2\ ^1B_1$ | $2\ ^1B_2$ | $3\ ^1B_2$ | $1\ ^1A_2$ | $2\ ^1A_2$ |
|---|---|---|---|---|---|---|---|---|---|
| COC | anion | 2.2010 | 2.2327 | 2.1934 | 2.1969 | 3.4568 | 3.4862 | 2.2007 | 2.2301 |
| COM | anion | 2.2045 | 2.2362 | 2.1970 | 2.2005 | 3.4584 | 3.4879 | 2.2042 | 2.2337 |
| COC | radical | 2.1836 | 2.2152 | 2.1760 | 2.1796 | 3.3855 | 3.4150 | 2.1833 | 2.2127 |
| COM | radical | 2.1872 | 2.2189 | 2.1797 | 2.1832 | 3.3874 | 3.4168 | 2.1869 | 2.2164 |

many carriers are believed to behave (McCall et al., 2010). Neither of the other anions in this study will have any electronic excitations, and none of the three have valence excitations.

Regardless, the high eBE for each of these three amines implies that they could be abundant anionic species in the ISM if the proper formation mechanism allows. However, only the mixed functional $NCNC_2H^-$ anion could form through a radiative attachment-like, dipole-bound process akin to that believed to create most of the known carbon-bearing anions detected in the ISM: $C_4H^-$, $C_6H^-$, $C_8H^-$, $C_3N^-$, and $C_5N^-$ (Brnken et al., 2007; Cernicharo et al., 2007; 2008; McCarthy et al., 2006; Remijan et al., 2007). Detection of stable $NCNCN^-$ in the ISM or in Titan's atmosphere will be aided with rovibrational data computed previously (Dubois et al., 2019), but that for $NCNC_2H^-$ may be of greater significance since it likely possesses dipole bound excited states necessary for both radiative attachment formation and DIB correlation. Its rovibrational spectral features will be determined in future work.

Finally, the "+6s6p2d" functions added at the COC to the aug-cc-pVDZ basis set conclusively can determine the presence of dipole bound states when comparing the EOM-CCSD excited state energies with the EOMIP-CCSD eBEs. This protocol will allow for clear predictions of dipole bound states in the future.

## CRediT authorship contribution statement

**Taylor J. Santaloci:** Conceptualization, Methodology, Investigation, Visualization, Writing - original draft, Writing - review & editing. **Ryan C. Fortenberry:** Conceptualization, Methodology, Resources, Formal analysis, Writing - original draft, Writing - review & editing, Supervision.

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## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper (Allouche, 2011).

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