

RESEARCH ARTICLE

Theoretical study of the helio hydrogen cyanide dication HeCNH^{2+}

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The structure and stability of the helio hydrogen cyanide molecular ion, HeCNH^{2+} , is investigated by standard quantum chemical methods. Single reference calculations are carried out using second-order perturbation theory (MP2), the coupled cluster expansion in the CCSD approximation, and the hybrid approach using a perturbative estimate of the triple excitation energy component designated CCSD(T). Multireference calculations using a complete active space (CASSCF) and a second-order perturbation theory estimate of correlation effects (CASPT2) are reported.

Keywords: helio hydrogen cyanide; HeCNH^{2+} ; inert gas molecules; interstellar molecules; MP2; CCSD; CCSD(T); CASSCF; CASPT2

1. Introduction

Of the various techniques available for the study of matter on a molecular scale, computational quantum chemistry has particular strengths and weaknesses. In principle, *ab initio* quantum chemical methods can be applied to any grouping of atoms irrespective of whether they form a stable molecule or not. This has been found invaluable, for example, in the study of interstellar radicals and ions particularly in cases where the species under investigation are not stable in the terrestrial laboratory [1] (see, for example, [2–6] for recent reviews on the subject of molecules in space).

Radicals, such as the cyanoethynyl and the butadiynyl radicals [7], and ions, such as the thioformyl ion [8], have been identified in interstellar environments [9–11] on the basis of *ab initio* quantum chemical calculations prior to their observation on Earth. The principle weakness of *ab initio* quantum chemical methods is the rapid increase in the complexity of the associated computations with the number of atoms and/or number of electrons in the system under study. The most abundant elements in the universe are those of the light atoms hydrogen, helium, carbon, nitrogen and oxygen. Contemporary non-relativistic quantum chemical methods can support accurate calculations on small molecular systems containing these light atoms. Helium is the second most abundant element in the universe and this led Wilson and Green [12] to suggest

that, in spite of it being the most inert of the inert gases, helium-containing ions could have sufficient stability to be observed in the interstellar medium. In particular, these authors suggested the HeCN^+ ion as a candidate since the cyano-group ensures that the system has a large dipole moment to enhance detection by radio-astronomy. Although the HeCN^+ ion has not been found in space, it has nevertheless emerged from subsequent studies that simple ions containing helium have a rich chemistry (see, for example, the recent review by Grandinetti [13]).

The structure and stability of helium-containing polyatomic cations have been investigated by a number of authors [12,14–20]. In a paper published in 1999, Olah *et al.* [19] found the helionitronium trication, HeNO_2^{3+} , to be unusually stable. These authors drew this conclusion from second-order many-body perturbation theory calculations. However, subsequent work by Eisfeld and Francisco [20] using multireference configuration interaction demonstrated that the wave function for this system may have ‘extreme multireference character’.

In this paper, an *ab initio* quantum chemical study of the structure and stability of the ground state of the HeCNH^{2+} ion is presented. The previous work summarised above points to the need for a thorough description of electron correlation effects including the use of a multireference formalism. It is well known that when truncated, as it must be in practical applications,

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multireference configuration interaction suffers from non-linear scaling with particle number (i.e. lack of extensivity). Although an *a posteriori* correction of the type suggested by Davidson [21–25] for the single reference case can be applied, this is only approximate. On the other hand, multireference many-body methods (i.e. perturbation theory and cluster expansions) are plagued by the ‘intruder state problem’ which can impair or even destroy convergence. Furthermore, it should be emphasised that, for novel species such as the ion under investigation here, the algebraic approximation must be implemented in a sequence of basis sets in order to explore the basis sets dependence of the electron correlation calculations and to estimate the complete basis set limit.

Most contemporary applications of quantum mechanics to the molecular electronic structure problem use what is termed the ‘theoretical model chemistry’ approach championed by Pople and his co-workers [26]. A composite theoretical model chemistry involves a series of compromises [27,28], based on the methods and basis sets employed and dictated by the computing resources available. Systematic comparison of the results supported by a given model with corresponding data derived from experiment may give that model a predictive capability in situations where experiment is difficult or impossible, or simply too expensive. However, when quantum chemical methods are used to study novel systems such as that investigated here the highest level of theory and basis which is feasible for a system of this size should be employed.

HeCNH²⁺ is a 14-electron system which is isoelectronic with the well characterised HCN molecule. The carbon and nitrogen atoms each have a 1s² core leaving a total of 10 ‘valence’ electrons. Of all the elements helium has the highest ionisation potential (24.587 eV) and the lowest polarisability (0.205 Å⁻³) [29] and forms very few neutral molecular species. Although helium will form clusters He_n, n ≥ 2, [30] only a few neutral partners, such as Hg [31,32] or endohedral C₆₀ complexes [33,34] are able to fix helium. A few compounds such as OBeHe [35] and RNBeHe [36] have been predicted to be stable in theoretical studies. Grandinetti [13] observes that for cationic binding partners ‘*the capability of fixing helium dramatically increases, and numerous singly- and multiply-charged cations containing one or more helium atoms have been experimentally or theoretically investigated*’.

2. Methodology

Calculations were performed for the ground state of the HeCNH²⁺ cation using ‘standard’ *ab initio*

quantum chemical methods. Specifically, we employed (i) single reference second-order many-body perturbation theory in its Møller–Plesset form, MP2; (ii) the coupled cluster expansion including single and double excitations from a single reference function, CCSD; (iii) CCSD with a perturbative estimate of the triple excitation energy component, CCSD(T); (iv) multi-configuration self-consistent field theory in the complete active space self-consistent field form, CASSCF; (v) second-order perturbation theory based on a CASSCF reference function, CASPT2.

The algebraic approximation [37,38] was realised using the correlation consistent basis sets developed by Dunning and his co-workers [39]. Specifically, we employed a polarised valence basis set of ‘quadruple zeta’ quality designated *cc-pVQZ*. The molecular basis set contains a total of 201 primitive Gaussian-type functions which are contracted to give a set of 170 contracted Gaussian-type functions. The basis sets were taken from the MOLCAS library and the GAUSSIAN and can be found on the EMSL Basis Set Library at <https://bse.pnl.gov/bse/portal>.

The MP2, CCSD, CCSD(T), CASSCF and CASPT2 calculations were carried out using the MOLCAS 7.2 program package [40]. Geometry optimisations for the CCSD(T) model were performed with the GAUSSIAN03 program package [41]. The MOLDEN 4.6 package [42] was used to visualise the results.

Single reference self-consistent field calculations gave the following ground state configurations

linear: 1σ²2σ²3σ²4σ²5σ²1π⁴

non-linear: 1a^{1/2}2a^{1/2}3a^{1/2}4a^{1/2}5a^{1/2}6a^{1/2}1a^{1/2}

C_s symmetry: 1a^{1/2}2a^{1/2}3a^{1/2}4a^{1/2}5a^{1/2}6a^{1/2}1a^{1/2}

Geometry optimisation was carried out for the MP2 model and the optimised geometries thus obtained were employed in CCSD and CCSD(T) calculations the results of which were labelled CCSD/MP2 and CCSD(T)/MP2, respectively. Geometry optimisation was also carried out for the CCSD(T) model.

The multireference calculations employed a complete active space of 12 orbitals to describe the 10 valence electrons, designated CASSCF(10e/12o). For the linear geometry, the active space was constructed from three bonding orbitals of σ symmetry and two bonding orbitals of π symmetry together with two non-bonding orbitals of π symmetry and five non-bonding orbitals of σ symmetry. Geometry optimisation was carried out both for the CASSCF model and for the CASPT2 model.

For both the single reference and multireference cases, the potential energy surfaces were explored and stationary points identified and characterised as a global minimum, local minima and transition states.

The dissociation of the structures determined in this way into fragments of the type $AB^+ + CD^+$ was studied by performing calculations for the supersystem $AB^+ \dots CD^+$ with the distance between the two fragments set to a large value (9000 Å). Other coordinates were optimised using 15 active orbitals to describe the 10 valence electrons in the CASSCF model. Then a second-order perturbation theory calculation using the geometry so determined was carried out using the CASPT2 method.

3. Results

A summary of the results of the quantum chemical calculations employing single reference models is collected in Table 1. Total electronic energies, correlation energies and structural parameters, i.e. bond lengths, bond angles and dihedral angles, are presented for the MP2, CCSD and CCSD(T) models. The MP2 model was used to explore the potential energy surface and a total of seven stationary points were identified. In addition to a global minimum, three local minima were found as well as three transition states. The geometries corresponding to these stationary points are shown in Figure 1. The global minimum corresponds to the linear structure HeCNH^{2+} shown in Figure 1(a) and labelled L . One of the local minima in the potential energy surface is associated with the non-linear structure HeNCH^{2+} in Figure 1(b) and labelled N and the other two local minima correspond to trigonal pyramidal configurations, labelled $T1$ and $T2$, and shown in Figure 1(c) and (d) with the formulae NC(He)H^{2+} and CN(He)H^{2+} , respectively. The three transition states corresponding to the formulae NC(He)H^{2+} , NC(He)H^{2+} and NC(He)H^{2+} , respectively, are displayed in Figure 1(e), (f) and (g). The energies for the CCSD and CCSD(T) models presented in Table 1 were calculated at the geometries determined by using the MP2 model and are labelled $E_{\text{CCSD}/\text{MP2}}$ and $E_{\text{CCSD(T)}/\text{MP2}}$. Energies obtained by optimising the geometries for the CCSD(T) model are labelled $E_{\text{CCSD(T)}}$. The $t1$ diagnostic suggested by Lee and co-workers [43,44] was used in the CCSD(T) calculations to determine whether a single reference wave function is adequate for each of the geometries examined. For the CCSD(T) calculations in which the geometry was optimised within that model, the $t1$ diagnostic took the values 0.0138 and 0.0352 for the L and N structures, respectively. For the $T1$ and $T2$ geometries, the $t1$ diagnostic was 0.0261 and 0.0267, respectively, whilst for the transition states $TS1$, $TS2$, $TS3$, the values recorded were 0.0226, 0.0835 and 0.0322. It can be seen that of the different structures studied, the L is best

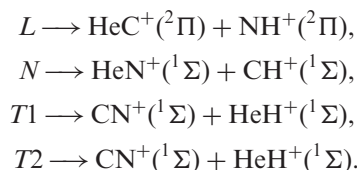
described by the CCSD(T). Reasonably low values of the $t1$ diagnostic (≤ 0.03) were measured for both of the trigonal pyramidal structures and the transition state $TS1$. However, for the non-linear geometry and the $TS2$ and $TS3$ transition states substantial multireference character is indicated. For these geometries, the single reference coupled cluster theory CCSD(T) is not as reliable as it is for the other structures.

The results of the quantum chemical calculations employing multi-reference models are summarised in Table 2.

In Table 3, the calculated total energies, in kJ mol^{-1} , associated with the structures displayed in Figure 1 are shown relative to the most stable structure, the linear configuration L . In this table it can be seen that the linear structure L HeCNH^{2+} is the most stable with other structures having energies lying $\sim 200 \text{ kJ mol}^{-1}$ or more above. Of the five different models employed in the present study, the largest differences in the calculated total energies occur for the MP2 model. For some of the structures studied the difference between the energies supported by the CCSD and CASPT2 models is quite large. For these structures some of cluster amplitudes were found to be larger than ~ 0.1 .

Three transition states were identified on the potential energy surface which correspond to the migration of the H or He atom from CN to NC. These transition states lie between the local minima and the global minimum. In Figure 2, the reaction path connecting the minima and transition structures is shown. The reaction paths between the non-linear structure N and the trigonal pyramidal structures $T1$ and $T2$ are shown in Table 4.

Dissociation energies corresponding to the following decay schemes were calculated:



For these calculations the CASSCF and CASPT2 models were employed. Three additional orbitals were included in the active space. The results of these calculations are given in Table 5. It can be seen that the decay channels in which the $T1$ or $T2$ structure decays into two diatomic cations, CN^+ and HeH^+ are strongly exothermic.

4. Conclusions

We have investigated the structure and stability of the helio hydrogen cyanide dication using standard

Table 1. Total electronic energies^a, correlation energies^a and geometries^b obtained from calculations using a single reference function. Geometries were optimised for the MP2 model giving the energy E_{MP2} . $E_{\text{CCSD/MP2}}$ and $E_{\text{CCSD(T)/MP2}}$ were evaluated at the geometry corresponding to E_{MP2} . Geometries were also optimised for the CCSD(T) model and the energies labelled $E_{\text{CCSD(T)}}$.

Structure	E_{MP2}	$E_{\text{CCSD/MP2}}$	$E_{\text{CCSD/MP2}}$	$E_{\text{CCSD(T)}}$	r_{MP2}	$r_{\text{CCSD(T)}}$	θ_{MP2}	$\theta_{\text{CCSD(T)}}$		
Linear L HeCNH ²⁺	-94.9291004	-94.9331789	-94.9515812	-94.9517595	HN	1.0683	1.0668	HNC	180.0	180.0
	-0.3749096	-0.3789882	-0.3973905	-0.3957184	CN	1.1406	1.1329	HeCN	180.0	180.0
					HeC	1.0826	1.0893			
Non-linear N HeNCH ²⁺	-94.8337300	-94.8529936	-94.8715113	-94.8733115	HC	1.1308	1.1372	HeNC	132.9	121.4
	-0.3413680	-0.3606113	-0.3791291	-0.3783791	CN	1.1890	1.2171	HCN	163.9	160.8
					HeN	1.0149	1.0584			
Trigonal pyramidal $T1$ NC(HeH) ²⁺	-94.8062968	-94.8431755	-94.8579476	-94.8580745	CH	1.1374	1.1414	NCHe	109.5	109.5
	-0.3100666	-0.3469707	-0.3617428	-0.3621031	CN	1.2961	1.3030	NCH	134.1	135.3
					CHe	1.1758	1.1910			
Trigonal pyramidal $T2$ CN(HeH) ²⁺	-94.7815910	-94.8198178	-94.8339876	-94.8346352	HN	1.0791	1.0797	CNHe	110.5	111.4
	-0.3067537	-0.3449808	-0.3591506	-0.3602527	CN	1.3773	1.3872	NCH	173.9	174.5
					CH	1.1468	1.1498			
Transition state $TS1$ NC(He)H ²⁺	-94.7918232	-94.8284594	-94.8431447	-94.8432779	NC	1.3091	1.3159	NCHe	68.8	67.8
	-0.3066705	-0.3426738	-0.3573590	-0.3574188	CHe	1.5633	1.6119	NCH	173.9	174.5
					CH	1.1468	1.1498			
Transition state $TS2$ CN(H)He ²⁺	-94.7532897	-94.7694552	-94.8036421	-94.8074154	CN	1.2290	1.2178	CNHe	147.0	22.3
	-0.3983124	-0.4149301	-0.4491169	-0.4458942	NHe	1.3700	2.6062	NCH	78.2	80.0
					NH	1.5766	1.3316			
Transition state $TS3$ CN(H)He ²⁺	-94.8006588	-94.8307419	-94.8483032	-94.8455633	CN	1.2324	1.2172	NCHe	137.2	151.6
	-0.3284562	-0.3598694	-0.3774307	-0.3941157	CH	1.2096	1.1384	NCH	97.0	79.1
					CHe	1.1195	1.2874			

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^aTotal electronic energies are in hartree.

^bBond lengths are in Ångstrom. Bond angles are in degrees.

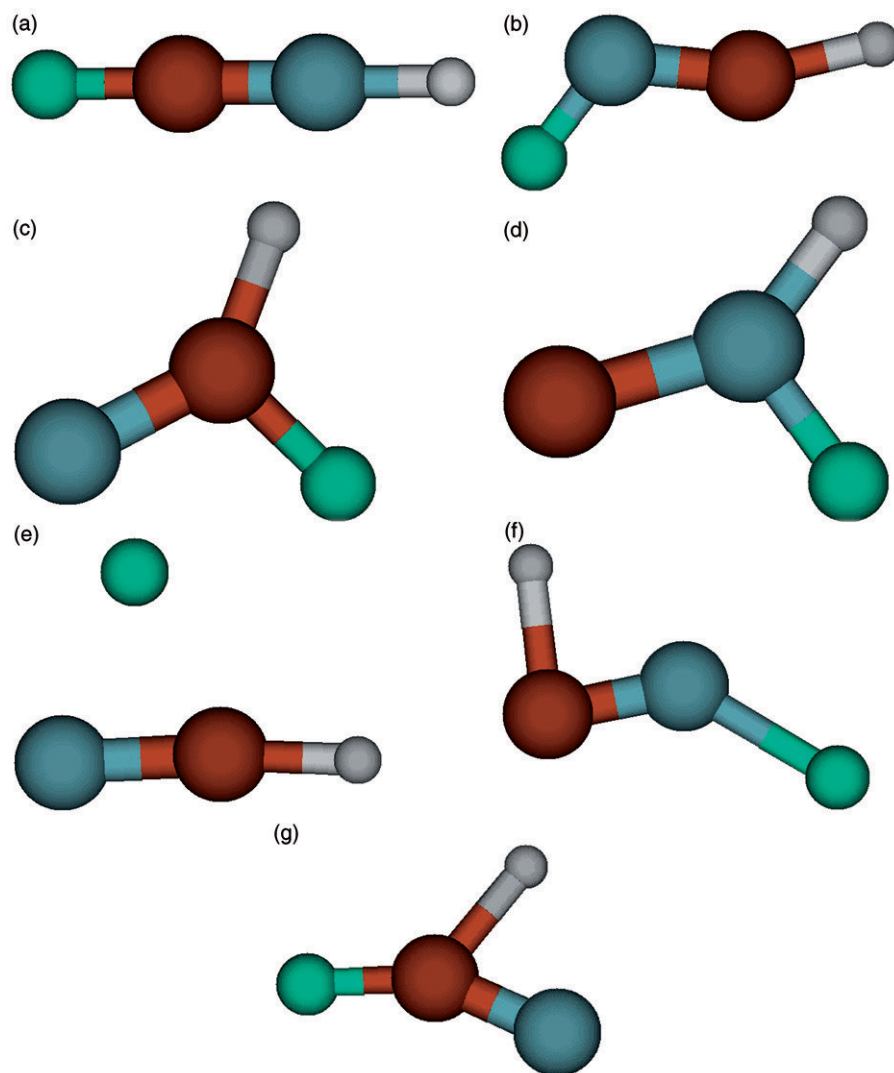


Figure 1. Geometries of stationary points on the potential energy surface of the HeCNH_2^{2+} dication: (a) linear L : HeCNH_2^{2+} ; (b) non-linear N : HeNCH_2^{2+} ; (c) trigonal pyramidal $T1$: NCHeH_2^{2+} ; (d) trigonal pyramidal $T2$: CNHeH_2^{2+} ; (e) transition state $TS1$: $(\text{HCN} \cdots \text{He})^{2+}$; (f) transition state $TS2$: HCNHe^{2+} ; (g) transition state $TS3$: HCNHe^{2+} .

Table 2. Total electronic energies^a and geometries^b obtained from calculations using a multi-reference function. Geometries were optimised for the CASSCF model giving the energy E_{CASSCF} . Geometries were also optimised for the E_{CASPT2} model giving the energy E_{CASPT2} .

Structure	E_{CASSCF}	E_{CASPT2}		r_{CASSCF}	r_{CASPT2}		θ_{CASSCF}	θ_{CASPT2}
Linear L HeCNH_2^{2+}	-94.7723331	-194.9363202	NH	1.0701	1.0665	CNH	180.0	180.0
			CN	1.1360	1.1337	HeCN	180.0	180.0
			HeC	1.0989	1.0889			
Non-linear N HeNCH_2^{2+}	-94.6929172	-94.8553807	HC	1.1422	1.1366	HeNC	121.0	121.1
			CN	1.2209	1.2189	HCN	160.1	160.4
			HeN	1.0772	1.0606			
Trigonal pyramidal $T1$ $\text{NC}(\text{HeH})_2^{2+}$	-94.6850509	-94.8394816	CH	1.1438	1.1422	NCHe	108.1	110.7
			CN	1.3113	1.3014	NCH	137.8	133.7
			CHe	1.2219	1.1843			

(continued)

Table 2. Continued.

Structure	E_{CASSCF}	E_{CASPT2}	r_{CASSCF}	r_{CASPT2}	θ_{CASSCF}	θ_{CASPT2}		
Trigonal pyramidal $T2$ $\text{CN}(\text{HeH})^{2+}$	-94.6529726	-94.8144955	HN	1.0870	1.0811	CNHe	110.0	113.9
			CN	1.3891	1.3855	NCH	143.4	139.4
			HeN	1.1957	1.1714			
$TS1$ $\text{NC}(\text{He})\text{H}^{2+}$	-94.6723976	-94.8244459	NC	1.3261	1.3163	NCHe	67.9	70.0
			CHe	1.6943	1.6044	NCH	174.9	174.2
			CH	1.1551	1.1503			
$TS2$ $\text{CN}(\text{H})\text{He}^{2+}$	-94.6723976	-94.7917849	CN	1.2251	1.2202	CNHe	137.5	141.4
			NHe	1.5910	1.5247	NCH	84.8	78.7
			NH	1.7186	1.6234			
$TS3$ $\text{CN}(\text{H})\text{He}^{2+}$	-94.6661576	-94.8294050	CN	1.2198	1.2202	NCHe	153.2	150.8
			CH	1.3123	1.2821	NCH	75.3	80.2
			CHe	1.1551	1.1392			

^aTotal electronic energies are in hartree.

^bBond lengths are in Ångstrom. Bond angles are in degrees.

Table 3. Calculated total energies, in kJ mol^{-1} , associated with the structures shown in Figure 1 relative to the most stable structure, the linear configuration L .

Energy	MP2	CCSD/MP2	CCSD(T)/MP2	CCSD(T)	CASSCF	CASPT2
$E(L)$	0.0	0.0	0.0	0.0	0.0	0.0
$E(N)$	250.4	210.5	210.2	205.9	208.5	212.5
$E(T1)$	322.4	236.3	245.8	246.0	229.2	254.2
$E(T2)$	387.2	297.6	308.7	307.5	313.4	319.9
$E(TS1)$	360.4	274.9	284.7	284.8	262.4	293.7
$E(TS2)$	461.6	429.9	388.4	378.9	363.0	379.5
$E(TS3)$	337.2	268.9	271.2	278.8	278.8	280.7

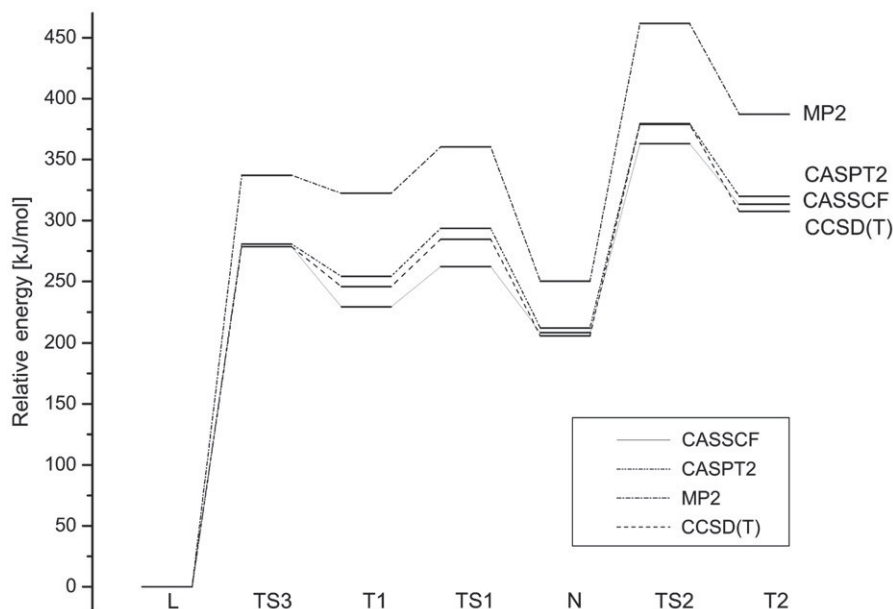


Figure 2. Reaction path connecting the minima and transition structures shown in Figure 1. Energies are given in kJ mol^{-1} .

Table 4. Reaction paths between the non-linear structure N and the trigonal pyramidal structures $T1$ and $T2$. There are three transition states, $TS1$, $TS2$ and $TS3$, which correspond to the migration of the H or He atom from CN to NC. Energies are given in kJ mol^{-1} .

Path	MP2	CCSD/MP2	CCSD(T)/MP2	CCSD(T)	CASSCF	CASPT2
$N \rightarrow TS1$	110.0	64.4	74.5	78.8	53.9	81.2
$N \rightarrow TS2$	211.2	219.4	178.2	173.0	154.5	167.0
$L \rightarrow TS3$	337.2	268.9	271.2	278.8	278.8	280.7
$TS1 \rightarrow T1$	-38.0	-38.6	-38.9	-38.8	-33.2	-39.5
$TS2 \rightarrow T2$	-74.4	-132.3	-79.7	-71.5	-49.6	-60.0
$TS3 \rightarrow T1$	-14.8	-32.6	-25.4	-32.8	-49.5	-26.5

Table 5. Dissociation energies given by the CASSCF(10e/15o) and CASPT2(10e/15o) models. Energies are given in kJ mol^{-1} .

Path	CASSCF	CASPT2
L	-15.3	36.4
N	192.8	162.9
$T1$	-544.5	-544.7
$T2$	-628.7	-610.3

ab initio quantum chemical methods. Both single reference and double reference models were employed together with a correlation consistent basis set of 'quadruple zeta' quality. The global minimum in the potential energy surface corresponds to the linear structure HeCNH^{2+} . Three local minima were identified as well as three transition states.

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