

Quantum chemical treatment of cyanogen azide and its univalent and divalent ionic forms

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Abstract

An explosive material, cyanogen azide (CN_4) and its univalent and divalent anionic and cationic forms have been studied quantum chemically by using different theoretical approaches. In this study, the structures considered have been screened for their relative stabilities. Also, they have been investigated whether the charged forms play a role in the usual explosion process or any electrical charging during storage cause explosion. Various quantum chemical properties are obtained and discussed. It has been found that the univalent cation and anion and divalent cation formations do not cause much change in the molecular structure as compared to the neutral cyanogen azide molecule, whereas the divalent anionic form exhibits drastic changes in the geometry, resulting in bond cleavage to eliminate nitrogen molecule.

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1. Introduction

Cyanogen azide (carbon pernitride) is an initiating explosive which has also been much investigated [1]. It is a clear colorless oily liquid and the pure azide detonates violently upon thermal, electrical or mechanical shock [2]. However, it can be handled relatively safely in solvents.

Structurally, cyanogen azide is a V-shaped molecule and it was determined that the angle at the middle N atom is 120° [3]. Its electron-density maps of bent bonds [4], He(I) photoelectron spectra [3], and bonding trends [5] have all been studied. In another study, the Ne(I) and He(I) photoelectron spectra (PE) of cyanogen azide have been recorded and their interpretation has been achieved by comparison with the PE spectrum of HN_3 and *ab initio* LCGO SCF MO calculation [6]. Deviations from Koopmans theorem of quite different magnitudes were found dependent on the type of ionization process applied [6]. However, its charged forms and their quantum chemical properties have not been studied yet to the best of our knowledge.

Fig. 1 shows the chemical structure of cyanogen azide molecule and numbering of the atoms. This molecule exhibits

explosive nature and unusual bonding character. In that respect, these properties make it an ideal candidate for a quantum chemical investigation. Many experimental data of the neutral molecule exist in the literatures [7–11], especially there are many studies concerning the data of infrared and Raman spectra of it [12–18]. On the other hand, as far as we know, no report on the univalent and divalent ionic forms of cyanogen azide molecule has appeared in the literature. In this study, the neutral and various charged forms of cyanogen azide have been considered for their relative stabilities to investigate whether the charged forms play any role in the explosion process.

2. Methods

Presently, the geometry optimizations of all the structures were achieved first by using MM2 molecular mechanics method [19–21] followed by semi-empirical PM3 and then treatment of certain quantum chemical methods (including *ab initio* and DFT-type treatments [22,23]). These levels of theories are, UHF/6-311(d), UHF/6-311G+(d), UMP2 (full)/6-31+G(d), UCCSD/6-31G+(d), G3, UB3LYP/6-31G(d), UB3LYP/aug-cc-pVDZ, UB3LYP/aug-cc-pVTZ, UB3LYP/aug-cc-pVQZ and ROB3P86/6-311+G(d) (also PM3(UHF) single point and geometry optimization calculations for heat of formation values). The exchange term of B3LYP consists of hybrid Hartree–Fock and

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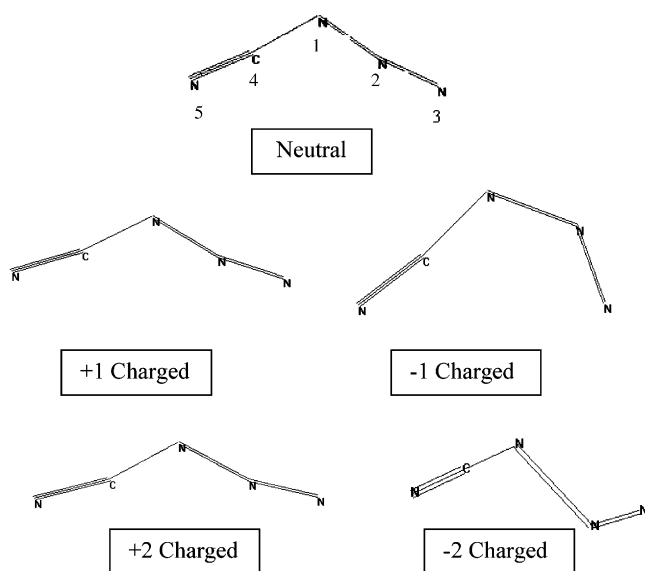


Fig. 1. The geometry optimized structures of cyanogen azide molecule (also numbering of the atoms shown), and its univalent and divalent forms considered. In the divalent anion form, due to technical reasons of the interface program, the dissociated N1–N2 bond appears as double bond.

local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [24,25]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [26] and Lee, Yang, Parr (LYP) correlation correction functional [27].

We employed Dunning's augmented correlation consistent basis sets, denoted aug-cc-pVXZ, (X = D, T, Q) [28] basis sets. Geometry optimizations for all the structures were achieved within B3P86 [29,30] at the level of 6-311+G(d) (restricted open-shell).

For each set of calculations, vibrational analyses were done. The normal mode analysis for each structure yielded no imaginary frequencies for the $3N - 6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths were thoroughly searched in order to find out whether any bond cleavage occurred or not during the geometry optimization process. All these computations were performed by using the Gaussian 98 package program [31].

3. Results and discussion

Although, the half-life of cyanogen azide (27% solution, in acetonitrile at room temperature) is about 2 weeks, in pure form it detonates violently upon thermal, electrical or mechanical shock [2]. In the present study, to get some insight at the molecular level about what happens when the cyanogen azide molecule is charged in an electrical field, the neutral, monovalent and divalent forms of it have been subjected to various quantum chemical treatments. Since, wave function of an atom (or molecule) is polarized when it is placed in a uniform electrical field (due to the attraction of electron cloud in the direction of the electric field) the charge distribution about the nucleus becomes asymmetric.

Thus, a better handling of the system necessitates the usage of polarization functions for the atoms of the system considered. The 6-31G(d) is the basis set which employs d-type functions for the heavy atoms. Note that 6-31G(d, p) level calculations provide in many cases quantitative results [21]. Since cyanogen azide does not contain any hydrogen atoms, then 6-31G(d) level of calculations should also be satisfactory for many purposes. Furthermore, to provide more accurate descriptions of anions, or neutral molecules with unshared pairs, basis sets may be augmented with so-called diffuse functions and these are intended to improve the basis set at large distances from the nuclei, thus better describing the barely bound electrons of anions. Hence, diffuse functions are indispensable for the proper description of anions.

The bond energies for N–N and N=N bonds are about 158 kJ/mol and 418 kJ/mol, respectively [32] and the following resonance structures can be written for cyanogen azide.



Thus N(1)–N(2) bond in character is in between single and double bond (see Fig. 1 for numbering of the atoms).

It is experimentally well proved fact that free electrons exist in combustion flames and gaseous detonations [33]. In some cases it is possible to quench detonation completely by an applied electrical field [33]. The applied electrical field causes polarization or ionization of the molecule thus changing properties of the bond even leading to bond rupture. However, this phenomenon is highly structure dependent and as indicated below for cyanogen azide, bond cleavage occurs in the case of dianion formation, but only some bond length changes happen in the case of the divalent cation. Explosive materials are more prone to such kind of electrical and magnetic effects. Thus, their response to such kind of effects is very important and vital for their storage and handling. On the other hand, after detonation, free electrons or charged particles are formed and according to the general principle of classical electromagnetic theory, that charged bodies in motion are accompanied by certain electromagnetic waves [34]. Hence, to study the charged forms of explosive materials at the molecular level by means of certain quantum chemical methods is very informative for many practical purposes.

The geometry optimized structures of cyanogen azide molecule and its ionic forms considered are shown in Fig. 1. This result is approximately consisting with all the levels of theory performed in this study. The neutral molecule displays some peculiar structural properties such as N1–C4–N5 and N1–N2–N3 bond angles are not expectedly linear but bent. As the charge develops the optimized geometry of cyanogens azide changes (see Fig. 1). Although, the mono and divalent cation formations are accompanied by moderate changes in geometry as compared to the neutral molecule, the anion forms exhibit drastic changes in the geometry. Table 1 shows the calculated and experimental geometric parameters of the neutral cyanogen azide molecule (since they exhibit certain parallelism, not all the results of the calculations are shown in Table 1). As seen there, the calculated and the experimental values are in well agreement in most of the cases. According to the experimental and calculated bond length values, the shortest bond length

Table 1
Calculated and experimental geometrical parameters of neutral cyanogen azide molecule

	UHF/6-311G(d)	UMP2/6-31+G(d)	UCCSD/6-31+G(d)	G3	ROB3P86/6-311+G(d)	UB3LYP/6-31G(d)	UB3LYP/ang-cc-pVQZ	Exp. ^a	Exp. ^b
N1–N2	1.259	1.259	1.273	1.257	1.249	1.254	1.246	1.252	1.261
N1–C4	1.345	1.352	1.365	1.351	1.341	1.347	1.339	1.312	1.355
N2–N3	1.082	1.157	1.132	1.157	1.124	1.132	1.118	1.133	1.122
C4–N5	1.131	1.186	1.170	1.184	1.158	1.166	1.154	1.164	1.155
N2–N1–C4	113.1	116.5	113.0	116.8	118.4	118	118.5	120.2	114.5
N1–N2–N3	172.3	169.9	170.6	169.9	170.2	169.0	170.7	–	169.2
N1–C4–N5	176.5	173.7	173.9	174.4	173.9	173.6	173.9	176.0	175.3
C4–N1–N2–N3	179.9	180.0	180.0	180.0	–179.9	179.9	179.9	–	180.0
N2–N1–C4–N5	–179.9	180.0	180.0	180.0	179.8	–179.9	179.7	180.0	180.0

Bond lengths are presented in Å and angles in degrees.

^a Ref. [35].

^b Ref. [14].

among them is N2–N3 bond length. Comparing the N1–N2 and N2–N3 bond lengths (both of them are double bonds), N1–N2 bond is found to be longer than N2–N3 bond. Furthermore, bond angle N1–C4–N5 is bigger than N1–N2–N3 bond angle (see Fig. 1 and Table 1). This result is consistent with all different theoretical levels of calculations performed and complies with the experimental data too. The calculated and observed values imply that the N2–N3 linkage should have a full π -bond but N1–N2 bond, possesses only a partial π -bond character. The bond angle constituted by C4–N1–N2 atoms has been calculated as 118° at UB3LYP/6-31G(d) level (the experimental value was reported as 120° [35] and 114° [14]). As it is evident from Table 1, in general there is a good agreement between most of the calculated and observed geometrical parameters of neutral cyanogen azide molecule. Note that HF and DFT equilibrium geometries of a ground state molecule are quite similar to one another (with bond-length difference from method to method usually no greater than 0.03 \AA for the first and second row atoms [19]).

Since, cyanogen azide molecule possesses a nitrogen atom (the third atom from each end) flanked by a doubly bonded nitrogens (N=N) and also by a C \equiv N moiety (all of which at first sight imply a linear geometry for these groups), a V-shaped geometry is expected for the whole molecule. However, this is not the case and the arms of generally V-shaped structure are not perfectly straight. In Fig. 1, it is observed that the optimized geometry of the charged species, especially the anionic species, is distorted much, so that the optimized geometry for the divalent anionic form of the molecule stands for the dissociated form at N1–N2 bond. Whereas, the divalent cation, still has a stable geometry contrary to the divalent anion form.

Table 2 shows the structural parameters for the neutral cyanogen azide molecule, as well as its univalent and divalent ionic forms calculated, at the levels of UB3LYP/6-31G(d), and UMP2 (full)/6-31+G(d) (the other calculation results are nearly similar to the values tabulated in Table 2, thus not included in the table). As seen in these tables, as the charge develops certain bonds are elongated or contracted as compared to the neutral state. The cation formation causes elongation of mainly N1–N2 and C4–N5 bonds for both the univalent and the divalent cationic forms (see Table 2). On the other hand, the cation formation causes contraction of N1–C4 and N2–N3 bonds for both the cationic forms. The results are consistent with all the different levels of calculations performed presently. When N1–C4–N5 angle is considered, one finds that as the positive charge develops to generate the univalent and divalent forms, the angle decreases (see Table 2). A similar behavior is exhibited by N1–N2–N3 bond angle.

As for the anionic species, N1–C4–N5 angle is less or very comparable to the respective angle in the neutral form, but greater (with the exception of UMP2 (full)/6-31+G(d) level result) in the divalent anion (note that the divalent anion in this study actually stands for a dissociated molecule. In other words it is a system of fragments or a hypothetical molecule having a very elongated bond). On the other hand, N1–N2–N3 bond angle is much less (ca. 41°) in the univalent form as compared to the neutral molecule. Whereas the univalent anion formation

Table 2
Structural parameters of cyanogen azide molecule, its univalent and divalent ions

Bond lengths and angles	Charge				
	0	+1	+2	-1	-2
N1–N2	1.254 (1.259)	1.303 (1.334)	1.319 (1.351)	1.398 (1.401)	2.593 ^a (2.761) ^a
N1–C4	1.347 (1.352)	1.295 (1.273)	1.270 (1.306)	1.332 (1.341)	1.262 (1.265)
N2–N3	1.132 (1.157)	1.120 (1.085)	1.126 (1.151)	1.200 (1.161)	1.142 (1.149)
C4–N5	1.166 (1.186)	1.199 (1.173)	1.237 (1.226)	1.181 (1.195)	1.240 (1.265)
N2–N1–C4	118.0 (116.5)	118.8 (114.5)	123.1 (117.5)	114.6 (111.2)	
N1–N2–N3	169.9 (169.9)	166.2 (168.8)	164.3 (164.3)	129.5 (134.8)	
N1–C4–N5	173.6 (173.7)	170.7 (173.5)	166.7 (163.1)	172.9 (173.8)	178.1 (172.1)
C4–N1–N2–N3	179.9 (180.0)	179.9 (179.9)	179.9 (179.9)	-0.001 (0.0)	
N2–N1–C4–N5	-179.9 (180.0)	-179.9 (179.9)	-179.9 (-179.9)	-179.9 (-179.9)	

Calculated parameters are at UB3LYP/6-31G(d) level. The values in parentheses calculated at UMP2 (full)/6-31+G (d) level. Bond lengths are presented in Å and angles in degrees.

^a Distance between the atoms, not the bond length.

goes parallel with the elongation of mainly N1–N2, N2–N3 and C4–N5 bonds and the contraction of the N1–C4 bond (see Table 2). The calculations within the limitations of the methods employed have revealed that in spite of the elongation of certain bonds while charge develops, no bond cleavage happens for the univalent and divalent cationic forms and also for the univalent anionic form of cyanogen azide.

In these systems the kind of atoms and structure of the molecule compensate the electron lost or electron gain in order to prevent bond rupture. On the other hand, as the divalent anionic state forms, it breaks into two parts about N1–N2 bond. N1–C4 bond is contracted as a result of dissociation. The calculated distance between N1–N2 atoms is 2.5–3.5 Å (2.55 Å at UB3LYP/aug-cc-pVDZ level). Hence, as a result of dissociation, CN₂ and N₂ fragments formed. Moreover, the charge calculations indicate that CN₂ fragment formed is a dianion.

In the neutral form, electron density is located mainly at N5 and N1 atoms. As it is expected, N2 atom has lower electron density (positively charged). Considering cationic forms one finds that C4 progressively gets more positive charge as the total charge develops and acquires a high charge value for the divalent cationic form, also this result is verified with the tabulated data in Table 3. Furthermore, Table 3 shows the Mulliken atomic charges of cyanogen azide molecule, as well as its univalent and divalent ions calculated at UCCSD/6-31+G(d) and UB3LYP/aug-cc-pVDZ levels, respectively. Unfortunately,

optimization failed in the case of divalent anion at the UCCSD/6-31+G (d) level of theory.

In Table 4, the data for the divalent anionic form reveal that approximately all the charges located in N–C–N part of the molecule (CN₂ = fragment). Note that this system stands for the decomposed structure.

Table 4 shows some calculated energies of cyanogen azide and some of its ions (zero-point energies are taken into account). As seen in the table, all the species at the optimized form stand for energetically stable systems. Note that the energy for the dianionic case actually stands for a composite (decomposed) structure of the fragments. In terms of energy considerations, stability order is -1 > 0 > +1 > +2 at UHF, UB3LYP, UMP2, UCCSD and G3 theoretical levels, however, stability order is -1 > +1 > 0 > +2 at ROB3P86/6-311+G(d) level of theory (see Table 4). Recall that in the case of divalent anion, it is not stable structurally (chemically), thus not included in the successive energies in the table. The energy difference between the lowest energy (univalent anion) and highest energy species (divalent cation) is 3100 kJ/mol at UB3LYP/aug-cc-pVDZ level of theory. On the other hand, lowest energies for the species are obtained in the cases of UB3LYP/aug-cc-pVQZ and B3P86/6-311+G(d) (restricted open-shell) level of theories among the theoretical levels employed in this study. Unfortunately, in the case of divalent anionic form of cyanogens azide, optimization failed at UCCSD/6-31+G(d) and UB3LYP/aug-cc-pVXZ (X = T, Q) level of theories so the corresponding energy data are missing

Table 3
Mulliken atomic charges of cyanogen azide molecule, its univalent and divalent ions.

Position	Atom	Charge				
		Neutral	+1	+2	-1	-2 ^a
1	N	-0.122 (-0.405)	0.092 (-0.100)	0.308 (0.118)	-0.265 (-0.647)	-0.586
2	N	0.647 (0.521)	0.707 (0.311)	0.761 (0.185)	0.164 (0.035)	-0.117
3	N	-0.451 (-0.101)	-0.174 (0.424)	0.078 (0.738)	-0.529 (-0.199)	-0.306
4	C	0.091 (0.350)	0.406 (0.382)	0.648 (0.523)	0.007 (0.452)	-0.369
5	N	-0.166 (-0.365)	-0.032 (-0.017)	0.206 (0.738)	-0.377 (-0.641)	-0.622

Calculated parameters at UB3LYP/aug-cc-pVDZ level. The values in parentheses obtained at UCCSD/6-31+G (d) level, at which optimization failed in the case of divalent anion.

^a For the dissociated system. See Fig. 1 for the numbering of atoms.

Table 4
Some calculated energies for cyanogen azide molecule, its univalent and divalent ions (energies in a.u., 1 hartree = 627.5 kcal/mol), the total electronic energies are corrected for ZPV(E)

Charge	UHF/6-311G(d)	UMP2/6-31+G(d)	UCCSD/6-31+G(d)	G3	ROB3P86/6-311+G(d)	UB3LYP/6-31G(d)	UB3LYP/aug-cc-pVDZ	UB3LYP/aug-cc-pVTZ	UB3LYP/aug-cc-pVQZ
0	-255.589119	-256.342332	-256.3294441	-256.940065	-257.055677	-256.982026	-257.020276	-257.082054	-257.099477
1	-255.244415	-255.893534	-255.9440638	-256.474895	-257.219536	-256.587889	-256.621276	-256.682376	-256.699639
2	-254.539450	-255.233332	-255.2527161	-255.775358	-256.489049	-255.878830	-255.912663	-255.972845	-255.989894
-1	-255.634764	-256.363308	-256.3882906	-256.940065	-257.726274	-257.027099	-257.093323	-257.150627	-257.167841
-2	-255.455223	-256.287923	-256.832068	-256.832068	-257.643104	-256.871047	-256.88933		

Empty spaces in the table mean that optimization failed so the energy data are not available. The energies for the dianion is for the dissociated system.

Table 5

The heat of formation (ΔH_f) values for the species considered

Charge	ΔH_f
0	509.222
+1	1494.087
-1	281.789
+2	3137.546
-2	772.922

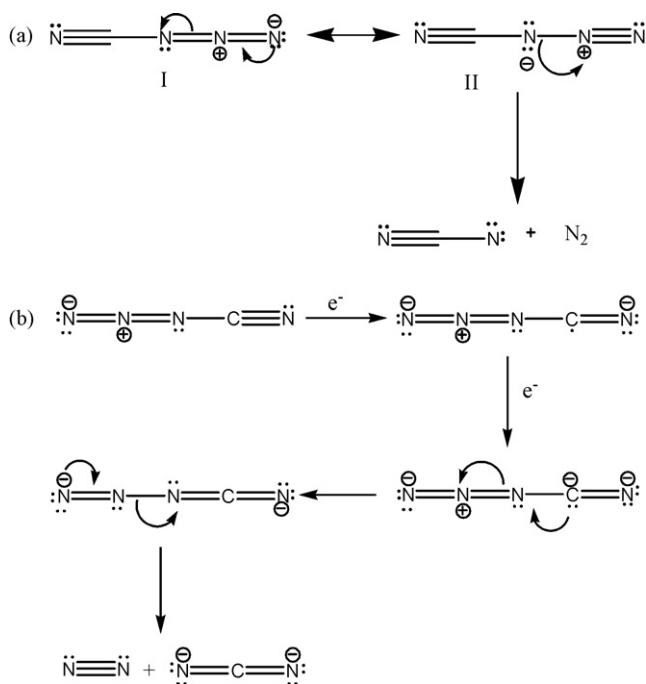
ΔH_f : obtained from PM3 (UHF) single point calculations based on the geometry optimized structures at UB3LYP/6-31G(d) level (energies in kJ/mol).

in Table 4. Note that G3 method known as the best one as compared to others [19] (shown in Table 4), however it is very time consuming.

The heat of formation values for the neutral and charged species have been calculated by using single point PM3 (UHF) calculation over UB3LYP/6-31G(d) optimized geometries. Resulting stability order in terms of the heats of formation values is found to be, $-1 > 0 > +1 > +2$ (the decomposed system is not included, see Table 5). In the case of divalent anion of cyanogen azide, the distance calculated as the supposed bond length of N1=N2 is 1.664 Å (it is much longer than the normal bond length of N1=N2 of the neutral molecule, which is 1.252 Å [35]).

Another approach to these systems, has been charging (+2, +1, -1, -2) of the geometry optimized structure of neutral cyanogen azide molecule (keeping the geometry fixed). Then, the single point total energy value increases (its total energy is represented by $E_i(\text{sp})$). If the corresponding total energy value of the geometry optimized structure of the neutral molecule in these calculations is represented by $E_0(\text{opt})$ is taken as the reference, $\Delta E = E_i(\text{sp}) - E_0(\text{opt})$ energy difference follow the order of $+2 > +1 > -2 > -1$. It means that cyanogen azide molecule is more tolerant to negative charging than the positive one in the fixed geometry. Note that E_i and E_0 are the total energies for the charged and neutral systems, respectively. Furthermore, $E_i(\text{sp})$ is obtained by single point calculation starting from the optimized geometry of the neutral system and charging. The UHF/6-311+G(d) and UB3LYP/6-31G(d) levels of theory predict the above mentioned order for ΔE . On the other hand, if these charged forms are allowed to optimize their geometries to minimize their total energy contents ($E_i(\text{opt})$), then $\Delta E_i = E_i(\text{opt}) - E_i(\text{sp})$ values (energy loss by geometry optimization) follow the order of $-2 > -1 > +2 > +1$. Note that -2 charged system is actually a fragmented structure. The calculations again were performed at the above mentioned levels of the theory.

In the mid-1960s Milligan et al. studied the photochemistry of matrix-isolated cyanogen azide N_3CN , a suitable precursor for the free nitrenes NCN and CNN . Due to its explosive nature, it was only synthesized in situ, by passing a gaseous mixture of BrCN or ClCN over NaN_3 [36]. It is well known from the literature [37,38], that photolysis of matrix-isolated (Ar, 12 K) cyanogens azide, N_3CN , led formation of expected nitrene NCN . As a result of the present calculations, it is evident that the initially formed divalent anionic species dissociates forming



Scheme 1.

two new structures, NCN= and N_2 . On the other hand, other charged forms are stable according to the calculations performed presently.

Experimental studies show that the N1-N2 bond is the weakest bond in the molecule [39]. According to the present calculations, the bond rupture of this bond takes place in the divalent anionic form. The valence bond formalism may give some clue why the divalent anionic form is decomposed rather than the neutral or cationic forms. As seen in Scheme 1a, canonical structure II leads to nitrene and nitrogen molecule formations. When the negative charge density on the N1 atom in the canonical structure II is high enough, the bond rupture takes place easily (see the Mulliken atomic charges of cyanogen azide molecule and its ions in Tables 4 and 5). Scheme 1a and b outline the thermal decomposition of the neutral cyanogens azide and the decomposition by negative charging, respectively. Note that in Scheme 1a and b, cyanogen azide skeleton, for the sake of simplicity, is shown linear albeit the fact that cyanogen azide is a V-shaped molecule. Furthermore, bond dissociation energy of N1-N2 for the neutral form is calculated (at G3 level) considering the fragmentation pattern shown in Scheme 1a. In the case of neutral cyanogen azide molecule BDE value is 63 kJ/mol. This value is quite low considering the average bond dissociation energy value for N-N and N=N bonds (158 kJ/mol and 418 kJ/mol, respectively) [32]. Indeed cyanogen azide molecule even in the neutral form is not very stable [2]. In the light of Scheme 1b, a similar calculation was carried out for N1-N2 bond (it is not real chemical bond because of its highly long value, 2.282 Å at G3 level) of cyanogen azide dianion. The result of the calculation revealed that bond dissociation energy of that hypothetical bond is 21 kJ/mol. Note that the homolytic BDE [40,41] is defined for the present case as $\text{BDE} = E(X) + E(R) - E(R-X)$, where E stands for the respective total electronic energy corrected for

Table 6
The α - and β -HOMO and α - and β -LUMO energies (ϵ) of cyanogen azide molecule and some of its ions (energies in 10^{-19} J, $\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$)

Energy	Charge		+1		+2		-1		-2 ^a	
	Alpha	Beta	Alpha	Beta	Alpha	Beta	Alpha	Beta	Alpha	Beta
HOMO	-13.0 (-18.3)	-13.0 (-18.3)	-26.4 (-33.6)	-26.1 (-31.5)	-38.9 (-45.6)	-38.9 (-45.6)	-0.3 (-7.5)	-0.9 (-7.1)	12.2 (5.7)	12.2 (5.7)
LUMO	-3.7 (2.0)	-3.7 (2.0)	-15.4 (-7.3)	-21.1 (-12.5)	-35.1 (-27.7)	-35.1 (-27.7)	7.8 (9.4)	5.9 (9.3)	15.3 (16.2)	15.3 (16.2)
$\Delta\epsilon$	9.3 (20.3)	9.3 (20.3)	11.0 (26.3)	5.0 (19.0)	3.8 (17.9)	3.8 (17.9)	8.1 (16.4)	6.8 (16.4)	3.1 (10.5)	3.1 (10.5)

Calculated at UB3LYP/6-31G(d) level. The values in parentheses calculated at UMP2 (fuII)/6-31+G (d) level.

^a For the dissociated system.

Table 7
Fundamental normal modes (cm^{-1}) of cyanogen azide calculated at different levels of theory and experimental values

UB3LYP/6-31G(d)	UHF/6-311G(d)	ROB3P86/6-311+G(d)	UMP2/6-31+G(d)	Experimental [42,43]	Assignment
170.2	193.2	171.9	162.5	184	N=N–C bend
453.9	524.4	461.4	416.6	451	N–C≡N bend
463.8	558.9	469.1	453.5	451	N–C≡N bend
523.1	597.2	513.0	473.1	520	N=N=N bend
662.4	771.2	666.2	660.9	666	N=N=N bend
921.5	983.4	917.1	922.8	929	N–C stretch
1351.5	1328.2	1348.9	1329.0	1253	N=N=N sym stretch
2305.8	2553.8	2289.2	2197.0	2208	N=N=N asym stretch
2350.9	2611.7	2338.7	2326.0	2239	C≡N stretch

the zero-point energy for each species involved in the general reaction shown as $R - X \rightarrow R + X$.

Table 6 contains the α - and β -type HOMO and LUMO energies obtained by means of the UB3LYP/6-31G(d) and UMP2/6-31+G(d) calculations, respectively. As seen in Table 6, the cation formation generally lowers all the molecular orbital energies of cyanogen azide, whereas the anion formation raises them up as expected. The effect of charging on the frontier molecular orbitals (the HOMO and LUMO) is more pronounced in the case of the anion rather than the cation. However, note that the dianionic case is a split system because of decomposition so its frontier orbital energies stand for the composite system.

Table 7 shows the calculated raw IR frequencies and experimental data [42,43] for the neutral cyanogen azide molecule considered. Whereas, fundamental normal modes (cm^{-1}) of neutral cyanogen azide molecule and its monovalent and divalent ions calculated at different levels of theory are given in Table 8. Regression analysis [44] was carried out for the observed and

calculated (unscaled) IR frequencies for the neutral cyanogen azide molecule. The experimental data cover statistical sample size of $n=9$ IR frequencies excerpted from the literature [42,43]. The details of the regression analysis can be found in Table 9. In all the cases, the coefficient of determination (R^2) value and the simple correlation coefficient (r_{YX}) are greater than 0.99. Therefore, the regression equations are all good. However, the tabulated F -distribution [45] value with $k-1$ and $n-k$ degrees of freedom (where n is the number of observations and k is the number of parameters estimated, $F_{1,7}$ presently) is 12.25 at 1% probability [45]. Thus, the regression equations involving UB3LYP/6-31 G(d) and ROB3P86/6-311+ G(d) results are more significant than the others because for those relevant $F_{1,7}$ values far exceed the tabulated value.

As mentioned in the introduction part, there are some studies concerning the IR spectra of cyanogen azide molecule [12–18], whereas there is no corresponding study about the charged forms of cyanogen azide molecule in the literature, to the best of our

Table 8
Fundamental normal modes (cm^{-1}) of neutral cyanogen azide molecule and its monovalent and divalent ions calculated at different levels of theory

UHF/6-311G(d)					ROB3P86/6-311+G(d)					UMP2/6-31+G(d)				
2	1	Neutral	-1	-2 ^a	2	1	Neutral	-1	-2 ^a	2	1	Neutral	-1	-2 ^a
183	174	193	223	104	176	172	172	186	66	166	167	162.5	179	84
340	404	524	282	115	246	369	461	274	68	262	490	416.6	260	140
405	421	559	535	136	350	430	469	469	146	343	537	453.5	445	163
468	431	597	674	244	423	448	513	588	347	371	564	473.1	531	304
637	695	771	810	783	574	635	666	733	630	577	799	660.9	716	534
899	775	983	954	800	816	875	917	848	638	763	863	922.8	835	573
1413	1271	1328	1173	1364	1322	1325	1349	1112	1234	1195	1485	1328.7	1111	1172
2040	1863	2554	1500	2089	1936	2019	2289	1701	1902	1929	2544	2196.8	2128	1852
2711	2429	2612	2430	2663	2257	2333	2339	2213	2169	2016	3910	2325.7	2517	1934

UB3LYP/6-31G(d)					UB3LYP/aug-cc pVDZ					UB3LYP/aug-cc-pVQZ			
2	1	Neutral	-1	-2 ^a	2	1	Neutral	-1	-2 ^a	2	1	Neutral	-1
175	170	170	186	37	171	168	170	204	65	174	172	173	204
264	356.1	454	270	72	234	350	453	215	86	249	368	467	216
335	416.3	464	457	128	310	407	462	533	130	335	427	477	540
413	432.2	523	577	326	402	427	515	575	361	416	443	540	586
574	627.3	662	704	650	580	636	667	608	645	581	642	678	605
789	834.9	922	807	652	789	835	922	815	658	789	836	919	794
1304	1291.1	1352	1090	1241	1285	1275	1337	1143	1222	1298	1286	1348	1147
1922	2023.1	2306	1680	1960	1905	2006	2284	1727	1948	1894	2006	2290	1732
2247	2293.3	2351	2215	2115	2232	2282	2331	2197	2108	2235	2287	2336	2201

^a For the dissociated system.

Table 9

Statistics of regressed equations for the observed vs. calculated IR frequencies for neutral cyanogens azide molecule

	UB3LYP/6-31G(d)	UHF/6-311G(d, p)	ROB3LYP/6-311+(d)	UMP2/6-31+G(d)
A	0.9411848	0.8620429	0.9488208	0.9620698
B	26.57587	19.48462	21.67725	33.19427
R ²	0.9991747	0.9965041	0.9990267	0.9978702
r _{YX}	0.9995872	0.9982505	0.9995132	0.9989346
F	8474.909	1995.362	7185.144	3279.704

Y = AX + B, where Y and X are observed and calculated IR frequencies in cm⁻¹, respectively.

knowledge. Since (to the best of our knowledge), no experimental data are available for the charged forms of cyanogen azide in the literature; we could not compare the calculated IR data with any experimental one.

4. Conclusion

In the present study, a highly explosive material, cyanogen azide and its monovalent and divalent ions have been investigated quantum chemically. The presently performed *ab initio* and DFT type calculations indicate that cyanogen azide and its monovalent cation, monovalent anion and divalent cation forms are stable in the isolated state. Although certain bonds undergo bond elongation or bond contraction parallel to the charge development in those systems, no bond cleavage happens. However, one should keep in mind that only the ions which are not in the bulk of the material are considered (single molecule or ion). In the case of the divalent anion form, bond cleavage takes place at N1–N2 bond. This decomposition pattern has some resemblance to the thermal decomposition of cyanogen azide molecule in solution which is a suitable precursor for the free nitrene, NCN. To the best of our knowledge, no report on the vibrational analysis on charged species of cyanogen azide exists in the literature. Thus, the present study sheds some valuable light on to this highly sensitive (sensitive to thermal, electrical and mechanical shocks) explosive and its univalent and divalent ions, by exploring their structural, energetic, electrostatic and vibrational properties.

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