An ab initio study on ethylenedinitramine and its monovalent ions

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Abstract

An explosive material, ethylenedinitramine (EDNA), its mono and di *aci* forms, as well as its monovalent cation and anion forms have been considered for 6-31G (UHF) type ab initio quantum chemical treatment in order to investigate the stability of EDNA in the neutral form and when charges develop on it exposed to electrical fields during the storage, handling or explosion process. The calculations indicate stable species. The *aci* forms are less stable than EDNA itself and the anion form is more stable than the neutral and cation forms. Although, the charge development is accompanied by some elongation or contraction of bonds and deviation of bond angles also as compared to the neutral state, no bond rapture occurs.
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1. Introduction

EDNA (ethylendinitramine, 1,4-dinitro-1,4-diazabutane) is a nitramine type highly important explosive [1–3]. Nitramines have long been used for technological as well as military purposes [1–5]. In practice, usually new energetic materials are designed by modifying known substances by addition and/or modification of explosophoric group(s) in the molecule(s). However, the research on the subject also accumulates in the direction of synthesis of brand new explosives as well as the development of theoretical methods. These help chemists to develop systematic and scientific approach, thus formulations of appropriate futuristic molecules having ameliorated properties for the desire. These properties might be good thermal stability, impact and friction sensitivity and enhanced explosive performance. The major aim of these methods, apart from being developed as predictive tool in general, is to provide some insight to understanding the molecules which are responsible for higher performance and which are not. Hence, the quantum chemical approaches at various level of sophistication might be helpful to visualize

certain aspects of explosion process. For example, electrostatic charges developed during the handling and processing of bulk powder such as explosive, propellant and pyrotechnic powders can be sufficient to cause ignition under certain conditions [6–8]. The propagation of detonation waves could be controlled by means of external magnetic and electrical fields [9]. The influence of these fields on the explosive material might cause polarization or ionization, which may be involved by some means of explosion mechanism. Some explosives, like RDX and TNT, because of their ring shaped geometries are comparatively rigid molecules. While nitrate esters and nitramines are not constrained in such a fashion and are "floppier". These molecules have more conformational states and might be expected that this would leave the nitrate esters and nitramines more susceptible to fragmentation in external fields [10]. Being a nitramine, the explosion process of EDNA could be triggered by charge development arising from exposure to external fields, static charging by friction or pressure.

Recently, nitramines have been considered for investigation of various properties of them. Especially, the stability and decomposition mechanisms have been the subject of some theoretical treatment [11–15]. Note that storage and handling stability of explosives are as important as their

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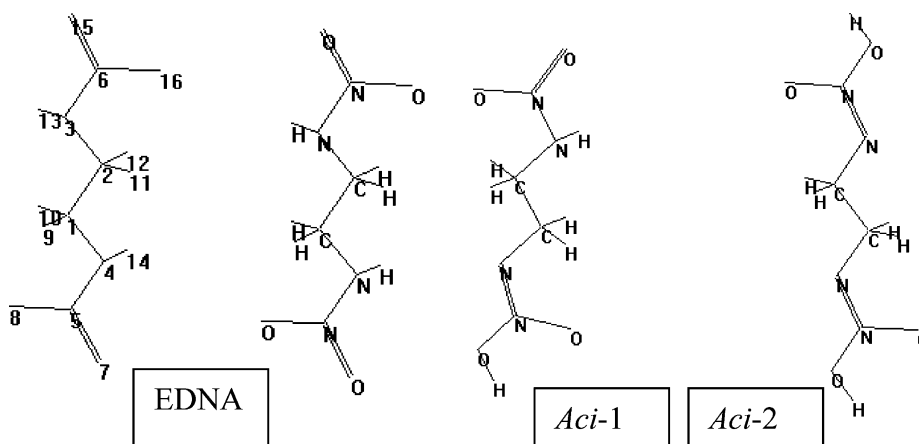*E-mail address:* lturker@metu.edu.tr.

Fig. 1. The chemical structures of EDNA and its *aci* forms.

blasting performances. One of the factors to be considered along this line is whether the development of static charges on the explosive material generates certain hot points. In the present study, to shed some light on the stability of an important nitramine, EDNA, to electrical charging and to investigate whether the charged forms play a role in the explosion process, the neutral as well as its monovalent ions have been subjected to quantum chemical analysis.

2. Method

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM+ method followed by semiempirical PM3 self-consistent fields molecular orbital (SCF MO) method [16,17] at the unrestricted Hartree-Fock (UHF) level [18] (by the application of the steepest-descent method followed by conjugate gradient methods, Fletcher-Reeves and Polak-Ribiere, consecutively; convergence limit of 4.18×10^{-4} kJ/mol and RMS gradient of $4.18 10^7$ kJ/m mol) and then by, ab initio treatment at the level of 6-31G [18,19] (UHF type, convergence limit 10^{-5} kcal/mol and RMS gradient of 10^{-3} kcal/A mol) by using Polak-Ribiere technique. The Raffenetti integral format (cut-off 1×10^{-10} Hartree) was used for two-electron integral control. For the molecular orbital initial guess, the core-Hamiltonian option [19,20] was applied with involvement of six d-orbitals. The geometry optimized structures were subjected to vibrational analysis (UHF, 6-31G) for the judgment of their stabilities. Furthermore, all the bond lengths were thoroughly searched. All these computations were performed by using the Hyperchem (release 5.1) package program.

3. Results and discussion

EDNA (Haleit) forms orthorhombic white crystals. EDNA is a nitramine type organic explosive and it was found that polynitro aliphatics containing at least one N–NO₂

(nitramine) linkage are more sensitive than nitroaliphatic explosives containing C–NO₂ linkage [5].

Krygowsky et al. have claimed that, in the crystalline state pyridylnitramines exist in the nitrimino forms [21,22] whereas a detailed ab initio study of N-(2-pyridyl)-nitramine, contrary to the structural data, favors the nitramino form [21,22]. Keeping these literature data in mind, presently, various forms of EDNA have been screened for their relative stabilities. In the case of EDNA, 1,3-proton tautomerism involving the shift of hydrogen from amino nitrogen to oxygen site (by analogy called mono and di *aci* forms) may be possible. Because of that the calculations extended to these forms. The chemical structures of EDNA and its tautomeric *aci* forms are shown in Fig. 1. Whereas, Table 1 shows some of the calculated energies of EDNA and its tautomeric *aci* forms. The geometry optimized structures of the *aci* forms are shown in Fig. 2. The data in Table 1 reveal that EDNA in its nitramine form is far more stable than its *aci* forms.

The stability order is EDNA > *Aci*-1 > *Aci*-2. Since the nitrimine forms are attainable via *aci* forms and they are less stable than EDNA, the nitrimine forms are not considered. Hence, in the present study, EDNA in nitramine form has been adopted to investigate the effect of charge development on the stability and some quantum chemical properties of it.

The geometry optimized structures based on 6-31G (UHF) type ab initio calculations (see Fig. 3) have C₂, C₁ and C₁ type molecular point groups for the neutral, cation and anion forms, respectively. Table 2 shows the calculated bond

Table 1
Some calculated energies for EDNA and its *aci* forms

Energy	EDNA	*Aci*-1	*Aci*-2
Total	−1564429	−1564407	−1564364
Electronic kinetic	1565811	1565773	1565664
EK, ee, and eN	−3029517	−2992808	−3008516
Nuclear repulsion	1465088	1428401	1444152
Viral	1.9991	1.9992	1.9991
Total (MP2)	−1567518	−1567382	−1567231

Energies in kJ/mol.
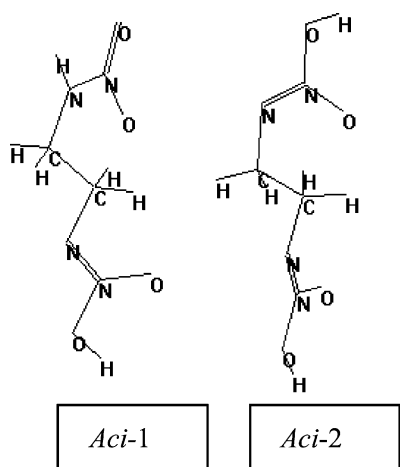
Fig. 2. The geometry optimized structures of the *aci* forms considered.

Table 2
Some calculated bond lengths (10^{-10} m) of the EDNA species considered

Bond	Neutral	Cation	Anion
C(1)—C(2)	1.532	1.540	1.533
C(1)—N(4)	1.456	1.497	1.453
C(1)—H(9)	1.079	1.077	1.083
C(1)—H(10)	1.080	1.078	1.091
C(2)—N(3)	1.456	1.442	1.450
C(2)—H(11)	1.079	1.082	1.076
C(2)—H(12)	1.080	1.080	1.078
N(3)—N(6)	1.330	1.385	1.303
N(3)—H(13)	0.993	0.995	1.013
N(4)—N(5)	1.330	1.296	1.420
N(4)—H(14)	0.993	1.006	0.997
N(5)—O(7)	1.233	1.314	1.343
N(5)—O(8)	1.231	1.305	1.302
N(6)—O(15)	1.231	1.242	1.250
N(6)—O(16)	1.233	1.247	1.242

lengths for the species considered. The calculated bond angles of EDNA species presently considered are shown in Table 3.

As seen in Table 3, as the charge develops certain bonds are elongated or contracted as compared to the neutral state. The cation formation causes elongation of mainly N(5)—O(8), N(5)—O(7), N(3)—N(6) bonds and contraction of N(4)—N(5) bond. Whereas, the anion formation goes parallel with the elongation of mainly N(5)—O(8), N(5)—O(7), N(4)—N(5) bonds and the contraction of N(3)—N(6) bond. The calculations within the limitations of the method employed have revealed that in spite of the elongation of certain bonds while charge develops no bond cleavage happens. The kind of atoms and structure of EDNA compensate an electron loss or gain to prevent bond rupture. Note that certain explosives are sensitive to electrical polarization or charge development [8,12]. In nitramine type explosives the initial decomposition step was claimed to be the scission of the N–N bond [23–25]. Thermodynamic studies show this is the weakest bond in the
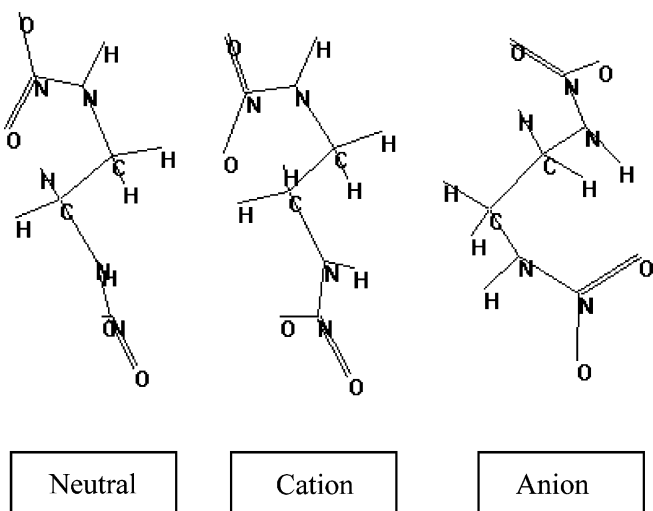
molecule [26]. According to the present calculations, in the cation formation N(3)–N(6) bond elongates while N(4)–N(5) bond contracts. Imamura et al. [25] showed by molecular dynamic studies that in certain nitramine type explosives, an intramolecular vibrational energy transfer occurs from one of the N–NO₂ moiety into the other N–NO₂ moieties or other parts of the molecule. However, the present study indicates much longer elongation in the N–O bonds of the NO₂ group which is flanked by the contracted N–N bond (N(4)–N(5)). The elongation of N–O bonds of the other NO₂ group which is linked to the elongated N–N bond (N(3)–N(6)) are not appreciable. These results indicate that the cation, is mainly in between mesomeric structures C_1 and C_2 in Scheme 1. Thus, a certain double bond character is to be associated with the

Table 3
Some calculated bond angles (degrees) of the EDNA species considered

Bond	Neutral	Cation	Anion
C(2)—C(1)—N(4)	111.902	111.514	111.623
C(2)—C(1)—H(9)	110.283	110.733	109.575
C(2)—C(1)—H(10)	109.890	111.360	107.695
N(4)—C(1)—H(9)	110.079	107.823	106.741
N(4)—C(1)—H(10)	105.772	105.407	113.065
H(9)—C(1)—H(10)	108.778	109.816	108.057
C(1)—C(2)—N(3)	111.906	108.022	112.044
C(1)—C(2)—H(11)	110.281	110.773	109.582
C(1)—C(2)—H(12)	109.892	110.598	110.593
N(3)—C(2)—H(11)	110.082	111.406	104.665
N(3)—C(2)-H(12)	105.772	107.479	109.988
H(11)—C(2)—H(12)	108.774	108.522	109.802
C(2)—N(3)—N(6)	122.208	117.485	122.584
C(2)—N(3)—H(13)	123.857	121.325	114.135
N(6)—N(3)—H(13)	113.083	111.958	118.414
C(1)—N(4)—N(5)	122.210	123.409	115.704
C(1)—N(4)—H(14)	123.857	122.294	115.002
N(5)—N(4)—H(14)	113.083	114.282	106.964
N(4)—N(5)—O(7)	116.872	120.176	114.413
N(4)—N(5)—O(8)	117.921	121.832	113.516
O(7)—N(5)—O(8)	125.202	117.992	123.943
N(3)—N(6)—O(15)	117.923	117.218	119.064
N(3)—N(6)—O(16)	116.870	117.594	118.162
O(15)—N(6)—O(16)	125.202	125.133	122.745

Fig. 3. The geometry optimized structures of EDNA and its monovalent ions.
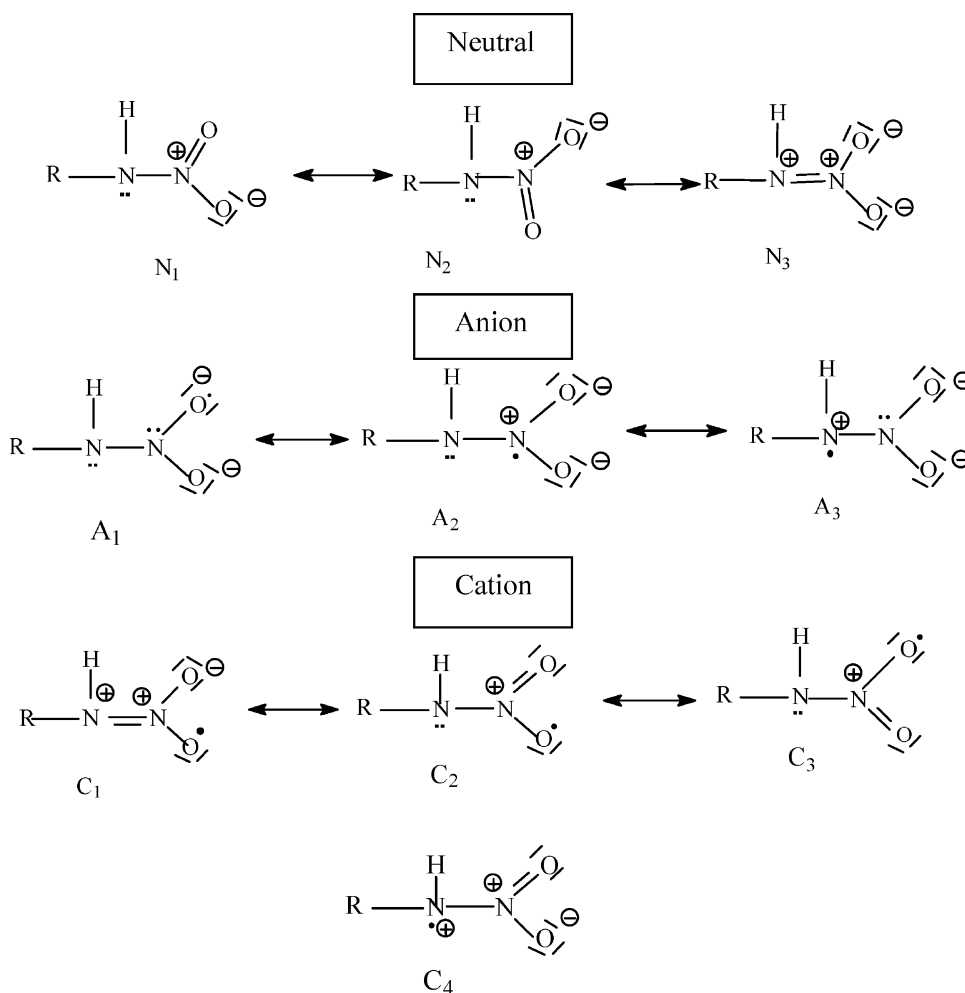
Scheme 1.

nitramine bond. As a result of this the adjacent N–O bonds elongate gaining more single bond character. However, predominant contribution of C_1 structure to the valance-bond hybrid makes the cation to be less stable than the neutral form (see Table 4).

In the case of the anion, all the N–O bonds are elongated as compared to the neutral state beside highly elongated N(4)–N(5) bond. The N–O bonds linked to N(5) are more elongated than the other N–O bonds. Since, all the bonds linked to N(5) are longer as compared to the neutral state, probably the anion is mainly described by the mesomeric structure in which none of the nitrogens carries a positive

charge. Then, lone-pair, lone-pair repulsions elongate the N(4)–N(5) bond whereas, the N–O bonds get longer due to the repulsions between the nitrogen lone-pair and the anionic charge (see structure A_1 in Scheme 1). Note that in the scheme structure C_4 arises when the cation formation occurs on the amino nitrogen, whereas structures C_1–C_3 arise if the nitro-oxygen atom loses an electron. In the scheme R stands for the rest of EDNA molecule. Table 4 shows some calculated energies of EDNA and its univalent ions. As seen in the table, all the species are stable. The 6-31G (UHF) type calculations at the MP2 level give the MP2 correlation energy for the neutral, cation and anion forms of EDNA as −3089.82, −2713.25 and −3008.64 kJ/mol, respectively. The table also includes the total energies having these MP2 correlation energies. With or without MP2 correlation energy, the stability order is anion > neutral > cation. Note that in each case the viral (−V/T) is very close to 2.

The valance-bond formalism may give some clue why the anion form is more stable than the neutral and cation forms. As seen in Scheme 1, no like charges appear on the adjacent atoms in any of the canonical structures in the case of anion form (thus anionic charge stabilized by many

Table 4
Some calculated energies of EDNA and its univalent ions

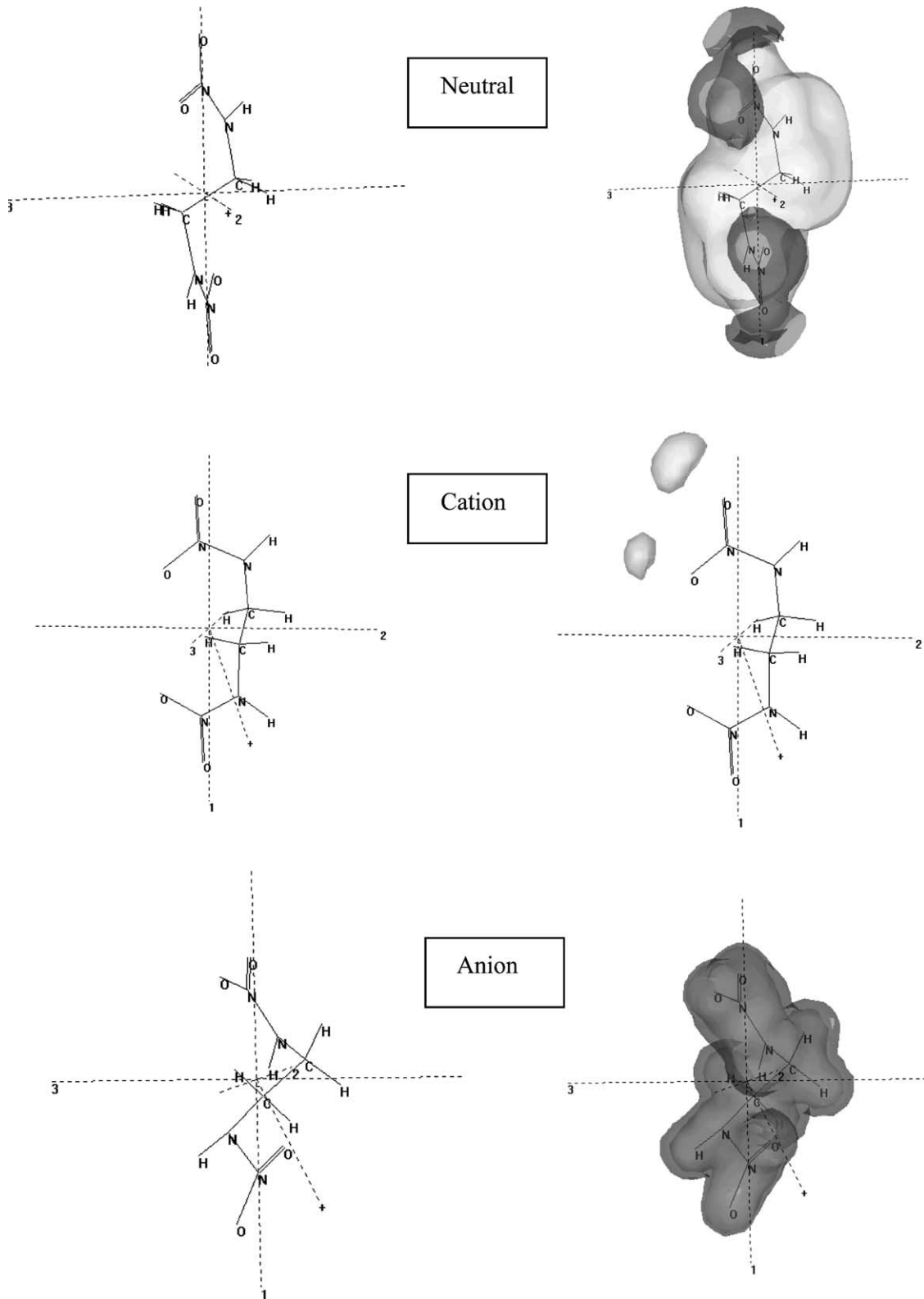| Energy	Neutral	Cation	Anion
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Total (MP2)	−1567518	−1566341	−1567539

Energies in kJ/mol.

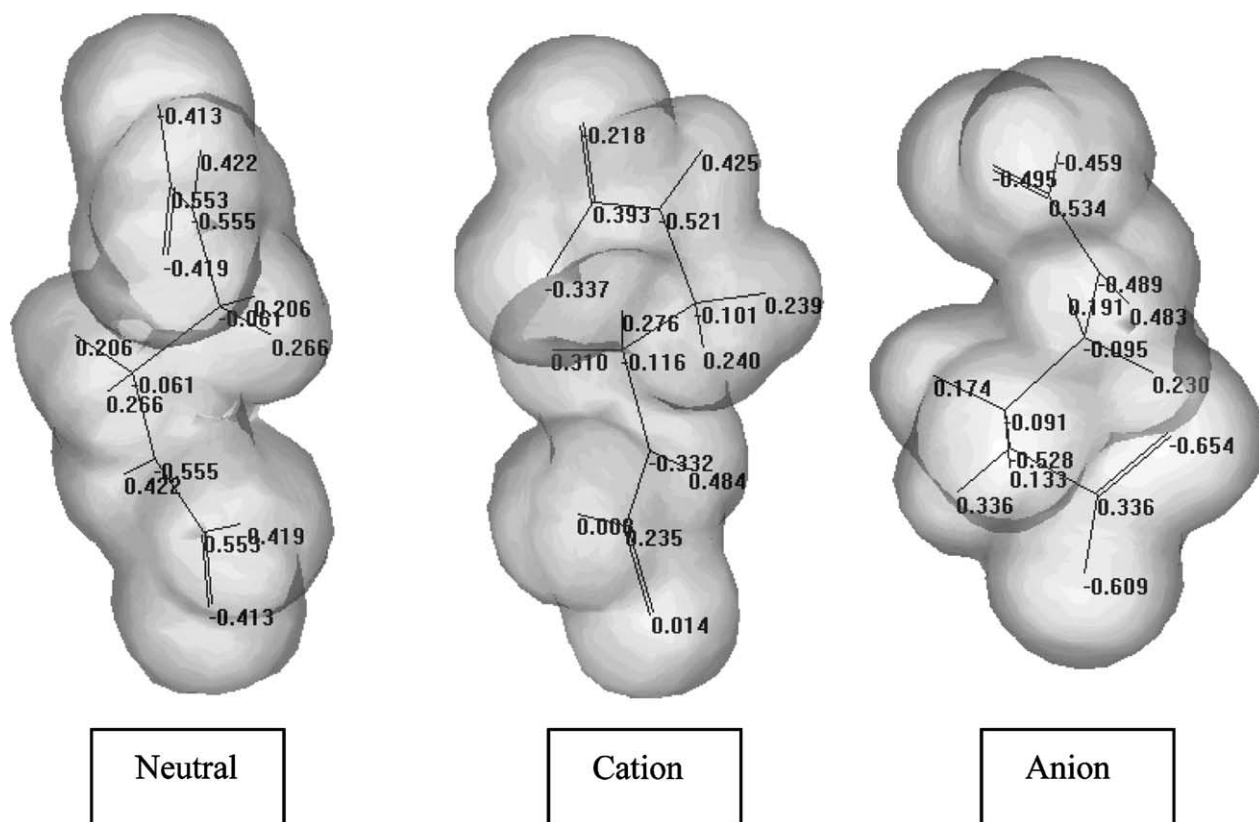Fig. 4. 3D-potential field maps of EDNA and its monovalent ions.

Fig. 5. 3D-charge density maps and charges of atoms of EDNA and its monovalent ions.

canonical structures), whereas the neutral and cation forms might have one which causes less stabilization for them.

Figs. 4 and 5 show the 3D-electrostatic potential field and charge density maps (as well as the atomic charges) for the species, respectively. As seen in Fig. 4, the dipole moment vector in the neutral form is along one of the axes of moment of inertia (shown as dashed lines). The tail and head of the dipole moments in the figure are shown by + and − signs, respectively. In the other, forms, the dipole moment vector originates somewhere in one of the octants of space and points to the origin of the axes of inertia.

The root mean square overlay error values of the univalent ions of EDNA compared to the neutral form are $0.8530723 \times 10^{-10}$ m and 1.684394×10^{-10} m for the cation and anion, respectively. The values indicate that as the charge develops to yield the anion, the structure of EDNA has been modified more as compared to the cation formation.

Table 5 contains the α- and β-type HOMO and LUMO energies obtained by means of the 6-31G (UHF) calculations. Note that the HOMO of the neutral molecule is a α-type orbital, however at the MP2 level of calculations the α- and

Table 5
The HOMO and LUMO energies of EDNA and its univalent ions

Neutral		Cation		Anion	
α-type	β-type	α-type	β-type	α-type	β-type
LUMO					
3.5009	3.5011	−7.1273	−8.0143	9.9920	9.9893
B	B	A	A	A	A
(3.5009)	(3.5009)	(−7.1274)	(−8.0150)	(9.9919)	(9.9921)
B	B	A	A	A	A
HOMO					
−19.3913	−19.3975	−23.9481	−23.7121	−6.7630	−7.7369
A	A	A	A	A	A
(−19.3449)	(−19.3949)	(−23.9509)	(−23.7138)	(−6.7625)	(−7.7361)
A	A	A	A	A	A

Energies in 10^{-19} J. Symmetries below the numerical data. Energies at the MP2 level are in parenthesis.
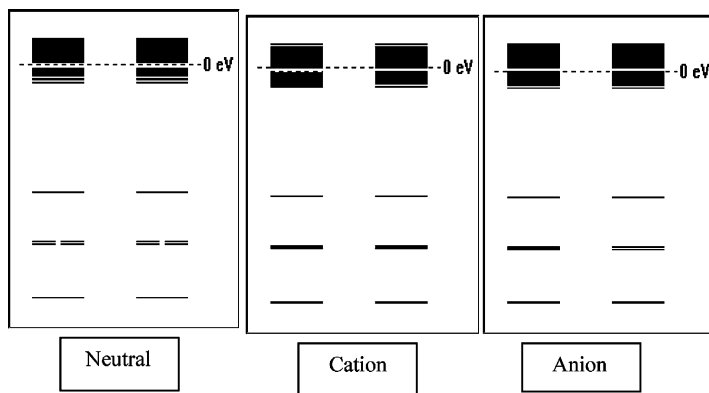
Fig. 6. The molecular orbital energy spectra of EDNA and its monovalent ions.

Table 6
The lowest and highest molecular orbital energy values and the range of α- and β-type orbital energies for the species considered

	Neutral	Cation	Anion
α-type	−899.07, 97.24	−913.83, 86.10	−891.54, 101.74
Range	996.31	999.93	993.28
β-type	−899.06, 97.25	−912.04, 86.12	−892.18, 101.95
Range	996.31	998.16	994.13

Energies in 10^{-19} J.

β-type HOMOs are degenerate. In a similar behavior the LUMO is of α-type but at the MP2 level of calculations the α- and β-type LUMOs are degenerate. In the case of cation, the HOMO (or the LUMO) is of β-type, irrespective of MP2 correlation is considered or not. As for the anion the HOMO of the species is an α-type orbital (irrespective of the MP2 correlation) whereas the LUMO is of β-type at the level of MP2 calculations.

Fig. 6 shows the molecular orbital energy spectra of the species presently considered. In all the cases, although low-lying molecular orbital energy levels are quite distinct, the others, irrespective of the occupied or unoccupied are very close to each other, resulting in a band like appearance. As seen in Tables 5 and 6, the cation formation generally lowers all the molecular orbital energies of EDNA whereas the anion formation raises them up. 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.

4. Conclusion

The presently performed ab initio type quantum chemical calculations indicate that EDNA and its monovalent cation and anion forms are stable in the isolated state. Although, certain bonds undergo bond-elongation (or bond contraction) parallel to the charge development no bond cleavage happens. However, one should keep in mind that only monovalent ions not in the bulk of the material are considered.

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