

Density functional theory calculations for [C₂H₄N₂O₆]⁽ⁿ⁾ (n = 0, +1, –1)

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Abstract

The structural and electronic properties of neutral and mono ionic structures of isolated ethylene glycol dinitrate (EGDN) [C₂H₄N₂O₆]⁽ⁿ⁾ (n = 0, +1, –1) have been investigated by performing density functional theory calculations at B3LYP level. The optimum geometry, vibrational frequencies, electronic structure and some thermo dynamical values of the structures considered have been obtained in their ground states. The calculations reveal that as the charge develops the bond lengths and angles change. In the anionic case charge accumulation causes NO₂ elimination as a result of esteric O–N bond cleavage.

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1. Introduction

Explosives differ widely in their power and sensitivity and only those of a comparatively safe nature can find practical applicability. However, high energy content is a desirable property of explosives although, usually higher the energy content less stable the molecule is. An explosive reaction differs from the others only by the large free energy of the molecule, the rapidity of its release and the accelerating effect of the decomposition products, which produce an explosion reaction [1].

It has been reported long time ago that free electrons exist in combustion flames and detonations [2]. Detonations are capable of generating large electromotive forces in external systems [2]. Also, it has been reported that electromagnetic radiation having “video” frequencies to “centimeter waves” accompany detonations [2,3]. All these observations, combined with the rule of classical electromagnetic theory stating that necessarily an electromagnetic wave accompanies to moving charges [4] reveal that abundance of free electrons and positive charges should be generated while a detonation happens.

Although, in most of the cases the detonation mechanism is not evident, whether first the ions form to generate “hot points” or ions form after detonation, it is a well known fact that when some explosives are exposed to some electrical fields they get polarized or ionized which may lead to explosion. For example, lead styphnate is a primary explosive and extremely sensitive to the discharge of static electricity [5–8]. Hence, it would be interesting to study the influence of ionization at the molecular level by means of quantum chemical methods.

Ethylene glycol dinitrate (EGDN) (C₂H₄N₂O₆) is the inorganic ester of ethylene glycol with nitric acid. It is one of the explosives having quite high power index (182, picric acid as the standard). Its explosion reaction is



As seen in the reaction, no oxygen is consumed or produced, thus EGDN is one of the explosives of oxygen sufficient type [1,5]. Recently, EGDN have accumulated considerable attention of researches also because of its additional non-explosive applications or properties [9–12]. Like pentaerythriol tetranitrate (PETN), EGDN has wide application in ammunition industry because it can participate in composition of certain explosive mixtures (like Semtex [13]). Some quantum chemical calculations at the level of AM1 method was performed by Crellin et

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al., on the compounds involved in the reaction of EGDN with $\text{Si}(\text{CH}_3)_3^+$ [10].

In the present study, EGDN and its univalent anion and cation forms have been subjected to quantum chemical analysis (DFT/B3LYP).

2. Method of calculation

In the present work, the ground state structural and electronic properties of the isolated neutral and mono ionic structures of EGDN $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ ($n=0, +1, -1$) have been investigated. The density functional theory (DFT) calculations have been performed at B3LYP level within the unrestricted formulation (open-shell system). All the calculations have been carried out by using the Gaussian-98 package program [14]. In the present calculations the density functional theory [15] with B3LYP exchange-correlation potential [16] and core effective potential basis (CEP-121G) [17,18] have been used. The exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [19]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [20] and Lee, Yang, Parr (LYP) correlation correction functional [21]. The BLYP method gives a better improvement over the SCF-HF results. Its predictions are in qualitative agreement with experiment. CEP-121G basis functions are becoming widely used in quantum chemistry, particularly in the study of compounds containing heavy elements [17,18].

The CEP basis sets have been used to calculate the equilibrium structures and spectroscopic properties of several small molecules [17,22–26]. The standard basis set of CEP theory, CEP-121G, was consistent for the entire series, consistent not only within the lanthanide series but also with the second and third row metals. The quantity of the CEP-121G basis set does not degrade when going from the second to third row of the periodic table. In the present calculations CEP-121G basis set which consists of 132 symmetry-adapted basis functions (including 6d, 10f orbitals) of asymmetry for the neutral molecule and for its ions has been considered. Totally, 180 primitive Gaussians have been used for all the molecules studied. The numbers of α - and β -electrons depend on the system. Table 1 contains the information for the basis set used. For all the species considered vibrational and structural analyses were done.

Table 1

Basis set, CEP-121G (6d, 10f), used in the calculations of $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ ($n=0, +1, -1$)

Quantity	$n=0$	$n=+1$	$n=-1$
No. of basis functions	132	132	132
No. of primitive gaussians	180	180	180
No. of α -electrons	29	29	30
No. of β -electrons	29	28	29

3. Results and discussion

Initiation of detonations mainly occurs by means of (i) initiation because of heat addition (possible only in primary explosives); (ii) initiation through shock waves (possible for all explosives). Other mechanisms like radiation or chemical effects are less important [27]. However, the external magnetic and electrical fields are capable of controlling the propagation of detonation waves [6]. The influence of these effects on the explosive molecules may cause polarization or ionization, which may trigger some explosion mechanisms. Some explosive molecules (like TNT and RDX) are comparatively rigid systems because of their ring shaped geometries, while nitrate esters or nitramines (e.g. NG, EGDN, PETN, etc.) are “floppier” thus possess more conformational states and might be expected that this would leave these molecules more susceptible to fragmentation. EGDN is a secondary type explosive which is qualitatively different from the primary explosives with respect to their chemical structures as well as to their detonative features.

In the present study, EGDN molecule and its mono ionic forms (\pm) have been subjected to DFT/B3LYP type quantum chemical analysis. Table 1 tabulates some data of the calculations. Figs. 1–3 show the geometry-optimized structures of these systems.

In Tables 2–4, one can find some bond lengths, bond angles and dihedral angles for these neutral and charged systems, respectively. Inspection of the bond length data (Table 2) indicates that certain bonds in the charged systems undergo contraction and elongation as compared to the respective bonds in the neutral form. For example, although 1,5 bond (O–NO₂) length is 1.47×10^{-10} m in the neutral form it elongates to 2.108×10^{-10} m (bond rupture) in the anionic case. On the other hand, the other O–NO₂ bond contracts. Also 1,4 bond (O–C) length decreases from 1.49×10^{-10} m (the neutral form)

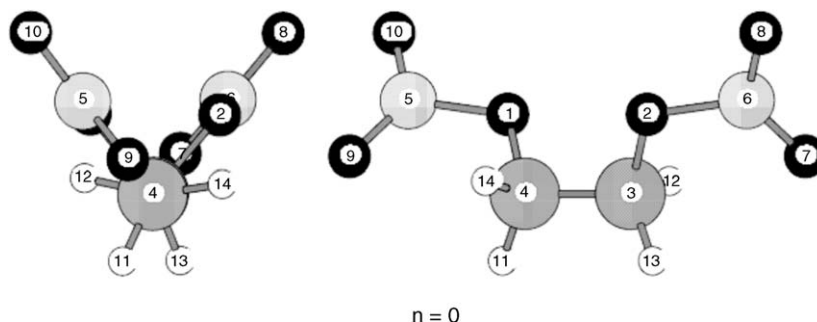


Fig. 1. Two different views of the optimized geometry of the structure, $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ ($n=0$), in its ground state. Dark gray colored big circles stand for carbon, light gray colored circles are for nitrogen, whereas black colored and white colored circles stand for oxygen and hydrogen atoms, respectively.

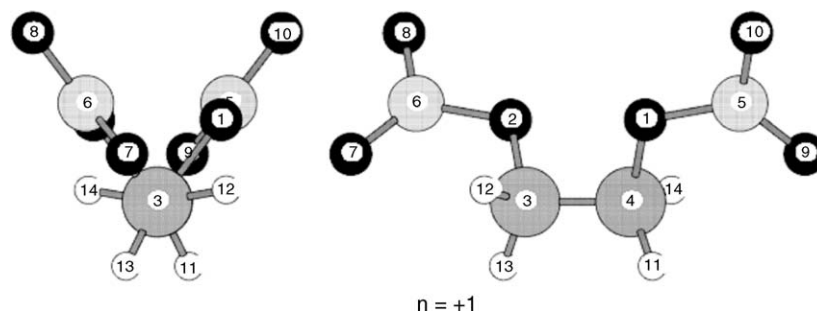


Fig. 2. The optimized geometry of the structure, $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ ($n=+1$), in its ground state. Colored representation of atoms is the same as Fig. 1.

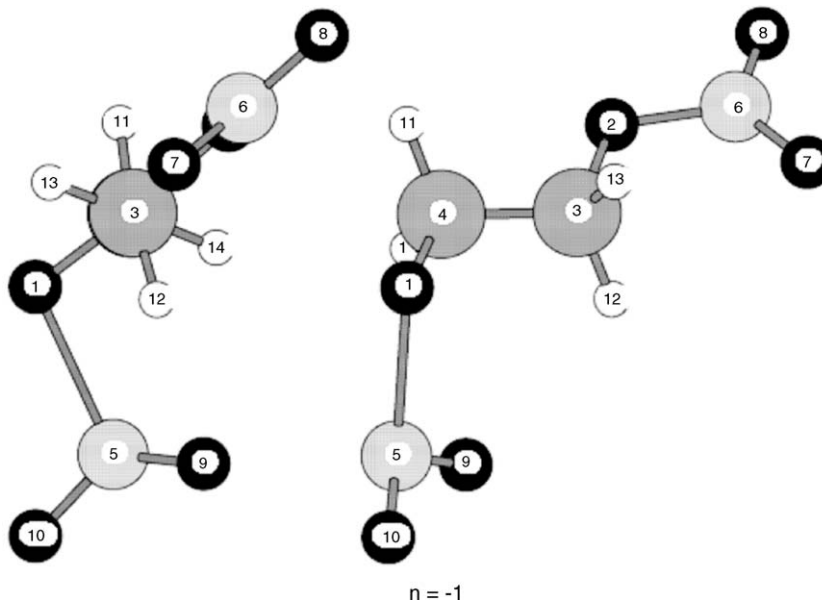


Fig. 3. The optimized geometry of the structure, $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ ($n=-1$), in its ground state. Colored representation of atoms is the same as Fig. 1.

to 1.434×10^{-10} m. Whereas, the other O–C bond (2,3) elongates. The C–C bond length also increases somewhat (Table 2) as compared to the neutral structure. The N–O bonds in the NO_2 moieties get longer as the anion forms. Also 2,3(C–O), 5,9(N–O) and 5,10(N–O) bonds exhibit some bond elongation. Since

Table 2
Optimized bond lengths (R , in 10^{-10} m) of the structures, $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ in their ground states

Quantity	Bond type	$n=0$	$n=+1$	$n=-1$
$R(1,4)$	O–C	1.494	1.523	1.434
$R(1,5)$	O–N	1.470	1.413	2.108
$R(2,3)$	O–C	1.494	1.523	1.533
$R(2,6)$	O–N	1.470	1.413	1.434
$R(3,4)$	C–C	1.528	1.526	1.548
$R(3,12)$	C–H	1.093	1.093	1.092
$R(3,13)$	C–H	1.095	1.095	1.094
$R(4,11)$	C–H	1.095	1.095	1.107
$R(4,14)$	C–H	1.093	1.093	1.101
$R(5,9)$	N–O	1.275	1.263	1.308
$R(5,10)$	N–O	1.259	1.298	1.287
$R(6,7)$	N–O	1.275	1.262	1.281
$R(6,8)$	N–O	1.259	1.298	1.276

See Figs. 1–3 for labels.

Table 3
Optimized bond angles (A , in degree) of the structures, $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ in their ground states

Quantity	$n=0$	$n=+1$	$n=-1$
$A(4,1,5)$	113	114	103
$A(3,2,6)$	113	114	116
$A(2,3,4)$	105	104	106
$A(2,3,12)$	110	109	108
$A(2,3,13)$	109	109	108
$A(4,3,12)$	112	113	111
$A(4,3,13)$	111	111	112
$A(12,3,13)$	110	111	112
$A(1,4,3)$	105	104	107
$A(1,4,11)$	109	109	111
$A(1,4,14)$	110	109	112
$A(3,4,11)$	111	111	110
$A(3,4,14)$	112	113	109
$A(11,4,14)$	110	111	109
$A(1,5,9)$	117	122	112
$A(1,5,10)$	113	114	112
$A(9,5,10)$	129	125	122
$A(2,6,7)$	117	122	119
$A(2,6,8)$	113	114	114
$A(7,6,8)$	129	125	127

See Figs. 1–3 for labels.

Table 4
Optimized dihedral angles (D , in degree) of the structures, $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ in their ground states

Quantity	$n=0$	$n=+1$	$n=-1$
$D(5,1,4,3)$	-178	-177	-89
$D(5,1,4,11)$	64	65	151
$D(5,1,4,14)$	-57	-56	30
$D(4,1,5,9)$	-1	-1	27
$D(4,1,5,10)$	179	179	168
$D(6,2,3,4)$	-178	-177	178
$D(6,2,3,12)$	-57	-56	-63
$D(6,2,3,13)$	64	65	58
$D(3,2,6,7)$	-1	-1	-1
$D(3,2,6,8)$	179	179	180
$D(2,3,4,1)$	79	76	-175
$D(2,3,4,11)$	-164	-168	-54
$D(2,3,4,14)$	-40	-42	65
$D(12,3,4,1)$	-40	-42	68
$D(12,3,4,11)$	77	74	-172
$D(12,3,4,14)$	-160	-160	-53
$D(13,3,4,1)$	-164	-168	-57
$D(13,3,4,11)$	-46	-52	63
$D(13,3,4,14)$	77	74	-178

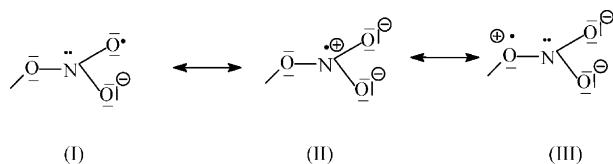
See Figs. 1–3 for labels.

Table 5
Calculated excess charge (in units of electron charge) on the atoms of the structures, $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ in their ground states

Atom label	Atom	$n=0$	$n=+1$	$n=-1$
1	O	-0.1415	-0.0756	-0.3545
2	O	-0.1415	-0.0755	-0.1455
3	C	-0.1606	-0.1810	-0.1789
4	C	-0.1606	-0.1810	-0.1026
5	N	0.0501	0.0681	0.0780
6	N	0.0501	0.0678	0.0332
7	O	-0.0905	0.0615	-0.1296
8	O	-0.0576	0.1120	-0.1408
9	O	-0.0905	0.0614	-0.3256
10	O	-0.0576	0.1120	-0.2869
11	H	0.1922	0.2558	0.0868
12	H	0.2079	0.2594	0.1962
13	H	0.1922	0.2558	0.1448
14	H	0.2079	0.2594	0.1253

See Figs. 1–3 for the labels.

lone-pair-lone-pair repulsion is greater than lone-pair-electron repulsion, 1,5 and 5,9 distances in the anion are greater than 5,10 distance (see Table 2 and Fig. 3). The following canonical structures by certain electron transfers can be written for the anion such that structure (I) may explain the variation of bond lengths (within the VB formalism).



The data in Table 5 reveal that the excess charge of the anion is mainly partitioned to oxygen atoms around the nitrogen atom (they have comparatively more negative charge than the respective atoms in the neutral EGDN).

Table 6
Some of the calculated energy values of the structures, $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ in their ground states

Quantity	$n=0$	$n=+1$	$n=-1$
Total energy (hartree)	-128.896	-128.483	-128.978
KE (hartree)	98.027	97.242	98.087
PE=E-N (hartree)	-887.202	-876.873	-881.719
EE (hartree)	367.038	356.985	369.905
N-N (hartree)	293.240	294.162	284.749
HOMO- α (hartree)	-0.347	-0.557	-0.065
LUMO- α (hartree)	-0.128	-0.330	0.000
HOMO-LUMO gap- α (eV)	5.959	6.177	1.769
HOMO- β (hartree)	-0.347	-0.494	-0.076
LUMO- β (hartree)	-0.128	-0.475	0.000
HOMO-LUMO gap- β (eV)	5.959	0.517	2.068
Zero-point vibrational energy (kJ/mol)	226.438	216.877	213.869

As for the cation case, again some bond elongation and contraction occur compared to the neutral case although this time changes are not as drastic as the anionic case. In the case of cation, 1,4(O-C); 2,3(O-C); 5,10(N-O); 6,8(N-O) bonds elongate as compared to the neutral case, whereas, 1,5(O-N); 2,6(O-N) bonds contract.

The C-H bonds in the cation are equal to the respective ones in the neutral form but in the anion case 3,12 and 3,13 bonds are shorter whereas 4,11 and 4,14 bonds are longer. As for the bond angles, $A(4,1,5)$ is slightly larger in the cation but appreciably smaller in the anion case compared with the neutral form. Also, $A(3,4,14)$, $A(1,5,9)$, $A(9,5,10)$ and $A(7,6,8)$ are smaller but $A(2,6,7)$ is bigger. In the case of the cation, $A(9,5,10)$ contracts from 129° (the neutral form) to 125° .

The dihedral angles are generally comparable in the neutral and charged forms. However, in the anion $D(5,1,4,3)$ is especially smaller whereas $D(5,1,4,11)$, $D(12,3,4,11)$ and $D(13,3,4,14)$ are appreciably greater as compared to the neutral form.

Table 6 outlines some of the calculated energies of the systems presently considered. The total energy values are negative irrespective of the charge, being the anionic case more stable

Table 7
Some of the calculated multipole elements of the structures, $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ in their ground states

Quantity	$n=0$	$n=+1$	$n=-1$
Dipole moment (Debye)			
X	0.000	0.000	6.154
Y	-4.004	-3.737	1.219
Z	0.000	0.000	-0.248
Total	4.004	3.737	6.279
Quadrupole moment (Debye-angle)			
XX	-77.519	-37.089	-113.365
YY	-55.168	-46.510	-65.841
ZZ	-57.595	-52.273	-63.492
XY	0.000	0.009	0.137
XZ	0.548	0.894	5.754
YZ	0.000	-0.001	-0.717

Table 8
Calculated vibrational frequencies, w (cm^{-1}) and IR intensities, I_r (km/mol) of the structures $[\text{C}_2\text{H}_4\text{N}_2\text{O}_6]^{(n)}$ in their ground states

$n=0$		$n=+1$		$n=-1$		$n=0$		$n=+1$		$n=-1$	
w_i	I_r	w	I_r	w	I_r	w	I_r	w	I_r	w	I_r
33	1	27	2	32	1	891	39	869	68	854	12
36	2	30	2	37	1	1030	29	938	2179	1009	110
50	1	48	1	43	1	1041	61	995	29	1065	11
125	4	113	29	83	2	1112	1	1001	207	1102	10
153	2	153	3	106	2	1187	478	1084	7	1140	325
198	0	182	0	137	6	1199	11	1173	43	1188	39
218	1	185	150	154	2	1223	4	1206	3	1199	263
256	3	258	6	193	5	1266	1	1234	317	1283	13
436	1	401	832	245	1	1383	2	1245	3	1322	248
504	2	464	7	318	24	1409	3	1259	14	1334	198
521	3	469	165	367	4	1499	0	1385	0	1384	37
638	2	601	0	413	18	1501	34	1415	1	1482	55
665	14	611	1651	547	75	1534	225	1480	2	1486	196
667	7	639	1642	633	8	1536	314	1481	14	1497	24
675	3	653	57	669	7	3047	1	3054	1	2916	196
808	316	659	890	682	118	3058	15	3063	0	3001	22
816	16	793	129	796	1	3129	8	3145	0	3059	17
879	220	794	3	822	196	3136	10	3152	1	3157	13

than the others. Keeping the bond length data shown in Table 2 in mind, the total energy value of the anionic case which is the most negative of all (Table 6) species should stand for the total energy of the fragmented system rather than the intact molecule. Indeed, the energy calculations result in the least positive nuclear repulsion (N–N energy in Table 6) energy for the anionic system because the fragmentation reduces the nuclear repulsion energy.

As for the frontier molecular orbital (FMO) energies of the systems considered, the anionic case possesses the highest (the least negative) HOMO and LUMO (α - and β -types) energies. Note that the anionic system is not an intact molecule but it is fragmented. Both the α - and β -types of the HOMO and LUMO of the neutral system are degenerate (-0.347 and -0.128 Hartree, respectively). Whereas, the cationic case has the lowest (the most negative) HOMO and LUMO (α - and β -types) energies. Thus, the FMO energies of the neutral system lie in between the corresponding energies of the cationic and anionic systems. This is quite expected result because in general positive charge development depresses the molecular orbital energies and negative charge development on the contrary, raises up the molecular orbital energy levels.

Table 7 contains the dipole moments and quadruple moments and their components. As seen there, the cation has the lowest and the anion has the highest dipole moment. The highest value in the anionic case may be due to elongation of the bonds as well as the charge distribution.

The vibrational analysis data are shown in Table 8. The low intensity vibrations occurring in between 1200 and 800 cm^{-1} can be attributed to C–C stretchings. The vibrations between 2900 and 3160 cm^{-1} should be the symmetrical and asymmetrical C–H stretchings. The C–H bendings should be assigned to vibrations between 1300 and 1400 cm^{-1} . The strong vibrations in the region of 1000 – 1266 cm^{-1} should be C–O stretchings. On the other hand, the vibrations occurring in between 1400 and 1536 cm^{-1} can be various N–O stretchings of these species.

The NO_2 bands occur at lower wave numbers in the cation and the anion cases as compared to the neutral one. Note that comparatively the intensity of these vibrations are considerably low in the cationic form. Of course these theoretical vibrational assignments are qualitative and the accuracy is highly dependent on the calculation method employed. However, the data are invaluable for comparative purposes because experimentally it should be impossible or very hard to record the IR spectra of the charged forms of EGDN.

4. Conclusion

The presently performed DFT/B3LYP type calculations indicate that EGDN mono anion undergoes bond cleavage. The esteric O–N bond is the primary site of the bond rupture. Whereas, in the cationic form no drastic changes in the bonds are notified. The present study indicates the importance of negative charge development on EGDN. Note that it is an oxygen sufficient and a powerful explosive material possessing high hazardous risk. Hence, its storage and transport should be done properly being cautious that the static charge development may trigger the explosion process. However, one should keep in mind that an explosion is a dynamic process and static methods can describe only a part of it. Nevertheless, still the quantum chemical methods of present kind yield valuable information about explosive materials.

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