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Effect of Electric Field on ANTA

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Abstract

The present study considers an insensitive explosive, ANTA, (5(3)-amino-3(5)-nitro-1H-1,2,4-triazole) which is optimized within the restrictions of DFT (B3LYP/cc-PVTZ and B3LYP/6-311++G(d,p)). The optimized structure is subsequently subjected to single-point semi empirical MNDO and/or PM3 level of calculations to visualize the effect of electric field which has been set to magnitudes of 0.001 and 0.01 au. Perturbations on the energy and dipole moment are investigated. Also, the directional effect of the field along the axes of inertia of the molecule has been investigated. Generally, the effect of the field is more pronounced along the principle axis of ANTA.

1. Introduction

Among various molecular properties, molecular hyperpolarizabilities, namely β and γ have attracted special attention of scientists for couple of decades. When light is incident on a material, the optical electric field, E, results in a polarization P of the material. The polarization can be expressed as the sum of the linear polarization component, P_L and nonlinear polarization P_{NL} [1-5].

$$P = P_L + P_{NL} \tag{1}$$

$$P_L = \chi^{(1)}.E \tag{2}$$

$$P_{NL} = \chi^{(2)}.EE + \chi^{(3)}.EEE + ... \tag{3}$$

The susceptibility tensors $\chi^{(n)}$ give the correct relationship for the macroscopic material. For individual molecules, the polarizability α, hyperpolarizability β, and second

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hyperpolarizability γ are defined as certain tensor quantities. The susceptibility tensors are weight averages of the molecular values.

Energy of polarizable molecule in a field E is [3,4];

$$\varepsilon(E) = \varepsilon^{(0)} - \mu^{(0)}E - \alpha E^2/2! - \beta E^3/3! + ... \quad (4)$$

Whereas dipole moment in a field E is,

$$\mu = \mu^{(0)} + \alpha E + \beta E^2/2! + ... \quad (5)$$

The polarizabilities can be formulated as derivatives of the dipole moment with respect to incident electric field [1].

$$\alpha_{ij} = (\delta\mu_i/\delta E_j)_{E\text{-->}0} \quad (6)$$

$$\beta_{ijk} = (\ \delta^2\mu_i/\delta E_j\delta E_k)_{E\text{-->}0} \quad (7)$$

$$\gamma_{ijkl} = (\delta^3\mu_i/\delta E_j\delta E_k\delta E_l)_{E\text{-->}0} \quad (8)$$

Examining these definitions, one can get various conclusions that molecules with a center of inversion will have no hyperpolarizability ($\beta=0$) whereas molecules with a large dipole moment and a means for electron density shift will have large hyperpolarizability [1]. In the literature there are various articles and levels of theoretical and experimental research about the polarizabilities and nonlinear optical behavior of certain materials [2, 6-12].

5-Amino-3-nitro-1H-1,2,4-triazole (also named as 3-amino-5-nitro-1H-1,2,4-triazole) known as ANTA or ANT is a very insensitive explosive molecule [13]. Its synthesis were described decades ago [14-16]. In addition to its potential use as an insensitive high explosive, ANTA has been shown to be a useful intermediate for the preparation of other explosives. A computational study has been reported on ANTA [17].

In the present study, ANTA molecule has been subjected to electric field of different strengths and the resultant polarization effects have been investigated.

2. Method of Calculation

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [18, 19] at the restricted level [20]. Then, the structure optimizations have been achieved within the framework of Hartree-Fock (HF) and finally by using density functional theory (DFT) at the levels of B3LYP/CC-PVTZ and B3LYP/6-311++G(d,p) (restricted closed-shell) [21, 22]. Note that 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 [23]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [24] and Lee, Yang, Parr (LYP) correlation correction functional [25]. 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 SPARTAN 06 [26].

The calculations related to polarizability have been done by means of single point semi- empirical MNDO and PM3 type calculations based on the optimized structures obtained by density functional approach at the levels of B3LYP/cc-PVTZ and B3LYP/6-311++G(d,p). The directional effect of electric field along the axes of inertia of ANTA molecule have been searched by using Hyperchem 06 program [27].

3. Results and Discussion

Asymmetric substitution of a conjugated chain with a donor group on one end and an acceptor group on the other end provides the noncenterosymmetry required for a second-order nonlinearity [28-33]. Since, only the time averaged asymmetrically induced polarization leads to second order nonlinear optical (NLO) effects, only molecules and materials lacking a center of symmetry can exhibit them [28]. The assumption is frequently made that the atoms or molecules are independently polarized by the light with no interatomic or intermolecular coupling [28]. ANTA molecule fulfils that condition. The optimized structure belongs to C1 point group (at both levels of calculations). Figure 1 shows the optimized structure of ANTA (B3LYP/6-311++G(d,p)). The B3LYP/cc-PVTZ level of calculation also leads to very similar optimized structure. Nonlinear polarization becomes more important with increasing field strength. Under normal conditions $\alpha E>\beta E>\gamma E$ where α, β and γ refer to polarizability, the first and second order polarizabilities, respectively.

When an electric field (EF) is applied, the electron distribution and molecular geometry are disturbed. The atomic polarizability arises due to geometrical disturbance. It is significantly smaller than the electronic polarizability. Note that orientation polarizability arises when the molecules have a permanent dipole moment. ANTA has the dipole moment of 8.42 debye (B3LYP/6-311++G(d,p)). Highly polarizable molecules respond strongly to the application of the field [3]. They become highly polarized and the centroid of negative charge is displaced [3].

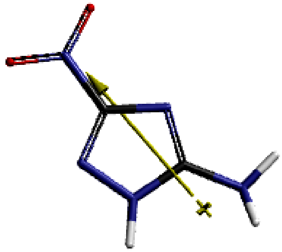

Figure 1. Optimized structure of ANTA (B3LYP/6-311++G(d,p)).

Figure 2 shows the bond lengths of ANTA molecule at two different level of calculations. The lengths differ only very slightly at two different level of calculations. In the present study value of the applied field is kept rather low just to prevent any disturbances of the molecular geometry.

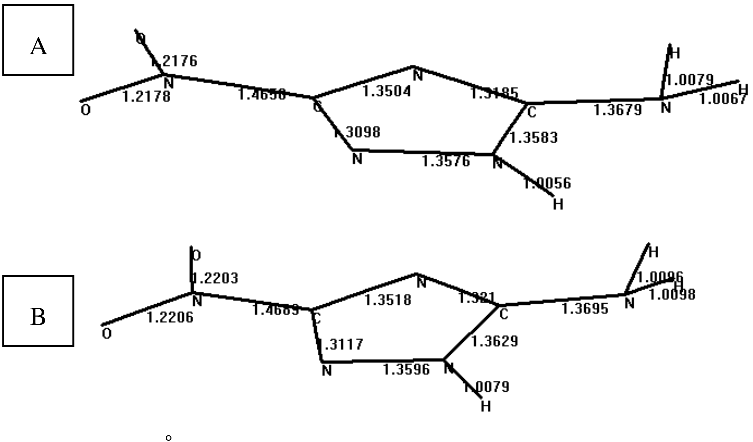

Figure 2. Bond lengths (Å) in ANTA. A: B3LYP/cc-PVTZ, B: B3LYP/6-311++G(d,p).

Tables 1A and 1B show the magnitude of dipole moment components as the polarization value increases ten times. The results indicate that the resultant magnitudes decrease as the polarization increases. This behavior holds for every level of calculations presented in the Tables 1A and 1B. Note that in the case of P:0.001 the individual components show parallelism in sign irrespective of the kind of method but when the polarizability value is increased to P:0.01 that property is lost, especially in the z-component.

The results of calculations related to polarizability of ANTA molecule are included in Tables 1-5.

Table 1A. Magnitude of dipole moment components (Applied electric field magnitude : 0.001).

	Method			
Field direction	MNDO// B3LYP/CC-PVTZ	PM3// B3LYP/CC-PVTZ	MNDO// B3LYP/6-311++G(d,p)	PM3// B3LYP/6-311++G(d,p)
X	-2.857011	-3.144356	-2.877493	-3.162892
Y	-0.551770	-0.672482	-0.540167	-0.662510
Z	0.456266	0.373758	0.442735	0.364013
Magnitude	2.945359 (7.485816)	3.237113 (8.227327)	2.961040 (7.525671)	3.251970 (8.265088)

In au units, Debye units in parenthesis.

Table 1B. Magnitude of dipole moment components (Applied electric field magnitude : 0.01).

	Method			
Field direction	MNDO// B3LYP/CC-PVTZ	PM3// B3LYP/CC-PVTZ	MNDO// B3LYP/6-311++G(d,p)	PM3// B3LYP/6-311++G(d,p)
X	2.855824	3.143499	2.876272	-3.162012
Y	0.551714	-0.672359	-0.540111	-0.662383
Z	0.456266	-0.373758	-0.442735	0.364013
Magnitude	2.944198 (7.482864)	3.236255 (8.225146)	2.959844 (7.522630)	3.251089 (8.262847)

In au units, Debye units in parenthesis.

If the molecule is considered to be in a uniform electric field aligned along one of the axis of the system, the values of the polarizabilities along that axis (μ_x , α_{xx} , β_{xxx} , γ_{xxx}) can be obtained by using eq.4. Tables 2A and 2B list the components of polarizability α, where E4 and dipole are the contributors of polarizability to energy and dipole moment, respectively. The results show that the average polarizability increases as the polarization value increases. Note that the diagonal elements exhibit parallelism in sign irrespective of the method applied but it does not hold for the off-diagonal elements.

Table 2A. Components of polarizability α (Applied electric field magnitude : 0.001).

Components of polarizability				
	Method			
	MNDO// B3LYP/CC-PVTZ		PM3// B3LYP/CC-PVTZ	
Field direction	E4	Dipole	E4	Dipole
XX	101.271402	77.834195	81.476646	81.469063
YY	91.634167	68.197510	68.203963	68.199057
ZZ	33.710802	10.277835	13.308350	13.306438
XY	-2.575101	-2.574591	-4.646400	-4.646921
XZ	-0.295551	-0.295574	0.699106	0.699903
YZ	-0.639497	-0.639470	-0.946444	-0.947303
Average polarizability	75.538790	52.103180	54.329653	54.324853

In au units.

Table 2B. Components of polarizability α (Applied electric field magnitude : 0.01).

Components of polarizability				
	Method			
	MNDO// B3LYP/CC-PVTZ		PM3// B3LYP/CC-PVTZ	
Field direction	E4	Dipole	E4	Dipole
XX	101.7738	78.31662	82.02514	82.00063
YY	92.02273	68.58571	68.59046	68.58603
ZZ	33.72485	10.2919	13.32381	13.32292
XY	2.624248	2.616245	-4.70991	-4.70272
XZ	-0.30399	-0.30407	0.703765	0.703272
YZ	0.647227	0.647182	-0.98461	-0.98452
Average polarizability	75.840467	52.398077	54.646472	54.636526

In au units.

Note that in Tables 2-5 the calculations were performed on B3LYP/cc-PVTZ based optimized structure employing MNDO and PM3 single point calculations.

The tensor components of the second order polarizability (β) are presented in Tables 3A and 3B.

Table 3A. Components of second order polarizability (β) (Applied electric field magnitude : 0.001).

	Method			
	MNDO// B3LYP/CC-PVTZ		PM3// B3LYP/CC-PVTZ	
Components	E4	Dipole	E4	Dipole
XXX	-91.410	-91.692	-213.595	-213.338
XYY	-2.402	-2.545	-39.188	-38.300
XZZ	19.676	19.837	25.744	25.087
YYY	81	80.908	137.637	137.165
YXX	69.617	69.413	136.644	136.297
YZZ	-0.629	-0.553	1.545	2.027
ZZZ	-1.989	-1.946	-6.933	-7.587
ZXX	-36.285	-36.327	-67.072	-67.029
ZYY	-5.295	-5.336	-11.387	-11.317

In au units.

Table 3B. Components of second order polarizability (β) (Applied electric field magnitude : 0.01).

	Method			
	MNDO// B3LYP/CC-PVTZ		PM3// B3LYP/CC-PVTZ	
Components	E4	Dipole	E4	Dipole
XXX	110.502	123.21	-227.681	-236.962
XYY	4.102	2.377	-41.699	-40.298
XZZ	-20.17	-20.153	26.704	26.764
YYY	81.257	80.684	137.69	136.409
YXX	67.865	53.423	135.603	115.885
YZZ	-0.838	-0.89	1.012	0.867
ZZZ	2.06	2.064	-6.979	-6.995
ZXX	35.96	36.152	-66.279	-65.82
ZYY	4.666	4.67	-10.848	-10.861

In au units.

The vector components of β and its value in the dipole moment are presented in Tables 4A and 4B. As seen in Tables 4A and 4B, the value of β in dipole moment increases as the polarizability value increased ten times. Also note that in each method applied, the value of β increases as the polarization increases. In the table components BI are expressed by the formula [2],

$$BI = (3/5)\ (BI11+BI22+BI33) \tag{9}$$

Table 4A. Vector component BI of second order polarizability (β). (Applied electric field magnitude : 0.001).

	MNDO// B3LYP/CC-PVTZ		PM3// B3LYP/CC-PVTZ	
BX	-44.482	-44.641	-136.224	-135.931
BY	89.993	89.861	165.496	165.294
BZ	-26.141	-26.165	-51.235	-51.56
Value of β in dipole moment.	22.239 $(0.193\ 10^{-30})$	22.414 $(0.194\ 10^{-30})$	92.024 $(0.797\ 10^{-30})$	91.744 $(0.794\ 10^{-30})$

In au, esu units in parenthesis.

Table 4B. Vector component BI of second order polarizability (β). (Applied electric field magnitude : 0.01).

	MNDO// B3LYP/CC-PVTZ		PM3// B3LYP/CC-PVTZ	
BX	56.661	63.26	-145.606	-150.298
BY	88.97	79.93	164.583	151.897
BZ	25.612	25.732	-50.464	-50.206
Value of β in dipole moment.	34.995 $(0.303\ 10^{-30})$	43.040 $(0.373\ 10^{-30})$	102.434 $(0.887\ 10^{-30})$	109.611 $(0.949\ 10^{-30})$

In au, esu units in parenthesis.

Tables 5A and 5B show the third order polarizability (γ) vector components involved in the calculation of averaged γ values as the applied polarizability value increased. The average value of γ is expressed as [2],

$$\text{Average Gamma}=(1/5)\ [XXXX + YYYY + ZZZZ + 2\ (XXYY + XXZZ + YYZZ)] \tag{10}$$

As seen in the tables γ strongly responds to the increase of polarizability.

Table 5A. Third order (γ) polarizability (Applied electric field magnitude : 0.001).

	MNDO// B3LYP/CC-PVTZ		PM3// B3LYP/CC-PVTZ	
Vector component	E4	Dipole	E4	Dipole
XXXX	19036.53	18511.04	19645.04	21602
YYYY	-1182.64	-1416.87	807.502	277.544
ZZZZ	28.791	103.402	144.857	603.88
XXYY	4074.776	3849.748	6465.778	5073.069
XXZZ	478.655	485.795	980.709	1609.056
YYZZ	193.231	137.359	465.796	1217.813
Value of γ	5475.20 (2.76561 10^{-36})	5228.67 (2.64109 10^{-36})	7284.39 (3.67946 10^{-36})	7656.66 (3.86750 10^{-36})

In au units. see units in parenthesis.

Table 5B. Third order (γ) polarizability (Applied electric field magnitude : 0.01).

	MNDO// B3LYP/CC-PVTZ		PM3// B3LYP/CC-PVTZ	
Vector component	E4	Dipole	E4	Dipole
XXXX	20689.91	21443.4	21134.63	21866.37
YYYY	-1188.39	-1181.03	764.001	759.483
ZZZZ	40.3	40.382	147.984	148.085
XXYY	4191.187	4184.982	6592.939	6583.735
XXZZ	480.476	480.259	959.381	958.45
YYZZ	202.522	202.355	472.516	471.987
Value of γ	5858.04 (2.95899 10^{-36})	6007.59 (3.0345310^{-36})	7619.26 (3.8486110^{-36})	7760.46 (3.9199310^{-36})

In au units. esu units in parenthesis.

Figure 3 shows the axes of inertia of ANTA molecule. In the figure, X-axis is along the longest principle axis of the molecule whereas Y axis is perpendicular to X-axis. The Z-axis is perpendicular to XY-plane.

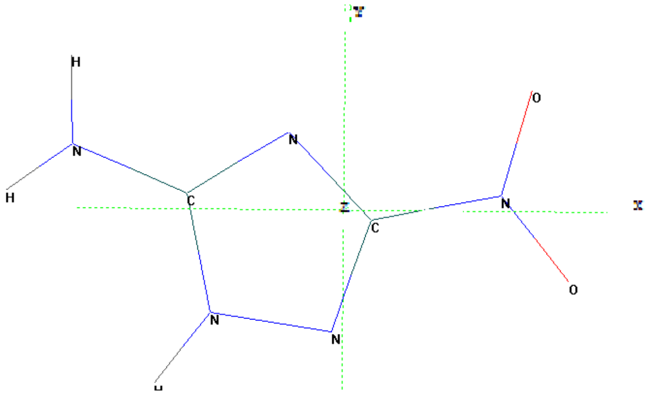

Figure 3. ANTA molecule and its axes of inertia.

Table 6 shows the effect of field applied along the axes of inertia (X,Y and Z) of ANTA molecule and strength on the dipole and its components. The components of the dipole are designated as x, y and z. The calculations have been performed at the level of MNDO//B3LYP/cc-PVTZ.

Table 6. Effect of field direction and strength on dipole and its components of ANTA molecule.

		E: 0.001				E: 0.01			
		Components				Components			
Field direction	Dipole	x	y	z	Total	x	y	z	Total
X	PointChg	-7.027	0.415	-0.881	7.094	-9.061	0.38	-0.836	9.108
	sp Hybrid	-1.137	0.171	-0.276	1.182	-0.913	0.168	-0.261	0.964
	Sum	-8.164	0.586	-1.157	8.266	-9.974	0.548	-1.096	10.049
Y	PointChg	-6.805	0.375	-0.807	6.863	-6.827	-0.012	-0.102	6.828
	sp Hybrid	-1.163	0.154	-0.294	1.21	-1.172	0	-0.438	1.251
	Sum	-7.969	0.529	-1.101	8.062	-7.999	-0.012	-0.54	8.017
Z	PointChg	-6.799	0.496	-1.028	6.894	-6.827	-0.012	-0.102	6.828
	sp Hybrid	-1.16	0.155	-0.274	1.202	-1.172	0	-0.438	1.251
	Sum	-7.959	0.651	-1.302	8.091	-7.999	-0.012	-0.54	8.017

Dipole in Debyes. E: Field strength in au units.

As seen in Table 6, the total value of the dipole moment increases if the field strength (F) is increased in the direction of the X-axis along which the donor (NH_2) and acceptor (NO_2) groups reside. The applied electric field perturbs the electron population in such a way that the value of dipole moment vector increases as the field strength is increased. However, increase of the field strength along the Y or Z axes slightly decreases the dipole moment value.

Figure 4 displays the effect of electric field on the molecular orbital energy spectra of

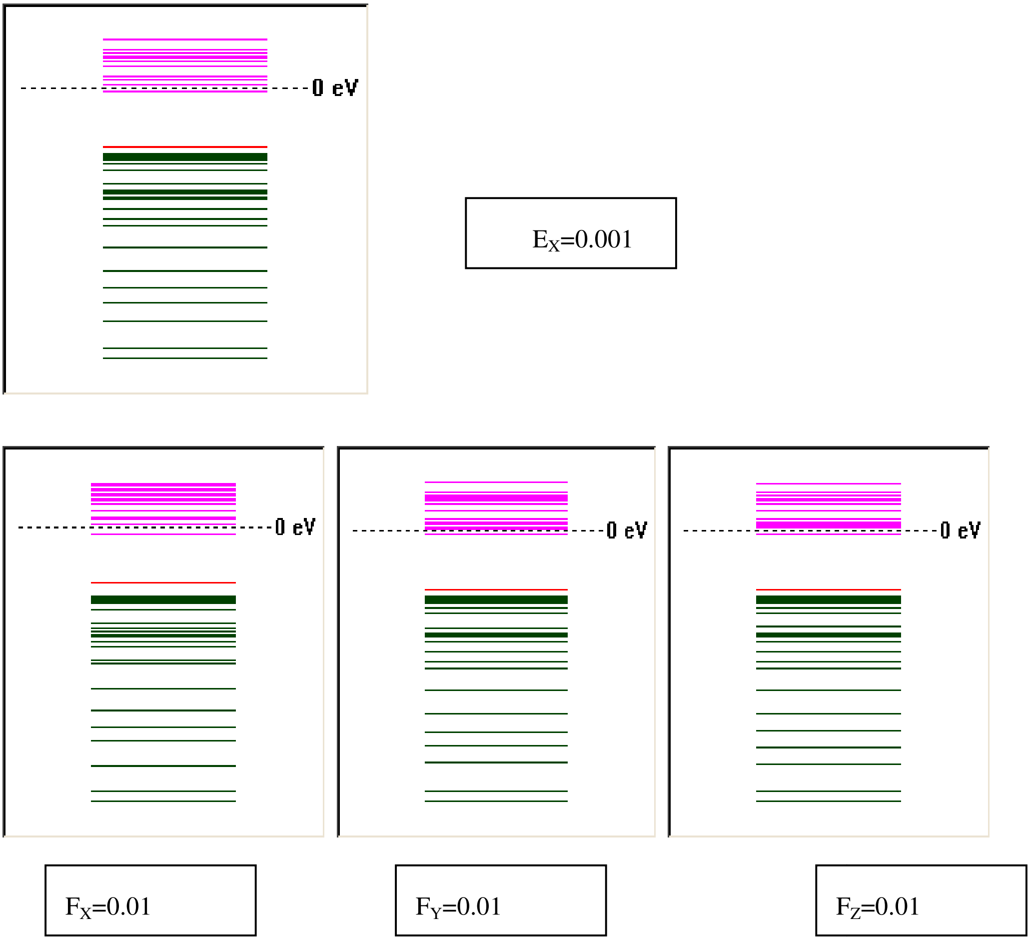

Figure 4. Effect of electric field on the molecular orbital energy spectra of ANTA molecule (Applied field in au units, MNDO// B3LYP/cc-PVTZ)).

ANTA molecule. In the case of F: 0.001 the distribution of molecular orbital energy levels does not exhibit discernable perturbation depending on the field direction. Whereas when F value is set to 0.01 au, the distribution standing for F_x case is different from the others.

Table 7 shows the effect of field strength on the HOMO, LUMO energies and the interfrontier molecular orbital energy gap (Δε) value of ANTA molecule. Note that $\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$. As seen in the table, as the field in X, Y and Z-directions increases the HOMO energy level raises up. Again the greatest effect occurs in case of X-direction. On the contrary, the LUMO energy decreases as the field strength increases in X, Y and Z-directions in all the cases. Consequently, the interfrontier molecular orbital energy gap value decreases as the field strength increases, keeping the direction be the same. The electron distribution can be distorted readily if the LUMO energy level lies close to the HOMO energy, so the polarizability is then large. If the LUMO lies high above the HOMO, an applied field cannot perturb the electron distribution significantly and the polarizability is low [34]. Note that the impact sensitivity of an explosive is related to Δε value such that decrease of it increases the sensitivity [35, 36]. Also note that in the case of ANTA the decrease in Δε is greater if the field direction lies along the X-axis.

Table 7. Effect of field strength on the HOMO, LUMO energies and Δε value of ANTA molecule.

Field direction	HOMO	LUMO	Δε
X	-10.315015	-0.930985	9.38403
	-9.722733	-1.29873	8.424003
Y	-10.375451	-0.901036	9.474415
	-10.358150	-0.920074	9.438076
Z	-10.378779	-0.894343	9.484436
	-10.358150	-0.920074	9.438076

The first and second entries in each row have E values of 0.001 and 0.01 in eV, respectively.

Figures 5 and 6 show the HOMO and LUMO patterns of ANTA molecule in two different field strengths. As seen in the figures the main effect of the increased field occurs on the LUMO pattern (on the carbon atom having the amino group) when it is set along the X- and Z-axes.

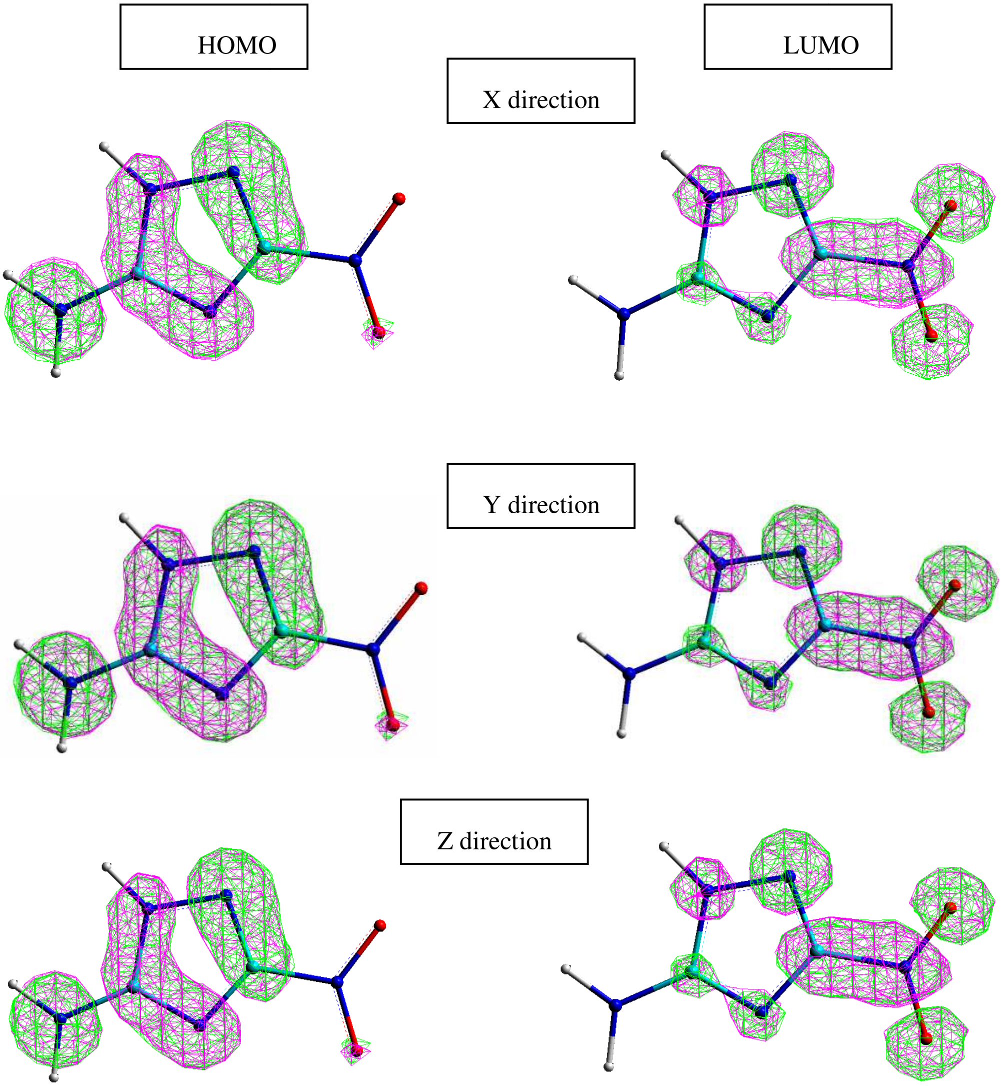

Figure 5. The HOMO and LUMO patterns of ANTA in F: 0.001 au. (MNDO//B3LYP/cc-PVTZ).

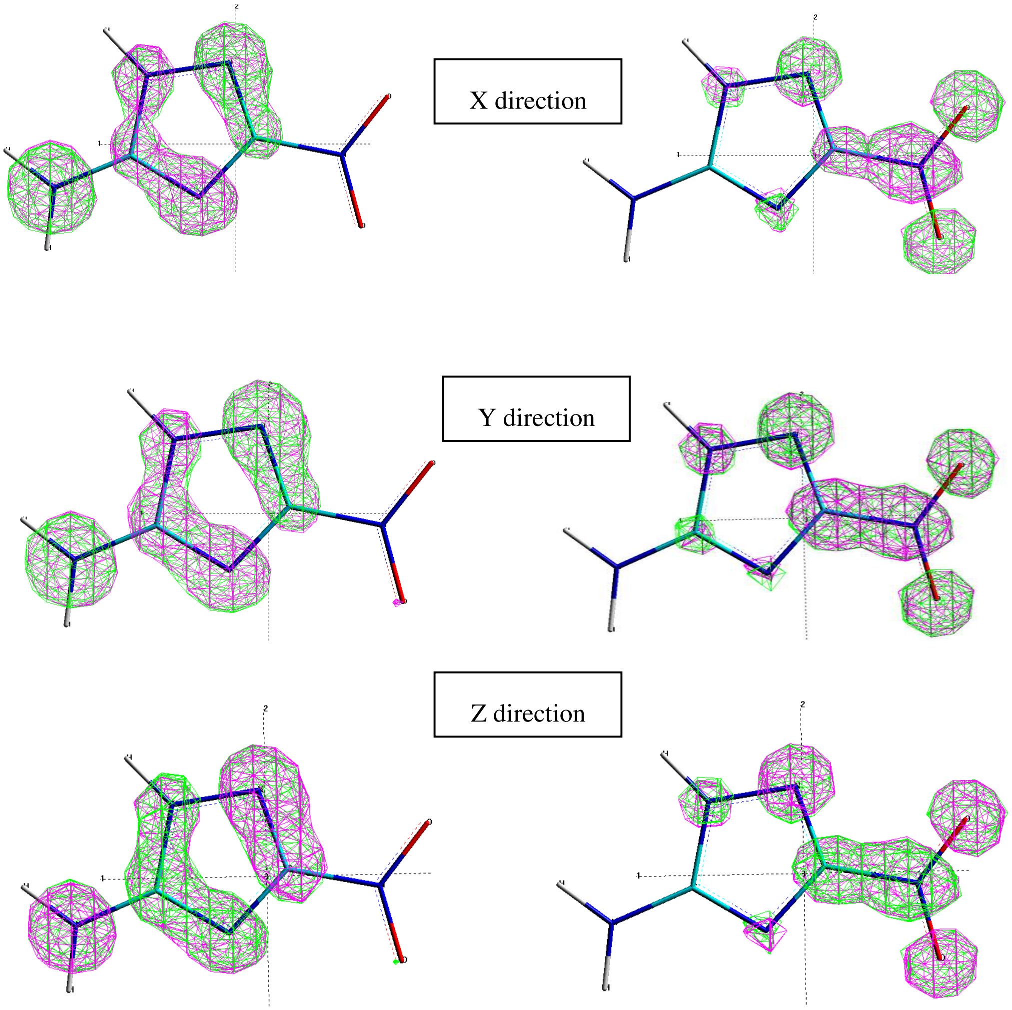

Figure 6. The HOMO and LUMO patterns of ANTA in F: 0.01 au. (MNDO//B3LYP/cc-PVTZ).

4. Conclusion

The present study on ANTA molecule has revealed that the applied electric field mainly affects ANTA when the direction of the field is set along the principle axis of the molecule. Then the HOMO energy level raises up whereas the LUMO level decreases. Meanwhile the interfrontier molecular orbital energy gap decreases as the magnitude of the field increases. So, the impact sensitivity of ANTA may increase by exposing it to an electric field. Obviously, *ab initio* methods are expected to yield reliable and quantitatively correct results. Note that semi empirical calculations tend to be qualitative unless the structure optimization is done by means of *ab initio*/DFT methods at high level basis sets.

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