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A quantum-mechanical investigation of functional group effect on 5,5'-disubstituted-1,1'-azobis(tetrazoles)

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ABSTRACT

The present work reports the detailed B3LYP/6-311++G(d,p) study of most stable transand cis configurations photoisomerization in the core system of computational photochemistry-the 5,5'-disubstituted-1,1'-azobis (tetrazole) molecules. All computations were carried out in gas phase at temperature 293.15 K and pressure 1 atm. Firstly; the potential energy surface (PES) of the ground state of the molecules has been directly optimized and scanned using a multistate multiconfiguration second-order perturbation theory. We characterize the cis and trans molecules geometric domains of the ground states. The imaginary frequencies were not shown in frequency computation analysis of the optimized molecules. Also we calculate the electronic and thermal energy, polarizability, equilibrium constant, HOMO-LUMO energies gap and chemical hardness of the configurations in the ground state. In general, the DFT results confirm the stability of the trans configurations among all structures. In the last section of this study, the detonation parameters of the compounds are calculated.

Keywords: Density functional theory; Azotetrazole; Configuration; Stability; Reactivity

INTRODUCTION

Tetrazoles are an important class of heterocyclic compounds and exhibit a wide range of applications in medicinal chemistry and the material sciences. For example, tetrazoles are regarded as isosteres of the carboxylic acid functionality in medicinal chemistry; they are applied in the material sciences and in chemical industry as propellants, explosives, and in photography [1-6]. Among these, tetrazole building blocks play a prominent role, considering their potential coordination modes [7].Nitrogen-rich, high energy density materials (HEDMs) derive most of their energy from their high positive heats of formation (the number of nitrogen atoms linked together is directly proportional to the performance of the compound) in contrast to classical explosives such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX), and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) that derive their energy from oxidation of the carbon backbone [8-10].The performance of an energetic material is largely a function of its oxygen balance (composition), density, and heat of formation, of which the two last are governed to some extent by the molecular structure [11].Tetrazole-based energetic materials have proven to be unique in that they combine a nitrogen-rich moiety, which also provides the compounds with relatively high densities, good thermal

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*Corresponding author: mnabati@ymail.com stabilities, and low sensitivities [12].The [2+3] cycloaddition of nitriles and azides is a reliable method for the synthesis of tetrazole derivatives [13].

An azo molecule undergoescis–trans photochemical isomerization following excitation to the S_1 (n→p*) and the S_2 (p→p*) states, providing the basis for various applications, such as light triggered switches and image storage devices [14-16]. These processes have been extensively investigated by various experimental methods, such as UV-visible absorption, Raman spectroscopy and NMR analysis [17-19]. From the experimental point of view, synthesis and determination of the properties of interest can be expensive and difficult. In this case, molecular modeling could help to find structures with desirable properties in a relatively short time [20].

Azo coupling reactions have been used to prepare useful azo-based energetic materials such as azotetrazoles, triazoles, and furazans and have even allowed the preparation of ten-linked nitrogen compound [21-23]. Thomas M. Klapotke and Davin G. Piercey synthesized and characterized 1, 1'-azobis (tetrazole) for the first time in 2011 [24]. In the present study, the effect of various substituents were investigated on the stability, reactivity and structural properties of the most stable cis and trans configurations of the 5, 5'- disubstituted -1, 1'- azobis (tetrazoles).

COMPUTATIONAL METHOD

The geometry optimizations and single point calculations of the most stable configurations of the 5, 5'-azotetrazole in gas phase have been carried out using the density functional theory (DFT) method [25] with Becke, 3-parameter, Lee-Yang-Parr (B3LYP) exchange correlation corrected functional [26] and the 6-311++G (d, p) basis set using the GAUSSIAN 03 program [27]. The imaginary frequencies were not shown in frequency computation analysis of the optimized molecules. The energies of the molecules were computed with a self-consistent field (SCF) convergence of 10^{-8}a.u. for the density matrix. For all compounds, we have studied trans and cis configurations concerning positions of functional groups in the molecules.

RESULTS AND DISCUSSION

In this work, we have presented the results of theoretical studying of the most stable cis and trans configurations of the 5,5'-disubstituted-1,1'-azobis(tetrazoles).

Structures of compounds are given in Figure 1. All considered compounds are presented in the Table 1. DFT calculations were performed to shed light on how the various substituents influence the stability and reactivity properties of the cis and transazotetrazoles. Key parameters: (i) polarizability, (ii) electronic and thermal energy, (iii) equilibrium constant, (iv) HOMO-LUMO energies gaps and (v) chemical hardness values were calculated.

Optimized Structures

The B3LYP/6-311++G(d, p) level of theory was employed to optimize all structures in gas phase during the present investigation. The bond lengths, bond angles and dihedral angles of the optimized structures are listed in Table 2. It can be seen from the data, the range of N6-N7 bond length of cis and trans configurations is 1.234-1.250 and 1.245-1257 Angstrom, respectively. And also, the N6-N7 bond length of cis configuration of each compound is shorter than the corresponding trans configuration. This can be related to the planar and non-planar structures of the trans and cis configurations. We know the conjugation of pi bonds of planar structures is better than the non-planar [28]. The results of the calculations showed that the longest and shortest N6-N7 bond in trans configuration are related to AABA and NAB structures. While, the shortest N6-N7 bond among all cis structures corresponds to NABN structure, which is 1.234 Å, and the longest N6-N7 is 1.250 Å and stands for AABA molecule. The same trends are obtained for bond lengths of the N1-N6 and N7-N8 bonds in cis structures and are longer than the trans configurations.

The data of the bond angles of the structures indicated that the N1-N6-N7 and N6-N7-N8 angles of the cis configurations are longer than the trans.

The N1-N6-N7-N8 dihedral angle data showed the planar and non-planar structure for trans and cis configurations, respectively. The torsion angle of the cis structures are in range of 0.8-8.684 degree. From the data of the Table 2, the N1-N6-N7-N8 torsion angles for cis configuration are in the following order: AABN > AAB > HAB > TAB > CAB > NAB > FAB > DAAB > MAB >AABA > AB > NABN. The AABN compound has the largest dihedral angle among all cis configurations.

Electronic Propertiez

The thermal and electronic energies (E), enthalpies (H) and Gibbs energies (G) for optimized structures of most stable cis and trans configurations of 5,5'-disubstituted-1,1'-azobis(tetrazoles) were calculated at B3LYP/6-311++G(d,p) level of theory and are listed in Table 3. We can see from the data, the trans configuration of each molecule is more stable than the cis configuration. The stability of trans structures to cis structures is in range of 7.2-17.5 kcal/mol. The stability order of trans-cis structures is: AAB > AABA > AABN > AB > DAAB > MAB > FAB > CAB > HAB > TAB> NAB > NABN.This stability order shows us that the electron-donating substituents give more stability to the trans configurations. It can be seen the trans configurations of compounds containing electron-donating groups such as amino groups have large negative thermal and electronic energy among all molecules. While, the NABN and NAB structures have the smallest trans-cis energy gap among all structures. AABN has both electron-donating and electron-withdrawing groups on its structure. Thetrans structure of this molecule is more stable than the cis because of the pull-push effect.

The equilibrium constants were computed by following formula [29]:

$$K = e^{\frac{-\Delta G^{\circ}}{RT}} \quad (1)$$

where T is temperature and R is gas constant.

The equilibrium constant value is depends on temperature, but is independent of the analytical concentrations of the species in a mixture [30]. The calculated equilibrium constants of the structures are shown in Table 3. The K values are changed between 2.8×10^4 and 3×10^{13}. And also, the equilibrium constant order for molecules is: AAB > AABA > AABN > AB > DAAB >MAB > FAB > HAB > CAB > TAB> NABN > NAB. This order is very similar to the stability order. The smallest equilibrium constant was found for NAB, and the biggest one for AAB.

Understanding of optical properties is very important in the designing of materials for signal processing, communication technology, optical memory devices and optical switches [31-33]. The strength of optical response depends on the electrical properties of the whole material, which for molecules can be related to the polarizability and dipole moment. Therefore, these are the properties that should be measured in order to assess the optical potential for molecules

[34].The dipole moment of molecule was obtained by following formula [35]:

$$p = p_0 + \alpha E + \frac{1}{2}\beta EE + \cdots$$

where p_0 is adipole moment without an electric field, α is a polarizability second-order tensor, β is the first in an infinite series of hyperpolarizabilities. The dipole moments, mean and anisotropic polarizabilities for most stable cis and trans configurations of the 5,5'-disubstituted-1,1'-azobistetrazoles are calculated and listed in Table 4. As expected, the dipole moment of cis configuration for each compound was found to be greater than trans. The data shows us the dipole moment of trans configuration of AABN and NAB molecules is more than the cis. The cis-trans dipole moment gap order is: AABA > AB > MAB > AAB > TAB > CAB > DAAB > HAB > FAB > NABN > AABN > NAB.It can be concluded the lowest cis-trans dipole moment gap is related to the compounds containing electron-withdrawing groups.

The polarizability tensor was firstly diagonalized and mean and anisotropic polarizabilities have been obtained using following formulas [36]:

$$\alpha_{mean} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (2)$$

$$\alpha_{anis} = \sqrt{\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{xx} - \alpha_{zz})^2}{2}}$$

where α_{xx}, α_{yy}, α_{zz} are diagonal elements of polarizability matrix. Our calculations indicate that the lowest and biggest mean and anisotropic polarizabilities have been obtained for the molecules containing electron-withdrawing and electron-donating substituents, respectively.

Molecular Properties

Energies of the HOMO and LUMO are important parameters in quantum chemical calculations. While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called "energy gap" that is an important parameter for structural stability. Higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles, while lower LUMO energy is essential for molecular reactions with nucleophiles [37].Computed frontier orbitals energies for most stable cis and trans configurations of 5,5'-disubstituted-1,1'-azobis (tetrazoles) are shown in Table 5. From the calculated results, we can see that the cis structures have more HOMO-LUMO energy gap than trans structures. This means the cis configuration of each molecule is more stable than trans. And also, It can be deduced the molecules containing electron-withdrawing substituents have a good reactivity with nucleophiles, while the electron-donating groups cause the reactivity of moleculeswith electrophiles. We also calculated chemical hardness (□), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) for all compounds. The data of the calculations are seen in Table 5. The □, μ, χ and ω parameters are obtained by following formulas [38]:

$$\eta = \frac{(\varepsilon_{LUMO} - \varepsilon_{HOMO})}{2}$$

$$\chi = \frac{-(\varepsilon_{LUMO} + \varepsilon_{HOMO})}{2}$$

$$\mu = \frac{(\varepsilon_{LUMO} + \varepsilon_{HOMO})}{2}$$

$$\omega = \frac{\mu^2}{2\eta}$$

From the data of the Table 5, it is observed that the chemical hardness for cis configurations is greater than the trans. While, the electrophilicity index of the trans structures is great. The chemical hardness and electrophilicity index for the cis and trans configurations are changed by following orders: the chemical hardness order for trans structures: HAB > FAB > AB > CAB > MAB > TAB > NABN > NAB > AABA > AAB > AABN > DAAB; the chemical hardness order for cis structures: TAB > CAB > MAB > FAB > AB > NAB > HAB > NABN > AABA > AAB > AABN > DAAB; the electrophilicy index order for trans structures: NABN>NAB >AABN>FAB > AB >CAB >MAB >HAB >TAB >DAAB > AABA> AAB; and the electrophilicity index order for cis structures: NABN > AABN > NAB > FAB > CAB > DAAB > AAB > AB > HAB > MAB > TAB > AABA. These chemical hardness orders show us the amino and nitro groups cause that the cis and trans molecules would be have more reactivity. And also it can be shown that the molecules containing electron-withdrawing groups have the biggest electrophilicity property. Then, these molecules could be having good reactivity with nucleophiles.

Figure 2 shows the correlation between chemical hardness (η) and total energy (E) of the cis and trans configurations of 5,5'-disubstituted-1,1'-azobis (tetrazoles). We can conclude from this Figure that the chemical hardness (η) and total energy (E) of the structures are independent of each other.

The correlation between electrophilicity index and total energy of the studied molecules is shown in Figure 3. It can be deduced that the electrophilicity property of both cis and trans structures increases when the stability increases.

Energetically Properties

High energetic density materials (HEDMs) may be categorized by the speed at which they expand. Materials that detonate (the front of the chemical reaction moves faster through the material than the speed of sound) are said to be "high explosives" and materials that deflagrate are said to be "low explosives". A wide variety of chemicals can explode; a smaller number are manufactured specifically for the purpose of being used as explosives. The remainder is too dangerous, sensitive, toxic, expensive, unstable, or decompose too quickly for common usage. In contrast, some materials are merely combustible or flammable if they burn without exploding [39].

Oxygen balance (OB_{100} or OB%) is an expression that is used to indicate the degree to which an explosive can be oxidized. If an explosive molecule contains just enough oxygen to form carbon dioxide from carbon, water from hydrogen molecules, all of its sulfur dioxide from sulfur, and all metal oxides from metals with no excess, the molecule is said to have a zero oxygen balance. The molecule is said to have a positive oxygen balance if it contains more oxygen than is needed and a negative oxygen balance if it contains less oxygen than is needed; the combustion will then be incomplete and large amount of toxic gases like carbon monoxide will be present [40]. The sensitivity, strength and brisance of an explosive are all somewhat dependent upon oxygen balance and tend to approach their maxima as oxygen balance approaches zero. The oxygen balance is calculated from the empirical formula of a compound in percentage of oxygen required for complete conversion of carbon to carbon dioxide, hydrogen to water, and metal to metal oxide. The procedure for calculating oxygen balance in terms of 100 grams of the explosive material is to determine the number ofmoles of oxygen that are excess or deficient for 100 grams of a compound [41].OB_{100} was calculated as follows [42]:

$$OB\% = \frac{-1600}{Mol.wt} \times \left(2a + \frac{b}{2} - c\right)$$

where:

a = number of atoms of carbon, b = number of atoms of hydrogen, c = number of atoms of oxygen.

	Stoichiometric ratio		
parameters	$c \geq 2a+b/2$	$2a+b/2>c \geq b/2$	$b/2>c$
N	$(b+2c+2d)/4MW$	$(b+2c+2d)/4MW$	$(b+d)/2MW$
M	$4MW/(b+2c+2d)$	$(56d+88c-8b)/(b+2c+2d)$	$(2b+28d+32c)/(b+d)$
Q	$(28.9b+94.05a+0.239\Delta H_f^{\circ})/MW$	$[28.9b+94.05(c/2-b/4) + 0.239\Delta H_f^{\circ}]/MW$	$(57.8c+0.239\Delta H_f^{\circ})/MW$

Furthermore, heat of formation (HOF), density (ρ), detonation velocity (D), and detonation pressure (P) are the important parameters to evaluate the explosive performance ofhigh energy materials and can be predicted by the following empirical Kamlet-Jacob equations [43]:

$$D=1.01(NM^{1/2}Q^{1/2})^{1/2}(1+1.3\rho)$$
$$P=1.558\rho^{2}NM^{1/2}Q^{1/2}$$

where D: detonation velocity in km/s, P: detonation pressure in GPa, ρ: density of a compound in g/cm^3, N: moles of gaseous detonation products per gram of explosive (in mol/g), M: average molecular weight of gaseous products (in g/mol), Q: chemical energy of detonation in kJ/g.

Here, the parameters N, M and Q were calculated according to the chemical composition of each explosive ($C_aH_bO_CN_d$). On the other hand, the density of each molecule was predicted from the molecular volume, while the molecular volume of each molecule was obtained from the statistical average of 100 single-point calculations for each optimized structures. The molar volume was defined as inside a contour of 0.001 electrons/Bohr^3 density that was evaluated using a Monte Carlo integration implemented in the Gaussian 03 package. This method has been successfully tested on various CHNO molecules and accurately predicts the explosive properties [44]. In the present study, single point molecular volume calculations at B3LYP/6-311++G (d, p) performed based on the B3LYP/6-311++G(d, p) geometry optimized structures. Table 6 collects the predicted V, ρ, Q, D and P values of the structures. The heats of formation (HOF) values were also calculated and listed in the table. It is shown that the density, velocity of detonation and detonation pressure of cis configuration of AB, MAB, FAB, CAB, AAB and AABA molecules are more than the trans. It is clear that the electron donating groups cause the trans molecules have high detonation properties. And also, the data of the Table 9 shows the detonation properties values of the cis structures of TAB, NAB, NABN, AABN, HAB and DAAB molecules are lower than the trans. This says the trans molecules containing electron-withdrawing and larger groups have more ρ, Q, D and P values than the cis molecules including same substituents. For RDX and HMX, experimental value of D and P are 8.75

km/s, 9.10 km/s and 34.70 GPa, 39.00 GPa, respectively [45, 46]. Comparing these values with most stable cis and trans configurations of the 5,5'-disubstituted-1,1'-azobistetrazoles, T-HAB has velocity of detonation value of 9.04 km/s and detonation pressure value of 37.41 GPa, one finds it to be as powerful explosive as the famous explosives HMX and RDX.

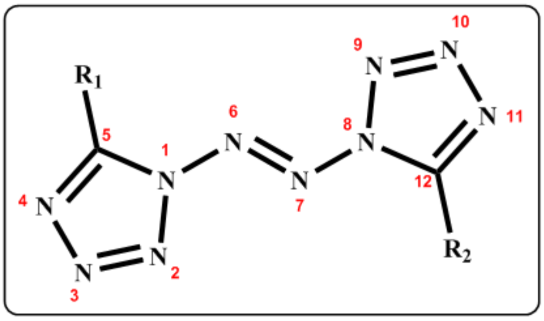
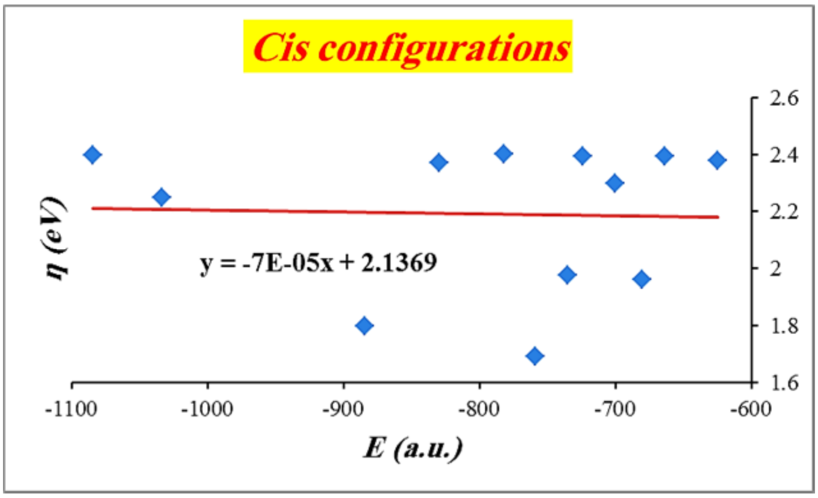


Fig. 1. Structure of studied 5,5'-disubstituted-1,1'-azobis(tetrazoles) with atomic numbering.



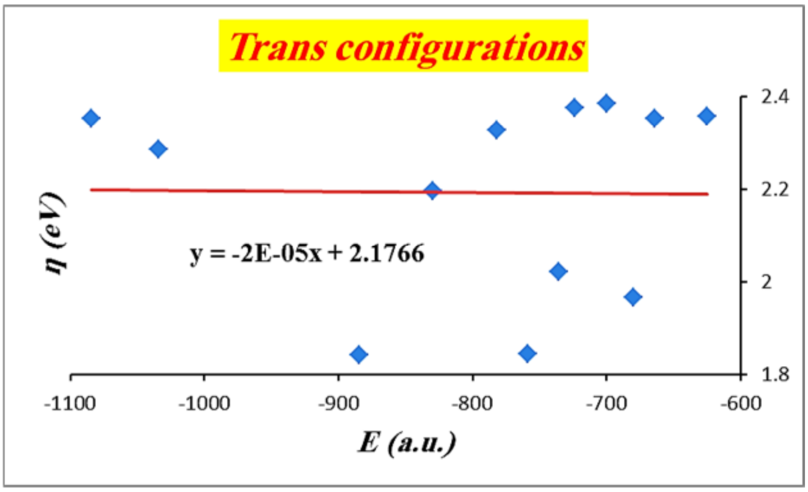


Fig. 2. Correlation between chemical hardness and total energy of studied 5,5'-disubstituted-1,1'-azobis (tetrazoles).

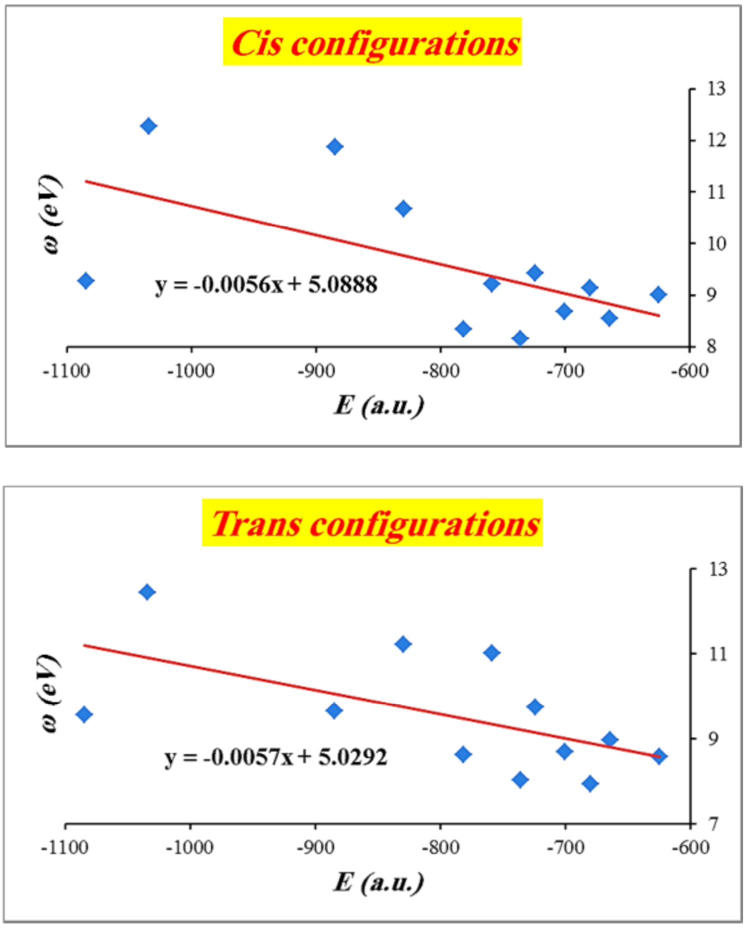


Fig. 3. Correlation between electrophilicity index and total energy of studied 5,5'-disubstituted-1,1'-azobis (tetrazoles).

Table 1. Studied molecules and their IUPAC names

	R_1	R_2	IUPAC name
AB	H	H	1,2-di(5H-tetrazol-1-yl)diazene
MAB	CH_3	H	(E)-1-(5-methyl-tetrazol-1-yl)-2-(5H-tetrazol-1-yl)diazene
TAB	tBu	H	(E)-1-(5-tert-butyl-tetrazol-1-yl)-2-(5H-tetrazol-1-yl)diazene
FAB	F	H	(E)-1-(5-fluoro-tetrazol-1-yl)-2-(5H-tetrazol-1-yl)diazene
CAB	Cl	H	(E)-1-(5-chloro-tetrazol-1-yl)-2-(5H-tetrazol-1-yl)diazene
AAB	NH_2	H	(E)-1-(5-amine-tetrazol-1-yl)-2-(5H-tetrazol-1-yl)diazene
AABA	NH_2	NH_2	1,2-bis(5-amine-tetrazol-1-yl)diazene
NAB	NO_2	H	(E)-1-(5-nitro-tetrazol-1-yl)-2-(5H-tetrazol-1-yl)diazene
NABN	NO_2	NO_2	1,2-bis(5-nitro-tetrazol-1-yl)diazene
AABN	NH_2	NO_2	(E)-1-(5-amine-tetrazol-1-yl)-2-(5-nitro-tetrazol-1-yl)diazene
HAB	OH	H	(E)-1-(5-hydroxy-tetrazol-1-yl)-2-(5H-tetrazol-1-yl)diazene
DAAB	NMe_2	H	(E)-1-(5-(*N,N*-dimethylamine)-tetrazol-1-yl)-2-(5H-tetrazol-1-yl)diazene

Table 2. Bond lengths (A°), bond angles (degree) and dihedral angles (degree) for the most stable configurations (cis and trans) of the molecules calculated at B3LYP/6-311++G(d,p) level of theory

	N1-N6	N6-N7	N7-N8	N1-N6-N7	N6-N7-N8	N1-N6-N7-N8	N6-N7-N8-C12	N7-N6-N1-C5
Trans								
AB	1.367	1.250	1.367	111.203	111.200	179.998	0.092	0.015
MAB	1.363	1.250	1.371	112.542	110.824	179.981	0.001	0.001
TAB	1.364	1.246	1.374	114.377	110.691	179.970	0.060	0.131
FAB	1.369	1.250	1.366	112.000	110.902	179.982	0.002	0.001
CAB	1.369	1.249	1.367	113.000	110.755	179.971	0.002	0.001
AAB	1.347	1.255	1.373	112.559	111.220	179.821	0.689	0.740
AABA	1.355	1.257	1.355	112.561	112.555	179.989	1.476	1.530
NAB	1.387	1.245	1.363	114.802	110.396	179.990	0.001	0.002
NABN	1.372	1.247	1.371	110.990	111.017	177.029	17.310	17.456
AABN	1.335	1.256	1.387	112.983	110.214	178.348	28.073	1.443
HAB	1.363	1.250	1.371	112.617	110.521	179.977	0.000	0.000
DAAB	1.354	1.251	1.377	114.051	110.313	178.572	3.619	11.770
Cis								
AB	1.388	1.241	1.394	124.968	125.106	4.177	174.100	41.778
MAB	1.388	1.242	1.389	125.213	124.797	4.325	38.974	172.064
TAB	1.396	1.242	1.385	123.633	125.136	5.047	30.556	162.301
FAB	1.401	1.240	1.381	123.688	125.152	4.455	34.980	170.638
CAB	1.406	1.240	1.378	122.731	125.449	4.896	28.942	163.940
AAB	1.398	1.246	1.385	120.444	123.954	5.506	173.915	65.615
AABA	1.405	1.250	1.359	118.934	125.204	4.309	178.407	69.820
NAB	1.447	1.235	1.363	119.393	126.303	4.482	8.800	141.721
NABN	1.439	1.234	1.371	119.782	124.781	0.789	179.683	87.133
AABN	1.370	1.242	1.441	122.171	118.189	8.684	145.111	50.788
HAB	1.399	1.243	1.384	121.279	124.315	5.426	173.302	60.311
DAAB	1.396	1.246	1.386	121.128	123.942	4.423	172.030	59.566

Table 3. Calculated sum of electronic and thermal energy (E), sum of electronic and thermal enthalpy (H), sum of electronic and thermal free energy (G) and equilibrium constant (K) at B3LYP/6-311++G(d, p) for the most stable configurations of the compounds

Compound	E (a.u.)	ΔE (kcal/mol)	H (a.u.)	ΔH (kcal/mol)	G (a.u.)	ΔG (kcal/mol)	*K*
*T-AB	-624.6809	-12.968	-624.6791	-13.025	-624.7694	-13.230	7.302×10^{9}
*C-AB	-624.6602		-624.6583		-624.7483		
T-MAB	-663.9586	-11.703	-663.9567	-11.696	-664.0536	-11.594	4.404×10^{8}
C-MAB	-663.9400		-663.9381		-664.0351		
T-TAB	-781.7487	-8.797	-781.7468	-8.790	-781.8587	-8.203	1.306×10^{6}
C-TAB	-781.7347		-781.7328		-781.8456		
T-FAB	-723.9474	-11.420	-723.9456	-11.483	-724.0399	-11.588	4.356×10^{8}
C-FAB	-723.9292		-723.9273		-724.0214		
T-CAB	-1084.3060	-10.757	-1084.3041	-10.750	-1084.4009	-10.950	1.458×10^{8}
C-CAB	-1084.2889		-1084.2870		-1084.3835		
T-AAB	-680.0340	-17.548	-680.0321	-17.541	-680.1280	-18.079	3.012×10^{13}
C-AAB	-680.0060		-680.0041		-680.0992		
T-AABA	-735.3861	-16.545	-735.3842	-16.537	-735.4856	-17.033	5.001×10^{12}
C-AABA	-735.3597		-735.3578		-735.4585		
T-NAB	-829.1945	-7.489	-829.1926	-7.482	-829.2930	-5.961	2.783×10^{4}
C-NAB	-829.1826		-829.1807		-829.2835		

Table 3. Continued

T-NABN	-1033.7180	-7.206	-1033.7161	-7.199	-1033.8298	-6.729	1.040×10^{5}
C-NABN	-1033.7065		-1033.7046		-1033.8191		
T-AABN	-884.5537	-13.728	-884.5518	-13.721	-884.6590	-15.002	1.530×10^{11}
C-AABN	-884.5318		-884.5299		-884.6351		
T-HAB	-699.9178	-10.400	-699.9159	-10.393	-700.0108	-11.465	3.527×10^{8}
C-HAB	-699.9012		-699.8993		-699.9925		
T-DAAB	-758.5386	-12.363	-758.5367	-12.355	-758.6436	-11.966	8.341×10^{8}
C-DAAB	-758.5189		-758.5170		-758.6245		

*T: Trans configuration, C: Cis configuration

Table 4. Calculated dipole moments μ (Debye), mean, and anisotropic polarizabilies α (a.u.) of the molecules obtained from B3LYP/6-311++G(d,p) computations

Compound	μ	$\Delta\mu$	α_{mean}	$\Delta\alpha$ mean	α_{anis}	$\Delta\alpha$ anis
*T-AB	0.0044	4.8840	61.8909	26.9167	94.3244	65.4516
*C-AB	4.8884		34.9742		28.8728	
T-MAB	1.2419	4.8282	67.8330	32.1302	108.6438	79.3625
C-MAB	6.0701		35.7028		29.2813	
T-TAB	2.1772	4.2801	48.6266	14.4829	60.1153	30.3259
C-TAB	6.4573		34.1437		29.7894	
T-FAB	1.0640	2.3039	49.0844	12.9813	66.5317	49.3124
C-FAB	3.3679		36.1031		17.2193	
T-CAB	0.2793	3.8307	51.1321	14.6588	69.0130	44.5959
C-CAB	4.1100		36.4733		24.4171	
T-AAB	2.1249	4.6045	76.3162	47.4819	115.0606	98.7473
C-AAB	6.7294		28.8343		16.3133	
T-AABA	0.0023	8.4386	91.9245	48.2786	127.6884	105.4112
C-AABA	8.4409		43.6459		22.2772	
T-NAB	2.5634	-1.6633	44.6734	2.6204	52.6934	40.8520
C-NAB	0.9001		42.0530		11.8414	
T-NABN	0.6813	1.0336	25.3171	3.0918	22.3731	9.4839
C-NABN	1.7149		22.2253		12.8892	
T-AABN	5.0290	-1.6461	55.8905	20.3544	70.3063	56.2083
C-AABN	3.3829		35.5361		14.0980	
T-HAB	2.1718	2.7701	66.4754	39.3174	101.8720	79.4313
C-HAB	4.9419		27.1580		22.4407	
T-DAAB	3.5634	3.2093	55.5901	26.8085	51.8439	42.3566
C-DAAB	6.7727		28.7816		9.4873	

*T: Trans configuration, C: Cis configuration

Table 5.HOMO/LUMO energies, electronegativities (χ), chemical potentials (μ), chemical hardnesses (η) and electrophilicity indexes of the molecules obtained from B3LYP/6-311++G (d, p) computations

Compound	HOMO (eV)	LUMO (eV)	GAP (eV)	χ (eV)	μ (eV)	η (eV)	ω (eV)
*T-AB	-9.0947	-4.3816	4.7131	6.7382	-6.7382	2.3565	9.633
*C-AB	-8.9292	-4.1710	4.7582	6.5501	-6.5501	2.3791	9.017
T-MAB	-8.8476	-4.1432	4.7044	6.4954	-6.4954	2.3522	8.968
C-MAB	-8.7921	-4.0055	4.7866	6.3988	-6.3988	2.3933	8.554
T-TAB	-8.6664	-4.0107	4.6557	6.3386	-6.3386	2.3278	8.630
C-TAB	-8.7352	-3.9326	4.8026	6.3339	-6.3339	2.4013	8.353
T-FAB	-9.1714	-4.4216	4.7498	6.7965	-6.7965	2.3749	9.725
C-FAB	-9.1042	-4.3201	4.7841	6.7122	-6.7122	2.3920	9.417

Table 5. Continued

T-CAB	-9.0525	-4.3473	4.7052	6.6999	-6.6999	2.3526	9.540
C-CAB	-9.0606	-4.2703	4.7903	6.6655	-6.6655	2.3951	9.275
T-AAB	-7.5529	-3.6232	3.9297	5.5881	-5.5881	1.9648	7.946
C-AAB	-7.9420	-4.0241	3.9179	5.9831	-5.9831	1.9590	9.137
T-AABA	-7.7197	-3.6766	4.0431	5.6982	-5.6982	2.0216	8.031
C-AABA	-7.6563	-3.7021	3.9542	5.6792	-5.6792	1.9771	8.157
T-NAB	-9.2092	-4.8181	4.3911	7.0137	-7.0137	2.1956	11.202
C-NAB	-9.4786	-4.7416	4.7370	7.1101	-7.1101	2.3685	10.672
T-NABN	-9.8256	-5.2556	4.5700	7.5406	-7.5406	2.2850	12.442
C-NABN	-9.6794	-5.1789	4.5005	7.4292	-7.4292	2.2502	12.264
T-AABN	-8.2122	-4.5256	3.6866	6.3689	-6.3689	1.8433	11.003
C-AABN	-8.3376	-4.7386	3.5990	6.5381	-6.5381	1.7995	11.877
T-HAB	-8.8212	-4.0524	4.7688	6.4368	-6.4368	2.3844	8.688
C-HAB	-8.6179	-4.0197	4.5982	6.3188	-6.3188	2.2991	8.683
T-DAAB	-7.4606	-3.7759	3.6847	5.6183	-5.6183	1.8426	8.566
C-DAAB	-7.2777	-3.8923	3.3854	5.5850	-5.5850	1.6927	9.214

*T: Trans configuration, C: Cis configuration

Table 6. HOFs, predicted densities and detonation properties of the molecules

Structures	OB_{100}	HOF (kJ/mol)	Q (kJ/g)	V* (cm^3/mol)	ρ (g/cm^3)	D (km/s)	P (GPa)
T-AB	-48.18	762.768	1097.895	109.598	1.515	7.238	20.829
C-AB	-48.18	818.902	1178.692	99.353	1.671	7.871	26.255
T-MAB	-71.07	568.397	754.445	122.367	1.471	6.473	16.328
C-MAB	-71.07	618.749	821.278	101.031	1.782	7.530	25.000
T-TAB	-122.46	98.587	106.084	131.837	1.685	4.318	7.945
C-TAB	-122.46	136.993	147.411	147.272	1.508	4.351	7.501
T-FAB	-39.12	604.885	785.535	118.201	1.557	6.290	16.018
C-FAB	-39.12	654.505	849.974	112.161	1.641	6.647	18.509
T-CAB	-36.00	767.280	916.866	113.939	1.755	6.805	20.231
C-CAB	-36.00	813.949	972.633	105.737	1.892	7.281	24.217
T-AAB	-48.60	734.059	968.976	123.101	1.471	7.022	19.215
C-AAB	-48.60	809.387	1068.410	114.509	1.581	7.549	23.307
T-AABA	-48.96	707.861	862.857	132.276	1.482	6.968	19.017
C-AABA	-48.96	778.679	949.181	111.364	1.761	8.021	28.162
T-NAB	-18.95	708.063	1273.102	116.770	1.807	8.388	31.286
C-NAB	-18.95	735.891	1304.618	142.584	1.480	7.369	21.655
T-NABN	0.00	652.174	1343.544	141.574	1.808	8.614	32.999
C-NABN	0.00	648.163	1339.800	143.945	1.779	8.511	31.904
T-AABN	-21.23	657.832	1159.282	118.228	1.912	8.587	34.538
C-AABN	-21.23	717.744	1222.628	133.395	1.695	7.998	27.348
T-HAB	-35.16	523.768	1263.480	96.011	1.896	9.044	37.407
C-HAB	-35.16	569.220	1323.153	102.405	1.778	8.744	33.663
T-DAAB	-88.00	478.482	546.932	146.397	1.428	6.578	16.515
C-DAAB	-88.00	531.979	608.082	153.056	1.366	6.564	15.935

*Average valu from 100 single-point volume calculations at the B3LYP/6-311++G(d,p) level.

Q: Heat of explosion, V: Volume of explosion, D: Velocity of detonation, P: Pressure of explosion.

CONCLUSIONS

This work studies the reactivity, stability and structural properties in the most stable cis and trans configurations of 5,5'-disubstituted-1,1'-azobis (tetrazoles). Our calculations show the following results:

a. The trans and cis configurations have planar and non-planar structures.

b. The trans configuration of all molecule is more stable than the cis.

c. The trans structures containing electron-donating groups have large negative thermal and electronic energy among all molecules.

d. The dipole moment of cis configuration for each compound is greater than the trans.

e. The lowest cis-trans dipole moment gap is related to the compounds containing electron-withdrawing groups.

f. The molecules containing electron-withdrawing and electron-donating substituents have the lowest and biggest mean and anisotropic polarizabilities, respectively.

g. The cis structures have more HOMO-LUMO energy gap than trans structures.

h. The molecules containing nitro and amino substituents have more reactivity among all compounds.

i. The molecules containing electron-withdrawing substituents have a good reactivity with nucleophiles, while the electron-donating groups cause the reactivity of molecules with electrophiles.

j. The chemical hardness and total energy of the structures are independent of each other.

k. The electrophilicity index of both cis and trans configurations increases when the stability increases.

l. The calculation of detonation performances of compounds showed the trans molecule containing hydroxyl substituent (T-HAB) is a powerful explosive as same the famous explosives HMX and RDX.

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REFERENCES

[1]. M. Mahkam, M. Nabati, A. Latifpour and J. Aboudi, Des. Monomers Polym.17, (2014) 453.

[2]. M. Mahkam, Z. Namazifar, M. Nabati and J. Aboudi, Iran.J. Org. Chem. 6, (2014)1217.

[3]. M. Nabati and M. Mahkam, Iran. Chem. Commun. 2, (2014) 164.

[4]. Y. Boland, D. A. Safin, B. Tinat, M. G. Babashkina, J. Marchand-Brynaert and Y. Garcia, New J. Chem. 37, (2013) 1174.

[5]. R. Sivabalan, M. Anniyappan, S. J. Pawar, M. B. Talawar, G. M. Gore, S. Venugopalan and Gandhe, J. Hazard. Mater.A137, (2006) 672.

[6]. H. A. Dabbagh, A. Najafi-Chermahini and S. Banibairami, Tetrahedron Lett. 47, (2006) 3929.

[7]. M. Nabati and M. Mahkam, J. Phys. Theor. Chem. IAU Iran 12, (2015) 33.

[8]. L. Mosca, R. S. Khnayzer, M. S. Lazroski, E. O. Danilov, F. N. Castellano and P. Anzenbacher Jr., Chem. Eur. J. 21, (2015) 4056.

[9]. H. M. Shim and K. K. Koo, Cryst. Growth Des.14, (2014) 1802.

[10]. X. Shi, J. Wang, X. Li, C. An, J. Wang and W. Ji, Defence Sci. J.65, (2015) 131.

[11]. D. Furman, R. Kosloff, F. Dubnikova, S. V. Zybin, W. A. Goddard, N. Rom, B. Hirshberg and Y. Zeiri, J. Am. Chem. Soc. 136, (2014) 4192.

[12]. Q. Zhang and J. M. Shreeve, Angew. Chem. Int. Ed. Engl.53, (2014)2540.

[13]. D. Kong, Y. Liu, J. Zhang, H. Li, X. Wang, G. Liu and Z. Xu, New J. Chem. 38, (2014)3078.

[14]. Y. C. Liu, K. T. Cheng, H. F. Chen and A. Y. G. Fuh, Opt. Express22,(2014) 4404.

[15]. V. Odent, M. G. Clerc, C. Falcón, U.

Bortolozzo, E. Louvergneaux and S. Residori, Opt. Lett.39, (2014) 1861.
[16]. J. Seo, J. W. Chung, J. E. Kwon and S. Y. Park, Chem. Sci. 5, (2014)4845.
[17]. R. Szabla, R. W. Gora, J. Sponer and J. E. Sponer, Chem. Eur. J.20, (2014) 2515.
[18]. B. Zietz, E. Gabrielsson, V. Johansson, A. M. El-Zohry, L. Sun and L. Kloo, Phys. Chem. Chem. Phys. 16, (2014)2251.
[19]. A. J. Gottle, F. Alary, I. M. Dixon, J. L. Heully and M. Boggio-Pasqua, Inorg.Chem.53,(2014) 6752.
[20]. H. Hashimoto, K. Kawamura, N. Igarashi, M. Takei, T. Fujishiro, Y. Aihara, S. Shimoi, M. Muto, T. Ito, K. Furutsuka, T. Yamasaki, J. Yui, L. Xie, M. Ono, A. Hatori, K. Nemoto, T. Suhara, M. Higuchi and M. R. Zhang, J. Nucl. Med.55, (2014) 1532.
[21]. F. F. Al-Blewi, H. A. Al-Lohedan, M. Z. A. Rafiquee and Z. A. Issa, J. Saudi Chem. Soc.18,(2014) 632.
[22]. J. Aboudi, Y. Bayat, Y. Abedi, M. Nabati and M. Mahkam, Iran. J. Chem. Chem. Eng. 34,(2015)In Press.
[23]. D. N. Tran, C. Battilocchio, S. B. Lou, J. M. Hawkins and S. V. Ley, Chem. Sci.6, (2015) 1120.
[24]. T. M. Klapotke and D. G. Piercey, Inorg. Chem. 50, (2011) 2732.
[25]. S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 58, (1980) 1200.
[26]. C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, (1988) 785.
[27]. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03. Revision B.01.Gaussian Inc. Wallingford. CT. (2004).
[28]. M. Nabati and M. Mahkam, Iran. Chem. Commun.2, (2014)129.
[29]. R. V. Eldik, T. Asano and W. J. L. Noble, Chem. Rev. 89, (1989)549.
[30]. M. Borkovec and G. J. M. Koper, Anal. Chem.72, (2000)3272.
[31]. M. Nabati and M. Mahkam, Iran. J. Org. Chem.6, (2014) 1397.
[32]. N. A. Wazzan, P. R. Richardson and A. C. Jones, Photochem. Photobiol. Sci. 9, (2010) 968.
[33]. R. Lindner, C. Wagner and D. Steinborn, J. Am. Chem. Soc.131, (2009)8861.
[34]. S.K. Yen, L.L. Koh, H.V. Huynh and T.S.A. Hor, Chem. Asian J.3, (2008)1649.
[35]. A. Dhiman, T. Muller, R. West and J.Y. Becker, Organometallics 23, (2004) 5689.
[36]. M. Nabati and M. Mahkam, Silicon (2015) published online.
[37]. M. Nabati and M. Mahkam, Iran. J.

Org. Chem. 6, (2014) 1331.

[38]. M. Mahkam, H. R. Kafshboran and M. Nabati, Des. Monomers Polym. 17, (2014)784.

[39]. Q. Wu, W. Zhu and H. Xiao, J. Mater. Chem.A2, (2014)13006.

[40]. C. Bian, M. Zhang, C. Li and Z. Zhou, J. Mater. Chem. A **2015,** 3, (2015) 163.

[41]. T. Sun, J. J. Xiao, Q. Liu, F. Zhao and H. M. Xiao, J. Mater. Chem.A2, (2014)13898.

[42]. P. Yin, J. Zhang, C. He, D. A. Parrish and J. M. Shreeve, J. Mater. Chem. A2, (2014) 3200.

[43]. M. J. Kamlet and S. J. Jacobs, J. Chem. Phys.48, (1968) 23.

[44]. Q. Wu, W. Zhu and H. Xiao, RSC Adv.4, (2014)3789.

[45]. T. Lu, Y. Yuan, X. He, M. Li, X. Pu, T. Xuand Z. Wen, RSC Adv.5, (2015) 13021.

[46]. D Chen, S. Huang, Q. Zhang, Q. Yu, X. Zhou, H. Li and J. Li, RSC Adv.5, (2015)32872.