DFT investigation of 1,1'-disubstituted-5,5'-azotetrazoles:a study of functional group effect

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Abstract: The idea behind most stable cis and trans configurations of an azo compound is photoisomerization of it under irradiation when non-polar trans configuration can be photoisomerized into the polar cis configuration. In the present study, the density functional theory (DFT) method with B3LYP exchange correlation corrected functional and the 6-311++G(d,p) basis set has been carried out to investigate the isomerization effect on the stability, reactivity and structural properties of 1,1'-disubstituted-5,5'-azotetrazoles. All computations were performed at 293.15 K and 1 atmosphere in gas phase. From our calculations, it is obtained that the trans configurations of all molecules are more stable than cis. Also, the dipole moment, chemical hardness (η), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) were calculated for all structures. The data shows that the stability oftrans and cis configurations have direct and indirect correlation with reactivity, respectively. The results also indicate that the trans and cis configurations of compounds have planar and non-planar structures, respectively.

Introduction

In recent years, the chemistry of nitrogen-rich compounds has received increasing attention [1-3]. One main group of nitrogen-rich compounds is related to the molecules containing tetrazole groups. A large number of tetrazole molecules have biological activity [4-7]. This group indicates as a stable isostere for the carboxylic acid [8]. And also, tetrazole compounds have high nitrogen content and can easily be oxygen balanced. Then, these high-nitrogen materials show energetic properties [9-11]. Because of the more nitrogen gas production per gramme after decomposition, they do not harm the environment [12]. So far, a great deal of tetrazole derivatives have been prepared and their properties were investigated both experimentally and theoretically [13-15].

Tetrazole based energetic compounds have good relationship between performance and sensitivity [16]. Fang Li and his coworkerssynthesized and characterized 1,1'-disubstituted-5,5'-azotetrazoles (substitutions: H, CH$_3$, tBu, Ph and NH$_2$) for the first time in 2012 [17]. The structure of compounds was studied by IR, NMR and X-ray crystallographic analyses. As we know, azo compounds have plenty of configurations but they show cis and trans configurations in the electronic ground state [18]. The trans configuration of an azo compound has more stability than the cis configuration [19]. These materials can undergo a reversible photoisomerization between cis and trans isomers [20]. Isomerization of the most stable configurations of azo compounds is carried out by excitation to the S$_1$ (n→π*) and the S$_2$ (π→π*) states [21]. These processes have been studied

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by UV-Vis absorption [22]. Synthesis, characterization

Optimized structures

Figure **1** indicates the structures of the 1,1'-disubstituted-5,5'-azotetrazoles presently considered.All considered compounds are presented in the Table **1**. The most stable cis and trans configurations of the molecules were optimized at B3LYP/6-311++G(d,p) level of theory. The structural data of the present compounds have been given in Table 2. The data of the three types of bonds in the present molecules, namely: C4-N6, N6-N7 and N7-C8 bonds are listed in Table **2**. As can be seen from the data, the C4-N6 and N7-C8 bonds lengths of cis configuration of each molecule are longer than the corresponding bonds lengths of the trans configuration. In contrast, the N6-N7 bond length of the trans configuration of molecules is longer than the corresponding bond length of thecis configuration of the compounds. The N6-N7 bond distance order of trans compounds is: AAB = AABA = AABN = HABH > MABM = TAB = HAB = AABH > MAB > AB > NAB > NABN. This bond distance order indicates that the electron withdrawing and electron donating groups reduce and increase the N6-N7 bond length, respectively. As for the cis form, the following order was found: AAB > MABM = TAB = AABA > MAB > AB = AABN = HAB = HABH > AABH > NAB > NABN. From this bond length order, it was found that the smallest N6-N7 bond is related to the nitro derivatives of 5,5'-azotetrazole.

It was obtained that the C4-N6-N7 and N6-N7-C8 angles for trans configuration of studied molecules are smaller than the cis configuration of them. In cis configurations, the tetrazole rings are near together and have high electrostatic repulsion. For this reason, the mentioned angles of cis molecules are grower.

From the data of the Table **2**, the C4-N6-N7-C8 torsion angles for cis configuration are in the following order: MABM > TAB > NABN > MAB > HABH > AAB > AB > AABH > HAB > NAB > AABN > AABA. It can be deduced that the compounds with electron-acceptor groups show high torsion angles, but the NH_2-substituted molecules present small angles because of the hydrogen bond between amino group of one tetrazole ring and nitrogen atom of another tetrazole ring. And also, it should be noted that planar structures were obtained for all optimized trans configurations.

Electronic properties

The computed thermal energies, enthalpies and Gibbs free energies for both the most stable trans and cis configurations of the molecules are given in Table **3**. Thermal energies differences (ΔE), enthalpy

and identification of the properties of these isomers are differences (ΔH) and Gibbs free energy differences (ΔG) were calculated and collected in the mentioned Table. As we know the compound with negative energy is stable. From the data of the Table **3**, trans configuration for each molecule is more stable than cis. The trans-cis stability order for molecules is: HABH > HAB = AAB > AB > MAB > TAB > MABM > AABH > AABA > AABN > NAB > NABN. It can be concluded that the trans-cis energy gap for compounds containing electron-withdrawing groups is smaller than the molecules containing electron-acceptor groups. The biggest and smallest energy gaps were found for HABH (-11.546 kcal/mol) and NABN (-5.71 kcal/mol) molecules, respectively.

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

$$K = e^{\frac{-\Delta G}{RT}}$$

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 data of the most stable trans and cis configurations of molecules is listed in Table 3. We can see the equilibrium constant range is 5.311×10^4-1.055×10^8. And also, the equilibrium constant order for molecules is: MABM > AABH > MAB > TAB > AABA > AB = AAB > HAB > NAB > HABH > AABN > NABN. The smallest equilibrium constant was found for NABN, and the biggest one for MABM. It can be deduced that the molecules containing electron-acceptor groups are more in trans state.

Polarizabilityis the ability for a molecule to be polarized. Polarizabilities determine the dynamical response of a bound system to external fields, and provide insight into a molecule's internal structure [31].Polarizability matrix components can be determined spectroscopically, but this data is poor because of a hard experimental procedure, especially for molecules with low or no symmetry [32]. For this reason, the quantum-mechanical modeling of molecules can help us in this study [33]. The dipole moments mean and anisotropic polarizabilities for most stable configurations of the molecules are calculated and listed in Table **4**. The dipole moment of molecule was obtained by following formula [34]:

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

Where p_0 is adipole moment without an electric field, α is a polarizability second-order tensor, β is the first in

difficult and expensive [23]. For this reason, molecular modeling of them could study the structures with their properties in a short time [24]. In the present study, the effect of various substituents were investigated on the stability, reactivity and structural properties of the 5,5'-azotetrazoles.
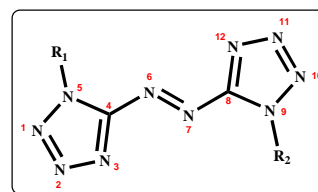
Results and discussion

Optimized structures
Figure **1** indicates the structures of the 1,1'-disubstituted-5,5'-azotetrazoles presently considered.

Figure 1: Structure of studied 1,1'-disubstituted-5,5'-azotetrazoles with atomic numbering.

All considered compounds are presented in the Table **1**.

Table 1: Studied molecules and their IUPAC names.

	R_1	R_2	IUPAC name
AB	H	H	1,2-di(1H-tetrazol-5-yl)diazene
MAB	CH_3	H	(E)-1-(1-methyl-1H-tetrazol-5-yl)-2-(1H-tetrazol-5-yl)diazene
MABM	CH_3	CH_3	1,2-bis(1-methyl-1H-tetrazol-5-yl)diazene
TAB	tBu	H	(E)-1-(1-tert-butyl-1H-tetrazol-5-yl)-2-(1H-tetrazol-5-yl)diazene
AAB	NH_2	H	(E)-1-(1-amine-1H-tetrazol-5-yl)-2-(1H-tetrazol-5-yl)diazene
AABA	NH_2	NH_2	1,2-bis(1-amine-1H-tetrazol-5-yl)diazene
NAB	NO_2	H	(E)-1-(1-nitro-1H-tetrazol-5-yl)-2-(1H-tetrazol-5-yl)diazene
NABN	NO_2	NO_2	1,2-bis(1-nitro-1H-tetrazol-5-yl)diazene
AABN	NH_2	NO_2	(E)-1-(1-amine-1H-tetrazol-5-yl)-2-(1-nitro-1H-tetrazol-5-yl)diazene
HAB	OH	H	(E)-1-(1-hydroxy-1H-tetrazol-5-yl)-2-(1H-tetrazol-5-yl)diazene
HABH	OH	OH	1,2-bis(1-hydroxy-1H-tetrazol-5-yl)diazene
AABH	NH_2	OH	(E)-1-(1-amine-1H-tetrazol-5-yl)-2-(1-hydroxy-1H-tetrazol-5-yl)diazene

The most stable cis and trans configurations of the molecules were optimized at B3LYP/6-311++G(d,p) level of theory. The structural data of the present compounds have been given in Table 2. The data of the three types of bonds in the present molecules, namely: C4-N6, N6-N7 and N7-C8 bonds are listed in Table **2**.

Table 2: Bond lengths (Aº), 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.

	N6-C4	N6-N7	N7-C8	C4-N6-N7	N6-N7-C8	C4-N6-N7-C8	N6-N7-C8-N9	N7-N6-C4-N5
Trans								
AB	1.390	1.259	1.390	114.001	114.001	179.996	179.996	179.995
MAB	1.386	1.260	1.391	114.468	113.769	180.000	179.995	179.992
MABM	1.387	1.261	1.387	114.217	114.216	179.971	179.930	179.942
TAB	1.387	1.261	1.391	114.316	113.540	179.982	179.939	179.900
AAB	1.376	1.262	1.390	115.477	113.620	178.836	178.691	177.941
AABA	1.377	1.262	1.391	115.588	112.780	178.295	176.361	177.776
NAB	1.393	1.258	1.389	112.870	114.193	175.635	178.663	158.351
NABN	1.395	1.256	1.395	112.980	112.980	172.077	156.574	156.575
AABN	1.373	1.262	1.391	115.614	112.525	174.939	161.262	178.013
HAB	1.384	1.261	1.390	113.541	114.059	180.000	180.000	179.998
HABH	1.384	1.262	1.384	113.569	113.565	179.994	179.998	180.000
AABH	1.391	1.261	1.385	113.225	113.558	179.552	179.010	178.866
Cis								
AB	1.405	1.252	1.405	121.753	121.756	13.484	147.712	147.678
MAB	1.402	1.253	1.406	121.950	121.530	13.961	145.129	150.928

MABM	1.403	1.254	1.403	121.650	121.650	14.496	148.111	148.144
TAB	1.405	1.254	1.408	121.250	121.522	14.410	144.276	148.249
AAB	1.390	1.256	1.403	123.627	121.934	13.585	144.359	164.808
AABA	1.392	1.254	1.410	125.142	123.204	1.977	69.636	168.003
NAB	1.414	1.248	1.402	122.219	121.197	9.741	165.650	115.957
NABN	1.408	1.246	1.408	120.929	120.928	14.102	143.959	143.926
AABN	1.386	1.252	1.413	122.395	121.734	8.898	110.543	172.911
HAB	1.404	1.252	1.404	121.749	121.930	13.389	152.054	145.956
HABH	1.403	1.252	1.403	121.735	121.732	13.734	149.924	149.983
AABH	1.408	1.250	1.405	121.020	121.138	13.412	152.060	137.041

As can be seen from the data, the C4-N6 and N7-C8 bonds lengths of cis configuration of each molecule are longer than the corresponding bonds lengths of the trans configuration. In contrast, the N6-N7 bond length of the trans configuration of molecules is longer than the corresponding bond length of the cis configuration of the compounds. The N6-N7 bond distance order of trans compounds is: AAB = AABA = AABN = HABH > MABM = TAB = HAB = AABH > MAB > AB > NAB > NABN. This bond distance order indicates that the electron withdrawing and electron donating groups reduce and increase the N6-N7 bond length, respectively. As for the cis form, the following order was found: AAB > MABM = TAB = AABA > MAB > AB = AABN = HAB = HABH > AABH > NAB > NABN. From this bond length order, it was found that the smallest N6-N7 bond is related to the nitro derivatives of 5,5'-azotetrazole.

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Electronic properties

The computed thermal energies, enthalpies and Gibbs free energies for both the most stable trans and cis configurations of the molecules are given in Table **3**.

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	-624.5990	-10.040	-624.5971	-10.040	-624.6885	-10.103	3.406×10^7
C-AB	-624.5830		-624.5811		-624.6724		
T-MAB	-663.8594	-9.915	-663.8575	-9.915	-663.9574	-10.417	5.836×10^7
C-MAB	-663.8436		-663.8417		-663.9408		
T-MABM	-703.1191	-9.475	-703.1178	-9.852	-703.2271	-10.919	1.055×10^8
C-MABM	-703.1040		-703.1021		-703.2097		
T-TAB	-781.6405	-9.789	-781.6386	-9.789	-781.7546	-10.291	4.705×10^7
C-TAB	-781.6249		-781.6230		-781.7382		
T-AAB	-679.8876	-10.730	-679.8857	-10.730	-679.9830	-10.103	3.406×10^7
C-AAB	-679.8705		-679.8686		-679.9669		
T-AABA	-735.1745	-7.907	-735.1726	-7.907	-735.2783	-10.228	4.225×10^7
C-AABA	-735.1619		-735.1600		-735.2620		
T-NAB	-829.0381	-6.526	-829.0362	-6.526	-829.1426	-7.342	2.977×10^5
C-NAB	-829.0277		-829.0258		-829.1309		
T-NABN	-1033.4771	-5.710	-1033.4752	-5.710	-1033.5964	-6.338	5.311×10^4

C-NABN	-1033.4680		-1033.4661		-1033.5863		
T-AABN	-884.3272	-6.714	-884.3253	-6.714	-884.4379	-7.091	1.935×10^5
C-AABN	-884.3165		-884.3146		-884.4266		
T-HAB	-699.7496	-10.730	-699.7477	-10.730	-699.8426	-8.534	2.305×10^6
C-HAB	-699.7325		-699.7306		-699.8290		
T-HABH	-774.9003	-11.546	-774.8984	-11.546	-774.9969	-7.216	2.400×10^5
C-HABH	-774.8819		-774.8800		-774.9854		
T-AABH	-755.0346	-8.095	-755.0327	-8.032	-755.1419	-10.668	8.980×10^7
C-AABH	-755.0217		-755.0199		-755.1249		

Thermal energies differences (ΔE), enthalpy differences (ΔH) and Gibbs free energy differences (ΔG) were calculated and collected in the mentioned Table. As we know the compound with negative energy is stable. From the data of the Table **3**, trans configuration for each molecule is more stable than cis. The trans-cis stability order for molecules is: HABH > HAB = AAB > AB > MAB > TAB > MABM > AABH > AABA > AABN > NAB > NABN. It can be concluded that the trans-cis energy gap for compounds containing electron-withdrawing groups is smaller than the molecules containing electron-acceptor groups. The biggest and smallest energy gaps were found for HABH (-11.546 kcal/mol) and NABN (-5.71 kcal/mol) molecules, respectively.

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

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data of the most stable trans and cis configurations of molecules is listed in Table **3**. We can see the equilibrium constant range is 5.311×10^4-1.055×10^8. And also, the equilibrium constant order for molecules is: MABM > AABH > MAB > TAB > AABA > AB = AAB > HAB > NAB > HABH > AABN > NABN. The smallest equilibrium constant was found for NABN, and the biggest one for MABM. It can be deduced that the molecules containing electron-acceptor groups are more in trans state.

Polarizabilityis the ability for a molecule to be polarized. Polarizabilities determine the dynamical response of a bound system to external fields, and provide insight into a molecule's internal structure [31]. Polarizability matrix components can be determined spectroscopically, but this data is poor because of a hard experimental procedure, especially for molecules with low or no symmetry [32]. For this reason, the quantum-mechanical modeling of molecules can help us in this study [33]. The dipole moments mean and anisotropic polarizabilities for most stable configurations of the molecules are calculated and listed in Table **4**.

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

Compound	μ	Δμ	α_{mean}	Δα mean	α_{anis}	Δα anis
T-AB	0.0002	4.9697	158.5455	19.7518	419.9407	237.3576
C-AB	4.9699		138.7937		182.5831	
T-MAB	1.0584	4.4520	179.4502	48.6721	472.6639	320.4815
C-MAB	5.5104		130.7781		152.1824	
T-MABM	0.0181	5.7343	305.1748	149.3684	835.6009	665.9224
C-MABM	5.7524		155.8064		169.6785	
T-TAB	1.8714	3.8238	164.4377	44.7703	415.8979	302.5408
C-TAB	5.6952		119.6674		113.3571	
T-AAB	1.0995	5.7280	152.8427	28.1385	267.8077	194.2757
C-AAB	6.8275		124.7042		73.5320	
T-AABA	2.0278	5.0541	283.3187	213.0292	635.5657	559.2429
C-AABA	7.0819		70.2895		76.3228	
T-NAB	3.0764	2.0023	129.1354	62.9303	215.5499	112.7095
C-NAB	5.0787		66.2051		102.8404	
T-NABN	1.3131	0.7120	38.8550	-20.0209	11.6646	-105.5626
C-NABN	2.0251		58.8760		117.2272	
T-AABN	3.9622	2.6146	145.1431	70.2512	220.0799	155.0988

C-AABN	6.5768		74.8919		64.9811	
T-HAB	1.8511	3.6086	1851.9531	1660.9634	5501.6416	5418.5839
C-HAB	5.4597		190.9897		83.0577	
T-HABH	0.0013	5.6393	2182.6912	1957.2972	6487.9430	6407.8755
C-HABH	5.6406		225.3940		80.0675	
T-AABH	0.7291	4.2075	438.1225	212.1795	1210.1921	1049.6356
C-AABH	4.9366		225.9430		160.5565	

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

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

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. As expected, the dipole moment of cis configuration for each compound was found to be greater than trans. The cis-trans dipole moment gap order is: MABM > AAB > HABH > AABH > AB > MAB > AABH > TAB > HAB > AABN > NAB > NABN. We can observe that the lowest dipole moment gaps between most stabecis and trans configurations of the molecules are 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 [35]:

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

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

Where α_{xx}, α_{yy}, α_{zz} are diagonal elements of polarizability matrix. The lowest and biggest mean and anisotropic polarizabilities have been obtained for the NABN and HABH molecules, respectively.

Molecular properties

Frontier molecular orbital (FMO) theoryis an application of molecular orbital (MO) theorydescribingHOMO-LUMOinteractions. This theory is very important in describing the reactivity of molecules [36]. Computed frontier orbitals energies for most stable cis and trans configurations of molecules are collected in Table **5**.

Table 5: HOMO/LUMO energies, electronegativities (χ), chemical potentials (μ), chemical hardnesses (   ) 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)	(eV)	ω (eV)
T-AB	-8.1292	-4.3321	3.7971	6.2307	-6.2307	1.8986	10.224
C-AB	-8.0639	-4.1960	3.8679	6.1300	-6.1300	1.9340	9.715
T-MAB	-7.9866	-4.1786	3.8080	6.0826	-6.0826	1.9040	9.716
C-MAB	-7.8954	-4.0322	3.8632	5.9638	-5.9638	1.9316	9.207
T-MABM	-7.8544	-4.0325	3.8219	5.9435	-5.9435	1.9110	9.243
C-MABM	-7.7357	-3.8790	3.8567	5.8074	-5.8074	1.9284	8.745
T-TAB	-7.7978	-4.0461	3.7517	5.9220	-5.9220	1.8759	9.348
C-TAB	-7.7569	-3.8826	3.8743	5.8198	-5.8198	1.9372	8.742
T-AAB	-8.0595	-4.2439	3.8156	6.1517	-6.1517	1.9078	9.918
C-AAB	-7.8456	-4.0948	3.7508	5.9702	-5.9702	1.8754	9.503
T-AABA	-7.8769	-4.0763	3.8006	5.9766	-5.9766	1.9003	9.398
C-AABA	-7.9776	-4.0423	3.9353	6.0100	-6.0100	1.9677	9.178
T-NAB	-8.4555	-4.7267	3.7288	6.5911	-6.5911	1.8644	11.651
C-NAB	-8.5561	-4.4611	4.0950	6.5086	-6.5086	2.0475	10.345
T-NABN	-8.8040	-5.0622	3.7418	6.9331	-6.9331	1.8709	12.846
C-NABN	-8.8710	-4.9030	3.9680	6.8870	-6.8870	1.9840	11.953
T-AABN	-8.3131	-4.6295	3.6836	6.4713	-6.4713	1.8418	11.369
C-AABN	-8.4443	-4.3182	4.1261	6.3813	-6.3813	2.0631	9.869
T-HAB	-8.0451	-4.2328	3.8123	6.1435	-6.1435	1.9062	9.900
C-HAB	-8.0696	-4.1827	3.8869	6.1262	-6.1262	1.9435	9.655
T-HABH	-7.9705	-4.1370	3.8335	6.0538	-6.0538	1.9168	9.560

C-HABH	-8.0740	-4.1691	3.9049	6.1216	-6.1216	1.9525	9.597
T-AABH	-7.8378	-4.0583	3.7795	5.9481	-5.9481	1.8898	9.361
C-AABH	-7.9648	-3.9732	3.9916	5.9690	-5.9690	1.9958	8.926

The HOMO/LUMO energies gap for cis configuration of compounds is greater than trans. The highest HOMO energy value is related to the both cis and trans configurations of the NABN compound. And also, chemical hardness (η), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) are calculated and collected in Table 5 for both most stable configurations of considered compounds. We can study the correlation between molecular properties and chemical quantities by mentioned parameters. The η, μ, χ and ω parameters are obtained by following formulas [37]:

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

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

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

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

It can be seen from the data of the Table 5, the chemical hardness of trans systems decreases in the following order: HABH > MABM > AAB > HAB > MAB > AABA > AB > AABH > TAB > NABN > NAB > AABN. And also, the chemical hardness order for cis molecules is: AABN > NAB > AABH > NABN > AABA > HABH > HAB > TAB > AB > MAB > MABM > AAB. It is deduced that the trans-HABH and cis-AABN molecules are the least reactive among the presented molecules. The trans-AABN and cis-AAB are more reactive than other compounds. From our calculations, the trans configurations have more reactivity than cis. It means that compounds tend to move from cis form to trans form.
Figure **2** shows the correlation between chemical hardness (η) and total energy (E) of the cis and trans configurations of 1,1'-disubstituted-5,5'-azotetrazoles.
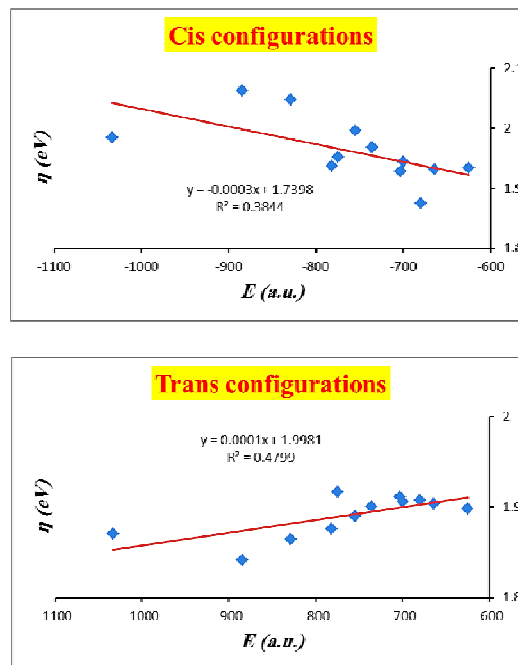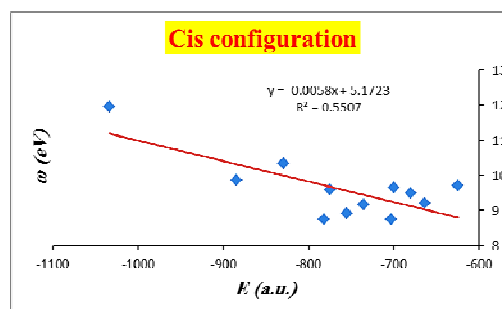

Figure 2: Correlation between chemical hardness and total energy of studied 1,1'-disubstituted-5,5'-azotetrazoles.

It can be seen that the reactivity of molecules decreases with increasing the stability in cis configurations. In contrast, the reactivity of trans configurations increases with increasing the stability of molecules.
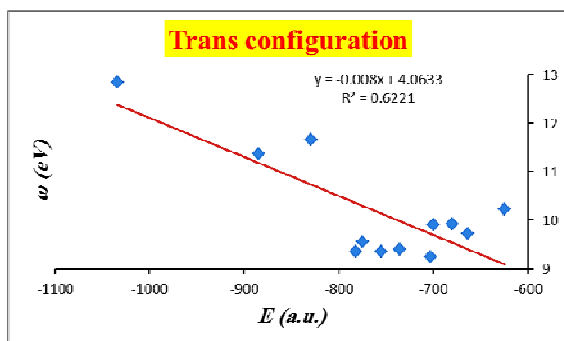The correlation between electrophilicity index and total energy of the studied molecules is shown in Figure **3**.

Figure 3: Correlation between electrophilicity index and total energy of studied 1,1'-disubstituted-5,5'-azotetrazoles.

We can see the electrophilicity index of both configurations increases with increasing the stability of compounds

Conclusions

In the present work, I performed a theoretical study on stability and reactivity of most stable cis and trans configurations of 1,1'-disubstituted-5,5'-azotetrazoles. The results indicate that the trans systems have planar structures. In contrast, the tetrazole rings of cis structures have dihedral angles about 10-15 degree. The structure of both configurations of all compounds is asymmetric. From the total energies data, it deduced that the stability for trans configurations is more than cis. The reactivity of trans and cis structures increases and decreases respectively, when the stability of compounds increases. And also, the electrophilicity property of both cis and trans configurations increases with increasing the stability of molecules.We can see the molecules containing withdrawing substituents have small trans-cis energy gaps and dipole moment gaps to the compounds with electron-donation groups.

Acknowledgments

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