RESEARCH ARTICLE

Calculation of Stabilization Energy of Tetrahedrane with its Nitrogen Substituted Derivatives by DFT Method and Driving an Empirical Relation Connect it with Charge Functions of the Molecule

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Abstract

In this work the strain energy of tetrahedrane and its nitrogen substituted molecules were calculated by isodesmic reaction method according to DFT quantum chemical fashion, the used basis set was 6-31G/B3-LYP, in addition all structures were optimized by RM1 semi-empirical method. From the obtained data we estimate an empirical equation connect between strain energy of the molecule with charge functions represented by dipole moment of the molecule plus accumulated charge density involved within the tetrahedron frame plus the number of nitrogen atoms. The results indicate the charge spreading factors by polarization and $n \rightarrow \sigma^*$ processes are the most important factors in decreasing the strain energy.

Keywords: *Tetrahedrane, Azaetrahedranes, Isodesmic reaction, Strain energy.*

Introduction

In many pharmaceutical compounds the medicinal activity attributed to the angular strain property that exist in its structure, an example for antibiotics are penicillin and cephalosporin family of antibiotics [1], which their activity comes from the opening of the beta lactam square ring inside the organism cell which disable [2]. Further one of the mechanisms of the deactivation of these antibiotics by the drug resistant bacteria is due to their ability to release beta lactamase enzyme which open the four membered rings outside the bacteria body [3]. Another example is the azirdine ring that exists in many antiviral and anticancer drugs which disturb the DNA synthesis in the targeted cells [4, 5].

The tetrahedrane system is one of the basic stereotactic systems [6]. It represents the simplest alicyclic organic compound, therefore occupies an exceptional importance in the field of structure and stability in the studying the geometry of these compounds. When carbon atoms occupy the corners of tetrahedral system obtain geometrical structure of particularly interest. The t-butyle alkylated derivative of the tetrahedrane compound was prepared by

Maier et al in 1978 [7], the resulting tetrahedrane is a multiple negative ion and is one of the few examples available for this active structure, also there are some derivatives are prepared and have a considerable degree of stability [6]. Furthermore, the mass spectrometry studies of some compounds suggest the formation of tetrahedrane systems as intermediate products [8]. In the past two decades, many unusual chemical structures in the outer space have been spectrally detected [9]. The presence of such structures has been identified as a shock and a motive for the re-reviewing of the formulas and theories of chemical bonding.

The structure of the nitrogen tetrahedrane (tetrazatetrahedrane) until these days represent a hypothetical unstable compound[10], but if we compare with other elements in the same group in periodic table we found phosphorous, arsenic and antimony can form this structure at least in the gaseous phase. It is probable to find this compound in the outer space extreme environment of low pressure and ionizing radiation [11]. Some sources [12] indicate that the stability of these elements in the

formation tetrahedral geometry is due to presence of d orbital, which works to increase the spread of the charge, which reduces the severity of dissonance and thus increase the stability [13]. As with the azatetrahedrane molecule, the nitrogen derivatives of the tetrahedral molecules are all hypothetical. Thus, the theoretical study of these structures is a rich field that contributes to the interpretation of the structure, stability and probability of such compounds.

The calculation of stability or energy functions in the Isodesmic reaction method is one of the tools adopted in the field of theoretical calculations. The essence of the effectiveness of this method is to eliminate potential errors or approximations by measuring the difference in a given characteristic when present in an environment and in the absence of such an environment [14].

Method of Calculation

In this research, a computer of the type of hp with processor Intel® core™ i5/1.7 GHz. was used. For building molecular geometries, geometry optimization, energy calculations we used HyperChem package version: (8.0.8 for Windows Modeling System). The calculation steps used in this program are as follows:

- The structure of the studied molecules was built using the HyperChem graphical user interface (GUI) according to the building tools adopted in the program.

- The geometry of the built molecules was determined by geometry optimization based on the use of the Polak-Ribiere (Conjugate gradient) algorithm and on the RMS gradient 0.1 Kcal / mol. The computational method used to optimize molecular geometry was RM1 to all molecules all calculations were carried out in the vacuum, the total charge for each molecule is 0 and the spin multiplicity = 1 and the convergence limit in the stand-alone domain accounts = 0.01. The values of the molecular geometry parameters of the molecules studied are shown in table [1]. Molecular geometry organized by route the previous procedure for calculating energy variables according to the method of DFT where the settings adopted in energy calculations are as follows: The orbital basis set function used is 3-21G with B3-LYP as an exchange correlation potential. The chosen basis function in this work was mentioned as the most practical basis function for this type of molecules in the [15] which were carried out by ab-initio method.

- The angular strain energy was calculated according to the isodesmic reactions method of the tertiary group of agencies:
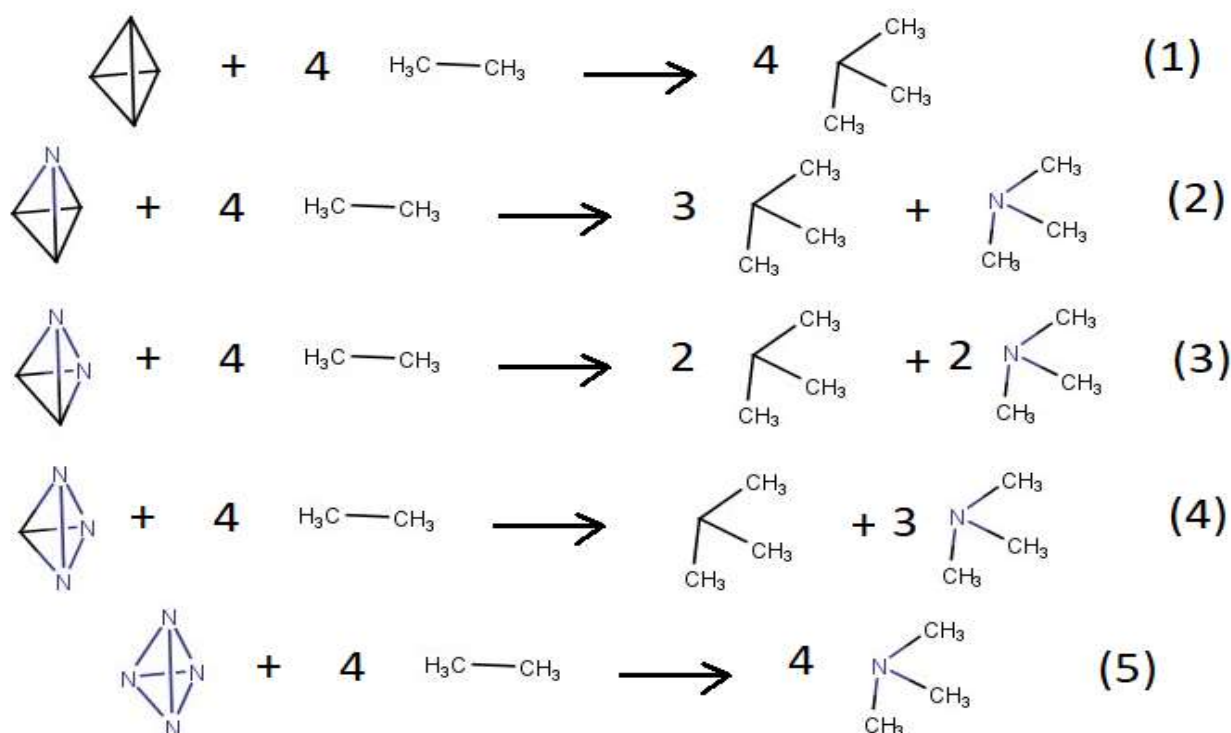
Discussion

Table [1] shows the molecular geometry parameters of the studied molecules (lengths and angles values), where it is observed the length of the C-H bond is increasing with increasing number of nitrogen atoms in these compounds, for C-C bonds there is a decrease in bond length as well as C-N and N-N bonds with increasing N atoms. These results show that the increase in the number of nitrogen atoms within the group of studied compounds reduces the length of bonds in these compounds due to the raising the effect of electronegativity factor in addition to the small atomic radius of nitrogen in comparison with carbon atom.

In [16] the bond lengths which calculated in several levels of DFT and ab-initio methods are close to the calculated geometry parameters in this work that calculatd by RM1 semiemperical method for tetrahedrane molecule. As expected all internal angles of the tetrahedran molecule were 60^0 reflecting the state of high symmetry of the stable state of the tetrahedrane molecule. This continues even in the azatetrahedrane compound, since in the flat triangle of carbon atoms the angle value of this triangle remains 60^0, this is the same case in a compound triazatethedhedrane in its ground state in the plane of nitrogen atoms.

In the state of internal angle of N-C-C or N-N-C they are slightly deviated from the value of 60^0 as a result of the symmetry breaking in the molecules that included these types of angles. External angles H-C-C and H-C-N show a general pattern of the behavior which is increasing their values by increasing the content of nitrogen atoms in the compound which can be attributed to the presence of loan pair on the nitrogen atom so the electrostatic repulsion that taking place

among those electronic centers in addition to bond charges act to increase the value of external bond angles in order to reduce the repulsion potential. In the calculating the energy functions of the studied molecules, the useful information about stability can be derived from the value of strain energy calculated according to the isodesmic reaction method, where the stability of the compound increased with raising nitrogen content in the compounds from tetrahydrane to triazetetrahedrane, this can be attributed to contribution of $n \rightarrow \sigma^*$ excitation in reducing the high electron density within the tetrahedral frame [15], in addition, the presence of the nitrogen atom with its loan pair causes a highly degree of polarization represented by increasing the value of the dipole moment as shown in Table (2). By moving from diazetetrahedrane to triazatetrahedrane we note that the change in the value of the dipole moment was not significant, but rather a slight decrease in value.

This is because the polarization of the bonds in the molecule worked against each other. In the case of tetraazatetrahedrane, the effect of contrast among the dipoles in the molecule reached a value close to zero. The relation of strain energy of the molecules with the dipole moment is shown in Figure (1).

To estimate the factor of increasing electropositive charge density in the tetrahedral frame on the strain energy we used the length of the external C-H bond as a parameter. As we mentioned previously, this bond increases by increasing the number of nitrogen atoms in the compound, although it is a slight increase, but it is almost constant as shown in Figure (2), by assuming that the interference between hydrogenic proton with tetrahedral frame charge is an electrostatic type, from Coulomb law:

Table 1: molecular geometry parameters for the studied molecules

	tetrahedrane	TN1	TN2	TN3	TN4
C-H/A	1.054	1.058	1.063	1.069	……..
C-C/A	1.493	1.479	1.463	…….	……..
C-N/A	…….	1.534	1.516	1.497	………
N-N/A	…..	………	1.582	1.560	1.535
H-C-C/deg	144.74	147.29	150.58	……..	…….
C-C-C/deg	60.00	60.00	…….	……..	…….
H-C-N/deg	…….	137.50	139.98	143.00	…….
N-C-N/deg	…….	…….	62.91	62.82	……
N-N-N/deg	……..	……..	………	60.00	60.00

Table 2: Energy functions calculated for the tetrahedrane molecular groups in addition to the reference molecules that used in isodesmic reaction calculations

| molecule	energy	Total E.	Elect.Kin.E.	ek eeandeN E.	Nuc.Rep.E.	Dipole	strain E.
	unit	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	Debye	(kcal/mol)
ethane		-50052.99	49602.68	-76725.69	26672.70	0.00	
isobutane		-99355.61	98491.95	-184418.16	85062.54	0.05	
trimethylamine		-109404.99	108322.83	-194978.18	85573.19	0.74	
T		-96970.36	96088.78	-163019.50	66049.13	0.00	134.13
TN		-107041.13	105997.93	-172304.65	65263.52	2.20	112.74
TN2		-117103.81	115923.12	-181659.40	64555.59	2.90	99.44
TN3		-127159.36	125865.93	-191120.92	63961.56	2.89	93.27
TN4		-137208.01	135840.04	-200793.40	63585.39	0.10	94.00
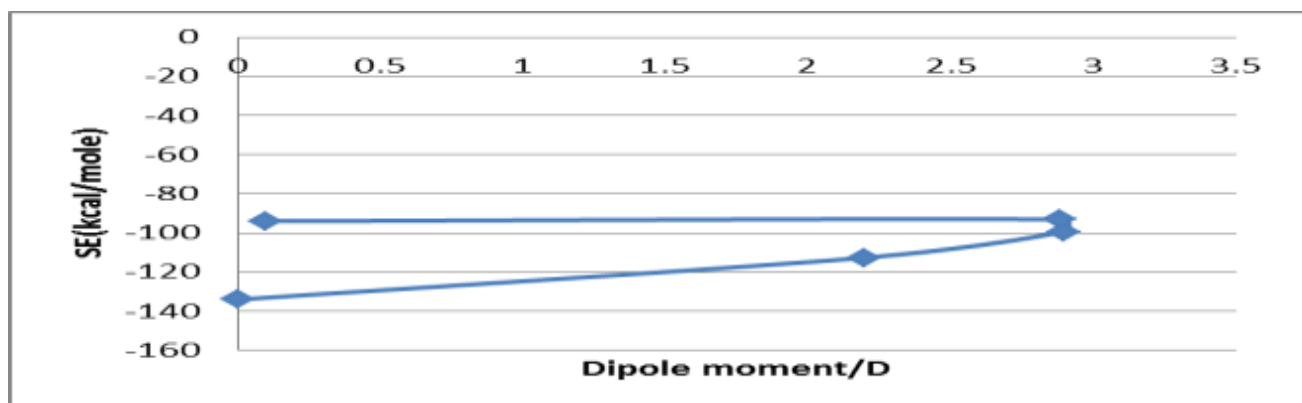
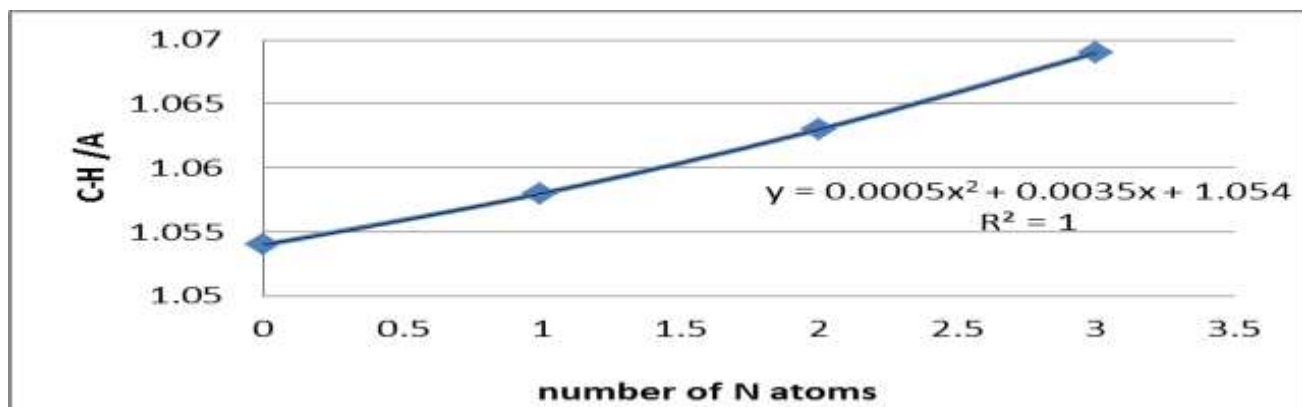**Figure 1: plotting stabilization energy vs. dipole moment for the tetrahedrane geometry molecules**

Figure 2: variation of C-H bond length with increasing of N atoms in the molecule

$$V = \frac{-Q_p \cdot Q_{frame}}{r_{C-H}} \dots\dots\dots\dots\dots\dots (6)$$

By going from tetrahedrane to its nitrogen derivatives we can conclude:

$$\frac{Q_{(frame)}0}{(r_{C-H})0} \approx \frac{Q_{(frame)}1}{(r_{C-H})1} \approx \frac{Q_{(frame)}2}{(r_{C-H})2} \approx \frac{Q_{(frame)}3}{(r_{C-H})3} \dots\dots (7)$$

The numbers appeared in the above equation refer to the number of N atoms in the frame. Clearly the ratio of the C-H bond lengths in the substituted compounds relative to the C-H bond length in the tetrahedrane which is used as a reference give a close value of the ratio of the frame charge in the substituted systems relative to the tetrahedral frame charge

$$\frac{Q_{(frame)}i}{Q_{(frame)}0} \approx \frac{(r_{C-H})i}{(r_{C-H})0} \dots\dots\dots (8)$$

Here (i) is the number if N atoms of the molecule. The previews equation was used as a parameter indicating the accumulated positive charge factor affecting the stability

of the studied frames. Special case of tetraazatetrahedrane molecule which does not carry any C-H bonds urge us to estimate the virtual proton equilibrium distance by plotting C-H of the molecule versus number of the N atoms in the studied molecules as in Figure(2), the quadratic equation resulted from this plot was used to calculate the virtual proton distance which was 1.076 A⁰.

The last proposed factor that took place in the stability of studied alicyclic systems was the number of nitrogen atoms which is referred by [15]. These three proposed parameters were merged in a linear empirical equation gives the strain energy of the tetrahedrane molecule and its nitrogenic derivatives as:

$$E_{strain} = a * DM + b * \frac{(r_{C-H})i}{(r_{C-H})0} + c * n_N + d \dots\dots\dots(9)$$

The first term in this equation reflects the contribution of the polarization factor represented by dipole moment parameter, the second term reflects the positive crowded charge factor represented by bond ratio parameter, the third term belongs to the number of nitrogen atoms, and the fourth one represents to constant parameter related to the geometry of the alicyclic system. The coefficients of this equation were determined by Excel solver method which gives the values:

$a = -4.63, b = 0.01, c = -9.56, d = 133.32$

the standard deviation was $1.229\ kcal/mole$.

The previous results indicate the geometry factor form the major source of the instability of these molecules. Also the polarization of the molecule and the existence of nitrogen atoms act to decrease the strain energy, the existence of nitrogen atoms is the most effective factor in the reducing of the instability of the molecules. A surprising result about the effect of accumulated positive charge was found less effective in reducing the strain energy, in fact it was found act to slightly increase the strain energy of the studied systems, so the charge spreading factors by polarization and $n \to \sigma^*$ processes are the most important factors in decreasing the strain energy.

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