DFT Study of 1*H*-tetrazolyl derivatives of tetrahedrane

Mehdi Nabati and Mehrdad Mahkam*

Chemistry Department, Faculty of Science, Azarbaijan Shahid Madani University, Tabriz, Iran

ABSTRACT

Tetrazole-containing compounds have been the subject of much recent research because of their potential as high energy density materials (HEDMs). In this work, theoretical studies on the 1*H*-tetrazolyl derivatives of tetrahedrane were done at the density functional theory (DFT) method with the 6-31G(d) basis set without any symmetrical restrictions in order to find the structural and energetically properties. Geometric and electronic structures, natural bond orbitals (NBOs) population, aromaticity of tetrazole rings, thermodynamic properties and detonation performances of these molecules have been studied using mentioned level of theory. Nucleus independent chemical shift (NICS) calculations show the tetrazole rings on the tetrahedrane system are aromatic. The heat of formation (HOF) values of all structures has been calculated by a proper isodesmic reaction. The HOFs are found to be correlative with the number of tetrazole groups. According to the results of the calculations, only tri-substituted derivative of tetrahedrane can be a viable candidate of high energy materials.

INTRODUCTION

Tetrahedrane is a platonic hydrocarbon with tetrahedral structure [1]. It is a most highly strained hydrocarbon and has an important role in the extension of the strain concept in organic chemistry. Due to this reason, this molecule is unstable and experimental data on it have been hard to obtain [2]. It can be used from this property to design of novel high energy density materials (HEDMs). The explosive function is dependent on many things such as density, volume of explosion, velocity of detonation, pressure of explosion and the number of moles and molecular weight of the gaseous products that one explosive produces under decomposition [3]. The nitrogen-rich groups such as tetrazole rings can increase the detonation properties of the explosive compounds [4]. Synthesis of these materials is very difficult and dangerous, but knowing of the structural and energetic properties of explosives makes easy the preparation of them [5]. In the present work, we report the theoretical study of the 1*H*-tetrazolyl derivatives of tetrahedrane. A particularly important method is to model a molecular system prior to synthesizing that molecule in the laboratory [6]. This is very useful mean because synthesizing a compound could

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*Corresponding author: mmahkam@yahoo.com

need months of labor and raw materials, and generates toxic waste [7]. A second use of computational chemistry is in understanding a problem more completely [8].

COMPUTATIONAL METHODS

All theoretical studies were carried out with the Gaussian 03 computational package [9]. The computational method employed for the tetrahedrane derivatives calculations is the same as that used previously for tetraherane: B3LYP/6-31G(d) level of theory. The term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [10] and Lee, Yang, Parr (LYP) correlation correction functional [11]. The geometry of structures was optimized without any structural or symmetry restrictions in the gas phase. Vibrational frequencies were calculated to determine the nature of the stationary points as well as the zero point and heat capacity corrections. Prediction the heat of formation (HOF) of the molecules was studied via the isodesmic reactions [12]. To calculate the density of structures, the molecular volume data was required. The molecular volume V was defined as inside a contour of 0.001 electrons/bohr^3 density. The computational molecular density ρ (ρ=M/V, where M = molecular weight) was also calculated. The computational molecular density ρ (ρ=M/V, where M = molecular weight) was also calculated. Oxygen balance (OB$_{100}$) is an expression that is used to indicate the degree to which an explosive ($C_aH_bO_cN_d$) can be oxidized [13]. OB$_{100}$ was calculated as follows:

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

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

RESULTS AND DISCUSSION

Structural properties study of the molecules

In this paper we studied 1*H*-tetrazolyl derivatives of tetrahedrane system. The studied molecules are depicted in Figure 1. As mentioned above, we were successful in computing the structural properties of the molecules with DFT method at 298.15 K and 1 atmosphere; therefore, we use the DFT method for computing the properties of the structures. The geometric structures of the studied molecules are shown in Figure 2. All calculations were performed at B3LYP/6-31G(d) level of theory. As seen from the Table 1, the dipole moment (μ) order is T2>T1>T3>T4>tetrahedrane for the structures. The bond lengths and angles data of the molecules have been given in Table 2. It is observed that the length of C-H bond of tetrahedrane backbone does not change by increasing of 1*H*-tetrazole number on the system (σ_{C-H}=1.075A°). As seen from the data, the length of C_T-C_T bond is longer than the length of C_H-C_T bond. The results of the calculations showed that the longest C-C bond among all the structures corresponds to C_T-C_T bond of molecule T4, which is 1.521A°, and the shortest C-C bond corresponds to C_H-C_H bond of molecule T1, which is 1.466A°. It is also observed that the shortest angle corresponds to C_T-C_H-C_T angle of molecule T3, which is 59.615 degree.

The molecular electrostatic potential (MEP) [14] is typically visualized through mapping its values onto the surface reflecting the molecules boundaries. The three-dimensional electrostatic potential maps of the structures are shown in Figure 3. The yellow-red loops and the blue loops indicate negative and positive charge development for a particular system respectively. As can be seen from the figures the negative charge is located on

the nitrogen elements of the tetrazole rings as expected due to the electron withdrawing character of theirs and positive charge is located on the tetrahedrane backbone and hydrogen atom that attached to the tetrazole rings.

The natural bond orbitals (NBOs) [15] data of the structures are listed in Table 3. It can be deduced from the data, the electron occupancy order of the C-C bonds is C_T-$C_T < C_T$-$C_H < C_H$-C_H for the molecules. It is also observed the C-C σ-bonds and the C-H σ-bonds are p-rich and s-rich, respectively. We can see, the tetrazole groups cause the carbon atoms use more p orbitals for formation of C-C bonds in tetrahedrane backbone.

Aromatic character is not a directly measurable or computable quantity [16]. This character can be obtained by NMR keyword in Gaussian software. Paul Schleyer and his coworkers proposed the use of nucleus independent chemical shift (NICS) computed with available quantum mechanics programs, as a new aromaticity/antiaromaticity criterion [17]. NICS calculations at the center of the rings were carried out on the molecule using the gauge invariant atomic orbital (GIAO) approach. NICS calculations were carried out to determine the aromaticity of tetrazole rings of the molecules [18]. The results of calculations are shown in Table 4. Negative and positive signs for NICS indicate the aromatic and anti-aromatic characters of the molecules, respectively. As can be seen from the data, tetrazole rings of the molecules have been found to be aromatic.

IR, UV-VIS and NMR study of the molecules

Spectroscopy methods are widely used in all fields of chemistry for determination of structure of molecules. The IR, UV-Vis and NMR spectra are basic properties of a compound. Figures 4 and 5 provide IR and UV spectra of the molecules, respectively.

T1: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 134.05 (1.60), 136.20 (2.39), 368.82 (0.16), 427.04 (0.44), 455.05 (9.77), 567.01 (72.54), 603.45 (27.82), 695.66 (10.93), 724.33 (4.99), 744.71 (2.84), 795.39 (22.83), 810.98 (25.03), 836.29 (43.46), 873.88 (3.85), 894.30 (5.43), 902.87 (0.91), 1013.42 (0.99), 1058.13 (0.27), 1061.87 (45.90), 1095.64 (11.39), 1136.93 (0.67), 1168.85 (7.13), 1233.23 (1.18), 1271.33 (2.09), 1356.74 (47.16), 1401.19 (16.07), 1500.71 (36.78), 1701.73 (170.51), 3352.43 (13.13), 3355.72 (15.52), 3383.11 (8.41), 3654.48 (67.24). NMR [nucleus shielding (ppm)]: H (22.4551, 28.7910, 28.7911, 29.0900), C (49.0228, 200.1359, 200.1374, 204.2996, 206.0690), N (-147.6854, -102.3083, -72.3582, 39.5918). UV: The wavelength of maximum absorption (λ_{max}) is 221.13 nm.

T2: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 35.64 (0.07), 82.45 (6.69), 88.53 (13.72), 130.32 (1.51), 147.20 (0.46), 187.32 (4.01), 313.09 (6.54), 381.98 (0.01), 396.43 (0.99), 419.50 (7.11), 483.16 (5.21), 583.97 (86.90), 590.05 (1.66), 675.05 (0.48), 691.39 (10.24), 713.04 (11.78), 728.04 (7.49), 743.12 (0.01), 744.52 (1.18), 820.02 (31.94), 823.92 (66.37), 849.95 (2.90), 880.79 (4.13), 888.20 (10.78), 1013.89 (1.62), 1024.57 (1.31), 1050.45 (1.86), 1061.47 (17.05), 1066.14 (14.67), 1091.88 (31.59), 1098.36 (22.56), 1100.77 (17.06), 1143.99 (1.85), 1188.72 (6.21), 1250.47 (2.72), 1264.55 (27.58), 1283.55 (0.56), 1336.59 (26.35), 1405.84 (22.81), 1422.43 (8.89), 1440.60 (1.27), 1515.12 (42.54), 1625.01 (287.29), 1750.45 (54.82), 3347.68 (20.82), 3366.56 (17.79), 3467.71 (296.83), 3650.05 (99.39). NMR [nucleus shielding (ppm)]: H (19.2761, 22.0450, 28.0907, 28.0907), C (49.3154,

53.4316, 190.5738, 190.5739, 200.0443, 203.8394), N (-148.7868, -142.8636, -109.7011, -108.4051, -77.6389, -65.9928, 27.6324, 40.7425). UV: The wavelength of maximum absorption (λ_{max}) is 244.22 nm.

T3: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 14.21 (8.42), 39.01 (1.25), 42.79 (8.26), 49.56 (4.21), 70.90 (7.10), 92.58 (17.08), 159.90 (1.85), 160.80 (0.46), 187.91 (2.21), 285.71 (4.73), 298.05 (8.14), 311.16 (8.16), 401.04 (0.99), 405.72 (2.55), 435.19 (0.23), 560.35 (2.59), 573.63 (18.58), 611.80 (75.33), 617.45 (62.48), 623.34 (12.05), 675.89 (15.60), 698.18 (15.27), 728.65 (19.39), 731.93 (13.74), 741.28 (0.33), 745.59 (1.76), 751.43 (0.22), 771.46 (6.09), 811.82 (71.70), 848.74 (12.60), 875.13 (5.19), 1009.91 (0.80), 1012.41 (1.15), 1022.68 (0.55), 1048.70 (3.96), 1054.44 (0.43), 1061.45 (2.11), 1066.56 (46.23), 1069.05 (28.93), 1087.44 (28.30), 1089.98 (22.18), 1093.11 (5.96), 1094.96 (3.61), 1231.72 (6.04), 1252.22 (6.26), 1263.30 (21.02), 1274.38 (11.08), 1284.43 (6.58), 1325.96 (6.25), 1414.94 (7.95), 1416.80 (24.67), 1425.52 (13.93), 1429.53 (2.19), 1445.23 (3.41), 1514.63 (16.69), 1618.16 (254.15), 1629.33 (203.50), 1798.60 (12.27), 3352.74 (28.09), 3481.77 (260.24), 3623.80 (89.68), 3637.30 (105.30). NMR [nucleus shielding (ppm)]: H (19.4262, 21.5037, 21.6066, 27.5591), C (51.7911, 54.1586, 54.6778, 182.27.51, 188.4299, 195.3901, 196.3289), N (-148.9673, -147.8604, -143.6145, -112.4500, -111.0855, -108.9025, -75.9250, -74.6419, -66.7417, 28.8667, 38.3574, 38.6239). UV: The wavelength of maximum absorption (λ_{max}) is 238.61 nm.

T4: IR [Harmonic frequencies (cm^{-1}), intensities (KM/Mole)]: 10.58 (0.28), 32.32 (0.08), 34.16 (3.90), 35.68 (8.66), 37.84 (16.29), 46.47 (3.52), 47.56 (4.16), 77.37 (7.35), 93.09 (16.96), 168.45 (3.30), 191.21 (1.23), 278.26 (1.59), 279.88 (4.80), 293.07 (9.32), 294.43 (1.57), 295.40 (5.35), 311.48 (8.48), 526.90 (7.89), 550.30 (3.15), 565.92 (13.38), 578.37 (33.93), 579.93 (0.45), 601.68 (60.66), 601.81 (65.09), 622.93 (58.73), 635.23 (2.94), 659.38 (20.15), 705.68 (4.62), 727.88 (23.97), 728.31 (9.52), 729.89 (15.80), 739.18 (0.67), 744.03 (0.36), 749.00 (0.55), 758.13 (0.08), 809.01 (0.03), 831.97 (72.14), 1008.71 (0.73), 1009.42 (0.03), 1012.41 (0.53), 1023.56 (0.44), 1037.31 (5.97), 1049.35 (2.97), 1054.75 (7.17), 1065.61 (2.64), 1066.09 (42.02), 1067.87 (49.52), 1072.61 (17.62), 1084.75 (18.84), 1087.24 (9.76), 1089.42 (26.47), 1092.61 (9.38), 1097.87 (37.43), 1203.25 (3.29), 1236.22 (2.56), 1253.39 (6.24), 1262.17 (20.79), 1268.16 (13.75), 1276.58 (4.34), 1282.65 (8.56), 1317.65 (2.02), 1411.82 (0.67), 1413.24 (21.71), 1415.06 (2.18), 1422.81 (21.02), 1430.12 (5.74), 1436.95 (0.59), 1447.84 (14.09), 1513.52 (3.34), 1601.78 (180.20), 1626.65 (158.06), 1628.49 (192.09), 1823.83 (1.82), 3452.45 (303.48), 3631.55 (116.50), 3632.29 (4.99), 3633.19 (165.65). NMR [nucleus shielding (ppm)]: H (19.0317, 21.0203, 21.7452, 21.7458), C (54.0596, 56.2707, 56.4206, 56.4212, 179.0706, 179.0729, 190.3671, 191.3109), N (-150.7990, -149.0954, -149.0922, -143.3631, -115.3794, -113.1980, -110.4827, -110.4817, -78.6430, -78.6430, -77.5786, -67.2055, 26.4519, 36.3145, 40.2825, 40.2859). UV: The wavelength of maximum absorption (λ_{max}) is 255.85 nm.

Table 1. Dipole moment of the structures

Molecules	μ_X (Debye)	μ_Y (Debye)	μ_Z (Debye)	μ_{Tot} (Debye)
Tetrahedrane	-0.0002	0.0001	0.0000	0.0002
T1	-5.1318	3.5777	0.0001	6.2559
T2	-6.0379	6.4456	0.0004	8.8319
T3	0.2813	-2.6662	3.9646	4.7860
T4	-0.2355	-0.0022	-1.0097	1.0368
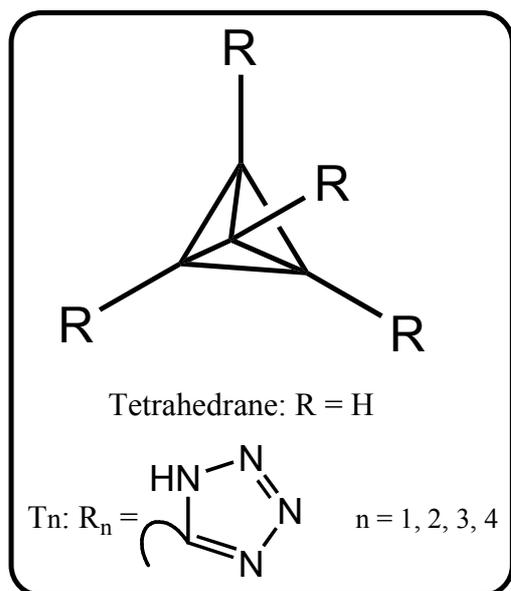
Fig. 1. Molecule structure of 1H tetrazolyl derivativies of tetrahedrane.

The frontier molecular orbital energies

Table 5 shows the frontier orbitals energies of the tetrazolyl derivatives of the tetrahedrane computed at B3LYP/6-31G(d) level of theory. And also, the electronic chemical potential (μ), the absolute hardness (η) and the electrophilicity character (ω) are defined as the reactivity indexes by following equations [19]:

$$\mu \ (eV) = (\varepsilon_{LUMO} + \varepsilon_{HOMO})/2$$
$$\eta \ (eV) = \varepsilon_{LUMO} - \varepsilon_{HOMO}$$
$$\omega \ (eV) = \mu^2/2\ \eta$$

It is obtained from the data, the energies of the frontier orbitals and absolute hardness of the molecules decrease and the electronic chemical potential of the molecules increase by increasing the number of tetrazole group on the tetrahedrane backbone. This is due to the electron withdrawing property of tetrazole groups. The index ω denotes electrophilicity power 1.62, 2.06, 1.52, 1.72, 1.64, 1.59, 1.22, 1.17 and 1.31 for C_2H_2, C_2HF, BH_3, HNO_3, CS_2, C_4H_4,

Azulene, Anthracene and Perylene respectively [20]. From the data, it is seen that the electrophilicity index of the molecules increase by increasing the number of tetrazole group on the tetrahedrane system.

Table 2. Bond lengths and angles of the structures calculated at B3LYP/6-31G(d) level

Bonds (A°)		Angles (degree)	
C-C (Tetrahedrane)	1.479	C-C-C (Tetrahedrane)	60.000
C-H (Tetrahedrane)	1.073	C-C-H (Tetrahedrane)	144.742
C_H-C_H (T1)	1.466	C_H-C_H-C_H (T1)	60.354
C_H-C_T* (T1)	1.489	C_H-C_H-C_T (T1)	60.526
C-H (T1)	1.074	C_H-C_T-C_H (T1)	58.948
C_H-C_H (T2)	1.480	C_H-C_H-C_T (T2)	59.948
C_H-C_T (T2)	1.478	C_H-C_T-C_H (T2)	60.105
C_T-C_T (T2)	1.484	C_H-C_T-C_T (T2)	60.283
C-H (T2)	1.075	C_T-C_H-C_T (T2)	60.045
C_H-C_T (T3)	1.474	C_T-C_T-C_T (T3)	59.662
C_T-C_T (T3)	1.488	C_H-C_T-C_T (T3)	59.659
C-H (T3)	1.075	C_T-C_H-C_T (T3)	59.615
C_T-C_T (T4)	1.521	C_T-C_T-C_T (T4)	59.674

*C_H and C_T are related to the carbon atoms that attached to hydrogen atom and tetrazole group respectively.

Heats of formation, predicted densities and detonation of the structures

Heat of formation (HOF) is an important property for a molecule in the area of energetic materials for determining detonation or propellant performance [21]. The HOF values were calculated at B3LYP/6-31G(d) level of theory and are listed in table 6. In this study, isodesmic reaction method is employed. The isodesmic reactions for HOF calculation are showed in Scheme 1.

For the isodesmic reactions, heat of reaction ΔH at 298 K can be calculated from the following equations [22]:

$$\Delta H_{298} = \Sigma\Delta H_{fP} - \Sigma\Delta H_{fR}$$
$$\Delta H_{298.15K} = \Delta E_{298.15K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT = \Sigma\Delta H_{fP} - \Sigma\Delta H_{fR}$$

where ΔH_{fP} and ΔH_{fR} are the heats of formation of products and reactants at 298 K, respectively. ΔE_0 and ΔZPE correspond

to the total energy difference and the zero point energy difference between products and reactants at 0 K, respectively. ΔH_T is the changes in thermal correction to enthalpies between products and reactants. $\Delta(PV)$ equals ΔnRT for reaction in gas phase.

For isodesmic reactions, $\Delta n=0$. As seen from the table, the HOF of the molecules increases by increasing the number of tetrazole group on the tetrahedrane system. The density of the each molecule was obtained from the molecular weight divided by the average molecular volume. The average mole volume of each compound was obtained from the

statistical average value of 100 molar volumes. The mole volume of each molecule, defined as the volume inside a contour of $0.001e/Bohr^3$ density, was calculated by Monte Carlo method in the Gaussian 03 program package. Velocity of detonation (D) and pressure of explosion (P) are the important factors for evaluating the detonation properties of energetic compounds. They can be predicted by the following empirical Kamlet-Jacob equations [23]:

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

	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	$(28.9b+94.05a+0.239\Delta Hf)/MW$	$[28.9b+94.05(c/2-b/4)+0.239\Delta Hf]/MW$	$(57.8c+0.239\Delta Hf)/MW$

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. The data of Table 6 show that the introduction of tetrazole group can improves the

detonation properties of the structures. 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 [24]. The RDX and HMX are the current standards for detonation behavior [25]. Comparing tetrazolyl derivatives of tetrahedran with RDX and HMX shows T3 can be an explosive.

Table 3. NBOs population calculated at B3LYP/6-31G(d) method

Bonds	Occupancy	Population/Bond orbital/Hybrids
C-C (tetrahedrane)	1.96065	50.00% C ($sp^{4.08}d^{0.01}$), 50.00% C ($sp^{4.08}d^{0.01}$)
C-H (tetrahedrane)	1.99730	63.67% C ($sp^{1.46}$), 36.33% H (s)
C_H-C_H (T1)	1.95096	50.34% C_H ($sp^{4.22}d^{0.01}$), 49.66% C_H ($sp^{4.16}d^{0.01}$)
C_H-C_T (T1)	1.94973	48.28% C_H ($sp^{3.86}$), 51.72% C_T ($sp^{3.70}$)
C-H (T1)	1.99703	64.15% C ($sp^{1.45}$), 35.85% H (s)
C_H-C_H (T2)	1.94867	50.00% C_H ($sp^{4.14}d^{0.01}$), 50.00% C_H ($sp^{4.14}d^{0.01}$)
C_H-C_T (T2)	1.92472	47.25% C_H ($sp^{4.28}d^{0.01}$), 52.75% C_T ($sp^{3.72}$)
C_T-C_T (T2)	1.91951	51.05% C_T ($sp^{4.81}$), 48.95% C_T ($sp^{4.86}d^{0.01}$)
C-H (T2)	1.99627	64.80% C ($sp^{1.42}$), 35.20% H (s)
C_H-C_T (T3)	1.91301	47.98% C_H ($sp^{4.59}d^{0.01}$), 52.02% C_T ($sp^{4.41}$)
C_T-C_T (T3)	1.92048	49.80% C_T ($sp^{3.82}d^{0.01}$), 52.20% C_T ($sp^{3.92}$)
C-H (T3)	1.99577	65.21% C ($sp^{1.40}$), 34.79% H (s)
C_T-C_T (T4)	1.87948	50.00% C_T ($sp^{4.93}d^{0.01}$), 50.00% C_T ($sp^{4.93}d^{0.01}$)
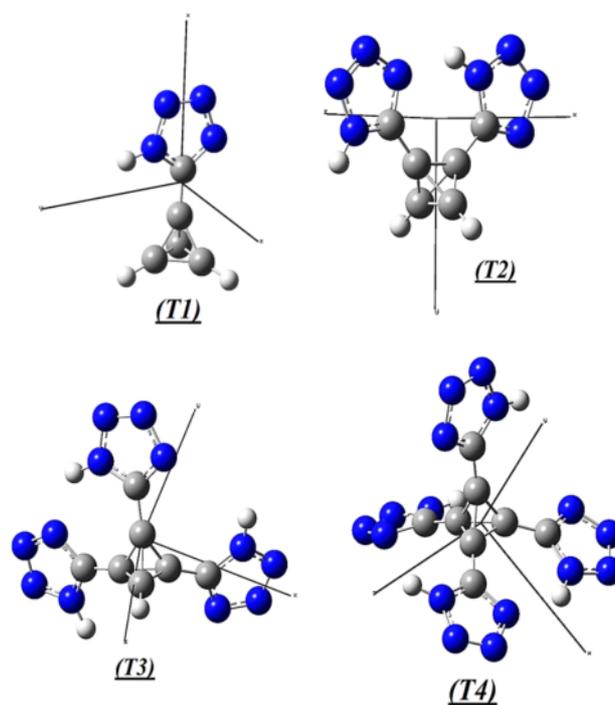
Fig. 2. The geometric structure of the molecules.
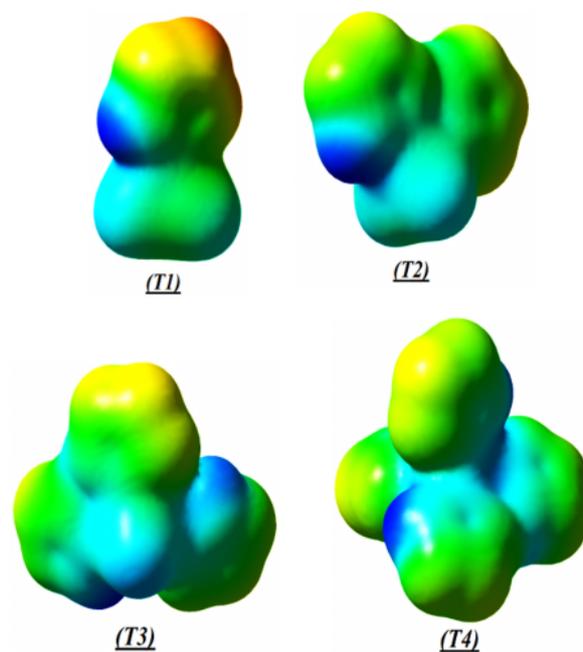
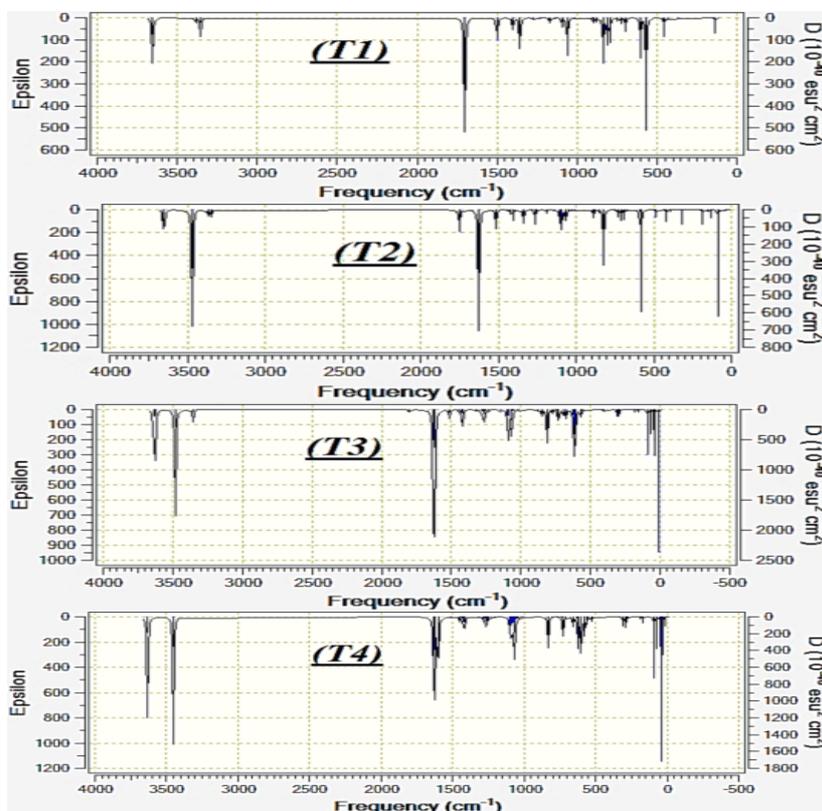**Fig. 3.** The 3-D electrostatic potential map of the structures.

Fig. 4. The IR spectra of structures.

Table 4. NICS index of the tetrazole groups of the structures calculated at B3LYP/6-31G(d) method

Molecules	NICS(0)
T1	-11.9
T2	-11.9
T3	-12.1
T4	-12.1

Table 5. The frontier orbitals energy and electrophilicity of structures

Structures	ε_{HOMO} (hartree)	ε_{LUMO} (hartree)	μ (eV)	η (eV)	ω (eV)
Tetrahedrane	-0.22038	0.11982	1.368	9.257	0.101
T1	-0.24027	-0.01626	3.490	6.096	0.999
T2	-0.25986	-0.05109	4.231	5.681	1.576
T3	-0.27962	-0.06439	4.680	5.857	1.870
T4	-0.28464	-0.08539	5.034	5.422	2.337
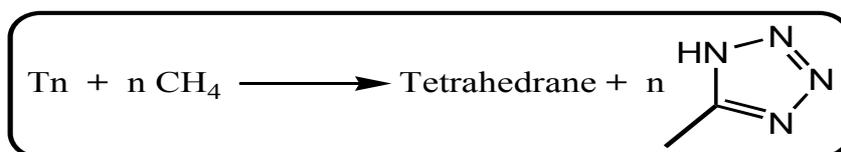
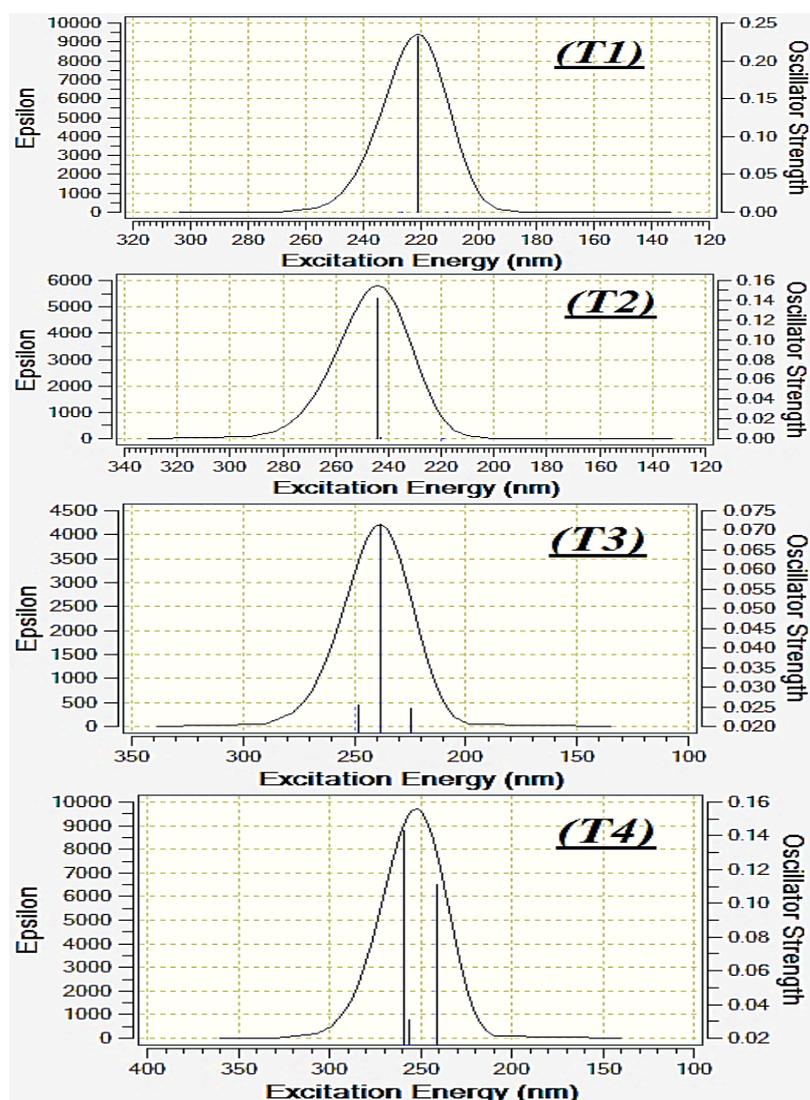**Scheme 1.** The isodesmic reaction for HOF calculations.

Fig. 5. The UV spectra of structures.

Table 6. Oxygen balance, HOF, predicted density and detonation properties of the structures

Structures	Energy (hartrees)	OB_{100}	HOF (kJ/mol)	Q (kJ/g)	V* (cm^3/mol)	ρ (g/cm^3)	D (km/s)	P (GPa)
Tetrahedrane	-154.576791	-307.51	582.897	2677.474	45.667	1.139	4.202	5.685
T1	-411.615320	-159.94	909.677	1811.115	82.037	1.463	6.869	18.315
T2	-668.657254	-119.11	1227.517	1560.049	111.390	1.688	7.595	24.600
T3	-925.692688	-99.97	1562.422	1458.279	129.276	1.981	8.493	33.823
T4	-1182.723886	-88.87	1908.450	1407.427	192.628	1.682	7.567	24.364

*Average valu from 100 single-point volume calculations at studied levels.
Q: Heat of explosion, V: Volume of explosion, D: Velocity of detonation, P: Pressure of explosion

CONCLUSIONS

In the present work, the 1H-tetrazolyl derivatives of tetrahedrane system have been studied by using quantum chemical calculations in order to find some novel potential candidates of explosives. Full geometrical optimization of the structures was performed using B3LYP/6-31G(d) level of theory. From the above calculations and analyses, the following conclusions can be drawn:

a. The dipole moment order is T2>T1>T3>T4>tetrahedrane for the compounds.

b. The molecular electrostatic potential (MEP) map shows the negative and positive charges are located on the nitrogen elements of the tetrazole rings and the tetrahedrane backbone, respectively.

c. All tetrazole rings of the structures are aromatic.

d. The NBO analyses show the more p orbital of carbon atoms uses for forming C-C bonds of the tetrahedrane system.

e. The HOF and electrophilicity power order is T4>T3>T2>T1>tetrahedrane as expected due to the electron withdrawing character of tetrazole groups.

f. The molecule T3 is viable candidate of high energy materials.

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