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A theoretical study of the structural and energetically properties on the 1,4-bis(1H-tetrazolyl)cubane: an ab-initio treatment

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Abstract: Quantum chemical studies on the 1,4-bis(1H-tetrazolyl)cubane were performed at the Hartree-Fock (HF) method with the 6-31G(d), 6-31G(d,p), 6-311G(d,p), 6-31+G(d,p) and 6-31G(2d,2p) basis sets without any symmetrical restrictions in order to find the structural and energetically properties. The structure of molecule was optimized, and thermodynamic analyses were also performed using the single point energy calculation and frequency analyses. Some important properties such as bond dissociation enthalpy, density, frontier orbital energy, thermodynamic parameters, natural bond orbital population, and heat of formation and detonation parameters were then calculated. Also, IR, UV-Vis and NMR spectra of the structure were simulated. Bond dissociation energy (BDE) was obtained through designed homolytic cleavage path. Heat of formation (HOF) was predicted through designed isodesmic reaction. The simulation results revealed that this compound exhibit excellent performance; and that is viable candidate of high energy density materials (HEDMs) but it can't be an explosive.

Keywords: 1,4-Bis(1H-tetrazolyl)cubane, Electrophilicity index, Bond dissociation energy, Heat of formation, Detonation properties.

Introduction

Cubane, pentacyclo[4.2.0.0^{2,5}.0^{2,8}.0^{4,7}]octane, is a strained cube-shaped molecule that includes eight carbon atoms and eight hydrogen atoms. In 1964, Philip Eaton and his coworkers reported the first successful synthesis of the cubane carbon skeleton [1]. This molecule is stable to electrophiles, nucleophiles, air and light. Molecular mechanics calculations show the C-C σ-bonds and the C-H σ-bonds are p-rich and s-rich, respectively. The ^{1}H-NMR shows one singlet peak at 4.0 ppm for it [2]. One of the most important properties of cage compounds is related to the detonation performances [3]. The first usage of cubane as source of high energy materials was introduced in the early 1980s by the U.S. army [4]. 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 [5]. Such groups like NO_2, NO, ONO_2, $NHNO_2$, NH_2 and nitrogen-rich rings like tetrazole increase the effectiveness of an explosive [6]. 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 [7]. In present work, we report the theoretical study of the 1,4-bis(1H-tetrazolyl)cubane. A particularly important method is to model a molecular system prior to synthesizing that molecule in the laboratory [8]. This is very useful mean because synthesizing a compound could need months of labor and raw materials, and generates toxic waste. A second use of computational chemistry is in understanding a problem more completely [9].

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Computational method

All of the calculations were performed with Gaussian 03 series of programs [10]. The molecule was fully optimized by Hartree-Fock (HF) with the 6-31G(d), 6-31G(d,p), 6-311G(d,p), 6-31+G(d,p) and 6-31G(2d,2p) basis sets without any symmetrical restrictions. Theoretical calculations have been performed in the gas phase at 298.15 K of temperature and one atmospheric pressure. The molecule was visualized with the GaussView 5.0 program [11]. Geometry was checked to be the minimal by method of the frequency analysis. For comparing of the bond strengths, hemolytic bond dissociation energy (BDE) calculations were performed in the mentioned levels. The studied methods were used to predict the HOFs of the molecule via isodesmic reactions [12]. The population analysis has also been performed by the natural bond orbital method at mentioned levels of theory using NBO keyword [13]. Aromatic character is not a directly measurable or computable quantity [14]. 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 [15]. NICS calculations at the center of the rings were carried out on the molecule using the gauge invariant atomic orbital (GIAO) approach [16]. To calculate the density of 1,4-bis(1H-tetrazolyl)cubane, the molecular volume data was required. The volume of molecule was defined as inside a contour of 0.001 electrons/bohr^3 density that was evaluated using a Monte Carlo integration. We performed 100 single-point calculations for the optimized structure of the molecule to get an average volume. 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 can be oxidized [17]. OB_{100} was calculated as follows:

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

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

Results and discussion

The geometry of 1,4-bis(1H-tetrazolyl)cubane:

There are many energetic compounds with most usages [18]. Their classification is according to the types of groups present in their structures like azides, nitro, nitramines etc [19]. However, a look into the high energy density materials reveals that the nitrogen-rich rings are more responsible for the energy character of the molecules [20]. Tetrazole, one of the major nitrogen-rich compounds, is a five membered ring with four nitrogen atom and one carbon atom [21]. If the tetrazolyl group is linked to a carbon atom in cubane structure, the detonation performance of the system could be increased by electron withdrawing property of the ring nitrogen atoms. As we mentioned above, we study here structural properties of the molecule: 1,4-bis(1H-tetrazolyl)cubane. The molecular structure with atomic numbers is showed in Figure **1**.

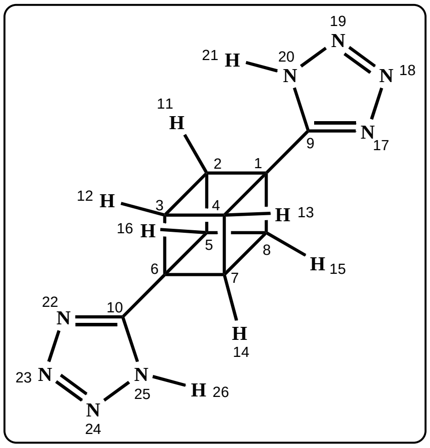


Figure 1: Molecule structure of 1,4-bis(1H-tetrazolyl)cubane with atomic numbering.

The geometry of molecule obtained at the HF/6-31G(d) level is displayed in Figure **2**. The dipole moment of the system is calculated at the HF method with the 6-31G(d), 6-31G(d,p), 6-311G(d,p), 6-31+G(d,p) and 6-31G(2d,2p) basis sets. As seen from the Table **1**, 1,4-bis(1H-tetrazolyl)cubane is a non-polar system. The natural atomic charges of the molecule at studied level of theory are listed in Table **2**. According to the data, the charge of the carbon atoms of the cubane skeleton is negative, whiles the charge of the carbon atoms of the tetrazole rings is positive. And also, the charge of the hydrogen atoms that attached to the tetrazole rings is more positive than the hydrogen atoms that attached to the cubane skeleton. It can be explained that the electron withdrawing property of the nitrogen atoms is more than carbon and hydrogen atoms. The bond lengths and angles data of the molecule have been given in Table **3**. In organic compounds, normal C_{sp3}-C_{sp3}, C_{sp3}-C_{sp2} and C_{sp3}-H bonds length is 1.54 A°, 1.50 A° and 1.10 A° respectively [22], whiles the results of the calculation by HF/6-31G(d) on the 1,4-bis(1H-tetrazolyl)cubane showed 1.556 A°, 1.473 A° and 1.080 A° respectively.

The N–N and N=N bond lengths are 1.341 A° and 1.250 A° respectively, whereas the normal N–N and N=N bond lengths are are 1.450 A° and 1.250 A° respectively [23].

Table 1: Dipole moment of the structure calculated at all studied methods.

Methods	μ_X (Debye)	μ_Y (Debye)	μ_Z (Debye)	μ_{Tot} (Debye)
HF/6-31G(d)	0.0000	0.0000	0.0062	0.0062
HF/6-31G(d,p)	0.0000	0.0000	0.0050	0.0050
HF/6-31G(2d,2p)	0.0000	0.0000	0.0040	0.0040
HF/6-31+G(d,p)	0.0000	0.0000	0.0046	0.0046
HF/6-311G(d,p)	0.0000	0.0000	0.0040	0.0040

Table 2: Natural atomic charges of the structure calculated at HF/6-31G(d) method.

Atoms	Natural Charge (e)	Atoms	Natural Charge (e)
C1	-0.11773	H16	0.24046
C2	-0.19758	C9	0.42799
C3	-0.18818	N17	-0.37341
C4	-0.19766	N18	-0.04778
C5	-0.19763	N19	-0.05051
C6	-0.11773	N20	-0.43887
C7	-0.19761	H21	0.44866
C8	-0.18818	C10	0.42799
H11	0.24048	N22	-0.37341
H12	0.25415	N23	-0.04778
H13	0.24044	N24	-0.05051
H14	0.24046	N25	-0.43887
H15	0.25415	H26	0.44866

Table 3: Bond lengths and angles of the structure calculated at HF/6-31G(d) level.

C1-C2	1.567	C4-C1-C9	126.369
C1-C4	1.567	**C8-C1-C9**	123.397
C1-C8	1.553	**C2-C3-C4**	90.326
C7-C8	1.556	**C2-C5-C8**	90.276
C5-C8	1.556	**C4-C7-C8**	90.276
C2-C5	1.556	**C1-C9-N17**	126.724
C2-C3	1.556	**C1-C9-N20**	126.039
C4-C7	1.556	**N20-C9-N17**	107.238
C2-H11	1.080	**C9-N17-N18**	106.348
C4-H13	1.080	**N17-N18-N19**	111.348
C8-H15	1.078	**N19-N20-C9**	108.507
C1-C9	1.473	**N19-N20-H21**	120.464
C9-N17	1.294	**C9-N20-H21**	131.028
C9-N20	1.335	**H11-C2-C1-C9**	-1.656
N17-N18	1.341	**H13-C4-C1-C9**	1.647
N18-N19	1.250	**H15-C8-C1-C9**	0.006
N19-N20	1.328	**C2-C1-C9-N17**	-118.882
N20-H21	0.994	**C2-C1-C9-N20**	61.107
C1-C2-H11	125.093	**C4-C1-C9-N17**	119.126
C1-C2-C5	89.627	**C4-C1-C9-N20**	-60.885
C1-C2-C3	90.066	**C8-C1-C9-N17**	0.115
C1-C4-H13	125.098	**C8-C1-C9-N20**	-179.896
C1-C4-C7	89.626	**C1-C9-N20-H21**	0.012
C1-C4-C3	90.066	**N18-N19-N20-H21**	179.989
C1-C8-H15	123.819	**C5-C2-C1-C9**	132.703
C1-C8-C5	90.118	**C7-C4-C1-C9**	-132.710
C1-C8-C7	90.116	**C5-C8-C1-C9**	-134.830
C2-C1-C9	126.360	**C1-C2-C3-C4**	0.096

*Bonds (A°), Angles (degree)

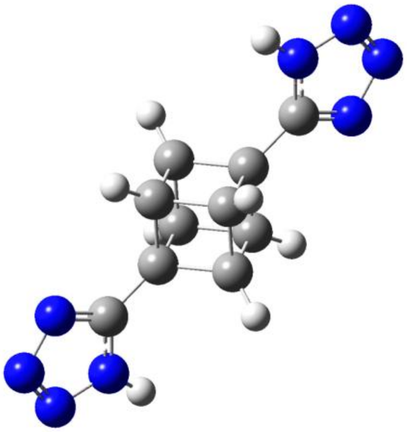


Figure 2: The geometric structure of the molecule

As seen from the Table **3**, the inernal C-C-C angles of cubane system are in the range of 89.6-90.1 degree and they aren't around the normal C-C-C angle which is known as 109.5 degree [24]. Therefore, the molecule has high angle strain. The dihedral angles show that the tetrazole rings are plane. For a better understanding of the 1,4-bis(1H-tetrazolyl)cubane structure, natural bond orbital (NBO) analysis has been performed at the HF/6-31G(d) level. NBO analysis is known as a method for studying hybridization in polyatomic wave functions [25]. NBOs show the nature of localized bonds and lone pairs of molecular structure [26]. The natural bond orbital calculation was carried out at HF/6-31G(d) level. The results of calculation are listed in Table **4**. The data show the carbon atoms in C-C and C-H bonds of cubane section are formed from $sp^{3.35}d^{0.01}$ and $sp^{2.20}$ hybrids, respectively. It gets rid of the angular strain in the structure, the more p orbital of carbon atoms uses for forming C-C bonds. And also, the hydrogen atoms have acidic property because the carbon atoms of cubane use more s orbital for forming C-H bonds. The molecular electrostatic potential (MEP) maps are very useful three dimensional diagrams of molecules [27]. They show the charge distributions of structures and charge related properties of compounds [28]. And also, they display the size and shape of structures [29]. The MEP is the force acting on a positive test charge (a proton) located at a given point p(x,y,z) in the vicinity of a molecule through the electrical charge cloud generated through the molecules electrons and nuclei [30]. The three-dimensional electrostatic potential map of the molecule is shown in Figure **3**. The red loops and the blue loops indicate negative and positive charge development for a particular system respectively. As can be seen from the figure 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 other sections of the molecule.

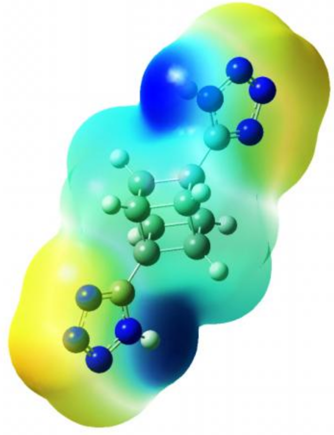


Figure 3: The 3-D electrostatic potential map of the structure.

Table 4: NBOs population calculated at HF/6-31G(d) method.

Bonds	Occupancy	Population/Bond orbital/Hybrids
σ(C5-C2)	1.98032	50.00% C5 ($sp^{3.35}d^{0.01}$), 50.00% C2 ($sp^{3.35}d^{0.01}$)
σ(C5-C6)	1.96800	47.80% C5 ($sp^{3.47}d^{0.01}$), 52.20% C6 ($sp^{3.39}d^{0.01}$)
σ(C5-C8)	1.98068	50.30% C5 ($sp^{3.32}d^{0.01}$), 49.70% C8 ($sp^{3.40}d^{0.01}$)
σ(C5-H16)	1.99387	62.53% C5 ($sp^{2.20}$), 37.47% H16 (s)
σ(C2-C3)	1.98067	50.30% C2 ($sp^{3.32}d^{0.01}$), 49.70% C3 ($sp^{3.40}d^{0.01}$)
σ(C2-H11)	1.99387	62.53% C2 ($sp^{2.20}$), 37.47% H11 (s)
σ(C2-C1)	1.96797	47.80% C2 ($sp^{3.47}d^{0.01}$), 52.20% C1 ($sp^{3.39}d^{0.01}$)
σ(C3-C6)	1.97259	47.59% C3 ($sp^{3.41}d^{0.01}$), 52.41% C6 ($sp^{3.31}d^{0.01}$)
σ(C3-H12)	1.99338	63.19% C3 ($sp^{2.17}$), 36.81% H12 (s)
σ(C3-C4)	1.98068	49.70% C3 ($sp^{3.40}d^{0.01}$), 50.30% C4 ($sp^{3.32}d^{0.01}$)
σ(C6-C10)	1.97908	49.63% C6 ($sp^{2.20}$), 50.37% C10 ($sp^{1.55}$)
σ(C6-C7)	1.96799	52.20% C6 ($sp^{3.39}d^{0.01}$), 47.80% C7 ($sp^{3.47}d^{0.01}$)
σ(C8-C1)	1.97259	47.59% C8 ($sp^{3.41}d^{0.01}$), 52.41% C1 ($sp^{3.31}d^{0.01}$)
σ(C8-C7)	1.98067	49.70% C8 ($sp^{3.40}d^{0.01}$), 50.30% C7 ($sp^{3.32}d^{0.01}$)
σ(C8-H15)	1.99338	63.19% C8 ($sp^{2.17}$), 36.81% H15 (s)
σ(C1-C4)	1.96802	52.20% C1 ($sp^{3.39}d^{0.01}$), 47.80% C4 ($sp^{3.47}d^{0.01}$)
σ(C1-C9)	1.97908	49.63% C1 ($sp^{2.20}$), 50.37% C9 ($sp^{1.55}$)

σ(C4-C7)	1.98032	50.00% C4 ($sp^{3.35}d^{0.01}$), 50.00% C7 ($sp^{3.35}d^{0.01}$)
σ(C4-H13)	1.99387	62.53% C4 ($sp^{2.20}$), 37.47% H13 (s)
σ(C10-N22)	1.98600	42.81% C10 ($sp^{2.08}$), 57.19% N22 ($sp^{1.62}d^{0.01}$)
π(C10-N22)	1.84085	38.04% C10 (p), 61.96% N22 (p)
σ(C10-N25)	1.99046	37.62% C10 ($sp^{2.51}d^{0.01}$), 62.38% N25 ($sp^{1.61}$)
σ(C7-H14)	1.99387	62.53% C7 ($sp^{2.20}$), 37.47% H14 (s)
σ(C9-N17)	1.98600	42.81% C9 ($sp^{2.08}$), 57.19% N17 ($sp^{1.62}d^{0.01}$)
π(C9-N17)	1.84085	38.04% C9 (p), 61.96% N17 (p)
σ(C9-N20)	1.99046	37.62% C9 ($sp^{2.51}d^{0.01}$), 62.38% N20 ($sp^{1.61}$)
σ(N22-N23)	1.98401	50.35% N22 ($sp^{2.82}d^{0.02}$), 49.65% N23 ($sp^{2.55}d^{0.01}$)
σ(N23-N24)	1.99143	48.87% N23 ($sp^{2.17}d^{0.01}$), 51.13% N24 ($sp^{1.99}d^{0.01}$)
π(N23-N24)	1.92399	48.55% N23 ($pd^{0.01}$), 51.45% N24 ($pd^{0.01}$)
σ(N24-N25)	1.98967	44.58% N24 ($sp^{3.04}d^{0.02}$), 55.42% N25 ($sp^{2.39}$)
σ(N25-H26)	1.99005	72.80% N25 ($sp^{2.11}$), 27.20% H26 (s)
σ(N17-N18)	1.98401	50.35% N17 ($sp^{2.82}d^{0.02}$), 49.65% N18 ($sp^{2.55}d^{0.01}$)
σ(N18-N19)	1.99143	48.87% N18 ($sp^{2.17}d^{0.01}$), 51.13% N19 ($sp^{1.99}d^{0.01}$)
π(N18-N19)	1.92399	48.55% N18 ($pd^{0.01}$), 51.45% N19 ($pd^{0.01}$)
σ(N19-N20)	1.98967	44.58% N19 ($sp^{3.04}d^{0.02}$), 55.42% N20 ($sp^{2.39}$)
σ(N20-H21)	1.99005	72.80% N20 ($sp^{2.11}$), 27.20% H21 (s)

Nucleus Independent Chemical Shift (NICS):

NICS calculations were carried out to determine the aromaticity of tetrazole rings of the molecule at the HF method with the 6-31G(d), 6-31G(d,p), 6-311G(d,p), 6-31+G(d,p) and 6-31G(2d,2p) basis sets. The results of calculations are shown in Table **5**. Negative and positive signs for NICS indicate the aromatic and anti-aromatic characters of the molecules, respectively. Negative “nucleus-independent chemical shifts” (NICSs) denote aromaticity (-11.5 for benzene, -11.4 for naphthalene); positive NICSs, antiaromaticity (28.8 for cyclobutadiene); small NICS, non-aromaticity (-2.1 for cyclohexane, -1.1 for adamantane) [31]. As can be seen from the data, tetrazole rings of the molecule have been found to be aromatic.

Table 5: NICS index of the structure calculated at all studied methods.

Theory levels	NICS(0)
HF/6-31G(d)	-13.21
HF/6-31G(d,p)	-13.16
HF/6-31G(2d,2p)	-13.37
HF/6-31+G(d,p)	-12.60
HF/6-311G(d,p)	-13.08

Infrared spectra:

Infrared spectroscopy is a simple and reliable method widely used in all fields of chemistry. The IR spectrum is one basic property of a compound, and also an effective measure to identify structures [32]. In order for a vibrational mode in a molecule to be "IR active," it must be associated with changes in the dipole moment [33]. Here, calculations of vibrational frequencies were carried out by using HF/6-31G(d) level. Figure **4** provides structure's IR spectra. A molecule can vibrate in many ways, and each way is called a vibrational mode [34]. For molecules with N number of atoms in them, linear molecules have 3N – 5 degrees of vibrational modes, whereas nonlinear molecules have 3N – 6 degrees of vibrational [35]. Then, 1,4-bis(1H-tetrazolyl)cubane, will have 72 degrees of vibrational modes.

Harmonic frequencies (cm^{-1}), IR intensities (KM/Mole)

20.0545 (26.1639), 21.2065 (0.0000), 59.7624 (5.1568), 62.8896 (13.0959), 138.3931 (0.0000), 148.0188 (0.0000), 254.6895 (0.0000), 345.1906 (0.0122), 374.5578 (14.4240), 413.4882 (0.0000), 431.2265 (9.3251), 462.2266 (0.0000), 625.7520 (199.4835), 630.2589 (0.0001), 718.4695 (7.8033), 730.3967 (0.0639), 765.6371 (0.0000), 767.7949 (0.0000), 807.1283 (0.0000), 807.4673 (15.0965), 834.1402 (0.0952), 837.8437 (0.0000), 883.6271 (0.0000), 930.8874 (0.0000), 931.4526 (0.0006), 934.2327 (6.5560), 940.3480 (7.0106), 961.7962 (0.0000), 965.8847 (0.0000), 997.1564 (0.3281), 1107.8046 (0.0000), 1118.2818 (0.1602), 1120.8761 (0.7249), 1120.9226 (0.0103), 1121.5473 (0.0000), 1137.0909 (20.1952), 1144.2211 (5.4136), 1145.1590 (0.0000), 1194.5084 (0.0000), 1196.7440 (91.0311), 1214.7343 (0.0034), 1216.4287 (0.0000), 1217.5760 (3.2642), 1254.6921 (0.0000), 1258.7775 (0.0000), 1264.1230 (0.0953), 1264.6796 (0.5480), 1266.3685 (0.0000), 1278.2995 (22.6658), 1293.4774 (0.0000), 1357.9167 (0.0000), 1363.0090 (0.0000), 1373.2092 (0.1630), 1377.5451 (2.2289), 1397.7054 (0.0000), 1416.6397 (6.5889), 1492.1799 (0.0000), 1500.1925 (35.3829), 1584.7566 (0.0000), 1585.2877 (44.3057), 1619.2556 (0.0000), 1620.4328 (34.9297), 1787.0850

(200.7654), 1788.5344 (0.0000), 3309.0639 (29.5325), 3310.2622 (0.0121), 3318.6018 (68.3505), 3320.1463 (0.0148), 3343.3562 (25.4302), 3346.5316 (0.0000), 3919.2755 (0.0002), 3919.2970 (222.3272).

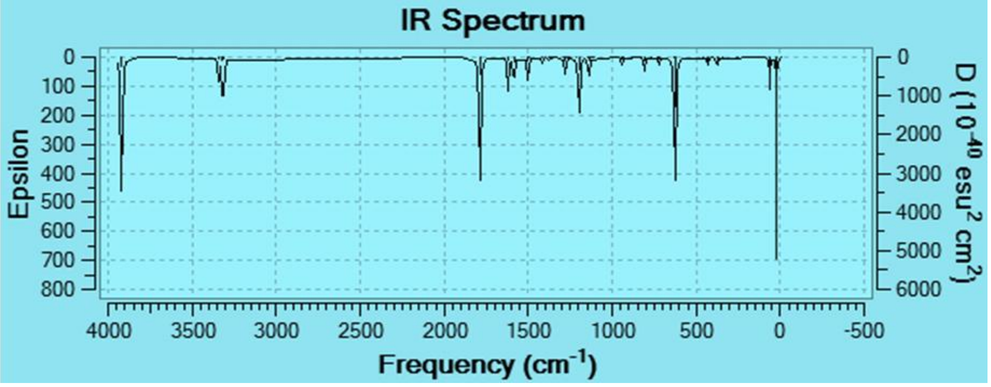


Figure 4: The IR spectra of structure.

It is remarkable that there are three very strong IR active modes. One is in 625.8 cm^{-1} frequency and is raised from the N-H bend of tetrazole groups. Second strong mode is in 1787.1 cm^{-1} frequency and it is related to the stretching vibration of C=N bonds. Finally, the third peak at 3919.3 cm^{-1} is caused mainly by the stretching of N-H bonds.

Nuclear magnetic resonance spectra:

Nuclear magnetic resonance (NMR) spectroscopy is a chief mean for determining the structure of organic molecules [36]. Here, nucleus shielding (ppm) for structure were calculated by using HF/6-31G(d) level of theory.

-151.7139 (N18 & N23), -108.1835 (N19 & N24), -50.0289 (N17 & N22), 22.8850 (H21 & H26), 28.1709 (H12 & H15), 29.0441 (H13), 29.0442 (H16), 29.0447 (H11 & H14), 50.5692 (C9 & C10), 69.1219 (N20), 69.1220 (N25), 159.0929 (C1 & C6), 160.5037 (C2), 160.5085 (C7), 160.5126 (C5), 160.5175 (C4), 162.5939 (C8), 162.5940 (C3).

Ultraviolet spectra:

Ultraviolet spectroscopy or spectrophotometry (UV) refers to absorption or reflectance spectroscopy in the ultraviolet spectral region [37]. This technique is used for the quantitative determination of various organic compounds and is carried out in solutions but solids and gases may also be studied [38]. Absorption of photons in the ultraviolet range is a result of excitation of ground state valence or bonding electrons into higher energy orbitals [39]. The molecule absorption was calculated at HF/6-31G(d) level. Figure **5** provides structure's UV spectra. The transitions are in 150-190 nm range and correspond to the $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions. The wavelength of maximum absorption (λ_{max}) is 160.91 nm and is related to the $n \rightarrow \pi^*$ transitions (-C=N-).

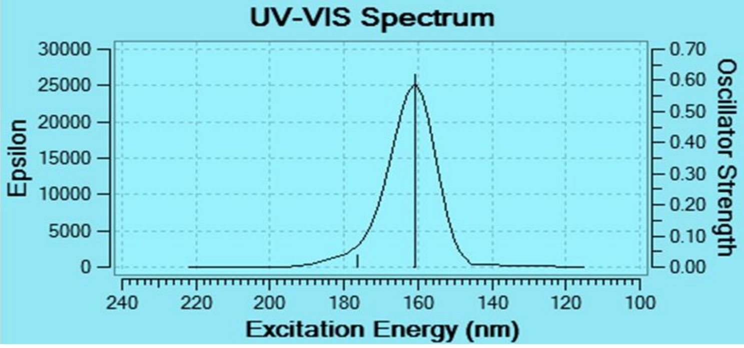


Figure 5: The UV spectra of structure.

The frontier molecular orbital energies:

Table **6** shows the HOMO and LUMO energies (ε) of the molecule computed at studied levels of theory. Figures **6** and **7** provide the frontier orbitals map. The HOMO is used if the reaction is with an electrophile, or Lewis acid, and the LUMO is used if reaction is with a nucleophile, or base [40]. The chemical reactivity is the molecular reactivity between two compounds [41]. For interaction of molecule with F$^-$ ion, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are [ε_{LUMO}(F$^-$) – ε_{HOMO}(molecule)] and

[ε_{LUMO}(molecule) – $\varepsilon_{HOMO}(F^-)$], respectively. From the data, we can see the $\Delta(\Delta\varepsilon_1 - \Delta\varepsilon_2) > 0$. Then, 1,4-bis(1H-tetrazolyl)cubane is considered as an electron acceptor (electrophilic). Pearson and Parr presented several chemical topics explaining the electronic reactivity of molecules [42]. These concepts (electronegativity, chemical potential, hardness and electrophilicity index) are obtained by theoretical calculations within the progressed structure of Hartree-Fock method [43]. The electronic chemical potential (the negative of the electronegativity, χ) of a molecule is defined by the following formal mathematical expression:

$$\mu \text{ (hartree)} = (\varepsilon_{LUMO} + \varepsilon_{HOMO})/2$$

Table 6: The frontier orbitals energy and electrophilicity of structure calculated at all studied methods.

Theory levels	ε_{HOMO} (hartree)	ε_{LUMO} (hartree)	μ (hartree)	η (hartree)	ω (hartree)	$\Delta\varepsilon_1$ (hartree)	$\Delta\varepsilon_2$ (hartree)
HF/6-31G(d)	-0.38722	0.12670	0.13026	0.51392	0.0165	1.93465	0.20414
HF/6-31G(d,p)	-0.38718	0.12650	0.13034	0.51368	0.0165	1.93461	0.20394
HF/6-31G(2d,2p)	-0.38389	0.12955	0.12717	0.51344	0.0157	1.55810	0.20789
HF/6-31+G(d,p)	-0.39222	0.04068	0.17577	0.43290	0.0357	0.92481	0.21874
HF/6-311G(d,p)	-0.38991	0.10953	0.14019	0.49944	0.0197	2.06019	0.21595

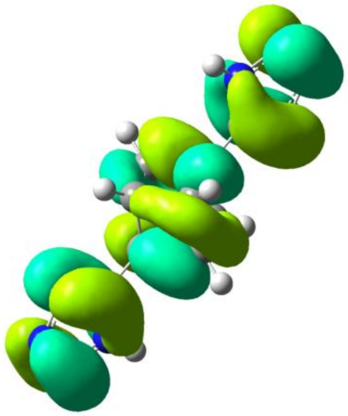


Figure 6: HOMO orbital map of the structure.

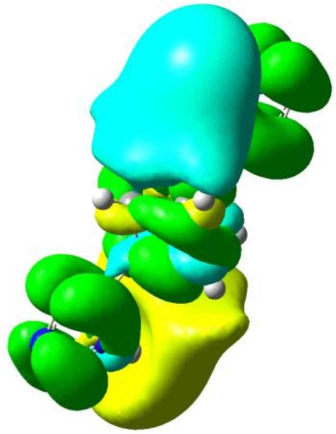


Figure 7: LUMO orbital map of the structure.

The μ (electronic chemical potential) shows the electron trend to migrate from the electronic cloud [44]. The absolute hardness η is branched from the μ [45]. The value of η for different molecules correlates with chemical hardness and softness obtained empirically [46]. A graphic definition of hardness is given as the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [47]. It is defined by the following formula:

$$\eta \text{ (hartree)} = \varepsilon_{LUMO} - \varepsilon_{HOMO}$$

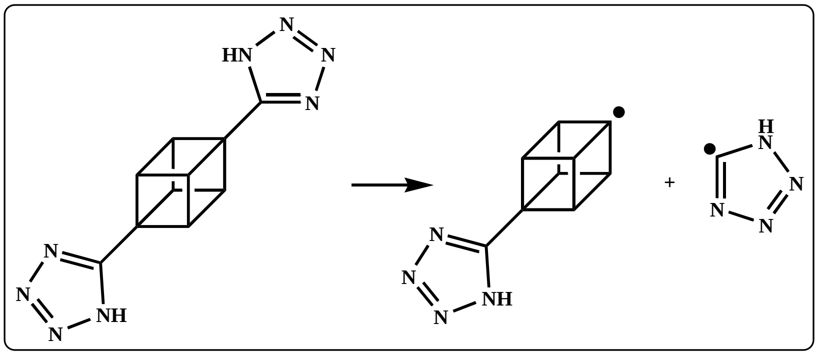
If $\eta > 0$, the charge transfer process is energetically favorable [48]. Finally, an electrophile is a compound attracted to electrons [49]. It participates in a chemical reaction by accepting an electron pair in order to bond to a nucleophile [50]. The index ω is defined as electrophilicity character that measures the energy stabilization when the system obtains an additional electronic charge from the environment [51]. This index is a kind of electrophilic power. The electrophilicity index ω given as:

$$\omega \text{ (hartree)} = \mu^2/2\,\eta$$

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 [52]. As we can see from the data, it is obtained that the 1,4-bis(1H-tetrazolyl)cubane has very low electrophilicity.

Bond Dissociation Energy (BDE) of the structure:

In organic chemistry, bond dissociation energy (BDE) shows the strength of a chemical bond [53]. It is expressed by the standard enthalpy change when a bond is cleaved by homolysis [54]. Indeed, BDE is the measure of energy needed to break apart one mole of covalently bonded molecules into a pair of radicals [55]. It does not depend on the path by which it occurs [56]. Bond dissociations investigation is essential and basic property for understanding the decomposition process of the high energy materials, since they are directly relevant to the stability and sensitivity of the high energy materials [57]. The homolytic bond dissociation of 1,4-bis(1H-tetrazolyl)cubane is shown in Scheme **1**. BDE calculations were performed at the HF method with the 6-31G(d), 6-31G(d,p), 6-311G(d,p), 6-31+G(d,p) and 6-31G(2d,2p) basis sets. The results of calculations are shown in Table **7**. As seen from the table, the homolytic bond dissociation energy of molecule is 85 kcal/mol. According to suggestion of Chung [58], the BDE more than 20 kcal/mol corresponds for a compound to be considered as a viable candidate of high energy density material (HEDM). Therefore, it can deduce that the molecule is viable candidate of HEDMs.



Scheme 1: The dissociation reaction for BDE calculation.

Table 7: Calculated total energies of the structures and fragments at the equilibrium geometries and resulting bond dissociation energies (BDE).

Theory levels	Parent energy (hartrees)	Fragment energy (hartrees)	1H-Tetrazole energy (hartrees)	BDE (kcal/mol)
HF/6-31G(d)	-818.409327	-562.201743	-256.055089	85.166
HF/6-31G(d,p)	-818.428343	-562.216697	-256.059270	85.100
HF/6-31G(2d,2p)	-818.464203	-562.240667	-256.071896	84.688
HF/6-31+G(d,p)	-818.447157	-562.228202	-256.066604	85.086
HF/6-311G(d,p)	-818.587257	-562.321526	-256.115171	84.085

Heats of formation, predicted densities and detonation of the structure:

The Enthalpy or heat of formation (HOF) is an important function for a molecule. There isn't any method to measure the absolute enthalpy and we have to measure changes in the HOF of the system [59]. One of the most important ways for calculation of the enthalpy of the molecule is defining the isodesmic reaction for the system. In isodesmic reaction, the numbers of bonds and bond types are preserved on both sides of the reaction [60]. The isodesmic reaction for HOF calculation is showed in Scheme **2**. For the isodesmic reaction, heat of reaction ΔH at 298 K can be calculated from the following equations:

$$\Delta H_{298} = \Sigma\Delta H_{f,P} - \Sigma\Delta H_{f,R}$$

$$\Delta H_{298.15K} = \Delta E_{298.15K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT$$

$$= \Sigma\Delta H^{\circ}_{f,P} - \Sigma\Delta H^{\circ}_{f,R}$$

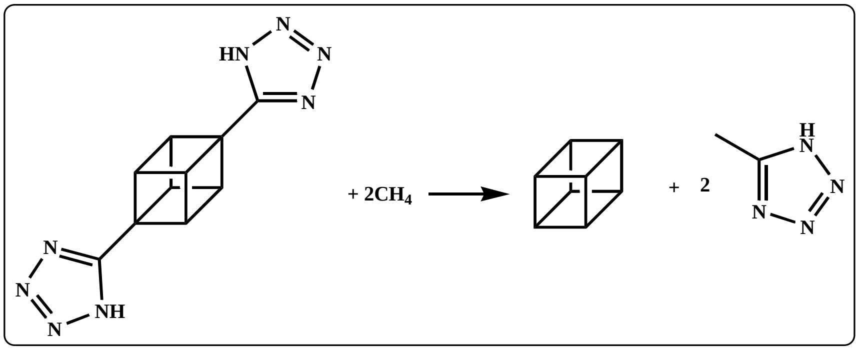
Where $\Delta H_{f,P}$ and $\Delta H_{f,R}$ are the heats of formation of products and reactants at 298 K, respectively. ΔE_0 and ΔZPE correspond to the total energy difference and the zero point energy difference between products and reactants at 0 K, respectively. ΔH_T is the changes in thermal correction to enthalpies between products and reactants. Δ(PV) equals ΔnRT for reaction in gas phase. For isodesmic reactions, Δn=0 [61]. As seen from the Table **8**, the HOF is 1350 kJ/mol for the structure at Hartree-Fock theory. Furthermore, density (ρ), detonation velocity (D), and detonation pressure (P) are the important parameters to evaluate the explosive performances of high energy materials ($C_aH_bO_cN_d$) and can be predicted by the following empirical Kamlet-Jacob equations [62]:

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

$$P=1.558\rho^2NM^{1/2}Q^{1/2}$$

	Stoichiometric ratio		
parameters	**c≥2a+b/2**	**2a+b/2>c≥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+0.239ΔH_f°)/MW	[28.9b+94.05(c/2-b/4)+0.239ΔH_f°]/MW	(57.8c+0.239ΔH_f°)/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 structures density was computed from the molecular volume, while the molecular volume for each structure was gained from the statistical average of 100 single-point calculations for optimized compound. The molar volume was defined as inside a contour of 0.001 e/Bohr^3 density that was evaluated using a Monte Carlo integration implemented in the Gaussian 03 package. The calculations were performed at the HF method with the 6-31G(d), 6-31G(d,p), 6-311G(d,p), 6-31+G(d,p) and 6-31G(2d,2p) basis sets. The results of calculations are shown in Table **8**. 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 [63]. The RDX and HMX are the current standards for detonation behavior. Comparing these values with 1,4-bis(1H-tetrazolyl)cubane shows it can't be an explosive.



Scheme 2: The isodesmic reaction for HOF calculation.

Table 8: Oxygen balance, HOF, predicted density and detonation properties of the structure at studied methods.

Theory Levels	OB$_{100}$	HOF (kJ/mol)	Q (kJ/g)	V* (cm^3/mol)	ρ (g/cm^3)	D (km/s)	P (GPa)
HF/6-31G(d)	-159.94	1350.059	1343.946	141.525	1.696	8.702	32.387
HF/6-31G(d,p)	-159.94	1350.316	1344.201	147.328	1.630	8.469	29.918
HF/6-31G(2d,2p)	-159.94	1350.057	1343.944	153.108	1.568	8.250	27.682
HF/6-31+G(d,p)	-159.94	1348.529	1342.422	162.876	1.474	7.916	24.449
HF/6-311G(d,p)	-159.94	1350.337	1344.222	157.014	1.529	8.112	26.325

*Average valu from 100 single-point volume calculations at studied levels.

Conclusion

In the present work, structural properties of the 1,4-bis(1H-tetrazolyl)cubane have been studied theoretically by using quantum chemical treatment. Full geometrical optimization of the structure was performed using Hartree-Fock theory (HF) at the 6-31G(d), 6-31G(d,p), 6-311G(d,p), 6-31+G(d,p) and 6-31G(2d,2p) basis sets. According to the results, we can be concluded as follows:

a. The charge of the carbon atoms of the cubane skeleton is negative.

b. The dihedral angles show that the tetrazole rings are plane.

c. It gets rid of the angular strain in the structure, the more p orbital of carbon atoms uses for forming C-C bonds.

d. The molecular electrostatic potential (MEP) map shows the negative charge is located on the nitrogen elements of the tetrazole rings.

e. Tetrazole rings of the molecule are aromatic.

f. There are three very strong IR active modes.

g. The wavelength of maximum absorption (λ_{max}) is 160.91 nm and is related to the $n \rightarrow \pi^*$ transitions (-C=N-).

h. 1,4-bis(1H-tetrazolyl)cubane is considered as an electron acceptor and has low electrophilicity.

i. The molecule is viable candidate of HEDMs.

j. 1,4-bis(1H-tetrazolyl)cubane can't be an explosive.

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