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# Theoretical studies on structure, material properties and spectrum of 3,4-Bis(1H-5-tetrazolyl)furoxan

Hong-Wei Xi<sup>1</sup>, Siti Zubaidah Binte Mohammad Mazian<sup>1</sup>, Hay Yee Serene Chan<sup>2</sup>, Huey Hoon Hng<sup>2</sup>, Ho Wee Goh<sup>3\*</sup>, Kok Hwa Lim<sup>1\*</sup>

<sup>1</sup>Singapore Institute of Technology, 10 Dover Drive, Singapore 138683

<sup>2</sup>Energetics Research Institute, Nanyang Technological University, 50 Nanyang Avenue, Singapore,

<sup>3</sup>ATREC Pte Ltd, 601 Rifle Range Road, Singapore 588398

## Abstract

Theoretical studies based on Density Functional Theory (DFT) were performed on the structure, the density and heat of formation of 3,4-Bis(1H-5-tetrazolyl)furoxan (H<sub>2</sub>BTF). Two planar conformational isomers, the Face-to-Back and the Back-to-Face, and one slightly twisted conformer, the Back-to-Back, had been predicted at the level of M06-2X/6-311+G(d,p). The Face-to-Back conformer is the most stable conformational isomer at its potential energetic surface. However, no stable Face-to-Face conformer, the planar or the tilted, could be found. Vienna Ab initio Simulation Package (VASP) in combination with molecular dynamics simulation was used to explore the stable crystal form and estimate the density for each of the stable conformational isomer. Two of them: Face-to-Back conformer adopting *P2*<sub>1</sub> (2.01 g/cm<sup>3</sup>) symmetry and Back-to-Back conformer adopting *Pna2*<sub>1</sub> symmetry (2.05 g/cm<sup>3</sup>) exhibited high densities. Their heats of formation were also predicted to be high at the same DFT level. The detonation pressures and velocities of these conformers, calculated by EXPLO5 program, are well above that of many advanced high energy density materials, hence displaying potential as explosives with good detonation performance. This study suggested that it could be worthwhile to investigate the possibility of growing denser polymorphs of H<sub>2</sub>BTF.

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\* Authors to whom correspondence should be addressed. *E-mail address:* [KokHwa.Lim@SingaporeTech.edu.sg](mailto:KokHwa.Lim@SingaporeTech.edu.sg) (Kok Hwa Lim); [gohhw@atrec.org](mailto:gohhw@atrec.org) (Ho Wee Goh).

To distinguish these denser polymorphs, IR spectra of H<sub>2</sub>BTF were reported herein.

Keywords: 3,4-Bis(1H-5-tetrazolyl)furoxan, HEDM, density, heat of formation, detonation property

## 1 Introduction

The tetrazole ring and furoxan ring are two worthy energetic building blocks in the design of new high energy density materials (HEDMs). Both, being rich in nitrogen, exhibit high heat of formation and the furoxan ring, in particular, has a superior oxygen balance over the tetrazole ring [1-6].

In 2012, a nitrogen-rich energetic monoanionic salt of 3,4-Bis(1*H*-5-tetrazolyl)furoxan (defined as H<sub>2</sub>BTF), which contained both tetrazole and furoxan rings, was first synthesized by Huang et al. [7]. In 2015, Zhai et al synthesized H<sub>2</sub>BTF by another method via cyclization reaction using 3,4-dicyanofuroxan and sodium azide as raw material [8].

The present authors found the chemical structure of H<sub>2</sub>BTF intriguing and worthy of further theoretical studies. Herein, Density Functional Theory (DFT) calculations were performed on conformers of H<sub>2</sub>BTF to obtain their optimized molecular and crystals structures and densities. Their heats of formation, detonation properties and IR spectra were also predicted and reported in this work.

## 2 Theoretical Method

Molecular geometries were fully optimized with DFT [9-10], by using M06-2X functionals developed by Zhao and Truhlar [11]), together with the 6-311+G(d,p) [12-13] basis set [14]. Vibrational frequency analyses were performed at the same level to characterize the stationary point as minima and to carry out zero-point-energy and thermal correction. The calculations were carried out using the computational chemistry software package Gaussian 09 [15].

Natural Population Analysis (NPA), Natural Bond Orbital (NBO) analysis [16] and Wiberg bond index (WBI) [17] were performed with DFT M06-2X wave functions. All the calculations were carried out using the NBO 5.0 package [18].

Quantum mechanics (QM) molecular volume, defined as the volume inside a contour of 0.001 electrons/ Bohr<sup>3</sup> density [19], was evaluated using a Monte Carlo integration. The QM molecular volume was taken as an average volume of 100 single-point

calculations.

It is known that the predicted density (QM density, gas phase) from QM calculations does not take into account intermolecular interactions and crystal packing. In addition, the technique would not be able to distinguish between different polymorphs of the same energetic material. To increase the accuracy of HEDMs prediction, a new technique was developed to include two consecutive steps: crystal packing of molecules and first-principle simulation of crystalline HEDMs, to evaluate the crystalline density of HEDM [20].

Firstly molecular dynamics (MD) simulations were performed by the Polymorph Predictor calculations (using Dreiding force field) to 11 common space groups ( $P2_1$ ,  $P2_1/m$ ,  $P-1$ ,  $P1$ ,  $P2_12_12_1$ ,  $Pbca$ ,  $Pbcn$ ,  $Pnam$ ,  $Pca2_1$ ,  $Pca2_1$  and  $C/c$ , above 80% crystal forms are under them) [21]. Then, out of 11 space groups, several more stable crystal forms were selected. Subsequent ab initio calculations using the Vienna Ab Initio Simulation Package (VASP) performed within generalized gradient approximation Perdew-Burke-Ernzerh (GGA-PBE) [22] as implemented within the package [23-25] the projector augmented wave method (PAW) [26-27] was used to describe the interaction between the atomic cores and electrons. From the VASP simulations, unit cell lattice parameters of HEDM crystals were attained and the crystalline density was obtained by dividing the mass of the unit cell by the volume of the unit cell.

## 3 Results and discussion

### 3.1 Molecular structure and chemical bond

Full geometry optimization found three stable minima of H<sub>2</sub>BTF on its potential energy surface (PES). Optimized structural parameters of the three conformational isomers, calculated at the level of M06-2X, are given in Table 1. The notations for the geometrical parameters are shown in Figure 1. Based on the relative positions of the two Hydrogen (H<sub>17</sub> and H<sub>18</sub>) and Oxygen (O<sub>6</sub>), two planar conformers are defined as Face-to-Back **1** (C<sub>s</sub> symmetry) and Back-to-Face **2** (C<sub>s</sub> symmetry) conformers. There is another non-planar conformer, defined as Back-to-Back

conformer **3** ( $C_1$  symmetry), (see Figure 1). The two tetrazolyl planes of Back-to-Back conformer **3** are tilted from the central furoxan plane at  $6.6^\circ$  and  $32.0^\circ$  (dihedral angle of  $D(N_9C_7C_1C_2)$  and  $D(N_{10}C_8C_2C_1)$ ) being  $-173.7$  and  $-148.0$ , see Table 1), respectively .

Figure 1 and Table 1 should be here

Back-to-Face **2** and Back-to-Back **3** local minima lies  $2.98$  and  $6.98$  kcal/mol above Face-to-Back **1** global minimum, respectively. The stability and planar structure of Face-to-Back **1** and Back-to-Face **2** originate from the intramolecular hydrogen bond and the conjugation effect spanning the tetrazole and furoxan ring. NBO analysis indicates that there are  $n_O \rightarrow \sigma_{HN}^*$  donor–acceptor interactions in Face-to-Back conformer **1** and Back-to-Face conformer **2** (see Figure 2). The second-order stabilization energies of  $n_{O9} \rightarrow \sigma_{H18N10}^*$  at Face-to-Back **1** and  $n_{O10} \rightarrow \sigma_{H17N9}^*$  in Back-to-Face **2** are  $12.21$  and  $11.23$  kcal/mol, respectively. Although there is another  $n_{O9} \rightarrow \sigma_{H18N10}^*$  donor–acceptor interaction in the Face-to-Back conformer, this interaction is very weak. The second-order stabilization energy is only  $1.28$  kcal/mol (see Figure 2). Since there is no weaker repulsion between lone pair orbitals of  $O_6$  and  $N_{15}$  in the Back-to-Face conformer **2**, its potential energy is slightly lower than that of Face-to-Back conformer **1** (see Figure 2).

Figure 2 should be here

M06-2X optimization found that there is *no* stable Face-to-Face minimum (the planar or the slightly tilted) on the  $H_2BTF$  PES, which is different from the experimental geometry [8]. Similar optimization at the level of B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) leads to the same conclusion as the M06-2X optimization. The hypothetical Face-to-Face planar structure **4** (see Figure 1) is a second-order saddle point with two degenerate imaginary frequencies.

To discuss the stability of conformers, the contra rotating PEC from planar Face-to-Face conformer to planar Back-to-Back conformer, whose rotational angles ( $\theta$ ) are defined as the  $D(N_9C_7C_1C_2)$  and  $D(N_{10}C_8C_2C_1)$  dihedral angle and potential energy is related to the Back-to-Back conformer **3**, was obtained by performing geometry optimization calculations (all the independent geometric parameters except  $\theta$  were optimized) at a set of selected  $\theta$  values ranging from  $-180.0^\circ$  and  $180.0^\circ$ .

The M06-2X contra rotation PEC from the Face-to-Face to the Back-to-Back is shown in Fig. 3. Along the skeleton of contra rotation PEC of H<sub>2</sub>BTF, there exists a minimum around  $\theta = 165.0^\circ$  and there is only one maximum (the planar Face-to-Face geometry). From the planar Face-to-Face conformer ( $\theta = 0.0^\circ$ ) to the planar Back-to-Back conformer ( $\theta = \pm 180.0^\circ$ ), the curve drops rapidly at first since there is the stronger repulsion between  $\sigma_{NH}$  orbitals at two tetrazole rings (see Figure 2). The trend of PES becomes more gentle from  $\theta = 45.0^\circ$  to  $\theta = 90.0^\circ$ . After  $\theta = 90.0^\circ$ , the potential energies of conformers gradually decrease since the conjugation effect between tetrazole and furoxan rings become stronger. There is one shallow minimum at  $\theta = 165.0^\circ$ . The planar structure of Back-to-Back conformer is sacrificed to avoid the repulsion between the two lone pairs of electrons at the two tetrazole rings.

Figure 3 should be here

### 3.2 Crystal form and density

The density of H<sub>2</sub>BTF in  $P2_12_12_1$  space group was previously reported to be 1.76 g/cm<sup>3</sup> [8]. However, other polymorphs could have existed, through rotation of the tetrazole rings relative to the furoxan ring, and therefore a more detailed theoretical study was performed in this work. As previously reported [20], the technique of VASP would be able to account for intermolecular interactions and

the different polymorphs within an energetic crystal and hence provide a more realistic prediction to its density.

The densities of three stable conformers, Face-to-Back **1**, Back-to-Face **2** and Back-to-Back **3**, are calculated at the level of QM, MD and VASP. They are defined as QM, MD and VASP density and are given in Table 2. For MD and VASP methods, the densities of two most stable crystal forms of three stable conformer are presented in order to avoid the perversion of density order between MD and VASP.

Table 2 should be here

Table 2 shows that the values of MD and VASP density is consistently higher than QM density. It is because the presence of hydrogen bonding of is conducive to higher crystal density than predicted by QM calculations.

Results of the calculation at the VASP level show that the two highest densities and their crystal forms of the H<sub>2</sub>BTF are 2.01 g/cm<sup>3</sup> with *P2*<sub>1</sub> symmetry (Face-to-back **1**, see Figure 4(a)) and 2.05 g/cm<sup>3</sup> with *Pna*<sub>21</sub> symmetry (Back-to-Back **3**, see Figure 4(b)). Such values are very close to the density of  $\epsilon$ -CL-20 (2.04 g/cm<sup>3</sup>) [28]. Thus far, there had been no practical molecule synthesized that exceeds the energy density of CL-20 discovered about 20 years ago. It is interesting that the non-planar Back-to-Back conformer **3** possess higher crystal density than planar Face-to-back conformer **1**. It may be the prevalence of intramolecular hydrogen bonding over stabilization through conjugation which contributed to the higher density.

Figure 4 should be here

Through QM densities at the level of M06-2X have more similar densities (1.73, 1.79 and 1.72 g/cm<sup>3</sup> for Face-to-Back **1**, Back-to-Face **2** and back-to-Back **3**, respectively) to the density in reference 8 (1.76 g/cm<sup>3</sup>), MD and VASP simulation

predicted different crystal forms from the experiment ( $P2_12_12_1$  space group, see Reference 8). It is because that  $H_2BTF$  structure found experimentally had one different geometry, whose tetrazole rings were slightly twisted relative to the central furoxan ring with face-to-face model from three present stable conformers based on the theoretical simulation. MD and VASP simulation indicate that the  $P2_12_12_1$  space group of  $H_2BTF$  is one of top two maximum densities of Back-to-Face conformer.

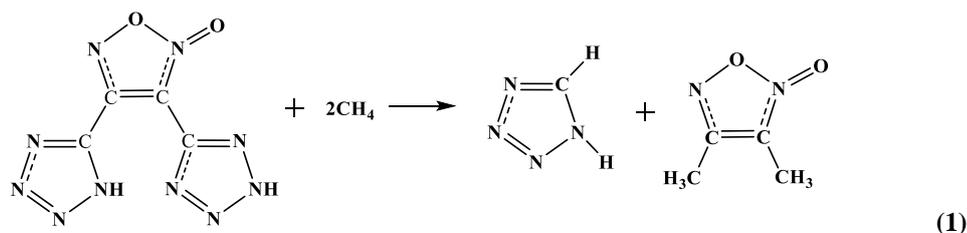
Our calculation also predicts the existence of the  $P2_12_12_1$  crystal form with crystal density at  $1.77 \text{ g/cm}^3$ . This is in congruence with previously reported results [8]. To sum up, our results show the possibility of other crystal forms that are higher in density and thermodynamically more stable. The crystal reported by Zhai et. al could be a kinetically driven product.

### 3.3 Heat of Formation

Heat of formation is another crucial physical property of an energetic material. It indicates the energy content of a material and is a critical parameter used in standard thermochemical codes to assess its potential detonation performance.

In recent years, QM is becoming an important technique to estimate the heat of formation of HEDM [29-30]. QM method predicts the gas-phase heats of formation based on Hess's law together with the use of experimental values of standard enthalpies of formation of reactants and products.

In order to obtain heat of formations of  $H_2BTF$  conformers, we build an isodesmic reactions (see below) to calculate the HOFs at the level of M06-2X/6-311+G(d,p):



For the isodesmic reaction, the heat of reaction  $\Delta H_{298}$  is calculated and corrected to 298 K based on the following equation:

$$\Delta H_{298\text{ K}} = \Delta E_{298\text{ K}} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

where  $\Delta E_0$  is the change in total energy between the products and the reactants at 0 K;  $\Delta ZPE$  is the difference between the zero-point energies (ZPEs) of the products and the reactants at 0 K;  $\Delta H_T$  is the thermal correction from 0 to 298 K.  $\Delta(PV)$  value is the PV work term and equals to  $\Delta nRT$ . The experimental heat of formation of tetrazole and furoxan rings are 76.5 kcal/mol<sup>-1</sup> [31] and 24.4 kcal/mol<sup>-1</sup> [32], respectively.

Table 3 should be here

Heat of formations of three stable conformers, Face-to-Back **1**, Back-to-Face **2** and Back-to-Back **3**, are given in in Table 3. The calculated values of the three conformers are found to have similar values of 184.80, 187.83 and 192.01 kcal/mol, which can be attributed to the difference in structural aspect of the three conformers. It is interesting to note that heat of formation of Back-to-Back **3** has the highest value. The heats of formation of the three stable conformers are significantly higher than that of TNT and RDX, by 79.45 kcal/mol and 59.20 kcal/mol (which were calculated by the same DFT method in this work), respectively. The relatively high heat of formations found for all the conformers suggest that H<sub>2</sub>BTF could be a promising HEDM candidate.

### 3.4 Detonation Performance

Detonation velocity (D) and detonation pressure (P) are essential performance parameters for an energetic material. Since experimental data is lacking for new

HEDMs, the detonation properties of many HEDMs are often predicted by applying the empirical equations [33] and thermochemical code [34]. In the present work, detonation parameters, D and P, were calculated using EXPLO5 [34]. EXPLO5 program uses Becker-Kistiakowsky-Wilson (BKW) equation of state for gaseous detonation products and Murnaghan or Cowan-Fickett's equation of state for solids products and EXPLO5 detonation parameter can be derived with the error less than 10% [35].

The detonation velocities of H<sub>2</sub>BTF conformers; Face-to-Back ( $P_{21}$ ), Back-to-Face ( $P_{na21}$ ) and Face-to-Face ( $P_{na21}$ ), are 9375, 8463 and 9620 m/s, respectively; the detonation pressures of Face-to-Back ( $P_{21}$ ), Back-to-Face ( $P_{na21}$ ) and Face-to-Face ( $P_{na21}$ ) polymorphs are 36.92, 28.64 and 39.30 GPa, respectively (see Table 4). It is noteworthy that Back-to-Face conformer has considerably lower performance properties than other two conformers.

The detonation velocities and pressures of Face-to-Back ( $P_{21}$ ) and Face-to-Face ( $P_{na21}$ ) polymorphs of H<sub>2</sub>BTF are above classical explosives such as TNT, RDX and HMX, whose detonation velocities, calculated using the same EXPLO5 program, are 6809, 8793 and 9179 m/s and detonation pressures are 18.70, 33.68 and 37.82 GPa (see Table 4). The detonation velocities and pressures of Face-to-Back ( $P_{21}$ ) and Face-to-Face ( $P_{na21}$ ) polymorphs of H<sub>2</sub>BTF are comparable to new theoretically predicted explosive molecules, for example, 3,4,5-trinitro-pyrazol-1-amine, with the detonation velocities and pressures calculated to be 9,230 m/s and 39.40 GPa [36]. Hence, the proposed H<sub>2</sub>BTF polymorphs show potential as HEDMs.

Table 4 should be here

### **3.5 Infrared (IR) vibrational spectrum**

Infrared (IR) spectrophotometry is often used to identify and study chemical structures of energetic materials. Though DFT studies have shown that simulated

infrared vibrational frequencies are close to their experimental results [37], DFT vibrational frequencies are usually slightly higher than those observed frequencies [38]. This may be attributed to the intermolecular interactions in solution and crystal that are not accounted for in DFT calculations. Moreover, DFT method calculates the vibrational frequencies only in harmonic mode. To accurately and reliably determine IR frequencies of H<sub>2</sub>BTF, a scaling factor between the simulated and the experimental data should account for the theoretical deviation. Since a uniform scaling factor for different systems may lead to the wrong assignment, a new set of transferable scaling factors for H<sub>2</sub>BTF have been proposed here.

At the M06-2X/6-311+G(d,p) level, the scaling factor of IR frequency suitable for H<sub>2</sub>BTF was evaluated according to the experimental IR frequency of some nitrogen-rich five-membered ring with similar structure to H<sub>2</sub>BTF. Furan, pyrrole, pyrazole and imidazole have been selected as the control; their IR frequencies will be compared with that of H<sub>2</sub>BTF.

Table 5 lists the top 5 IR frequencies for furan, pyrrole, pyrazole and imidazole derived from experimental data and M06-2X/6-311+G(d,p) calculations as well as the IR frequencies of the three conformers of H<sub>2</sub>BTF (see supporting information for detailed table). From Table 5, we can see that the calculated IR frequencies are in qualitative agreement with their corresponding experimental IR frequencies. The optimum scaling factor  $\lambda$  are obtained through a least-squares procedure by minimizing the residual error between the experimental and calculated vibrational frequencies:

$$\lambda = \frac{\sum_i^N \omega_i^{th} \omega_i^{exp}}{\sum_i^N (\omega_i^{th})^2} \quad (6)$$

where  $\omega_i^{th}$  are the computational IR frequencies derived from the M06-2X/6-311+G(d,p) calculations and  $\omega_i^{exp}$  are the experimental IR frequencies.

Table 5 should be here

Based on the data from Table 5 and equation 6, the evaluated IR frequency scaling factor  $\lambda$  is 0.96, Using Multiwfn software [39], IR spectra of Face-to-Back **1**, Back-to-Face **2** and Back-to-Back **3**, are corrected with the scale factor of 0.96 and plotted in Fig.5.

Figure 5 should be here

Generally, the IR spectra of the three conformers are distinctly different from one another, suggesting IR could well differentiate the 3 different conformers. The ring C=C and C=N stretching vibrations observed in the region 1613-1587 and 1519-1462  $\text{cm}^{-1}$  and the vibrations of NH and CH groups in the range 3500 - 3220  $\text{cm}^{-1}$  are in good agreement with presence of the tetrazole rings.

## 4 Conclusion

DFT calculations of H<sub>2</sub>BTF reported in this work predict stable planar conformers, the Face-to-Back and Back-to-Face, and one slightly twisted Back-to-Back conformer, which were not previously reported. Face-to-Back conformer is found to be the most stable conformer of the potential energetic surface of H<sub>2</sub>BTF since there is  $n_{\text{O}} \rightarrow \sigma_{\text{HN}}^*$  donor-acceptor interactions and there is no the weak repulsion between lone pair orbitals of O and N. It is interesting that the Face-to-Face conformer that was previously reported, the planar or the slightly tilted, was found not to be stable based on DFT and *ab initio* calculation. We ascribed the instability to the repulsion between  $\sigma_{\text{NH}}$  orbitals of two tetrazole rings.

The present work further suggests that it may be worthwhile to study the crystallization of H<sub>2</sub>BTF compound to crystallize out the more thermodynamically stable and yet experimentally evasive polymorphs and use IR spectra as a supporting technique. The polymorphs appeared promising as they potentially

possess higher density and heat of formation, and hence detonation performance, as compared to classical energetic materials such as RDX and HMX.

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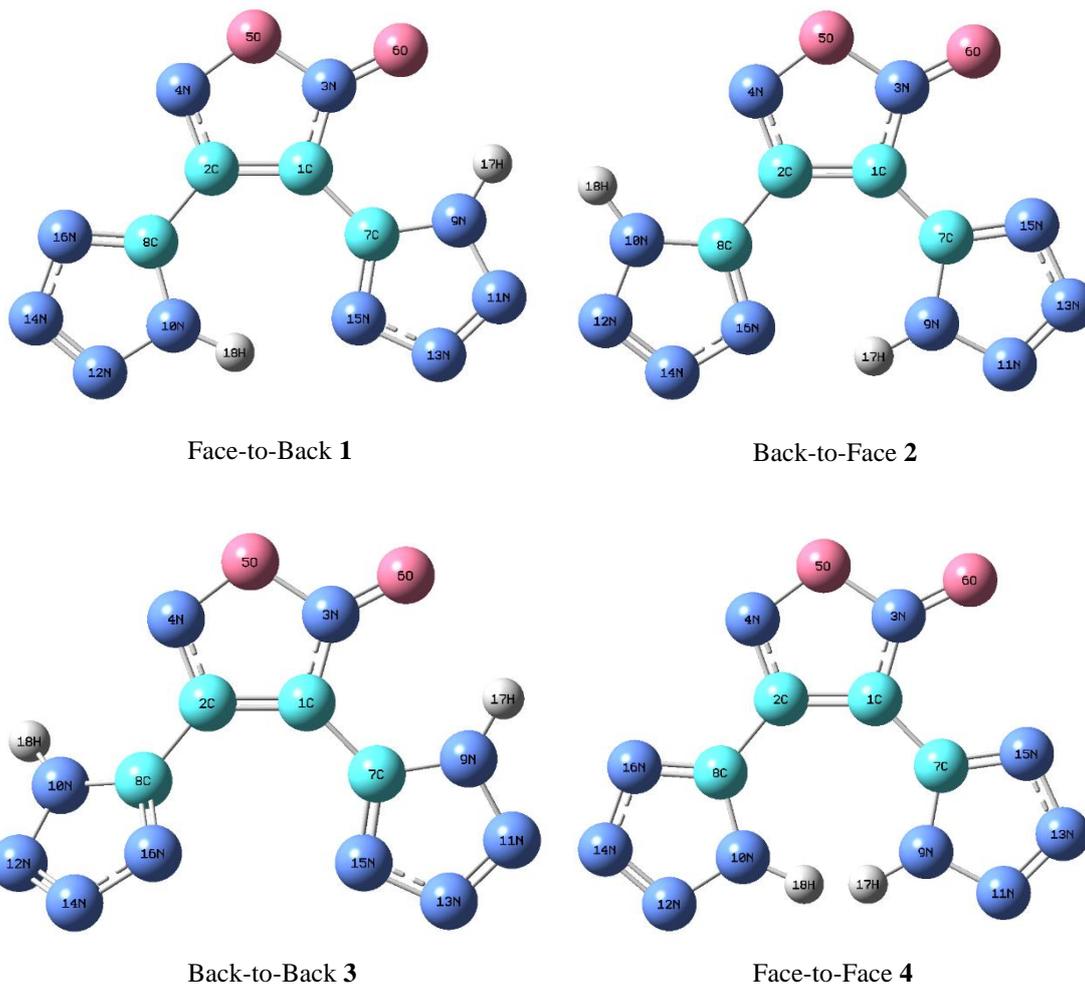


Fig. 1 Molecular structures and notations of conformers, Face-to-Back 1, Back-to-Face 2 and Back-to-Back conformers 3, optimized at the M06-2X/ 6-311+G(d,p) level and hypothetical Face-to-Face planar structure 4.

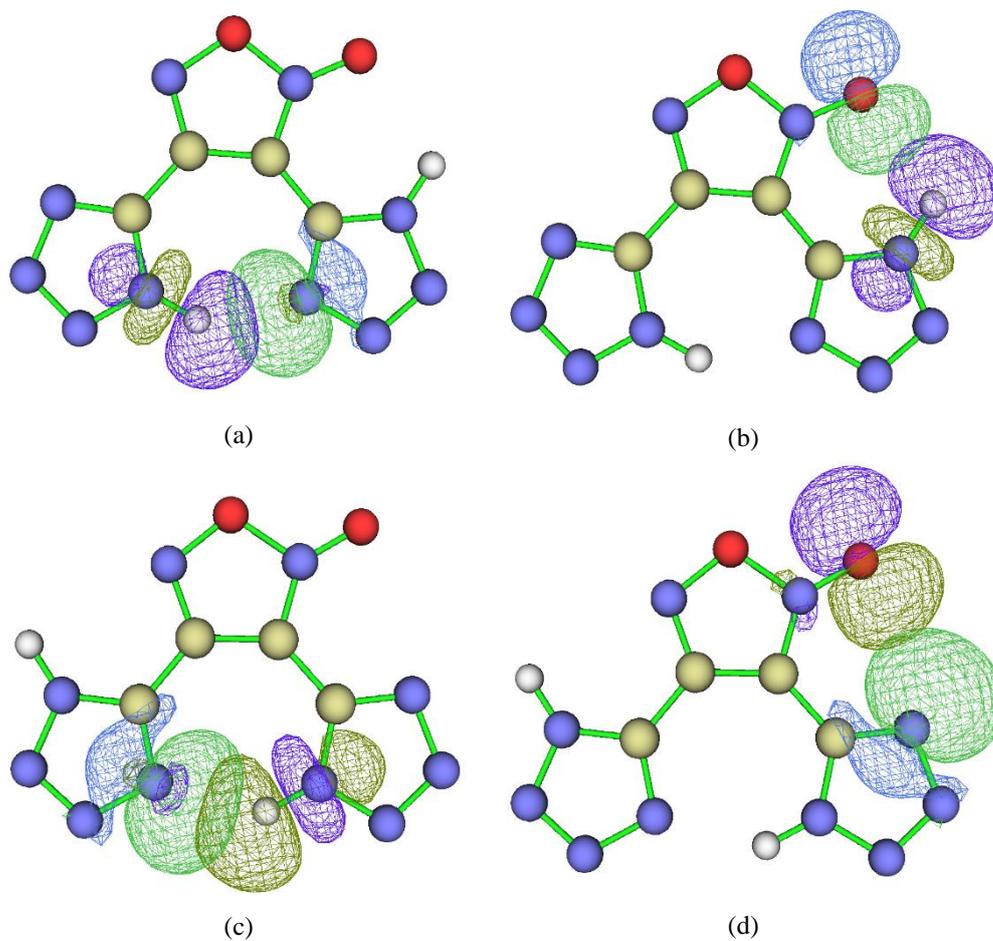


Fig. 2 (a)  $n_{\text{N}} \rightarrow \sigma_{\text{HN}}^*$  donor-acceptor interactions of  $\text{N}_{15} \dots \text{H}_{18}\text{N}_{10}$  hydrogen-bond at Face-to-Back conformer **1**. (b)  $n_{\text{O}} \rightarrow \sigma_{\text{HN}}^*$  donor-acceptor weak interactions at Face-to-Back conformer **1**. (c)  $n_{\text{N}} \rightarrow \sigma_{\text{HN}}^*$  donor-acceptor interactions of  $\text{N}_{16} \dots \text{H}_{17}\text{N}_9$  hydrogen-bond at Back-to-Face conformer **2**. (d) The repulsion between lone-pair NBO orbit of  $\text{O}_6$  and  $\text{N}_{15}$  at Back-to-Face conformer **2**.

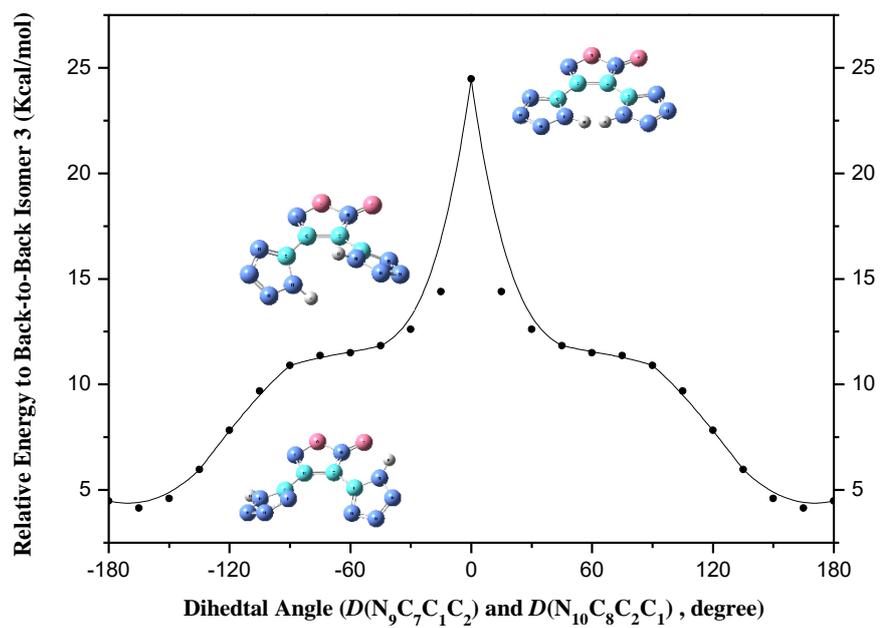
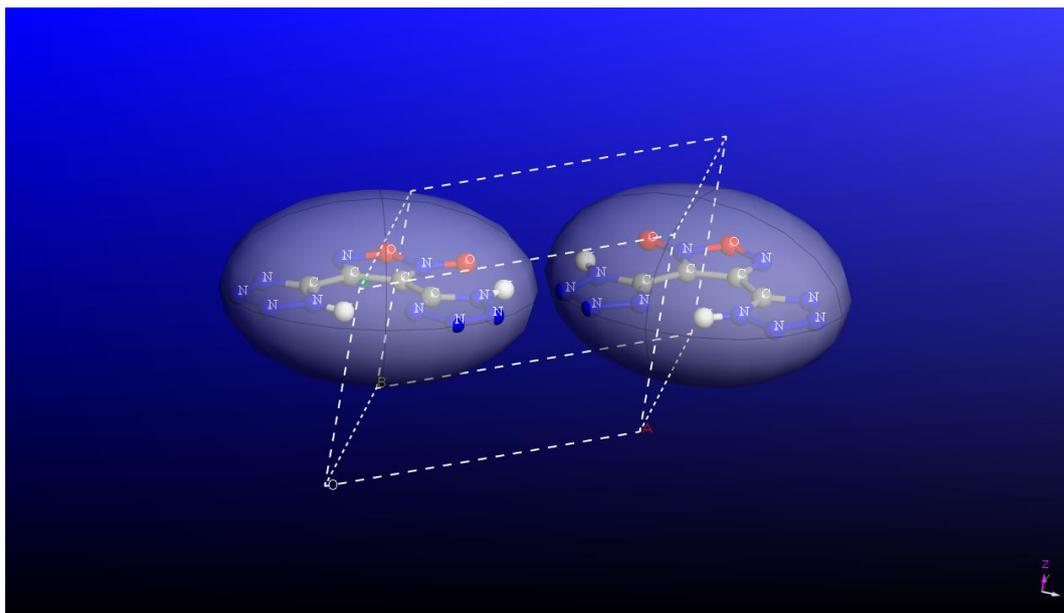
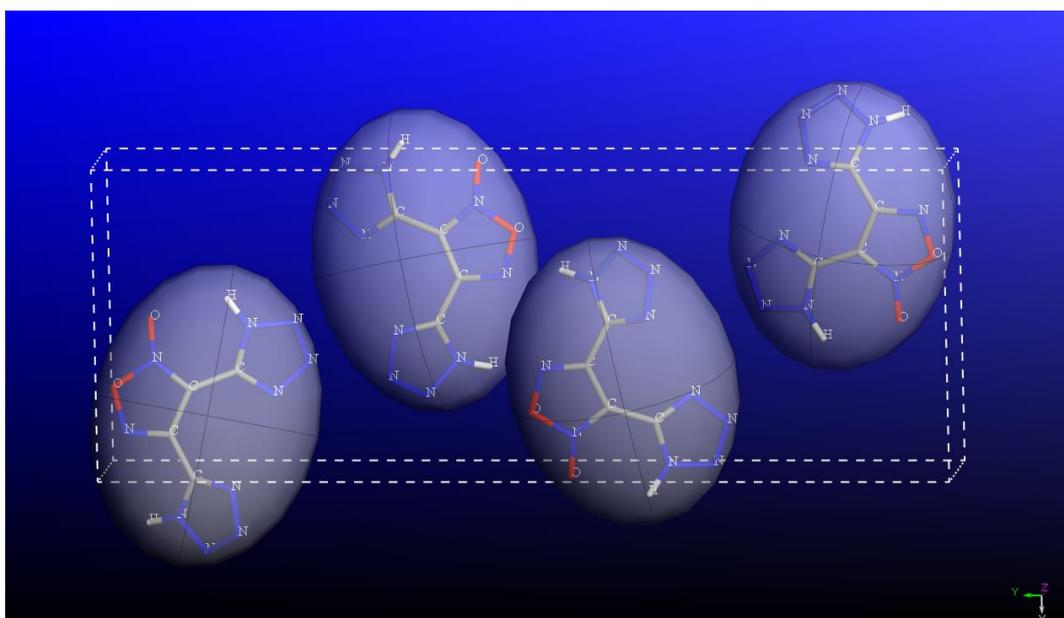


Fig. 3 The contra rotating potential energy curve from planar Face-to-Face conformer to planar Back-to-Back conformer the internal rotation angle is defined as the dihedral angle of  $D(N_9C_7C_1C_2)$  and  $D(N_{10}C_8C_2C_1)$ .

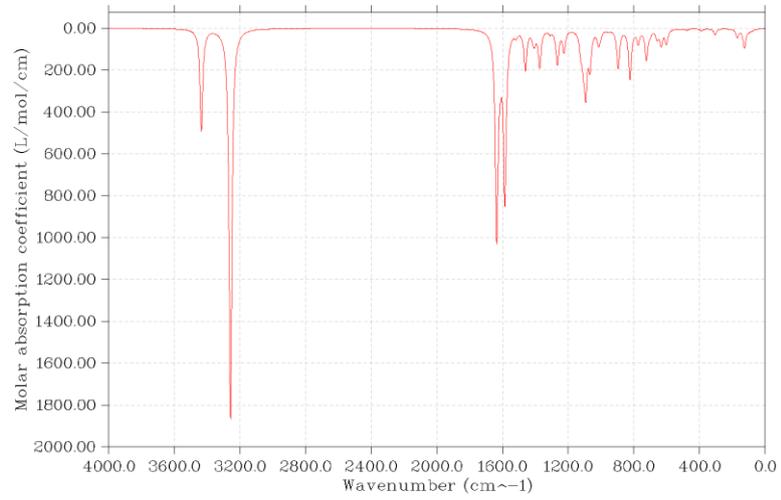


(a)

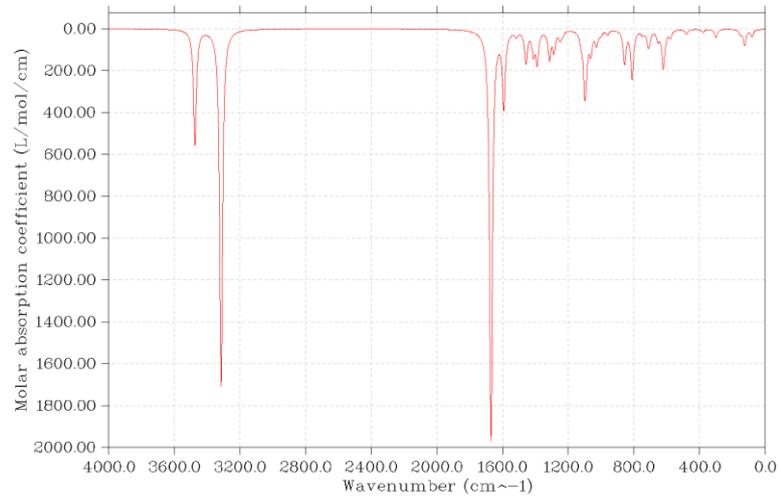


(b)

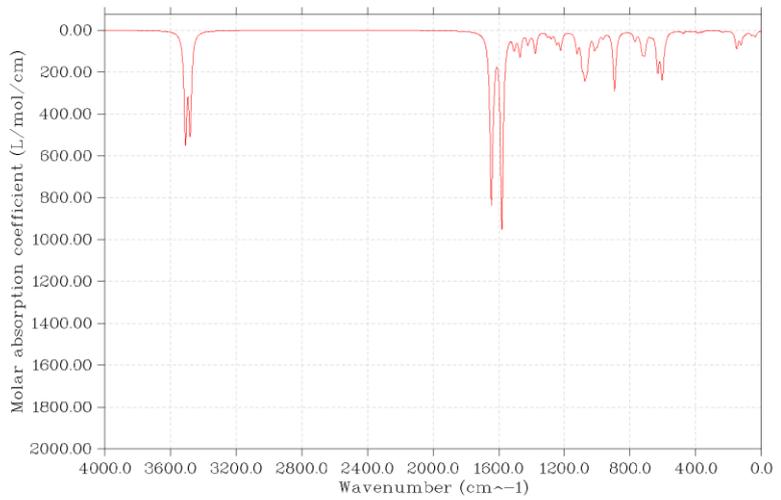
Fig. 4. Molecular packing diagrams of the unit cells of Face-to-Back ( $P2_1$  group, a) and Back-to-Back ( $Pna2_1$  group, b) conformational isomers



(a) IR spectrum of



(b) IR of Face-to-Back 2



(c) IR of Back-to-Back 3

Fig. 5. IR spectra of Face-to-Back 1, Back-to-Face 2 and Back-to-Back 3, drawn using Multiwfn software.

Table 1. Geometric parameters, optimized at the M06-2X/6-311+G(d,p) level, for three conformational isomers of H<sub>2</sub>BTF, Face-to-Back, Back-to-Face and Back-to-Face conformers (for notations see Fig. 1; bond distances (*R*, in Å) and dihedral angles (*D*, in degrees)).

Conformer	<i>R</i> (C <sub>1</sub> N <sub>3</sub> )	<i>R</i> (C <sub>1</sub> C <sub>7</sub> )	<i>R</i> (C <sub>7</sub> N <sub>9</sub> )	<i>R</i> (C <sub>7</sub> N <sub>15</sub> )	<i>R</i> (C <sub>1</sub> C <sub>2</sub> )	<i>R</i> (N <sub>3</sub> O <sub>5</sub> )	<i>R</i> (N <sub>3</sub> O <sub>6</sub> )	<i>D</i> (N <sub>9</sub> C <sub>7</sub> C <sub>1</sub> C <sub>2</sub> )	<i>D</i> (N <sub>10</sub> C <sub>8</sub> C <sub>2</sub> C <sub>1</sub> )
Face-to-Ba ck 1	1.326 (1.301) <sup>a</sup>	1.440 (1.458) <sup>a</sup>	1.343 (1.344) <sup>a</sup>	1.315 (1.313) <sup>a</sup>	1.430	1.378	1.219	180.0	0.0
Back-to-Fa ce 2	1.339 (1.299) <sup>a</sup>	1.447 (1.455) <sup>a</sup>	1.346 (1.341) <sup>a</sup>	1.316 (1.311) <sup>a</sup>	1.424	1.418	1.194	0.0	180.0
Back-to-Ba ck 3	1.326 (1.300) <sup>a</sup>	1.443 (1.456) <sup>a</sup>	1.346 (1.344) <sup>a</sup>	1.312 (1.308) <sup>a</sup>	1.424	1.389	1.217	-173.3	-148.0

<sup>a</sup> Corresponding bond length at another corresponding ring. <sup>b</sup> *R*(C-C) ranges from 1.430 to 1.458 Å, *R*(C-N) from 1.299 to 1.346 Å and *R*(N-N) ranges from 1.277 to 1.350 Å. <sup>c</sup> C=C, C=N and O=N bond lengths in CH<sub>2</sub>=CH<sub>2</sub>, CH<sub>2</sub>=NH and O=NH are 1.326, 1.263 and 1.190 Å, respectively (at M06-2X/6-311+G(d,p) level). <sup>d</sup> C-C, C-N and O-N bond lengths in CH<sub>3</sub>-CH<sub>3</sub>, CH<sub>3</sub>-NH<sub>2</sub> and OH-NH<sub>2</sub> are 1.527, 1.462 and 1.422 Å, respectively (at M06-2X/6-311+G(d,p) level).

Table 2. Molecular volume (at cm<sup>3</sup>/mol) and QM density (at g/cm<sup>3</sup>) at the M06-2X/6-311+G(d,p) level and top two maximum density MD density (at g/cm<sup>3</sup>) and VASP density (at g/cm<sup>3</sup>) of crystal form of different conformational isomers of Tetrazolyfuroxan.

Conformer	Molecular volume (cm <sup>3</sup> /mol)	QM Density (g/cm <sup>3</sup> )	MD density (g/cm <sup>3</sup> ) <sup>a</sup>	crystal form <sup>a</sup>	VASP density (g/cm <sup>3</sup> )
Face-to-back	128.29	1.73	1.86	<i>Pna2</i> <sub>1</sub>	1.86
			2.01	<i>P2</i> <sub>1</sub>	2.01
Back-to-Face	123.93	1.79	1.81	<i>P2</i> <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	1.77
			1.81	<i>Pna2</i> <sub>1</sub>	1.81
Back-to-Back	129.34	1.72	1.77	<i>Pca2</i> <sub>1</sub>	1.77
			1.80	<i>Pna2</i> <sub>1</sub>	2.05

Table 3. The QM heat of formation (HOF, at kcal/mol) calculated at the M06-2X/6-311+G(d,p) level based on the Hess circle together with the experimental values of standard enthalpies of formation of reactants and products.

	Face-to-Back 1	Back-to-Face 2	Back-to-Back 3
HOF	184.80	187.83	192.01

Table 4. The detonation velocity ( $D$ , at km/s) and detonation pressure ( $P$ , at GPa) of the most stable polymorph of three conformers of H<sub>2</sub>BTF and TNT, RDX, HMX<sup>a</sup>, which are calculated using EXPLO5 computer program.

	Face-to-Back 1 ( $P2_1$ )	Back-to-Face 2 ( $Pna2_1$ )	Back-to-Back 3 ( $Pna2_1$ )	TNT	RDX	HMX
$D$	9375	8463	9620	6809	8793	9179
$P$	36.92	28.64	39.40	18.70	33.68	37.82

<sup>a</sup> The densities of TNT, RDX, HMX are 1.65, 1.80 and 1.90 g/cm<sup>3</sup>, respectively; the heats of detonation of TNT, RDX, HMX are -4380, -5712 and -5674 kJ/kg, respectively.

Table 5: Top 5 IR frequencies for Nitrogen-rich five-membered ring compounds, Furan, Pyrrole, Pyrazole and Imidazole, obtained from calculations and experiments and for three stable conformers of H<sub>2</sub>BTF simulated at the level of M02-2X and corrected with scaling factor.

Furan <sup>a</sup>		Pyrrole <sup>a</sup>		Pyrazole <sup>b</sup>		Imidazole <sup>c</sup>		Face-to-back		Back-to-Face		Back-to-Back	
Theory	Experiment	Theory	Experiment	Theory	Experiment	Theory	Experiment	Simulated	Scaled IR <sup>d</sup>	Simulated	Scaled IR <sup>d</sup>	Simulated	Scaled IR <sup>d</sup>
613.99	599.60	502.97	474.61	575.20	516	549.01	509	54.44	52.27	44.27	42.50	39.05	37.49
626.13	602.85	629.88	614.01	641.82	623	649.07	628	84.30	80.93	84.88	81.48	61.00	58.56
762.65	721.50	642.09	620.67	702.13	674	684.95	664	104.03	99.87	86.59	83.13	85.27	81.86
777.31	744.65	714.39	692.20	769.45	745	744.06	724	131.35	126.10	130.86	125.62	106.65	102.38
884.68	837.59	745.80	722.13	868.58	833	841.92	812	135.41	130.00	132.84	127.53	130.69	125.46

<sup>a</sup> Furan and Pyrrole, see Ref [40]. <sup>b</sup> Pyrazole, see Ref [41]. <sup>c</sup> Imidazole, see Ref [42]. <sup>d</sup> Scaled to 0.96.