3,4-Bis(3-tetrazolylfuroxan-4-yl)furoxan: A Linear C–C Bonded Pentaheterocyclic Energetic Material with High Heat of Formation and Superior Performance

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ABSTRACT: The design and preparation of new nitrogen-rich heterocyclic compounds are of considerable significance for the development of high-performing energetic materials. By combining nitrogen-rich tetrazole and oxygen-rich furoxan, a linear C–C bonded pentaheterocyclic energetic compound, 3,4-bis(3-tetrazolylfuroxan-4-yl) furoxan (BTTFO), was synthesized using a facile and straightforward method. Comprehensive X-ray analysis reveals the key role of hydrogen bonds, π−π interactions, and short contacts in the formation of dense packing of BTTFO and explains why a long chain-shaped molecule has a high density. This multicyclic structure incorporating three furoxan and two tetrazole moieties results in an exceptionally high heat of formation (1290.8 kJ mol−1) and favorable calculated detonation performances (vD, 8621 m s−1, P, 31.5 GPa). The interesting structure and fascinating properties demonstrated the feasibility of a linear multicyclic approach as a high-energy-density skeleton. Additionally, the thermodynamic parameters, electrostatic potential (ESP), and frontier molecular orbitals were also studied to get a better understanding of structure−property correlations.

INTRODUCTION

Since the first synthetic explosive, 2,4,6-trinitrophenol, was prepared by Woulfe in 1771,1 the design and synthesis of new high-energy-density materials used as explosives, propellants, and pyrotechnics have been one of the most interesting and challenging subjects for synthetic chemists worldwide.2,3 The nitro group has been playing a vital role in the development process of energetic materials. A majority of energetic compounds belongs to polynitro compounds, such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10, 12-hexazaisowurtzitane (CL-20), which derive their energy mainly from the oxidation of carbon and hydrogen frameworks during combustion and detonation.1,2 Although introducing more nitro groups into a single molecule has been proved to be an effective way to promote the detonation performances greatly, the synthesis becomes more difficult owing to multiple steps and also causes serious environmental issues as a result of the large-scale use of HNO3 or HNO3/H2SO4. Moreover, structural stability always becomes worse along with an excess of nitro groups within a molecule, which further leads to high sensitivity and low thermal decomposition temperature. Therefore, more considerable effort should be devoted to developing new environmentally benign and insensitive energetic materials.3,4 In recent years, five-membered nitrogen-containing heterocycles have been widely recognized as ideal scaffolds for the construction of new high-energy-density compounds.5,6 Not only does the nitrogen-containing azoles bring the environmental benefit of releasing mainly N2 upon decomposition, but it also significantly increases the heat of formation and thermal stability and reduces sensitivity because of inherently energetic C–N and N–N bonds and π-conjugated systems.6 More importantly, the combination of azoles with various energetic groups like amino, nitro, nitramino, azido, and polynitromethyl could produce a considerable variety of energetic materials, which have diverse properties and meet different demands of application. Compared with single heterocyclic structures, C–C bonded bis(heterocyclic)7,8 triheterocyclic9,10 and even tetraheterocyclic11 compounds usually have a higher heat of formation, good sensitivity, and better thermal stability derived from larger π-conjugated systems. Typical examples for these kinds of compounds are illustrated in Figure 1.
Among the class of five-membered nitrogen-containing heterocycles, tetrazole- and furoxan-based compounds have usually shown increased densities and superior performances in comparison with triazole, diazole, furazan derivatives. The highly energetic nature of tetrazole and furoxan has resulted from their unique structural features; tetrazole possesses a higher nitrogen content (N% = 80.1%) among the five-membered rings, resulting in the high gas-phase enthalpy of formation of the tetrazole ring ($\Delta H_f = 333.3$ kJ mol$^{-1}$). Furoxan not only has a high oxygen balance ($\Omega_{(CO)} = -18.6\%$) but also has a “latent” nitro group within one side of its ring, which is an effective structural unit that is itself an explosive group. The combination of furoxan with tetrazole via C–C bond benefits from the high enthalpy of formation of the tetrazole and the good oxygen balance of furoxan. By introducing a furoxan ring into bistetrazole, the density and heat of formation of 3,4-bis(1H-5-tetrazolyl)furoxan (BTFO$^\ddagger$) can be increased by approximately 0.07 g cm$^{-3}$ and 100 kJ mol$^{-1}$ than those of 5,5′-bistetrazole (BT)$^\ddagger$ (Figure 2), respectively. However, although incorporating more furoxan and tetrazole moieties into a molecule through C–C bonds would be expected to possess both high nitrogen and oxygen contents with concomitant desired excellent energetic properties, few linear C–C bonded pentacyclic arrays of energetic molecules consisting of furoxan and tetrazole rings have been prepared successfully until now. This has largely stemmed from the perception that energetic compounds featuring linear polycyclic structures are not advantageous to pursue since long linear molecular structures will prevent the formation of dense three-dimensional packing and usually lead to achieving a low crystal density.

Herein, we report an example of the synthesis, structure, and energetic properties of a linear C–C bonded pentaheterocyclic compound 3,4-bis(3-tetrazolylfuroxan-4-yl)furoxan (BTTFO) with two outer tetrazole rings connected via a trifuroxan skeleton. Encouragingly, the effective combination between a trifuroxan skeleton and a tetrazole ring not only further enhances the heats of formation but also achieves a high density of 1.82 g cm$^{-3}$, which are significantly higher than that of bicyclic BT and tricyclic BTFO. The high density and enthalpy of formation of BTTFO finally lead to superior detonation performances.

**RESULTS AND DISCUSSION**

**Synthesis and Spectroscopy.** The synthetic route toward BTTFO is shown in Scheme 1. 4,5-Dicyanofuroxan (1) was synthesized in a high yield starting from commercially available cyanoacetic acid.$^\ddagger$ Our group has successfully constructed the trifuroxan skeleton featuring nitro and fluorodinitromethyl moieties, both of them showing outstanding performances.$^\ddagger$ The synthesis of the intermediate 3,4-bis(3-cyanofuroxan-4-yl) furoxan (4) has already been described in our recently published report,$^\ddagger$ mainly involving addition, diazotization, and cycloaddition reactions. The final step involves a ring closure reaction in a [2+3] dipolar azide–nitrile cycloaddition reaction at 80 °C in water to give BTTFO with a high yield of 83.3%.

BTTFO was characterized and confirmed by multinuclear ($^1$H, $^{13}$C) NMR spectroscopy (Figures S1 and S2). The $^1$H NMR spectrum of BTTFO·H$_2$O revealed one broad peak at 3.93 (2 H, NH) in dimethyl sulfoxide (DMSO)-$d_6$. The $^{13}$C($^1$H) NMR spectrum showed eight different signals for the chemically different carbon atoms. As expected, the carbon atoms in BTTFO appear as three sets of resonances. One set of resonances of carbon atoms adjacent to N-oxide in furoxans are observed in the range of 106.1–107.7 ppm, while the downfield-shifted three signals that appeared at 142.4–146.7 ppm belong to the other carbon atoms of the furoxan rings. The last set of resonances of tetrazole moieties in BTTFO are observed at 146.0 and 146.7 ppm, respectively, which are significantly higher than that of bicyclic BT and tricyclic BTFO. The high density and enthalpy of formation of BTTFO finally lead to superior detonation performances.

**Single-Crystal X-ray Diffraction.** Single crystals suitable for X-ray diffraction measurements were obtained by slow evaporation of a methanol solution of BTTFO at room temperature. Single-crystal X-ray diffraction data were recorded on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation with o $\theta$ scans. The structures were solved with the ShelXT program$^\ddagger$ and refined with the ShelXL program$^\ddagger$. The crystallographic data and refinement details are summarized in Table S1. The final atomic coordinates, bond lengths, bond angles, thermal parameters, and hydrogen bond distances and angles are summarized in Tables S2-S5. The ORTEP$^\ddagger$ diagram is shown in Figure 3. The crystal packing is shown in Figure 4. The packing of the title compound is shown in Figure 5. The Hirshfeld surface analysis was performed on the title compound using the CRYSTAL17$^\ddagger$ program.

**Figure 1.** C–C bonded energetic compounds consisting of nitrogen-containing heterocycles.

**Figure 2.** Combination of furoxan with tetrazole via a C–C bond leading to superior energetic compounds.
temperature. Selected crystallographic data, measurement parameters, refinement details, and CCDC numbers are given in Table S1 in the Supporting Information. The cif file is deposited with CCDC nos. 1987360.

BTTFO crystallizes as colorless blocks with two different conformational BTTFO molecules and two water molecules in the orthorhombic space group P2₁2₁2₁, as shown in Figure 3a.

![Figure 3](image)

Figure 3. (a) Single-crystal X-ray structure of BTTFO·H₂O encompassing different conformers A and B, viewed down the a axis. (b) Flat folded conformers A and B viewed down a perspective.

Surprisingly, although the crystals contain one water molecule per BTTFO molecule, it still has a fairly high calculated density of 1.79 g cm⁻³ at 296 K. The C–C bonds connecting the five aromatic rings in BTTFO are involved in a conjugated π electron system, and therefore their average lengths (1.46 Å) are shorter than the standard C=C single bond length (1.54 Å). Although the whole molecular structure is not planar, the aromatic rings in BTTFO are involved in a conjugated π system, and therefore their average lengths (1.46 Å) are distinctly shorter than typical parameters of aromatic face-to-face π-interactions (<4.00 Å). Moreover, the interlamellar spacing of the molecular chain is further shortened through short attractive intermolecular contacts (N20···N21 and O10···N22 for conformer A; N6···N7, N10···N13, N10···N14, and O6···N13 for conformer B; symmetry codes: i = −1 + x, y, z. The details are given in Table 1) as depicted with dotted lines in Figure 4a,b. The one-dimensional molecular chains formed by conformers A and B further assemble into an oval-shaped dimeric molecular column via two hydrogen bonds (Table 2).
and four short contacts (Table 1) from the interference of conformers A and B (Figure 4c). The water molecules are inserted into the molecular columns and perform bridging connection functions by the formation of six significant hydrogen bonds (Table 2). Finally, the hydrogen bonds, as well as intermolecular contacts, drive the adjacent molecular columns, forming a dense three-dimensional assembly (Figure 4d). Hence, the unique stacking of BTTFO intensively involved in hydrogen bonds, π−π interactions, and short contacts contributes significantly to a closer arrangement and explains why the C−C bonded linear pentacyclic BTTFO has a relatively high density.

Kinetic and Thermodynamic Parameters. Decomposition kinetic parameters are important indicators affecting the stability and safety performances of energetic materials. The Kissinger and Ozawa methods were employed to determine the kinetic parameters of BTTFO. The Kissinger and Ozawa equations are as follows:43,44

$$\frac{\ln \beta_i^2}{T_p^2} = \ln \frac{AR}{E_k} + \frac{E_k}{RT_p}$$ (1)

$$\log \beta_i + \frac{0.4567E_k}{RT_p} = C$$ (2)

where $T_p$ is the peak temperature, $K$; $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$); $\beta$ is the linear heating rate, °C min$^{-1}$; $A$ is the pre-exponential factor, and $C$ is a constant.

Based on the multiple nonisothermal differential scanning calorimetry (DSC) curves measured at four different heating rates of 5, 10, 15, and 20 °C min$^{-1}$ (Figure 5), the values of the apparent activation energies $E_k$ and $E_\varphi$, pre-exponential factor $A_\varphi$ and linear correlation coefficients $R_k$ and $R_\varphi$ of the exothermic decomposition process were determined. As can be seen, the apparent activation energies obtained from Kissinger’s method ($E_k = 131.3$ kJ mol$^{-1}$) and Ozawa’s method ($E_\varphi = 132.5$ kJ mol$^{-1}$) are in good agreement. The linear correlation coefficients ($r_k = 0.9930$ and $r_\varphi = 0.9929$) close to 1 also show that the results are credible. Moreover, the high activation energy ($E$) indicates that BTTFO is quite stable.

The initial decomposition temperature ($T_{p0}$) is the peak temperature corresponding to $\beta = 0$, which is obtained as 235.9 °C using eq 3.45 The entropy of activation ($\Delta S^\#$), enthalpy of activation ($\Delta H^\#$), and free energy of activation ($\Delta G^\#$) obtained using eqs 4–6 are 158.6, 129.3, and 48.6 kJ mol$^{-1}$, respectively, where $T = T_{p0}; E = E_k; A = A_\varphi; k_B$, the Boltzmann constant, is 1,3807 × 10$^{-23}$ J K$^{-1}$; and $h$, the Planck constant, is 6.626 × 10$^{-34}$ J s$^{-1}$.46,47

$$T_{p0} = T_p + b\beta_i + c\beta_i^2 + d\beta_i^3$$ (3)

$$A = k_B T \exp \left( \frac{\Delta S^\#}{R} \right)$$ (4)

$$\Delta H^\# = E - RT$$ (5)

$$\Delta G^\# = \Delta H^\# - T\Delta S^\#$$ (6)

Physicochemical and Energetic Properties. The physicochemical and detonation properties, such as density, the heat of formation, sensitivity, and detonation performances of BTTFO were investigated and are summarized in Table 3. It should be noted that dried BTTFO does not absorb water

| Table 2. Hydrogen Bonds Present in BTTFO·H$_2$O |
|--------|--------|--------|--------|
| D−H−⋯A | d(D−H) Å | d(H−A) Å | d(D−H−A) Å | z(D−H−A) Å |
| N11−H11−N23 | 0.96(4) | 1.96(4) | 2.89(4) | 162.7(3) |
| N15−H15−N30 | 0.89(2) | 2.11(2) | 2.94(2) | 154.9(3) |
| O14−H14A−N24 | 0.80(6) | 2.19(6) | 2.98(5) | 170.1(6) |
| N1−H1−O14 | 0.91(4) | 1.74(4) | 2.63(5) | 165.9(4) |
| O13−H13A−N26 | 0.72(5) | 2.40(5) | 3.00(4) | 142.7(5) |
| O13−H13B−N17 | 0.89(6) | 2.41(6) | 3.03(5) | 126.7(5) |
| O13−H13B−O10 | 0.89(6) | 2.14(6) | 2.96(4) | 152.2(5) |
| N23−H23−O13 | 0.88(5) | 1.78(5) | 2.64(4) | 165.9(5) |

"Hydrogen-bonding interactions within the dimeric structure.  "Hydrogen-bonding interactions between BTTFO and H$_2$O.  Symmetry operators: ii = 1 − x,0.5 + y, 0.5 − z; vii = x, 1 + y, z; viii = 1 − x, −0.5 + y, 0.5 − z; ix = 1 + x, y, z; x = −0.5 + x, −0.5 − y, −z.

**Figure 5.** DSC curves at different heating rates.  

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c01048)

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from the air. The density of dried BTTFO was measured using a gas pycnometer in an atmosphere of helium (25 °C). Encouragingly, though BTTFO has a long linear molecular structure, it has a relatively high density of 1.82 g cm⁻³, which is significantly higher than BT (1.69 g cm⁻³) and BTFO (1.76 g cm⁻³) and comparable to that of the polynitro compound RDX (1.80 g cm⁻³). The heat of formation of BTTFO was calculated based on compatible isodesmic reactions using the Gaussian 09 programs (details are given in the Supporting Information). Derived from three furoxan and two tetryazole rings, BTTFO shows exceptionally high positive heats of formation of 1391.4 kJ mol⁻¹, much higher than those of RDX (863 kJ mol⁻¹), BT (531.7 kJ mol⁻¹), and BTFO (727.8 kJ mol⁻¹). Since BTTFO incorporates three oxygen-rich furoxan rings, it has a relatively good oxygen balance (Ω_(CO) = −12.3 %), considering no nitro group within the BTTFO molecule.

The sensitivities toward impact and friction were determined experimentally according to the BAM method. BTTFO shows a moderate impact (8 J) and friction sensitivities (290 N), which are close to those of RDX and distinctly lower than BTFO. The detonation properties of BTTFO were evaluated using the EXPLO5 6.04 program. The high density and high heat of formation result in remarkable detonation performances of BTTFO. Calculated detonation velocity (v_D = 8621 m s⁻¹) and detonation pressure (P = 31.5 GPa) are superior to the corresponding values for BT (v_D = 8094 m s⁻¹, P = 23.3 GPa) and BTFO (v_D = 8154 m s⁻¹, P = 26.0 GPa) and are in the range of RDX (v_D = 8823 m s⁻¹, P = 35.1 GPa). These properties make it one of the promising energetic materials with good detonation performance.

Computational Structural Considerations. To gain more insights into the electronic structural properties as well as explain the reason that BTTFO shows much lower impact sensitivity than BTFO, the electrostatic potential (ESP) and the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) orbitals were calculated based on the B3LYP/6-31+g(d,p) method with an optimized structure. It is extensively used since the computed ESP is generally relevant to the impact sensitivity of energetic materials. The surface extent and the intensity of these electropositive potential surfaces are coherent with higher impact sensitivity. In Figure 6a, it can be clearly seen that the positive ESP region of BTTFO is smaller and shows lower charge separation than that of BTFO; this is in good agreement with the experimental result of the relatively lower impact sensitivity of BTTFO than that of BTFO. ESP analysis convincingly demonstrated that larger \(\pi\)-conjugated systems can effectively reduce the sensitivity of energetic materials. In addition, the HOMO of the molecule is distributed both on tetryazole rings and adjacent furoxan rings, while the LUMO is mainly localized on the central furoxan ring (Figure 6b). The energy gap between the HOMO and the LUMO is 3.86 eV, which shows molecular stability and is in good agreement with the DSC experimental results.

CONCLUSIONS

In summary, a C–C bonded linear pentaheterocyclic energetic compound 3,4-bis(3-tetrazolylfuroxan-4-yl) furoxan (BTTFO) was synthesized by employing a convenient and straightforward method. BTTFO was comprehensively characterized, especially single-crystal X-ray diffraction. The pivotal role of hydrogen bonds, \(\pi\)–\(\pi\) interactions, as well as short contacts in the formation of dense three-dimensional (3D) arrangement is expounded detailedly, which explains the reason for a long linear compound showing a relatively high density of 1.82 g cm⁻³. As expected, oval-shaped molecular structure with five high nitrogen and oxygen rings endow BTTFO with a great standard molar enthalpy of formation of 1290.8 kJ mol⁻¹, a high decomposition temperature of 201.8 °C, and moderate sensitivity. BTTFO has highly desirable calculated detonation properties (v_D = 8621 m s⁻¹, P = 31.5 GPa), which are superior to those of high-nitrogen-content bicylic BT and tricyclic BTFO analogues. The nonisothermal kinetic and thermodynamic parameters of BTTFO have been studied, with the apparent activation energy, entropy of activation, enthalpy of activation, and free energy of activation of 131.3, 158.6, 129.3, and 48.6 kJ mol⁻¹, respectively. The computational results in terms of ESP and HOMO–LUMO orbitals support the relationship between the structure and properties of the target compounds. The versatile structural features based on a C–C linked linear multicyclic motif provide a potential option for the future exploration of building blocks for new HEDMs.

EXPERIMENTAL SECTION

Caution. While we have experienced no issues in the syntheses and characterization of these materials, appropriate protective measures should be used. Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn.

General Methods. Unless otherwise specified, all commercially available reagents were purchased from chemical suppliers without further purification. H and C NMR spectra were recorded on 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers. The melting and decomposition points (onset) were obtained on a differential scanning calorimeter (TA Instruments Company, Model DSC-Q200) at a flow rate of 50 mL min⁻¹. About 0.5 mg of the sample was sealed in aluminum pans for DSC. Infrared spectra were obtained from KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000–400 cm⁻¹. Elemental analyses (C, H and N) were performed on a VARI-El-3 elemental analysis instrument. The impact and friction sensitivities were determined following the BAM method.

Crystallographic Measurements. The single-crystal X-ray experiment was performed on a Bruker Apex II CCD diffractometer equipped with graphite-monochromatized Mo Kα radiation (\(\lambda = 0.71073\) Å) using \(\omega\) and \(\phi\) scan modes. The
structures were solved by direct methods using SHELXTL and refined by means of full-matrix least-squares procedures on \( F^2 \) with the program SHELXL-97. All nonhydrogen atoms were refined with anisotropic displacement parameters. Experimental details of crystal data, data collection parameters, and refinement statistics are summarized in Table S1. The H atoms were found and refined. CCDC-1987360 for BTTFO·H\(_2\)O contains the supplementary crystallographic data for this paper, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif.

**Synthesis.** Compound 4 was prepared according to our recently published procedure.\(^1\)

3,4-Bis(3-tetrazolylfuroxan-4-yl)furoxan. To a solution of NaN\(_3\) (0.28 g, 4.2 mmol) in water (10 mL), 3,4-bis(3-cyanofuroxan-4-yl) furoxan (0.4 g, 1.2 mmol) and ZnCl\(_2\) (0.36 g, 1.2 mmol) were added in sequence at room temperature. The reaction mixture was stirred for 6 h. Afterward, a precipitated product was filtered off, and the filtrate was evaporated with EtOAc (15 mL × 2). After the combined organic phase was evaporated, the obtained solid was recrystallized from water to afford BTTFO (0.39 g, 83.3%). DSC (5 °C min\(^{-1}\): 201.8 °C (dec.); IR (KB): \( \tilde{\nu} = 3445, 1624, 1562, 1457, 1440, 1415, 1003, 971, 939, \) and 789 cm\(^{-1}\); \(^1\)H NMR (DMSO-\(d_6\): 500 MHz, 25 °C, tetramethylsilane (TMS)): \( \delta = 3.93 \) (s, H, NH) ppm; \(^{13}\)C NMR (DMSO-\(d_6\): 125 MHz, 25 °C, TMS): \( \delta = 146.75, 146.31, 146.02, 145.77, 142.44, 107.74, 107.60, \) and 106.11 ppm; elemental analysis found: C 24.46, H 0.43, and N 49.89.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif.

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