Molecular and Crystal Features of Thermostable Energetic Materials: Guidelines for Architecture of “Bridged” Compounds

Hui Li, Lei Zhang, Natan Petrutik, Kangcai Wang, Qing Ma, Daniel Shem-Tov, Fengqi Zhao, and Michael Gozin

†Science and Technology on Combustion and Explosion Laboratory, Xi’an Modern Chemistry Research Institute, Xi’an 710065, China
‡School of Chemistry, Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel
§CAEP Software Center for High Performance Numerical Simulation, Beijing 100088, China
∥Institute of Applied Physics and Computational Mathematics, Beijing 100088, China
¶Laboratory of Materials Chemistry, Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang, 621900 Sichuan, China

Supporting Information

ABSTRACT: Extensive density functional theory (DFT) calculation and data analysis on molecular and crystal level features of 60 reported energetic materials (EMs) allowed us to define key descriptors that are characteristics of these compounds’ thermostability. We see these descriptors as reminiscent of “Lipinski’s rule of 5,” which revolutionized the design of new orally active pharmaceutical molecules. The proposed descriptors for thermostable EMs are of a type of molecular design, location and type of the weakest bond in the energetic molecule, as well as specific ranges of oxygen balance, crystal packing coefficient, Hirshfeld surface hydrogen bonding, and crystal lattice energy. On this basis, we designed three new thermostable EMs containing bridged, 3,5-dinitropyrazole moieties, HL3, HL7, and HL9, which were synthesized, characterized, and evaluated in small-scale field detonation experiments. The best overall performing compound HL7 exhibited an onset decomposition temperature of 341 °C and has a density of 1.865 g cm⁻³, and the calculated velocity of detonation and maximum detonation pressure were 8517 m s⁻¹ and 30.6 GPa, respectively. Considering HL7’s impressive safety parameters [impact sensitivity (IS) = 22 J; friction sensitivity (FS) = 352; and electrostatic discharge sensitivity (ESD) = 1.05 J] and the results of small-scale field detonation experiments, the proposed guidelines should further promote the rational design of novel thermostable EMs, suitable for deep well drilling, space exploration, and other high-value defense and civil applications.

INTRODUCTION

As our civilization progresses and expands, the need for natural resources and minerals, as well as deeply buried fossil fuel, gases, and oil, is followed by an ever-growing consumption and demand. For efficient extraction of raw petroleum, perforating guns, based on shaped explosive charges, are commonly used to start the oil flow. These shaped explosives ensure efficient penetration into the well-surrounding soil, allowing easier and faster access to the soil-imbedded deposits. Deep charges, based on highly thermostable energetic materials, are being vastly used on the verge of their thermostable threshold at a depth of 6 km where the temperature reaches 230 °C. The expected depletion of easily accessible natural minerals, fossil fuel, gases, and oil reservoirs around the world is driving the oil and gas industry to explore and reach deposits as deep as 10 km. This encourages the pursuit for novel highly thermostable energetic materials capable of operating in the deep well environment. When currently used explosives in perforation guns are subjected to conditions beyond their temperature–time stability limits, they start to gradually decompose, resulting in a significantly deteriorated performance or even detonation failure.

On the other end of the spectrum, thermostable energetic materials are essential to satisfy the safety requirements of in-space operating systems. For example, the Apollo spacecraft was installed with more than 210 pyrotechnic devices serving a variety of applications, including launch escape tower separation, booster stage separation, as well as lunar module separation and landing gear deployment. These mission-critical tasks’ success completely relies on the performance of highly thermostable energetic materials (EMs), such as 1,2-bis(2,4,6-trinitrophenyl)ethene (HNS; C8, Figure 13), exhibiting a decomposition temperature (Td) of 318 °C.

With this ever-growing demand for new and improved EMs, the discovery of new materials mainly relies on an experimental
smart-screening approach. Nevertheless, the technological progress of current computational power can be harnessed to assist the development of EMs with desired properties. There are several important molecular design strategies to obtain explosives with improved thermostability. Beyond preparation of explosive salts, a popular approach is the introduction of amino groups to aromatic carbocyclic and heterocyclic rings in structures of neutral explosive molecules. Another important methodology for enhancing heat resistance relies on the connection of two or more energetic rings together, directly or through various “bridges”. The later design methodology was extensively explored by Shreeve in condensing N,N'-alkylene-bridged symmetric and asymmetric bis-azoalexol, Klapotke in utilizing a bis(1,3,4-oxadiazole)-bridging moiety between two trinitro-benzene rings, Pagoria, and other investigators.

With the rapid improvement in methods for molecular and crystal modeling, the direct simulation of crystal properties, rather than properties of isolated molecules, becomes more feasible. Utilizing supercomputers, empirical guidelines and rules, derived from energetic crystals, can become powerful tools for the molecular and crystal design of the future EMs. Principles for crystal engineering of insensitive EMs were described by Chaoyang Zhang, who studied the crystal packing—impact sensitivity relationships, working toward efficient strategies for designing high-performance insensitive EMs. A set of guiding principles for architecting new explospheres with desired properties were reported by Qinghua Zhang in his research focused on accelerating the discovery of insensitive EMs by the use of a “materials genome” approach. Attempts of a comprehensive end-to-end design of novel bridged explosives were also reported by Kuklja and co-workers. In a series of publications, they presented a methodical design, synthesis, and characterization of 1,2,4-oxadiazole-bridged explosives, showing advantages of calculation-based systematic properties—structure analysis. Furthermore, extensive studies addressing the influence of molecular design and structure on the thermal stability of high-energy compounds were performed by Manelis and co-workers.

In our perspective, the aforementioned molecular-level approaches in the field of EMs are significant steps forward, reminiscent of the impact created by the ground-breaking Lipinski’s “Rule of Five”. The latter set of critical guidelines for the desired molecular structural features revolutionized pharmaceutical research, becoming a key guiding molecular-design methodology for the development of novel pharmaco-phases and orally active therapeutic agents. Since heat-resistant explosives are typically solid crystalline organic materials, their mechanical sensitivity, thermostability, and detonation properties greatly depend on the interactions between individual molecules in crystals, as well as the crystals’ size and shape.

Here, we report the design, synthesis, and performance evaluation of three new thermostable explosives—1,2-bis(3,5-dinitropyrazol)ethane (HL3), 5,5′-bis(3,5-dinitropyrazol)-2,2′-bi(1,3,4-oxadiazole) (HL7), and 4,4′-(3,5-dinitropyrazolyl)-methane (HL9), in which two bis(3,5-dinitro-1H-pyrazole) moieties were connected to each other via their C-4 carbon by ethylene, bis(1,3,4-oxadiazole), and methylene bridges, respectively. The molecular designs of these new compounds were based on a comprehensive analysis of X-ray crystallography data and thermal properties of 60 previously reported EMs (Figures 13−17). For more methodological processing of the structural data, all EMs in this study were divided into five representative families: (Family A) single-ring explosives; (Family B) “bridgeless” explosives, in which two energetic rings are connected directly to each other; (Family C) explosives, in which two energetic rings are connected via a “simple bridge”; (Family D) explosives, in which two energetic rings are connected via a “complex bridge”; and (Family E) “fused-rings” explosives, in which two energetic rings are connected via more than a single “bridge”.

By analyzing the crystallographic data of 60 reported EMs and conducting high-throughput density functional theory (DFT) calculations on supercomputers, we searched for the most influential molecular and crystal level parameters that would show a certain level of correlation with these EMs’ thermostability. In the present work, the thermostability of explosive crystals was defined by DSC-measured onset temperature, at which structural changes and decomposition are initiated in these crystals. At the molecular level, we examined correlations of the type of the “bridge” (if present) in the molecule, the reactivity of this “bridge” and other bonds in the molecule, as well as molecular oxygen balance (OB) with respect of the thermostability of the corresponding EM. At the crystal level, valuable correlations were found between EMs’ thermostability and intermolecular parameters including the crystal’s packing coefficient (PC), hydrogen bonding amount in a crystal, and crystal’s lattice energy (LE).

By deducing common parameters and features (explosives thermostability general trends—ETGTs) found in the molecular and crystal structures of the reported EMs, we implemented these guidelines into the design of three new thermostable EMs (HL3, HL7, and HL9). Computational detonation performance, as well as small-scale field detonation experiments, showed the validity of our ETGT approach for the design of a new generation of top performing thermostable EMs for deep drilling and space applications. In the future, this approach may significantly contribute to the design of novel EMs, utilizing machine learning methodologies.

### RESULTS AND DISCUSSION

**Synthesis.** Based on our guidelines for the architecture of “bridged” thermostable explosives, we developed synthetic methodologies for the preparation of three new compounds. The first compound, 1,2-bis(3,5-dinitro-pyrazol)ethane (HL3; Figure 1), was prepared in three steps, starting with synthesis of 1-(ethoxymethyl)-4-methyl-3,5-dinitropyrazole (HL1) in 94% yield. We considered straightforward synthetic approaches...
for the preparation of 1,2-bis(3,5-dinitropyrazol)ethane (HL3), via a nitration of 1,2-bis(1H-pyrazolyl)-ethane. However, since no synthetic methodology was reported for the latter compound, we eventually decided to utilize a similar oxidative coupling strategy typically used for preparation of 1,2-bis(2,4,6-trinitrophenyl)-ethane (a precursor of 1,2-bis(2,4,6-trinitrophenyl)ethane; HNS) from 2-methyl-1,3,5-trinitrobenzene (TNT). This oxidative coupling reaction allows formation of a carbon–carbon bond between two nitro-activated methyl groups of TNT and, in our case, of methyl-1,3,5-trinitrobenzene (TNT). This oxidative coupling reaction allows formation of a carbon–carbon bond between two nitro-activated methyl groups of TNT and, in our case, of compound HL1, using KOrBu base in THF, which is followed by addition of bromine, to produce key intermediate 1,2-bis(1-ethoxymethyl)-3,5-dinitro-pyrazole (HL2) in 94% yield. The protection step was found to be necessary, as all attempts to make a direct transformation from compound 4-MDNP to the target compound HL3 were unsuccessful under a broad range of reaction conditions and temperature regimes. The final conversion of compound HL2 to the target compound HL3 was performed in 88% yield, by utilizing trifluoroacetic acid solution in CH2Cl2 as a deprotecting agent, leading to an overall yield of 77% for HL3, while starting from 4-MDNP.

The second energetic compound, 5,5′-bis(3,5-dinitro-1H-pyrazol-4-yl)-2,2′-bi(1,3,4-oxadiazole) (HL7; Figure 2), was prepared in four steps, starting with a synthesis of 3,5-dinitro-1H-pyrazole-4-carboxylic acid (HL4) in 67% yield, via selective methyl group oxidation of 4-MDNP with Na2Cr2O7·2H2O under acidic conditions. The oxidation reaction was followed by two-step transformation of HL4 acid into the corresponding 3,5-dinitropyrazole-4-carboxyhydrazide (HL5) in 74% yield: first, by reacting the acid HL4 with thionyl chloride; next, with 1H-benzo[d]-[1,2,3]triazole; and then, by treating in situ formed (1H-benzo[d][1,2,3]triazol-1-yl)(3,5-dinitro-1H-pyrazol-4-yl)-methanone with NH2NH2·H2O. Subsequently, carbonyl hydrazide HL5 was converted into the key intermediate N′1,N′2-bis(3,5-dinitro-1H-pyrazole-4-carboxyl)oxalohydrazide (HL6) in 75% yield, by reacting compound HL5 with oxalyl chloride. Attempts to react freshly prepared 3,5-dinitro-1H-pyrazole-4-carboxyl chloride with oxalyl dihydrazide, utilizing a similar methodology described for the preparation of 5,5′-bis(2,4,6-trinitrophenyl)-2,2′-bi(1,3,4-oxadiazole) (TKX55), did not result in our case in the formation of the key intermediate HL6, and the starting oxalyl dihydrazide was recovered from our reaction mixtures. The final simultaneous bis-cyclization of two adjacent 1,3,4-oxadiazole rings was achieved by treating compound HL6 with H2SO4 oleum, which led to formation of the target 5,5′-bis(3,5-dinitro-pyrazol)-2,2′-bi(1,3,4-oxadiazole) (HL7) in 83% yield.

The synthesis of the third new energetic compound in this study, 4,4′-(3,5-dinitropyrazolyl)methane (HL9; Figure 3), was achieved in two steps, starting with thermal isomerization of hydrobromide salt of 1,1′-dipyrrozolylmethane (DPM) into 4,4′-dipyrrozolymethane (HL8) key precursor, in 56% yield. Our initial strategy to prepare compound HL8 included one-pot reaction of pyrazole with CH3Br, which included a tedious sublimation-based purification step. However, due to expected scalability issues of such a protocol, we eventually preferred technologically simpler isomerization of the isolated DPM route. The key precursor HL8 was then fully nitrated to form the target explosive 4,4′-(3,5-dinitropyrazolyl)methane (HL9) in 51% yield, using a fuming HNO3 in H2SO4 oleum nitration mixture at 100 °C. All new energetic compounds HL3, HL7, and HL9, as well as their precursors and intermediates, were comprehensively characterized by 1H and 13C NMR, mass spectrometry, infrared spectroscopy, and elemental analysis (Figures S4–S18, Supporting Information). 13C NMR spectra of HL7 showed a peak at 93.7 ppm that was assigned to the C-4 ipso-carbons of 3,5-dinitropyrazolyl rings of this compound. In comparison, we found that C-4 carbons of 3,5-dinitropyrazolyl rings in HL3 and HL9 have chemical shifts of 113.9 and 110.2 ppm.
ppm, respectively. These observations were explained on the basis of the electron density calculations, which showed that the valence charge density at the 3,5-dinitropyrazolyl rings in HL7 is somewhat higher than in HL3 and HL9 (Figure 4). Quantitatively, the Mulliken charges surrounding the C-4 carbons in 3,5-dinitropyrazolyl rings were calculated to be 3.85, 3.95, and 3.89 e for HL3, HL7, and HL9, respectively, matching our $^{13}$C NMR results, as higher electron density around a certain carbon atom should result in the upfield chemical shift for this atom.

**X-ray Crystallography.** We further analyzed the structure of compounds HL3, HL7, and HL9 by X-ray crystallography. In addition, for comparison and comprehensive analysis purposes, a crystal structure of 4-MDNP was obtained. Although the synthesis of the latter compound was previously described by Shevelev, its crystallographic structure was not reported. 4-MDNP crystals suitable for X-ray diffraction studies were obtained by crystallization from ethanol. 4-MDNP crystallizes in the monoclinic space group $P2_1/C$, with four molecules in each unit cell ($Z = 4$) and a density of 1.674 g cm$^{-3}$ (CCDC 1910475; Figure 5). All the non-hydrogen atoms of the 4-MDNP molecule are located in the same plane (Figure 5a,b), while each 4-MDNP molecule interacts with two adjacent molecules through N−H···N and N−H···O hydrogen bonds (HBs), forming flat nanobands with a width of 1.1 nm (Figure 5c). These nanobands are interacting with each other via van der Waals interactions, creating a wavelike layered three-dimensional structure (Figure 5d). The distance between two nearby methyl groups belonging to two different nanobands in the same layer is 3.879 Å and significantly longer than the length of the alkane single C−C bond.

The intermolecular N−H···N and N−H···O HBs were also clearly illustrated from the red spots on the Hirshfeld surface as shown in Figure 5e and from the spikes on the bottom left in the 2D-fingerprint as shown in Figure 5f. In Figure 6g, the individual interatomic contacts percentage contribution confirms the conclusion, in which HBs possess 41.9% of the total weak interactions of the 4-MDNP crystal. The hydrogen bonding attraction makes the molecules associated with a lattice energy of 25.22 kcal mol$^{-1}$ and a packing coefficient of 71.92%.

**HL3** crystals suitable for X-ray diffraction studies were obtained by crystallization from ethanol. HL3 crystallizes in the monoclinic space group $P2_1/C$, with two molecules in each lattice cell ($Z = 2$) and a density of 1.809 g cm$^{-3}$ (CCDC 1910476; Figure 6). Only a half molecule of HL3 is contained in the asymmetric unit, demonstrating relatively high structural symmetry of HL3. The molecular structure of HL3 could be seen as two 4-MDNP moieties connected by a single sp$^3$−sp$^3$ C−C bond, forming a “step”-connected two parallel planes structure (Figure 6a,b). The length of this C−C bond is 1.532 Å, which is much shorter than the in-plane band-to-band closest methyl–methyl groups distance in the crystal structure of 4-MDNP (3.879 Å). Similar to 4-MDNP, in the crystal structure of HL3, each molecule interacts with four adjacent molecules through N−H···N and N−H···O HBs, forming two-dimensional layers as shown in Figure 6c. These two-dimensional layers are also interacting with each other via van der Waals interactions, creating a wavelike layered three-dimensional structure (Figure 6d). Due to the much shorter distance between two methylene groups in HL3 versus the methyl–methyl distance in 4-MDNP, the packing of the HL3 crystal is tighter, leading to a higher crystal density obtained for HL3.

The intermolecular N−H···N and N−H···O HBs were also confirmed in Hirshfeld surface analysis as shown in Figure 6e and 2D-fingerprint as shown in Figure 6f. The thicker spikes and shorter $d_1 + d_2$ values in Figure 6f suggest that the HBs in HL3 are greater in number and stronger as compared to those in the 4-MDNP crystal. As shown in Figure 6g, the HBs take 46.6% of the total weak interactions in HL3, which is 4.7% higher comparing to 4-MDNP. This leads HL3 to have a higher lattice energy (46.68 kcal mol$^{-1}$) and an improved packing coefficient (76.25%).

**HL7** crystals suitable for X-ray diffraction studies were obtained by crystallization from ethanol. All attempts to obtain solvent-free crystals of HL7 were unsuccessful under a broad range of solvent conditions including of ethanol, acetone, ethyl acetate, and even fuming nitric acid. HL7 crystals crystallized from the mentioned solvent were all found to be the HL7 hydrate or HNO$_3$ solvated HL7. HL7 dihydrate crystallizes in the monoclinic space group $Cc$, with four molecules in each lattice cell ($Z = 4$) and density of 1.854 g cm$^{-3}$ (CCDC 1910477; Figure 7). There is a single molecule of HL7 and two molecules of water located in an asymmetric unit. In the molecular structure of HL7, two 1,3,4-oxadiazole rings of the bridge are positioned in the same plane, while the 3,5-dinitropyrazolyl rings are connected with the 1,3,4-oxadiazole rings through C−C bonds with dihedral angles of 61.7° and 78.3°, respectively. Each HL7 molecule interacts with four adjacent water molecules through N−H···O and O−H···O HBs, forming water-bridged interactions between HL7 molecules and creating a layered structure.

The asymmetry of the spikes in Figure 7f is caused by the unequal electronic structure when looking outward and inward of the Hirshfeld surface as shown in Figure 7d. Due to the

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Figure 4. Analysis of the valence charge density distribution in compounds HL3 (A), HL7 (B), and HL9 (C). The electron density maps are shown in the plane of one of the 3,5-dinitropyrazolyl rings of these compounds.
presence of water molecules, the lattice energy significantly increase to 85.90 kcal mol⁻¹ while the packing coefficient decreases to 74.87%.

**HL9** crystals suitable for X-ray diffraction studies were obtained by crystallization from ethanol. **HL9** crystallizes in the monoclinic space group P2₁/C, with four molecules in each lattice cell (Z = 4) and density of 1.820 g cm⁻³ (CCDC 1910478; Figure 8). There is a single molecule of **HL9** located in an asymmetric unit. In the molecular structure of **HL9**, the 3,5-dinitropyrazolyl rings are positioned in two different planes, with a dihedral angle of 85.4°. Each **HL9** molecule interacts with four nearby-located **HL9** molecules through HBs of N–H···O (2.214 Å) and N–H···O (2.034 Å), forming nanobands, which in turn are creating a layered structure. Compared to **HL7**, both the amount and strength of the hydrogen bonding interactions of **HL9** are slightly improved, as shown in Figure 8e,f. However, due to the lower symmetry of the crystal (SGN 9) as compared to that of **HL7** (SGN 14), **HL9** has a similar crystal packing coefficient of 73.43%.

**Physicochemical and Energetic Properties.** The thermal behavior of compounds **HL3**, **HL7**, and **HL9** was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) at a heating rate of 5 °C min⁻¹. Each of these compounds showed a single intense exothermic decomposition peak without melting (Figures S17 and S18; Supporting Information). Decomposition of the

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**Figure 5.** Crystal structure and structure analysis of 4-MDNP. (a) Top view of the 4-MDNP molecule. (b) Side view of the 4-MDNP molecule. (c) Hydrogen bonding interaction within a single “layer” of 4-MDNP molecules in a crystal structure of this compound. (d) Side view of wavelike stacking between two “layers” of 4-MDNP molecules in a crystal structure of this compound. Intermolecular interactions analysis for crystals of 4-MDNP. (e) Hirshfeld surface. (f) Fingerprint plot. (g) Individual atomic contact percentage contribution to the Hirshfeld surface.
energetic compound from its solid state, rather than the liquid phase, is highly desirable for a compound which could be considered as a potential heat-resistant explosive since the rate of degradation is significantly enhanced when the substance is placed as a molten phase. The onset decomposition temperatures for HL3, HL7, and HL9 were determined to be 351, 341, and 262 °C, respectively, while the peak decomposition temperatures were observed at 359, 343, and 269 °C, respectively. Thus, the thermal performance of HL3 and HL7 was found to be significantly better than that of commonly used thermostable explosive HNS (Td 318 °C; Table 1), and comparable or even better than LLM-105 (Td 345 °C), suggesting the potential usability of HL3 and HL7 compound as new heat-resistant EMs.

The densities of EMs HL3, HL7, and HL9 were measured by gas pycnometer at ambient temperature and found to be 1.805, 1.865, and 1.810 g cm⁻³, respectively, higher than the reference thermostable HNS explosive (1.740 g cm⁻³). Furthermore, evaluations of the sensitivity by standard BAM methods to impact, friction, and electrostatic discharge for the newly synthesized thermostable EMs show significantly higher stability than HNS in all safety parameters, while HL7 shows comparable safety to LLM-105 (Table 1). The enthalpies of formation (ΔHf) of HL3, HL7, and HL9 were calculated by the isodesmic reactions approach, using Gaussian 09 software, and found to be 184.3, 446.5, and 224.2 kJ mol⁻¹, respectively. The relatively higher calculated ΔHf of compound HL7 could be explained by the presence of two adjacent 1,3,4-oxadiazole rings constructing its bridged structure.

The calculated VODs for HL3, HL7, and HL9 were 8234, 8517, and 8357 m s⁻¹, respectively. The maximum detonation pressures for HL3, HL7, and HL9 were 28.6, 30.6, and 29.7 GPa, respectively.

Energetic Evaluation and Detonation Experiments. In order to evaluate the energetic properties of materials HL3 and HL7 versus reference materials, small-scale reactivity tests (SSRTs) were performed. SSRTs measure the performance of EMs, allowing preliminary evaluation without requiring scaled...
up synthesis for full-scale detonation tests. In our experiments, 9.0 g of a powdered EM was pressed with a pressure of 0.5 ton, using a hydraulic press, at room temperature, into a stainless steel (316) cylinder with an outer diameter of 28 mm, 4 mm wall thickness, and 2 mm thickness at the bottom (Figure 9a). A pressed charge was placed on an aluminum (3003) witness plate, to measure the brisance of the evaluated EM via the volume of the postdetonation dent mark. The pressed charge was initiated with a standard detonator, consisting of 850 mg of RDX and 150 mg of PbN₃ (Figure 9c,d). The detonation of the pressed charge was carried out in open air, 1 m above the ground. The charge generated a shock wave, followed by a pressure blast that was recorded by three pressure sensors (ENDEVCO), each positioned 1.0 m away from the charge (Figure 9e). Voltage signals from the sensors, obtained via a standard signal amplifier, were recorded on an analog oscilloscope and translated into real-time pressure values. All the detonation experiments were filmed with a high-speed camera (Phantom v610), operated at 10 000 frames s⁻¹ (selected frames are presented in Figure 9f–i). Reference detonations with nonenergetic (9.0 g of water) and representative energetic charges (9.0 g of HNS) were also conducted. Subsequently, the dent marks on the witness plates (Figure 10a–d) were mapped with the assistance of a three-dimensional laser scanner (Nikon MMDx 50) attached to a robotic measuring arm (MCAx 20) to produce maximum precision point cloud files (STL) that were converted to solid objects (Figure 10e–h). The diameters, depths, and volumes of these objects were calculated by dedicated software (SolidWorks; Figure 10i–l).

Obtained pressure changes were found to match the expected behavior of an unconfined high explosive, characterized by a rapid pressure increase at the shock front, followed by a quasiexponential decay back to an ambient pressure (Figure 11). A negative phase follows, in which the pressure is less than ambient, characterized by oscillations between negative and positive overpressure fading away after about 2 ms.
The recorded detonation pressure for water, as a non-energetic reference, was measured with a maximal overpressure of 9.80 KPa, which is attributed to the booster, leaving a very shallow dent with a volume of only 0.20 cm³ (Figures 10i and 11a; Table 2), and the cylindrical body remaining fractured but intact. For HNS, HL3, and HL7 only the bottoms of the metal cylinders were recovered, while the body of the cylinders was fully fragmented, as evident from the high-speed video recordings. Results for the reference HNS explosive have shown a maximal measured detonation overpressure of 29.84 KPa (Figure 11; Table 2), with a clear dent on the witness plate with a volume of 2.21 cm³, a depth of 4.47 mm, and a diameter of 37.08 mm (Figure 10b,f,j; Table 2). Evaluation of newly synthesized thermostable EMs HL3 and HL7 showed a higher maximal recorded detonation overpressure of 32.64 and 32.08 KPa, respectively (Figure 11b; Table 2). While the measured dent volume for HL7 was 2.17 cm³, with a depth of 4.25 mm and a diameter of 37.61 mm (Figure 10d,h,l; Table 2) implying a great brisance capability correlating with its detonation overpressure, the dent volume of HL3 was found

Table 1. Properties of Compounds HL3, HL7, HL9, and Reference Explosives

| compound | $T_d$ (°C) | $\rho$ (g cm⁻³) | $\Delta H_f$ (kJ mol⁻¹) | VOD (m s⁻¹) | $P_e$ (GPa) | IS° (J) | FS° (N) | ESD° (J) |
|----------|-----------|-----------------|------------------------|-------------|-------------|--------|--------|---------|
| HL3      | 351       | 1.805           | 184.3                  | 8,234       | 28.6        | 10     | 352    | 1.12    |
| HL7      | 341       | 1.865           | 446.5                  | 8,517       | 30.6        | 22     | 352    | 1.05    |
| HL9      | 262       | 1.810           | 224.2                  | 8,357       | 29.7        | 14     | 352    | 0.98    |
| HNS      | 318       | 1.740           | 78.2                   | 7,612       | 24.3        | 5      | 240    | 0.8     |
| LLM-105  | 345       | 1.910           | -12.0                  | 8,560       | 33.4        | 28     | >360   | 1.02    |

a Onset decomposition temperature by DSC (heating rate of 5 °C min⁻¹). b Density measured by helium gas pycnometer (at 25 °C). c Calculated standard molar enthalpy of formation. d Calculated velocity of detonation. e Calculated detonation pressure. f Impact sensitivity evaluated by a drop hammer (2.5 kg) BAM technique. g Friction sensitivity evaluated by a BAM technique. h Electrostatic discharge sensitivity.
to be lower, of $1.31 \, \text{cm}^3$, with a depth of $2.59 \, \text{mm}$ and a diameter of $34.25 \, \text{mm}$ (Figure 10c,g,k; Table 2). Although HL3 had greater detonation overpressure than both HL7 and HNS, the emanating low volume and low diameter of the dent on the witness plate can be attributed to lower brisance as a result of lower achieved density under equal mechanical compression (0.5 ton) applied during the preparation of all charges.33

Our field experiments showed that HL7 EM exhibited brisance and detonation overpressure comparable to HNS, while being more insensitive and thermostable, strongly supporting the validity of the bridged molecular design approach for new heat-resistant explosives. We believe that properly pressed HL3 EM could exhibit comparable performance while having superior thermostability.

**Ab Initio Molecular Dynamics Calculations.** In order to study the initial kinetics of the chemical bonds under heating stimulus, we performed *ab initio* molecular dynamics simulations with the HASEM package for the optimized structures of HL3, HL7, HL9, and HNS crystals. We employed the canonical (NVT) ensemble to simulate the heating of the systems from 0 to 1000 K for 10 000 steps, with the time step set as 0.2 fs. For each iteration of the atomic positions, the density matrix tolerance was set to be $5.0 \times 10^{-6}$ e, and the atomic force tolerance was 0.04 eV Å$^{-1}$. The potential energy, pressure, and temperature of the four systems converged from $\sim$300 steps. From then on, the temperature of each system was constrained at around 1000 K. We assumed that the chemical bond broke when it was stretched beyond the cutoff percentage relative to the equilibrium state. The breaking of the chemical bonds for each molecule was counted within the simulation duration, as shown in Figure 12. The breaking of chemical bonds occurred competitively between the first and second weakest bonds, which are shown in detail in Tables S2 and S3 of the Supporting Information. The total count of bond breaking indicated that the order of the thermostability of the four compounds was HL3 > HL7 > HNS > HL9, which was satisfactorily consistent with the

Figure 9. (a) View of an exemplary pressed EM charge witness plate. (b) Witness plate. (c) Assembly of a system prior to detonation. (d) Schematic presentation of the charge detonation setup. (e) Schematic presentation of the field measurement setup including high-speed video camera and pressure sensors. (f–i) Frames from high-speed video clip of the detonation experiment of HL7 (f, frame before detonation; g, first frame of detonator initiation; h, frame of the main charge initiation; i, frame of the maximum fire ball).
experiments as determined by DSC and TGA techniques. Note that the chemical kinetics shown in Figure 12 would vary with the temperature and heating rate.

Molecular and Crystal Structure Assessment and Categorization of the Reported and Newly Synthesized EMs. For the better understanding of how molecular and crystal structures could be correlated with EMs’ thermostability, a collection of 60 reported explosives was divided into five different families. Each family contains molecules with specific structural features, in which the type of the “bridge” (if present) served as the primary selection criterion (Figures 13–17). Based on this criterion, the categorization and comprehensive properties studies of these EMs allowed us to propose reasonable designs for new bridged thermostable explosives: HL3, HL7, and HL9.17

Table 2. Results of Detonation Experiments for Compounds HL3, HL7, Inert, and Energetic References

| material | exp. maximal overpressure [kPa] | dent diameter [mm] | dent depth [mm] | dent volume [cm³] |
|----------|---------------------------------|---------------------|-----------------|-------------------|
| 1 water  | 9.80                            | 31.32               | 0.45            | 0.20              |
| 2 HNS    | 29.94                           | 37.08               | 4.47            | 2.21              |
| 3 HL7    | 32.08                           | 37.61               | 4.97            | 2.17              |
| 4 HL3    | 32.64                           | 34.25               | 2.59            | 1.31              |

Figure 10. (a–d) Postdetonation dent marks on witness plates with the remaining bottom of the stainless-steel cylinder. (e–h) Three-dimensional mapping of dent marks for water, HNS, HL3, and HL7, respectively. (i–l) Side view of three-dimensional SolidWorks objects of the dent marks and their diameters and depth; corresponding SolidWorks calculated volumes are shown in Table 2.

Figure 11. (a) Measured detonation pressures for inert (water) and energetic reference (HNS) charges. (b) Compared measured detonation pressures for HL3, HL7, and HNS charges.
DFT CALCULATIONS

General Methodology. Density functional theory (DFT) calculations were performed to determine and compare the physicochemical properties of 60 previously reported and 3 newly synthesized EMs (Figures 11–15) on a molecular level (Gaussian 09 and HASEM software) and on a crystalline material level (HASEM software). The reliability of the HASEM software in describing EMs’ crystal structures, energetics, mechanical parameters, thermodynamic properties, detonation performance, and sensitivity under external stimulus has been extensively verified by the comparison with experiments and CCSD(T) results. In addition, the HASEM software was constructed based on the J parallel Adaptive Structured Mesh applications Infrastructure (JASMIN), thereby allowing the high-efficient parallel computing of large-scale systems on modern supercomputers. The investigated properties included covalent bonding characteristics, such as type, distribution, length, strength, and decomposition location; molecular characteristics, such as bridging configuration (type of bridging) and bridge reactivity, oxygen balance, molecular size, and heat of formation; crystal structure characteristics, such as crystal volume, lattice lengths, lattice angles, crystal density, packing coefficient, crystal space group, and number of molecules located in each unit cell; as well as characteristics of crystal lattice energy (LE; lattice energy) and material energetic performance, such as detonation velocity, detonation pressure, heat of explosion, and explosion temperature. LE is defined as the energy difference between the total energy of constituent molecules in each free state and the total energy of the crystal.

To study crystal packing arrangements in all EMs mentioned in this work, we calculated the intermolecular interactions (CrystalExplorer software), which included the enclosed...
volume, surface area, globularity, and asphericity of the Hirshfeld surface of each molecule. The Hirshfeld surface area is an alternate measure of the molecular size, resembling the molecular weight. The contribution to the Hirshfeld
surface from each individual atomic contact was also quantified and analyzed.

Taking the lattice parameters and atomic coordinates from single-crystal X-ray diffraction analysis as input, the geometries of the 63 EMs were optimized on the basis of the conjugate gradient method. The calculated structures were considered by us as fully optimized, when the residual forces were less than 0.03 eV Å$^{-1}$, and the stress components were less than 0.1 GPa for each structure. All parameters of the fully optimized calculated structures showed a very high level agreement with the experimental parameters of the same compounds obtained by X-ray crystallography (Figure 18). For lattice lengths, lattice angles, and cell volumes, the linear correlation coefficients between the calculated and experimental values were 0.999, 0.992, and 0.999, respectively, with the standard errors of 0.17 Å, 0.69°, and 22.73 Å³, respectively. These minute discrepancies between the calculated and the experimental values show the reliability and robustness of the calculation methods that were used in this work.

**Molecular Level Correlations.** Our first evaluated correlation was the type of the bridge, connecting two energetic rings, versus the examined EM’s thermostability. The full temperature range correlation graph for all 63 EMs included in this study is shown in Figure S31 (SI), while Figure 19a presents a focused temperature range version of the Figure S31 (SI) full temperature range graph. In Figure 19a only the EMs with thermostability above 250 °C (defined by us as thermostable) are included. Analyzing the distribution of the various thermostable compounds among all EMs included in this study, we found that only 44% among single ring EMs (Family A) could be described as thermostable, while the remaining 66% of these materials would have thermostability below 250 °C (Figure 19b). In contrast, all bridged EMs (Families B–E) showed typically better statistics (above 46%) in being thermostable than single-ring compounds, with Family D (EMs in which two energetic rings are connected via a “complex bridge”) and Family E (“fused-rings” EMs) show the highest probabilities of 82% and 67%, respectively, of the compounds in these families being stable above 250 °C. These findings clearly show that the inclusion of bridges into molecular structures of EMs, and in particular “complex” bridges and “fused” rings, should lead to improved thermostability of the resulted molecules versus nonbridged single-ring versions of related EMs. The “bridge” approach should provide a promising and effective methodology for the molecular design of the heat-resistant explosives. One of the possible underlying physical mechanisms of the bridge-related thermostability phenomena could be a significantly improved heat conductivity and distribution within a bridged or a “fused” molecular structure of thermostable EM. Therefore, one of our new molecules, HL7 (a member of Family D), was designed to incorporate the bis(1,3,4-oxadiazole) complex bridge, as its structural features to attain an improved thermostability.

Searching for additional parameters that could be responsible for thermostability on a molecular level, we calculated the stability of all bonds present in molecular structures of all EMs.
in our study. The results of these calculations, including compounds’ crystal structures of which contained solvents, and calculated solvent-free crystal structures of the same compounds, are shown in Tables S6 and S7 (SI). These calculations allowed us to pinpoint the most plausible locations of the first and the second chemical bonds that would undergo seizure upon molecule decomposition. One of the parameters that may significantly influence the thermostability of a molecule could be whether these chemical bonds are broken at the bridges or at the energetic ring terminals.

Therefore, we introduced two criteria to examine a hypothesis of the bridge bonds seizure-related thermostability. These criteria, defined as “Does the first bond break at the bridge” and “Does the second bond break at the bridge”, were plotted versus corresponding EM thermostability in a three-dimensional arrangement (Figure S32; Supporting Information), and its focused version is shown in Figure 19c. We found that, based on these criteria, the thermostability trend was clear, especially in cases of EMs with both the first and the second chemical bond seizures at the bridge (“Yes/Yes” columns, Figure 19c,d) which were found to be predominantly thermostable (73% out of all compounds in this group). Two of our new compounds, HL3 and HL7, belong to this specific category, in which EMs from Family D (“complex” bridge) and Family E (“fused” rings) are mainly prevalent. In our perspective, the underlying physical mechanism of the bridge bond seizure-related thermostability provides an alternate route, a type of a sacrificial buffer zone, to otherwise initial disintegration of the energetic ring terminals, upon exposure of the bridged energetic molecule to the thermal stimulus. Thus,

![Figure 19](image-url)
in our opinion, one of the proposed guidelines for the design of new thermostable EMs should be introduction of a sacrificial “complex” bridge moiety or “fused” rings arrangement, into a molecular structure of the target explosive.

Following more general observations of the location of the weakest bonds during thermal decomposition, we closely checked the chemistry and the strength of these bonds. For these purposes, the lengths and strengths of all covalent bonds in all 63 examined EMs were calculated (1842 bonds in total; Tables S2 and S3; Supporting Information). The types and statistical distribution of the first and second weakest bonds are shown in Figure 20a and Figure S32 and Table S7 (SI). We found that the C−NO2 bond was by far the most prevalent type of the first weakest bond, with length in the range 1.38−1.56 Å and the bond strength ranging from 71.63 to 128.23 kcal mol−1. The bridge bonds, such as C−C, C−O, and C−N, with the lengths in the range 1.37−1.56 Å and the strengths ranging from 50.69 to 129.07 kcal mol−1, are very likely to be the first or the second weakest bonds in the examined bridged EMs. In addition, C−O, C−N, N−N, and N−O bonds in heterocycle moieties of the relevant EMs (1.37−1.42 Å; 62.97−116.97 kcal mol−1) can also function as the weakest bonds. As shown in Figure 20a, EMs with C−C bridge bonds, C−NO2, or heterocyclic bonds, as their weakest bonds, have more than 50% probability to be thermostable.

Also, a general correlation was found between the value of the weakest bond strength and the thermostability in all relevant EMs (Figure S32; Supporting Information), and more focused correlations are shown in Figure 20b, presenting data for EMs with thermostability above 250 °C. For example, compounds D5 (TKX55) and E2 (2,3,5,6-tetranitro-4H,9H-dipyrazolo[1,5-a:5′,1′-d][1,3,5]triazine), were calculated to have the same weakest bond type (C−O bonds in their 1,3,4-oxadiazole rings) that has very close bond strengths of 98.72 and 96.84 kcal mol−1, respectively, making these explosives exhibit a similar thermostability of 335.011 and 340.8 °C, respectively (a pink cluster, Figure 20b). Explosives C2 (bis[2,4,6-trinitrophenyl]amine),38 E2 (2,3,5,6-tetranitro-4H,9H-dipyrazolo[1,5-a:5′,1′-d][1,3,5]triazine),38 and HL9 were calculated to have

Figure 20. (a) Distribution of the 1st and the 2nd weakest bonds among various types of covalent bonds in all 63 EMs mentioned in this study. (b) Focused temperature range (>250 °C) correlations between the strength of the 1st weakest bond and the thermostability in all 63 EMs (full temperature range correlations are shown in Figure S32; Supporting Information). (c) Distributions of all 63 EMs with respect to the strength of their 1st weakest bond.
C–NO$_2$ and bridged bonds to be the first and second weakest bonds, with the corresponding bond strength distributed in the narrow range 95.91−100.12 kcal mol$^{-1}$, showing a close thermostability of these explosives of 254.0, 261.2, and 261.9 °C, respectively (a purple cluster, Figure 20b). On a molecular level, there is a certain degree of structural resemblance between C2 and E2 EMs, which have 1,3,5-trinitrobenzene and 3,4-dinitro-1H-pyrazole energetic rings, respectively, connected by a bridging NH group, and HL9 that has two 3,5-dinitro-1H-pyrazole energetic rings, connected by a bridging CH$_2$ group.

Figure 20c presents a percentage distribution of thermostable EMs among all examined explosives, with respect to these explosives’ first weakest bond strength. We found a clear relationship between the weakest bond strength and the thermostability of the examined EMs. This relationship indicated that the increase in the strength of the weakest covalent bond in the molecule would lead to an overall stronger molecular structure, less prone to decomposition and therefore more stable to external stimuli, including heat. However, this obvious conclusion regarding the bond strength was never previously quantified for EMs. Following this analysis, we think that the design of molecular structures in which the weakest bond strength would be above 95 kcal mol$^{-1}$ could be an effective methodology to achieve EMs with improved thermostability.

EMs typically contain both oxidizing and reducible functional groups or components in their structure or composition. The oxygen balance (OB) is a calculated parameter that is used to describe to which degree a certain EM or its formulation could be oxidized, with OB equal to 0% considered as the exact amount of oxygen atoms present in EM for the complete oxidation of all oxidizable atoms to carbon dioxide and water leading to the best performance, but with a price of a high sensitivity. The results of OB calculations exhibited a remarkable correlation with EMs’ sensitivity to mechanical impact and the detonation performance, making OB values among critical parameters in design of new explosives. Thus, we plotted correlation between OBs of all EMs in this study with respect to their thermostability (Figure 21a and Figure S34; Supporting Information). We draw a similarity cluster for compound HL3 (a purple oval, Figure 21a) that included single ring EMs A4 (TATB), A13 (DADNPO), and A15 (ANPZ), as well as bridged EMs D8$^{22}$ and D10 (PYX),$^{44}$ which are among the best performing heat-resistant explosives, with thermostability in the range 350.7−366.4 °C and OB values in the range from −62.3 to −48.0%. In the second cluster for compound HL7 (a pink oval, Figure 21a) we included, closely positioned in terms of its parameters, a single ring explosive A14 (LLM-105).$^{25}$ Thermostability of both A14 and HL7 compounds was in the range 345.3−340.8 °C, with close OB values of −37.0% and −39.1%, respectively, strongly indicating that the “bridged” approach could be a viable alternative to the molecular design of thermostable EMs based on closely positioned alternating nitro and amino groups on the same aromatic ring. In the third cluster (a colorless oval, Figure 21a), we included structurally related (bridged dinitropyrazolyl rings) compounds E2 and HL9 that exhibit very close thermostability of 261.2 and 261.9 °C, respectively, and have similar OB values of −35.2% and −39.0%, respectively. We found that for thermostable EMs (with thermostability above 250 °C) the typical OB values were in the range from −80% to −30% (the “island of thermostability”), with prevalence of the thermostability going down, as OB values get closer to −30% (Figure 21b).

Although we could not find an obvious correlation between molecular weight of all examined EMs and their thermostability (Figure S35; Supporting Information), bridged explosives with molecular weight above 550 Da were clearly thermostable, supporting our previous statement regarding the capability of a molecule to dissipate heat by an appropriate molecular structure.

Crystal Level Correlations. In addition to molecular structures of various solid EMs, since these materials are used in bulk, their crystal structures and in-crystal molecular interactions play a great role in EMs’ detonation performance, mechanical and thermal stability, and processability. Following our studies related to different aspects of molecular level...
correlations, we expanded our investigation toward in-crystal arrangements and interactions of these energetic molecules. The first examined parameter was a crystal packing coefficient (PC), which quantifies the fraction of the volume in a crystal that is occupied by hard sphere atoms. The PC parameter was reported to be in a good correlation with a range of physicochemical properties of EMs.53 The results of correlation between EMs’ crystal PC and their thermostability showed that many heat-resistant explosives occupy a relatively narrow packing range between 73% and 77% (focused correlations for EMs with thermostability above 250 °C are shown Figure 22a; full range correlations for all EMs in this study are shown in Figure S36; Supporting Information). Compound HL3 has a similar PC value (76.3%) to heat-resistant explosives A14 (LLM105) and E1,13 where HL7 has a very close PC value (74.9%) to analogous D5 (TKXX55; a pink cluster, Figure 22a). Interestingly, compound HL9 was found to have a close PC value (73.4%) to explosive C2 (a purple cluster, Figure 22a), showing further correlation between these two bridged EMs to the above-mentioned molecular stability studies presented in Figure 22b. From Figure 22b that took into account all EMs in this study, we can learn that, for EMs with a higher probability to be thermostable, the preferable crystal PC values should be above 73%, with all our newly synthesized bridged compounds HL3, HL7, and HL9 fitting perfectly into the optimum range of PC values.

We further looked into correlations between the number of molecules found in each unit cell of all EMs mentioned in this study and these EMs’ thermostability (Figure S37; Supporting Information). We found that the prevalent number of molecules in the primitive cells of thermostable EMs was 2, 4, and 8 (Figure S37c; Supporting Information). A correlation between the space group number (SGN) of crystal structures of the examined EMs and their thermostability showed that most of these compounds have P21/c (SGN 14), P21/n (SGN 14), and P212121 (SGN 19) symmetries. As a general observation, the thermostable EMs have low crystal symmetry, highly disordered packing arrangements, and in narrow thermostability ranges, compared to non-thermostable compounds that have more ordered and higher symmetry structures.
with a space group number below 19 (Figure S38; Supporting Information). Notably, two of our newly synthesized HL3 and HL9 compounds were found to match both the prevalent number of molecules in the primitive cell and the space group number criteria, having 2 and 4 molecules in their crystal cell and the SNG of 14, similar to heat-resistant explosives A15 (ANPZ), D6, A14 (LLM105), and several others.

As in the above-mentioned case of no obvious correlation between the molecular weight of examined EMs and their thermostability (Figure S35; Supporting Information), we could not observe a clear trend in attempts to find a correlation between the Hirshfeld surface area of each molecule in a crystal and the examined EMs’ thermostability (Figure S39; Supporting Information). Thermostable bridged explosives from the Family D, with the Hirshfeld surface area above 400 Å², were found in this range, further supporting the hypothesis that molecular size is related to the capability of a molecule to dissipate the heat.

Hydrogen bonding is known to be an important factor governing EM’s reactivity to external stimuli. Therefore, we evaluated a correlation between the hydrogen bonding population (HBP, measured in %) and hydrogen bonding area (HBA, measured in Å²) on a Hirshfeld surface for all 63 EMs mentioned versus these compounds’ thermostability (Figure S40, Supporting Information). By analyzing the distribution of the thermostable EMs among all evaluated EMs, with respect to their HBPs, we determined that their preferred HBP values should be in a range between 20% and 70%. This is consistent with a previous theoretical work that intermolecular HBs between hydroxylammonium cations and anions are primarily responsible for the increase in the PC of energetic ionic salts.55 The highest probability of an EM to be thermostable was found in explosives having HBP in the relatively narrow range 50–70%. The latter group of explosives includes single-ring compounds, such as A4 (TATB), A15 (ANPZ), A13 (DADNPO), and A14 (LLM105), as well as some bridged EMs, such as D5 (TKX55), E9,47 D7,45 and D9.53

Our further analysis of correlation between EMs’ HBAs and their thermostability showed that heat-resistant explosives prevalently have HBA values in a range between 90 and 180 Å² (Figure 23). Grouping compounds with similar HBA and thermostability properties together, we could draw three different clusters for each of HL3, HL7, and HL9 explosives. The pink cluster that includes HL3, A13 (DADNPO), D6, and D10 (PYX), the HBA values are 136.51, 133.06, 136.69, and 134.63 Å², respectively, where the corresponding thermostability of these explosives was 351.0, 354.0,35 362.0,40 and 360.0 °C,44 respectively (Figure 23a). We can also point out a similarity between compound HL7 (with calculated solvent-free crystal structure) and explosives E1 and A14 (LLM105; the purple cluster), as well as similarity of HL9 to E2 (the colorless cluster).

An additional crystal parameter affecting EM’s solid-state properties is the lattice energy (LE), which is a quantification parameter of crystal packing forces, as well as a crystal’s intermolecular association strength. We studied a correlation between the LE (measured in kcal mol⁻¹) in all mentioned EMs in this study, versus these compounds’ thermostability (Figures 24A and Figure S41, Supporting Information). By analyzing the distribution of the thermostable EMs among all evaluated EMs, with respect to their LEs, we determined that their preferred LE values should be above 25 kcal mol⁻¹.

Among explosives having close LEs and thermostability values, we found compounds such as single-ring A13 (DADNPO) and A14 (LLM105); A15 (ANPZ) and “complex-bridge” D10 (PYX); as well as fused-rings E4 and bridgeless polynitropyrazole isomers B2 and B4. Our newly synthesized explosive HL3 has an outstanding thermostability of 351.0 °C because of its very high LE of 46.68 kcal mol⁻¹. While our newly synthesized solvent-free explosives HL7 and HL9 are both falling in the narrow range 35–40 kcal mol⁻¹, the significant difference in their thermostability could be explained by different molecular structures of their bridges, overpowering the influence of their crystal structures.

**CONCLUSIONS**

A general objective of this research was to explore and map features and advantages of “bridged” molecular structures on the thermostability of a broad range of energetic materials (EMs) and then to implement deduced guidelines for the design of new thermostable explosives.

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Figure 24. (a) Focused temperature range (>250 °C) correlation between the lattice energy and the thermostability of all evaluated EMs (full range correlations are shown in Figure S41; Supporting Information). (b) Distribution of the thermostable EMs, with respect to their lattice energy for each molecule, among all 63 EMs mentioned in this study.
On the molecular level, our first design guideline for the improvement of the thermostable properties of EMs is the introduction of a sacrificial “complex” bridge moiety or “fused” rings arrangement into the structure of the new explosive. We found a clear correlation between the value of the weakest bond strength and the thermostability of the EMs. This correlation was never reported previously. The bridged EMs having C=C bridge bonds, C=NO, or heterocyclic bonds, as their weakest bonds, show more than 50% probability to be thermostable, while the design of molecules with the weakest bond strength above 95 kcal mol\(^{-1}\) could be an effective methodology to achieve improved thermostability. With respect to the oxygen balance parameter, we found that the optimum OB values for thermostable EMs should be in the range from \(-80\%\) to \(-30\%\) (the “island of thermostability”).

In terms of the crystal structure-related parameters, we found a good correlation between the thermostability and the crystal packing coefficient, which for thermostable explosives should be the narrow range 73–77%. In the case of the thermostability correlation with Hirshfeld surfaces’ hydrogen bonding population (HBP) and hydrogen bonding area (HBA) parameters, relatively narrow ranges with distributions of 50–70% and 90–180 \(\text{Å}^2\), respectively, were observed.

An additional examined crystal level parameter was the crystal’s lattice energy (LE), which was found to be above 25 kcal mol\(^{-1}\) in the evaluated thermostable EMs.

On the basis of our comprehensive study of various molecular level and crystal level parameter correlations with the thermostability of 60 reported EMs, three new insensitive, thermostable, and high-performing energetic materials, having bridged molecular structures, HL3, HL7, and HL9, were designed, synthesized, characterized, and evaluated in small-scale field detonation experiments. We found that best overall performing compound HL7 exhibited a remarkable onset decomposition temperature of 341 °C and has a density of 1.865 g cm\(^{-3}\). It has a calculated velocity of detonation and maximum detonation pressure of 8517 m s\(^{-1}\) and 30.6 GPa, respectively.

Considering HL7’s impressive safety parameters (IS = 22 J, FS = 352, and ESD = 1.05 J) and results of fast camera-monitored small-scale field detonation experiments, we believe that our proposed molecular and crystal guidelines and criteria for the design of thermostable explosives could be a valuable and indispensable asset in the architecture of future thermostable energetic materials, pushing the relevance of our conclusions to the higher technology readiness level.

**ASSOCIATED CONTENT**

† Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsscienc.9b01096.

Materials, synthesis, and analytical data including NMR, MS, DSC, FTIR, elemental analysis, X-ray crystallography, as well as detailed of detonation and computational studies, supplementary figures, and tables (PDF)

Video S1: detonation experiment of HL7 (ZIP)

**AUTHOR INFORMATION**

Corresponding Authors
*E-mail: zhang_lei@iapcm.ac.cn.
*E-mail: cogozin@gmail.com.

**ORCID**

Lei Zhang: 0000-0002-7722-565X
Michael Gozin: 0000-0003-0897-1760

**Notes**

Note that the DFT calculation and data analysis of molecular and crystal features of the series of explosives allowed the definition of key descriptors of thermostability.

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**REFERENCES**

(1) Larcher, D.; Tarason, J. M. Towards Greener and more Sustainable Batteries For Electrical Energy Storage. Nat. Chem. 2015, 7, 19.

(2) (a) Galante, E.; Haddad, A.; Marques, N. Application of Explosives in the Oil Industry. Int. J. Oil Gas Coal Technol. 2013, 1, 16. (b) Barker, J. M. In Thermally Stable Explosive System for Ultra-High-Temperature Perforating, Society of Petroleum Engineers, SPE 166179, the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, USA, 2013; 166179. (c) Abdel-Aal, H. K.; Aggour, M. A.; Fahim, M. A. Petroleum and Gas Field Processing; CRC Press: New York, 2015; pp 41–51.

(3) Majorowicz, J.; Nieuwenhuis, G.; Unsworth, M.; Phillips, J.; Verveda, R. In High Temperatures Predicted in the Granite Basement of Northwest Alberta – An Assessment of the EGS Energy Potential, Proceedings of 39th Workshop on Geothermal Reservoir Engineering, Stanford, USA, February, 2014.

(4) (a) Kilmer, E. E. Heat-Resistant Explosives for Space Applications. J. Spacecr. Rockets 1968, S, 1216. (b) Tang, Y.; He, C.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. Aminonitro Groups Surrounding a Fused Pyrazolotriazine Ring: A Superior Thermally Stable and Insensitive Energetic Material. ACS Appl. Energy Mater. 2019, 2, 2263.

(5) (a) Brauer, K. In Present and Future Applications of Pyrotechnic Devices and Pyrotechnic Systems for Spacecraft”, 19th Congress of the International Astronautical Federation, New York, USA, October, 1970. (b) Hwang, D. H.; Han, J. H.; Lee, J.; Lee, Y.; Kim, D. A Mathematical Model for the Separation Behavior of a Split Type Low-Shock Separation bolt. Acta Astronaut. 2019, 164, 393.

(6) (a) Shipp, K. G. Reactions of \(\alpha\)-Substituted Polynitrotoluenes. I. Synthesis of \(2,2',4,4',6,6'-\text{Hexanitrostilbene}\). J. Org. Chem. 1964, 29 (9), 2620. (b) Rieckmann, T.; Völker, S.; Lichtblau, L.; Schirra, R. Investigation on the Thermal Stability of Hexanitrostilbene by Thermal Analysis and Multivariate RSegression. Chem. Eng. Sci. 2001, 56 (4), 1327–1335. (c) Gilbert, E. The Preparation of Hexanitrostilbene from Hexanitrobenzyl. Propellants, Explos., Pyrotech. 1980, 5, 168.

(7) (a) Agrawal, J. P. Past, Present & Future of Thermally Stable Explosives. Cent. Eur. J. Energy 2012, 9 (3), 273–290. (b) Agrawal, J. P. High energy materials: propellants, explosives and pyrotechnics; Wiley-VCH Verlag GmbH: Germany, 2010; pp 1–464.

(8) (a) Yin, P.; Zhang, J.; Parrish, D. A.; Shreeve, J. M. Energetic N,N'-Ethylene-Bridged Bis(nitropyrazoles): Diversified Functionalities and Properties. Chem. - Eur. J. 2014, 20, 16529.

(9) Kumar, D.; Tang, Y.; He, C.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. Multipurpose Energetic Materials by Shuffling Nitro Groups on a 3,3'-Bipyrrole Monety. Chem. - Eur. J. 2018, 24, 17220.

(10) Klapötke, T. M.; Witkowski, T. G.; Wilk, Z.; Hadzik, J. Experimental Study on the Heat Resistant Explosive \(5,5'\)-Bis\((2,4,6\)-trinitrophenyl\))-2,2'-bi\((1,3,4\)-oxadiazole\) (TKX-55): the Jet Penetration Capability and Underwater Explosion Performance. Cent. Eur. J. Energ. Mater. 2016, 13, 821.
(11) Klapötke, T. M.; Witkowski, T. G. S,5′-Bis(2,4,6-trinitrophenyl)-2,2′-bi(1,3,4-oxadiazole) (TKX-55): Thermally Stable Explosive with Outstanding Properties. *ChemPlusChem* 2016, 81, 357.

(12) (a) Tsyshchevsy, R.; Pagoria, P.; Zhang, M.; Racoveanu, A.; Parrish, D. A.; Smirnov, A. S.; Kuklja, M. M. Comprehensive End-to-End Design of Novel High Energy Density Materials: I. Synthesis and Characterization of Oxadiazole Based Heterocycles. *J. Phys. Chem. C* 2017, 121, 23865. (b) Tsyshchevsy, R.; Pagoria, P.; Smirnov, A. S.; Kuklja, M. M. Comprehensive End-to-End Design of Novel High Energy Density Materials: II. Computational Modeling and Predictions. *J. Phys. Chem. C* 2017, 121, 23865. (c) Tsyshchevsy, R.; Smirnov, A. S.; Kuklja, M. M. Comprehensive End-to-End Design of Novel High Energy Density Materials: III. Fused Heterocyclic Energetic Compounds. *J. Phys. Chem. C* 2019, 123, 8688.

(13) (a) Kroonblawd, M. P.; Sewell, T. D.; Maillet, J. B. Characteristics of Energy Exchange Between Inter- and Intra-molecular Degrees of Freedom in Crystalline 1,5,5′-Triamin-2,4,6-Trinitrobenzene (TATB) with Implications for Coarse-Grained Simulations of Shock Waves in Polyatomic Molecular Crystals. *J. Chem. Phys.* 2016, 144 (6), No. 064501. (b) Mostafá, S. G.; Schultz, A. J.; Kofke, D. A. Very Fast Averaging of Thermal Properties of Crystals by Molecular Simulation. *Phys. Rev. E* 2015, 92, No. 043303. (c) Pulido, A.; Chen, L.; Kaczorowski, T.; Holden, D.; Little, M. A.; Chong, S. Y.; Slater, B. J.; McMahon, D. P.; Bonillo, B.; Stackhouse, C. J.; Stephenson, A.; Kane, M. C.; Clowes, R.; Hasell, T.; Cooper, A. I.; Day, G. M. Functional Materials Discovery Using Energy-Structure-Function Maps. *Nature* 2017, 543, 657. (d) Musil, P.; De, S.; Yang, J.; Campbell, J. E.; Day, G. M.; Ceriotti, M. Machine learning for the structure–energy–property landscapes of molecular crystals. *Chem. Sci.* 2018, 9, 1289.

(14) (a) Ma, Y.; Zhang, A.; Zhang, C.; Jiang, D.; Zhu, Y.; Zhang, C. Crystal Packing of Low-Sensitivity and High-Energy Explosives. *Cryst. Growth Des.* 2014, 14, 4703. (b) Zhang, C.; Wang, X.; Huang, H. π-Stacked Interactions in Explosive Crystals: Buffers against External Mechanical Stimulation. *J. Am. Chem. Soc.* 2008, 130, 8359. (c) Tian, B.; Xiong, Y.; Chen, L.; Zhang, C. Relationship between the crystal packing and impact sensitivity of energetic materials. *CrystEngComm* 2018, 20, 837.

(15) Wang, Y.; Liu, Y.; Song, S.; Yang, Z.; Qi, X.; Wang, K.; Liu, Y.; Zhang, Q.; Tian, Y. Accelerating the Discovery of Inensitive High-Energy-Density Materials by a Materials Genome Approach. *Nat. Commun.* 2018, 9, 2444.

(16) (a) Manelis, G. B.; Nazin, G. M.; Rubtsov Yu, I.; Strunin, V. A. Thermal Decomposition and Combustion of Explosives and Propellants; Taylor & Francis: New York, 2003. (b) Manelis, G. B.; Nazin, G. M.; Rubtsov Yu, I.; Strunin, V. A. Performance of DFT, MP2, and RHF/MRCI Theoretical Predictions for the Oxidation Polymers. *Coord. Chem. Rev.* 2019, 392, 49. (b) Tian, A.; Ni, H.; Ji, X.; Tian, Y.; Liu, G.; Ying, J. Influence of Pendant 2-1,2,4-triazol-4-yl-ethylamine and Symmetrical Bis(pyrrozal) Ligands on Dimensional Extension of POM-Based Compounds. *RSC Adv.* 2017, 7, 30573. (c) Tian, A.; Yang, Y.; Ying, J.; Li, N.; Liu, X.; Zhang, J. W.; Wang, X. L. The Key Role of –CH₂ Steric Hindrance in Bis(pyrrozal) Ligand on Polyoxometalate-based Compounds. *Dalt. Trans.* 2014, 43, 8405.

(21) (a) Bellamy, A. J. Synthesis of Hexanitrostilbene (HNS) using a Kenics Static Mixer. *Org. Process Res. Dev.* 2010, 14, 632. (b) Lu, T.; Yao, K.; Mao, Y.; Xu, J.; Wang, P.; Lu, M. A Novel and Efficient Synthesis of Hexanitrostilbene by N-Hydroxypthalimide/FeCl₂-Catalyzed Aerobic Dehydrogenation of Hexanitrobenzyl. *J. Energ. Mater.* 2013, 31, 217. (c) Wang, P.; Lu, T. T.; Lu, M. A Green and Effective Approach of Two-Step 2,2′,4,4′,6,6′-Hexanitrostilbene Preparation and Its Industrial Scale Study. *Org. Process Res. Dev.* 2016, 20, 688.

(22) Zaitssev, A. A.; Kortusov, I.; Dalinger, I.; Kachala, V.; Popova, G.; Shevelev, S. Nitropyrazoles 15. The use of methoxymethyl group as a protecting group for the synthesis of 4-methyl-3-nitro-5-R-pyrazoles. *Russ. Chem. Bull.* 2009, 58, 2118.

(23) Zaitssev, A. A.; Vatsadze, I.; Dalinger, I.; Kachala, V.; Nelyubina, Y. V.; Shevelev, S. Nitropyrazoles 15. Synthesis and some transformations of 1-(2,4-dinitrophenyl)-4-methyl-3,5-dinitropyrazole. *Russ. Chem. Bull.* 2009, 58, 2109.

(24) Zaitssev, A. A.; Cherskova, T. I.; Dalinger, I.; Kachala, V. V.; Strelenko, Y. A.; Fedyanin, I. V.; Solkan, V. N.; Shikineva, T. V.; Popova, G. P.; Shevelev, S. A. Nitropyrazoles. *Russ. Chem. Bull.* 2007, 56, 2074.

(25) (a) Trofimenko, S. G. Solid Polymers with One Oxadiazole Ring and their Coordination Chemistry. *J. Am. Chem. Soc.* 1970, 92, 5118. (b) Wheate, N. J.; Broomhead, J. A.; Collins, G.; Day, A. I. Thermal Rearrangement of N-Substituted Pyrazoles to 4,4′-Diarylpyrazole-methane and 1,2,4,4′,6,6′-Triarylpentazole. *J. Chem. Soc.* 2001, 54, 141.

(26) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. Tables of Bond Lengths Determined by X-ray and Neutron Diffraction. Part I. Bond Lengths in Organic Compounds. *J. Chem. Soc., Perkin Trans. 2* 1987, 51.

(27) Urbański, T.; Vasudeva, S. K. Heat Resistant Explosives. *J. Sci. Ind. Res.* 1978, 37 (5), 250.

(28) Wang, H. B.; Wang, Y. H.; Li, Y. X.; Liu, Y. C.; Tan, Y. X. Scale-up Synthesis and Characterization of 2,6-diamino-3,5-dinitropyrazine-1-oxide. *Def. Technol.* 2014, 10, 343.

(29) Singh, B.; Malhotra, R. Hexanitrostilbene and its Properties. *Def. Sci.* 1983, 33, 165.

(30) (a) Dorofeeva, O. V.; Osiha, E. L. Performance of DFT, MP2, and Composite ab initio Methods for the Prediction of Enthalpies of Formations of CHON Compounds Using Isodesmic Reactions. *Comput. Theor. Chem.* 2017, 1106, 28. (b) Xu, Z.; Cheng, G.; Yang, H.; Ju, X.; Yin, P.; Zhang, J.; Shreeve, J. M. A. Accurate Synthesis of Energetic Furazan-Functionalized 5-Nitroimino-1,2,4-Triazoles. *Angew. Chem., Int. Ed.* 2017, 56, 5877.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2013.
(32) Suceska, M. EXPLO S; Brodarski Institute: Zagreb, Croatia, 2013.

(33) (a) Pimbley, G. H.; Bowman, A. L.; Fox, W. P.; Kershner, J. D.; Mader, C. L.; Urizar, M. J. Investigating Explosive and Material Properties by Use of the Plate Dent Test; Los Alamos Scientific Laboratory: Los Alamos, New Mexico, 1980. (b) Fren, D. Predicting the Plate Dent Test Output in Order to Assess the Performance of Condensed High Explosives. J. Energ. Mater. 2017, 35, 20.

(34) (a) Fedyanin, I. V.; Lyssenko, K. A. New Hydrogen-bonded Supramolecular Synthon: A Case Study of 2,4,6-trinitroaniline. CrystEngComm 2013, 15, 10086. (b) Thallapalli, P. K.; Jetti, R. K.; Katz, A. K.; Carrell, H. L.; Singh, K.; Lahiri, K.; Kotha, S.; Boese, D.; Resjari, G. R. Polymorphism of 1,5-Trinitrobenzene Induced by a Trisindane Additive. Angew. Chem., Int. Ed. 2004, 43, 1149.

(35) Kohno, Y.; Hiyoshi, R. I.; Yamaguchi, Y.; Matsumoto, S.; Koseki, A.; Takahashi, O.; Yamazaki, K.; Ueda, K. Molecular Dynamics Studies of the Structural Change in 1,3-Diamino-2,4,6-trinitrobenzene (DATB) in the Crystalline State under High Pressure. J. Phys. Chem. A 2009, 113, 2551. (d) Nair, U. R.; Gore, G. M.; Sivabalan, R.; Pawar, S. J.; Asthana, S. N.; Venugopalan, S. Preparation and Thermal Studies on Tetratinodibenzo Tetrazapentalene (TACTOT): A Thermally Stable High Explosive. J. Hazard. Mater. 2007, 143, 500.

(36) (a) Rohač, M.; Zeman, S.; Růžička, A. Crystallography of 2,2′,4′,6,6′-Hexanitro-1,1′-biphenyl and Its Relation to Initiation Reactivity. Chem. Mater. 2008, 20, 3105. (b) Tang, Y.; He, C.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. Amino Derivatives of Octanitro-2,4,6,8-tetraoxa-1,3,5,7-tetrabenzenacyclooctaphane and its Derivatives: Thermally Stable Explosives with Outstanding Properties. New J. Chem. 2017, 41, 5764.

(37) (a) Zeng, Z.; Guo, Y.; Twambley, B.; Shreeve, J. M. Energetic Polyzole Polynitrobenzenes and Their Coordination Complexes. Chem. Commun. 2009, 6014. (b) Zhang, Y.; Zhou, C.; Wang, B.; Zhou, Y.; Xu, K.; Jia, S.; Zhao, F. Synthesis and Characteristics of Bis(nitrofurazano)furan (BNFF), an Insensitive Material with High Energy-Density. Propellants, Explos, Pyrotech. 2014, 39, 809. (c) Li, H.; An, C. W.; Du, M. Y. J. Chin. J. Explos. Propell. 2016, 39, 58.

(38) (a) Vorob’ev, A. V.; Kacarevič, A.; Sibley, G. A.; Platt, A. G. Stabilization of Energetic Materials by Introducing Nitrogen-Containing Ions. J. Phys. Chem. B 2019, 123, 13939.

(39) Zeman, S.; Rohač, M.; Friedl, Z.; Růžička, A.; Lyčka, A. Crystallography and Structure–Property Relationships of 2,2′,4′,6′,6′-Octanitro-1′-terphenyl (ONT). Propellants, Explos, Pyrotech. 2010, 35, 130.

(40) Wei, J.; Li, F.; Xu, J.; Peng, X. Synthesis and Thermal Stability of New Polynitrostilbenes. Aust. J. Chem. 2015, 68, 919.

(41) Klappete, T. M.; Stierstorfer, J.; Weyrauther, M.; Witzkowski, T. G. Synthesis and Investigation of 2,6-Bis(picrylamino)-3,5-dinitro-1,2,4-triazine Derivatives Containing Azole Functional Groups. Dalton Trans. 2015, 44, 13939.

(42) Zeman, S.; Rohač, M.; Friedl, Z.; Růžička, A.; Lyčka, A. Crystallography and Structure–Property Relationships of 2,2′,4′,6′,6′-Octanitro-1′-terphenyl (ONT). Propellants, Explos, Pyrotech. 2010, 35, 130.

(43) Wei, J.; Li, F.; Xu, J.; Peng, X. Synthesis and Thermal Stability of New Polynitrostilbenes. Aust. J. Chem. 2015, 68, 919.

(44) Klappete, T. M.; Stierstorfer, J.; Weyrauther, M.; Witzkowski, T. G. Synthesis and Investigation of 2,6-Bis(picrylamino)-3,5-dinitro-1,2,4-triazine Derivatives Containing Azole Functional Groups. Dalton Trans. 2015, 44, 13939.

(45) Altmann, K. L.; Chafin, A. P.; Merwin, L. H.; Wilson, W. S.; Gilardio, R. Chemistry of Tetrazapentalenes. J. Org. Chem. 1999, 63, 3352.

(46) Yin, P.; Zhang, J.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. PolynitroFunctionalized Dipyrzyolo-1,3,5-triazinanines: Energetic Polycyclization toward High Density and Excellent Molecular Stability. Angew. Chem. 2017, 129, 8960.

(47) Tang, Y.; He, C.; Imler, G. H.; Parrish, D. A.; Shreeve, J. M. Ring Closure of Polynitroazoles via an N,N’-alkylene Bridge: Towards High Thermally Stable Energetic Compounds. J. Mater. Chem. A 2018, 6, 8382.

(48) Zhang, L.-J.; Jiang, S.-L.; Yu, Y.; Long, Y.; Zhao, H.-Y.; Peng, L.-J.; Chen, J. Phase Transition in Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) under Static Compression: An Application of the First-Principles Method Specialized for CHNO Solid Property Relationships. J. Phys. Chem. B 2016, 120, 11510. (b) Zhang, L.; Wu, J.-Z.; Jiang, S.-L.; Yu, Y.; Chen, J. From Intermolecular Interactions to Structures and Properties of a Novel Cocrystal Explosive: A First-Principles Study. Phys. Chem. Chem. Phys. 2016, 18, 269600. (c) Zhang, L.; Yao, C.; Yu, Y.; Jiang, S.-L.; Sun, C. Q.; Chen, J. Stabilization of the Dual-Aromatic cycloNS-Anion by Acidic Entrapment. J. Phys. Chem. Lett. 2019, 10, 2378. (d) Zhang, L.; Jiang, S.-L.; Yu, Y. Revealing Solid Properties of High-energy-density Molecular Cocrystals H2Q from the Cooperation of Hydrogen Bonding and Molecular Polarizability. Sci. Rep. 2019, 9, 1257. (e) Zhang, C.; Sun, C.; Hu, B.; Yu, C.; Lü, M. Synthesis and Characterization of the Pentazalene Cyanogen NC3N− in [N(N2)6]H3O3(NH4)4Cl. Science 2017, 355, 374. (f) Zhang, L.; Yao, C.; Yu, Y.; Wang, X.; Sun, C. Q.; Chen, J. ChemPhysChem 2019, 20, 2525. (g) Zhang, L.; Yu, Y.;
Xiang, M. A Study of the Shock Sensitivity of Energetic Single Crystals by Large-Scale Ab Initio Molecular Dynamics Simulations. *Nanomaterials* 2019, 9, 1251.

Zong, H.-H.; Zhang, L.; Zhang, W.-B.; Jiang, S.-L.; Yu, Y.; Chen, J. Structural, Mechanical Properties, and Vibrational Spectra of LLL-105 Under High Pressures from a First-Principles Study. *J. Mol. Model.* 2017, 23, 275.

Mo, Z.; Zhang, A.; Cao, X.; Liu, Q.; Xu, X.; An, H.; Pei, W.; Zhu, S. JASMIN: A Parallel Software Infrastructure for Scientific Computing. *Front. Comput. Sci. China* 2010, 4, 480.

Wolff, S. K.; Grimwood, D. J.; McKinnon, J. J.; Turner, M. J.; Jayatilaka, D.; Spackman, M. A. *CrystalExplorer 3.1*; University of Western Australia, 2012.

Hestenes, M. R.; Stiefel, E. L. Methods of Conjugate Gradients for Solving Linear Systems. *Journal of Research of the National Bureau of Standards* 1952, 49, 409.

He, P.; Zhang, J.-G.; Wang, K.; Yin, X.; Zhang, T.-L. Combination Multinitrogen with Good Oxygen Balance: Molecule and Synthesis Design of Polynitro-Substituted Trazolotriazine-Based Energetic Compounds. *J. Org. Chem.* 2015, 80, 5643.

Lin, H.; Yang, D.-D.; Lou, N.; Zhu, S.-G.; Li, H.-Z. Computational Design of High Energy Density Materials with Zero Oxygen Balance: A Combination of Furazan and Piperazine Rings. *Comput. Theor. Chem.* 2018, 1139, 44.

Zhang, J.; Mitchell, L. A.; Parrish, D. A.; Shreeve, J. M. Enforced Layer-by-Layer Stacking of Energetic Salts towards High-Performance Insensitive Energetic Materials. *J. Am. Chem. Soc.* 2015, 137, 10532.

Zhang, W.; Zhang, J.; Deng, M.; Qi, X.; Nie, F.; Zhang, Q. A Promising High-Energy-Density Material. *Nat. Commun.* 2017, 8, 181.

McKinnon, J. J.; Jayatilaka, D.; Spackman, M. A. Towards Quantitative Analysis of Intermolecular Interactions with Hirshfeld Surfaces. *Chem. Commun.* 2007, 3814.

McKinnon, J. J.; Mitchell, A. S.; Spackman, M. A. Hirshfeld Surfaces: A New Tool for Visualising and Exploring Molecular Crystals. *Chem. - Eur. J.* 1998, 4, 2136.

Meng, L.; Lu, Z.; Ma, Y.; Xue, X.; Nie, F.; Zhang, C. Enhanced Intermolecular Hydrogen Bonds Facilitating the Highly Dense Packing of Energetic Hydroxylammonium Salts. *Cryst. Growth Des.* 2016, 16, 7231.