

Prediction of the Crystal Packing of Di-Tetrazine-Tetroxide (DTTO) Energetic Material

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Previous calculations suggested that di-tetrazine-tetroxide (DTTO), aka tetrazino-tetrazine-tetraoxide, might have a particularly large density (2.3 g/cm³) and high energy release (8.8 kJ/kg), but it has not yet been synthesized successfully. We report here density functional theory (DFT) (M06, B3LYP, and PBE-ulg) on 20 possible isomers of DTTO. For the two most stable isomers, **c1** and **c2** we predict the best packings (i.e., polymorphs) among the 10 most common space groups for organic molecular crystal using the Universal force field and Dreiding force field with Monte Carlo sampling. This was followed by DFT calculations at the PBE-ulg level to

optimize the crystal packing. We conclude that the **c1** isomer has the *P2₁2₁2₁* space group with a density of 1.96 g/cm³, while the **c2** isomer has the *Pbca* space group with a density of 1.98 g/cm³. These densities are among the highest of current energetic materials, RDX (1.81 g/cm³) and CL20 (2.01 g/cm³). We observe that the stability of the polymorphs increases with the density while the planarity decreases. © 2015 Wiley Periodicals, Inc.

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Introduction

High energy density materials (HEDM) have many important applications as propellants and explosives. It is desirable to increase energy density while decreasing sensitivity in HEDM. Previous calculations^[1–4] suggested that di-tetrazine-tetroxide (DTTO) might have a particularly large density (greater than 2.0 g/cm³), high-energy release, and detonation properties. Despite these strong interests, it has not yet been synthesized successfully.

To provide critical parameters for synthesizing these materials, we predicted the most stable isomers of DTTO using density functional theory (DFT) at the M06 and B3LYP level. Then, we used Monte Carlo sampling with classical force fields to identify the most favorable packings for the 10 most common space groups for organic molecular crystal. Finally, the most stable packings were optimized at the DFT PBE-ulg level to predict the optimized crystal structure and densities.

Methods

Nonperiodic DFT methodology (B3LYP and M06)

Quantum Mechanical calculations were carried out using the M06^[5] and B3LYP^[6,7] hybrid functionals as implemented in the Jaguar code.^[8] For structure optimization, we used 6–311G**++ basis set for C, N, and O.^[9,10] All geometries were optimized using the analytic Hessian to determine that the local minima have no negative curvatures (imaginary frequencies). The vibrational frequencies from the analytic Hessian were used to calculate the zero-point energy and temperature corrections to the enthalpy.

Periodic DFT methodology (PBE-ulg)

We performed periodic DFT calculations using Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional including the low gradient London dispersion correction

(PBE-ulg) implemented in the VASP package.^[11–14] We found that a kinetic energy cutoff of 600 eV for the plane wave expansions gives excellent convergence of the total energies, energy differences, and structural parameters. Reciprocal space was sampled using the Γ -centered Monkhorst–Pack scheme with a resolution of $2\pi \times 1/40 \text{ \AA}^{-1}$. The convergence criteria were set to a 1×10^{-6} eV energy difference for solving the electronic wave function and a 1×10^{-3} eV/Å force for geometry optimization.

Monte Carlo annealing method

Rather than searching all 230 space groups, we considered the 10 space groups: *P2₁/c* (36.0%), *P-1* (13.7%), *P2₁2₁2₁* (11.6%), *P2₁* (6.7%), *C2/c* (6.6%), *PBCA* (3.5%), *C2* (1.5%), *PNA21* (1.4%), *PBCN* (1.0%), and *Cc* (<1.0%) that account for 83% of the organic molecular solids.^[15,16]

The MC simulated annealing process contains two stages: heating and cooling. First, we start the heating process of the system from the minimum temperature of 300 K to maximum temperature of 60,000 K with a constant heating factor of

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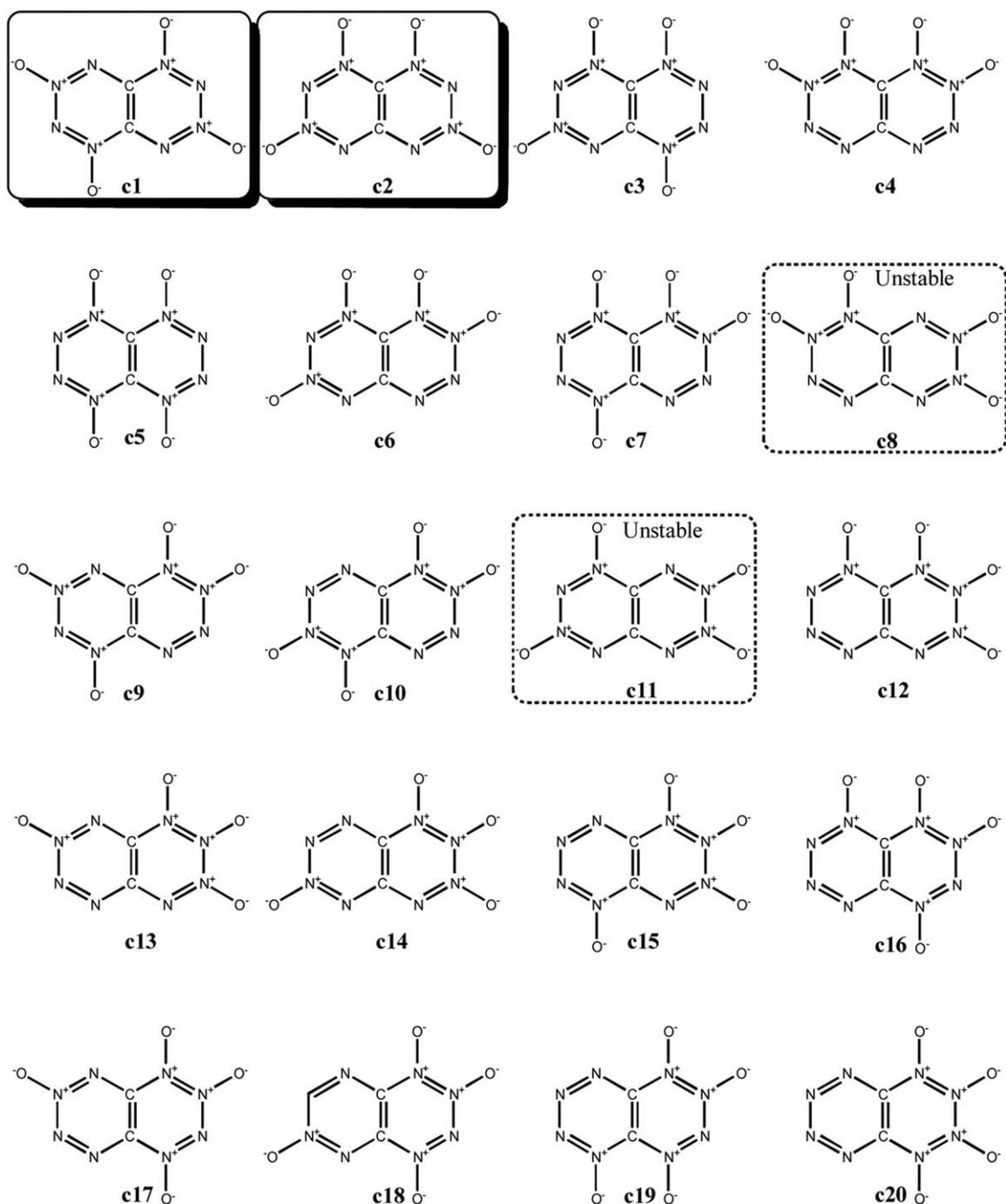


Figure 1. Isomers of DTTO analyzed to find the most stable molecular structure. All isomers are stable except for **c8** and **c11**, which rearrange into more stable molecules (Fig. 2) that do not have the DTTO backbone.

0.025. After the structure reaches the maximum temperature, we turn to the cooling stage with a cooling factor of 0.001.

For each MC trial step, we include the following steps to optimize the crystal structure. First, we make random changes of the orientation of the rigid molecule within the constraints of the space group. Then, we make random changes in the lattice vectors within the constraints of the space group. Furthermore, we allow the system to minimize the van der Waals interaction by changing cell parameters. Rigid molecule translation is maintained during these processes to obtain the best

crystal packing. Finally, the energy and density of the structure are calculated and used in conjunction with the Metropolis algorithm to determine whether the newly generated structure should be accepted or rejected. Any structure with a density lower than 0.3 g/cm^3 is always rejected.

This MC annealing process makes 6000 total trials, leading to ~ 3000 accepted structures, which are then used for further geometry optimization using two force fields (Dreiding^[17] and UFF^[18]). The symmetry constraints are maintained when varying the cell parameters in the geometry optimization. The

Table 1. Relative energies, E (kcal/mol) of the 20 DTTO isomers with respect to **c1** at 0 K.^[a]

Isomer	E B3LYP	E M06	Isomer	E B3LYP	E M06
c1	0.0	0.0	c11 ^[b]	3.0	2.4
c2	0.8	0.6	c12	15.3	15.6
c3	14.5	15.6	c13	0.1	0.3
c4	17.6	18.0	c14	0.5	0.8
c5	33.3	35.5	c15	8.4	8.8
c6	8.7	8.8	c16	22.5	23.9
c7	18.3	19.2	c17	5.4	18.0
c8 ^[b]	1.0	0.7	c18	9.5	22.6
c9	2.5	2.2	c19	23.0	36.1
c10	12.7	12.9	c20	31.7	44.7

[a] Previous studies on isomers **c1**–**c5** used the G3MP2B3 method^[4] with constrained symmetry. [b] These structures are not stable; that is, they transform into structures that do not have a DTTO backbone (Fig. 2).

lowest energy structures for 10 space groups were used for QM optimization at the PBE-ulg level.

Results and Discussion

QM calculation of the most stable isomer for DTTO

Previous calculations on DTTO isomers considered only five isomers (labeled **c1** to **c5**) with high molecular symmetries.^[4] In contrast, we predicted the energy of all 20 possible DTTO isomers, making no symmetry constraints, assuming only that C and N are present in the ring (Fig. 1).

First, the structures for all 20 isomers were optimized using the B3LYP and M06 flavors of DFT, leading to the energies in Table 1. Our energetics for **c1** to **c5** were consistent with previous estimates,^[4] although we allowed the geometry to relax without symmetry constraints. All 20 isomers were stable except for **c8** and **c11**. These two transformed into the structures shown in Figure 2, with open rings, which were more stable by 12 and 18 kcal/mol, but would not be good candidates for energetic materials. Thus, we did not consider them further.

Of the remaining 18 isomers, four (**c1**, **c2**, **c13**, and **c14**) had stabilities within 1.0 kcal/mol of each other from both B3LYP and M06. However, we chose to study the packing of only **c1** and **c2**, because **c13** and **c14** have three adjacent nitroxides, which we expect to be less stable when packed into a crystal.

Next, we analyzed the bonds and charges of **c1** and **c2** to understand their differences. The electrostatic potential (ESP) analysis is summarized in Figure 3 and Supporting Information Figure S1. Both B3LYP and M06 predicted that **c1** was 0.6–0.8

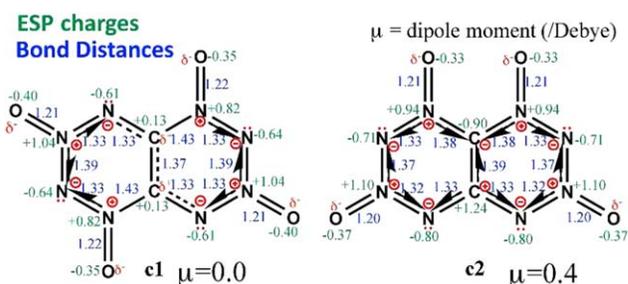


Figure 3. The bond character of isomers **c1** and **c2** based on ESP charges and bond distances.

kcal/mol more stable than **c2** (Table 1). Combining the ESP charges and bond distances led to the bond character suggested in Figure 3. The isomer **c2** depicted therein has alternating positive and negative character for the N and C framework atoms so that all CN and NN bonds have similar dipolar character. This led to a net dipole moment of 0.4 Debye for **c2**. In contrast, isomer **c1** had the central CC bond separating the N^+ and N^- atoms, leading to a resonance in the trans NCCN unit. The net result was that **c1** was more stable and did not have a dipole moment.

Determining the best candidates for packing of DTTO isomers into crystals using Monte Carlo annealing

We explored the 10 most common space groups for molecular systems [Periodic DFT methodology (PBE-ulg)] to predict the packing of the **c1** and **c2** isomers into crystals (i.e., polymorphs). For each of these 10 space groups, we first carried out Monte Carlo sampling of over 6000 packings for each of the 10 space groups using fixed molecular structures. Then, using both the UFF^[18] and Dreiding^[17] force fields, we minimized the most stable structures while allowing the molecules and the lattice to relax. The predicted structures are compared in Supporting Information Figures S1 and S2. The results are compared in Supporting Information Tables S1–S4. From these tables, we concluded that the Dreiding force field gives more consistent results. We then selected the best structure from each of the five best space groups for further DFT calculations.

Density functional studies of the stability of the DTTO packing

Starting with the top five polymorphs for the isomers **c1** and **c2** generated from the Monte Carlo sampling using the Dreiding force field, we used DFT to optimize the structures. Here, we used the PBE-ulg method,^[11] in which the van der Waals

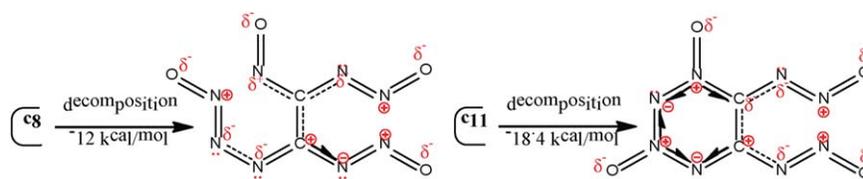


Figure 2. The isomers **c8** and **c11** are unstable. They rearranged into the more stable structures shown here. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

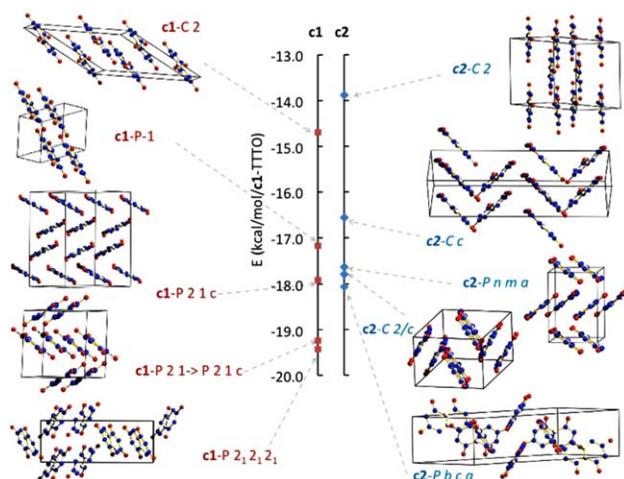


Figure 4. The most stable structures for **c1** and **c2** are shown, ranked by their QM energy. We found for these polymorphs that the stability of the polymorphs increased as the density and the planarity decreased.

attraction was corrected using the UFF C6 parameters damped with the low gradient form. We found that in most cases the space group obtained from the FF was maintained after QM optimization. We monitored the symmetry at the beginning and at the end of the calculation with a tolerance in the deviation of 0.001 Å. The exception for **c1** is that the $P2_1$ structure found with the FF minimized to $P2_1/c$ for QM. Additionally, the **c2** structure obtained for the $P2_12_12_1$ space group using the FF minimized to the $Pnma$ space group after QM.

The most stable structures are shown in Figure 4 and Table 2. The PBE-ulg method predicted **c1** to be 1.2 kcal/mol more stable than **c2**, whereas B3LYP predicted **c1** to be 0.8 kcal/mol more stable than **c2**, and M06 predicted **c1** to be 0.6 kcal/mol more stable than **c2**. Thus, all DFT methods predict the same trend for the free molecule. Table 2 included a useful way to look at relative energies referenced to the most stable molecule (defined as the energy relative to **c1** [or $\Delta(c1)$]), to determine the global rank. This comparison can be done because **c1** and **c2** are isomers, with the same number of atoms and

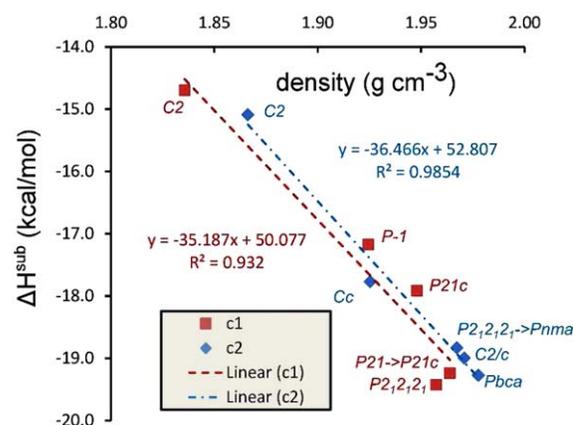


Figure 5. Most stable structures for **c1** and **c2** ranked by their QM energy. The stability increased with the density for these polymorphs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electrons. The polymorphs from DTTO isomers **c1** and **c2** show stabilities that increase with the density (Fig. 5 and Table 2). These results show that the stability increases as the density and the planarity decreases for these polymorphs. Thus among the **c1** and **c2** polymorphs, the most stable polymorph was the one with the highest density, **c1**: $P2_12_12_1$ with density 1.96 g/cm³, and **c2**: $Pbca$ with density 1.98 g/cm³. The energy content of **c1**: $P2_12_12_1$ is 6.31 kJ/g, and 6.32 KJ/g for **c2**: $Pbca$, if one assumes they are decomposed to CO₂ and N₂, which is 150% higher than that of trinitrotoluene (TNT) (4.2 kJ/g).

Song et al.^[4] predicted that that the most stable polymorph for **c1** was $P2_12_12_1$ with density of 2.3 g/cm³. Indeed, our studies found this space group to be the most stable, but with a much lower density, 1.96 g/cm³. The Song study used DFT-local density approximation (LDA) to describe crystal packing, which does not treat dispersion forces properly.

The **c1** and **c2** polymorphs were very similar except that **c2**: $Pbca$ was nonplanar whereas **c1**: $P2_12_12_1$ was more planar. A similar behavior was found for the polymorphs of FOX-7 where three polymorphs (α -, β -, and γ -) were closely related

Table 2. Predicted properties from DFT: PBE-ulg.

Structure	ρ (g/cm ³)	$\Delta H_{\text{sub}}^{\text{sub}}$ (kcal/mol)	$\Delta(c1)$ (kcal/mol) ^[a]	Local rank	Global rank
c1 :Molecule	–	–	0.0	–	–
c1 : $P2_12_12_1$	1.96	–19.4	–19.4	1	1
c1 : $P2_1/c$ ^[b]	1.96	–19.2	–19.2	2	2
c1 : $P2_1/c$ ^[c]	1.95	–17.9	–17.9	3	4
c1 : $P-1$	1.93	–17.2	–17.2	4	7
c1 : $C2$	1.84	–14.7	–14.7	5	9
c2 :molecule	–	–	+1.2	–	–
c2 : $Pbca$	1.98	–19.3	–18.1	1	3
c2 : $C2/c$	1.97	–19.0	–17.8	2	5
c2 : $Pnma$ ^[d]	1.97	–18.8	–17.6	3	6
c2 : Cc	1.93	–17.8	–16.6	4	8
c2 : $C2$	1.87	–15.1	–13.9	5	10

Heat of sublimation ($\Delta H_{\text{sub}}^{\text{sub}}$, kcal/mol/DTTO), density (ρ , g/cm³), and rank for the five predicted DTTO crystals shown in Figure 4. The energy difference of **c2** with respect to **c1** is $\Delta(c1)$ (kcal/mol). [a] This shows the energy of the isomer **c2** packing compared with the best packing of isomer **c1**. [b] This is the global minimum. We started with space group $P2_1$ from the FF but QM minimized to $P2_1/c$. [c] This is a local minimum for this space group; the initial structure from FF had the same space group. [d] The initial space group from the FF was $P2_12_12_1$ but QM minimized this to find $Pnma$ as the ground state.

and quite similar, but the planarity of the individual FOX-7 layers increased from α -, via β - to γ -. It was found experimentally that γ -, the one with the most planar layers, was the least stable at mild thermodynamic conditions.^[15]

The **c2:Pbca** polymorph has a density of 1.98 g/cm³, which can be compared with the density of RDX of 1.81 g/cm³ and CL20 of 2.01g/cm³. In contrast for isomer **c1**, the most stable polymorph **c1:P2₁2₁2₁**, had a density of 1.96 g/cm³. CL-20 has one of the highest densities of all nitramines and exists in several polymorphs forms, with the ϵ phase being the desired one. This phase is the one with the most detonation velocity and the highest density, however, it is not the most stable thermodynamically.^[16] Thus, we believe the isomers of DTTO **c1** and **c2** are excellent candidates for synthesis.

Conclusion

We predicted the most stable phases of one of the most promising high-energy materials, DTTO. The most stable polymorphs **c2:Pbca** and **c1:P2₁2₁2₁**, had densities of 1.98 and 1.96 g/cm³, respectively. These densities are among the highest of current energetic materials, RDX (1.81 g/cm³) and CL20 (2.01g/cm³). Thus, the energy content of the **c1** polymorph is 6.31 kJ/g and 6.32 KJ/g for the **c2** polymorph, which is 150% higher than that of TNT (4.2 kJ/g). We observed a useful relation, which is that the stability of the polymorphs increased as the density and the planarity decreased.

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Keywords: crystal structure prediction · density functional theory · PBE-ulg · Monte Carlo sampling · energetic materials

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Additional Supporting Information may be found in the online version of this article.

- [1] J. S. Murray, M. C. Concha, P. Politzer, *Mol. Phys.* **2009**, *107*, 89.
- [2] P. Politzer, J. Martinez, J. S. Murray, M. C. Concha, A. Toro-Labbe, *Mol. Phys.* **2009**, *107*, 2095.
- [3] P. Politzer, J. S. Murray, J. M. Serninario, P. Lane, M. E. Grice, M. C. Concha, *J. Mol. Struct. (Theochem)* **2001**, *573*, 1.
- [4] X. L. Song, J. C. Li, H. Hou, B. S. Wang, *J. Comput. Chem.* **2009**, *30*, 1816.
- [5] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
- [6] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [7] C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [8] Y. H. Jhon, M. Cho, H. R. Jeon, I. Park, R. Chang, J. L. C. Rowsell, J. Kim, *J. Phys. Chem. C* **2007**, *111*, 16618.
- [9] M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265.
- [10] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650.
- [11] H. Kim, J. M. Choi, W. A. Goddard, *J. Phys. Chem. Lett.* **2012**, *3*, 360.
- [12] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558.
- [13] G. Kresse, J. Furthmuller, *Comput. Mater. Sci.* **1996**, *6*, 15.
- [14] G. Kresse, J. Furthmuller, *Phys. Rev. B* **1996**, *54*, 11169.
- [15] J. Evers, T. M. Klapotke, P. Mayer, G. Oehlinger, J. Welch, *Inorg. Chem.* **2006**, *45*, 4996.
- [16] R. L. Simpson, P. A. Urtiew, D. L. Ornellas, G. L. Moody, F. J. Scribner, D. M. Hoffman, *Propell. Explos. Pyrot.* **1997**, *22*, 249.
- [17] S. L. Mayo, B. D. Olafson, W. A. Goddard, *J. Phys. Chem.* **1990**, *94*, 8897.
- [18] A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, W. M. Skiff, *J. Am. Chem. Soc.* **1992**, *114*, 10024.

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