

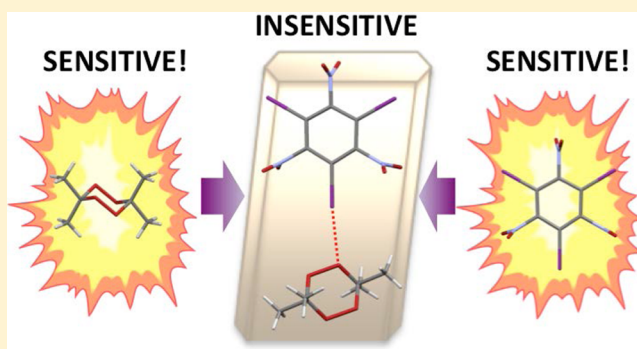
Energetic–Energetic Cocrystals of Diacetone Diperoxide (DADP): Dramatic and Divergent Sensitivity Modifications via Cocrystallization

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S Supporting Information

ABSTRACT: Here we report a series of energetic–energetic cocrystals that incorporate the primary explosive diacetone diperoxide (DADP) with a series of trihalotrinitrobenzene explosives: 1:1 DADP/1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB), 1:1 DADP/1,3,5-tribromo-2,4,6-trinitrobenzene (TBTNB), and 1:1 DADP/1,3,5-triiodo-2,4,6-trinitrobenzene (TITNB). Acetone peroxides are attractive for their inexpensive and facile synthesis, but undesirable properties such as poor stability, intractably high sensitivity and low density, an indicator for low explosive power, have limited their application. Here through cocrystallization the density, oxygen balance, and stability of DADP are dramatically improved. Regarding sensitivity, in the case of the DADP/TCTNB cocrystal, the high impact sensitivity of DADP is retained by the cocrystal, making it a denser and less volatile form of DADP that remains viable as a primary explosive. Conversely, the DADP/TITNB cocrystal features impact sensitivity that is greatly reduced relative to both pure DADP and pure TITNB, demonstrating for the first time an energetic cocrystal that is less sensitive to impact than either of its pure components. This dramatic difference in cocrystal sensitivities may stem from the significantly different halogen–peroxide interactions seen in each cocrystal structure. These results highlight how sensitivity is defined by complex relationships between inherent bond strengths and solid-state properties, and cocrystal series such as that presented here provide a powerful experimental platform to probe this relationship.



■ INTRODUCTION

Cocrystallization is proving to be a powerful tool for creating less-sensitive explosives, as well as modifying and optimizing other properties of energetic materials, a class of materials including explosives, propellants and pyrotechnics. While traditional strategies for energetic materials development have relied on the synthesis of novel energetic compounds and the optimization of their (polymorphic) solid forms, cocrystallization presents an elegant means to improve the performance of energetic materials without requiring new chemical synthesis. Cocrystals of 2,4,6-trinitrotoluene (TNT),¹ 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX),² and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)³ have clearly demonstrated the capacity for modifying materials properties through cocrystallization, and work cocrystallizing multiple energetic materials, notably 1:1 CL-20/BTF,⁴ 1:1 CL-20/TNT,⁵ and 2:1 CL-20/HMX,⁶ has yielded novel and attractive high-power explosives.

These examples have demonstrated how cocrystallizing secondary, i.e., low sensitivity, explosives can produce other novel secondary explosives with low and reduced sensitivity. There is, however, also need to develop improved primary explosives: high-sensitivity energetic materials used to trigger

the detonation of safer and higher power secondary explosives. While most existing examples of energetic cocrystals have represented reductions in sensitivity compared to the more sensitive component by exhibiting sensitivities between the two cocrystal formers, the use of cocrystallization to increase sensitivity and produce primary explosives from secondary explosives would be of great value toward replacing less attractive alternatives currently in use such as lead azide and lead styphnate. Unfortunately, little is still understood about how chemical and solid-state characteristics affect the physical sensitivity of energetic materials, though it is understood that both are important.

■ RESULTS AND DISCUSSION

Interest in using cocrystallization as a strategy to produce primary explosives led us to consider the use of recently reported energetic cocrystals of diacetone diperoxide (DADP) with each of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) and 1,3,5-tribromo-2,4,6-trinitrobenzene (TBTNB) in this role

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(Figure 1).⁷ These cocrystals combine DADP, an easily synthesized explosive with high sensitivity, low density, and

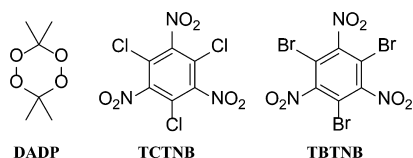


Figure 1. Chemical structures of DADP, TCTNB, and TBTNB.

high volatility, with trihalotrinitrobenzenes that offer high density and low volatility. While energetic cocrystals in general exhibit sensitivities that are equal to or lower than the average of their pure components, the presence of the highly labile peroxide bond in DADP was suspected to limit the reduction in sensitivity normally afforded via cocrystallization. Thus, DADP cocrystals were expected to retain the high sensitivity of DADP and yield novel, cocrystalline primary explosives. After successfully generating the 1:1 DADP/TCTNB cocrystal (**1**) (Figure 2) and the 1:1 DADP/TBTNB cocrystal (**2**), we sought a DADP cocrystal with the novel compound 1,3,5-triiodo-2,4,6-trinitrobenzene (TITNB, Scheme 1).

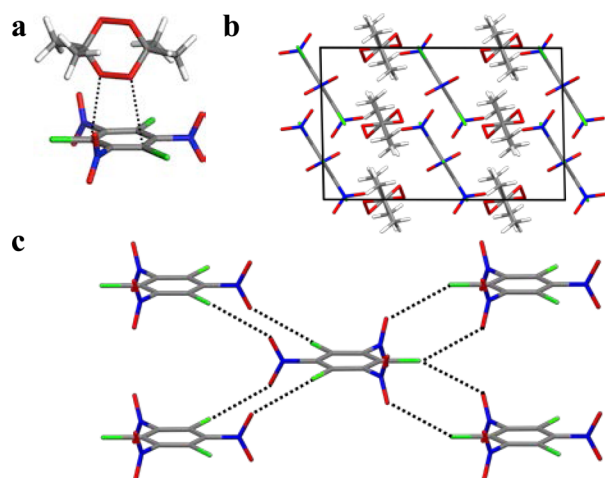
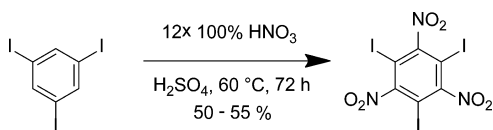


Figure 2. Cocrystal structure of 1:1 DADP/TCTNB (**1**) with the peroxide disorder removed for clarity. (a) Peroxide-aromatic ring interaction, (b) unit cell viewed down the *b* axis, and (c) chlorine-nitro interactions.

Scheme 1. Synthesis of TITNB



TITNB was chosen for cocrystallization with DADP because it was expected to impart greater density than either of TCTNB or TBTNB and cocrystallize via peroxide interactions similar to those seen in **1** and **2**, though it was unclear whether a cocrystal incorporating DADP and TITNB would be isostructural to **1** and **2**. Direct nitration of 1,3,5-triiodobenzene was attempted first for preparing TITNB or its potential precursors. While a similar method is viable for producing TCTNB from 1,3,5-trichlorobenzene, TBTNB cannot be produced directly from 1,3,5-tribromobenzene and must instead utilize a dinitro

intermediate.⁸ Fortunately, like TCTNB, TITNB was found to be obtainable directly from 1,3,5-triiodobenzene (1,3,5-triiodobenzene was prepared via published routes⁹). With the use of an excess of white fuming nitric acid, mild heat, and extended reaction times, TITNB was produced from 1,3,5-triiodobenzene in one step (Scheme 1, see Supporting Information). This compound was found to be very thermally stable, forming pale yellow crystals that melt at approximately 400 °C.

Like TCTNB and TBTNB, TITNB was found to form a cocrystal with DADP. The 1:1 DADP/TITNB cocrystal (**3**) was formed by the solvent mediated transformation of a 3:1 mixture of solid DADP and solid TITNB shaken under acetonitrile. Blocky, pale yellow needles of **3** are produced by this method and easily identified and isolated for characterization by X-ray diffraction. Notably, the cocrystal is not isostructural to **1** and **2**, though the halogenated trinitrobenzenes all show remarkably similar structures and supramolecular interactions, particularly TBTNB and TITNB.

The cocrystal structure of **3** is wholly distinct from those of **1** and **2** and features a novel halogen bonding interaction. While **1** and **2** both feature interactions between the peroxide oxygen atoms and the electron-deficient aromatic rings of TCTNB and TBTNB (Figure 2a), the peroxide moieties in **3** instead interact with the iodine atoms of TITNB (Figure 3a). At a distance of

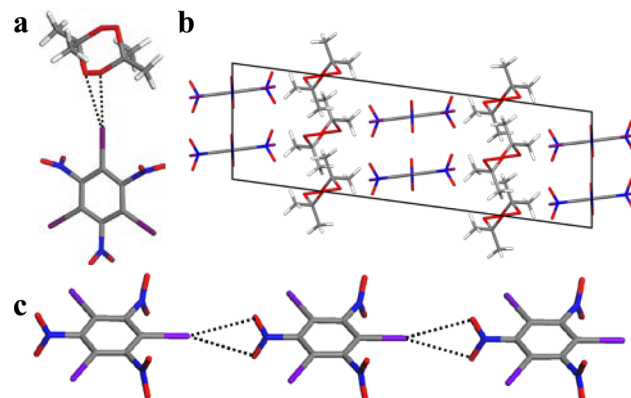


Figure 3. Cocrystal structure of 1:1 DADP/TITNB (**3**), with the peroxide disorder removed for clarity. (a) Peroxide-iodine interaction, 2.95 Å (b) unit cell viewed down the *b* axis, and (c) iodine-nitro interactions.

2.95 Å, this interaction is 0.55 Å shorter than the combined van der Waals radii of oxygen and iodine (3.5 Å). This interaction produces C–I⋯O angles of approximately 171° for the nearer peroxide oxygen and 161° for the more distant, which aligns the oxygen atoms toward the sigma-hole of iodine and indicates that this is a halogen bonding interaction. Though many different types of halogen bonding interactions are reported, to the best of our knowledge no halogen-peroxide interaction has been reported prior. This interaction propagates throughout the cocrystal structure, with each peroxide moiety of DADP interacting with an adjacent TITNB iodine atom to form infinite chains. These contribute to a crystal structure of molecular layers stacked perpendicularly to the rings of TITNB (Figure 3b). This packing contrasts to the parallel stacking of **1** and **2** (Figure 2b).⁷ The third iodine atom of each TITNB molecule in **3** interacts with a nitro group of an adjacent TITNB molecule, also forming infinite linear chains, though these involve only TITNB (Figure 3c).

While the reasons for **3** adopting a different crystal structure than **1** and **2** are not obvious, the markedly shorter intermolecular interactions in **3** are clearly significant for the energy of the system and suggest a more stabilized structure. The three shortest intermolecular interactions in **3** are iodine-peroxide oxygen atom contacts that are 19%, 16%, and 7% shorter than the combined van der Waals radii of iodine and oxygen. In comparison, the halogen-ring interactions in **1** and **2** are each no more than 4% shorter than their respective combined van der Waals radii. This trend continues as, in general, **3** features shorter intermolecular interactions than **1** or **2** (Figure 4a).

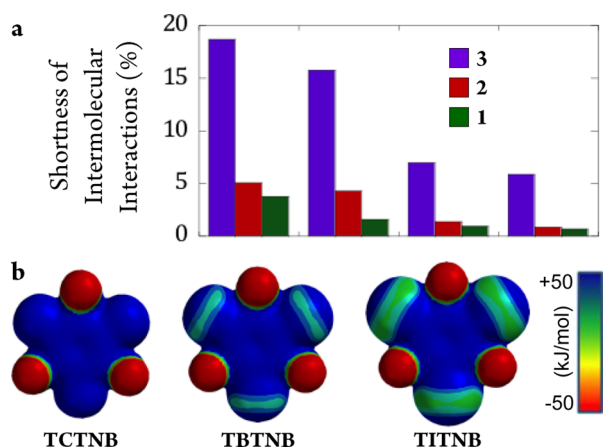


Figure 4. Supramolecular analysis of **1**, **2**, and **3**. (a) Comparison of the shortest intermolecular contact distances in **1**, **2**, and **3** as the percentage less than the combined van der Waals radii. (b) Electrostatic potential maps by AM1 semiempirical calculation.

The markedly short intermolecular interactions present in **3** will influence the energy of this cocrystal. If these interactions are indeed attractive, they could explain the increased stabilization to that crystal structure relative to those of **1** and **2** that is evidenced in several materials properties (see the following discussion). It is perhaps surprising then that TCTNB and TBTNB were not seen to form DADP cocrystals that are isostructural to **3**. This is particularly puzzling in the case of TBTNB, which chooses the structure of **1** rather than that of **3** and ultimately produces cocrystal **2**, which is unstable.⁷ It may be that the increased polarizability of iodine relative to bromine and chlorine facilitates its enhanced interaction with peroxy oxygen atoms.^{10–14} Also, it may be that the size of iodine makes its electron-deficient regions accessible in ways that those of chlorine and bromine in TCTNB and TBTNB are not (Figure 4b). Regardless of the reason, the pronounced shortness of I...OO contacts in **3** strongly suggest that these interactions are a significant stabilizing force in the cocrystal.

One method for probing the relative stabilities while also testing the practical usefulness of these cocrystals is to measure the volatility of DADP as it sublimates from these cocrystals. While DADP is attractive for its economical and facile synthesis, this explosive also exhibits undesirable high volatility and sublimates readily at room temperature.^{15–17} Fortunately, cocrystallization provides an opportunity to improve this property.

Vapor pressure experiments were performed by loading pure DADP or its cocrystals into aluminum DSC pans with 50 μm

diameter holes in their lids. The rate of mass loss by these samples was then observed using a TA Instruments Q50 thermogravimetric analysis instrument. Samples were heated to 40 °C at a rate of 20 °C/min and held isothermally for 16 h under a 30 mL/min flow of nitrogen gas. To compare the DADP cocrystals with pure DADP, relative partial vapor pressures for the experimental conditions described above were calculated using a modified Langmuir equation and then estimated by using previously reported vapor pressure values for DADP at 40 °C (see Supporting Information).^{18–20}

The cocrystals each exhibit a reduced partial pressure for DADP, demonstrating the stabilizing effect of cocrystallization (Figure 5). Cocrystal **3** provides the greatest reduction in

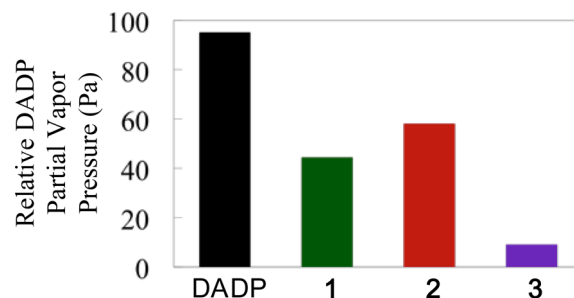


Figure 5. Relative partial vapor pressures of DADP generated from pure crystals and cocrystals.

DADP volatility, dropping its atmospheric relative partial pressure by an order of magnitude from 95.2 to 9.10 Pa (at 40 °C). This change is consistent with the presence of stronger interactions in **3** relative to **1** and **2**; in particular, the iodine-peroxy interaction could be responsible for this dramatic reduction in DADP loss while the ring-peroxy interactions of **1** and **2** may provide a similar but weaker stabilization. However, regardless of their modes, these examples each demonstrate how cocrystallization can suppress the undesirable volatility of energetic materials like DADP.

As expected, extending the cocrystal series to produce **3** yields a novel explosive material with better oxygen balance and higher density than the two previously reported cocrystals. Both oxygen balance and density play important roles in dictating the explosive power of an explosive and, in general, an oxygen balance near to zero and a high density are desirable.²² Due to the mass added by the iodine substituents, the oxygen balance of **3** is -40.0% , significantly better than the -63.7% of **1** and -49.5% of **2** and, for reference, better than common explosives TNT (-74.0%) and TATB (-55.8%). The room temperature crystallographic density of **3** is 2.26 g/cm³ (Table 1), which is, as expected, higher than the densities of **1** and **2**

Table 1. Crystallographic Density and Calculated Packing Coefficients (PC) for All Cocrystals and Cocrystal Formers at Room Temperature

compound	density (g/cm ³)	PC (%)
1	1.55	72.8%
2	1.94	74.8%
3	2.26	84.2%
DADP	1.31	79.6%
TCTNB	1.92	74.7%
TBTNB	2.40	69.9%
TITNB	2.82	68.4%

(1.55 and 1.94 g/cm³, respectively). This density places **3** among the densest organic explosives and is notably even higher than the 2.04 g/cm³ density of ϵ -CL-20, a current benchmark for high-density organic explosives. Though one should note that increased density afforded through heavier atoms may not necessarily increase explosive power, high density is desirable for other purposes such as enhanced target penetration.

The increase in density from **2** to **3** is not attributed only to the substitution of bromine with iodine but also an increased molecular packing efficiency of the new cocrystal structure. This is clear from a comparison of packing coefficients, percentages representing the fraction of occupied space in the crystal unit cell measured as the total molecular volume divided by the unit cell volume.²¹ The packing coefficient of **1** and **2** are 72.8% and 74.8%, respectively, which are unsurprisingly similar numbers given that these crystals are isostructural. The packing coefficient of **3** is significantly higher at 84.2% and has the distinction of being the only cocrystal here to have a packing coefficient substantially higher than both cocrystal formers. This relative increase is likely another result of the short iodine-peroxy interactions that are unique to the crystal structure of **3**.

A key property defining a secondary explosive is sensitivity. As a primary explosive is responsible for triggering the detonation of a larger mass of secondary explosive, it is important that the primary explosive detonates reliably when initiated. This typically requires high sensitivity. To make relative comparisons of overall sensitivity, impact sensitivities were measured for the pure and cocrystalline materials presented here. These were analyzed using a drop-hammer style apparatus designed to accommodate small masses. Samples were struck with a freefalling 5 lb weight dropped from variable heights.²³ Each material was tested using 2 \pm 0.2 mg samples. A Brucon Analysis was conducted on the “up-and-down” drop test results for each material using a step size of 2 cm and 20 drops per material (see Supporting Information). Error is reported from the analysis and is generally equal or less than the step size of the test, indicating a degree of reliability. It must be stressed that this is a nonstandard testing apparatus and the results given here are intended to be used only for relative comparisons. The impact sensitivity is given here as $h_{50\%}$, the height from which impact was 50% likely to cause detonation as calculated from the Brucon Analysis (Figure 6). Sensitivity was not measured for **2** because the unusual metastability of this material led to difficulties in producing a reliably phase-pure sample.⁷

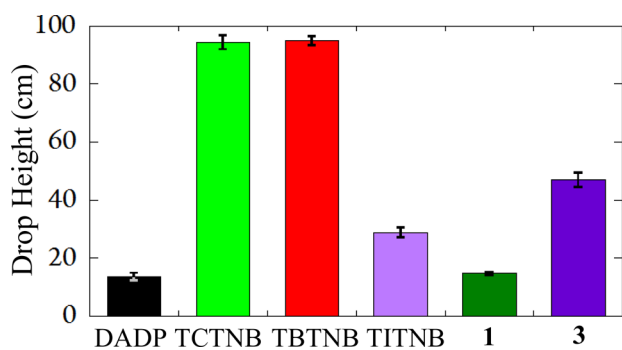


Figure 6. Relative impact sensitivity of explosive pure solids and cocrystals as $h_{50\%}$.

DADP is known for having high sensitivity. By the drop test described here, pure solid DADP exhibited an $h_{50\%}$ of only 13.5 \pm 1.3 cm. This sensitivity is believed to be due to the highly labile peroxide oxygen–oxygen bond in this compound. The inherent instability of this bond is also believed to be the reason why these compounds are explosive even in solution while the vast majority of other energetic compounds become non-explosive in solution.¹⁷

Each of the trihalotrinitrobenzenes exhibited lower sensitivities than DADP. Drop tests revealed nearly identical $h_{50\%}$ values for TCTNB and TBTNB of 94.3 \pm 2.4 and 94.9 \pm 1.6 cm, respectively, significantly higher and less sensitive than pure DADP. TITNB exhibited an $h_{50\%}$ of only 28.8 \pm 1.8 cm, revealing it to also be less sensitive than DADP but more sensitive than both TCTNB and TBTNB. While it was expected that each of these compounds would exhibit much lower sensitivity than DADP given the low-sensitivity seen from other aromatic explosives such as TNT and TATB,^{24–26} it is surprising that TITNB is so much more sensitive than TCTNB and TBTNB. This is made more surprising by the similarity of the crystal structure of TCTNB, TBTNB, and TITNB; each pure crystal structure features very similar halo-nitro interactions that form stacked planes of parallel aromatic rings. In particular, TBTNB and TITNB are nearly isostructural (see Supporting Information). Furthermore, the high thermal stability of TITNB, which was observed by DSC to melt at ca. 400 °C, gave even more reason to expect lower sensitivity as higher melting point materials are generally less sensitive. While it is common for materials with high thermal stability to have low impact sensitivities, this is not always the case. Lead azide, for example, is a well-known primary explosive with high impact sensitivity but is thermally stable up to 350 °C. From this example and others such as TITNB it is clear that the molecular mechanisms of explosive initiation can differ for thermal and mechanical stimuli.

Turning to the sensitivity of the cocrystals, it is seen that **1** exhibits disproportionately high sensitivity, and a low $h_{50\%}$, far more on par with DADP than TCTNB. Cocrystal **1** exhibits an $h_{50\%}$ value of 14.7 \pm 0.5 cm, which is only 1.2 cm higher (slightly less sensitive) than that of pure DADP but 79.6 cm lower (much more sensitive) than the $h_{50\%}$ value of TCTNB. While the sensitivity of this cocrystal was expected to be increased relative to that of pure TCTNB, a shift to nearly the level of pure DADP was unexpected. Previously reported energetic-energetic cocrystals have exhibited sensitivity that are either reduced or nearer to an average of their components. The very high impact sensitivity of **1** makes it viable as a primary explosive and demonstrates the potential of cocrystallization to produce a novel material with many improved properties such as density, oxygen balance, and volatility, while doing little to disturb other desirable properties, here sensitivity.

Cocrystal **3** possesses sensitivity far lower than either DADP or TITNB, an unprecedented observation. The cocrystal exhibits an $h_{50\%}$ of 47.0 \pm 2.5 cm, far greater (less sensitive) than both the 13.5 cm of DADP and the 28.8 cm of TITNB. This result is notable as a first example of two relatively high sensitivity explosives combining to form a cocrystal explosive with much lower sensitivity. One can speculate that this reduction in sensitivity is the result of the apparently strong iodine-peroxide interactions seen throughout the cocrystal structure. Indeed, no such halo-peroxy interactions are present in the cocrystal structure of **1**, which is dramatically more

sensitive than 3. Furthermore, as speculation on the origins of the relatively high sensitivity of pure TITNB looks toward iodine for being the most significant difference between this compound and TCTNB/TBTNB, it may be reasonable to think that the I...OO interactions of 3 help to stabilize not only the labile peroxy moieties of DADP but also the I–C bonds of TITNB.

This series of cocrystals provides unique data useful for the studies on the origin of sensitivity in solid-state energetic materials, which remains poorly understood and an area of ongoing debate. Theories have been put forth attempting to correlate sensitivity with the strength and number of intermolecular interactions present in the explosive,^{25,27} the presence of slip planes,²⁴ the crystal packing,^{26,28} the bond dissociation energy of the weakest covalent bond present,^{29–31} the oxygen balance,³² decomposition temperature,³³ the distribution of electron density^{34,35} and even the free volume available within the crystal lattice.³⁶ The low sensitivity of 2:1 CL-20/HMX is hypothesized to be the result of increased stability afforded through the intermolecular interactions observed in that cocrystal structure.^{7,37} These cocrystals present a variety of data points in this realm where minor changes to chemistry coupled with more dramatic changes in solid-state interactions are seen to generate very dramatic changes in sensitivity. For example, in combining TCTNB with DADP to produce 1 it seems that chemical considerations dominate as the high sensitivity of DADP, believed to be due to the peroxy bond, is maintained almost perfectly. Conversely, when TITNB and DADP form 3 the dramatic reduction in sensitivity shows clearly that stabilizing solid-state effects can also dominate the sensitivity of a material. This may imply that models seeking to predict sensitivity must be correlated to both effects, though it remains to be elucidated how to weigh these factors.

CONCLUSIONS

Here three energetic cocrystals are presented that demonstrate the application of cocrystallization as a strategy for realizing enhanced primary explosives by incorporating secondary explosives. Existing DADP cocrystals 1:1 DADP/TCTNB (1) and 1:1 DADP/TBTNB (2) were evaluated, while the novel energetic compound TITNB was synthesized in order to extend this series into a new cocrystal, 1:1 DADP/TITNB (3). Cocrystal 3 provides a denser, less oxygen-deficient, less volatile, and less sensitive DADP-based explosive and also stands out as a unique example of an energetic cocrystal that exhibits the dramatic synergy of being less sensitive than either of its pure components. This is suspected to be due to unique halogen bonds in the cocrystal structure that brings iodine atoms of TITNB into close contact with the unstable peroxide oxygen atoms of DADP. The dramatic differences in sensitivity afforded by the cocrystal presented here may offer insights toward developing a model for energetic material sensitivity that unites both chemical and solid state considerations.

ASSOCIATED CONTENT

Supporting Information

Experimental methods, crystallographic data, Raman spectra, powder X-ray diffraction patterns, and thermal data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (21) Packing coefficients were calculated by using the following equation: $C_k = ZV_{\text{mol}}V_{\text{cell}}^{-1}$, where C_k is the packing coefficient, Z is the number of molecules in the unit cell, V_{mol} is the molecular volume (\AA^3), and V_{cell} is the volume of the unit cell. Molecular volume was calculated with Spartan '10 version 1.0.1 (Wave function, Inc.), which employs van der Waals radii of 1.8855 \AA for bromine, 1.5138 \AA for fluorine, 1.9200 \AA for carbon, 1.2000 \AA for hydrogen, 1.5500 \AA for nitrogen, and 1.5200 \AA for oxygen.
- (22) The oxygen balance for organic materials can be calculated using the following equation: $-32(a + f + 0.25(b - e) - d/2)/\text{MW}$, where

a, *b*, *c*, *d*, *e*, and *f* are the number of carbon, hydrogen, oxygen, halogen, and sulfur atoms, respectively, and MW is the molecular weight.

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