The use of co-crystal technology for stabilizing energetic materials

The use of co-crystallizations is emerging as a new avenue for modifying the solid-state properties of a wide range of high-value chemicals, such as agrochemicals, pharmaceutics, dyes, and nutraceuticals, in such a way that certain physical properties can be “dialed-in” without reducing the intrinsic performance of the active ingredient itself. A co-crystallization is often defined as the synthetic process that allows two or more neutral molecular compounds to exist together in a crystalline material in definite stoichiometric quantities. The synthesis of a co-crystal relies exclusively on non-covalent interactions such as hydrogen- and halogen- bonding as well as on other reversible intermolecular forces.

Fig. 1. Blocking the acidic protons of EDNA via hydrogen bonding to suitable co-formers.

Technologies based on co-crystallizations are now also beginning to find applications in the arena of energetic materials for modifying, improving, and enhancing the properties of existing explosives, propellants, or fireworks.

Ethylenedinitramine (EDNA), also known as Haleite, is often referred to as the first entirely American high explosive and it is more powerful than the very well-known TNT. The general use of EDNA is restricted due to its relatively high chemical reactivity, caused by the presence of two highly acidic protons. Thus, EDNA is corrosive and can, over time, react with metals and metal salts which may in turn produce completely new and unknown materials with completely unpredictable properties. Unexpected changes of the chemical and physical nature of an energetic

material as a function of time should be avoided at all costs when it comes to transporting, processing, and storing of the material.
In this study, a co-crystallization approach was adopted in order to ‘block’ the acidic protons in an attempt to reduce the chemical instability while retaining some of the valuable energetic characteristics associated with EDNA itself. The acidic protons of EDNA were utilized as effective hydrogen-bond donors and they acted as a synthetic gateway to the synthesis of a series of new co-crystals of EDNA.

Fig. 2. EDNA is corrosive towards copper (left) but a co-crystal of EDNA (right) does not display any unwanted or unpredictable chemical instability with respect to the same metal.

The hydrogen-bond acceptors in each co-former act as a "supramolecular protecting group" (Fig. 1) thereby making EDNA more chemically stable and less acidic. An analysis of the physical properties of the EDNA co-crystals demonstrates that density, thermal properties, impact sensitivity, and detonation velocity and pressure could be modified through co-crystallizations (in some cases in a highly predictable manner). Furthermore, qualitative corrosion tests conducted with copper metal suggested that co-crystals of EDNA are not chemically reactive, because they have been effectively ‘buffered’ by the co-formers in the solid state, Figure 2.

In summary, co-crystallizations with EDNA resulted in multi-component crystalline solids with significantly lowered chemical reactivity and much improved stability with minimal negative impact on the energetic performance of the active ingredient. This clearly suggests that systematic co-crystallizations can allow for fine-tuning of several properties that are critical for safe and effective storage, handling, and processing of molecular solids.

Publication

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performance and improved chemical stability.
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