Two Energetic Cocrystals of TNT/cyclohexane and picric acid/triethylamine

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ABSTRACT

Cocrystal engineering provides an attractive approach to fine-tune performance characteristics of existing energetic materials at the molecular level instead of synthesizing novel energetic materials. In this study, two energetic cocrystals of TNT/cyclohexane in a 3∶2 ratio (cocrystal I) and picric acid/triethylamine in a 1∶1 ratio (cocrystal II) were prepared by solvent-evaporating method and their crystal structures were characterized by single X-ray diffraction (XRD). Electrostatic potential surfaces and molecular volumes of TNT-cyclohexane and picric acid-triethylamine were calculated by DFT method. Results showed that strong electrostatic attraction promoted the formation of TNT/cyclohexane cocrystal and picric acid/triethylamine cocrystals. Great changes of density, packing coefficient and the critically performance criteria of energetic materials were observed through cocrystallization. Packing coefficients of cocrystal I increased greatly relative to pure TNT and cyclohexane by 7.69% and 12.92%, respectively, and packing coefficients of cocrystal II increased greatly relative to pure picric acid and pure triethylamine by 6.83% and 5.18%, respectively. The increase of packing coefficients is due to strong intermolecular interactions and intense molecular arrangement in the crystal motif. Though the packing coefficients of cocrystal I and cocrystal II increased greatly, the densities of cocrystal I and cocrystal II decreased relative to pure TNT and picric acid because of low densities of cyclohexane and triethylamine. Namely, improvement in packing coefficients does not necessarily means to form high-density energetic cocrystals. Both cocrystals exhibit layered crystal structure and molecules linked by relatively strong hydrogen bonds. Such bonding is prevalent in energetic cocrystals and it was believed that such layered structures allow energy to be dissipated efficiently throughout the crystal thereby reducing the likelihood of initiation via hot-spots. The impact sensitivity test of both cocrystals showed that impact sensitivities of cocrystals greatly decreased compared to the most sensitive components of TNT and picric acid, even with 10kg test drop, H_{50} of cocrystals is over 100cm. The similarity in crystal structure and electrostatic potential surface of TNT and picric acid offered some insights into the cocrystal design of these kinds of energetic materials.