

**A Quantum-Chemical Investigation into the Complexation of HMX dimeric systems
within the HMX-CL-20 Co-Crystal**

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Physical-chemical microscopic properties of dimeric complexations of two molecular explosives CL-20 and HMX were analyzed with the goal of posing the foundations for a fundamental understanding of the nucleation mechanism of the CL-20:HMX (2:1) co-crystal. Wavefunction-based approximations (Hartree Fock (HF)) and density functional theory (DFT) approximations (B3LYP and B3LYP-GD3) were adopted in conjunction with the 6-311G(d,p) and aug-cc-pVDZ basis sets. Preliminary comparisons of various properties derived from single-point energy calculations for the molecules as they pack in the co-crystal and geometric relaxation calculations for the isolated monomers allowed for an assessment of the influence that the crystalline environment has on the molecular complexation that will eventually lead to the formation of a first crystalline nucleation seed from which the growth of the material can generate. Subsequently, energy calculations were performed on several homospecies and heterospecies dimeric systems via 1D rigid scan (*i.e.*, single-point) procedures able to construct 1D potential energy surfaces. An initial comparison of the 1D-PES scans across the approximated methods showed the importance of describing the properties of the complexation mechanisms with theoretical approximations able to describe the non-covalent nature of the intermolecular interactions; in addition, this approach provided for a visual appreciation of the dramatic differences in the methods' ability to properly describe weak intermolecular forces. From a relatively small amount of discrete energy values, numerical extrapolation of equilibrium geometries and energies allowed for an accurate description of the complexating systems. In conjunction with other projects within the Valenzano research group, this work poses grounds for the understanding of the crystalline nucleation mechanism in organic solids together with an original, practical, yet reliable computational practice having the potential for extension toward other oligomeric systems.