

*Quantitative approaches to crystal engineering: Applications to mechanical properties*

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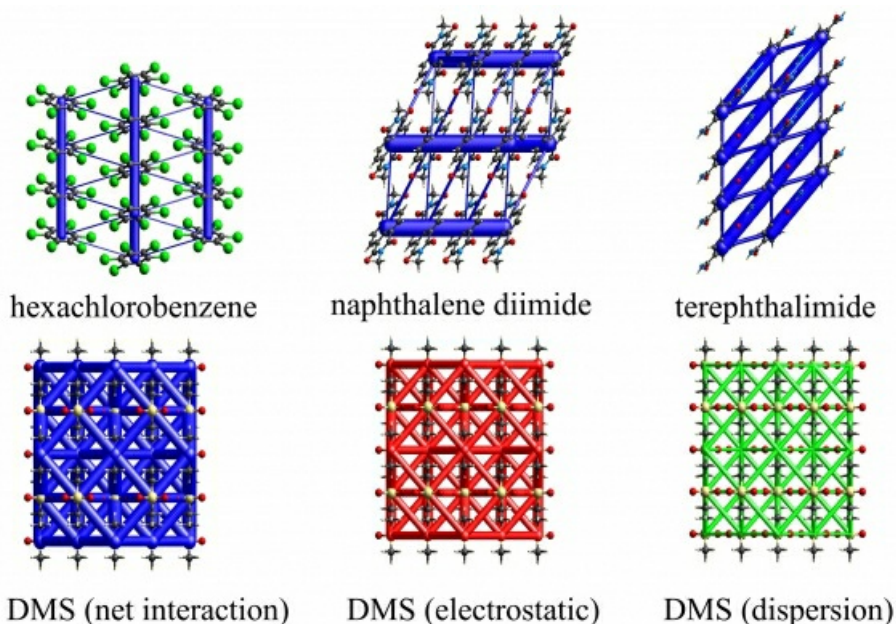
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Over the last two decades, crystal engineering has evolved from its early stage of attempting to understand the grammar of crystal packing into applying such insights for the design of useful crystal forms. Nevertheless, the pursuit of crystal engineering is still largely based on qualitative structural intuitions and trial-and-error approaches. In this context, the 'energy framework' analysis, [1] a method we recently introduced, has been found useful for the visualization and understanding of crystal packing in terms of intermolecular interaction topology – leading to a more quantitative approach to crystal engineering. I will demonstrate the utility of this technique in crystal engineering and applications in various contexts such as the identification of supramolecular recognition units, understanding isostructurality, polymorphism and enantiomorphism. Moreover, we show that mechanical properties such as bending/shearing in molecular crystals [2,3] can also be correlated with the topology of intermolecular interactions as manifested in their energy frameworks.[1] The anisotropy in the strengths of crystal packing can be visualized as the anisotropy in the 'energy frameworks', making it an efficient tool to predict bending/ shearing behaviour in crystals. To demonstrate this, several crystals that exhibit interesting mechanical properties have been analyzed in terms of energy frameworks. In addition, we also present an intriguing observation of plastic-bending in dimethyl sulfone crystal that defies this common trend, showing nearly isotropic energy frameworks. In order to rationalize the observed bending behaviour of the crystal, we performed X-ray charge density studies and variable temperature neutron crystallography. H···H dihydrogen interactions and differences in electrostatic complementarity between molecular layers have been found to facilitate the bending behaviour in this case.

[1] Turner M. J., Thomas S. P., Shi M. W., Jayatilaka D., Spackman M. A. (2015), *Chem. Commun*, 51, 3735.

[2] Reddy C. M., Rama Krishna G., Ghosh S. (2010), *Crystengcomm*, 12, 2296.

[3] Panda M. K., Ghosh S., Yasuda N., Moriwaki T., Mukherjee G. D., Reddy C. M., Naumov P. (2015), *Nat. Chem.*, 7, 65.



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