

## A computational study of differences in phosphoramide/thiophosphoramide structures

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Investigating the impact of substituent variations on molecular packing has been a topic of interest in the field of crystal engineering [1,2]. Based on the Kitaigorodskii close packing model [3], the exchanging of non-polar substituents with almost similar sizes may lead to the production of isostructures. For polar substituents, the molecular arrangement deeply depends on the electrostatic potential of the substituents [4]. In this study, a Cambridge Structural Database survey is considered to find analogous phosphoramide and thiophosphoramide structures with the three equal amine groups (P(X)(R)<sub>3</sub>, X = O, S). Two pairs of similar phosphoramide/thiophosphoramide structures are found  $(R = N(NH_2)(CH_3))$  (I/II) and  $NHCH_2C_6H_5$  (III/IV)), and the structural analysis is carried out using the energy framework calculations to explore similarities and differences arisen from O/S exchange. The results show that the structures with smaller and more polar substituents (I/II) have completely different molecular packing maps (space groups =  $Pbca/P6_3$ ), while in the structures with bulkier and less polar substituents (III/IV), despite the overall differences in the crystal packing maps, there are some similarities. Particularly, the strongest assemblies are similar and are constructed through NH...X=P hydrogen bonds with total interaction energies of -116.7/-100.3 kJ/mol and nearly equal electrostatic energies (-70.2/-68.5 kJ/mol). The differences in III/IV are related to the greater tendency of the P=O group to attract NH units, which makes one other assembly with a total interaction energy of -45.4 kJ/mol.

## References

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