# P25 Determination of the enthalpy of sublimation of the caffeine polymorphs

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The study of the crystalline structures of a substance and their physical properties is an important field of research with applications in the development of new medicines, explosives, paints, and electronics [1]. Thus, it is important to develop the ability to predict the properties of crystal forms of a compound (e.g., different polymorphs where molecules are assembled with different packings), to design materials with optimal properties for a given application. Promising methods to achieve this goal include the use of computational techniques, like molecular dynamics simulations. These are based on intermolecular force fields, which, employing simple atom-atom interaction potentials, can be used to predict many properties of materials. However, due to the empirical nature of these force fields, they need to be validated against benchmark experimental data, like molar enthalpies of sublimation ($\Delta_{sub}H^{o}$) and crystal structure unit cell parameters [2]. Although results of this type can be found in the literature, $\Delta_{sub}H^{o}$ data that can be safely assigned to specific crystal structures are rarely found. This may be one of the main causes of the discrepancies often found between $\Delta_{sub}H^{o}$ values reported by different authors. Thus, the development of a benchmark database of enthalpies of sublimation for specific crystal structures of materials is a crucial step for the development of theoretical methods. With this objective in mind, this work describes the revaluation of the enthalpy of sublimation of the different polymorphs of caffeine (Figure 1), to which previous results span a range of ~10 $kJ{\cdot}mol^{-1}$ [3]. The experiments were performed by Calvet microcalorimetry using samples characterized by powder X-ray diffraction and differential scanning calorimetry.

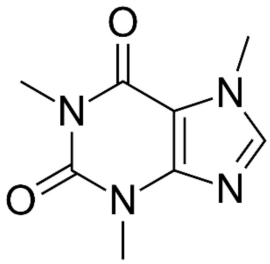

**Figure 1**. Molecular structure of caffeine.

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**References:** [1] A.J. Cruz-Cabeza, N. Feeder, R.J. Davey; *Commun. Chem.* **2020**, 3, 10-13. [2] C.E.S. Bernardes, A. Joseph; *J. Phys. Chem. A* **2015**, 119, 3023-3034. [3] W. Acree, J.S. Chickos; *J. Phys. Chem. Ref. Data.* **2016**, 45, 033101.