MS31-P18

Computional studies of droperidol / benperidol solid solution phase formation.

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Goal of the research is to rationalize and find one common ground how to predict formation of solid solutions between chemically similar molecules and how to explain formation or absence of mentioned phase (structural and energy aspects).

Experimentally it is confirmed that several of the chemically similar benperidol and droperidol solvates yield solid solutions with limited solubility [1], however there is lack of insight on theoretical studies, since solid solutions if one of the least researched solid phase. The analysis of crystal structures have been accompanied for a while with various computational techniques – for instance with calculations of total unit cell energy we can explain why one structure is more favourable, it is possible to simulate solid solutions with various compositions and find limitations for compound solubility in each other by comparing total unit cell energy, as well as simulated structures allow to compare bond angles and lengths.

References:

1.Berzins, A. & Actins, A. 2016. Cryst. Growth Des., 16, 1643-1653.

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Structure and conformation of photosynthetic pigments and related compounds

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Normal-coordinate Structural Decomposition (NSD) has been used to study the role of distortions of tetrapyrroles in biochemical mechanisms.[1] In the Senge group, NSD has been used to determine the extent that different modes of distortions contribute in 3D structures of similar but distinct porphyrinoid macrocycles.[2] In this project we are intending to conduct a detailed comparative analysis of chlorophyll related molecules at a small molecule, high resolution level. Additionally, we will also establish how effective the NSD is by determining specific 3D features of porphyrins, chlorins, and their metal derivatives. With this in mind we used the Cambridge Structural Database[3] to obtain the X-ray crystal structures of free base 5,10,15,20-tetraphenylporphyrins (**TPP**); free base 2,3,7,8,12,13,17,18-octaethylporphyrins (**OEP**); free base porphyrins with increasing β-substituted ethyl groups (**XETPP**) (X = 0–8); free base chlorins with increasing β-substituted ethyl groups (**XETPC**) (X = 0–8) and the Zn(II) derivatives of the four groups mentioned above. The NSD of these compounds were then obtained using the NSDGUI developed by Shelnutt and co-workers.[4]

Chlorophylls and porphyrins have been shown to exhibit a wide range of different macrocycle conformations. These can occur by metalation, steric effects of peripheral or axial ligands, N-substitution, protonation, and π-aggregation in the environment. The compounds listed above were discussed in terms of their out-of-plane (oop) and in-plane (ip) distortion modes. In the TPPs, the main oop distortion mode is *wav*(x). In OEPs, the main oop mode is *wav*(y). Factors such as solvent, axial ligands, and π-interactions influence the 3D structure of these compounds, resulting in a comprehensive preference for each distortion mode based off interactions. OKOQUA (OEP) is solvated with a tetracyanoquinodimethane solvent that approximately triples the *wav*(x) distortion mode compared to the non-solvated OEP. Increasing the number of ethyl chains on the β carbons in the XETPPs increases the oop distortion, which is clearly seen in the *sad* distortion. In the XETPCs (X = 2), increases of roughly 1.0 Å exist in the *sad* mode compared to corresponding porphyrins. When X = 4(cis), decreases in distortion occur when ethyl chains are on the reduced pyrrole and increases are observed when ethyl chains are on the non-reduced pyrrole. The insertion of a Zn(II) results in a *wav*(x) decrease in TPP of 0.1 Å. This can be rationalized by the N-Zn(II) bond which contracts the porphyrin core. Additionally, it should be noted that peripheral substitutions have a larger impact on 3D structure than Zn(II) metal in-