Oral presentation

The curious case of the white pigment leucopterin in the wings of butterflies: crystal structure analysis by combination of X-ray diffraction with solid-state NMR and DFT-D calculations

F. Bravetti[1,2], L. Tapmeyer[1], K. Skorodumov[1], E. Alig[1], S. Habermehl[1], R. Hühn[1], S. Bordignon[2], A. Gallo[2], C. Nervi[2], R. R. Chierotti[2], M. U. Schmidt[1]

[1]*Institut für Anorganische und Analytische Chemie, Goethe-Universität, Max-von-Laue-Str. 7, 60438 Frankfurt am Main, Germany,*

[2]*Dipartimento di Chimica e Centro di Eccellenza NIS, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 Torino, Italy*

federica.bravetti@unito.it

Leucopterin (LCPT, Fig. 1), $C_6H_5N_5O_3$, member of the class of pteridines, is the white pigment in the wings of *Pieris brassicae* butterflies [1]. This is particularly interesting, since in nature as well as in industry, organic white pigments are rather scarce compared to inorganic white pigments, because (I) inorganic pigments such as $CaCO_3$ or TiO_2 are easy to synthesise industrially; also plants and animals can easily produce $CaCO_3$ or other inorganic pigments; (II) inorganic pigments generally have a much higher refractive index than organic pigments, leading to a better light scattering and to a better hiding power, *i.e.,* they are of a more intense white. The hiding power depends on the difference of the refractive index between pigment and air and on the particle size, which is optimal at around 0.5 µm. The wings of the *Pieris* butterflies contain small scales and empty spheres with a thickness of 0.7-2 µm surrounded by air. The beads have a very high refractive index, with values above 2.0 across the visible wavelength range [2].

The optical properties of pigments are strongly related to their crystal structures. Thus, to understand the function of LCPT in the wings of butterflies, its crystal structure was investigated combining powder and single-crystal diffraction data with solid-state NMR (SSNMR) and DFT-D calculations. LCPT crystallises in two phases, which differ for the content of water, *i.e.* hemihydrate and anhydrate. The crystal structure of the hemihydrate was solved by single-crystal XRD, but hydrogen atoms positions were still uncertain. Furthermore, LCPT is characterised by tautomerism: indeed, *at least 17 possible tautomers* can exist. The tautomeric state was elucidated by multinuclear high-resolution SSNMR experiments and DFT-D optimisations. ^{15}N spectra showed the presence of one NH_2 and three NH groups, and one unprotonated N atom, which agreed with the ^{1}H and ^{13}C spectra. The final tautomeric state was assessed analysing ^{1}H-^{1}H atom proximities in the ^{1}H 2D spectrum [3]. The results of lattice energy minimisations with DFT-D, performed independently of SSNMR on the 17 most chemically reasonable tautomeric forms, were in agreement. In LCPT hemihydrate, which is the stable form at ambient conditions, the molecules form an extremely efficient molecular packing resulting in an *extraordinarily high density* of 1.909 kg/dm^3. Only few organic compounds, consisting of C, N, H and O only, have a density of 1.909 kg/dm^3 or higher at ambient conditions. Most of them are nitro compounds, frequently used as explosives. The high density of LCPT hemihydrate might explain the observed light scattering and opacity of the wings of *Pieris brassicae* and several other butterflies.

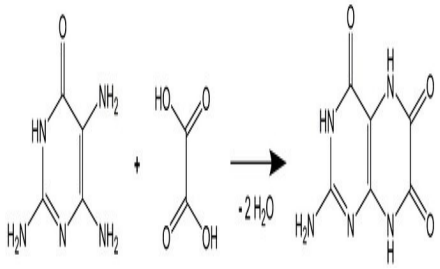

Figure 1. Molecular structure of leucopterin.

[1] Bravetti, F.; Tapmeyer, L.; Skorodumov, K.; Alig, E.; Habermehl, S.; Hühn, R.; Bordignon, S.; Gallo, A.; Nervi, C.; Chierotti, M. R. & Schmidt, M. U. (2023). *IUCrJ*, **10**, 448-463.

[2] Wilts, B. D.; Wijnen, B.; Leertouwer, H. L.; Steiner, U. & Stavenga, D. G. (2017). *Adv. Opt. Mater.* **5**, 1600879.

[3] Bravetti, F.; Bordignon, S.; Alig, E.; Eisenbeil, D.; Fink, L.; Nervi, C.; Gobetto, R.; Schmidt, M. U.; Chierotti, M. R. (2022). *Chem. Eur. J.*, **28**, e202103589.