Cocrystal of 4,4’-azopyridine and diphenic acid: synthesis and high-pressure investigation

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Organic cocrystals are of great interest to both the research community and industry, as their design and synthesis offer a relatively easy route to modify physicochemical properties of solid matter [1]. They were found to have interesting optical, electrical and stimuli-responsive properties [2], and their formation is often employed in the pharmaceutical industry with an aim to obtain crystal forms of active pharmaceutical ingredients (APIs) of desired solubility and stability [1]. Recently, a cocrystal showing exceptional negative linear compressibility (NLC), of a magnitude usually observed for framework materials was reported [3]. Such significant NLC was observed for the cocrystal of fumaric acid and 1,2-bis(4-pyridyl)ethane (ETY) and resulted from unconstrained deformation of a wine rack motif a motif that elongates in one direction as it flattens. Indeed, the wine rack is one of several motifs which presence is often associated with NLC, others being herringbone and zig-zag motifs. The deformation of these motifs is associated with a hinging motion, that can take place either about a hydrogen-bond or be the result of changes in the conformation of a molecule. Therefore, selecting coformers, of which at least one is V-shaped and have conformational flexibility allowing it to mimic the work of a hinge can be applied for intentional synthesis of NLC organic materials [4]. On the other hand, it was previously shown that the exchange of the coformers in NLC cocrystals can be used to modify the magnitude of NLC, provided the newly-introduced molecules are structurally similar to the replaced ones and their presence does not prevent the formation of the NLC-promoting motif [5].

Herein we introduce a novel cocrystal based on 4,4’-azopyridine (AZO) and diphenic acid (DIP), where molecules aggregate to form zig-zag chains (Fig. 1). The crystal of AZO·DIP was investigated under pressure to assess its behaviour and to study the response of a zig-zag motif to compression. Results were contrasted with a high-pressure study of recently-synthesised cocrystal of DIP and ETY. Its crystal structure is similar to that of AZO·DIP, but the conformation of ETY offers larger flexibility, and was observed to be highly affected by pressure increase.

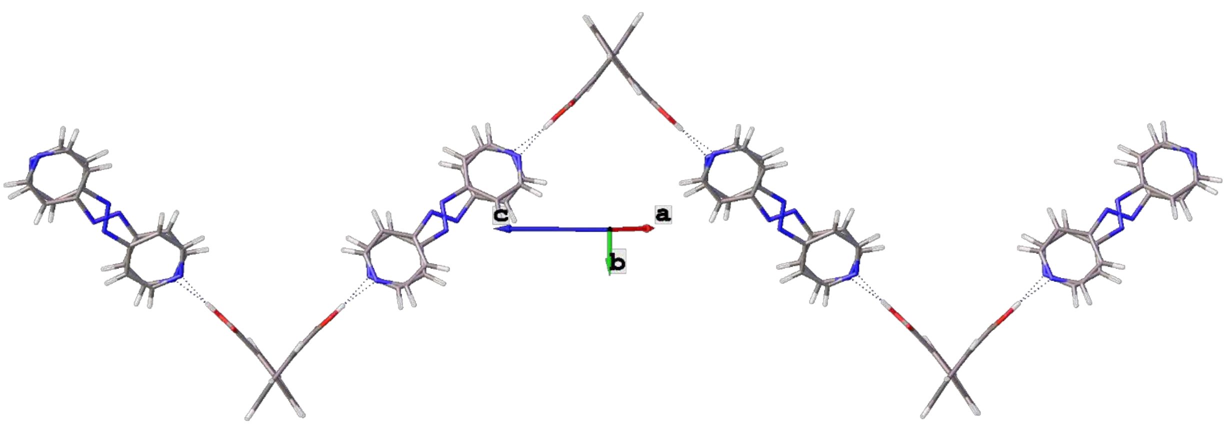

Figure 1. Zig-zag motif formed by disordered AZO and DIP molecules in crystal structure of AZO·DIP at 0.1 MPa/298 K.

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