

Electronic supporting information

Crystal structure determination and disorder of cytenamide form I (CYT I)

Supplementary crystal data (CYT I)

Diffraction data were collected on a Bruker-Nonius FR591 rotating anode diffractometer at 120(2) K using Mo-K α radiation. The structure was solved by direct methods using the program SIR92.¹ Data were merged with SORTAV.² Full-matrix least-squares structure refinement against F^2 was performed using the program CRYSTALS.³ All non-H atoms were refined anisotropically. H-atoms were found on a difference Fourier map and were initially refined with soft restraints on the bond lengths and angles to regularise their geometry and $U_{\text{iso}}(\text{H})$ (in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

1. A. Altomare, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
2. R. H. Blessing, *J. Appl. Cryst.*, 1997, **30**, 421.
3. P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487.

Supplementary disorder data (CYT I)

Three peaks of conspicuous electron density near the high-symmetry site were located on a difference Fourier map. Based on their heights and separations, these were assigned to O and C atoms of an ethanol moiety. However, refinement of their positions failed to yield a satisfactory model. Given that the solvent of crystallisation (industrial methylated spirits) has >1 component, the possibility that methanol and/or water could also be present in the cavities cannot be excluded, further complicating the modelling of disorder.

Accordingly, an unsolvated model was refined (Fig. S1), using PLATON/SQUEEZE to correct for the contribution of the disordered solvent to the diffraction pattern. A total of 6 e⁻ was found in 3 voids of ca. 128 Å³ each. These were located at (0,0,-0.012), (1/3,2/3,0.393) and (2/3,1/3,0.060). The electron count is not consistent with a reasonable solvent stoichiometry, but the void volume can accommodate a small molecule such as methanol, ethanol or water. It is well-known that the number of recovered electrons in the solvent area is strongly dependent on the quality of the low-angle reflections. Though a complete, merged data set was fed into the program, the overall quality of the data is not ideal and the ratio of observed/unique reflections is only ca. 50%. The electron count was not taken into account for calculation of density, F(000) and related crystal data.

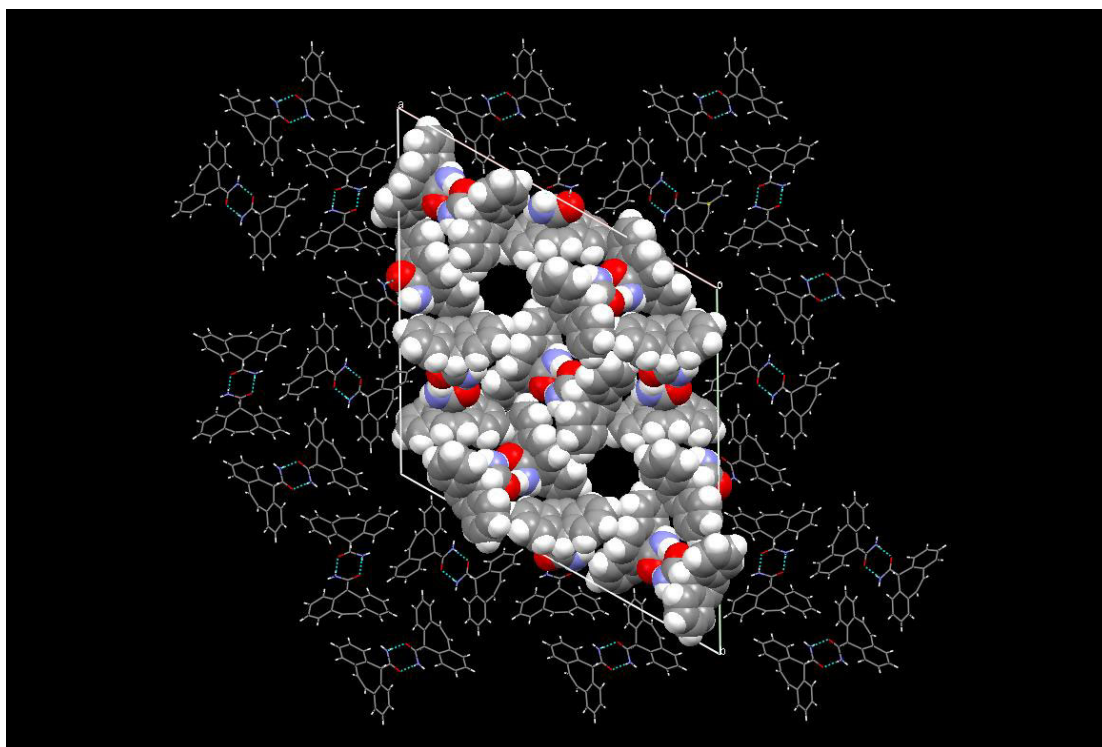


Fig. S1. The final refined crystal structure of CYT I, viewed along the *c*-axis, with the unit cell contents space-filled to highlight the void volume of the channel structure (this is the same view of CYT I provided in manuscript Fig. 4).