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Lattice interactions and aggregation in solution—can the two be related?

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Dedicated to Professor Jean-Marie Lehn on the occasion of his 75th birthday

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ABSTRACT

Comparison is made of the crystal structures of two different solvates of a molecule containing both H-bond donor and acceptor sites, which is found either as a monomer or a hexamer. The solid state features are analysed with respect to the behaviour seen in solutions in the same solvents as found in the crystal lattices. Dimethylsulfoxide appears to be particularly effective in preventing aggregation not only through H-bond acceptance but also through contacts at S which may block H-bond acceptor sites adjacent to donors.

Introduction

The remarkable growth in the amount of structural data provided by both powder and single-crystal X-ray diffraction measurements over the past 2–3 decades has augmented even further the importance of such data as one of the foundations of contemporary chemistry and biochemistry.[1] Over this recent period, however, a significant change has been the use of crystallography to provide not only the structure of the constituents of a crystalline lattice but also an analysis of the usually relatively weak and labile interactions that occur between them.[2] The latter has led to a proliferation of descriptive terminology such as CH...O bonding,[3] the weak hydrogen bond,[4] CH–π bonding,[5] aromatic–aromatic interactions,[6] halogen bonding,[7] chalcogen bonding[8] and so forth, all unnecessary in the sense that these interactions all have the same origin, the mutual interactions of electrons and nuclei, but perhaps useful in that they may aid in the design of new materials with desired properties.[9] Usually, these secondary interactions are described, like conventional bonds, in terms of two-centre contacts, whether or not the centres are separated by a distance which is less than the sum of the van der Waals radii being a criterion of their importance to the structure. This can be misleading, since the shortest H-bonds (in the 2-centre sense), for example, may not necessarily be the strongest[10] and a short 2-centre separation may actually be repulsive because it is simply a consequence of stronger interactions elsewhere.[11] Thus, various theoretical treatments[10–14] have been developed which enable the treatment of secondary bonding in terms of delocalised interactions and which provide criteria for assessing the importance of 2-centre contacts.

One of the issues which has long been of importance is that of the relationship between a molecular structure found in the crystal and that found in other phases involving the molecule.[15] A particular question is what bearing a detailed analysis of a crystal lattice may have on understanding the nature of the molecule in solution. With, for example, the primary coordination sphere of solvated cations,[16] there is very close agreement between the results of diffraction measurements on solutions and crystals but for neutral molecules appropriate experiments are difficult to conduct and a detailed understanding of molecular solvation remains elusive despite, for example, the significance of the isolation of different crystalline solvates of biologically active species[17] and the strong interest in theoretical modelling of solvent structure in solutions.[18–24] A recent study[25] of the hexameric form of a molecule originally characterised, in the crystalline and solution states, as monomer, has, however, provided an unusual example of a close correlation between crystal structures and the consequences of solvation.

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Discussion

Many contemporary problems have their origins in long-studied aspects of solution behaviour[23] and the perspectives of supramolecular chemistry[26] have offered new ways to interpret what are indeed highly complex phenomena. The compound ≪Bis-C3≫ (Fig. 1(a)) was originally synthesised for examination of its capacity to form supramolecular polymers through H-bonding interactions.[27] It is of rather low solubility in most solvents, presumably because this is limited by the self-interactions possible for a species containing both H-bond donor and acceptor sites, although it is quite soluble in the good H-bond acceptor solvent dimethylsulfoxide (DMSO). Crystallisation from DMSO by addition of CH_3CN gives material of composition Bis-C3·2DMSO·CH_3CN, indicating that both these solvents interact with Bis-C3. A single crystal, X-ray structure determination[27] showed that the molecule adopts a conformation of C_2 symmetry (Fig. 1(b)) in the solid state and provided details of the interactions of the two solvents with Bis-C3.

Use of CrystalExplorer[14] to search for labile interactions in Bis-C3·2DMSO·CH_3CN shows that, as concluded originally,[27] there are no stacking interactions of the aromatic units, and reveals as well

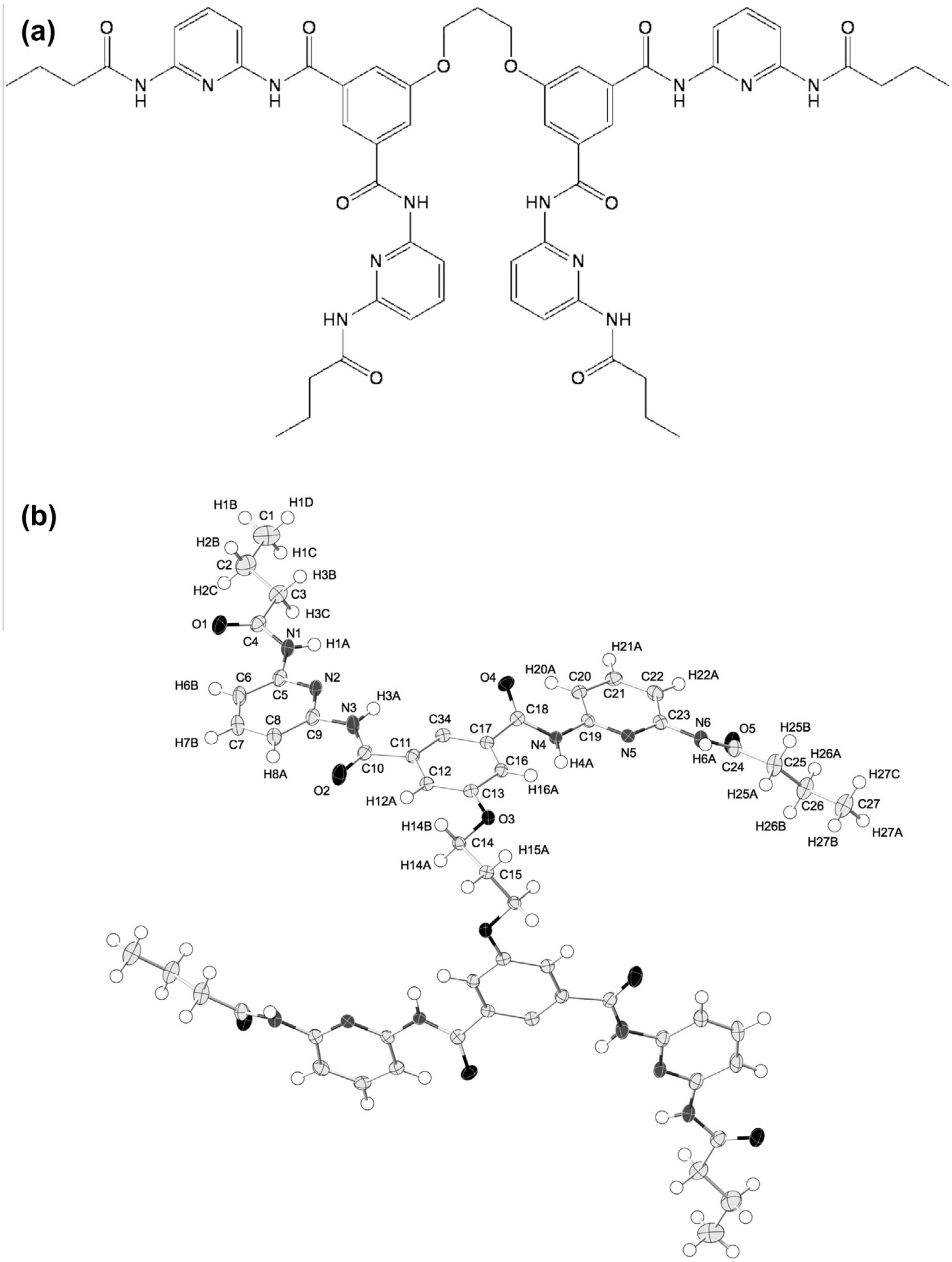

Figure 1. The octa-amido-tetra-pyridyl species ≪Bis-C3≫ shown (a) in the form of an idealised structural diagram and (b) as found in the crystal lattice of Bis-C3·2DMSO·CH_3CN, viewed down the molecular C_2 axis and with atom numbering shown. (Probability displacement ellipsoids at the 50% level.)