The Cyanuric Acid–Biuret Co-crystal: a New Type of Hydrogen-bonded System Formed between a Molecule and Its Solution-phase Decomposition Product

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Crystallization from a warm solution of biuret in methanol–water yields a monophasic sample of 1 : 1 co-crystals of biuret and its decomposition product cyanuric acid; these co-crystals are constructed from two types of hydrogen-bonded array consisting of, respectively, linear chains of cyanuric acid molecules and chains of alternating cyanuric acid and biuret molecules.

A major goal of solid state chemists at present is to develop a systematic rationalization of the factors that control the packing of organic molecules in the crystalline state,[1] the motivation being, at least in part, the design of crystalline organic solids with specific properties for materials applications. Unfortunately, the optimum crystal structure formed by a given molecule often arises from the interplay of several factors of approximately equal importance, rendering it difficult to derive a systematic understanding of the molecular packing arrangement. The hydrogen bond,[2–5] however, is generally stronger than the other types of intermolecular force found in organic molecular crystals, and frequently controls the packing arrangement; as a consequence, the structures of hydrogen-bonded crystals can often be rationalized simply by identifying the preferred modes of interaction of the potential hydrogen-bond donor and acceptor groups present (see, for example, the recent work of Etter and coworkers[6,7]). As shown elsewhere,[8] structural studies of hydrogen-bonded

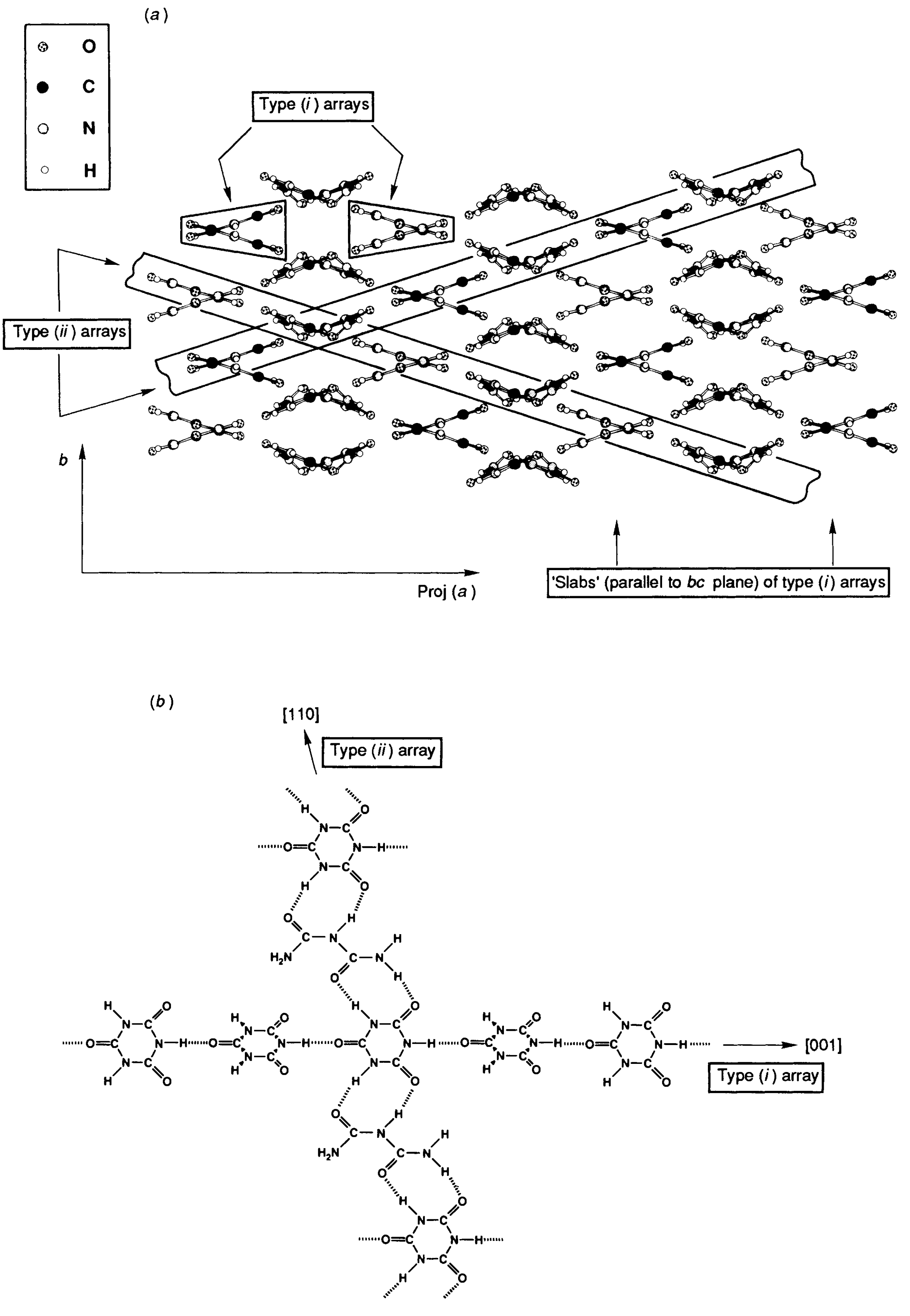

Fig. 1 (*a*) Crystal structure of the cyanuric acid–biuret co-crystal viewed along the crystallographic *c*-axis (parallel to the type (*i*) arrays of cyanuric acid molecules). The *b*-axis lies in the plane of the page, and the *a*-axis is directed beneath the plane of the page [proj (*a*) represents the projection of the *a*-axis on the plane of the page]. The type (*ii*) arrays (consisting of alternating biuret and cyanuric acid molecules) are aligned along the [110] and [1$\bar{1}$0] directions. The two different orientations of the cyanuric molecules (*i.e.* A and B molecules) within each type (*i*) array are clearly evident. (*b*) Schematic representation showing the hydrogen-bonding scheme in the type (*i*) and type (*ii*) arrays. The plane of the page represents the crystallographic ($\bar{1}$10) plane. Note that each cyanuric acid molecule in the structure represents the intersection of a type (*i*) array and a type (*ii*) array.

co-crystals (*i.e.* crystals that contain more than one type of molecule) can be particularly informative in this regard. In this paper, the crystallographic properties of a new hydrogen-bonded co-crystal (consisting of a 1 : 1 molecular ratio of cyanuric acid and biuret) are reported and discussed in the light of the motivations introduced above. This co-crystal is additionally interesting in that it can be prepared by crystallization from a solution containing *only* biuret as the solute; cyanuric acid is produced as a decomposition product of biuret under the conditions of the crystallization. The ability to form the co-crystal in this way suggests that the co-crystal formation and the decomposition of the biuret may occur over comparable timescales. To our knowledge, this method of preparation of the cyanuric acid–biuret co-crystal represents a unique example of co-crystal formation between a molecule and its solution-phase decomposition product.

Co-crystals (characterized by MS, solution ^{1}H NMR, solid state ^{13}C CPMAS NMR, and X-ray diffraction techniques) containing cyanuric acid and biuret in a 1 : 1 molecular ratio were initially prepared by slowly cooling a solution of biuret in methanol–water (2 : 1 v/v) from 60 °C to room temperature. The same crystalline phase (characterized by powder X-ray diffraction) has also been prepared by the same crystallization procedure from an aqueous solution of biuret and cyanuric acid. (Note that an aqueous solution of biuret yields crystals of biuret hydrate[9] following this crystallization procedure; the presence of methanol is evidently crucial for the partial decomposition of biuret to cyanuric acid to occur.)

The crystal structure[†] of the cyanuric acid–biuret co-crystal (Fig. 1) consists of an 'interwoven' pattern of intersecting hydrogen-bonded networks, built from two basic types of hydrogen-bonded array: (*i*) essentially linear arrays of cyanuric acid molecules aligned end-to-end and running parallel to the crystallographic [001] direction (*c*-axis); and (*ii*) arrays (again essentially linear) composed of alternating cyanuric acid and biuret molecules running parallel to either the [110] direction or the $[1\bar{1}0]$ direction. Neighbouring cyanuric acid molecules within an array of type (*i*) are linked by N–H···O=C hydrogen bonds (N–H···O angle *ca.* 172°); the orientation of the molecular plane alternates along these chains between +17.6° (denoted A type cyanuric acid molecules) and −17.6° (denoted B type cyanuric acid molecules) with respect to the (010) plane (*ac* plane) [see Fig. 1(a)]. Defining the 'direction' of the type (*i*) arrays by the direction in which the axial C=O group points, half the type (*i*) arrays are directed along the positive *c*-axis (denoted ↑ arrays) whereas the other half are directed along the negative *c*-axis (denoted ↓ arrays). From the viewpoint of future discussion, it is instructive to note that there are four different 'types' of cyanuric acid molecule (*i.e.* A↑, A↓, B↑ and B↓), all of which are crystallographically equivalent, but have different orientations with respect to the crystallographic reference frame. As seen from Fig. 1(*a*), arrays of type (*i*) are regularly arranged with 'slabs' that are parallel to the (100) plane (*bc* plane), with adjacent type (*i*) arrays in these slabs having opposite orientations (*i.e.* ↑ and ↓). Individual type (*i*) arrays in neighbouring slabs are linked to each other *via* bridging biuret molecules. In this way, the arrays of type (*ii*), consisting of alternating cyanuric acid and biuret molecules, are formed. Again, there are four different orientations of the biuret molecule; a given array of type (*ii*) contains only one orientation of biuret molecule and only one of the four different orientations of cyanuric acid molecule identified earlier. There are two different type (*ii*) arrays aligned along the [110] direction; one involves *only* A↑ type cyanuric acid molecules and the other involves *only* A↓ type molecules. Likewise, there are two different type (*ii*) arrays aligned along the $[1\bar{1}0]$ direction, one involving *only* B↑ type cyanuric acid molecules and the other involving *only* B↓ type molecules. The hydrogen-bonding arrangement within the type (*ii*) arrays is of the familiar eight-membered ring type [see Fig. 1(*b*)] commonly found for amide–amide interactions.[10] Each cyanuric acid molecule [see Fig. 1(*b*)] is involved in one type (*i*) array and one type (*ii*) array, and thus all of its available hydrogen-bond donor and acceptor groups are utilized. The biuret molecules utilize both of their hydrogen-bond acceptor (C=O) groups but only two of the five available hydrogen-bond donor (N–H) groups. The biuret NH_2 group that does not form any hydrogen bonds is planar with the C=O group to which it is bonded; the other C(O)NH_2 group of the biuret molecule deviates significantly from planarity.

A method (based upon the application of graph set analysis) for the systematic description of the topological features of hydrogen-bonded systems has been developed recently by Etter and co-workers.[6,7] For reference, the designation of the cyanuric acid–biuret co-crystal according to this method is given in footnote ‡.

The 'pure' crystalline phase of cyanuric acid[11–14] also contains hydrogen-bonded arrays of type (*i*), in which all the cyanuric acid molecules are co-planar and the N–H···O=C system is perfectly linear [both of these features contrast with the analogous type (*i*) arrays in the cyanuric acid–biuret co-crystal reported here]. The direct transverse interaction (*via* eight-membered hydrogen-bonded rings) between cyanuric acid molecules in neighbouring type (*i*) arrays in the 'pure' cyanuric acid structure is replaced, in the cyanuric acid–biuret co-crystal, by a similar interaction with the intervening biuret molecules. Clearly the provision of two amide groups functioning as hydrogen-bond donors and acceptors in the biuret molecule is crucial to the construction and propagation of the type (*ii*) arrays interlinking the type (*i*) chains of cyanuric acid molecules; and furthermore, there is considerable potential for exploiting this structural feature in the design of other hydrogen-bonded networks. For example, replacement of the biuret molecules with other molecules possessing an appropriate pair of amide functional groups should form the basis of a 'crystal engineering' strategy for inducing, in a controlled and premeditated manner, specific packing arrangements (*e.g.* parallel or anti-parallel) of type (*i*) arrays of cyanuric acid

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[†] *Crystallographic data* for the cyanuric acid–biuret co-crystal: $(C_3H_3N_3O_3)_4 \cdot (C_2H_5N_3O_2)_4$; monoclinic, space group *C*2/*c* (No. 15); $a = 20.650(14)$, $b = 6.634(4)$, $c = 13.404(7)$ Å, $\beta = 101.18(4)°$; $V = 1801(2)$ Å^3; $Z = 4$; $F(000) = 960$; Mo-Kα radiation; μ(Mo-Kα) = 1.04 cm^{-1}; 1332 observed diffractometer data $[F > 3\sigma(F)]$ in the ranges $h = 0$–28; $k = 0$–9; $l = -17$–17. Structure solved by direct methods and difference Fourier techniques and refined by full-matrix least-squares analysis to $R = 0.0383$, $R_w = 0.0359$ {using weighting scheme $0.3540/[\sigma(F)^2 + 0.0001F^2]$}. Positions of H atoms refined freely; isotropic atomic displacement parameter refined for H atoms; anisotropic atomic displacement parameters refined for non-H atoms. Atomic coordinates, bond lengths and angles, and atomic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] The cyanuric acid–biuret (CA–B) co-crystal contains four different hydrogen-bond motifs (defined on the basis of the chemical nature of the hydrogen-bond donor and acceptor groups involved, and specified here in order of decreasing priority[7]): CA(N–H)···CA(C=O); CA(N–H)···B(C=O); B(>N–H)···CA(C=O); B(–NH_2)···CA(C=O). The graph set assignments for each of these motifs within the structure are, respectively, $C(6)$, $C_2^2(10)$, Ds and D; thus, considering the structure as a first-order network,[7] the graph set assignment for the structure is $DDC_2^2(10)\,C(6)$. Treating the type (*i*) and type (*ii*) arrays as separate first-order networks, the graph set assignments are $C(6)$ and $DDC_2^2(10)$, respectively. Within the type (*ii*) arrays, two different second-order networks, each designated as $R_2^2(8)$, can be identified. Each of these second-order networks is constructed from two different hydrogen-bond motifs, and each corresponds to one of the eight-membered hydrogen-bonded rings discussed earlier. (Note that, throughout this paper, the term 'array' has been used in a general sense, and does not necessarily carry the precise meaning assigned to this term in ref. 7).

molecules. Investigations on the design and structural characterization of systems of this type are in progress.

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