

## Novel Hydrogen-Bonded Host Lattices Built of Urea and the Elusive Allophanate Ion

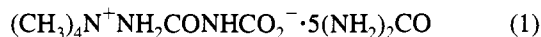
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Allophanic acid (ureidoformic acid,  $\text{NH}_2\text{CONHCOOH}$ ) is a fugitive compound which is known only in the form of its derivatives. Ester-like organic allophanates have been prepared from primary, secondary, and tertiary alcohols and from phenols,<sup>1</sup> whereas inorganic allophanate salts are unstable and easily hydrolyzed by  $\text{H}_2\text{O}$  to  $\text{CO}_2$ , urea, and carbonate.<sup>2</sup> The relatively stable carbonyl-O diprotonated form of allophanic acid was directly observed in an investigation of the behavior of alkyl allophanates in  $\text{FSO}_3\text{H}-\text{SbF}_5/\text{SO}_2$  ("Magic Acid"/ $\text{SO}_2$ ) solution,<sup>3</sup> and the kinetics and catalysis of consecutive reactions of organic isocyanates with alcohols and phenols to give carbamates, allophanates, and eventually isocyanurate were reported recently.<sup>4</sup> Nevertheless, to our knowledge the literature hitherto contains no crystallographic structural information on the elusive allophanate ion.

Our interest in urea adducts stems from an attempt to generate different inclusion topologies such as networks of intersecting tunnels, two-dimensional interlamellar regions within a layered structure, isolated cages, and systems of interconnected cages by incorporating additional components into the construction of the hydrogen-bonded host lattice. In the isomorphous complexes  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{X}^-\cdot(\text{NH}_2)_2\text{CO}\cdot 2\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{CN}$ ), the quaternary ammonium cations are sandwiched between puckered layers constructed from the cross-linkage of planar zigzag chains of hydrogen-bonded urea molecules by the water molecules and halide/pseudo-halide anions.<sup>5</sup> The planar zigzag urea ribbon in this structure contrasts with the relatively open framework in tetragonal urea<sup>6</sup> and the helical spirals in both the urea channel adducts and the isomorphous series  $(n-\text{C}_3\text{H}_7)_4\text{N}^+\text{X}^-\cdot 3(\text{NH}_2)_2\text{CO}\cdot \text{H}_2\text{O}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ).<sup>7</sup> In the present work, we report the preparation and structural characterization of two novel crystalline complexes containing host lattices built of urea molecules and allophanate ions:



Tetramethyl- and tetra-*n*-propylammonium hydroxides were prepared from their corresponding chloride salts by reaction with an equivalent molar quantity of sodium hydroxide in absolute ethanol. Then each hydroxide and urea were mixed in a molar ratio of 1:2, and a minimum quantity of water was added to dissolve the solid. After compressed air was allowed to bubble through the solution for about 3–4 h, the latter was subjected to slow evaporation at room temperature in a desiccator charged with Drierite to yield colorless crystals of the desired product,

(1) Blohm, H. W.; Becker, E. I. *Chem. Rev.* 1952, 51, 471–504.

(2) Bougault, J.; Leboucq, J. *Bull. Soc. Chim. Fr.* 1930, 47, 594–605.

(3) Olah, G. A.; Ku, A. T.; Olah, J. A. *J. Org. Chem.* 1971, 36, 3582–3584.

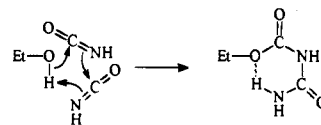
(4) Schwetlick, K.; Noack, R. *J. Chem. Soc., Perkin Trans. 2* 1995, 395–402.

(5) Mak, T. C. W.; McMullan, R. K. *J. Inclusion Phenom.* 1988, 6, 473–481.

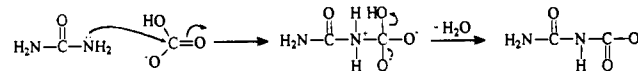
(6) Pryor, W.; Sanger, P. L. *Acta Crystallogr.* 1970, A26, 543–558.

(7) (a) Rosenstein, D.; McMullan, R. K.; Schwarzenbach, D.; Jeffrey, G. A. *Am. Cryst. Assoc. Abstr. Papers (Summer Meeting)*; 1973; p 152. (b) Mak, T. C. W. Unpublished data.

### Scheme 1

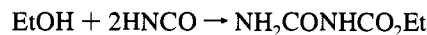


### Scheme 2



which was subjected to structural characterization by X-ray crystallography.<sup>8</sup>

Since ethanol was present in the synthesis of both compounds, the following reactions presumably took place:<sup>1</sup>



Ethyl allophanate is formed from the concerted reaction involving two molecules of isocyanic acid and one molecule of the alcohol.<sup>9</sup> In alkaline solution the allophanate anion  $\text{NH}_2\text{CONHCO}_2^-$  is formed by hydrolysis of the ester (Scheme 1).

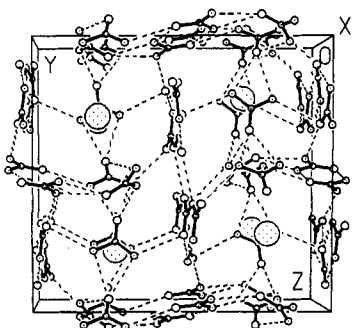
Alternatively, the allophanate ion may be generated by dehydration of the mixture of urea and bicarbonate according to the mechanism depicted in Scheme 2.

In the three-dimensional network structure of **1** (Figure 1), each tetramethylammonium cation is enclosed in a box-like cage, the separation between individual pairs of opposite walls being 8.3 ( $b/2$ ), 7.8 ( $c/2$ ), and 7.3 Å, respectively. The allophanate ion and one independent urea molecule composed of atoms C(1), O(1), N(1), and N(2) [hereafter conveniently referred to as **C(1)**] are joined together by a pair of  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds to form a structural unit. Repetition of this unit in the  $a$  direction generates a hydrogen-bonded zigzag ribbon, and a pair of adjacent ribbons related by an inversion center are cross-linked by additional  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds to form a nearly planar double ribbon (Figure 2). Two such double ribbons which are arranged parallel to the (010) plane constitute a pair of opposite walls of the hexahedral cage. Another pair of walls is formed by straight chains of urea molecules extending along the [101] direction, which are derived from two independent urea molecules **C(2)** and **C(3)** that are alternately linked by hydrogen bonds in a head-to-tail mode (Figure 3). The third pair of walls of the cage is constructed from urea molecules **C(4)** and **C(5)**.

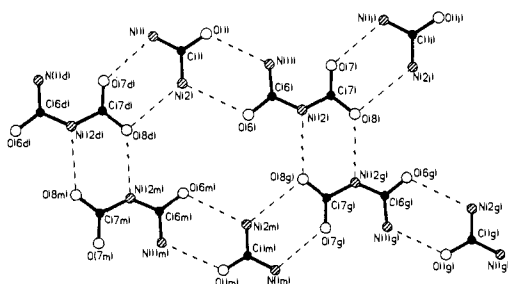
The hydrogen-bonding scheme in **2** is shown in Figure 4. Of the three independent urea molecules in the asymmetric unit, two [**C(2)** and **C(3)**] are linked by a pair of  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds while the third, namely, **C(1)**, forms an  $\text{O}(1)\cdots\text{H}-\text{N}(5)$

(8) Crystals of  $(\text{CH}_3)_4\text{N}^+\text{NH}_2\text{CONHCO}_2^- \cdot 5(\text{NH}_2)_2\text{CO}$  (**1**) belong to space group  $P2_1/n$  (No. 14) with  $a = 9.553(4)$  Å,  $b = 16.715(7)$  Å,  $c = 15.576(5)$  Å,  $\beta = 94.14(1)^\circ$ ,  $V = 2480(2)$  Å<sup>3</sup>,  $D_{\text{calcd}} = 1.246$  g cm<sup>-3</sup>, and  $Z = 4$ . A selected crystal ( $0.52 \times 0.52 \times 0.54$  mm) was mounted inside a 0.7 mm Lindemann glass capillary. Intensity data were collected at 291 K on a Siemens R3m/V diffractometer using Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å,  $2\theta_{\text{max}} = 50^\circ$ . The structure was solved by the direct method and refined (SHELXTL-PC package) to  $R = 0.059$ ,  $R_w = 0.087$ , for 2397 observed reflections [ $|F_o| > 4\sigma(|F_o|)$ ]. The tetramethylammonium ion was found to be disordered by rotation about the N(13)–C(8) bond, and its scattering power was represented by N(13), C(8), and half-carbon atoms C(9), C(10), and C(11). Crystals of  $(n-\text{C}_3\text{H}_7)_4\text{N}^+\text{NH}_2\text{CONHCO}_2^- \cdot 3(\text{NH}_2)_2\text{CO}$  (**2**) belong to space group  $Cc$  (No. 9) with  $a = 8.811(2)$  Å,  $b = 18.156(3)$  Å,  $c = 16.394(8)$  Å,  $\beta = 97.15(1)^\circ$ ,  $V = 2602.2(8)$  Å<sup>3</sup>,  $D_{\text{calcd}} = 1.199$  g cm<sup>-3</sup>, and  $Z = 4$ . A selected crystal ( $0.40 \times 0.50 \times 0.60$  mm) was mounted inside a 0.5 mm Lindemann glass capillary. Structure analysis based on intensity data with  $2\theta_{\text{max}} = 45^\circ$  yielded  $R = 0.038$  and  $R_w = 0.053$  for 3925 observed reflections [ $|F_o| > 4\sigma(|F_o|)$ ].

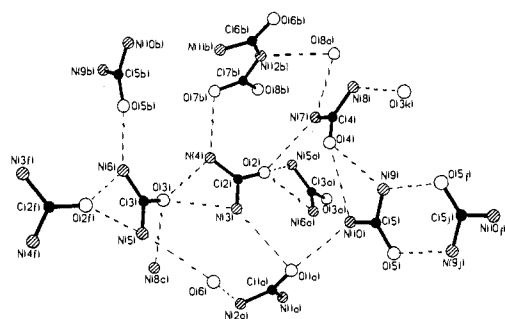
(9) Close, W. J.; Spielman, M. A. *J. Am. Chem. Soc.* 1953, 75, 4055–4056.



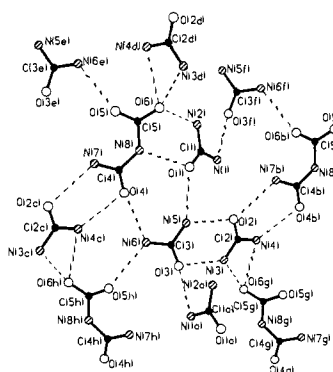
**Figure 1.** Crystal structure of  $(\text{CH}_3)_4\text{N}^+\text{NH}_2\text{CONHCO}_2^- \cdot 5(\text{NH}_2)_2\text{CO}$  (**1**). Broken lines represent hydrogen bonds, and the enclosed  $(\text{CH}_3)_4\text{N}^+$  ions are represented by large dotted circles.



**Figure 2.** Perspective view of a portion of the planar double ribbon built by urea molecules and allophanate ions in **1**.

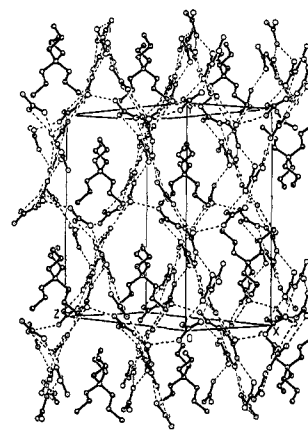


**Figure 3.** Head-to-tail hydrogen-bonded chains extending along the  $[101]$  direction and the shoulder-to-shoulder dimer of urea in the crystal structure of **1**.

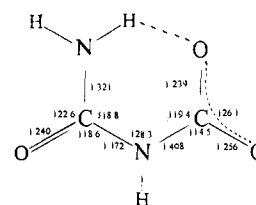


**Figure 4.** Perspective view of a portion of the wide urea-allophanate ribbon linked by hydrogen bonds in  $(n\text{-C}_3\text{H}_7)_4\text{N}^+\text{NH}_2\text{CONHCO}_2^- \cdot 3(\text{NH}_2)_2\text{CO}$  (**2**).

acceptor hydrogen bond with C(3). In this arrangement, atoms N(6), O(1), and N(2), belonging to two urea molecules, lie on the same side to match atoms O(4), N(8), and O(6) of the allophanate ion. Together as a repeating unit, these four molecules generate a wider ribbon running through the structure in the direction of  $[110]$ . At a location which is one-half translation away along the  $c$  axis, there is a similar ribbon which



**Figure 5.** Crystal structure of **2** showing two series of urea-allophanate ribbons running parallel to the  $[110]$  and  $[\bar{1}10]$  directions and their interlinkage by hydrogen bonds to form channels extending parallel to the  $[101]$  direction.



**Figure 6.** Molecular configuration and averaged dimensions of the allophanate ion in **1** and **2**. The standard deviations of individual bond lengths and angles are  $0.004 \text{ \AA}$  and  $0.3^\circ$ , respectively.

extends in the  $[\bar{1}10]$  direction. Finally, intermolecular hydrogen bonding weaves these two crossed series of ribbons into a three-dimensional framework containing open unidirectional channels, as shown in Figure 5. A single columnar stack of well-ordered  $(n\text{-C}_3\text{H}_7)_4\text{N}^+$  cations is accommodated in each channel, which has an approximately elliptical cross section shape (Figure 5), with effective major and minor axes of  $5.2/2$  and  $6.0/2 \text{ \AA}$ , respectively.

The heretofore uncharacterized allophanate ion adopts a planar configuration that facilitates the formation of an intermolecular  $\text{N-H}\cdots\text{O}$  hydrogen bond (Figure 6). The relative instability of the parent allophanic acid is consistent with this hydrogen-bonded ring structure, as protonation at the exocyclic carboxyl oxygen would result in an overall reduction of  $\pi$ -electron delocalization.

In summary, we have shown that the allophanate ion can be generated *in situ* and stabilized in the crystalline state through hydrogen-bonding interactions with its nearest neighbors, and that novel anionic host lattices can be constructed from urea molecules and allophanate ions as building blocks, which readily adopt different topologies for the accommodation of tetraalkylammonium ions of various sizes. By employing organic cations as templates and suitable counteranions as ancillary host material, with or without neutral molecules such as  $\text{H}_2\text{O}$  as a third component, the "lattice engineering" of new urea and thiourea inclusion compounds by self-assembly may be further explored.

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**Supporting Information Available:** Parameters of data collection and structure analysis for **1** and **2** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any masthead page for ordering information and Internet access instructions.