CHEMCOMM
Communication
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Rhodizonate and croconate dianions as divergent hydrogen-bond acceptors in the self-assembly of supramolecular structures†

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Received (in Cambridge, UK) 18th May 2001, Accepted 9th June 2001
First published as an Advance Article on the web 9th August 2001

The $C_5O_5{}^{2-}$ and relatively unstable $C_6O_6{}^{2-}$ dianions, each serving as a hub for binding with a set of convergent NH donor groups of four phenylurea molecules, have been generated *in situ* and stabilized in nearly isostructural hydrogen-bonded host lattices.

Recently we initiated a program to explore the use of the non-benzenoid aromatic oxocarbons $C_nO_n{}^{2-}$ (n = 3, deltate; n = 4, squarate; n = 5, croconate; n = 6, rhodizonate),[1] each bearing a planar set of divergent hydrogen-bond acceptor sites, in combination with urea or thiourea, for the construction of anionic host frameworks that accommodate quaternary ammonium cations. In the series of inclusion complexes $[Et_4N^+]_2C_4O_4{}^{2-}\cdot 2Et_4N^+\cdot HCO_3{}^-\cdot 4(NH_2)_2CO\cdot 6H_2O$,[2] $[Pr^n{}_4N^+]_2C_4O_4{}^{2-}\cdot 6(NH_2)_2CO\cdot 2H_2O$,[3] $[Et_4N^+]_2C_4O_4{}^{2-}\cdot 4(NH_2)_2CS\cdot 2H_2O$,[4] $[Et_4N^+]_2C_4O_4{}^{2-}\cdot 6(NH_2)_2CS$[6] and $[Et_4N^+]_2C_4O_4{}^{2-}\cdot 2(NH_2)_2CS\cdot 2H_2O$,[6] direct linkages between squarate and urea/thiourea exhibit the hydrogen bonding patterns I–IV shown in Fig. 1, which are further connected with the commonly occurring infinite urea/thiourea chains or ribbons[5] to generate two- or three-dimensional host networks.

Attempts to obtain analogous croconate and rhodizonate inclusion complexes with urea (and thiourea) have so far been unsuccessful. We then proceeded on the hypothesis that an oxocarbon dianion could be stabilized by surrounding it with the maximum number of convergent NH donor sites, and to do so it would be necessary to disrupt the intermolecular association between urea molecules. We therefore decided to replace urea with phenylurea, whose bulky and hydrophobic substituent is expected to prevent, or at least suppress, the formation of urea ribbons. Furthermore, the rhodizonate dianion readily undergoes oxidative ring contraction through an α-oxo alcohol rearrangement,[6] which is related to the well known benzil–benzylic acid rearrangement,[7] to produce the croconate ion. Accordingly we developed a simple method to generate the rhodizonate ion *in situ* and incorporate it and its ring-contracted croconate product into the host lattices of new inclusion compounds $[Bu^n{}_4N^+]_2C_6O_6{}^{2-}\cdot 4PhNHCONH_2$ **1** and $[Bu^n{}_4N^+]_2C_5O_5{}^{2-}\cdot 4PhNHCONH_2$ **2**, respectively.‡

In the crystal structure of **1**,§ four crystallographically independent phenylurea molecules are directly connected to the rhodizonate ion *via* separate pairs of strong N–H$_{anti}$···O hydrogen bonds in the range of 2.834–2.933 Å [ring motifs **A**, **B**, **C** and **D**; graph set $N_2 = R_2^2(9)$][8] to form a pseudo-centrosymmetric, slightly twisted X-shaped pentamer (Fig. 2). One pair of opposite phenylurea molecules (designated as type A) are nearly coplanar with the rhodizonate ion, as shown by the relevant torsion angles C46–N5···O3–C3 0.6°, C46–N6···O4–C4 18.9°, C60–N9···O6–C6 23.5° and C60–N10···O1–C1 −8.2°, while the other pair (type B) are inclined to it at about 45°. Adjacent pentamers are joined together by pairs of strong N–H$_{syn}$···O hydrogen bonds between urea fragments (N5···O10 2.913 Å and N9···O8 2.969 Å) in a complementary manner [**E**, $N_2 = R_2^2(8)$] to generate a wide rhodizonate–phenylurea ribbon, which is further strengthened by additional strong N–H$_{anti}$···O hydrogen bonds (N3···O10 3.063 Å and N7···O8 3.083 Å) to produce two other ring motifs [**F** and **G**, $N_2 = R_4^2(8)$]. This wide ribbon runs parallel to the [1$\bar{1}$0] direction, and the hydrophilic amido fragment of the type A phenylurea molecule participates in the construction of its zigzag 'pseudo rhodizonate–urea' backbone in a 'chain of rings' pattern $C_3^3(12)[R_2^2(9)R_2^2(8)\ R_2^2(9)]$. The phenyl rings of type A urea molecules and whole urea molecules of type B protrude outward from the backbone, and stacking of the wide ribbons leads to a system of grated, broken-walled channels each accommodating two parallel columns of well ordered tetra-*n*-butylammonium cations (Fig. 3).

The hydrogen bonding pattern in the crystal structure of **2**§ (Fig. 4) is very similar to that in **1** (Fig. 2), and the cyclic pentameric structural unit with an oxocarbon core is basically retained, so that the pair of inclusion compounds exhibit an interesting isostructurality relationship.[9] However, the croconate ion is disordered about an inversion center, and it adopts two equally populated orientations. Consequently, there are only two independent phenylurea molecules in the asymmetric unit of **2**, and the length of the *c*-axis is about half of that in **1**. In addition to the conventional N–H···O hydrogen bonds, the croconate-based pentamers are consolidated by the charged-assisted C–H···O hydrogen bonds, whose metric parameters (C19···O5 3.282 Å, H19···O5 2.497 Å, C19–H19···O5 142.3°, H19···O5–C5 135.6°; C8···O2 3.341 Å, H8···O2 2.568 Å, C8–

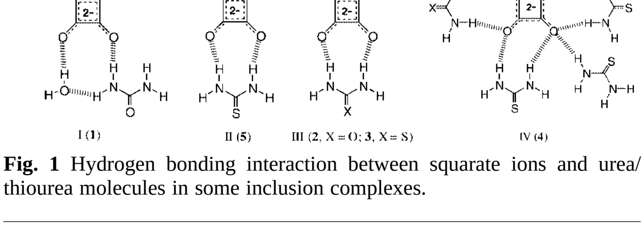

Fig. 1 Hydrogen bonding interaction between squarate ions and urea/thiourea molecules in some inclusion complexes.

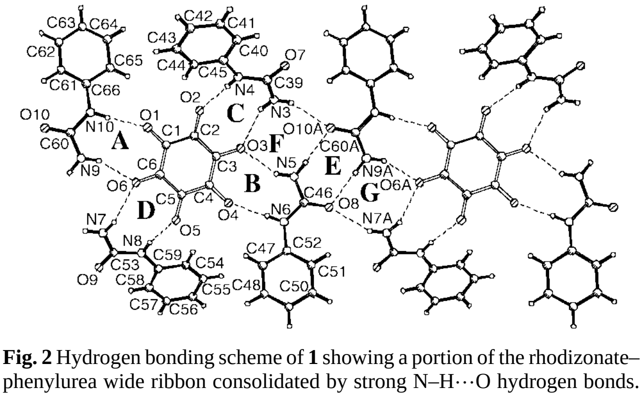

Fig. 2 Hydrogen bonding scheme of **1** showing a portion of the rhodizonate–phenylurea wide ribbon consolidated by strong N–H···O hydrogen bonds. The phenyl rings lie on opposite sides of the zigzag ribbon; half of them are nearly co-planar with the ribbon, and the other half are inclined at 45°. The orientation of these two kinds of phenyl rings is further illustrated in Fig. 2. Symmetry transformation: A (−*x*, −*y*, −*z*).

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† Dedicated to Dr. Tze-Lock Chan on the occasion of his retirement.

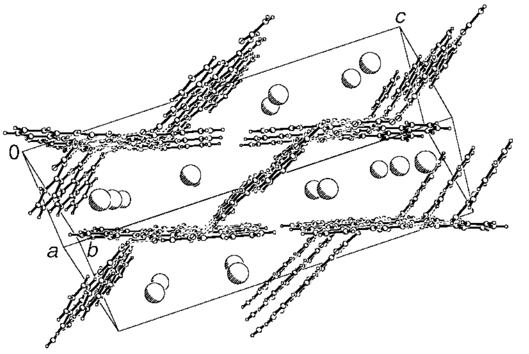

Fig. 3 The crystal structure of **1** showing the one-dimensional 'broken-walled' channel system. The well ordered tetra-*n*-butylammonium cations (represented by large shaded circles for clarity) are arranged in two parallel columns in the $[1\bar{1}0]$ direction. Half of the phenylurea molecules reach out of the plane of each rhodizonate–phenylurea ribbon, functioning as spacers which effectively separate the double cationic columns. The cross-section of the parallelogram-shaped channel is *ca.* 11.6 × 19.2 Å.

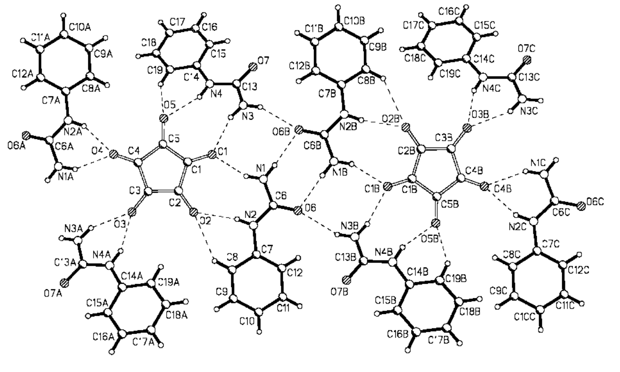

Fig. 4 Hydrogen bonding scheme of **2**, showing a wide croconate–phenylurea ribbon running parallel to the *b*-axis. The disordered croconate dianion lies at an inversion center; for clarity, one orientation is shown on the left and the other on the right. Symmetry transformations: A ($1 - x, -y, 1 - z$), B ($1 - x, 1 - y, 1 - z$) and C ($x, 1 + y, z$).

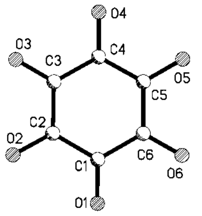

Fig. 5 Structure of $C_6O_6^{2-}$ in **1**. Bond lengths (Å) and angles (°) with esds in parentheses: O(1)–C(1) 1.234(4), O(2)–C(2) 1.247(4), O(3)–C(3) 1.252(4), O(4)–C(4) 1.251(4), O(5)–C(5) 1.258(4), O(6)–C(6) 1.250(4), C(1)–C(2) 1.449(5), C(1)–C(6) 1.458(5), C(2)–C(3) 1.443(5), C(3)–C(4) 1.421(5), C(4)–C(5) 1.424(5), C(5)–C(6) 1.447(5); O(1)–C(1)–C(2) 120.1(4), O(1)–C(1)–C(6) 120.5(4), C(2)–C(1)–C(6) 119.4(4), O(2)–C(2)–C(3) 120.0(4), O(2)–C(2)–C(1) 120.8(4), C(3)–C(2)–C(1) 119.2(4), O(3)–C(3)–C(4) 120.4(4), O(3)–C(3)–C(2) 119.2(4), C(4)–C(3)–C(2) 120.5(4), O(4)–C(4)–C(3) 119.7(4), O(4)–C(4)–C(5) 118.9(4), C(3)–C(4)–C(5) 121.4(4), O(5)–C(5)–C(4) 120.8(4), O(5)–C(5)–C(6) 120.1(3), C(4)–C(5)–C(6) 119.1(4), O(6)–C(6)–C(5) 119.5(4), O(6)–C(6)–C(1) 120.4(4), C(5)–C(6)–C(1) 120.1(4).

H8···O2 140.9°, H8···O2–C2 164.4°) are comparable to those in the most probable ranges (C···O 3.3–3.4 Å, H···O 2.2–2.6 Å, C–H···O 150–160° and H···O–C *ca.* 120°).[10]

The present study provides the first reasonably precise molecular dimensions of the rhodizonate dianion, which lends support to the aromaticity of this non-benzenoid cyclic oxocarbon. Notably, the measured C–C bond lengths [1.421(5)–1.458(5) Å; see Fig. 5] of the rhodizonate in **1**, which exhibits approximate D_{6h} molecular symmetry, are significantly shorter than the corresponding values (1.488 and 1.501 Å) in $Rb_2C_6O_6$[11] and the calculated values (1.500 and 1.501 Å) for the C_2 structure of this dianion.[12] Compound **1** provides yet another example of the use of urea and its derivatives for stabilizing elusive molecular anions such as allophanate[13] and dihydrogen borate[14] in a hydrogen-bonded host lattice.

In summary, we have shown that the supramolecular approach to the synthesis of solids may lead to the stabilization, by way of crystal engineering, of a reactive covalent species, and this strategy holds good promise for further development.

This work was supported by Hong Kong Research Grants Council Earmarked Grant Ref. No. CUHK 4206/99P.

Notes and references

‡ *Synthesis*: phenylurea[15a] and tetrahydroxy-1,4-quinone hydrate[15b] were prepared according to literature procedures. For **1**, tetrahydroxy-1,4-quinone hydrate was dissolved in a small amount of absolute ethanol (E-Merck, 99.8%) in a stoppered flask, to which two molar equivalents of aqueous tetra-*n*-butylammonium hydroxide solution (40 wt% in water, Aldrich) were added. The solution was stirred until all solid material had completely dissolved. Five molar equivalent of phenylurea was then added and stirred for a while. The solution was concentrated under vacuum to yield a brownish orange solid. The solid was next re-dissolved in a minimum amount of absolute ethanol. After filtration, the deep orange red solution was evaporated in a dessicator charged with anhydrous calcium chloride. Rose-red polyhedral crystals of **1** (yield *ca.* 50%) were obtained after about one week. Mp 125.4–130.6 °C. IR (KBr): 3390, 3338, 3271, 3205, 3075, 2956, 2871, 1696, 1652, 1598, 1545, 1500, 1444, 1343, 1247, 756, 696 cm^{-1}. It was found that when **1** was exposed in air, its reddish color gradually faded and completely turned to pale yellow in *ca.* 3 h, therefore, a selected crystal from a freshly prepared sample was sealed in a 0.5 mm glass capillary for X-ray analysis. For **2**, having noticed the color change of **1** in air, a small amount of warm absolute ethanol was added to re-dissolve the immersed crystals. After the solution was kept inside a locker for another three weeks, a crop of brownish yellow rectangular prisms of **2** was deposited in *ca.* 60% yield. Compound **2** proved to be stable in air for an indefinite period. Mp 128.3–134.5 °C. IR (KBr): 3339, 3271, 3201, 3076, 2957, 2874, 1695, 1595, 1545, 1509, 1445, 1343, 1250, 755, 698 cm^{-1}.

§ CCDC reference numbers 163266 and 163267. See http://www.rsc.org/suppdata/cc/b1/b104386m/ for crystallographic data in CIF or other electronic format.

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