Generation and Stabilization of D_{6h} and C_{2v} Valence Tautomeric Structures of the Rhodizonate Dianion in Hydrogen-Bonded Host Lattices**

Chi-Keung Lam and Thomas C. W. Mak*

Dedicated to Dr. Tze-Lock Chan
on the occasion of his 60th birthday

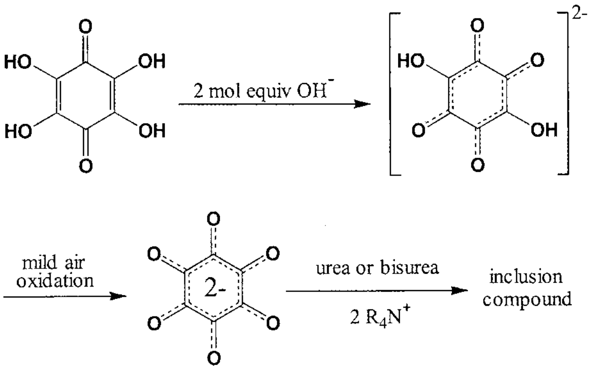
The monocyclic oxocarbon dianions, $C_nO_n^{2-}$ ($n = 3$, deltate; $n = 4$, squarate; $n = 5$, croconate; $n = 6$, rhodizonate), constitute a series of nonbenzenoid aromatic systems whose historical significance and interesting chemistry are well-documented in several books and reviews.[1] A wealth of spectroscopic and X-ray crystallographic data are available for numerous squarate[2] and croconate[3] metal complexes, including a recent report on the crystal structure of $K_2C_5O_5 \cdot 2H_2O$.[4] On the other hand, owing to the relative instability of the deltate and rhodizonate dianions, very meager structural information has been gathered for these two species.[5–7] Until now, the known rhodizonate compounds consist of salts of the alkali metals, alkaline earth metals, transition elements, and ammonium ions. It is noteworthy that the only well-characterized rhodizonate salts are $K_2C_6O_6$ and $Rb_2C_6O_6$, whose X-ray structures were described in a doctoral dissertation published in 1965[7] and widely quoted in the literature.[1]

For over four decades, interest in the whole family of oxocarbon dianions has focused on their aromaticity and molecular structure. The latest theoretical studies indicated that aromaticity decreases with increasing ring size, and that $C_6O_6^{2-}$ possesses only a small degree of aromatic character.[8] Furthermore, while it is firmly established that the squarate and croconate ions have planar D_{nh} structures, infrared spectroscopy[6] and X-ray analysis[7] indicates that the rhodizonate ion conforms to idealized D_{6h} geometry in $Rb_2C_6O_6$, but nonplanar D_{3d} and C_2 forms coexist in $K_2C_6O_6$.[1, 7]

In the course of our systematic investigation on inclusion compounds of urea and thiourea with quaternary ammonium salts,[9] we found that an elusive anionic species such as allophanate[10] or dihydrogen borate[11] can be generated in situ and stabilized in a hydrogen-bonded host lattice. In our follow-up studies, the squarate ion proved to be an effective divergent multisite hydrogen-bond acceptor for supramolecular assembly.[12] Against this background, we planned the synthesis (Scheme 1, starting with tetrahydroxy-1,4-quinone rather than rhodizonic acid) of two air-stable crystalline inclusion compounds of tetra-n-butylammonium rhodizonate with urea derivatives, namely **1** and **2**, and determined their X-ray structures.[13]

$[(n\text{-}C_4H_9)_4N^+]_2C_6O_6^{2-} \cdot 2\,m\text{-}OHC_6H_4NHCONH_2 \cdot 2\,H_2O$ **1**

$[(n\text{-}C_4H_9)_4N^+]_2C_6O_6^{2-} \cdot 2\,NH_2CONHCH_2CH_2NHCONH_2 \cdot 3\,H_2O$ **2**



Scheme 1.

In the host lattice of **1**, the planar rhodizonate dianion resides at an inversion center, being directly linked to a pair of (3-hydroxyphenyl)urea molecules through pairs of N–H···O (**A**, $N_2 = R_2^2(9)$)[14] and phenyl C–H···O (**B**, $N_2 = R_2^1(6)$) hydrogen bonds to form a puckered trimer (Figure 1). The trimer is consolidated by a pair of bridging water molecules that form strong O–H···O hydrogen bonds (**C**, $N_3 = R_3^2(8)$ and **D**, $N_2 = R_1^2(5)$) with the hydroxy and rhodizonate carbonyl groups to generate a pentamer. Adjacent pentamers are further connected together by strong O–H···O and N–H···O hydrogen bonds (**E**, $N_3 = R_3^2(8)$ and **F**, $N_4 = R_4^4(14)$) to produce a wide, puckered ribbon running parallel to the a axis. Well-ordered $(n\text{-}C_4H_9)_4N^+$ ions are accommodated between broken sinusoidal layers formed by the alternately stacked puckered ribbons, with an interlayer spacing of about 8.0 Å.

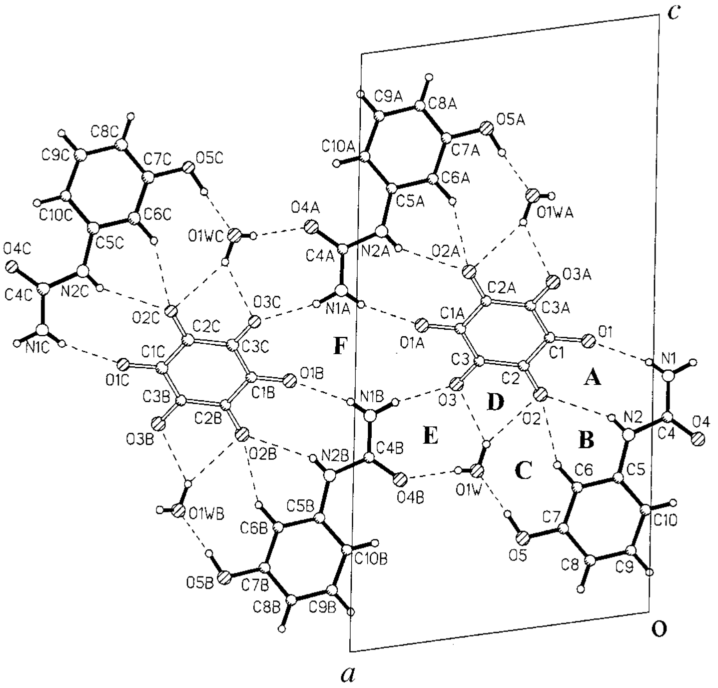


Figure 1. Projection down the b axis showing extensive hydrogen bonding interactions around the centrosymmetric rhodizonate dianion in the host lattice of $[(n\text{-}C_4H_9)_4N^+]_2C_6O_6^{2-} \cdot 2\,m\text{-}OHC_6H_4NHCONH_2 \cdot 2\,H_2O$ (**1**). Symmetry transformations: A: $1-x, 1-y, 1-z$; B: $1+x, y, z$; C: $2-x, 1-y, 1-z$.

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In the host lattice of **2**, two independent 1,1′-ethylenediurea molecules are directly bound to the rhodizonate dianion, which occupies a general position, by four pairs of strong N–H···O hydrogen bonds (**A**, **B**, **C**, and **D**, $N_2 = R^2_2(9)$) to yield a trimer (Figure 2). Adjacent trimers related by simple translation along the *a* axis are connected together by pairs of amido N–H···O hydrogen bonds in the usual shoulder-to-shoulder manner[9] (**E**, $N_2 = R^2_2(8)$) to produce a zigzag ribbon, which is further consolidated by three independent water molecules through additional strong O–H···O hydrogen bonds to generate two new motifs (**F**, $N_4 = R^2_4(8)$ and **G**, $N_5 = R^4_5(13)$). Two antiparallel ribbons related by $\bar{1}$ are cross-linked by pairs of N–H···O (**H**, $N_2 = R^2_2(8)$) hydrogen bonds to yield a double ribbon with large voids (**I**, $N_8 = R^8_8(36)$). Adjacent double ribbons related by the *c* translation are interwoven with three additional ring motifs (**J**, $N_4 = R^4_4(22)$, **K**, $N_3 = R^3_3(8)$ and **L**, $N_6 = R^4_6(12)$) by strong N–H···O and O–H···O hydrogen bonds to generate a highly corrugated layer. Well-ordered $(n\text{-}C_4H_9)_4N^+$ ions are sandwiched between adjacent layers with an interlayer spacing of about 7.8 Å.

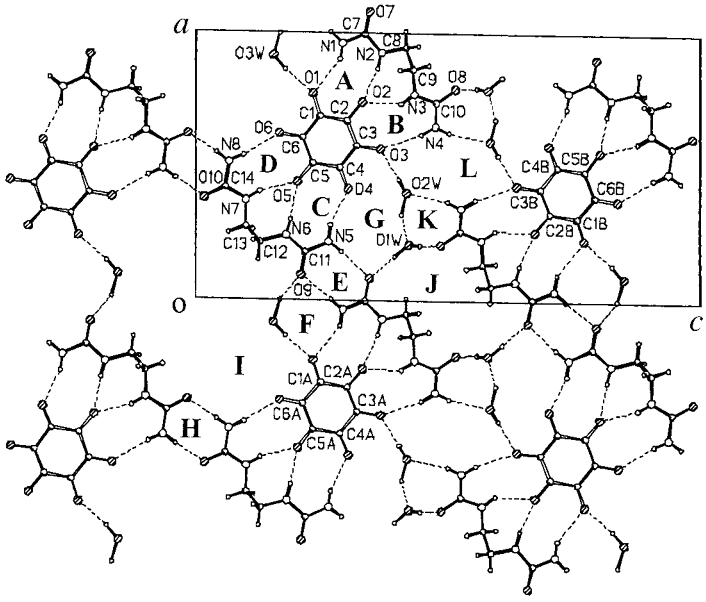

Figure 2. Projection down the *b* axis showing the hydrogen bonding interactions within the puckered rhodizonate–bisurea–water layer of $[(n\text{-}C_4H_9)_4N^+]_2C_6O_6^{2-}\cdot 2\,NH_2CONHCH_2CH_2NHCONH_2\cdot 3\,H_2O$ (**2**). Symmetry transformations: A: $x-1, y, z$; B: $-x, 1-y, 1-z$.

A recent theoretical study concluded that while the oxocarbon dianions $C_nO_n^{2-}$ ($n = 3-5$) all favor D_{nh} symmetry, the $C_6O_6^{2-}$ ground state has C_2 symmetry, and all isomeric structures are very close in energy, for example, the energy difference is 0.34 kcal mol^{-1} between the D_{6h} and nonplanar C_2 forms.[8b] Notably the measured dimensions of the relatively unstable $C_6O_6^{2-}$ species in **1** and **2** (the mean deviation from planarity is 0.020(4) and 0.010(3) Å for **1** and **2** respectively) nearly conform to idealized D_{6h} and C_{2v} molecular symmetry, corresponding to distinct valence tautomeric structures that manifest nonbenzenoid aromatic and enediolate character, respectively (Figure 3).

The measured C–C bond lengths in **1** (1.440(5)–1.442(5) Å) and **2** (1.404(5)–1.472(5) Å) are markedly shorter than those (1.488 and 1.501 Å) in $Rb_2C_6O_6$[7] and the computed values (1.500 and 1.501 Å) for the C_2 structure,[8b] implying that π-electron delocalization in the aromatic ring of $C_6O_6^{2-}$ is much more extensive than hitherto recognized. The strong negative charge-assisted hydrogen bonding interaction between rhodizonate and 1,1′-ethylenediurea causes the latter to assume a less stable *gauche* conformation, in preference to its favored *anti* conformation. Occurrence of the charge-localized structure of $C_6O_6^{2-}$ in **2**, as well as its noticeable deviation from idealized C_{2v} molecular symmetry, can be attributed to unequal hydrogen bonding interaction with its two neighboring bisurea donors and a pair of water molecules (Figure 2). The present finding would seem to provide a challenge for further theoretical work on monocyclic oxocarbon dianions and related species, despite the fact that the most recent publication on this topic appeared only a year ago.[8b]

Experimental Section

General: Tetra-*n*-butylammonium hydroxide (40 wt% in water) was purchased from Aldrich. (3-Hydroxyphenyl)urea,[15] 1,1′-ethylenediurea,[16] and tetrahydroxy-1,4-quinone[17] were prepared according to literature methods. IR spectra were recorded of KBr pellets on a Nicolet Impact 420 FT-IR spectrometer in the region of 4000–400 cm^{-1}. Melting points (uncorrected) were measured on a IA 9100 Electrothermal Digital Melting Point Apparatus.

Bis(tetra-*n*-butylammonium) rhodizonate–(3-hydroxyphenyl)urea–water (1/2/2) (**1**): To a 50 mL round-bottomed flask containing tetrahydroxy-1,4-quinone (0.035 g, 0.168 mmol), two molar equivalents (0.71 mL) of tetra-*n*-butylammonium hydroxide (40 wt% in water, diluted to 0.486 M) were added. The flask was stoppered and the solution stirred until all solid material had been completely dissolved. (3-Hydroxyphenyl)urea (0.102 g) was then added to the deep orange-brown solution and stirred for about half an hour. The solution was concentrated to dryness under reduced pressure, and the solid residue redissolved in absolute ethanol. The filtrate was allowed to evaporate in a dessicator charged with anhydrous calcium chloride. Well-formed deep brownish red polyhedra were obtained in

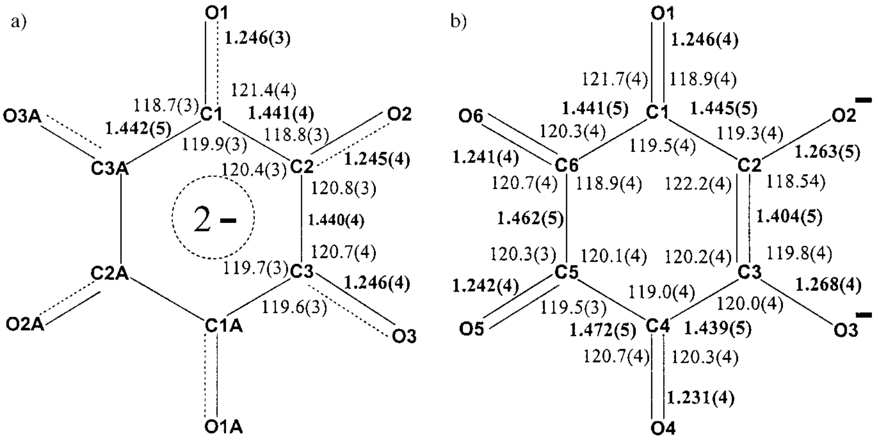

Figure 3. Bond lengths and angles of the a) D_{6h} and b) C_{2v} valence tautomers of the rhodizonate dianion in **1** and **2**, respectively.

nearly quantitative yield after about one week. The crystals were found to be stable in air. M.p. 148 – 150 °C (decomp); IR(KBr): $\tilde{\nu} = 3435$ (s, br), 3315 (ms, sh), 3261 (ms, sh), 3091 (w, sh), 2961 (m, sharp), 2874 (w), 1699 (s, sharp), 1678 (m, sh), 1604 (s, sharp), 1547 (vs, sharp), 1522 (vs, sh), 1494 (s, sh), 1353 (m, sh), 1327 (m, br), 1178 (m, sharp), 1158 (m, sharp), 875 (m, sharp), 778 (m, sharp), 699 (w) cm^{-1}; C, H, N analysis calcd for $[(n\text{-}C_4H_9)_4N^+]_2C_6O_6^{2-} \cdot 2\,m\text{-}OHC_6H_4NHCONH_2 \cdot 2\,H_2O$ ($M_r = 993.32$): C 62.88, H 9.33, N 8.46; found: C 62.48, H 9.37, N 8.41.

Bis(tetra-*n*-butylammonium) rhodizonate – 1,1′-ethylenediurea – water (1/2/3) (**2**): The above procedures were employed using tetrahydroxy-1,4-quinone (0.051 g), tetra-*n*-butylammonium hydroxide (1.00 mL), and 1,1′-ethylenediurea (0.107 g). Air-stable rose red prisms were obtained in nearly quantitative yield after about ten days. M.p. 187.9 – 191.5 °C, IR(KBr): $\tilde{\nu} =$ 3426 (vs, br), 3295 (s, sh), 3100 (w, sh), 2958 (m, sharp), 2873 (w), 1666 (s, sharp), 1550 (vs, sharp), 1521 (vs, sh), 1360 (w, sharp), 1158 (w, sharp), 790 (w, sh), 702 (m, sh), 543 (ms, br) cm^{-1}; C, H, N analysis calcd for $[(n\text{-}C_4H_9)_4N^+]_2C_6O_6^{2-} \cdot 2\,NH_2CONHCH_2CH_2NHCONH_2 \cdot 3\,H_2O$ ($M_r =$ 999.34): C 55.29, H 9.88, N 14.01; found: C 54.18, H 10.04, N 13.81. The results of elemental analysis are in better agreement with the presence of an extra water molecule in the structural formula of **2**, which might be due to absorption of atmospheric moisture by the mailed sample.

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A Practical and Highly Efficient Aminohydroxylation of Unsaturated Carboxylic Acids**

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Dedicated to Professor Harry H. Wasserman on the occasion of his 80th birthday

Osmium-catalyzed aminohydroxylation is a powerful synthetic transformation that allows conversion of olefins to commonly occurring β-amino alcohols. Products obtained by this route are important intermediates in the synthesis of natural products, pharmaceutically important compounds,

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