Letter

Electrostatic compression on non-covalent interactions: the case of π stacks involving ions†

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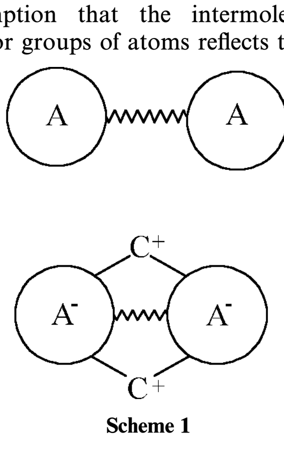
The short interplanar π-stacking separation observed in crystalline alkali hydrogen squarate salts is demonstrated to arise from electrostatic compression due to the alkali–squarate interactions and not from cohesive interactions between π systems of the squarate anions; the behaviour is generalised to π stacking within electrostatic environments.

In the study of supramolecular organisation in molecular or ionic crystals, it is common practice to focus the analysis on interatomic distances shorter than the sum of the van der Waals radii. Whether short distances are indicative of stabilizing or destabilizing interactions depends on the attractive or repulsive nature of the forces acting between the atoms.[1] Energy partitioning over selected groups of interactions is often a misleading approach since crystal cohesion is the result of a global (free) energy minimization and the existence of short intermolecular distances are often a *consequence* of truly relevant interactions, such as those between ions in crystalline salts.

Along this line of thought, we have recently shown[2] that interionic C–H$^-$···O$^-$ and O–H$^-$···O$^-$ interactions between small anions in the solid state do not correspond to stable intermolecular bonds, even though the distances between donor and acceptor groups are *shorter* than the corresponding distances between the equivalent neutral groups.[2] The shortening effect is a manifestation of *electrostatic compression* arising from attractive next-neighbour anion–cation [A$^-$···C$^+$] interactions, which largely overcompensate the combined effect of next-neighbour [A$^-$···A$^-$] and [C$^+$···C$^+$] repulsions and allows deeper penetration into the repulsive walls of neighbouring atoms. This concept is depicted in Scheme 1.

The implications of the above are quite relevant: (*i*) the common assumption that the intermolecular separation between atoms or groups of atoms reflects the strength of the *local* interaction is not directly transferable from neutral to ionic environments and (*ii*) the fact that *electrostatically compressed* interactions retain the directionality of the original neutral (uncompressed) interactions may be turned into a useful tool in crystal engineering[3] where reproducible crystal-directed synthetic strategies are sought and robust ionic materials[4] are often preferred to purely molecular ones.[5]



Scheme 1

In this communication we report the discovery that *π-stacks involving anions* are intrinsically unstable although the separation between the π systems is shorter than in graphitic-like arrangements formed by neutral molecules (see below). It is well known that π–π interactions, though weak, play an important role in the crystal packing of organic,[6a] organometallic[6b] and inorganic[6c] systems, as well as in biological systems.[7]

We have examined the family of alkali hydrogen squarate salts,[8] MHC_4O_4 (M = Li, Na, K, Cs, see Table 1) and observed that (*i*) all these crystalline materials form hydrogen squarate stacks in which the anions overlap to various extents; (*ii*) the $[HC_4O_4]^-$ chains are connected *via* O–H$^-$···O$^-$ interactions;[2] (*iii*) the O···O separations span a fairly large range (2.417–2.503 Å) apparently unrelated to the type of alkali cations, although the shortest one is with Li$^+$; (*iv*) the separation between squarate planes is considerably shorter than in neutral systems (range 3.13–3.34 *vs.* 3.43 and 3.46 Å in coronene and hexabenzocoronene,[9] respectively) and increases slightly on increasing the cation size. While points (*ii*) and (*iii*) can be understood on the basis of the same reasoning as in the case of the O–H$^-$···O$^-$ chain in KHC_2O_4,[2] the intriguing problem of the existence of interplanar π separations between the small $[HC_4O_4]^-$ anions shorter than in neutral systems needs to be addressed.

We have searched the CSD[10] for π interactions between squaric acid, squarate and hydrogen squarate units. We have found 11 crystals in which the interplanar separation between anions falls within the small distance range of 3.150–3.340 Å, in agreement with the data in Table 1.[11]

In order to rationalise the short π stacking separations in these crystals, we have carried out a *crystal packing functional*

Table 1 Summary of interionic structural parameters (in Å) for crystalline MHC_4O_4 (M = Li, Na, K, Cs)

Compound	d O···O	d O···O_w	d O_w···O_w	d O···M	Stack
$LiHC_4O_4 \cdot H_2O$	2.417	2.709	2.709	2.063	3.130
$NaHC_4O_4 \cdot H_2O$	2.503	2.785	3.605	2.345	3.155
$KHC_4O_4 \cdot H_2O$	2.472	2.730	3.857	2.850	3.205
$CsHC_4O_4$	2.482	—	—	3.123	3.315

group analysis,[12] based on *ab initio* computations of first-neighbour interaction energies. $CsHC_4O_4$ has been chosen as the representative case, because the absence of hydration water simplifies the computations. Crystalline $CsHC_4O_4$ presents two primary packing motifs (Fig. 1): (*a*) a stack of hydrogen squarate anions $[A^-]$ next to columns of Cs^+ cations and (*b*) an anionic ribbon containing short $O–H^- \cdots O^-$ interactions. A first glimpse at the nature of the $A^- \cdots A^-$ interactions can be obtained by looking at the electronic charge distribution on the anion. A Mulliken population analysis at the HF/6-31 + g(2d,2p) level[13] shows that the negative charge is delocalised over the whole anion, with a slightly more negative charge on the deprotonated oxygen atom.[14] A better perception of the nature of the interanion interaction is obtained by observing that the molecular electrostatic (MEP) map[15a] of the isolated anion (Fig. 2), computed at the HF/6-31 + g(2d, 2p) level, shows that the electrostatic potential is negative all around the anion (except in the regions close to the nuclei). Therefore, the electrostatic component of the $A^- \cdots A^-$ interaction is repulsive in all regions relevant for intermolecular interactions.

The validity of this analysis has been substantiated by computing at the HF/6-31 + g(2d,2p) level the interaction energies for the $A^- \cdots A^-$ and $Cs^+ \cdots Cs^+$ pairs with the geometry of motif (*a*) resulting in repulsions of 68 and 39 kcal mol^{-1}, respectively. When the computation is performed at the MP2/6-31 + g(2d,2p) level to include the effect of electron correlation, the results are 61 and 39 kcal mol^{-1}, respectively. When the same computation is done for the whole neutral A_2C_2 tetramer of motif (*a*) [*e.g.*, $Cs^+ \cdots \{\pi\text{-}[HC_4O_4]^-\}_2 \cdots Cs^+$] the interaction is stable: 212 and 220 kcal mol^{-1} at the HF/6-31 + g(2d,2p) and MP2/6-31 + g(2d, 2p) levels, respectively.[15b] Thus, the stacking in crystalline $CsHC_4O_4$ is a consequence of the $Cs^+ \cdots [HC_4O_4]^-$ stabilising interactions, which result from the balance between interanion repulsions and anion–cation attractions, and does not reflect a preferential cohesive π interaction between the anions. The short interplanar separation appears to have the same origin as the interanion hydrogen-bond-like interactions: the electrostatic compression brings the squarate planes to a separation shorter than between neutral systems. We have completed our analysis by applying the same procedure to motif (*b*), {*e.g.*, $[Cs^+ \cdots \{\cdots [HC_4O_4]^- \cdots [HC_4O_4]^- \cdots\} \cdots Cs^+]$}, Fig. 1(*b*). This A_2C_2 tetrameric unit is also stable (201 and 208 kcal mol^{-1} at the HF/6-31 + g(2d,2p) and MP2/6-31 + g(2d,2p) levels, respectively), while the $A^- \cdots A^-$ as well as the $Cs^+ \cdots Cs^+$ interactions are again repulsive.

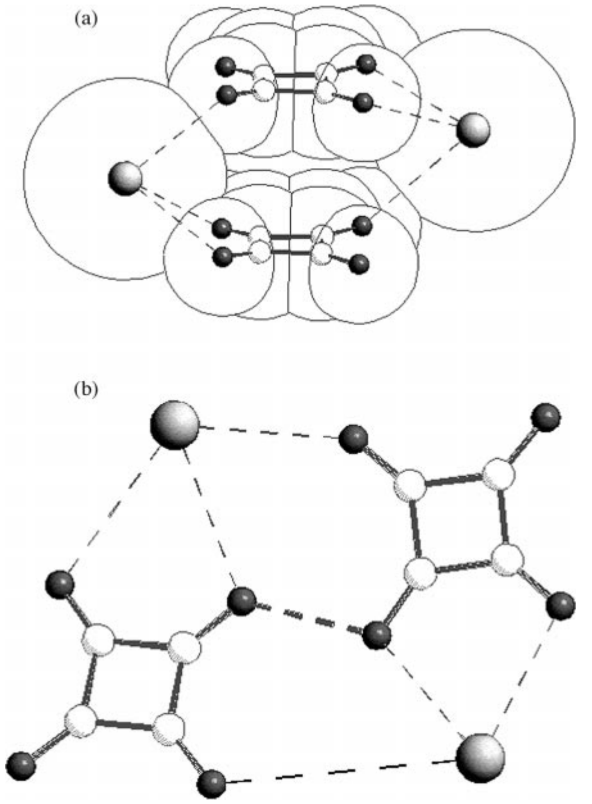


Fig. 1 The two primary packing motifs in the $Cs_2(HC_4O_4)_2$ subunit of crystalline $CsHC_4O_4$: (*a*) stacks of hydrogen squarate anions next to columns of Cs^+ cations, $[Cs^+ \cdots \{\pi\text{-}[HC_4O_4]^-\}_2 \cdots Cs^+]$ and (*b*) an anionic ribbon containing short $O–H^- \cdots O^-$ interactions $[Cs^+ \cdots \{\cdots [HC_4O_4]^- \cdots [HC_4O_4]^- \cdots\} \cdots Cs^+]$. The orientation of the ions is the same as in the observed crystal structure. The hydrogen atom participating in the short $O–H^- \cdots O^-$ interaction is not shown as it is not observed in the X-ray analysis.

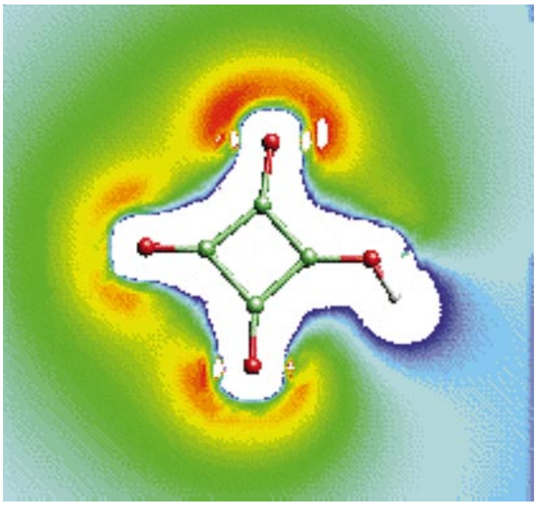


Fig. 2 The molecular electrostatic (MEP) map of the $[HC_4O_4]^-$ anion computed at the HF/6-31 + G(2d,2p) level. Only the negative portion of the MEP is plotted for simplicity (going from 0 to −173 kcal mol^{-1}) using the following color code: dark blue corresponds to zero, light blue, green, and yellow are used for increasing negative values, while red is used for the most negative regions (the white region in the interior indicates the position of the MEP minima).

It is worth stressing that, although the *stabilizing* contribution of interanionic π interactions may be *cancelled* by the presence of a strong electrostatic field, the directionality of the interactions is *retained*. Thus, while crystal cohesion is determined by the balance of attractive and repulsive ionic interactions (as in NaCl, for instance) the actual structure is controlled by the optimization of π-stack and $O–H^- \cdots O^-$ interactions. This idea is important not only for the crystal engineering of materials for their conductive and magnetic properties,[16] and in supramolecular chemistry,[17] but also in biostructural chemistry,[7] given that most of biological activity takes place in electrolyte solutions.

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Notes and references

† Supplementary material available: list of the 11 compounds obtained from the CSD search used in the current analysis. For direct electronic access see http://www.rsc.org/suppdata/nj/1999/577/, other-

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