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[22] The preferred orientation of the inorganic particles was confirmed by an analysis of the crystallographic ultrastructure of immature crystallites harvested 60 min after the induction of template assembly using established techniques for the collection and analysis of crystals which mitigate against any disruption of their alignment relative to the template.[23] In the present case, all crystals produced single-crystal electron diffraction patterns corresponding to the $<01.2>$ zone of calcite, thereby confirming the morphological assignment.
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Interanionic O–H···O Interactions: The Charge Density Point of View**

Piero Macchi,* Bo B. Iversen, Angelo Sironi, Bryan C. Chakoumakos, and Finn K. Larsen*

Interanion $^{\delta-}O–H \cdots O^{\delta-}$ interactions in the solid state have been the subject of recent scientific discussion. On the basis of in vacuo calculations on isolated anions and on the global repulsion between a pair of them, Braga et al.[1] suggested that the H···O "contacts" should be regarded as pseudo hydrogen bonds, in spite of the very short O···O and H···O distances.[2–5] In their view, the conformation adopted by two anions in the solid state minimizes the repulsion[6] but does not produce a chemical bond, and the stability of the crystal structure is due only to cation–anion attractions (the overall effect was called a tugboat effect). If confirmed, this hypothesis would have far-reaching implications for the understanding of hydrogen bonds (HB) and intermolecular

[*] Dr. P. Macchi,[+] Prof. F. K. Larsen, Dr. B. B. Iversen
Department of Chemistry
University of Aarhus
8000 Aarhus C (Denmark)
Fax: (+45) 86-19-6199
E-mail: piero@csmtbo.mi.cnr.it, kre@kemi.aau.dk
Prof. A. Sironi
Dipartimento di Chimica Strutturale e Stereochimica Inorganica
Via Venezian 21, 20133 Milano (Italy)
Dr. B. C. Chakoumakos
Solid State Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831 (USA)
[+] Permanent address:
Dipartimento di Chimica Strutturale e Stereochimica Inorganica
Via Venezian 21, 20133 Milano (Italy)
Fax: (+39) 02-7063-5288

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interactions. However, Steiner, who used the structure correlation method,[7] did not find reasons for considering these interactions significantly different from other O–H···O hydrogen bonds; in fact, IR absorption spectra, intermolecular distances, and structural changes occurring in the anion skeleton conform with the expectations for classical HBs. Thus, he dismissed the hypothesis of an H···O repulsion and focused instead on the covalent nature of this type of "charge-assisted" HB.[8]

In our opinion, the controversy can be well assessed by studying the electron-density distribution of a pertinent crystal, since unambiguous HBs can be characterized in detail with this technique.[9] It is now well established[10] that atomic multipolar expansions can be used to reconstruct the charge density $\rho(\boldsymbol{r})$, through reciprocal space fitting[11] of structure factors derived from accurate low-temperature X-ray diffraction data.[12] The advantage of this method is that a molecule can be modeled within the crystal and subsequently "extracted" (pseudomolecule); thus, each molecular building block can be studied in isolation from the others but with the same *shape* that it has in the crystal. Properties of the pseudomolecule such as the electrostatic potential can be calculated and compared with the corresponding values of the isolated molecule. Alternatively, the total $\rho(\boldsymbol{r})$ can be partitioned according to the quantum theory of atoms in molecules (QTAM),[13] which provides an unambiguous definition of chemical bonding by means of the bond path.[14] Having this in mind, we performed extensive X-ray ($T = 11$ K) and neutron ($T = 15$ K) diffraction measurements on single crystals of potassium hydrogenoxalate,[15] the most widely addressed example of $^{\delta-}$O–H···O$^{\delta-}$ so far.[1a],[7] KHC_2O_4 crystallizes in infinite chains of $HC_2O_4^-$ with short interanion H···O and O···O distances; the cations are coordinated to oxygen atoms of different chains (Figure 1). The optimized geometry of the isolated anion calculated at the HF level[16] shows important differences to that measured in the solid state: a) the O–H distance is 0.945 Å (0.968 Å at the MP2 level), much shorter than our neutron-diffraction value (1.060(2) Å); b) the HB acceptor C=O bond is shorter than in the crystal, while the C–O(H) bond is longer (Figure 1). Therefore, in agreement with the observations of Steiner,[7] a detailed comparison of geometrical features does not support the hypothesis of a pseudo hydrogen bond.[17]

A major point in the work of Braga et al.[1a] was the shape of the computed electrostatic potential $\Phi(\boldsymbol{r})$[18] of the isolated anion. Since a negative envelope completely surrounds $HC_2O_4^-$, an electrostatic repulsion was expected to exist in intermolecular contacts between two neighboring hydrogenoxalate anions. However, in the experimental pseudomolecule, $\Phi(\boldsymbol{r})$[19] is clearly different. In the vicinity of the hydrogen atom, the negative lobe is absent, and at the (expected) position of the HB acceptor oxygen atom, $\Phi(\boldsymbol{r})$ is positive (Figure 2d). It is also important to note that the atomic charges are unevenly distributed both in the isolated $HC_2O_4^-$ and in the dianionic dimer $[(HC_2O_4)_2]^{2-}$. No matter what partitioning is applied to the theoretical density, the H atom is always positively charged;[20] indeed, this is confirmed by the

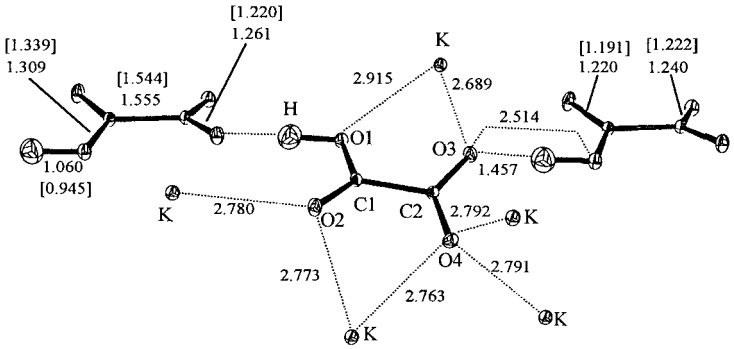

Figure 1. ORTEP view of the surrounding of a $HC_2O_4^-$ ion in the crystal (atomic ellipsoids at 70% probability level for all atoms). Distances from the X-ray/neutron model are reported in Å (standard uncertainties are less than 0.002 Å for all bonds). Figures in brackets are the distances of the HF/6-31 + G(2d,2p) optimized geometry of the isolated anion.[17]

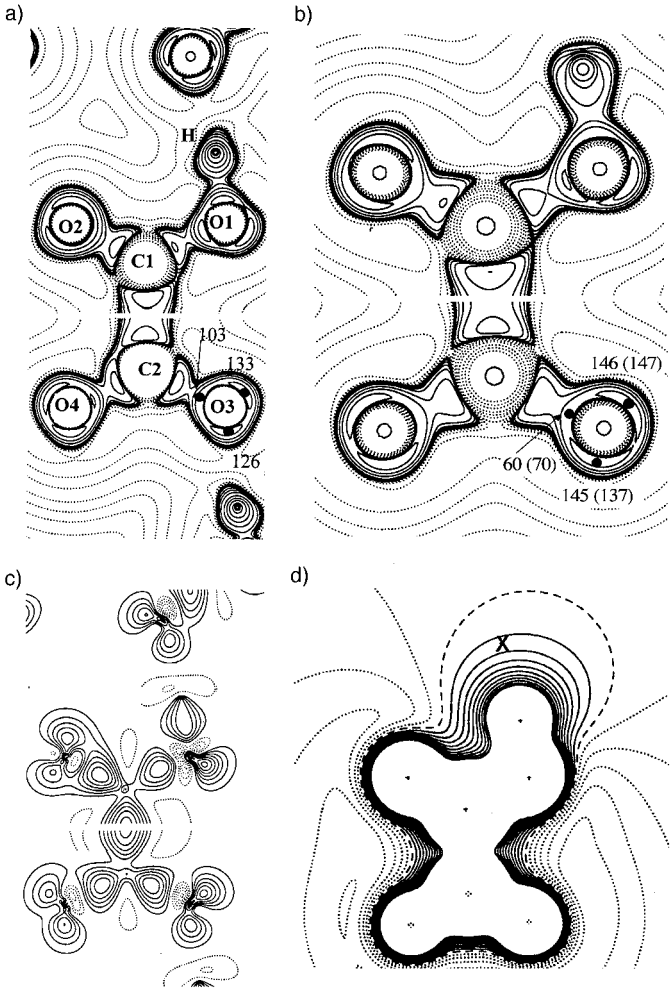

Figure 2. Drawings are composites of two molecular planes (O1-O2-H and O3-C2-O4) intersecting perpendicular to the C1–C2 bond; solid lines are positive contours. a) Experimental $L(\boldsymbol{r}) = -\nabla^2\rho(\boldsymbol{r})$ distribution (contours at $\pm 2.0, 4.0, 8.0 \times 10^x$ e Å^{-5}, $x = -2, -1, 0, 1$); maxima of $L(\boldsymbol{r})$ for O2 and O3 are reported. b) Theoretical $L(\boldsymbol{r})$ of the isolated anion (HF/6-31 + G(2d,2p)) in the solid state conformation; maxima for O2 and O3 are indicated (in parenthesis: those of O3 in the dimer). c) Static deformation map (contour intervals 0.1 e Å^{-3}); d) Electrostatic potential of the $HC_2O_4^-$ pseudomolecule from the refined X-ray model (contour intervals 0.05 e Å^{-1}, truncated at 0.5 e Å^{-1}; $\Phi(\boldsymbol{r}) = 0$ contour is a dashed line); the position of O3′ in the crystal orientation is marked by **X**.

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experimental monopolar charge.[21] On the basis of atomic electrostatic moments, a global anion–anion repulsion was calculated theoretically for $[(HC_2O_4)_2]^{2-}$;[1c] however, using the experimental multipoles,[22] we found that this is mainly due to O···O contributions, whereas the H···O3′ interaction is attractive. (Because atomic pairwise terms are not reported in ref. [1c], a complete comparison with the theoretical calculations in that paper is not possible.) Thus, according to all the partitioning schemes adopted, no electrostatic H···O repulsion can be anticipated.

The most substantial evidence of a "true" HB between the H and O atoms comes from the topological analysis of $\rho(\boldsymbol{r})$ in the crystal. Indeed, for all models tested, a bond path between H and O was always found. The quantities calculated at the bond critical point (bcp, a saddle point of $\rho(\boldsymbol{r})$ necessarily found along a bond path) indicate a rather large electron density and an incipient covalency (Table 1). The total energy density $H(\boldsymbol{r})$ is negative and relatively large; at the same time, the kinetic energy density is much smaller ($G(\boldsymbol{r}_{bcp}) = 0.381\ h\,Å^{-3}$) than what would be predicted for closed-shell type HBs (for $d_{H\cdots O} = 1.457$ Å, $G(\boldsymbol{r}_{bcp}) = 0.577\ h\,Å^{-3}$ [9e]). However, the features of $L(\boldsymbol{r}) = -\nabla^2\rho(\boldsymbol{r})$ (Figure 2a) suggest that considerable electrostatic interaction must also take place. In agreement with what is indicated by the geometry, the intramolecular O–H bond is clearly weakened: $\rho(\boldsymbol{r}_{bcp})$, $|\nabla^2\rho(\boldsymbol{r}_{bcp})|$, and $|H(\boldsymbol{r}_{bcp})/\rho(\boldsymbol{r}_{bcp})|$ are smaller than in the isolated molecule, whereas $G(\boldsymbol{r}_{bcp})/\rho(\boldsymbol{r}_{bcp})$ is larger.

Table 1. Properties at the bond critical point (bcp) of the HB system in the crystal (from the experimental X-ray model) and theoretical results for the isolated anion and the dianionic dimer, both calculated on the solid-state conformation.[a]

	O–H			H···O	
distance		1.060(2) Å		1.457(2) Å	
	monomer	dimer	crystal	dimer	crystal
$\rho(\boldsymbol{r})$ [e Å^{-3}]	1.97	1.81	1.89(5)	0.51	0.54(3)
$\nabla^2\rho(\boldsymbol{r})$ [e Å^{-5}]	−39.9	−38.4	−30.4(3)	4.16	2.03(10)
$H(\boldsymbol{r})/\rho(\boldsymbol{r})$ [h e^{-1}]	*−1.58*	*−1.71*		*−0.27*	
	[−1.73]	[−1.69]	[−1.60]	[−0.32]	[−0.44]
$G(\boldsymbol{r})/\rho(\boldsymbol{r})$ [h e^{-1}]	*0.16*	*0.22*		*0.85*	
	[0.32]	[0.20]	[0.48]	[0.89]	[0.71]

[a] The exact $H(\boldsymbol{r})$ and $G(\boldsymbol{r})$ can be evaluated only from the theoretical wavefunction (in italics); alternatively, these quantities can be estimated semiempirically[25] for both the theoretical and the experimental density (in square brackets).

The polarization of lone pairs involved in hydrogen bonds has been widely studied in the past (see refs. [3, 5c] for work on O–H···$O^{\delta-}$ and $^{\delta-}$O–H···$O^{\delta-}$ systems). This feature is recognized in the deformation maps (Figure 2c) and also in the $L(\boldsymbol{r})$ distribution. In fact, relative to the isolated molecule, both lone pairs of O3 are associated with smaller $L(\boldsymbol{r})$ maxima (Figures 2a and 2b); that pointing toward H is more polarized than that pointing toward K^+.[23] The calculated dianionic dimer shows the same feature, but, of course, only in the direction of the H atom (Figure 2b, values in parentheses).[24] We may conclude that many features of the topological analysis of the charge density indicate that $^{\delta-}$O–H···$O^{\delta-}$ behaves as a strong HB.

According to the above results, a polarization of the electron density in the $HC_2O_4^-$ molecular fragment occurs in the crystal by two mechanisms: 1) mainly electrostatic (the K···O interactions); 2) partially covalent (the HB). It can be concluded that when a molecule undergoes such a strong polarization, gas-phase calculations cannot predict its "properties" in the crystal, even if the solid-state conformation is used. A more empirical structural correlation is a better alternative for examining the chemical bonding, because suitable indexes are retrieved in the correct phase. Moreover, global (interfragment) interaction energies may fail to explain local parameters such as interatomic distances, and this can be particularly misleading in crystal engineering terms. A cluster of anions is obviously unstable, and only the addition of cations eventually allows the formation of a bound state; however, this does not hamper the formation of a bond between atoms of different anions, that is, a local atom–pair attractive interaction in the context of a global repulsion (when only the anions are considered). In view of the experimental observations reported here and using a more adequate definition of a chemical bond, we find no basis for claiming "the break-down of the strength/length analogy", as advocated in reference [1].

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[18] $\Phi(\boldsymbol{r}) = \sum_M \frac{Z_M}{|R_M - r|} - \int \frac{\rho(r')}{|r - r'|} d\boldsymbol{r}'$ ($\boldsymbol{R}_M$ are nuclear positions, and Z_M nuclear charges).

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[20] $q(H) = 0.58$ (QTAM); 0.29 (Mulliken); 0.41 (charge fitting the potential); 0.51 (NBO). Similar charges are found in the dimer. Note that in ref. [1a] Mulliken charges of O(H) and H were given as a single charge ($q(OH) = -0.19$).

[21] $q(H) = 0.38(2)$. In addition, a significant population was refined in the 4s orbital of K (0.51(5)e), which implies a partial charge transfer. A model with constrained molecular charges (+1 for K, −1 for HC_2O_4) did not show significant differences in the HB region.

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A New Kinetic Template Synthesis of Triphosphacyclodecanes**

Peter G. Edwards,* Paul D. Newman, and David E. Hibbs

Although the first macrocycles containing solely phosphorus atoms in the ring were reported nearly thirty years ago, there are surprisingly few studies on the coordination chemistry of these potentially very interesting ligands, especially when compared to the intensely studied nitrogen analogues. Early preparations including those of Horner et al.[1] and Kyba et al.[2] were by metal-free solution or high dilution methods, and were nonstereoselective giving a mixture of all possible isomers of the macrocycles. For the smallest triphosphorus macrocyclic ring system ([11]aneP_3) known to date, Kyba et al. achieved the separation and characterization of all isomers; for the *syn*,*syn*,*anti* ligand isomer vigorous conditions (boiling xylenes) were required for the inversion of the phosphorus center and formation of facially coordinated complexes.[3] More recently, metal template approaches by Horner and Kunz,[4] Stelzer et al.,[5] Norman et al.,[6] and us[7] have been studied in order to direct the cyclization step. For facially capping triphosphanes, the template allows control of the stereochemistry at the phosphorus centers; however, liberation of the macrocycle is commonly nontrivial and to date, only 12-membered triphosphamacrocycles have been obtained as the free ligands by this method, albeit stereospecifically.[7] Variations in ring size are difficult to achieve by the established $M(CO)_3$ templates (M = Group 6 metal) which does not allow manipulation and control of steric (or electronic) influences upon the cyclization step; the 12-membered ring is the smallest obtained by this method and attempts to decrease ring size by cyclization of vinyl phosphanes have failed in our hands.[8] We are interested in facially capping triphosphanes in which the phosphorus lone pairs are fixed in the favored all-*syn* orientation forcing remaining coordination sites in their complexes into mutually *cis* orientations.

This has prompted us to seek new template methods for the formation of triphosphamacrocycles to allow access to smaller ring sizes and rational high-yield routes to selectively functionalized ligands. We have chosen to investigate $[\eta^5\text{-}CpFe(L)_3]^+$ (L = monodentate or arene ligand; Cp = η^5-C_5Me_5) complexes as potential templates since they are readily prepared and form facial trisphosphane complexes which tend to have good air-stability.[9] Of particular interest is that substituents on the Cp ring may be widely varied which may allow manipulation of steric influences upon the *trans*-coordinated phosphanes. Herein we report the synthesis of

[*] Prof. P. G. Edwards, Dr. P. D. Newman, Dr. D. E. Hibbs
Department of Chemistry
Cardiff University
PO Box 912
Park Place, Cardiff, CF10 3TB (UK)
Fax: (+44) 2920-874-030
E-mail: Edwardspg@cardiff.ac.uk

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