How to make weak hydrogen bonds less weak

Dario Braga* and Fabrizia Grepioni*

Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

Letter

Interionic C—H···O hydrogen bond distances have been investigated in organometallic and inorganic salts showing that the average lengths unequivocally follow the order $[(\mathrm{M})\mathrm{C—H}]^+\cdots[\mathrm{O}]^- < (\mathrm{M})\mathrm{C—H}\cdots\mathrm{O}$ (M = first row transition metal) and $[(\mathrm{PPh_4})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^- < [(\mathrm{PPN})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^- < [(\mathrm{BPh_4})\mathrm{C—H}]^-\cdots[\mathrm{O_M}]^+$, which is the order of decreasing charge assistance to the weak hydrogen bonds.

Weak hydrogen-bonding interactions, in particular those of the C—H···O type, constitute a topic of great current interest.[1] The effect of charge on weak C—H···O hydrogen bonds has always been assumed, but never substantiated.[2] In this paper we address the question of charge assistance on a statistical basis by investigating the Cambridge Structural Database (CSD).[3] In recent years, data mining of the organometallic section of the CSD afforded a wealth of new information on intermolecular interactions that have no counterpart in the organic area because of the involvement of metal atoms or metal-bound ligands.[4] $\mathrm{C—H}^{\delta+}\cdots\mathrm{O}^{\delta-}$ bonds in which the donor system belongs to an organometallic cation and the acceptor to an organic anion have been widely exploited to engineer novel crystalline materials.[5]

We have searched the CSD for intermolecular and interionic C—H···O distances for metal-bound C—H systems [(M)C—H, M = first-row transition metal] in neutral, (M)C—H···O, and charged systems, $[(\mathrm{M})\mathrm{C—H}]^+\cdots[\mathrm{O}]^-$, respectively (Scheme 1).† Numerical results are summarized in Table 1, while histograms are shown in Fig. 1. It is immediately apparent that mean values as well as lowest (10%) and highest (90%) quantiles are appreciably shorter when the interaction is "charge-assisted" than in the corresponding neutral cases [2.629(15), 2.347/2.874 *versus* 2.741(12), 2.491/2.968 Å]. The lowest 10% quantiles (corresponding to the 10% shortest separations) are in both cases much shorter than van der Waals contact distances (H 1.2, O 1.5, H···O 2.7 Å). It is useful to stress that C—H···O hydrogen bonds, though weak, are directional and they are numerous in organometallic crystals because of the abundance of C—H donors (amongst arene and cylopentadienyl ligands, for instance), hence the electrostatic contribution to the C—H···O bonding makes these interactions valuable to crystal engineering.[6]

To put the metrical analysis in a somewhat broader perspective we have also chosen to compare C—H···O interactions involving the cations $\mathrm{PPh_4}^+$ and PPN^+ and the anion $\mathrm{BPh_4}^-$ and O acceptors in anionic and cationic transition-metal complexes $[\mathrm{O_M}]$ (see Scheme 1). The reason for this choice is apparent, $\mathrm{PPh_4}^+$, PPN^+ and $\mathrm{BPh_4}^-$ are among the most commonly used counter ions for the crystallization of charged organometallic species.

The comparison of the average structural parameters reported in Table 1 affords a rather consistent picture: the H···O distances, in both average and percentile values, follow the order $[(\mathrm{PPh_4})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^- < [(\mathrm{PPN})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^- < [(\mathrm{BPh_4})\mathrm{C—H}]^-\cdots[\mathrm{O_M}]^+$ which is the order of decreasing electrostatic reinforcement of the C—H···O interaction. Histograms showing the three types of length distributions are reported in Fig. 2. The difference between neutral and "charge-assisted" C—H···O hydrogen bonds is confirmed. The comparison between $\mathrm{BPh_4}^-$ and $\mathrm{PPh_4}^+$ is particularly educative since the donor group is *the same*, namely a C—H system from a phenyl group bound to B and P atoms, respectively. The $[(\mathrm{BPh_4})\mathrm{C—H}]^-\cdots[\mathrm{O_M}]^+$ represents a situ-

Table 1 Comparison of structural parameters for (M)C—H···O, $[(\mathrm{M})\mathrm{C—H}]^+\cdots[\mathrm{O}]^-$, $[(\mathrm{PPh_4})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^-$, $[(\mathrm{PPN})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^-$ and $[(\mathrm{BPh_4})\mathrm{C—H}]^-\cdots[\mathrm{O_M}]^+$ intermolecular/ interionic distances[a]

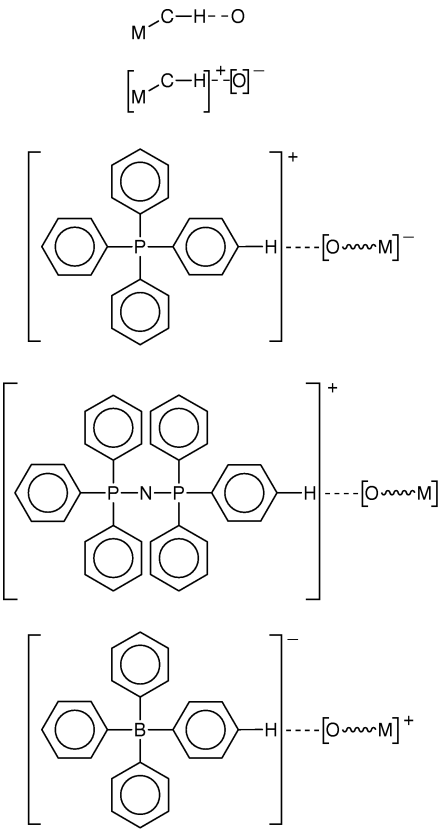
Sample Range $2.0 < \mathrm{H}\cdots\mathrm{O} < 3.0$ Å	Number of observations Min/mean(esds)/Å	Median Low/high quantiles (10/90)
(M)C—H···O	220 2.287/2.741(12)	2.766 2.491/2.968
$[(\mathrm{M})\mathrm{C—H}]^+\cdots[\mathrm{O}]^-$	163 2.088/2.629(15)	2.641 2.347/2.874
$[(\mathrm{PPh_4})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^-$	2058 2.058/2.700(4)	2.714 2.428/2.950
$[(\mathrm{PPN})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^-$	3502 2.077/2.723(3)	2.743 2.475/2.944
$[(\mathrm{BPh_4})\mathrm{C—H}]^-\cdots[\mathrm{O_M}]^+$	290 2.256/2.756(9)	2.775 2.551/2.949

[a] M = First-row transition metal; PPN = bis(triphenylphosphine)iminium.

---

* E-mail addresses: dbraga@ciam.unibo.it, grepioni@ciam.unibo.it, URL http://catullo.ciam.unibo.it

† CSD intermolecular searches based on a cut-off distance of 3.0 Å and on a cut-off angle of 110° for $[(\mathrm{PPh_4})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^-$, $[(\mathrm{PPN})\mathrm{C—H}]^+\cdots[\mathrm{O_M}]^-$, $[(\mathrm{BPh_4})\mathrm{C—H}]^-\cdots[\mathrm{O_M}]^+$ ($\mathrm{O_M}$ indicates that the oxygen atom belongs to an organometallic or coordination complex), and for $[(\mathrm{M})\mathrm{C—H}]^+\cdots[\mathrm{O}]^-$ and (M)C—H···O ['(M)C' indicates a metal-bound C atom with M = first-row transition metal]; C—H distances normalized to the neutron derived value of 1.08 Å; duplicate hits manually removed.



Scheme 1 A schematic representation of the interactions (M)C—H···O and $[(M)C—H]^+···[O]^-$ (metal-bound C atoms with M = first row transition metal) and $[(PPh_4)C—H]^+···[O_M]^-$, $[(PPN)C—H]^+···[O_M]^-$, $[(BPh_4)C—H]^-···[O_M]^+$ (O_M indicates that the oxygen atom belongs to an organometallic or coordination complex)

ation of "charge-opposition" to the C—H···O bonds and, in fact, this group of data is characterized by average distance values longer also with respect to the neutral sample. Note also that PPN^+, another very common counter ion for the crystallization of organometallic ions, is in between the two extremes defined by BPh_4^- and PPh_4^+. This can be understood in terms of a reduced polarization of the C—H systems arising from the fact that the charge is "shared" by six outer phenyl groups and by the P—N—P system. As a matter of fact it has been previously demonstrated that PPN^+ behaves, when packing with large anions carrying a small charge, very much like a neutral system.[7]

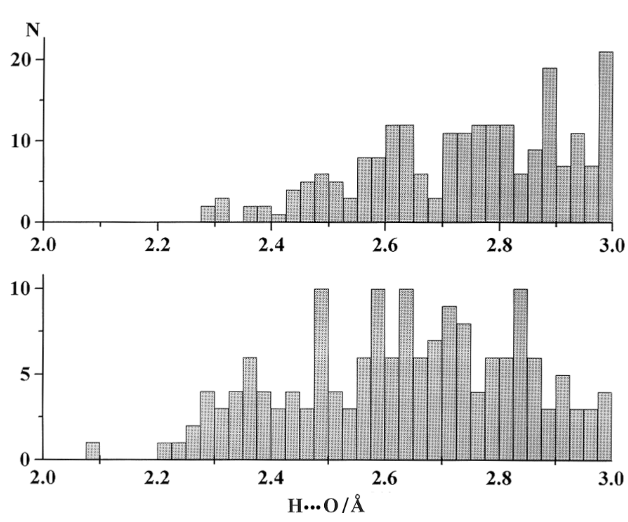


Fig. 1 Histograms of the two distributions of (C)H···O distances for neutral (M)C—H···O (top) and $[(M)C—H]^+···[O]^-$ (bottom). See Table 1 for mean values (M = first-row metal)

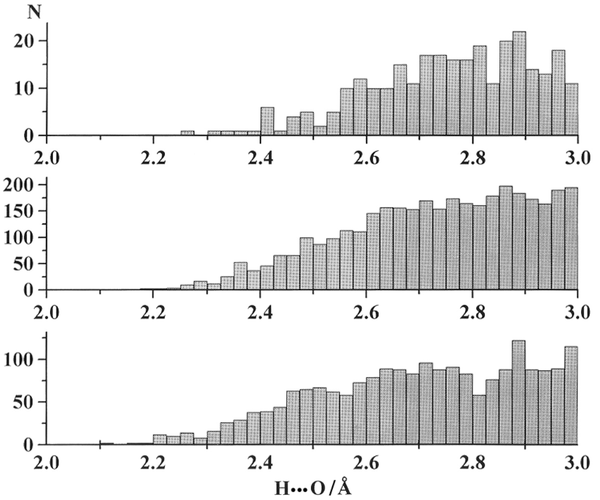


Fig. 2 Histograms of the distributions of (C)H···O distances for "charge-assisted" $[(PPh_4)C—H]^+···[O_M]^-$ (bottom) and $[(PPN)C—H]^+···[O_M]^-$ (middle) and for "charge-opposed" $[(BPh_4)C—H]^-···[O_M]^+$ (top) interactions (O_M = oxygen atom belonging to an organometallic or coordination complex). See Table 1 for mean values

In terms of angularity, all these interactions follow the trend expected for hydrogen bonds, *viz.* the C—H···O angle opens up as the distance between donor and acceptor decreases (see http://www.rsc.org/suppdata/njc/1998/1159).

Whether some C—H···O distances can be considered true hydrogen bonds or van der Waals interactions is still a controversial issue. The problem arises precisely from the fact there is no "rule of thumb" to follow when dealing with weak interactions. This is confirmed by our study. We have not only demonstrated the effect of "charge-assistance" on weak bonding, but also that the (C)H···O distance criterion is unsafe if the effect of ionic charges is neglected. An example of breakdown of the so-called hydrogen bond length/strength analogy has been recently reported.[8] Based on theoretical *ab initio* calculations of the unrestricted Hartree–Fock type, it has been possible to show that the shortest C—H···O interaction in crystalline $[(\eta^6—C_6H_6)_2Cr]^+[CrO_3(OCH_3)]^-$ cannot hold together anions because of the strong Coulombic repulsion between them. Similar observations have been made in the case of negatively charged hydrogen-bond-like $O—H^{(-)}···O^{(-)}$ interactions in chains formed by hydrogen oxalate anions.[9]

In general, however, when the donor is a cation and the acceptor an anion, there is no controversy. The positive charge carried by the cation decreases the shielding of the proton on the donor C—H groups and makes it more acidic; simultaneously, the presence of a negative charge on the acceptor increases its nucleophilicity. The net result is a strengthening of the weak bonds, which, being numerous in organometallic crystals because of the abundance of C—H donors, may play a key role in controlling crystal construction and stability.

Acknowledgements

DB and FG acknowledge financial support by M.U.R.S.T. (projects *Supramolecular Devices*) and University of Bologna (projects *Innovative Materials*).

References

1 (*a*) G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441; (*b*) T. Steiner, *Chem. Commun.*, 1997, **727**; (*c*) D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1997, **30**, 81.

2 (*a*) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, 1997; (*b*) L. Brammer, D. Zhao, F. T. Ladipo and J. Braddock-Wilking, *Acta Crystallogr., Sect. B*, 1995, **51**, 632; (*c*) C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 397.

3 F. H. Allen and O. Kennard, *Chemical Design Automation News*, 1993, **8**, 31.

4 D. Braga, F. Grepioni, E. Tedesco, K. Biradha and G. R. Desiraju, *Organometallics*, 1997, **16**, 1846 and references therein; G. Aullon, D. Bellamy, L. Brammer, E. A. Bruton and A. G. Orpen, *Chem. Commun.*, 1998, 653; D. Braga, F. Grepioni and E. Tedesco, *Organometallics*, 1998, **17**, 2669.

5 See, for example, D. Braga, A. Angeloni, F. Grepioni and E. Tagliavini, *Organometallics*, 1997, **16**, 5478; D. Braga and F. Grepioni, *Chem. Commun.*, 1998, 911; D. Braga, F. Grepioni and L. Maini, *Angew. Chem., Int. Ed. Eng.*, 1998, **37**, 2240.

6 G. R. Desiraju, *Chem. Commun.*, 1997, 1475; D. Braga and F. Grepioni, *Chem. Commun.*, 1996, 571; D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.

7 (*a*) D. Braga, F. Grepioni, P. Milne and E. Parisini, *J. Am. Chem. Soc.*, 1993, **115**, 5115; (*b*) D. Braga, F. Grepioni and E. Parisini, *J. Chem. Soc., Dalton Trans.*, 1995, 287.

8 D. Braga, F. Grepioni, E. Tagliavini, J. J. Novoa and F. Mota, *New J. Chem.*, 1998, **22**, 755.

9 D. Braga, F. Grepioni and J. J. Novoa, *Chem. Commun.*, 1998, 1959.

Received 6th *July* 1998;
Letter 8/06554C