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X−H⋯π (X = O, N, C) Hydrogen Bonds in Organometallic Crystals

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Summary: The intermolecular interactions between X−H donors (X = C, N, O) and electron-rich π-ligands (alkynes, arenes, and cyclopentadienyl ligands) in crystalline organometallic complexes have been investigated from data retrieved from the Cambridge Structural Database. Intermolecular X−H⋯π interactions are weak hydrogen bonds following the common order of acidity $H_{OH} > H_{NH} > H_{CH}$ but become more effective packing determinants when "charge-assisted" by the presence of an ionic charge $(X−H^{\delta+}⋯π^{\delta-})$.

Introduction

The great structural diversity of organometallic systems, arising from the variability of oxidation states, ligand−metal bonding, and types of ligands, is reflected in the types and patterns of hydrogen bonding and other intermolecular interactions established by organometallic molecules and ions in the solid state.[1] With organometallic species the capacity to form hydrogen bonds is not confined to the traditional acceptor and donor groups of organic molecules. We have devoted part of our recent research efforts to a systematic investigation of hydrogen bonding in organometallic crystals, in particular of donors and acceptors which have no counterpart in the organic chemistry field.[2]

This note reports a study of hydrogen bonds of the X−H⋯π (X = C, N, O) type. The acceptor groups are alkynes, cyclopentadienyl groups, and unsaturated rings belonging either to the ligands in neutral and charged complexes or to counterions in ionic crystals.

X−H⋯π interactions have been the subject of several theoretical,[3] spectroscopic,[4] and structural studies.[5,6] Furthermore, O−H⋯π and N−H⋯π interactions have

been shown to take part in the folding of biological macromolecules,[7] competing with the π−π stacking interactions. The T-shaped arrangement in crystalline acetylene[8a] and the well-known herringbone feature in the packing of aromatic molecules[8b,d] are a consequence of the optimization of C−H⋯π interactions. X−H⋯π interactions in organic crystals have been the subject of database analyses.[9,10] The role of ionic charge has also been discussed.[11]

We have investigated the distribution and geometry of intermolecular X−H⋯π interactions (X = O, N, C) by searching the Cambridge Structural Database (CSD).[12a] Mean values of X⋯π and H⋯π distances and X−H⋯π angles with reference to the electron density centroid of the unsaturated system[12b] are reported in Table 1 for X = O, N, and C, together with the number of crystal structures (entries) and intermolecular contacts (observations) found in each case.[12c] Except for the cases where the number of entries is too small to yield reliable statistical data (e.g. for X = O and $π_{C≡C}$),

(1) (a) Braga, D.; Grepioni, F. *J. Chem. Soc., Chem. Commun.* **1996**, 571. (b) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.,* in press.

(2) (a) Braga, D.; Grepioni, F.; Sabatino, P.; Desiraju, G. R. *Organometallics* **1994**, *13*, 3532. (b) Braga, D.; Biradha, K.; Grepioni, F.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156. (c) Biradha, K.; Desiraju, G. R.; Braga, D.; Grepioni, F. *Organometallics* **1996**, *15*, 1284. (d) Braga, D.; Grepioni, F.; Tedesco, E.; Biradha, K.; Desiraju, G. R. *Organometallics* **1996**, *15*, 2692. (e) Braga, D.; Grepioni, F.; Tedesco, E.; Biradha, K.; Desiraju, G. R. *Organometallics* **1997**, *16*, 1846. (f) Braga, D.; Grepioni, F.; Desiraju, G. R. *J. Organomet. Chem.* **1997**, *548*, 33. (g) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1997**, *27*, 51.

(3) (a) Takagi, T.; Tanaka, A.; Matsuo, S.; Maezaki, H.; Tani, M.; Fujiwara, H.; Sasaki, Y. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1015. (b) Cheney, B. V.; Schulz, M. W.; Cheney, J.; Richards, W. G. *J. Am. Chem. Soc.* **1988**, *110*, 4195. (c) Brédas, J. L.; Street, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7001. (d) Brédas, J. L.; Street, G. B. *J. Chem. Phys.* **1989**, *90*, 7291. (e) Rzepa, H. S.; Smith, M. H.; Webb, M. L. *J. Chem. Soc., Perkin Trans. 2* **1994**, 703. (f) Man-Fai Fan; Lin, Z.; McGrady, J. E.; Mingos, D. M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 563. (g) Kim, K. S.; Lee, J. Y.; Choi, H. S.; Kim, J.; Jang, J. H. *Chem. Phys. Lett.* **1997**, *265*, 497.

(4) (a) Block, P. A.; Jucks, K. W.; Pedersen, L. G.; Miller, R. E. *Chem. Phys.* **1989**, *139*, 15. (b) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 942. (c) Rodham, D. A.; Suzuki, S.; Suenram, R. D.; Lovas, F. J.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Nature* **1993**, *362*, 735. (d) Zwier, T. S. *Annu. Rev. Phys. Chem.* **1996**, *47*, 205 and references therein.

(5) (a) Mootz, D.; Deeg, A. *J. Am. Chem. Soc.* **1992**, *114*, 5887. (b) Muller, T. E.; Wing-Kin Choi, S.; Mingos, D. M. P.; Murphy, D.; Williams, D. J.; Wing-Wah Yam, V. *J. Organomet. Chem.* **1994**, *484*, 209. (c) Pilkington, M.; Wallis, J. D.; Smith, G. T.; Howard, J. A. K. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1849. (d) Allen, F. H.; Howard, J. A. K.; Hoy, V. J.; Desiraju, G. A.; Reddy, D. S.; Wilson, C. C. *J. Am. Chem. Soc.* **1996**, *118*, 4081.

(6) (a) Hardy, A. D. U.; MacNicol, D. D. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1140. (b) Nishio, M.; Hirota, M. *Tetrahedron* **1989**, *45*, 7201. (c) Hanor, T. A.; Jennings, W. B.; Proctor, L. D.; Tolley, M. S.; Boyd, D. R.; Mullan, T. *J. Chem. Soc., Perkin Trans. 2* **1990**, 25. (d) Atwood, J. L.; Hamada, F.; Robinson, D.; Orr, G. W.; Vincent, R. L. *Nature* **1991**, *349*, 683. (e) Rzepa, H. S.; Webb, M. L.; Slawin, M. Z.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 765. (f) Hanton, L. R.; Hunter, C. A.; Purvis, D. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1134. (g) Atwood, J. L.; Bott, S. G.; Jones, C.; Raston, C. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1349. (h) Hunter, R.; Haueisen, R. H.; Irving, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 566. (i) Ferguson, G.; Gallangher, J. F.; Glidewell, C.; Zakaria, C. M. *Acta Crystallogr.* **1994**, *C50*, 70. (j) Adams, H.; Carver, F. J.; Hunter, C. A.; Osborne, N. J. *Chem. Commun.* **1996**, 2529. (k) Adams, H.; Harris, K. D. M.; Hembury, G. A.; Hunter, C. A.; Livingstone, D.; McCabe, J. F. *Chem. Commun.* **1996**, 2531. (l) Fujimoto, T.; Yanagihara, R.; Kobayashi, K.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2113.

(7) (a) Ming Fong, T.; Cascieri, M. A.; Hong Yu; Bansal, A.; Swain, C.; Strader, C. D. *Nature* **1993**, *362*, 350. (b) Liu, S.; Ji, X.; Gilliland, G. L.; Stevens, W. J.; Armstrong, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7910. (c) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101. (d) Mitchell, J. B.; Nandi, L.; McDonald, I. K.; Thornton, J. M. *J. Mol. Biol.* **1994**, *239*, 315 and references therein.

(8) (a) McMullan, R. K.; Kvick, Å.; Popelier, P. *Acta Crystallogr.* **1992**, *B48*, 726. (b) Gavezzotti, A.; Desiraju, G. D. *Acta Crystallogr.* **1988**, *B44*, 427. (c) Gavezzotti, A.; Desiraju, G. D. *J. Chem. Soc., Chem. Commun.* **1989**, 621. (d) Gavezzotti, A. *Chem. Phys. Lett.* **1989**, *161*, 67.

Table 1.   Mean Values of X−H---π (X = O,N,C) Hydrogen Bonds Based on Database Analysis[a]

X−H---π	no. of entries	no. of observns	X---π (Å)	H---π (Å)	X−H---π (deg)
O−H---$\pi_{C\equiv C}$	4	4	3.42	*2.85*	119.0
O−H---π_{Cp}	1	1	3.26	*2.36*	159.2
O−H---π_{Ph}	41	49	3.41(3)	2.66(3)	143(3)
N−H---$\pi_{C\equiv C}$	3	3	3.34	*2.36*	164.3
N−H---π_{Cp}	4	6	3.63	*2.71*	156.2
N−H---π_{Ph}	103	176	3.50(1)	2.71(1)	145(1)
C−H---$\pi_{C\equiv C}$	229	229	3.795(9)	2.854(7)	148.1(9)
C−H---π_{Cp}	12	15	3.71(3)	2.80(3)	144(3)
C−H---π_{Ph}	24	77	3.69(2)	2.79(2)	142(2)

[a] Mean standard errors in parentheses for statistically significant samples.

estimated standard deviations of the mean values are also provided. Although the samples differ very much in population, H---π distances follow roughly the order O < N < C. This is particularly evident when the π-acceptor is the phenyl ring (π_{Ph}), for which a large number of structures has been found. The H---π_{Ph} distances increase on the average on passing from X = O (2.66(3) Å) to X = N (2.71(1) Å) and to X = C (2.79(2) Å). In contrast, for a given donor there is no clear-cut dependence on the nature of the acceptor. This applies also to the cyclopentadienyl ring, which is characteristic of organometallic species and has no counterpart in organic chemistry.

Figure 1 reports the distributions of intermolecular X−H---π_{Ph} angles versus H---π_{Ph} distances for X = O and N, while, for the sake of clarity, the scattergram in Figure 2 shows only the more abundant case of C−H---$\pi_{C\equiv C}$ angles versus H---$\pi_{C\equiv C}$. These scattergrams reproduce all the characteristic features of weak H-bonds: as the length decreases, the interactions approach linearity.

(9) Viswamitra, M. A.; Radhakrishnan, R.; Bandekar, J.; Desiraju, G. R. *J. Am. Chem. Soc.* **1993**, *115*, 4868.

(10) (a) Steiner, T.; Starikov, E. B.; Amado, A. M.; Teixeira-Dias, J. J. C. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1321. (b) Steiner, T.; Starikov, E. B.; Tamm, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 67. (c) Steiner, T.; Tamm, M.; Lutz, B.; van der Maas, J. *Chem. Commun.* **1996**, 1127. (d) Steiner, T.; Tamm, M.; Grzegorzewski, A.; Schulte, N.; Veldman, N.; Schreurs, A. M. M.; Kanters, J. A.; Kroon, J.; van der Maas, J.; Lutz, B. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2441. (e) Subramaniam, K.; Lakshmi, S.; Rajagopalan, K.; Koellner, G.; Steiner, T. *J. Mol. Struct.* **1996**, *384*, 121. (f) Steiner, T.; Lutz, B.; van der Maas, J.; Veldman, N.; Schreurs, A. M. M.; Kroon, J.; Kanters, J. A. *Chem. Commun.* **1997**, 191.

(11) (a) Bakshi, P. K.; Linden, A.; Vincent, B. R.; Roe, S. P.; Adhikesavalu, D.; Cameron, T. S.; Knop, O. *Can. J. Chem.* **1994**, *72*, 1273. (b) Bakshi, P. K.; Sereda, S. V.; Knop, O.; Falk, M. *Can. J. Chem.* **1994**, *72*, 2144.

(12) (a) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 204. (b) Data were retrieved from the April 1997 update version of the CSD. Only entries presenting atomic coordinates, including those of the hydrogen atoms, and for which *R* < 0.10 were retained. O−H---π, N−H---π, and C−H---π interactions were searched with selection criteria based on normalized H---π intermolecular distances below 3.0 Å from the centroid of the unsaturated system ($\pi_{C\equiv C}$, π_{Cp}, π_{Ph} for alkynes, cyclopentadienyl ligands, and phenyl groups). Geometrical queries for X = C are given in the Supporting Information as representative examples. Both neutron and X-ray determinations for X = N, O, C (for C−H---$\pi_{C\equiv C}$) were considered, while for the more abundant cases of C−H---π_{Cp} and C−H---π_{Ph} only neutron structures were considered. To analyze the charge effect, two separate searches were carried out on neutral and charged species for each type of X−H---π interaction. Duplicate hits were manually screened and removed. (c) Mean values on intermolecular separations depend on the interval; since the cutoff distances are the same for all types of donors, internal comparisons are meaningful. (d) Kroon, J.; Kanters, A. *J. Mol. Struct.* **1975**, *24*, 109.
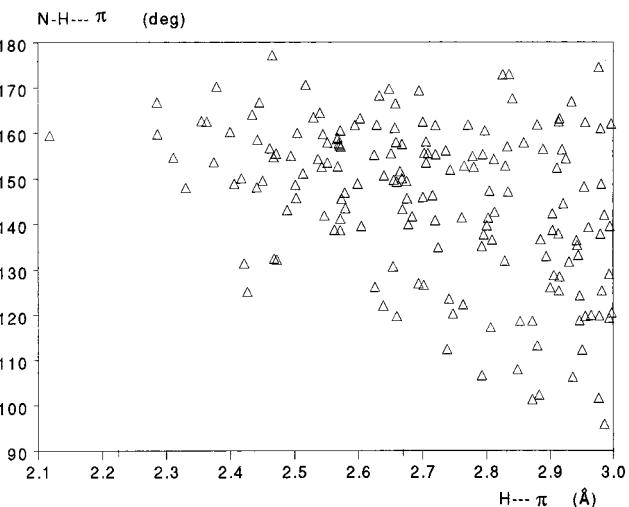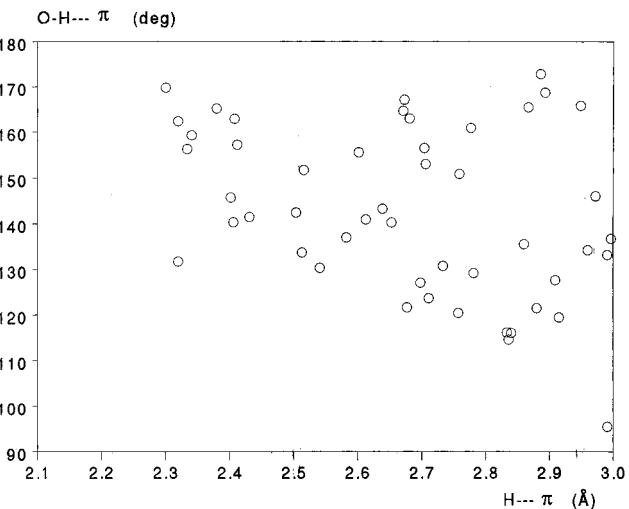

Figure 1. Scattergrams of O−H- - -π_{Ph} angles versus (O)H- - -π_{Ph} distances (a, top), and of N−H- - -π_{Ph} angles versus (N)H- - -π_{Ph} distances (b, bottom), where π_{Ph} indicates the phenyl ring centroid.
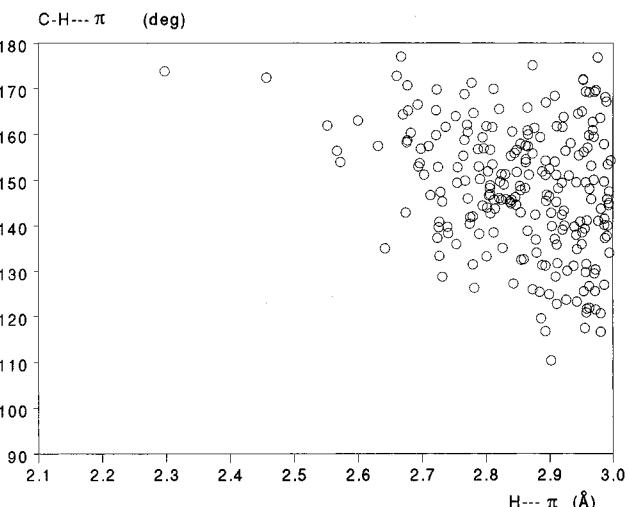
Figure 2. Scattergram of C−H- - -$\pi_{C\equiv C}$ angles versus (C)H- - -$\pi_{C\equiv C}$ distances.

In the case of phenyl or cyclopentadienyl rings it is convenient to study the distribution of the θ angle, formed by the π−H vector and the plane of the ring as illustrated in Chart 1 for an X−H---π_{Ph} interaction.
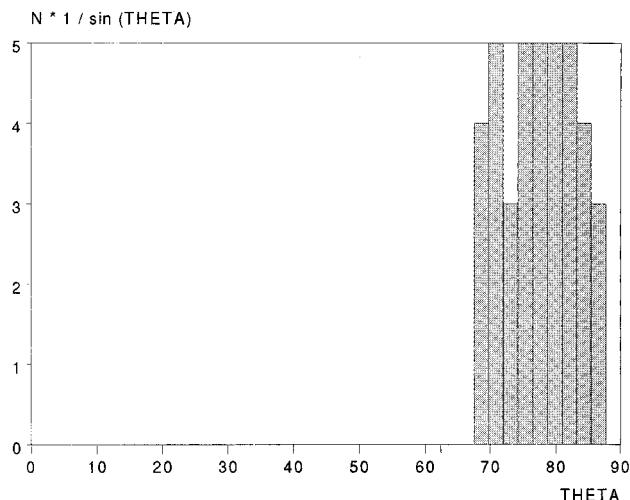
Figure 3. Histogram of θ angles (see Chart 1 for definitions) taken with their absolute values and corrected for the solid-state angle, relative to O−H- - -π_{Ph} interactions.

Chart 1
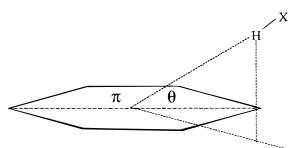
The use of the polar angle θ allows us to see how the H---π vector is oriented with respect to the ring plane. As an example, the distribution of θ (absolute) values for the O−H---π_{Ph} interactions after conical correction[12d] is shown in Figure 3. Similar distributions are obtained for X = N, C and π = cyclopentadienyl, phenyl. In all cases there is a strong preference for θ angle values around 80°.

This type of analysis, however, does not allow us to discriminate between an approach of the X−H donor toward the center of the ring system (in the cases of π_{Cp} and π_{Ph}) and an approach directed toward C−C bonds on the ligand rim. This latter type of interaction has been discussed on several occasions[9] and is also observed in our samples.

The hydrogen bond acceptor behavior of the cyclopentadienyl ligand, so typical of organometallic molecules, is similar to that of phenyl rings.

X−H---π Interactions in Ionic Crystals and Effect of Charge Assistance. Hydrogen bonds are interactions of chiefly electrostatic nature. In the case of X−H---π interactions, as in all other weak hydrogen bonds, we expect X−H$^{\delta+}$---$\pi^{\delta-}$ bonds to be shorter than neutral X−H---π or X−H$^{\delta-}$---$\pi^{\delta+}$ cases. To examine this aspect, separate CSD searches of X−H---π_{Ph} interactions on ionic and neutral complexes have been carried out for X = O, N, C. The results are grouped in Table 2 according to the neutral or positively or negatively charged nature of donors and/or acceptors.

In the case of X = O, 23 out of 42 structures with H---π_{Ph} distances below 3.0 Å are of hydrates, while in 7 cases the O−H group belongs to a metal-coordinated aquo ligand. As expected, water can approach π_{Ph} clouds more easily than any other O−H donor.

Figure 4 shows the distribution of (X−)H---π_{Ph} distances for charged and neutral organometallic systems
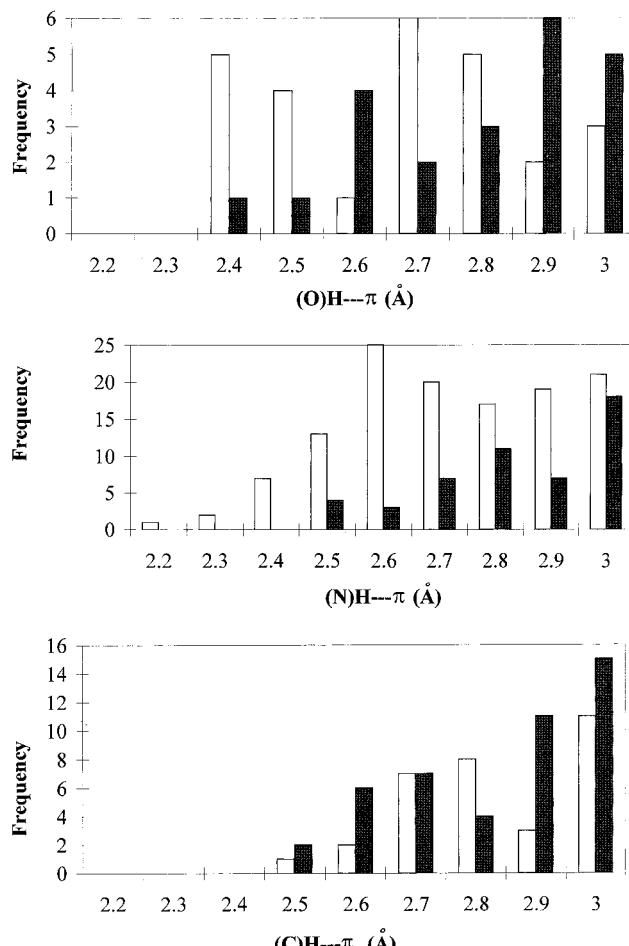

Figure 4. Distribution of (X)H- - -π_{Ph} distances for charged and neutral organometallic compounds (empty and solid bars, respectively): (a, top), X = O; (b, middle) X = N; (c, bottom) X = C.

Table 2. Number of Structures Containing Neutral and Charged X−H---π_{Ph} (X = O,N,C) Hydrogen Bonds

	⬡	⬡(+)	⬡(−)
O−H	22	2	12
N−H	45		
C−H	16		
O−H$^{\delta+}$		1	5
N−H$^{\delta+}$		9	48
C−H$^{\delta+}$		4	4
O−H$^{\delta-}$			
N−H$^{\delta-}$			1
C−H$^{\delta-}$			

(empty and filled bars, respectively). Table 2 and Figure 4 show that charged fragments are present in ca. 50% of the complexes for X = O, and N, leading to slightly shorter hydrogen bonds with respect to neutral systems both when *the acceptor is negatively charged* (mainly for X = O) and *the donor is positively charged* (X−H$^{\delta+}$---$\pi^{\delta-}$ type common for X = N). Negatively charged acceptors are most commonly found in crystals of the BPh$_4^-$ anion (7 cases for X = O, 39 for X = N). The X−H$^{\delta+}$---$\pi^{\delta+}$ situation is found in very few compounds. In the case of carbon donors, charged C−H$^{\delta+}$---$\pi_{Ph}^{\delta-}$ hydrogen bonds are less common. Furthermore, the charge effect seems to be less appreciable than in the
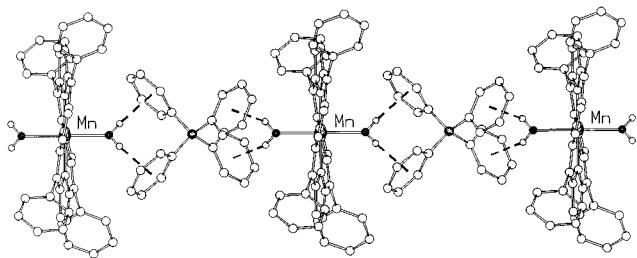
Figure 5. Bridging of BPh_4^- anions, via O−H- - -π_{Ph} hydrogen bonds, of [(tetraphenylporphyrin)Mn(H₂O)₂]⁺ cations in crystalline [(tetraphenylporphyrin)Mn(H₂O)₂]-[BPh₄] (drawn after ref 13 from coordinates available in the CSD).

cases of O−H and N−H donors, as shown by the comparison of (C-)H---π_{Ph} distances for ion pairs or neutral species in Figure 4c. We have found that the BPh_4^- counterion commonly acts as an X−H---π_{Ph} hydrogen bond acceptor (mainly when X = N) and appears to play a "noninnocent" role in determining the ion arrangement in crystals. As an example, Figure 5 shows the pattern of O−H---π_{Ph} interactions in crystalline [(tetraphenylporphyrin)Mn(H₂O)₂][BPh₄],[13] where the BPh_4^- anions "bridge" (H---π_{Ph} = 2.341 Å) cations via coordinated water molecules along the *c* axis.

Conclusions

We have shown on the basis of a CSD analysis that X−H---π hydrogen bonds in organometallic crystals are common. These interactions conform to the order of acidity observed in typical hydrogen bonds ($H_{OH} > H_{NH} > H_{CH}$) and show a tendency toward linearity at shorter

(X−)H---π distances. C−H---π hydrogen bonds, though weaker than N−H---π and O−H---π, behave in very much the same way whenever sufficiently acidic C−H donors are present.

The presence in the subset of organometallic structures retrieved from CSD of ca. 50% of ionic compounds has allowed an evaluation of the "charge effect" affecting the X−H---π hydrogen bond. Either donors or acceptors can carry a positive charge, while seldom are negatively charged X−H moieties observed. In most cases charge-assisted (X−H$^{\delta+}$---$\pi^{\delta-}$) interactions present shorter distances than neutral X−H---π bonds. This represents a clear-cut manifestation of the essentially electrostatic nature of X−H---π hydrogen bonds. Because of the abundance of ionic complexes, "charge assistance" to weak hydrogen bonds is a relevant phenomenon in organometallic solids.[14]

Supporting Information Available: A table giving geometrical questions for the search of intermolecular X−H---π interactions with X = C and π = phenyl (neutron data) (1 page). Ordering information is given on any current masthead page.

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(13) Turner, P.; Gunter, M. J.; Skelton, B. W.; White, A. H.; Hambley, T. W. *J. Chem. Res., Synop.* **1996**, *18-19*(1) (Eng).

(14) For other examples of the effect of charge assistance on organometallic hydrogen bonding see: (a) Braga, D.; Angeloni, A.; Grepioni, F.; Tagliavini, E. *Organometallics* **1997**, *16*, 5478. (b) Grepioni, F.; Cojazzi, G.; Draper, S. M.; Scully, N.; Braga, D. *Organometallics* **1998**, *17*, 296 and references therein.