Donor and acceptor strengths in C—H···O hydrogen bonds quantified from crystallographic data of small solvent molecules

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The influence of donor and acceptor strengths on mean distances in C—H···O hydrogen bonds is quantified in a crystallographic database study. Small solvent molecules are used as donors, which are cocrystallized in organic and organometallic crystals. This system provides chemically homogeneous sets of C—H groups, allowing better defined statistical analysis compared to studies based on molecular fragments. Eight kinds of O-atom acceptors are considered, ranging from the very strong acceptor P═O to the weak acceptor M—CO (M = transition metal atom). For the strongest donor considered, chloroform, mean hydrogen bond distances vary by *ca.* 0.5 Å as the acceptor strength is varied from P═O to M—CO. For the weak donor acetone, this variation is only *ca.* 0.1 Å. It is confirmed that even weakly polar C—H groups can donate, and that the O-atoms of M—CO groups can accept C—H···O hydrogen bonds.

The general properties of intermolecular C—H···O interactions are at this time the subject of intense research, and several reviews are already available.[1–5] It is found that C—H···O interactions possess all characteristics of hydrogen bonds, including complex properties such as cooperativity within hydrogen bond arrays.[6] Because carbon acidities span a range of over 50 orders of magnitude, the strength of C—H···O hydrogen bonds covers a wide range which overlaps with 'normal' O—H···O hydrogen bonds for more acidic C—H donors,[7–9] and merges with van der Waals interactions for the weakest C—H donor types. It could be shown that for C—H···O contacts in crystals, mean C···O distances correlate with the conventional C—H acidity (in DMSO).[10] Notably, even for C—H of methyl groups, the angular characteristics of C—H···O contacts show weak preference for linearity, indicating weakly hydrogen-bonding character.[11] Because weak hydrogen bonds are primarily electrostatic interactions, they operate also at long distances exceeding the van der Waals separation: for alkynyl donors, contacts with H···O distances of 2.9 Å still show clearly the spectroscopic effects of hydrogen bonding.[12]

The influence of donor strength on mean C—H···O hydrogen bond distances has been described by Desiraju and co-workers in a series of crystallographic database analyses.[10,13,14] Related data were only recently reported for C—H···Hal^- hydrogen bonds.[15] The influence of acceptor nature is more difficult to quantify, and has long resisted detection from crystallographic data. In a preliminary communication, it was shown that for C—H···O contacts formed by solvent molecules cocrystallized in organic crystal lattices, mean H···O distances clearly depend on the acceptor nature.[16] The system of cocrystallized solvent molecules is exceptionally well suited for such a study because it provides chemically homogeneous sets of C—H donors, such as $CHCl_3$, CH_2Cl_2, *etc.* Furthermore, solvent molecules can relatively freely orient in crystal lattices and effects of steric hindrance are smaller than for C—H donors that are part of larger molecules. In the present contribution, the concept of the initial communication is followed, but the work is expanded to a comprehensive form by including organometallic crystal structures and considering a larger set of acceptors. This does not only widen the scope, but it also increases the number of analysed contacts by almost a factor of four (from 311 to 1183), thereby considerably improving the statistical significance of the results. The study is based on 'normalised' X—H bond lengths, that is on bond lengths adjusted to corresponding neutron diffraction values. This procedure should be generally used in statistical hydrogen bond studies.[17]

It is necessary to give a comment on the terminology used. The quantities that are analysed in crystallographic database studies, *i.e.* distances and angles, are purely geometrical. Mean donor–acceptor separations in D—H···A hydrogen bonds are related to a number of physical and chemical properties of the groups involved, but do not directly measure them. For example, the geometric solid state property of mean H···A separations in crystals is correlated to the chemical property of D—H acidity,[10] but this is only a correlation and not a strict dependency. H···A separations in crystals are influenced by many effects, and acidities vary from solvent to solvent. The terms 'donor strength' and 'acceptor strength' are used here solely to characterise distance properties of donor–acceptor combinations in the solid state, meaning that a strong donor (or strong acceptor) will on average attract a given partner to a shorter distance than a weak one. Characterizing the relationships of strengths to properties such as acidity and basicity in solution, partial charges on H and on O, interaction energy, *etc.*, is non-trivial and not the subject of this study.

Results

To obtain results of statistical significance, only organic solvent molecules can be considered that are found cocrystallized in a relatively large number of crystal structures. Futhermore, these crystal structures must be chemically diverse so that C—H···O interactions are formed with a wide variety of acceptor types. Finally, the solvent molecules must not show a too strong tendency for disorder. Only five kinds of molecules fulfil all these requirements: chloroform, dichloromethane, acetonitrile, dimethyl sulfoxide and acetone. Benzene, unfortunately, is unsuitable because of its notorious tendency to disorder. The terminal alkyne group, C≡C—H, is also included in the set of donors because it is one of the very few molecular residues that is in almost all molecules fully accessible to intermolecular contacts.

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Compared to the previous communication, the range of acceptor strengths is widened by including the strong acceptors P=O and H_2O, and the weak acceptor M—CO (M = transition metal atom; only terminal CO ligands considered). For the latter functional group, the potential to accept C—H···O hydrogen bonds has been shown only recently.[18,19] Further subdivision of the acceptors, such as (CC)C=O, (NC)C=O, (OC)C=O, instead of $>$C=O, or primary, secondary and tertiary hydroxy groups instead of C(sp^3)—OH, would be desirable in principle, but is not feasible because of the limited numbers of crystal structures. Many important O-atom acceptors such as C(sp^2)—OH, N—OH, P—OH, —O—O—, bridged CO ligands, could not be considered because the available crystal structures are too few for analysis of statistical significance.

As the first step of the analysis, the sequence of C—H donors strengths is determined based on the mean distances to the acceptors O, N and Cl^-, Table 1 (Cambridge Structural Database,[20] January 1998 update). Because the data for O and N acceptors are averaged over all chemical types of O and N atoms, respectively, this is only a rough initial description. Ideally, the sequence of donor strengths should be the same for all acceptor types, and this is actually observed in Table 1, with the exception of minor uncertainties for the methyl donors. For the three stronger donor types, the sequence is clearly $CHCl_3 > C{\equiv}C{-}H > CH_2Cl_2$, and for the weak methyl donors, it appears to be $N{\equiv}C{-}Me >$ DMSO $>$ acetone.

In the second step, a ranking of strengths is set up for the eight types of O-atom acceptors under study. This is performed by determining mean hydrogen bond distances with the conventional donors H_2O and $-NH_3^+$, which occur in very large numbers of crystal structures, Table 2. The acceptors H_2O, C=O and S=O have very similar mean distances to the donors, but for the other acceptors the ranking of strengths is unambiguous: $P{=}O > H_2O \geqslant C{=}O \geqslant S{=}O > C(sp^3){-}OH > C{-}O{-}C > {-}NO_2 > M{-}CO$. Within this sequence, the mean hydrogen bond distances vary by *ca.* 0.5 Å from the strongest to the weakest acceptors. The poor acceptor strength of the nitro group is in accordance with a recent database and theoretical study on N/O—H···O_2N hydrogen bonds.[21]

If the six C—H donors in Table 1 are combined with the eight O-atom acceptors in Table 2, this leads to a 6 × 8 matrix of 48 possible donor–acceptor combinations. The mean hydrogen bond distances for these combinations are given in Table 3, the total number of contacts for each acceptor type is given in Table 4. In the lines of Table 3, the effect of donor strength on mean hydrogen-bond distances can be seen, and in the columns the corresponding effect of acceptor strengths. Because donors and acceptors are arranged in sequence of falling strengths, the strongest hydrogen bonds are formed with the combinations in the top left corner, and the weakest hydrogen bonds with those in the bottom right corner of the matrix. When looking at the numerical values, it must be considered that for many of the donor–acceptor combinations, only very few examples occur in crystal structures, leading to large standard uncertainties of the mean contact distances. The effect of donor strengths can be best seen in the lines for C=O, C(sp^3)—OH and C—O—C acceptors, for which the largest numbers of contacts are found, and also in the line for P=O, for which the effect is strongest. Within the lines, the mean H···O and C···O separations systematically increase from the left to the right. The effect of acceptor strength is best seen for the more acidic donors, in particular for chloroform. In essence, the sequences of donor and acceptor strengths that were initially set up in Tables 1 and 2 lead to a self-consistent picture in Table 3. It appears that the sequence of acceptor strengths derived from O/N—H···O hydrogen bonds is fully valid also for C—H···O interactions.

The effect of acceptor strength is qualitatively the same for all kinds of donors, *i.e.*, the mean hydrogen-bond distances systematically increase down the columns from P=O to M—CO. Quantitatively, however, there are large differences between the different donors. If the acceptor strength is reduced from P=O to M—CO, the mean H···O distance increases by 0.52 Å for the strongest donor, $CHCl_3$, but only by 0.12 Å for the weakest, acetone. For the other donor types, this value systematically falls with falling donor strength, Table 5. This shows that hydrogen bonds from strong donors are strongly influenced by variations of acceptor strength, whereas hydrogen bonds from weak donors are influenced only slightly. On the other hand, it is of importance that C—H···O contacts even of the weakest donors in the set are not completely insensitive to variations of acceptor nature (insensitivity would be an indication that such contacts do not

Table 1 Database results:[a] mean H···A and C···A distances/Å in hydrogen bonds of different C—H donors to the acceptors O (all types),[b] N (all types)[b] and Cl^-. The chemically more important distance is H···A

Donor	O acceptors	N acceptors	Cl^- acceptors
Mean H···A distance			
$CHCl_3$	2.31(1) [222]	2.37(3) [32]	2.38(3) [16]
C≡C—H	2.40(2) [145]	2.40(6) [12]	2.56(4) [8]
CH_2Cl_2	2.492(8) [356]	2.53(2) [58]	2.59(3) [34]
N≡C—Me	2.567(9) [323]	2.59(1) [114]	2.72(3) [20]
DMSO	2.56(1) [203]	2.65(2) [18]	2.94 [3]
Acetone	2.60(1) [92]	2.64(3) [11]	2.98 [1]
Mean C···A distance			
$CHCl_3$	3.24(1) [222]	3.34(3) [32]	3.41(2) [16]
C≡C—H	3.35(1) [145]	3.36(5) [12]	3.58(4) [8]
CH_2Cl_2	3.347(8) [356]	3.45(2) [58]	3.54(2) [34]
N≡C—Me	3.40(1) [323]	3.47(2) [114]	3.68(3) [20]
DMSO	3.45(1) [203]	3.57(3) [18]	3.86 [3]
Acetone	3.48(1) [92]	3.63(2) [11]	3.88 [1]

[a] Standard uncertainties are given in parentheses (given only for $n_{H\cdots A} > 3$), data quantities $n_{H\cdots A}$ are given in brackets. Numerical values are given for normalized H-atom positions. [b] Excluded are N and O atoms directly bonded to metal atoms, or carrying a positive charge.

Table 2 Database results:[a] mean H···O and D···O distances/Å in hydrogen bonds of H_2O and $-NH_3^+$ donors to various O-atom acceptors

Acceptor	H_2O donor	$C{-}NH_3^+$ donor
Mean H···O distance		
P=O	1.871(7) [374]	1.856(7) [336]
H_2O	1.903(3) [3002]	1.918(8) [325]
$>$C=O	1.903(3) [3280]	1.918(6) [1035]
$>$S=O	1.906(7) [650]	1.936(12) [162]
C(sp^3)—OH	1.921(5) [795]	2.00(2) [130]
C—O—C	2.018(11) [307]	2.07(2) [72]
C—NO_2	2.158(12) [175]	2.19(2) [37]
M—CO	2.29 [2]	2.35 [3]
Mean C···O distance		
P=O	2.793(5) [374]	2.817(4) [336]
H_2O	2.808(2) [3002]	2.851(5) [325]
$>$C=O	2.823(2) [3280]	2.839(3) [1035]
$>$S=O	2.824(5) [650]	2.859(7) [162]
C(sp^3)—OH	2.834(4) [795]	2.90(1) [130]
C—O—C	2.894(8) [307]	2.94(1) [72]
C—NO_2	2.988(9) [175]	3.05(2) [37]
M—CO	3.04 [2]	3.24 [3]

[a] Standard uncertainties are given in parentheses (given only for $n_{H\cdots O} > 3$), data quantities $n_{H\cdots O}$ are given in brackets. Numerical values are given for normalized H-atom positions.

Table 3 Database results:[a] mean H···O and C···O distances/Å in hydrogen bonds of different C—H donors and various O-atom acceptors

	$CHCl_3$	C≡C—H	CH_2Cl_2	N≡C–Me	DMSO	Acetone
Mean H···O distance						
P=O	1.97 [2]	2.02 [5]	2.27(7) [6]	2.40(4) [4]	— [0]	2.49 [2]
H_2O	2.11 [1]	2.11 [3]	2.16 [2]	2.65 [3]	2.73 [3]	2.61(9) [4]
$>C=O$	2.22(3) [52]	2.29(3) [40]	2.41(2) [123]	2.53(3) [42]	2.52(2) [73]	2.60(2) [67]
$>S=O$	2.25(6) [21]	2.50(6) [9]	2.40(4) [31]	2.57(3) [14]	2.57(2) [58]	2.53(8) [5]
C(sp^3)–OH	2.31(8) [5]	2.40(3) [31]	2.47(11) [4]	2.52(6) [11]	2.52(2) [73]	2.53(19) [4]
C—O—C	2.33(5) [16]	2.45(4) [19]	2.55(2) [57]	2.56(2) [56]	2.65(4) [4]	2.64(3) [14]
C—NO_2	2.52(6) [4]	2.63(3) [6]	2.48(4) [15]	2.59(3) [17]	2.60(3) [22]	2.57(5) [5]
M—CO	2.49(3) [20]	2.48(12) [4]	2.57(1) [176]	2.63(3) [21]	— [0]	2.61(2) [29]
Mean C···O distance						
P=O	3.03 [2]	3.06 [5]	3.19(7) [6]	3.36(5) [4]	— [0]	3.30 [2]
H_2O	3.09 [1]	3.15 [3]	3.22 [2]	3.41 [3]	3.61 [3]	3.57(11) [4]
$>C=O$	3.18(2) [52]	3.28(2) [40]	3.27(2) [123]	3.36(3) [42]	3.43(2) [73]	3.48(2) [67]
$>S=O$	3.22(5) [21]	3.45(5) [9]	3.31(4) [31]	3.36(4) [14]	3.47(2) [58]	3.39(11) [5]
C(sp^3)–OH	3.28(11) [5]	3.35(3) [31]	3.42(7) [4]	3.35(4) [11]	3.43(2) [73]	3.43(15) [4]
C—O—C	3.26(4) [16]	3.35(2) [19]	3.44(2) [57]	3.44(2) [56]	3.63(3) [4]	3.58(4) [14]
C—NO_2	3.48(7) [4]	3.45(4) [6]	3.33(4) [15]	3.25(5) [17]	3.47(3) [22]	3.31(5) [5]
M—CO	3.32(4) [20]	3.47(11) [4]	3.40(1) [176]	3.45(4) [21]	— [0]	3.52(3) [29]

[a] Standard uncertainties are given in parentheses (given only for $n_{H \cdots O} > 3$), data quantities $n_{H \cdots O}$ are given in brackets. Numerical values are given for normalized H-atom positions.

represent hydrogen bonds at all: for pure van der Waals contacts, one would expect to find the value 0.0 in Table 5).

Analogous observations can be made for the effect of donor strength on hydrogen bonds to different acceptors. For the strong acceptors P=O and H_2O, the H···O distances increase by *ca.* 0.5 Å if the donor is varied along the lines. For the weak acceptors NO_2 and M—CO, this variation is much smaller, only *ca.* 0.1 Å (Table 6).

It is of some interest to look at the top left corner of Table 3 which contains the strongest hydrogen bonds. It is not surprising that the shortest C—H···O hydrogen bond in the data sample (H···O = 1.88 Å) is formed by the combination of the strongest donor with the strongest acceptor considered, Cl_3C—H···O=P. This crystal structure, an organometallic phosphine,[22] is shown in Fig. 1. The second Cl_3C—H···O=P hydrogen bond in the sample is somewhat longer, H···O = 2.06 Å, C···O = 3.14 Å.[23] Remarkably short C—H···O hydrogen bonds are also formed if the alkyne donor, C≡C—H, is combined with the strong acceptors O=P and H_2O; since examples have been discussed in the original literature, they need not be shown here again (ref. 8 for P=O, ref. 9 for H_2O acceptors). Finally, the combination of the chloroform donor and the water acceptor also leads to short C—H···O hydrogen bonding; the only example in crys-

Table 4 The structural data set. Numbers of C—H···O contacts analysed for the different acceptor types (summed over all donors)

Acceptor	$n_{C\text{—}H \cdots O}$
P=O	19
H_2O	16
$>C=O$	397
$>S=O$	138
C(sp^3)—OH	128
C—O—C	166
C—NO_2	69
M—CO	250

Table 5 Difference of mean H···O distances/Å to P=O and M—CO acceptors (using data in Table 3)

Donor	$(H \cdots O)_{M\text{—}CO}$ minus $(H \cdots O)_{P=O}$
$CHCl_3$	0.52
C≡C—H	0.46
CH_2Cl_2	0.30
N≡C—Me	0.22
Acetone	0.12

Table 6 Difference of the mean H···O distances of hydrogen bonds formed by $CHCl_3$ and acetone to given acceptors (using data in Table 3)

Acceptor	$(H \cdots O)_{CHCl_3}$ minus $(H \cdots O)_{acetone}$
P=O	0.52
H_2O	0.50
$>C=O$	0.38
$>S=O$	0.28
C(sp^3)—OH	0.22
C—O—C	0.31
C—NO_2	0.05
M—CO	0.12

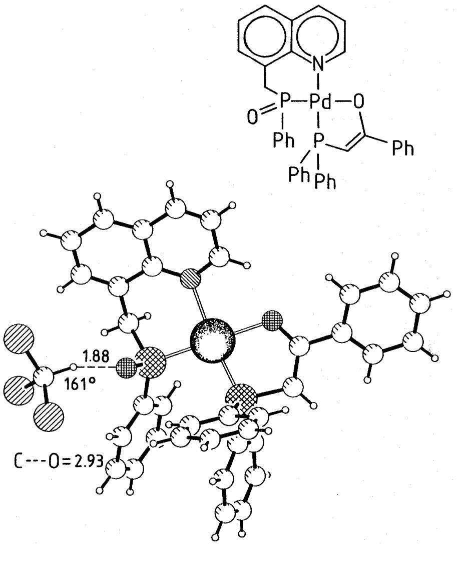

Fig. 1 The shortest hydrogen bond contained in the structural data set, donated from a $CHCl_3$ molecule to a P=O acceptor bonded to a Pd atom. Crystal structure determined by Braunstein and coworkers.[22] Numerical values are given for a normalized H-atom position

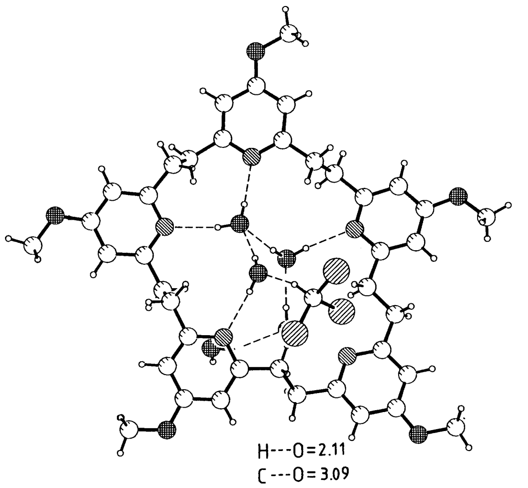

Fig. 2 The only hydrogen bond in the CSD which is donated from $CHCl_3$ to H_2O, occurring in a pyridinophane crystal structure containing one $CHCl_3$ and five water molecules. Crystal structure determined by Vögtle and co-workers.[24] Numerical values are given for a normalized H-atom position

tals is found in a pyridinophane structure containing chloroform as well as water molecules[24] (Fig. 2).

There has been some debate in the recent literature as to whether C—H···N interactions deserve generally the classification as 'hydrogen bonds'.[25–27] The data in Table 1 show that the effect of C—H donor strength in C—H···N contacts is the same as the effect in C—H···O contacts. It is of interest to see whether there is also an effect of N-atom acceptor strength. Because the number of relevant C—H···N contacts in the CSD is about a factor of 10 smaller than that of C—H···O contacts, a detailed analysis similar to that in Table 3 cannot be performed. However, at least for the acceptors C=N—C and N≡C—C, it can be shown that the influence of the acceptor type on H···N distances is similar for C—H···N and O—H···N hydrogen bonds, *i.e.* contacts to C=N—C are systematically shorter than to N≡C—C (Table 7).

Conclusions

It is shown that in intermolecular C—H···O contacts, the mean H···O separations depend strongly on the natures of both contact partners. Earlier studies on donor strengths of different C—H groups are confirmed.[10,13,14] The sequence of acceptor strengths found for conventional O/N—H···O hydrogen bonds (Table 2) is valid also for C—H···O interactions (Table 3). It is, furthermore, confirmed that even weakly polar C—H groups such as those in $—CH_3$ can donate, and that the O atoms of M—CO groups can accept (albeit weak) C—H···O hydrogen bonds.

Table 7 Database results:[a] mean H···N distances/Å in hydrogen bonds of different C—H donors and two kinds of N-atom acceptors. The conventional donor $C(sp^3)$—OH is included for comparison

	C—N=C	N≡C—C
$CHCl_3$	2.42(5) [16]	2.53 [2]
CH_2Cl_2	2.49(5) [13]	2.59(6) [8]
N≡C—Me	2.60(5) [10]	2.61(1) [112]
DMSO	2.61(2) [8]	2.67(9) [9]
$C(sp^3)$—OH	1.888(6) [418]	2.02(2) [35]

[a] Standard uncertainties are given in parentheses (given only for $n_{H\cdots O} > 3$), data quantities $n_{H\cdots O}$ are given in brackets. Numerical values are given for normalized H-atom positions.

It has been stated repeatedly that the influence of acceptor strength (or acceptor basicity) on C—H···O hydrogen bond distances is small compared to the influence of donor acidity.[2,16] The results in Table 3 suggest that this view should be modified: it appears that the variation range of mean donor–acceptor distances due to variation of donors (0.5 Å; Table 5) is just as broad as that due to variation of acceptors (0.5 Å; Table 6). Earlier observations have been made for the O-atom types that occur in organic crystals most frequently, such as C=O, C—OH and C—O—C. These represent only a small section of the range of acceptor strengths (and of O-atom basicities), so that the observed variation of mean H···O distances could be only small (*ca.* 0.1–0.2 Å). The early analyses of C—H donor strengths,[13,14] in contrast, did not suffer much from truncating the acidity range: structural data on strong ($CHCl_3$) and very weak ($—CH_3$) C—H donors are readily available in large quantities, so that a pronounced effect of donor strength became immediately obvious.

The functional groups and molecules in Table 3 cover neither the whole range of C—H acidities, nor the whole range of O-atom basicities. Considerably stronger carbon acids than $CHCl_3$ are known, such as HCN, $CH(NO_2)_3$, and $CH(CN)_3$. Notably, in the only crystal structure of a $CH(NO_2)_3$ complex, a very short C—H···O hydrogen bond is formed although the acceptor is one of the weaker types, C—O—C (H···O = 2.00 Å, C···O = 2.94 Å).[7] Similarly, stronger O-atom acceptors than P=O are known, such as $C—O^-$ in phenolate ions.[28] This suggests that the formation of even shorter C—H···O hydrogen bonds should be possible than the shortest known today. Experimentally, this could be realised for example by cocrystallisation of a P=O acceptor molecule such as triphenylphosphinoxide with a carbon acid stronger than $CHCl_3$.

Finally, it is noted that in the preceding short communication, the acceptor $—NO_2$ has been ranked at a high position between C=O and S=O.[16] This is peculiar because in O/N—H···O hydrogen bonds, the acceptor strength of the nitro group is poor.[21] In the present analysis, this ranking is not confirmed and the nitro acceptor is placed at the weak end of the scale, between C—O—C and M—CO. The previous ranking is interpreted as a statistical artifact.

Database Analysis

The study is based on the organic and organometallic crystal structures archived in the Cambridge Structural Database (CSD),[20] January 1998 update with 175 093 entries. Only ordered and error-free structures with *R*-values < 0.08 were used. H-atom positions were normalized using the CSD default X—H bond lengths. M—CO acceptors are defined as carbonyl ligands bonded to exactly one transition metal atom. Carbonyl ligands bonded to more than one metal atom were not considered. O- and N-atom acceptors directly bonded to metal atoms were generally disregarded. D—H···A contacts were considered to distance cut-off values of 2.8 Å for D = C and A = O/N, 3.0 Å for D = C, A = Cl^-, and 2.4 Å for D = N/O and A = O. No angle cut-off criteria were used. Comments and warnings concerning the use of cut-off criteria have been published previously.[2] Because of their structural importance, two crystal structures were included that did not pass the quality criteria defined above: the partially disordered structure of the complex triphenylsilylacetylene–triphenylphosphinoxide containing short C≡C—H···O=P hydrogen bonds,[8] and a structure with $R = 0.084$ containing a Cl_3C—H···O=P hydrogen bond.[23] The total number of contacts included in Table 3 is 1183, compared to 311 in the corresponding table of the preliminary report.[16]

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