Effect of Acceptor Strength on C–H···O Hydrogen Bond Lengths as revealed by and quantified from Crystallographic Data

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In C–H···O hydrogen bonds, the average C···O and H···O separations depend on the nature of the acceptor O atoms: they obey the trends observed as for the conventional O–H and N–H donors, with a ranking of acceptor strengths C=O > NO_2 > S=O > C–OH > C–O–C.

In O–H···O hydrogen bonds, the average O···O and H···O separations depend on the chemical nature of the O–H donor, and also, though to a lesser extent, on that of the O acceptor. For instance, hydrogen bonds donated by carboxylic acids are on the average shorter than those donated by alcohols. Similarly, hydrogen bonds accepted by carbonyl groups are shorter than those accepted by hydroxy groups.[1] From the large amounts of crystallographic data available, even subtle differences between donor–acceptor combinations like hydroxy–water, water–hydroxy and water–water can be described.[2] For the case of the weaker C–H···O hydrogen bonds,[3–6] it was analogously shown that the mean donor–acceptor separations depend on the nature of the C–H donor,[7,8] and even a correlation with the carbon acidity (pK_a in Me_2SO) could be established.[9] A complementary dependency on the acceptor properties (*e.g.* the O basicity) is to be expected, but has as yet not been definitely proven. In the present study, this effect is established and quantified for the first time, using structural data of polar organic solvent molecules.

To demonstrate the effect of acceptor basicity on C–H···O hydrogen bond lengths, the hydrogen bonds donated from invariant C–H donors to different acceptor types must be analysed statistically. The average C···O (and H···O) distances should then be shorter for strong acceptors such as carbonyl groups than for weaker acceptors like ether O atoms. As this effect will be weak, suitable data must be selected with care. Relatively small chemical variations can change the C–H acidity significantly[9,10] and obscure the weaker effect resulting from acceptor basicity. Consequently, the set of donor molecules should be chemically as homogeneous as possible. Furthermore, effects due to steric hindrance by or within bulky substituents[9] must be avoided. These requirements are best satisfied by the small molecules of polar organic solvents, which are often found co-crystallized in molecular crystal structures. They supply relatively large quantities of data on identical C–H donors in varying crystal environments.

At the outset, organic crystal structures containing co-crystallized solvent molecules were screened for C–H···O hydrogen bonds (Cambridge Structural Database;[11] quality criteria: no disorder, $R \leqslant 0.08$; hydrogen bond criteria: H···O < 2.8 Å for normalized H position with C–H 1.08 Å, angle at H > 90°; for comments on these criteria, see refs. 1, 5, 6, 12). Only solvent molecules with exactly one chemical type of H atoms were regarded. A total of five different solvents yielded sufficiently large sets of structural data (chloroform, dichloroethane, acetonitrile, dimethyl sulfoxide, acetone). The data sets of other solvents were either too small or were excessively dominated by only one type of acceptor. In addition, the ethynyl molecular residue bonded to C(sp^3) was included for comparison as it has been shown to be an exceptionally useful model system in hydrogen bonding studies.[5,12] The total data set contains 209 molecules (or residues) in 182 crystal structures, Table 1.

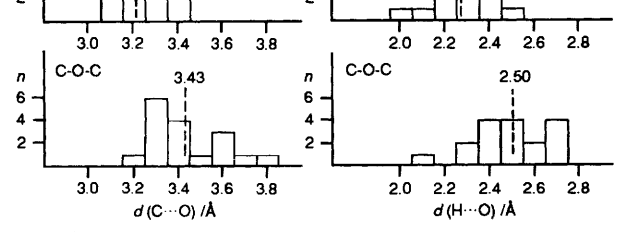

Fig. 1 Histograms of C···O (left) and H···O (right) separations in C–H···O hydrogen bonds donated by CH_2Cl_2 and accepted by C=O (top) and C–O–C (bottom). Data for normalized H positions (C–H bond length 1.08 Å) and H···O < 2.8 Å. Dashed lines show the mean values of the distributions.

Table 2 lists the mean C···O and H···O distances for hydrogen bonds from all six donor types to five specific acceptor types (C=O, NO_2, S=O, C–OH, C–O–C), as well as the average for all O acceptors. C···O and H···O are not equivalent parameters because most hydrogen bonds are nonlinear (for comprehensive discussion of C–H···O hydrogen bond geometries, see refs. 4–8). Of these two distances, H···O is the chemically more relevant one; it is, however, less reliably determined than C···O even after normalisation of the C–H bond length to the ideal value.

The effect of donor acidity is impressively shown in the columns of Table 2. Averaged over all O acceptors, the mean C···O separation is a short 3.16 Å for chloroform. It increases for molecules of lower acidity and is 3.52 Å for the poor methyl donors of acetone. The difference in the mean hydrogen bond distances between the strongest and the weakest donors in the data set is therefore more than 0.35 Å. The effect of acceptor basicity, though less pronounced, can clearly be observed in the rows of Table 2: for all six donor types, the hydrogen bonds to C=O are shorter than those to C–OH and C–O–C acceptors by about 0.1 Å or more. As an example, the distribution of the hydrogen bond separations is shown in Fig. 1 for interactions of dichloromethane with C=O and C–O–C acceptors. Apart from the shift to higher values from C=O to C–O–C acceptors, Fig. 1 also illustrates that even for constant donor–acceptor combinations, the hydrogen bond geometries are soft and cover wide ranges.

Table 2 suggests a ranking of acceptor strengths C=O > NO_2 > S=O > C–OH > C–O–C (preliminary at present owing to the limited quantity of data). This is exactly what would be expected on the basis of the polarity of these groups.

Table 1 The data sample[a]

	Formula	$n_{(\mathrm{Struct.})}$	$n_{(\mathrm{Molec.})}$
Chloroform	$CHCl_3$	21	22
Dichloromethane	CH_2Cl_2	31	40
Acetonitrile	CH_3CN	25	33
Dimethyl sulfoxide	$(CH_3)_2SO$	28	32
Acetone	$(CH_3)_2CO$	31	33
Ethynyl residue	C(sp^3)–C≡CH	46	49

[a] Organic solvent molecules co-crystallized in molecular crystal structures and acting as hydrogen bond donors in C–H···O interactions. The ethynyl molecular residue is included for comparison.

Table 2 Mean C···O and H···O separations (Å) for C–H···O hydrogen bonds to various acceptor types (with H···O < 2.8 Å, for normalized H positions)[a]

Donor	C=O	NO_2	S=O	C–OH	C–O–C	All O
Mean C···O						
$CHCl_3$	3.16 (3) [13]				3.26 (4) [3]	3.16 (2) [22]
CH_2Cl_2	3.21 (3) [13]	3.32 (4) [7]	3.3 (1) [3]	3.51 (5) [3]	3.43 (4) [17]	3.33 (2) [54]
$C(sp^3)–C≡CH$[b]	3.28 (2) [15]			3.37 (4) [22]	3.38 (4) [8]	3.35 (2) [49]
CH_3CN	3.33 (6) [7]	3.31 (6) [13]		3.42 (9) [4]	3.37 (3) [18]	3.35 (2) [47]
$(CH_3)_2SO$	3.41 (2) [25]	3.45 (4) [18]	3.51 (3) [26]	3.44 (3) [11]	3.59 (6) [3]	3.46 (1) [85]
$(CH_3)_2CO$	3.49 (2) [32]			3.55 (5) [8]	3.61 (4) [8]	3.52 (2) [54]
Mean H···O						
$CHCl_3$	2.22 (5) [13]				2.31 (4) [3]	2.22 (3) [22]
CH_2Cl_2	2.27 (4) [13]	2.41 (5) [7]	2.4 (1) [3]	2.6 (1) [3]	2.50 (4) [17]	2.41 (2) [54]
$C(sp^3)–C≡CH$[b]	2.24 (3) [15]			2.41 (5) [22]	2.44 (6) [8]	2.37 (4) [49]
CH_3CN	2.44 (7) [7]	2.55 (4) [13]		2.44 (7) [4]	2.46 (4) [18]	2.49 (2) [47]
$(CH_3)_2SO$	2.51 (2) [25]	2.57 (3) [18]	2.56 (2) [26]	2.61 (4) [11]	2.63 (6) [3]	2.56 (1) [85]
$(CH_3)_2CO$	2.60 (2) [32]			2.69 (2) [8]	2.69 (3) [8]	2.62 (2) [54]

[a] Standard errors of the mean values given in parentheses, n_{CH} given in square brackets. Note that for H···O, the standard errors refer to the normalized (*i.e.* theoretical), not to the experimental H positions. Data for acceptors with $n < 3$ are not given individually, but included in the column for 'all O'. [b] Molecular residue.

In essence, this study supports the view that C–H···O interactions possess all characteristic properties of hydrogen bonds.[1,5] As in the conventional hydrogen bonds donated by O–H and N–H, a pronounced effect of donor strength and also a weaker complementary effect of acceptor strengths on average hydrogen bond distances is inferred.

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