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Not all short C–H···O contacts are hydrogen bonds: the prototypical example of contacts to $C{=}O^+{-}H$

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Intermolecular contacts between C–H groups and the charged moiety $X{=}O^+{-}H$ show a pronounced negative directionality, *i.e.* short contacts are associated with strongly bent angles; this indicates that these interactions do not represent hydrogen bonds, although they are occasionally short with H···O distances down to 2.5 Å.

After a long period of dispute, it has in recent years become accepted that directional and cohesive C–H···O interactions represent hydrogen bonds.[1,2] Because carbon acidities span a very wide range,[3] the strengths of C–H···O hydrogen bonds cover also a wide range that overlaps at one end with strengths of O–H···O hydrogen bonds,[4] and on the other end it merges with van der Waals interactions.[5] In this context, it is of importance to ask whether *all* short C–H···O contacts are hydrogen bonds, or if there are exceptions. This matter has been addressed by several authors. In particular, short intramolecular C–H···O contacts,[6] short contacts with second-nearest neighbours,[7] compressed C–H···O interactions[8] and inter-anion C–H···O contacts[9] have been mentioned as possibly destabilizing. All these studies, however, remained limited in scope. In the present work, a whole class of short C–H···O contacts that do not represent hydrogen bonds will be presented, and structural consequences of this lack of hydrogen bond nature will be shown. The analytical tool used is the crystal correlation method, which has not been applied for this purpose before.

In hydrogen bonding X–H···A, it is a prerequisite that the acceptor A is a basic entity, and the donor X–H must be at least slightly acidic. Alternatively, in an electrostatic approach, one can give as a basic requirement that the acceptor A must carry a negative partial charge, or at least must have a sterically accessible region of negative charge concentration. This would mean that intermolecular contacts $X{-}H\cdots A^{\delta+}$ do not fulfill the primary conditions for hydrogen bonding, and even if they occur experimentally, they should not be classified as hydrogen bonds. To look into the matter of intermolecular C-H···O contacts that are not hydrogen bonds, contacts to O atoms of the kind $O^{\delta+}$ are, therefore, a relevant system. Candidates are the O atoms in species like H_3O^+ and $X{=}OH^+$. In the latter, the positive charge need not be localized on the O-atom, but charge delocalization with substantial contribution of the resonance form $X{=}OH^+$ should be sufficient. Examples are systems like $P{=}OH^+ \leftrightarrow P^+{-}OH$, $>N{-}C{=}OH^+ \leftrightarrow\ >N^+{=}C{-}OH$, and so on.

In crystals, there is not even one example of a short contact $X{-}H\cdots O^{\delta+}$ formed by an O–H or N–H group.‡ However, relatively short contacts of C–H groups to $O^{\delta+}$ do occur occasionally within frameworks of strong hydrogen bonds and ionic interactions. As an example, the crystal structure of acetamidium nitrate[10] is shown in Fig. 1. A methyl C–H group forms a short contact to a nitrate O atom (H···O = 2.28 Å), which is clearly suggestive of a $C{-}H\cdots O^{\delta-}$ hydrogen bond. This C–H group also forms an inter-cation $C{-}H\cdots O^{\delta+}$ contact with H···O = 2.60 Å. When considering only interatomic distances, this contact too might be interpreted as a weak hydrogen bond, and such a view could even be supported by the suitable orientation of the electron lone pair of the protonated amide O atom. On the other hand, when looking at the overall electrostatic situation, and when considering the complete absence of related $O/N{-}H\cdots O^{\delta+}$ 'hydrogen bonds' in crystals, this $C{-}H\cdots O^{\delta+}$ interaction would rather be taken as forced by optimization of the strong interionic interctions. In view of such conflicting arguments, further evidence in favour of or against the interpretation as a hydrogen bond is clearly needed.

One of the characterstics of hydrogen bonding is the *directionality*. In optimal geometry, the donor is oriented linearly at the acceptor, and any deviation from linearity incurs an energetic disadvantage. The weaker hydrogen bond types can be easily distorted from optimal geometry so that large deviations from linearity occur frequently, but a statistical preference for linearity is discernible even for the very weak C–H···O hydrogen bonds formed by methyl groups.[11] This property can be used as a test criterion in assessing whether a particular type of intermolecular C–H···O contact is a hydrogen bond or not. In a CSD analysis‡ of intermolecular $C{-}H\cdots O^{\delta+}$

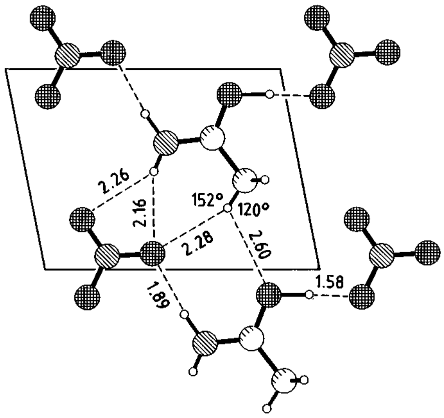

Fig. 1 Crystal structure of acetamidium nitrate (ref. 10); geometries are given for normalized H atom positions.

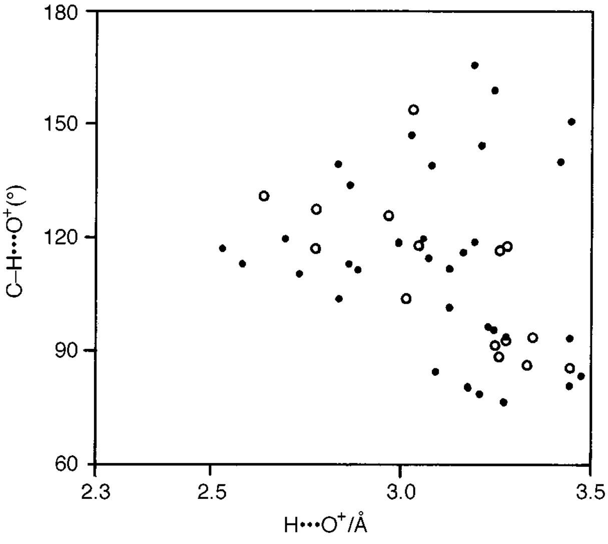

Fig. 2 Scatterplot of C–H···O angles against H···O distances in C–H···O contacts involving fragments (●) **1** and (○) **2**.

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Table 1 The structural data set under study

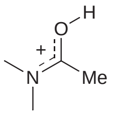
CSD reference code‡	Ref.	C=O$^+$H type	C–H type	Charge on CH donor molecular	Counterion to C = O$^+$H	Shortest H···O$^{\delta+}$/Å
BIFKEG	12(*a*)	**2**	> CH$_2$	0	NO$_3^-$	2.64
BIFKIK	12(*a*)	**2**	> CH$_2$	0	ClO$_4^-$	2.78
CAPRLC	12(*b*)	**1**	> CH$_2$	+1	Cl$^-$	2.59
DAHRAF	12(*c*)	**2**	–CH$_3$	+1	F$_3$C-SO$_3^-$	2.97
ENANLC	12(*d*)	**1**	> CH$_2$	+1	Cl$^-$	2.86
FUVMUE	12(*e*)	**1**	–CH$_3$	+1	F$_3$C-SO$_3^-$	2.73
MACMHC	12(*f*)	**1**	–CH$_3$	+1	Cl$^-$	3.08
MACMNO	10	**1**	–CH$_3$	+1	NO$_3^-$	2.60
VAYLAI	12(*g*)	**1**	–CH$_3$	+1	NO$_3^-$	2.53

Table 2 Mean geometries of different kinds of C–H···O interactions with H···O < 3.0 Å as compared with C–H···H–C van der Waals contacts

Interaction type	[*n*]	H···O (Å)	C···O (Å)	C–H···O/H (°)
C≡C–H···O=C[a]	44[a]	2.36(4)	3.31(2)	152(2)
C=CH$_2$···O=C[a]	124[a]	2.67(1)	3.56(2)	143(1)
CH$_2$–CH$_3$···O=C[a]	767[a]	2.761(6)	3.590(7)	137.1(7)
CH$_2$–CH$_3$···H–C[a]	3975[a]			128.6(3)
C–H···O$^{\delta+}$	15	2.78(4)	3.45(5)	121(3)

[a] From ref. 11.

contacts, data quantities sufficient for statistical analysis were found only for the O atoms in OH groups of the cationic fragments **1** and **2**, which represent protonated acetamide and



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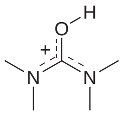

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urea skeletons. In both fragments, the positive charge is delocalized, but this involves only small groups of atoms. Fragments which allow charge dilution over larger atom groups than in urea were generally not considered.

For C–H···O contacts formed by fragments **1** and **2**, the scatterplot of C–H···O angles against the H···O distance is shown in Fig. 2, and some additional information is given in Table 1. The overall appearence of the scatterplot is very different from those obtained for hydrogen bonds. For these, short contacts are associated with relatively linear angles.[1] The shortest contacts in Fig. 2 have H···O distances slightly longer than 2.5 Å, but are all associated with strongly bent angles around 120°. No C–H···O$^{\delta+}$ contact is found which is at the same time short and linear, and relatively linear angles occur only at long distances > 3.0 Å. This could be termed a 'negative directionality', which is clearly incompatible with a hydrogen bond nature of the interaction. In order to compare the typical contact geometry with those of clear C–H···O hydrogen bonds and of C–H···H-C van der Waals contacts, mean distances and angles are listed for H···O < 3.0 Å in Table 2. The van der Waals contacts have isotropic directionality characteristics, associated with a mean C–H···H angle of 128.6°.[11] C–H···O hydrogen bonds are on average more linear than van der Waals contacts, whereas C–H···O contacts of fragments **1** and **2** are more bent, with a mean angle of 121(3)°. This indicates that these C–H···O contacts are neither hydrogen bonds, nor are they of the van der Waals type, but the H atom is rather repelled by the O atom, in a sense pushed out of the way.

A look at Table 1 shows that the data sample is chemically diverse. Most of the C–H···O contacts represent inter-cation interactions, but there are also examples of C–H groups in uncharged molecules. This means that the interaction is not specific to a particular narrow family of molecules, or to cation–cation contacts, but is of more general relevance. Actually, short but bent C-H···O$^{\delta+}$ contacts are found in the CSD also for O-atoms in P = OH$^+$, S = OH$^+$ and H$_3$O$^+$ but for these, the data quantities are too small to allow reasonable statistical analysis. It is of importance that the C–H groups involved are all of the very weakly polar types > CH$_2$ and –CH$_3$ (Table 1), for which the unfavourable electrostatic interaction H$^{\delta+}$···O$^{\delta+}$ is expected to be only relatively weak. The more polar kinds of C–H[3,5] apparently avoid short contacts to O$^{\delta+}$ as efficiently as do the strongly polar groups O–H and N–H.

The data in Fig. 2 and Table 2 clearly show that contacts of the kind C–H···O$^{\delta+}$ should not be considered as hydrogen bonds, even though they are occasionally relatively short. It is not the contact distances that lead to this conclusion, but the contact *directionalities*. A look at the data quantities in Table 2 also shows that short C–H···O$^{\delta+}$ contacts are a rare phenomenon when compared to C–H···O hydrogen bonding. There are two important conclusions: (i) not every single short C–H···O contact occurring in crystals is a hydrogen bond, and (ii) considering only contact distances is an unsuitable approach in the analysis of hydrogen bonds, and of intermolecular interactions in general.

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Notes and references

‡ Cambridge Structural Database (CSD),[13] spring 1998 update with 181 309 entries, ordered and error-free organic crystal structures with *R* < 0.08, H-atom positions normalized.

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