# Strength and Linearity of C–H · · · O Bonds in Molecular Crystals: a Database Study of Some Terminal Alkynes

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An analysis of 105 and 622 C–H · · · O bond geometries retrieved from 69 alkyne and 131 alkene structures in the Cambridge Structural Database shows that more acidic C–H groups tend to form stronger bonds but that even weak C–H · · · O bonds have pronounced linearity.

There is evidence that C–H · · · O interactions are electrostatic in nature,[1—5] and if these weak interactions are indeed 'hydrogen bond-like,' they should be shorter and possibly more linear, the more acidic the C–H group. Accordingly, it has long been supposed that terminal alkynes should form strong C–H · · · O bonds.[6] Early crystallographic studies by Sim failed to support this suggestion fully, mainly because (in retrospect) the number of examples studied was insufficient.[7,8] More recently, C–H · · · O bond lengths in nine terminal alkynes were correlated with corresponding $\nu_{C-H}$ values.[9] This communication deals with the analysis of a much larger number of C–H · · · O geometries in 69 alkyne and 131 alkene structures which were retrieved from the Cambridge Structural Database.[10]

The third version of the Database (69691 entries) is particularly well-suited to the analysis of intermolecular geometry. The search question for all error-free, diffractometer-data crystal structures with $R < 0.10$ containing a –C≡C–H residue with a non-bonded contact to an oxygen atom such that the C · · · O distance $d$ lies in the range $2.8 < d$

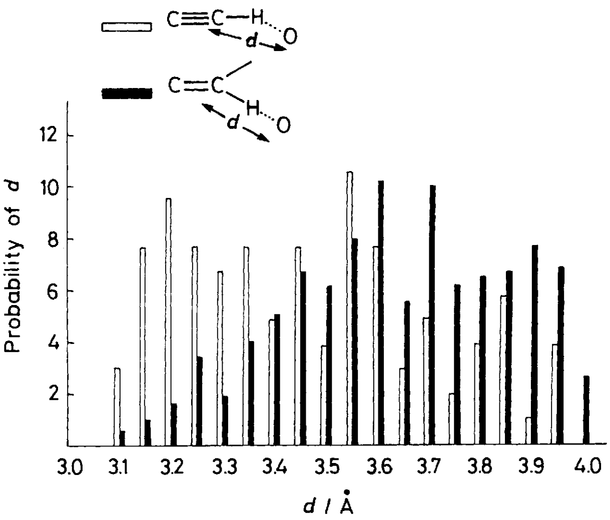

**Figure 1.** Histogram of C ··· O distances ($d$) for C–H ··· O hydrogen bonds from alkyne (unshaded) and alkene (shaded) C–H groups. The populations are expressed as percentages of observations (probabilities). The bars at, say 3.5 Å, represent contacts between 3.475 and 3.525 Å.

$< 4.0$ Å and with a C–C ··· O angle $\phi$ such that $75 < \phi < 180°$, yielded 105 such contacts. Restricting the range of $\phi$ ensures that the contact is of the C–H ··· O type. A similar query was framed for contacts from a $-\overset{|}{C}=\overset{|}{C}-H$ residue to an oxygen atom. In view of the larger number of anticipated hits, only ordered structures with $R < 0.075$ were considered whereupon 622 hits were obtained.

Figure 1 is a graphical representation of these results. The mean $d$ values for C ··· O distances from –C≡C–H and $-\overset{|}{C}=\overset{|}{C}-H$, 3.46 and 3.64 Å, cannot be accounted for on the basis of differing C–H bond lengths in the two cases. Further, Figure 1 shows that the two histograms are considerably offset and that most of the shorter contacts in the range 3.00—3.40 Å arise from alkyne C–H groups. However, the alkyne $d$ distribution is bimodal in that there are also 'normal' or longer contacts in the range 3.45—3.75 Å. In contrast, most of the C–H ··· O contacts from alkene C–H groups may be considered 'normal' since they are clustered in a unimodal distribution in the range 3.4—4.0 Å. Even the small number of alkene C–H ··· O contacts in the range 3.1—3.4 Å seem to arise from compounds where the hydrogen atoms are more acidic than usual (a typical example being VDURID, 5-vinyl-2′-deoxyuridine,[11] $d = 3.19$ Å).

In both cases, the C–C ··· O angles $\phi$ are readily obtained from the crystallographic data. These values, along with those of the mean $d$ obtained above, were used to estimate the C–H ··· O angles, $\theta$, assuming that the C–C–H angles are 180 and 120° for alkynes and alkenes respectively and that the C–H distance is 1.08 Å.[1] It is known that the probability of occurrence of these $\theta$ angles is a function of $\sin \theta$[2,12] and so the angular distributions were corrected for this geometrical factor. The results in the two cases are revealing; there is a 50% (alkyne) and 60% (alkene) probability that the C–H ··· O angle $\theta$ lies in the range 165—180°, in other words that the C–H ··· O bond is a linear contact. Even though a number of simplifying assumptions have been made in these calculations, the distribution is so strongly biased towards a linear C–H ··· O contact that it is noteworthy. A fact which is of even greater significance is that the weaker (longer) C–H ··· O contacts from alkene C–H groups are as linear as (in fact slightly more linear than?) the shorter contacts from alkyne C–H groups. Taylor and Kennard have shown that C–H ··· O contacts are, in general, linear while C–H bonds tend to point in the direction of the oxygen lone pairs for both $sp^3$ and $sp^2$ hybridised oxygens.[1] The present study shows that these characteristics are shared by both strong and weak C–H ··· O bonds. In a sense, this is already known indirectly from the large number of crystal structures whose packing arrangements may be understood only by a consideration of weak but directional C–H ··· O interactions.[3,13—15]

It is well known that electrostatic forces between approaching molecules (prior to crystallisation) are effective at distances longer than those at which dispersion forces are important. Therefore the fact that even weak C–H ··· O interactions are directional in nature seems to indicate that they are electrostatic. It is completely possible that they have an orienting effect on molecules before the influence is felt of the van der Waals forces which will eventually determine the packing of hydrocarbon moieties in the crystal. To conclude, C–H ··· O bonds may be said to resemble O–H ··· O and N–H ··· O bonds far more than has been supposed generally. Further, C–H ··· O bonds, even when quite long, do not seem to lose their linear character. Finally, it is in order to comment on the great utility of the Cambridge Structural Database in transforming crystallographic information into chemical information.

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