Reduction of Thermal Vibrations by C–H···X Hydrogen Bonding: Crystallographic Evidence for Terminal Alkynes

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For 51 terminal alkyn groups in 42 crystal structures, the correlation of displacement parameters with C–H···X hydrogen-bond distances shows that thermal vibrations are reduced due to hydrogen bonding even for long C···X separations between 3.6 and 3.8 Å and H···X separations between 2.6 and 2.8 Å.

It now is widely accepted that it is reasonable to classify cohesive C–H···X interations as 'hydrogen bonds', [1–3] and numerous examples have been reported where they decisively influence crystal packing arrangements and coordination geometries.[4–6] Neutron diffraction data of crystalline hydrates have shown that for hydrogen bonds donated by water molecules, thermal vibrations of the donor are reduced and crystallographic displacement parameters correlate with the hydrogen-bond distances.[7] In the present study this effect is shown the first time for a C–H hydrogen-bond donor.

An earlier attempt to find a dependence of H-atom thermal displacement parameters on H···O separations in C–H···O interactions in carbohydrate neutron crystal structures showed no obvious correlation;[8] this might be due to the rigidly confined orientation of the studied C(sp^3)–H groups. A more promising model system to detect the anticipated effect are the terminal alkynes; this is because the –C≡C–H group is one of the strongest (*i.e.* most acidic) C–H hydrogen bond donors[9] and at the same time it exhibits pronounced vibrational freedom. Geometric and spectroscopic properties of C≡C–H···X interactions have been surveyed previously[3,10] and will not be discussed here.

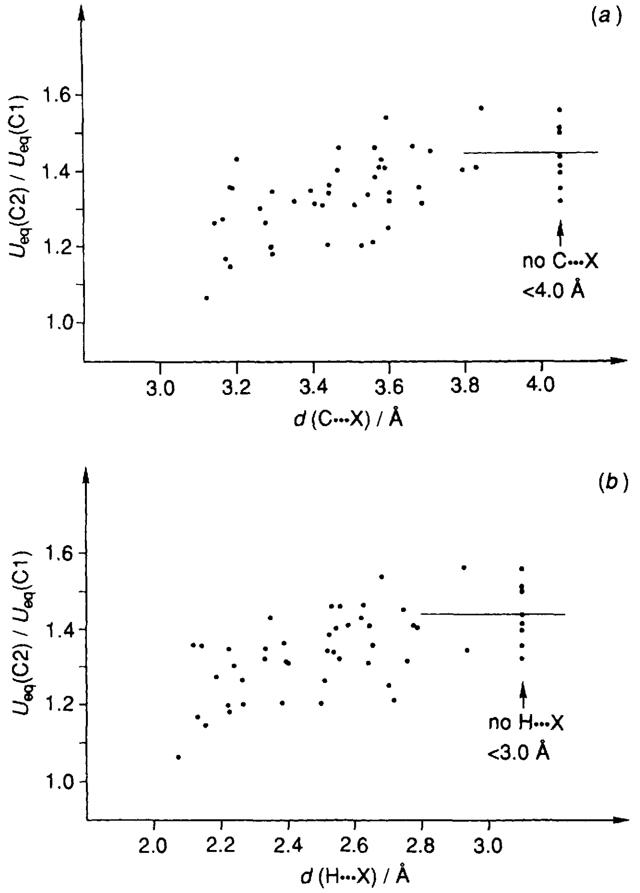

Fig. 1 (*a*) Correlation of the quantity $U_{eq}(C2)/U_{eq}(C1)$ of C≡C–H groups with the C···X distance (angle at H is always >90°). For three-centre hydrogen bonds, only the component with the shorter H···X separation is considered. The horizontal line shows the mean value for C≡C–H groups with no C···X contact shorter than 3.8 Å (Table 1). (*b*) Correlation of $U_{eq}(C2)/U_{eq}(C1)$ with the H···X distance for 'normalized' H positions: as the location of H is determined unreliably with X-rays, theoretical H positions based on linear C≡C–H groups and a C–H bond length[13] of 1.07 Å are used. The horizontal line shows the mean value for C≡C–H groups with no H···X contact shorter than 2.8 Å (Table 1).

The appropriate method to correlate thermal vibrations of a fragment –C1≡C2–H with hydrogen bonding is to study the mean-square displacements of C1, C2 and H perpendicular to the C≡C bond after subtraction of effects due to rigid-body librations of the molecules as a whole. This method is tedious[7] and requires the anisotropic displacement parameters U_{ik}. In most crystal-structure publications, only the equivalent isotropic displacement parameters U_{eq} (*i.e.* spherical approximations) are given; for the H atom, U values cannot be reliably determined from X-ray diffraction at all. Consequently, a simpler method of analysis has to be used, which is based only on U_{eq} of C1 and C2. The absolute values of U_{eq} are not useful in this context, as rigid-body vibrations cannot be subtracted. The ratio $U_{eq}(C2)/U_{eq}(C1)$, however, at least qualitatively reflects the vibration behaviour of –C1≡C2–H: if it is close to 1.0, C1 and C2 vibrate with similar amplitudes, indicating that the orientation of the fragment is steady; if it is > 1.0, the terminal C2 vibrates more vigorously than C1, indicating fluctuations of the –C≡C–H orientation. For C≡C–H groups engaged in hydrogen bonding, $U_{eq}(C2)/U_{eq}(C1)$ is expected to become smaller with increasing strength of the hydrogen bond, which confines the C≡C–H orientation.

Crystal structures of terminal alkynes with H atom positions given, C≡C not placed on crystallographic symmetry elements, reported C≡C–H angles > 160° and R <0.07 were extracted from the Cambridge Structural Database[11] (71

Table 1 Mean values of the quantity $U_{eq}(C2)/U_{eq}(C1)$ for given C···X and H···X intervals of C1≡C2–H···X hydrogen bonds [for normalized H positions; see legend of Fig. 1(*b*)]

C···X/Å	*n*	⟨C···X⟩	⟨$U_{eq}(C2)/U_{eq}(C1)$⟩
$d < 3.2$	7	3.16(1)	1.23(4)
$3.2 \leqslant d < 3.4$	9	3.29(2)	1.29(3)
$3.4 \leqslant d < 3.6$	18	3.52(2)	1.35(2)
$3.6 \leqslant d < 3.8$	7	3.68(2)	1.38(2)
$3.8 \leqslant d$	10	—	1.45(3)

H···X/Å	*n*	⟨H···X⟩	⟨$U_{eq}(C2)/U_{eq}(C1)$⟩
$d < 2.2$	6	2.13(2)	1.23(4)
$2.2 \leqslant d < 2.4$	12	2.30(2)	1.29(2)
$2.4 \leqslant d < 2.6$	11	2.52(1)	1.35(2)
$2.6 \leqslant d < 2.8$	12	2.70(2)	1.38(3)
$2.8 \leqslant d$	10	—	1.44(3)

Distances given in Å, standard errors of the mean values given in parentheses.

X-ray crystal structures). Of these, values for displacement parameters are given in the original publications for 51 C≡C–H groups in 42 crystal structures. If anisotropic displacement parameters were given, they were transformed to equivalent isotropic ones. The crystal structures were screened for C–H···X hydrogen bonds with angles at H $> 90°$ (X = O, N, halogens and the midpoint of π-bonds[12,13]). The correlations of U_{eq}(C2)/U_{eq}(C1) with the corresponding C2···X and the H···X separations are shown in Fig. 1 disregarding the nature of X.

Even though there is a considerable scatter of data points, Fig. 1 clearly shows that U(C1)/U(C2) continuously reduces with shortening hydrogen-bond distances, indicating reduction of thermal vibrations (note that C···X and H···X are not equivalent parameters because most hydrogen bonds are bent to some degree). To quantify this behaviour, the data were divided into five sets each with increasing C···X and H···X separations. The mean values of U(C1)/U(C2) smoothly decrease with shorter C···X and H···X separations, Table 1, as the reduction of thermal vibrations gradually becomes more pronounced.

It is of importance that even for the sets with long separations, C···X between 3.6 and 3.8 Å and H···X between 2.6 and 2.8 Å, thermal vibrations are slightly, but significantly reduced compared to C≡C–H groups without (or extremely long) hydrogen-bonding contacts. This (again) clearly shows the long-range character of the C–H···X hydrogen bond. If C–H···X interactions are identifed in crystal structures from geometric parameters, a cut-off value in H···X as long as 2.8 Å, or even longer, is therefore justified and necessary.

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References

1 R. D. Green, *Hydrogen Bonding by* C–H *groups*, Wiley, New York, 1974.

2 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.

3 G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.

4 Z. Berkovitch-Yellin and L. Leiserowitz, *Acta Crystallogr., Sect. B*, 1984, **40**, 159.

5 C. V. K. Sharma, K. Panneerselvam, T. Pilati and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1992, 832.

6 Th. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1993, **115**, 4540.

7 A. Eriksson and K. Hermansson, *Acta Crystallogr., Sect. B*, 1983, **39**, 703.

8 Th. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1992, **114**, 10146.

9 V. R. Pedireddi and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1992, 988.

10 G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1990, 454.

11 F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers and D. G. Watson, *Acta Crystallogr., Sect. B*, 1979, **35**, 2331.

12 A. C. Legon, P. D. Aldrich and W. H. Flygare, *J. Chem. Phys.*, 1981, **75**, 625.

13 R. K. McMullan, Å. Kvick and P. Popelier, *Acta Crystallogr., Sect. B.*, 1992, **48**, 726.