Hydrogen atom behaviour imaged in a short intramolecular hydrogen bond using the combined approach of X-ray and neutron diffraction†

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Received (in Montpellier, France) 5th May 2009, Accepted 8th July 2009
First published as an Advance Article on the web 4th November 2009
DOI: 10.1039/b908915b

The short intramolecular hydrogen bond in dibenzoylmethane has been studied by variable temperature neutron and X-ray single-crystal diffraction. Fourier difference maps have been used to image both the nuclear and electronic density of the hydrogen bond, in addition to determination of the refined positions obtained from the maxima of these densities. The nuclear density obtained from the neutron diffraction data shows an asymmetric position of the hydrogen atom in the hydrogen bond which is invariant as a function of temperature. The electronic density imaged from X-ray measurements, on the other hand, shows a migration of the bonding density from an asymmetric position at low temperatures to an almost centred position at room temperature.

Introduction

It is well known that neutron diffraction is the definitive tool for accurately locating hydrogen atom positions in crystalline materials. However recent work has shown that X-ray diffraction, and in particular imaging of hydrogen atoms using difference Fourier maps, can provide complementary and valuable information on the electron density in materials containing hydrogen bonds.[1] Variable temperature diffraction measurements can often yield interesting trends where the hydrogen is seen to migrate across the hydrogen bond,[1–3] or seen to populate a second position in the form of disorder.[4,5] Of particular relevance here is the class of short, strong hydrogen bonds, which tend to have a characteristic flat single minimum potential surface in which the proton is contained and is therefore often prone to exhibit migration across the hydrogen bond as a function of temperature.[1] These are thus a prime example of potentially "tuneable" hydrogen bonds, whose evolution as a function of environment (chemical or physical) may be able to be harnessed in behaviour such as hydrogen transfer.

Neutron and X-ray diffraction are in fact probing different effects, the former being sensitive to nuclear positions and the latter to the electron density and thus in the case of hydrogen, the bonding density. A systematic combined approach can thus yield a more complete picture of the characteristics of a hydrogen bond. Availability of neutron diffraction is limited, particularly for multi-condition diffraction studies, requiring time at central facilities, and has often been considered a time consuming measurement. However, recent improvements in instrumentation have allowed relatively routine variable temperature and variable pressure measurements to be carried out within a reasonably short allocation of time.[6,7] In particular, using the instrument used in the present work, SXD at ISIS, in many cases a full data set can now be acquired in a few hours with its current complement of 11 area detectors.

In parallel, advances in detector sensitivity for X-ray diffractometers has resulted in routine detection and location of hydrogen atoms where it is often possible to refine both the atomic positions and the isotropic thermal parameters. As is well known, however, the atomic position for a hydrogen atom refined from X-ray diffraction data tends to be drawn towards the atom to which it is bonding resulting in a shorter bonded distance than that which would be observed with neutron diffraction. Where there is some ambiguity about the hydrogen atom behaviour, particularly in the case of disorder and often manifesting in an anomalously large isotropic thermal parameter for the hydrogen atom of interest, direct visualisation of the electron density in the form of Fourier difference maps may yield more insight and a clearer understanding of the behaviour of the bonding density. This can have significant implications for the understanding of bonding effects, for example in strong hydrogen bonds the maximum of the electron density peak may not be fully representative of the bonding density, as demonstrated for the case of urea phosphoric acid.[1] This previous study of an intermolecular hydrogen bond utilised the powerful combination of X-ray and neutron diffraction, and we use the same combination of techniques here in studying a short, strong intramolecular hydrogen bond. Previous work has indicated that this so-called "anomalous" hydrogen atom behaviour frequently occurs in short hydrogen bonds.[8]

β-Diketo resonance-assisted hydrogen-bonded systems have been much studied utilising both experimental and theoretical techniques to develop models for the relative stability of the tautomeric forms.[9,10] A general preference has been found for the enol forms and the keto form is only found to exist where the enol form is sterically hindered.

The title material, dibenzoylmethane, has been extensively studied due to its potential to exist in different tautomeric forms, as the β-diketo tautomer or the β-keto-enol. Three

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† CCDC reference numbers 739586–739597. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b908915b

polymorphs are known and all have been found to exist in the enol form.[11–14] The presence of a geometrically constrained short, strong intramolecular hydrogen bond (O···O ~2.46 Å) creates an enol ring where the hydrogen could be theoretically located closer to either of the two crystallographically distinct oxygen atoms or in a central position.

Since the first structure determination of dibenzoylmethane in 1966,[11] there has been some debate as to whether the hydrogen atom sits in a central location between the two oxygens, or in an asymmetric position. Initial X-ray diffraction measurements were in contradiction,[11,12] but a neutron determination found the hydrogen atom to be placed asymmetrically at room temperature with a large anisotropic thermal parameter observed along the direction of the bond.[15] NMR studies have added to the debate, suggesting the presence of a double minimum potential with a fast exchange between the two tautomers.[16] This, however, could be difficult to observe using a time-averaged technique such as diffraction where the two possible positions for the hydrogen atom in each of the tautomers would be constrained to be located very close to one another due to the fixed geometry of the hydrogen bond.

Experimental

Crystals of dibenzoylmethane were grown from slow evaporation of acetonitrile. X-Ray data sets were collected at 100, 160, 200, 240, 280 and 293 K on a Rigaku R-axis/RAPID image plate diffractometer equipped with an Oxford cryosystems N_2 low temperature device, using graphite monochromated CuKα radiation (λ = 1.54186 Å). Neutron data were collected on the SXD instrument at the ISIS spallation neutron source, using the time-of-flight Laue diffraction method.[17] This method uses a wavelength-sorted white neutron beam combined with large area position-sensitive detectors to allow a large volume of reciprocal space to be measured in a single-crystal setting or frame. The full data collection process consists of a series of frames collected with a stationary crystal-detector arrangement. The crystal was mounted inside a Displex closed cycle refrigerator on a (ϕ, χ) orienter. At the time of data collection, SXD had two position-sensitive detectors and 20 frames were collected at 100, 160, 200, 240, and 280 K. 43 frames were collected at 123 K.

Dibenzoylmethane crystallises in the orthorhombic *Pbca* space group with Z = 8.‡ Thermal ellipsoid plots showing the neutron and X-ray determined structures at 100, 200, and 280 K are shown in Fig. 1. All other refinement details are available in the CIFs.

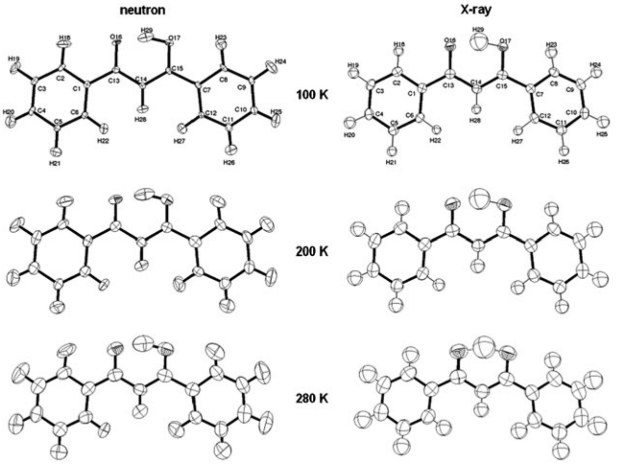

Fig. 1 Thermal ellipsoid plots showing the variation as a function of temperature for both the neutron and X-ray structure determinations. The thermal parameters for the hydrogen atom involved in the intramolecular hydrogen bond are seen to increase in size for both cases the position remains asymmetric for the neutron data but becomes approximately central in the X-ray data at 280 K. The thermal ellipsoids are plotted at the 50% probability level.

Results and discussion

The atomic positions of the heavy atoms show consistency between the neutron and X-ray diffraction structure determinations as would be expected. One of the phenyl rings is almost coplanar with the enol bridge but the other is twisted by approximately 18° at 100 K. This is consistent with the previously determined structures.[11,12,15] The two possible enol tautomers therefore create a different environment for the hydrogen atom involved in the intramolecular hydrogen bond. The phenyl rings both show a tendency to move towards a more coplanar conformation as the temperature is increased.

The neutron crystal structure does not show any unusual behaviour of the short, strong hydrogen bond as a function of temperature. The thermal ellipsoid is significantly elongated along the hydrogen bond at all temperatures and this elongation increases in size as the temperature is increased as would be expected. However the centre of the nuclear density appears to be invariant through the temperature range studied adopting an asymmetric position within the hydrogen bond (Fig. 2 (top)). This suggests that the potential surface for the hydrogen can be described as a weakly asymmetric flat single minimum characteristic of such a short, strong hydrogen bond and consistent with that previously suggested by Gilli *et al.*[9]

The electron density associated with the hydrogen atoms, found using the difference Fourier synthesis from the X-ray data, yields additional information that further informs our understanding of this hydrogen bond. The position of the maximum of the electron density associated with the hydrogen involved in the hydrogen bond shows a migration of the

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‡ *Crystal data* at 100 K: formula $C_{15}H_{12}O_2$, M = 224.25 g mol^{-1}. All X-ray data were measured on a Rigaku R-axis/RAPID diffractometer (image plate area detector, Cu radiation, graphite monochromator). Neutron data were collected using the SXD instrument at the RAL ISIS facility.[17] The X-ray structures were solved with the program SHELXS[18] and refined using SHELXL.[19] The neutron structures were refined using SHELXL[19] from the previously determined X-ray coordinates. The difference Fourier maps have been generated with WinGX.[20] *X-Ray* (100 K): orthorhombic, space group *Pbca*, a = 8.6251(5), b = 10.6442(8), c = 24.3193(16) Å, V = 2232.7(3) $Å^3$, Z = 8, ρ = 1.334 g cm^{-3}, μ = 0.704 mm^{-1}, F(000) = 944. A total of 7911 reflections ($6.85° < \Theta < 58.93°$) were collected, 1580 unique (R_{int} = 0.0222), R = 0.0356 for 2541 reflections with $I > 2\sigma(I)$ and R = 0.0328 for all reflections, ρ_{el} (max, min) = 0.113 and −0.160 e $Å^{-3}$. *Neutron* (100 K): orthorhombic, space group *Pbca*, a = 10.6442(8), b = 24.3193(6), c = 8.6251(5) Å, V = 2232.7(3) $Å^3$, Z = 8, ρ = 1.333 g cm^{-3}, F (000) = 53. 1473 reflections were collected (1473 unique), R = 0.0777 for all 1473 reflections, ρ (max, min) = 0.141 and −0.151 fm $Å^{-3}$.

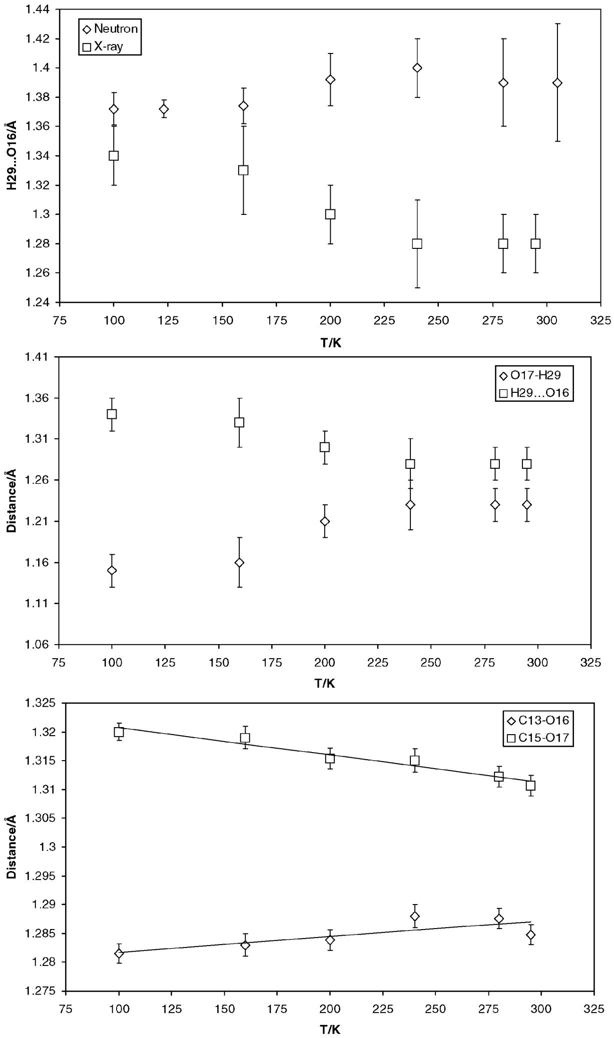

Fig. 2 (top) The variation in the H···O hydrogen bond distance as a function of temperature for both the neutron and X-ray diffraction refined structures. The neutron distance remains invariant through the temperature range studied but the X-ray data show a shortening on increasing temperature; (middle) the variation of the hydrogen bond O–H and H···O distances as a function of temperature for the X-ray data sets. The distances are calculated using the hydrogen atom position located by the maximum in the Fourier difference map; (bottom) the variation in the double bond and single bond C–O distances for the X-ray data set. The double bond is seen to lengthen and the single bond to shorten.

position of this density from an asymmetric position within the hydrogen bond at low temperatures, to an almost central position at higher temperatures, also borne out in this case by the hydrogen atom position refined directly from the X-ray data (Fig. 2 (middle)). This is a measure of the bonding density rather than the nuclear density as obtained from neutron diffraction. The size of the isotropic thermal parameter is larger than observed for the other hydrogen atoms in the structure but this is often observed in strong hydrogen bonds. The relative change in size of this isotropic thermal parameter as a function of temperature is consistent with that also observed for the hydrogen atom determined by neutron diffraction, and for the other hydrogen atoms in the structure. This can be seen by comparison of the U_{eq} values from the neutron data with the albeit less reliable U_{iso} values from the refined X-ray structure.

The oxygen–oxygen distance is found to be invariant as a function of temperature. However, the length of the C–O single bond is seen to slightly decrease and the C=O double bond slightly increase, an indication of these bonds becoming, respectively, slightly more double bonded in character in the case of the single bond and slightly more single in character in the case of the double bond (Fig. 2 (bottom)). Whilst the lengthening of the double bond could be attributed to temperature effects, the relative shortening of the single bond with increasing temperature would not be anticipated. This further suggests a change in bonding density within the cyclic hydrogen bond, with the bonding density tending to become more delocalised as the temperature is increased.

Whilst the hydrogen atom positions determined from X-ray diffraction are less reliable than those found using neutron diffraction, imaging of the electron density of a hydrogen atom through a Fourier difference map can add extra information. Difference Fourier maps were thus calculated for each of the measured X-ray and neutron data sets using the phases generated from a model with the hydrogen atom contained within the short, strong hydrogen bond removed (Fig. 3). In this way any bias introduced by imposing a model for the hydrogen atom behaviour is removed; such imaging of hydrogen atom density has been shown to be effective in allowing an understanding of hydrogen atoms in situations such as this.[1,8]

The Fourier difference maps generated for the neutron diffraction data, probing the nuclear density, clearly show only one maximum for the hydrogen atom at all temperatures. There is no evidence of two positions which would indicate proton disorder and the existence of both tautomers. This is in support of the fully refined positions where the proton position is found to be asymmetrically located at all temperatures. It is still possible that two sites for the proton exist, as suggested by NMR,[16] but the two positions may be located spatially sufficiently close to one another that it is not possible to resolve them from a technique such as neutron diffraction.

The Fourier difference maps calculated from the X-ray data probe the electron density, hence allowing a visualisation of the bonding density in the hydrogen bond. These maps clearly show a well defined, more or less symmetric, distribution of electron density about the central point. The electron density is extended along the hydrogen bond and this is as would be expected for a hydrogen atom involved in a short, strong hydrogen bond. However, the evolution of this density with temperature in the presence of *invariant* nuclear positions suggests that the electron density associated with the hydrogen atom in this case is reflective also of the hydrogen *bonding* density in this material. In this work we make no attempt to model further these data, instead emphasising that the evolution of the electron density reflects both the potential shape and, crucially, changes in the hydrogen bonding electron density.[1] Both the Fourier difference maps and the refined hydrogen atom positions determined

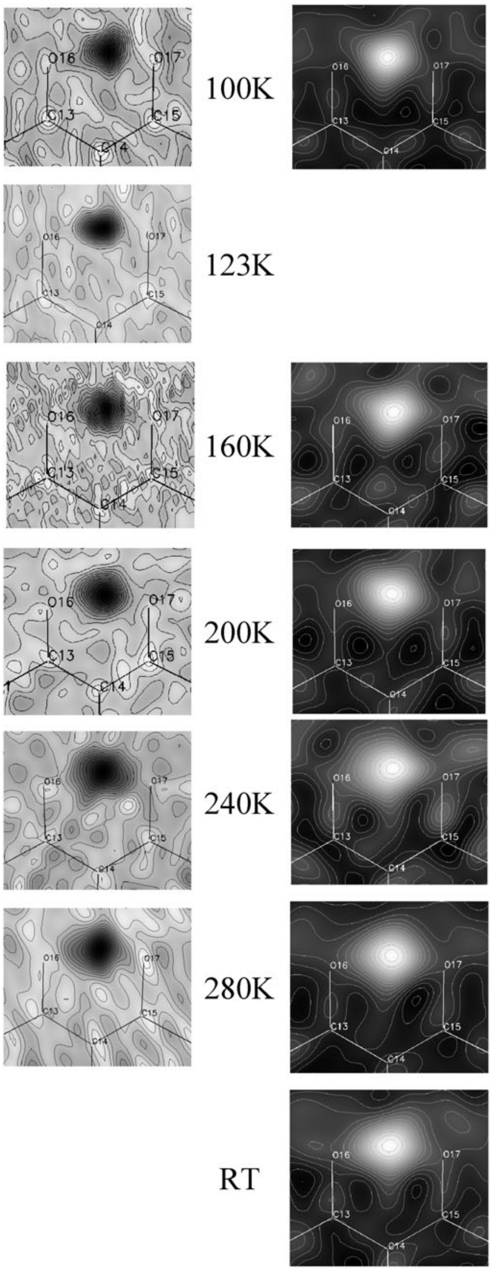

Fig. 3 Fourier difference maps ($F_o - F_c$) obtained at variable temperatures from both neutron (left) and X-ray (right) diffraction data. The X-ray maps were calculated using data collected to a resolution of 0.9 Å^{-1}. All maps were calculated using phases with the hydrogen atom of interest removed from the model and through the plane generated by the atoms O16, O17, C13, C14, and C15. Note that the hydrogen peaks are negative in the neutron diffraction maps.

through the X-ray diffraction data show a trend in the position of the hydrogen atom with the covalent bond length increasing and the hydrogen bond length decreasing until an almost central position is taken at 300 K. This indicates the complementary information available from the neutron data, showing *asymmetric nuclear* positions in the short, strong hydrogen bond and from the X-ray data, showing a *symmetric shared electron density* defining the hydrogen bonds.

Conclusions

Variable temperature neutron diffraction is still the definitive method for determining hydrogen atom positions in systems where there may be interesting evolution of the proton behaviour. However, X-ray diffraction Fourier difference maps are able to add complementary information into the behaviour of the electron density of hydrogen atoms.

For the case of dibenzoylmethane, the neutron data suggest that the nuclear position is invariant as a function of temperature (between 100 and 280 K). However, the X-ray diffraction data suggest that the electron density behaves differently as a function of temperature, moving towards a more central position within the hydrogen bond as the temperature reaches 280 K. This is backed up by the other geometric trends in the structure, the observation that the carbon–oxygen double bond appears to lengthen and the single bond shorten suggesting an increase in the delocalisation around the cyclic intramolecular hydrogen bond. The neutron diffraction data and the X-ray diffraction data are essentially probing different effects, with a consistent interpretation of the observations that the nuclear density does not appear to change as a function of temperature, while the electron density appears to show an increase in the covalent nature of the hydrogen bond. *These combined, variable temperature, neutron and X-ray diffraction observations are thus directly probing the evolving nature of the hydrogen bond.*[1]

This short, strong hydrogen bond is in some sense a special case as it is an intramolecular hydrogen bond and thus constrained to be short by the geometry of the molecule. Previous observations in urea–phorphoric acid[1] have shown that the observed migration of nuclear and electron densities in a short intermolecular hydrogen bond can occur to different extents, but the current work extends this finding by indicating that the electron density in a short intramolecular hydrogen bond redistributes about apparently fixed neutron positions as a function of temperature. Whether a similar effect would be seen in a short, strong intermolecular hydrogen bond remains to be seen. However, the application of combined variable temperature X-ray and neutron Fourier difference maps clearly has the potential to yield interesting insight into the chemistry of hydrogen bonds in a systematic manner.

Acknowledgements

Access to ISIS is provided through STFC. The X-ray data were collected on a diffractometer on loan to the University of Glasgow from Rigaku as part of a diffraction development programme. Kenneth Shankland is thanked for discussion.

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