Temperature dependence of proton transfer in 4-chlorobenzoic acid

Chick C. Wilson,*[a] Xuelian Xu,[b] Alastair J. Florence[b] and Norman Shankland[b]

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The energy asymmetry associated with hydrogen atom transfer in the O–H···O hydrogen bond of crystalline 4-chlorobenzoic acid has been determined from the temperature dependence of the hydrogen atom site occupancy factors, refined using single-crystal neutron diffraction data; the energy asymmetry ($\Delta H^{\circ}/R$) is estimated to be 200 ± 15 K, a factor of *ca.* 2.6 greater than the value obtained for benzoic acid.

Benzoic acid (BA) and 4-chlorobenzoic acid (CBA) both crystallise as hydrogen-bonded (H-bonded) dimers and dynamic H-atom transfer within the H-bonds mediates the interconversion of two inequivalent dimeric forms (see schematic, Table 1). At temperatures below *ca.* 40 K, the dynamics in BA are dominated by incoherent tunnelling and it is the physics of tunnelling (rather than the chemistry of BA) which has made the crystal structure a focus of attention for physicists over the years.[1–5]

NMR relaxometry measurements have provided some of the most accurate values for the energy asymmetry, $\Delta H^{\circ}/R$,† of the double minimum potential in BA.[4,5] Furthermore, independent corroboration of the NMR estimates for BA has been provided through refinement of the site occupancy factors (SOFs) of the disordered H-atoms in the course of a neutron single-crystal structure determination.[6] The consistency between the results of these two independent approaches is illustrated in Fig. 1, which combines NMR and neutron diffraction data for BA in the temperature range 10.8–175 K. The agreement is good, although it is notable that as SOF H1A decreases, and hence the contribution of atom H1A to the overall neutron scattering intensity decreases, the error associated with the diffraction estimate of ln(SOF H1/SOF H1A) in Fig. 1 increases to the extent that data below 28 K are unreliable. In contrast, the precision of the NMR measurement at 16.9 K is excellent, and well maintained down to the lowest temperature in the NMR investigation (10.8 K). A linear fit to the combined data sets yields a value for the energy asymmetry, $\Delta H^{\circ}/R = 78 \pm 2$ K, in good agreement with previous NMR estimates.[4,5] In summary, there are two good reasons for complementing NMR analyses of proton transfer with neutron structure refinement:

(i) the temperature dependence of the refined SOFs provides an independent estimate of the energy asymmetry, in a complementary temperature range;

(ii) the refinement process outputs atomic positional parameters that enable the geometry of the H-bond to be detailed. To this end, neutron diffraction has a clear advantage over X-ray diffraction in that H-atom parameters are determined with superior accuracy and precision in a neutron structure refinement.

The present investigation set out to determine the temperature dependence of the refined SOFs in CBA from single-crystal neutron diffraction data. CBA has recently been studied by NMR relaxometry and the energy asymmetry associated with the double H-atom transfer was estimated to be 187 ± 5 K in the temperature range 37.0–46.5 K *i.e.* a factor of *ca.* 2.4 greater than the corresponding value for BA.[7] The objective of this investigation, therefore, was to provide an independent estimate of the energy asymmetry for CBA. Accordingly, neutron diffraction data were collected on the SXD single-crystal diffractometer at ISIS[8,9] for CBA at five temperatures in the range 100–298 K.[10] Structure refinements were carried out with the GSAS program,[11] using the previously published structure[12] and fully anisotropic displacement parameters on all atoms except the H-bonded atom, H1. The position of this atom was refined over two sites, H1 and H1A, in the manner described previously for BA,[6] with the SOFs constrained to sum to unity and isotropic temperature factors constrained to be equal. Three additional CBA data sets were collected on SXD at 80, 40 and 20 K, in an attempt to get closer to the temperature range of the NMR experiment.[7] However, stable refinements could not be obtained with the two-site model due to the low occupancy of the minor site and these data are not considered further here.

In the refined crystal structure of CBA at 100 K, significant deviations from idealised aromatic geometry include:

(i) a marked widening of the internal ring angle at the C-atom bond to chlorine (121.99(18)°);

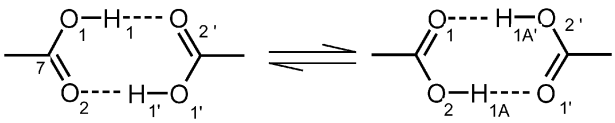
(ii) a concomitant narrowing of the angles *ortho* to this (118.69(18)° and 118.90(19)°).

These marked distortions from the ideal sp^2 geometry are, in fact, entirely in keeping with expectations based on Domenicano's assessment of structural substituent effects in benzene derivatives.[13] Following Domenicano and utilising the angular substituent parameters for –Cl and –COOH, the equivalent predicted internal ring angles of 122.1° and 118.7° are within one standard uncertainty of the observed values.

As with BA, the two dimeric configurations of CBA are energetically inequivalent in the anisotropic crystal field and

[a] *Department of Chemistry and WestCHEM Research School, University of Glasgow, Glasgow, UK G12 8QQ. E-mail: C.C.Wilson@chem.gla.ac.uk; Fax: +44 141 330 4888; Tel: +44 141 330 8522*
[b] *Department of Pharmaceutical Sciences, University of Strathclyde, Glasgow, UK G4 0NR*

Table 1 Selected distances (Å) for CBA in the temperature range 100–298 K (primed and unprimed atoms related by a crystallographic centre of inversion; standard uncertainties in parentheses)[a]



	T/K				
Parameter	298	250	200	133	100
C7–O1	1.272(6)	1.274(7)	1.275(6)	1.282(5)	1.285(3)
C7–O2	1.245(7)	1.244(8)	1.238(7)	1.237(5)	1.229(3)
O1···O2′	2.608(8)	2.583(10)	2.587(8)	2.581(6)	2.588(4)
O1–H1	1.011(17)	0.98(3)	0.983(16)	0.994(10)	0.997(6)
O2–H1A	0.79(4)	0.88(7)	0.79(6)	0.76(7)	0.83(5)
H1···O2′	1.600(17)	1.61(3)	1.607(16)	1.592(10)	1.595(6)
H1A···O1′	1.84(5)	1.71(8)	1.80(7)	1.85(7)	1.81(6)
H1···H1′	2.20(2)	2.15(4)	2.20(2)	2.178(13)	2.206(8)
H1A···H1A′	2.15(6)	2.28(12)	2.34(10)	2.17(10)	2.04(8)
SOF H1	0.754(20)	0.75(4)	0.793(22)	0.882(17)	0.911(12)
SOF H1A	0.246(20)	0.25(4)	0.207(22)	0.118(17)	0.089(12)
H1,1A U_{iso}	0.0621(30)	0.065(5)	0.0481(31)	0.0369(21)	0.0314(12)

[a] For comparison, the O1···O2′ distance in BA at 100 K is 2.606(4) Å.

the energy asymmetry is evaluated from the temperature dependence of SOF H1 and SOF H1A. CBA structure refinements at 100, 133, 200, 250 and 298 K gave SOF H1 = 0.911(12), 0.882(17), 0.793(22), 0.75(4) and 0.754(20). A linear fit to these data (Fig. 2) yields a value for the energy asymmetry, $\Delta H^{\circ}/R$ = 200 ± 15 K, in good agreement with the more precise NMR estimate of 187 ± 5 K, obtained over the complementary temperature range 37.0–46.5 K.

The H-bond distance parameters for CBA are listed in Table 1. As the crystal temperature is decreased from 298 K to 100 K, the observed C7–O1 distance apparently increases (+0.013(7) Å), with an accompanying decrease in the C7–O2 distance (−0.016(8) Å). In fact, this is simply a consequence of the temperature-dependent change in the proportion of the two possible dimer configurations (as evidenced by the trend in the SOFs in Table 1), which results in a temperature-dependent averaging of the observed C–O distances. Otherwise, there is little change in the H-bond distance geometry with temperature and the difference between the largest and smallest measurements of H1···O2′ distance (0.018(32) Å) is not significant. Similarly, in the range 100–250 K, the difference between the largest and smallest measurements of O1···O2′ distance (0.007(7) Å) is not significant (note: no

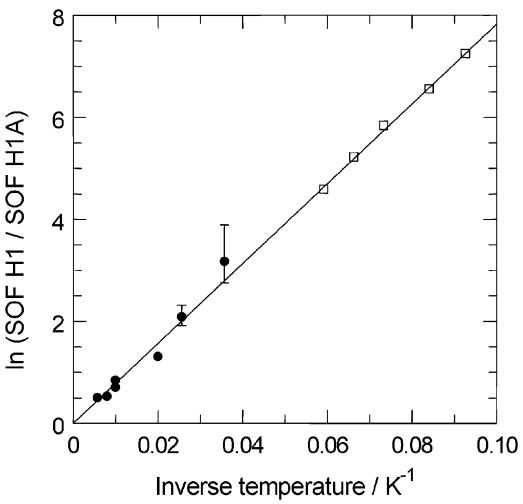


Fig. 1 A van't Hoff plot showing the temperature-dependence of the two dimer configurations of BA. The linear fit to the NMR data (□, 10.8 ≤ *T* ≤ 16.9 K; data from ref. 4) plus SXD data (●, 28 ≤ *T* ≤ 175 K; data from ref. 6, supplemented with additional measurements at 28, 39 and 100 K) gives $\Delta H^{\circ}/R$ = 78 ± 2 K (intercept = −0.005 ± 0.08). Error bars are shown only where the size of the bar is greater than the size of the associated symbol.

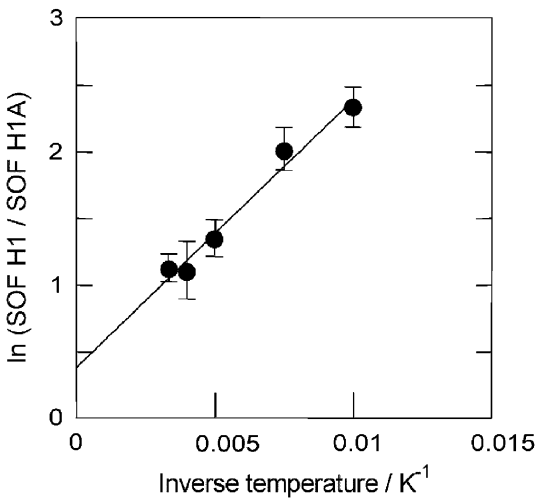


Fig. 2 A van't Hoff plot showing the temperature-dependence of the two dimer configurations of CBA. The SXD neutron diffraction data (●) were fitted to give $\Delta H^{\circ}/R$ = 200 ± 15 K (intercept = 0.38 ± 0.12). Given that there is no evidence of a phase change in CBA over the temperature range of interest, no physicochemical significance is ascribed to the non-zero intercept.

physicochemical significance is ascribed to the slightly longer distance measured at 298 K).

In summary:

(i) the energy asymmetry associated with concerted H-atom transfer within the H-bonds of crystalline CBA has been determined by single-crystal neutron diffraction, independent of NMR relaxometry and over a complementary temperature range;

(ii) the value of the CBA energy asymmetry, $\Delta H^{\circ}/R$, is estimated to be 200 $\pm$ 15 K, in good agreement with the determination from high precision NMR relaxometry analysis.[7]

The agreement between the asymmetry values determined from NMR and single crystal neutron diffraction, previously found for BA, is thus reproduced here for CBA. This confirms the complementarity of these two experimental methods for examining this important proton disorder/transfer phenomenon. Parallel computational modelling of these carboxylic acid systems in the anisotropic crystalline environment is also in progress;[14] preliminary results of this work indicate that the difference in asymmetry values between BA and CBA does not result from electronic distributions within the molecules, but rather from the packing of the dimers in the crystal, and the influence of various intermolecular interactions.

Acknowledgements

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10 Crystal data: $C_7H_5ClO_2$, M = 156.6; needle crystallised from ethanol solution, 2.25 × 1.75 × 1 mm; triclinic, $P\bar{1}$; a = 14.210(6)–14.368(9) Å, b = 6.072(2)–6.132(4) Å, c = 3.747(1)–3.778(2) Å; α = 87.68(3)–87.46(5)°, β = 100.32(3)–100.50(4)°, γ = 93.00(3)–92.94(4)°; V = 317.5(2)–326.7(3) Å^3, Z = 2; T = 100, 133, 200, 250, 298 K; μ(neutron) = 0.63 + 0.79λ cm^{-1}; max. sin θ/λ = 0.52–0.92 Å^{-1}; 1178–3198 reflections measured; 671–1804 unique reflections used in refinements (R_{int} = 0.055–0.070), with 135 refinable parameters; final $wR(F)$ = 0.054–0.064 (all data). It should be noted that the method of data collection occasionally allows for the observation of very high sin θ/λ reflections, even when no real attempt has been made to measure in this region. For that reason, the sin θ/λ limits of the data are diffcult to estimate exactly. CCDC reference numbers 280795–280799. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601123c.
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†The term 'energy asymmetry', expressed in temperature units (K), is chosen to be consistent with the terminology and units used elsewhere in the literature on double H-atom transfer in BA.