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Asymmetric hydrogen bonds in a centrosymmetric environment. III. Quantum mechanical calculations of the potential-energy surfaces for the very short hydrogen bonds in potassium hydrogen dichloromaleate

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In the crystal structure of potassium hydrogen dichloromaleate there are two short hydrogen bonds of 2.44 Å. The 'heavy-atom' structure is centrosymmetric (space group $P\bar{1}$) with centers of symmetry in the middle of the O—O bonds, suggesting centered hydrogen bonds. However, earlier unconventional types of refinements of the extensive neutron data taken at 30, 90, 135, 170 and 295 K demonstrated that the H atoms are actually non-centered in the hydrogen bonds, although the environment is centrosymmetric. Traditionally it has been assumed that the hydrogen distribution adopts the same symmetry as the environment. Reviewing these unusual results it was considered of great interest to verify that the non-centered locations of the H atoms are reasonable from an energy point of view. Quantum mechanical calculations have now been carried out for the potential-energy surfaces (PES) for both the centered and non-centered locations of the H atoms. In all cases the non-centered positions are closer to the energy minima in the PES than the centered positions, and this result confirms that the structure is best described with non-centered H atoms. There is virtually perfect agreement between the quantum-mechanically derived reaction coordinates (QMRC) and the bond-order reaction coordinates (BORC) derived using Pauling's bond-order concept together with the principle of conservation of bond order. [Part I: Olovsson *et al.* (2001). *Acta Cryst.* B**57**, 311–316; Part II: Olovsson *et al.* (2002). *Acta Cryst.* B**58**, 627–631.]

1. Introduction

It seems to be generally assumed that the hydrogen distribution in a centrosymmetric 'heavy-atom' structure adopts the same symmetry as the environment and that the H atom is accordingly located precisely at the center of symmetry (or is statistically or dynamically distributed around the center). In the following the term 'centered H atom' is used to describe a situation where the H atom is located at the center of symmetry and on the O···O line. In order to test whether this is a strict rule, the crystal structure of potassium hydrogen dichloromaleate was earlier determined with neutron diffraction at 30, 90, 135, 170 and 295 K by Olovsson *et al.* (2001, 2002). There are two crystallographically independent H atoms in two very short hydrogen bonds, 2.437 (2) and 2.442 (2) Å at 30 K. Several different types of refinements were applied in the previous investigations, including an unconventional model with all atoms except hydrogen constrained to $P\bar{1}$, but with hydrogen allowed to refine without any constraints in $P1$. The standard uncertainties and significance tests clearly showed that the 'heavy atom' structure is best described as centrosymmetric. However, even when the heavy-atom structure was constrained to be perfectly centrosymmetric the protons still refined to off-centered positions. This structure was described as 'pseudo-centrosymmetric with non-centered H atoms'.

Another remarkable feature was that the H-atom distribution was found to be different at higher temperatures (170 and 295 K) compared with at lower temperatures (30 and 90 K), although no phase transition was observed on lowering the temperature (*cf.* Fig. 1). At higher temperatures one H atom (H2) is closer to one of the maleate ions (*M*), whereas the other one (H4) is closer to maleate ion M^{i} (related to *M* by a center of symmetry). At the lower temperatures both H atoms are closer to M^{i}; for details see Olovsson *et al.* (2001, 2002). At the higher temperatures there are accordingly only dichloromaleate^{-1} ions, whereas at lower temperatures there are dichloromaleic acid molecules and dichloromaleate^{-2} ions in the structure. The heavy-atom structure is practically identical at the different temperatures and there seems to be no obvious reason for this difference in the H-atom distribution. In order to investigate if any abnormal changes could be detected at some intermediate temperature the unit-cell parameters were determined in great detail by X-ray diffraction in the whole temperature range from 30 to 295 K. The data points of the cell parameters as a function of temperature were found to fall on two different straight lines with a sudden change in the slope around 135 K. Attempts were made to observe some phase change at this temperature by DTA and DSC analysis, but the results were negative. It appears likely that the difference in H-atom distribution at the high and low temperatures observed in our earlier investigations is related to the sudden change in the slope of the unit-cell parameters with temperature at 135 K.

Considering the unconventional refinement procedure and the remarkable results summarized above – asymmetric hydrogen bonds in a centrosymmetric environment – it appears of great interest to verify that the non-centered locations of the H atoms in the hydrogen bonds are reasonable from an energy point of view also. Potential-energy calculations have now been carried out as a function of the OH distances for both non-centered and centered locations of the H atoms in the hydrogen bonds.

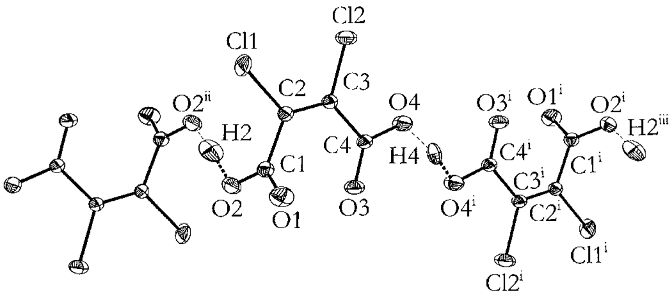
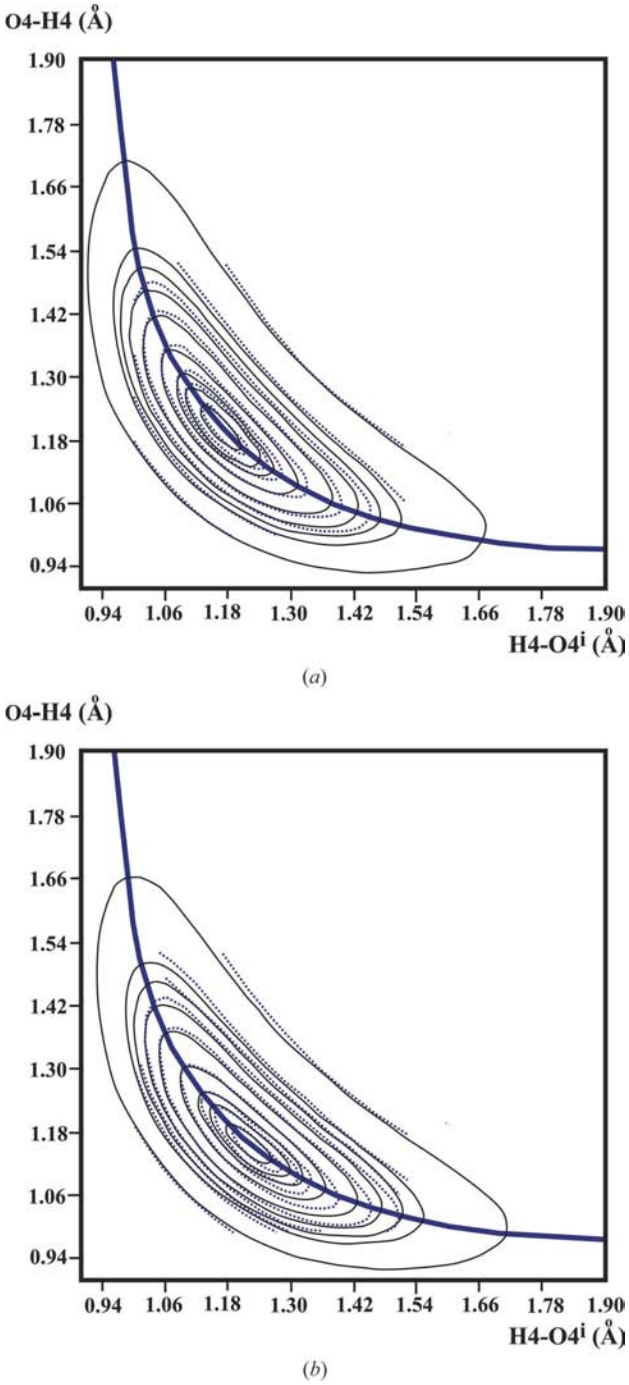


Figure 1
The hydrogen bonds and numbering of the atoms in the hydrogen-bonded network. The H atoms are off-centered in a centrosymmetric heavy-atom environment; at 295 and 170 K (as shown) the H2 atom is closer to molecule *M* but H4 is closer to molecule M^{i} (M^{i} is related to *M* by a center of symmetry; atoms are denoted O4$^{\mathrm{i}}$, O3$^{\mathrm{i}}$ *etc.*); at 90 and 30 K both H atoms are closer to molecule M^{i} (figure reproduced from Olovsson *et al.*, 2002). Symmetry codes: (i) $-x-1, -y-1, -z+1$; (ii) $-x, -y, -z$; (iii) $x-1, y-1, z+1$.



(*a*)

(*b*)

Figure 2
Comparison of the energy plots as a function of the OH distances for O4H4O4$^{\mathrm{i}}$ at 30 K calculated at the B3LYP/6-31G** and B3LYP/6-31++G** levels of theory (solid and dotted lines, respectively). (*a*) Non-centered proton location and (*b*) centered proton location in the hydrogen bond. Contour levels: 0.4, 1.3, 2, 4, 8, 13, 17, 21, 42 kJ mol^{-1} (0.1, 0.3, 0.50, 1, 2, 3, 4, 5, 10 kcal mol^{-1}).

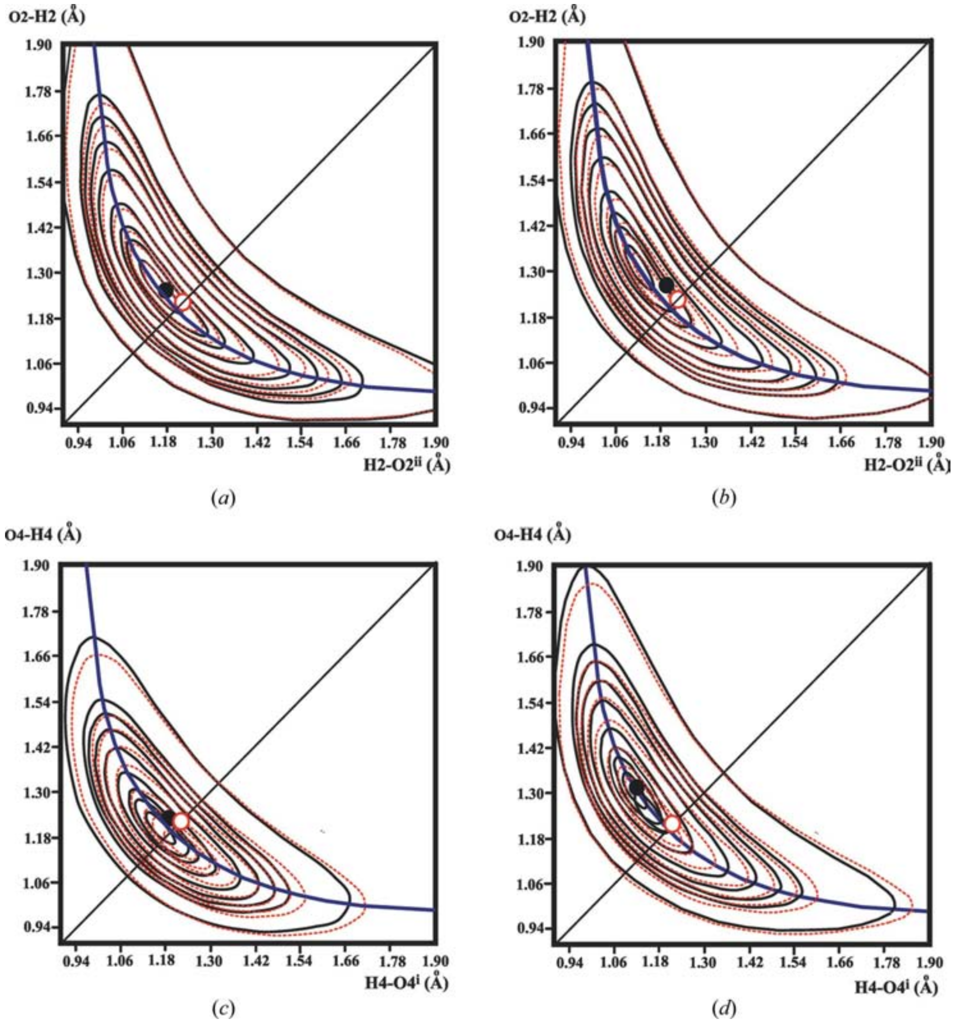
2. Theoretical calculations

2.1. Potential-energy surfaces (PES)

Quantum chemical calculations were carried out using the *GAUSSIAN*03 (Gaussian Inc., 2004) system. The calculations were first made at the B3LYP/6-31G** level of theory for an extended OH range (0.90–1.90 Å). As it may be argued that this method is insufficient to obtain reliable PES, the calculations were subsequently repeated in a more limited range of OH, in which the minimum is located (1.00–1.50 Å) at the B3LYP/6-31++G** level, including the diffusion functions. It turned out that both levels of calculation give almost identical PES.

The crystallographically determined coordinates for all atoms, except the H atom involved in a hydrogen bond, were kept fixed and the potential-energy surface was generated for oxygen–hydrogen distances in successive 0.01 Å steps. The calculations were performed for both hydrogen bonds in potassium dichloromaleate ($O2H2O2^{ii}$ and $O4H4O4^{i}$, *cf.* Fig. 1) using the experimental neutron structure solved with non-centered and centered locations of the protons. The proton was then moved along the O2—H2 and $O2^{ii}$—H2 directions in the first hydrogen bond, and along the O4—H4 and $O4^{i}$—H4 directions in the second hydrogen bond, where these directions were defined by the oxygen and hydrogen positions taken from the structure determination. The structure in the calculations has included the two dichloromaleate anions directly involved in the hydrogen bond in question and two potassium cations closest to the hydrogen bond.

The minimum-energy proton transfer path has been derived by locating the points of lowest energy in the theoretical potential energy diagram (‘the reaction coordinates’, QMRC) and fitting a curve through these points. The crystallographically determined position of the H atom is marked in the PES diagram as a filled circle for the non-centered and an unfilled circle for the centered location of the proton.



(*a*) (*b*) (*c*) (*d*)

Figure 3
Comparison of the energy plots as a function of the OH distances for potassium dichloromaleate. (*a*) $O2H2O2^{ii}$ at 30 K, (*b*) $O2H2O2^{ii}$ at 295 K, (*c*), $O4H4O4^{i}$ at 30 K, (*d*) $O4H4O4^{i}$ at 295 K. Full-drawn lines: non-centered proton; dotted lines: centered proton location in the hydrogen bond. The filled and unfilled circles correspond to non-centered and centered locations of the proton, respectively. The BORC curve is drawn as a thick line; the QMRC curve is indistinguishable from the BORC curve. Contour levels: 0.4, 1.3, 2, 4, 8, 13, 17, 21, 42 kJ mol^{-1} (0.1, 0.3, 0.50, 1, 2, 3, 4, 5, 10 kcal mol^{-1}).

2.2. Bond order

A general introduction to the application of Pauling's bond-order concept and the derivation of the bond-order reaction coordinates (BORC) has been given in previous papers (Olovsson, 2006; Majerz & Olovsson, 2007). The BORC curve is the general, theoretical reaction path which should be followed by the proton moving along the hydrogen bond. The selection of parameters in the Pauling relation $d(\rho) - d(1) = \Delta d = -a\ln\rho$, where $d(\rho)$ is the interatomic distance for a fractional bond with bond order ρ and $d(1)$ is the corresponding single bond length, has been described for different types of hydrogen bonds in a previous paper (Olovsson, 2006). For OHO hydrogen bonds the following reference distances were selected: $d(l)$ = 0.957 Å, the spectroscopically determined equilibrium value (r_e) for the O—H distance in the free water molecule (Benedict *et al.*, 1956), $d(0.5)$ = 1.200 Å, half the distance in a symmetrical O--H--O bond, which has been set equal to 2.400 Å; this is considered to be a representative experimental value for the shortest linear bonds of this type. These values give $a(\mathrm{O}) = 0.351$ Å. The BORC curve for OHO bonds is obtained by plotting $R(\mathrm{O1H}) = 0.957–0.351 \ln(1 - \rho)$ *versus* $R(\mathrm{O_2H}) = 0.957–0.351 \ln\rho$, with ρ taken in suitable small steps.

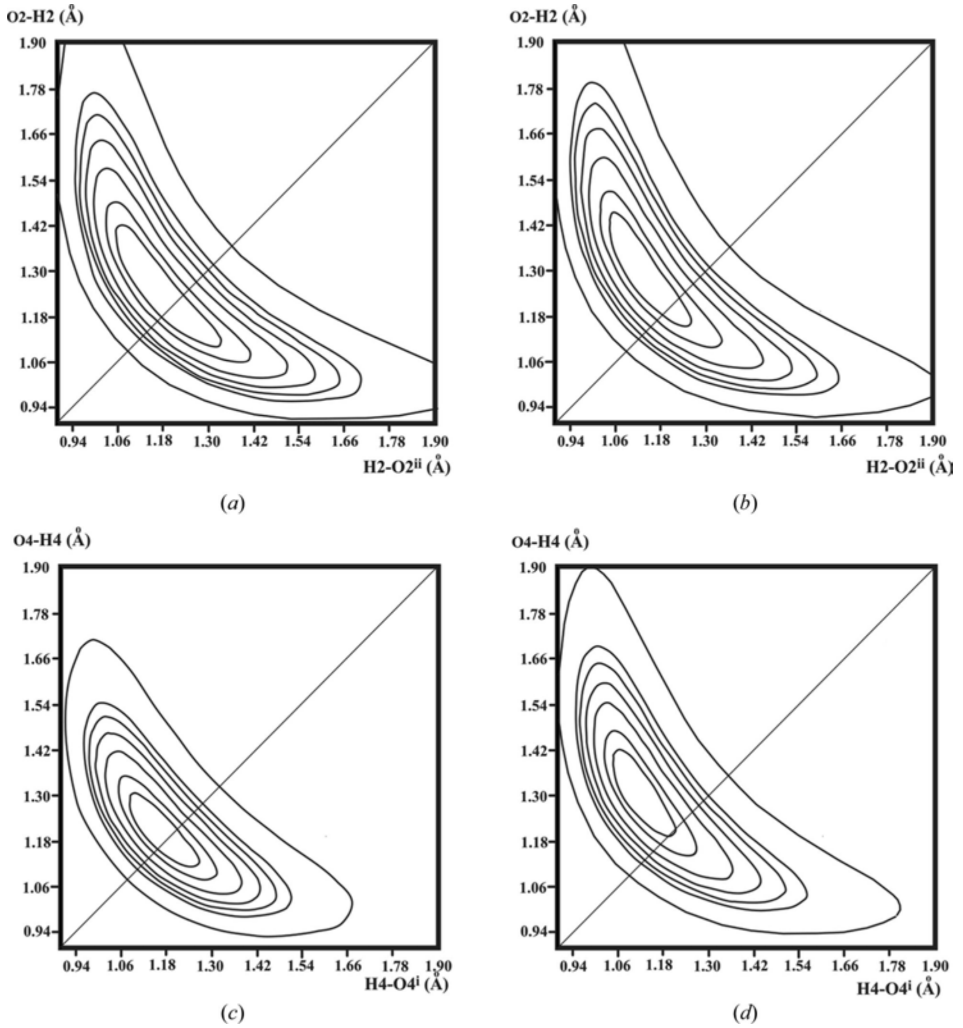
3. Results

The hydrogen bonds and numbering of the atoms is shown in Fig. 1. A comparison of the potential-energy diagrams calculated at the B3LYP/6-31G** and B3LYP/6–31++G** levels of theory is shown for the O4H4O4$^{\mathrm{i}}$ bond at 30 K in Fig. 2. The two methods give almost identical PES in the other cases also (in Fig. 3) and are therefore not illustrated here. Figs. 3(*a*)–(*d*) compare the potential-energy diagrams at 30 and 295 K of the non-centered and centered cases (shown with the extended OH range, using the B3LYP/6-31G** method).

The BORC curve for the OHO hydrogen bond in question is included in all the plots. The curve representing the minimum-energy proton-transfer path, QMRC, deviates < 0.01 Å from the BORC curve and is therefore not distinguishable in the diagrams. A location of the proton at the lowest energy also means that the proton is located on the BORC curve. As the BORC curve passes through the energy minima for both symmetric and asymmetric structures both centered and non-centered locations of the proton are allowed from the point of view of conservation of the O—H bond order. The low values of the energy contours in Fig. 3 show that moving of the proton between a centered and non-centered location can be easily realised. It would be expected that for symmetric structures the potential-energy diagram should be mirror-symmetric around the diagonal line drawn in the figures, but for all the analyzed hydrogen bonds the energy minimum is located off the diagonal, not only for asymmetric but even for symmetric hydrogen bonds. This unexpected result means that the position of the proton in the short hydrogen bond would tend to deviate from the center even if the heavy atom structure is centrosymmetric. An important question is why the contours in PES calculated for symmetric structures are not mirror-symmetric around the diagonal line in the OH/HO diagram. It has probably been caused by including into the calculations two potassium cations which are remote from the hydrogen bond, but which can influence the energy, and the proton location in a short hydrogen bond is very sensitive to even small energy changes.

Comparison of the location of filled and unfilled circles relative to the diagonal line in Fig. 3 shows the change in energy if the proton moves away from the symmetry center. When the structure is refined with all atoms except hydrogen in the space group $P\bar{1}$, but with hydrogen allowed to refine without any constraints in the space group $P1$, the non-centered locations of the protons (filled circles) in all cases are closer to the energy minima in PES. This means that even if the energy does not exclude non-centered or centered locations of the protons the fact that the non-centered positions are closer to the energy minimum in PES suggests that these positions are more correct. The full drawn and dotted contours close to the energy minima (the non-centered and centered cases) are most similar for the O2H2O2$^{\mathrm{ii}}$ hydrogen bond.

The temperature evolution of PES in Fig. 4 illustrates the sensitivity of the two hydrogen bonds to temperature. The contour lines for



(*a*) (*b*)

(*c*) (*d*)

Figure 4
Temperature changes of the potential-energy diagrams for the non-centered OHO hydrogen bonds. (*a*) O2H2O2$^{\mathrm{ii}}$ at 30 K, (*b*) O2H2O2$^{\mathrm{ii}}$ at 295 K, (*c*) O4H4O4$^{\mathrm{i}}$ at 30 K, (*d*) O4H4O4$^{\mathrm{i}}$ at 295 K. Contour levels: 2, 4, 8, 13, 17, 21, 42 kJ mol^{-1} (0.50, 1, 2, 3, 4, 5, 10 kcal mol^{-1}).

the O2H2O2^{ii} hydrogen bond do not undergo any essential changes. For O4H4O4^{i} the location of the energy minimum as well as the general shape of the contour lines change significantly. These changes are possibly connected with changes in the asymmetry in the hydrogen bonds: For O2H2O2^{ii} the O—O distance elongates slightly from 2.437 (2) Å at 30 K to 2.453 (2) Å at 295 K. The O2—H2 and H2—O2^{ii} bond lengths are 1.268 (12) and 1.185 (12) Å, respectively, at 30 K; the O2—H2 and H2—O2^{ii} distances are 1.214 (15) and 1.259 (15) Å, respectively, at 295 K. (Note that H2 has moved over from O2^{ii} to O2 at 295 K.) For O4H4O4^{i} the O—O distance is almost the same, 2.442 (2) and 2.445 (2) Å, at the two temperatures, but the asymmetry of the hydrogen bonds is more significantly different with temperature: the O4—H4 and H4-O4^{i} bond lengths are 1.253 (15) and 1.201 (15) Å at 30 K, and 1.327 (13) and 1.129 (13) Å at 295 K, respectively.

The changes in the PES diagrams seem to be sensitive to the location of the H atom in the hydrogen bridge and thus appear to be a very useful tool in deciding between the non-centered or centered location of the proton.

For one particular system the proton moves along the QMRC curve which passes through the points of lowest energy in the theoretical potential-energy diagram. As mentioned earlier QMRC, deviates < 0.01 Å from the BORC curve. The BORC curve is the general, theoretical reaction path which should be followed by the proton moving along the hydrogen bond.

4. General remarks

Potassium hydrogen dichloromaleate is a unique case where it has been possible to refine the proton in a non-centered location in a centrosymmetric heavy-atom structure. It seems quite likely that similar results may also be obtained in other very short and virtually symmetric hydrogen bonds if the same type of refinements are attempted. Naturally it may be questioned if there is in such a case actually a very small deviation from centrosymmetry also in the heavy-atom structure which is so small that it is statistically insignificant. The present PES analysis confirms the experimental results for potassium hydrogen dichloromaleate and the unconventional refinement model used to analyse the experimental neutron structure. The analysis of the PES diagram not only confirms the non-centered location of the proton in the short hydrogen bond, but also shows how far it is from the energy minimum. The lowest contours in the energy plot are far from the plot diagonal. The low values of the energy levels indicate that a non-centered location of the proton may have a neglible effect on the heavy-atom structure.

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