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PAPER

The influence of potassium cation on a strong OHO hydrogen bond†

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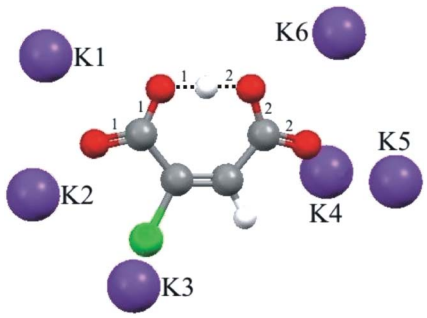
The influence of the potassium cation on the OHO hydrogen bond in potassium chloromaleate was investigated. Theoretical methods commonly used for investigating hydrogen bonds, such as the analysis of electron density at the hydrogen bond critical points, and the calculation of the shape of the potential energy curves and potential energy surfaces, show that the strong OHO hydrogen bond can be modified by the potassium cation located around the chloromaleate anion.

Introduction

Weak molecular interactions can be responsible for molecular conformation or for the packing of molecules in a crystal.[1] When looking for a very weak interaction, the question of whether a cation located in the vicinity of a hydrogen bond can influence the proton and electron density of the hydrogen bridge should be answered. The influence of a remote charge on the hydrogen bond is an important problem in biological systems,[2] and particularly the influence of potassium cations on OHO hydrogen bonds concerns potassium channels and thus transport through membranes.[3]

Because the strongest hydrogen bonds are the most sensitive to environment,[4] the best object for investigating the influence of a cation should be a hydrogen bond that is as strong as possible. The strength of a hydrogen bond decreases in the series starting from OHO through OHN to NHN. Other hydrogen-bonded systems are significantly weaker.[5] One of the strongest OHO hydrogen bonds known so far is the intramolecular hydrogen bond in potassium chloromaleate.[6] In the O···O bridge of length 2.403(3) Å, the proton is located very close to the bridge center, and the O···H distances are 1.206(5) and 1.199(5) Å. The strong hydrogen bond is almost linear, with an OHO angle of 175.4(4)°. The chloromaleate anion is surrounded by six potassium cations close to the carbonyl oxygens and therefore not very far from the proton of the hydrogen bond.[6]

The structure of a chloromaleate anion with a very strong hydrogen bond surrounded by six potassium cations can be used as an example of a very strong hydrogen bond, in which the influence of the cation should be the most significant. The distances of the potassium cations from the chloromaleate oxygen atoms were discussed in ref. 6, but more important are their distances from the proton in the hydrogen bridge. The distances are as follows: HK1 = 4.393, HK2 = 5.372, HK3 = 6.419, HK4 = 5.485, HK5 = 5.423 and HK6 = 3.910 Å. This system allows the checking of whether the potassium cation can influence the hydrogen bond and how short the distance between the cation and the proton should be to influence the hydrogen bond.



Computational details

For the crystal structure of the monochloromaleate anion, as well as the anion with different combinations of potassium cations surrounding it, the proton position and the geometry of the hydrogen bond was optimized at the DFT B3LYP/6-311G(d,p) level of calculation using the Gaussian03 package.[7] The rest of the molecule was kept fixed, as in the solid state. The wave function evaluated for every structure was used as the input to the AIM2000 program[8] with all the default options.

The potential energy curve for proton motion in the hydrogen bridge was performed as adiabatic, with all the atoms fixed for the solid state structure, except for the proton in the hydrogen bridge, the O–H distance of which was successively changed in 0.01 Å steps. The potential energy surfaces were calculated using crystallographically determined coordinates for all atoms except for the H atom involved in the hydrogen bond. The potential energy surface was generated for oxygen–hydrogen distances successively changed in 0.04 Å steps.

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Table 1 Calculated structural parameters (Å, °)

	Optimization of proton position		Optimization of hydrogen bond			
Positions of K^+	OH(1)	OH(2)	OH(1)	OH(2)	O···O	OHO
0	1.4788	1.2576	1.2432	1.1296	2.3709	175.437
1	1.7549	1.0265	1.3996	1.0319	2.4304	176.505
2	1.7328	1.0435	1.3490	1.0490	2.3957	174.914
3	1.6203	1.1338	1.2849	1.0888	2.3714	174.966
4	1.0595	1.7099	1.0612	1.3406	2.4005	176.264
5	1.0727	1.6932	1.0087	1.3295	2.3968	176.145
6	1.0092	1.7750	1.0324	1.3838	2.4153	176.894
1,2	1.8322	0.9692	1.4481	1.0082	2.4549	176.134
1,6	1.2366	1.5010	1.1990	1.1956	2.3934	176.379
2,3	1.7692	1.0157	1.3624	1.0363	2.3961	174.596
3,4	1.0987	1.6611	1.0853	1.3045	2.3881	175.568
4,5	0.9955	1.7933	1.0253	1.3901	2.4143	176.511
5,6	0.9659	1.8334	1.0106	1.4143	2.4240	176.997
1,2,3	1.8532	0.9540	1.4513	1.0030	2.4527	175.803
1,2,6	1.6881	1.0785	1.3580	1.0608	2.4171	175.694
2,3,6	1.1947	1.5477	1.1419	1.2438	2.3833	174.792
4,5,6	0.9326	1.8799	0.9941	1.4425	2.4359	177.072
1,2,3,4,5,6	1.1079	1.6498	1.0760	1.3409	2.4151	175.523

Results and discussion

To investigate if the presence of a potassium cation can influence the hydrogen bond in chloromaleate anions, two methods were used. The first was optimization of the proton position in the separate anion, as well as the anion surrounded by potassium cations located against the anion, as in the solid state. To check which cation most influences the hydrogen bond, optimization was performed for every single cation in the structure. Optimization of the hydrogen bond was performed using two methods. In the first one, the geometry including the O···O distance, was kept constant and only the proton position was optimized. In the second method, optimization was performed for the geometry of the hydrogen bridge. Both optimization methods illustrate situations that can take place in real systems with hydrogen bonds, where the energy can be delivered and modify the hydrogen bond or only the proton can be adapted to the hydrogen bond surroundings. The combinations of cations listed in Table 1 were used. The influence of the cations on the intramolecular hydrogen bond in chloromaleate is seen in the change in OH distances. An additional tool to verify the cation's influence is examination of the AIM parameters,[9] which are very sensitive to the hydrogen bond's strength and are therefore very often used in hydrogen bond investigations.[10]

The second method of investigating the influence of potassium cations on the chloromaleate anion is the calculation of adiabatic potential energy curves for proton motion in the hydrogen bridge for different combinations of potassium cations. If the presence of a cation changes the hydrogen bond, the potential energy curve changes its shape and location of the minimum. Finally, the potential energy surfaces for changing OH lengths in the hydrogen bridge were also calculated for different locations of the potassium cations.

Influence of the potassium cation on the geometry of the OHO hydrogen bridge. The results of optimization of the proton position and the results of optimization of the hydrogen bridge are listed in Table 1. A comparison of the OH distances in a separate chloromaleate anion with those when one or more potassium cations are present shows that every cation located as in the crystal structure changes the position of the proton in the hydrogen bridge. No OH distance listed in Table 1 is identical to that for the separate anion, which means that even the K3 cation, 6.419 Å away from the proton, influences the hydrogen bond. It could be expected that if the distance between the cation and the proton were smaller, the cation's influence would be more significant. This is true only for the shortest and longest distances. The presence of K2, K4 and K5, located at similar distances from the proton, change the OH bond lengths, but this change does not correlate with the H–K^+ distance. An analogous influence of the potassium cation on OH distances is also seen for structures with an optimized OHO bridge geometry.

If the geometry of the hydrogen bond is optimized, the influence of the potassium cation modifies not only the location of the proton between the oxygens but also the O···O distance and OHO angle (Table 1). The changes of the O···O bridge length are related to the difference between the OH distances by the second order polynomial ($O\cdots O = 0.3416d^2 + 0.0081d + 2.3747$, $R^2 = 0.8047$) and are analogous to the experimental results for the hydrogen bonds with a systematic change of the hydrogen bond strength.[11,12] A comparison of the O···O lengths in Table 1 with the experimental value (2.403(3) Å) shows that the presence of the potassium cation can cause both shortening and lengthening of the O···O distance compared to the crystal structure. In the separate chloromaleate anion, the O···O distance is the shortest. Elongation of O···O is connected with the presence of the cations at position 1 and 6, which are very close to the hydrogen bond. Cations at other locations allow shortening of the hydrogen bridge, but not as significantly as for the separate anion. Shortening of the hydrogen bond is connected with its linearization and the location of the proton close to the hydrogen bridge centre.

The influence of potassium cations can change the geometry of the hydrogen bond. If energy is delivered, modification of the O···O bridge is also possible. If this modification is not possible, the presence of the cation is expressed by the shifting of the proton along the O···O bridge. Comparison of the OHs in Table 1 shows that if the hydrogen bridge can be modified, the proton moves in a narrower range around the hydrogen bond centre than for a hydrogen bond in which the geometry is kept constant.

The OH bond lengths listed in Table 1 change over a broad range of values, and the evolution of the values is typical of a changing hydrogen bond strength. In Fig. 1 is shown the correlation linking the two OHs in the chloromaleate anion altered by the presence of the potassium cations listed in Table 1.

The correlation of the optimized proton position in the fixed hydrogen bond is similar, but not identical, to the general correlation linking OH bonds in the OHO hydrogen bridge.[12] The difference is connected with the fact that only the proton position is optimized when the O···O bridge length is kept constant. The proton moves along the quantum mechanical reaction coordinate (QMRC) curve, which for intramolecular hydrogen bonds is not identical to the BORC curve.[13] For systems in which not only the proton position but also the geometry of the hydrogen bridge can be optimized, the OH bond lengths are located along the bond order coordinate curve (BORC). Proton valency in the intramolecular hydrogen bond can be protected if the shifting of the proton is connected not only to the change of OH lengths

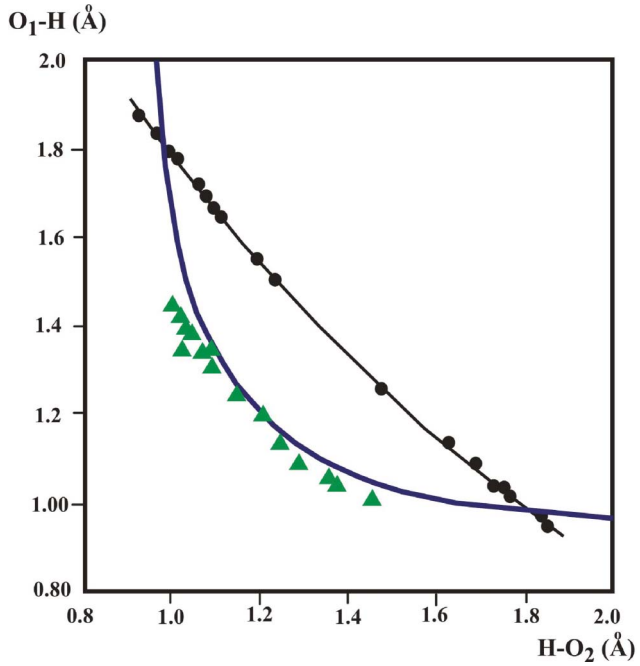

Fig. 1 Correlation between the OH distances in the structures and the optimized proton position. Blue solid line: BORC curve, black circles: optimized position of the proton in the crystal structure, green triangles: optimized geometry of the hydrogen bridge.

but also to the adaptation of the hydrogen bridge. This statement leads to a more general conclusion that a constant proton valency in intramolecular hydrogen bonds is possible in a non-adiabatic process when energy is delivered to the system so that the geometry of the hydrogen bond can be adapted to the shifting of the proton. Although the points obtained in Fig. 1 with optimization of the hydrogen bond parameters follow the BORC curve, they are not precisely located on it. Probably, optimization of the geometrical parameters that are sensitive to the proton transfer could shift the points precisely to lie on the BORC curve.

AIM analysis of the structures with optimized proton positions. Despite the differences in OH evolution in chloromaleate and the BORC curve, it can be seen that the presence of the potassium cations located near the chloromaleate anion can cause proton transfer in the short intramolecular OHO hydrogen bond, and the evolution of the OH bonds is typical of that reflecting changes in hydrogen bond strength. A very good method in theoretical investigations of hydrogen bonds is atom in molecule (AIM) analysis. The most important parameters in AIM analysis are connected with the bond critical points (BCPs). The values of electron density at the BCPs for the bonds participating in the chelate ring formed by the intramolecular OHO hydrogen bond are listed in Table 1 and Table 2 (ESI†), and the correlations of electron densities are shown in Fig. 2. The electron densities are correlated with the difference in the OH bond lengths, which is the best parameter for the strength of the hydrogen bond. For the strongest bonds, the OH distances are equal.

A d value of −1 means that the proton is located at O1 and a value of 1 at O2. The values of the electron density at the BCPs of OH bonds are the most sensitive to hydrogen bond strength. When the proton is located at O1, the BCP of OH1 reaches a maximum

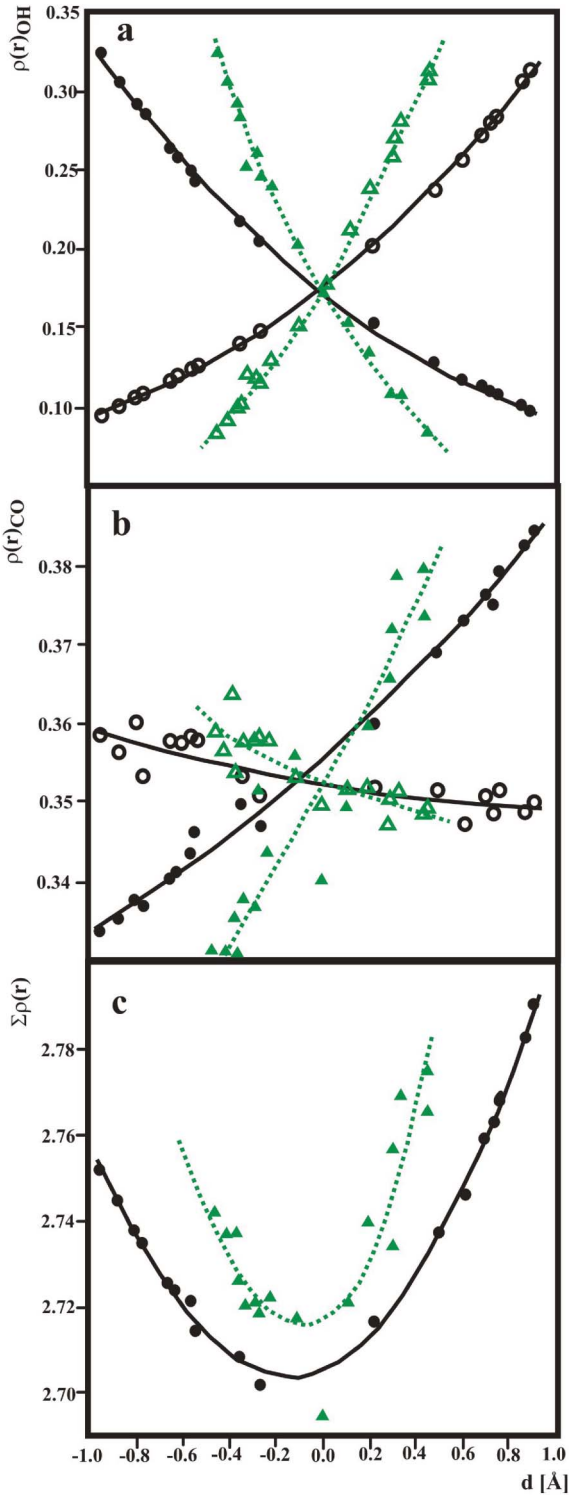

Fig. 2 Correlations of electron densities at BCPs with the difference of OH in the hydrogen bridge d = OH(1)–OH(2); a: BCP of OH, b: C–O, c: sum of electron densities in the chelate ring formed by the OHO hydrogen bond. Black circles: optimized position of the proton in the crystal structure, green triangles: optimized geometry of the hydrogen bridge.

and that of OH2 a minimum. For the strongest hydrogen bond, both values of electron density are equal. This correlation is typical of hydrogen bonds in which the proton's location in the hydrogen

bridge changes because of the different strength of the hydrogen bond.[14] The electron density at the BCPs of other bond lengths is sensitive to proton transfer in the OHO bridge, depending on the location distance to the OH. The electron density of C–O bonds is very sensitive. Correlations for both C–O bonds cross at an equal OH distance, but the correlation lines are different. The correlation for C–O1 is more sensitive to shifting of the proton, which can be caused by the presence of the chlorine atom at the carbon close to the C–O. The C–C and C═C bonds are not sensitive to proton transfer. For C═O bonds, the correlation of electron density with the difference in OH length changes in very limited range and is not clear. Very characteristic is the sum of all the electron densities in the chelate ring formed by the OHO intramolecular hydrogen bond, also including the electron density at the chelate ring's critical point. The parabolic shape of this correlation, with a minimum at zero, suggests that for the strongest hydrogen bond, the very mobile electrons can be easily removed from the maleate anion.

It is characteristic that electron density for the structures with optimized proton positions changes in the same range as the densities for the optimized hydrogen bridge. The correlations in Fig. 2 are different because the OH bond lengths change in a narrower range.

Besides the electron density at the BCPs, AIM analysis delivers other parameters describing the electron density. In Fig. 3 are shown correlations of the ellipticity (ε_b) of the electron clouds at the BCPs of the OH bonds, as well as correlations of the distance of the BCP from the bond center (d(BCP)). The first parameters describe the instability of the hydrogen bond.[15] The shift of the BCP from the bond midpoint indicates polarization of the bond. The location of the proton at the oxygen is connected with high stability and high polarization of the OH bond. Shifting the proton causes an increase in bond instability but a decrease in polarization. A central location of the proton in the hydrogen bridge is needed to equalize the stability and polarization of both OH bonds. A similar trend is represented by the cylindrical symmetry of the electron density at the OH BCPs. Shifting the proton from the oxygen atom to the hydrogen bridge center is connected with decreasing its cylindrical symmetry.

A very important parameter delivered by AIM theory is the potential (V(r)) and kinetic (G(r)) energies of the electrons at the BCP.[16] The potential energy can be interpreted as the pressure exerted on the electrons at the BCP and the kinetic energy as the pressure exerted by the electrons at the BCP. The kinetic energy illustrates the mobility of the electrons. According to the correlation of the two energies for chloromaleate anion shown in Fig. 4, the location of the proton at the oxygen atom is connected with a low value of the potential energy and a high value of kinetic energy. Shifting the proton to the hydrogen bond center is connected with an increase in potential energy and a decrease in kinetic energy. Similarly to the AIM parameters discussed previously for the strongest hydrogen bonds, the energies for both OH are equal.

AIM analysis of the crystal structure with different locations of potassium cations. To check if the electron cloud in the chloromaleate anion can be influenced by potassium cations located in the vicinity, the electron densities at the BCPs of the anion were calculated for different locations of the K^+.

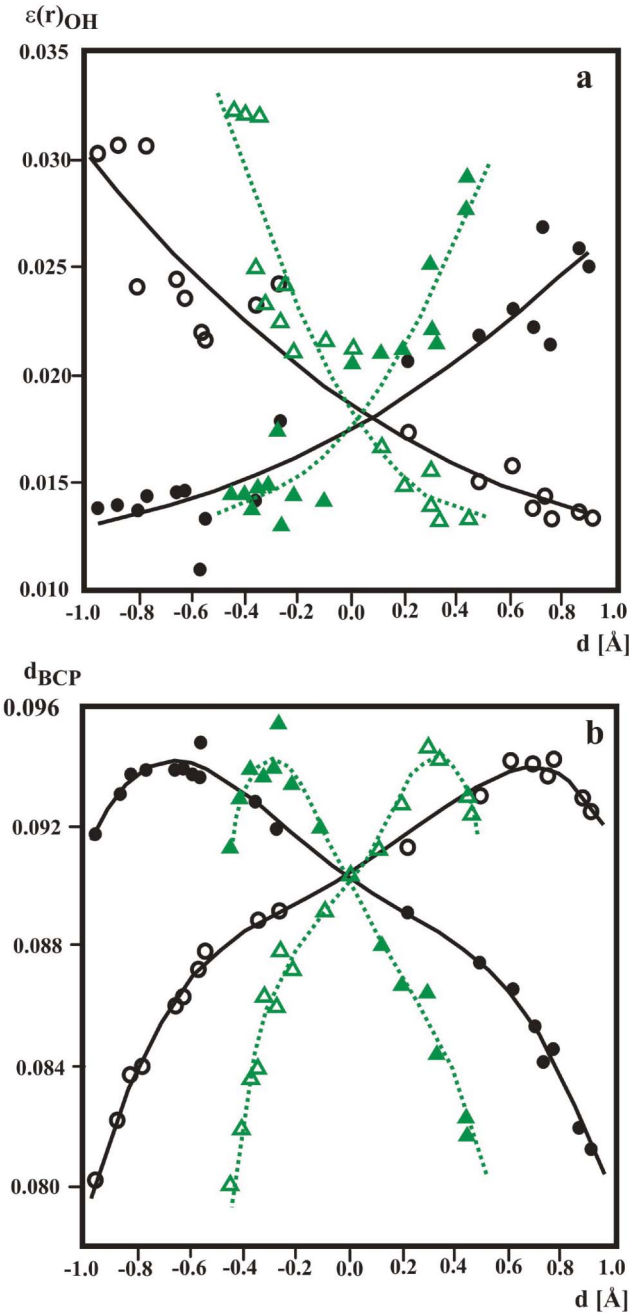

Fig. 3 a: the ellipticity of electron density at BCPs of the OH bonds, b: distance of the BCP from the bond center of OH bonds correlated with the difference between OH distances. Points marked as in Fig. 2.

The electron densities at the BCPs of the OH bonds change in a very narrow range of values, but the influence of the cations is evident. Other bonds of the chloromaleate anion are not sensitive to K^+. The only exception is the C═O bonds, in which the π electrons can be modified by the presence of the cations. The correlation between electron densities at the BCPs of both OH bonds for the structures with the optimized proton position and the solid-state structure is shown in Fig. 5. If the proton is moved by the potassium cations, both electron densities change in a very broad range along a curve analogous to that for the OH bond length. It is characteristic that even if the hydrogen bond can

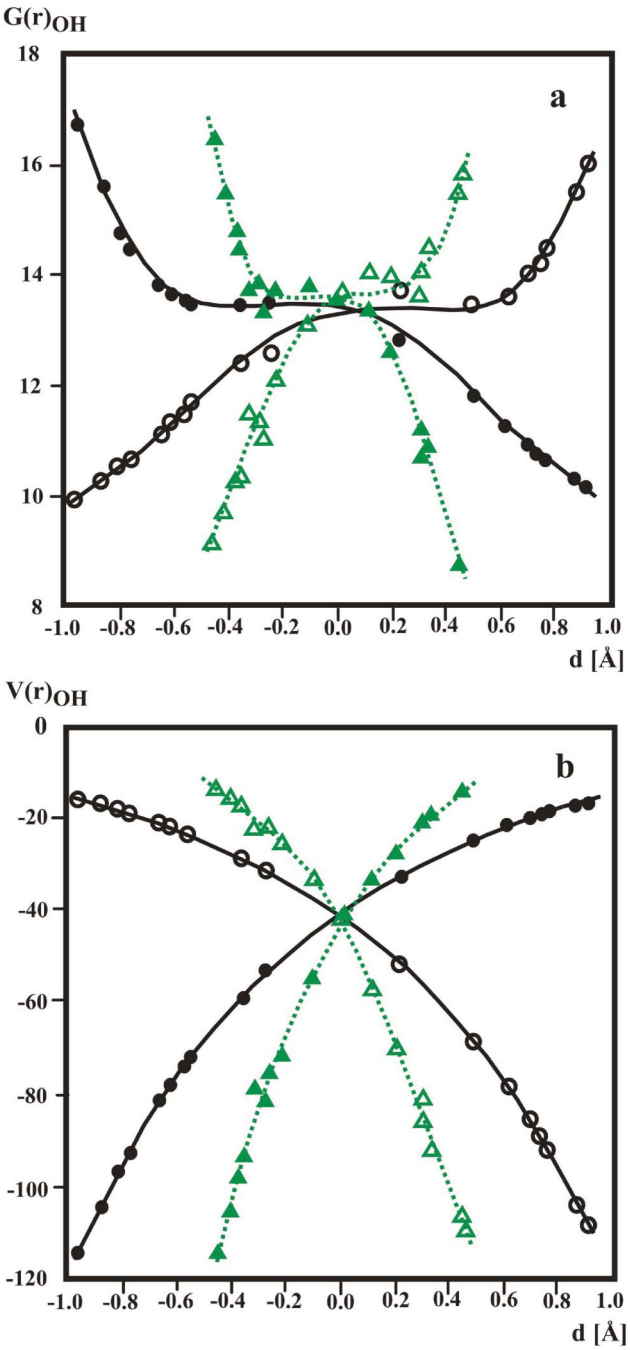

Fig. 4 (a) Kinetic and (b) potential energies of electrons at the BCPs of the OH bonds as a function of the differences in OH distances. Points marked as in Fig. 2.

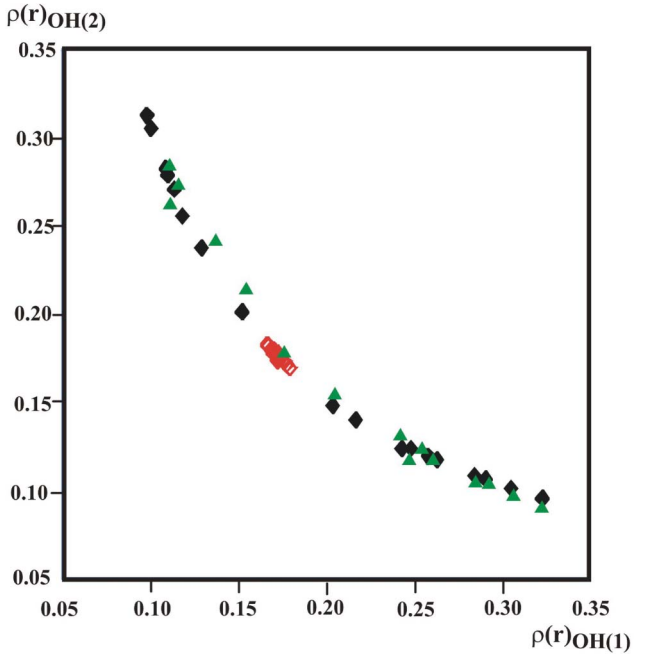

Fig. 5 Correlations between electron densities at the BCPs of OH bonds. Black points: structures with optimized proton position; red: empty points in the center of the correlation, structures with different locations of the potassium cations; green triangles: optimized geometry of the hydrogen bridge.

be adapted to the environment in a non-adiabatic process, the correlation linking both electron densities at the OH critical points is identical to that obtained for the structure in which only the proton can be shifted by the potassium cations surrounding the hydrogen bond. If the structure is kept constant and the cation's presence can only modify the electron cloud without shifting the proton in the hydrogen bond, the change in electron densities is very small, but it is very characteristic that the correlation points are located in the central range of the correlation curve, determined by the moving proton. The electron densities obtained for the structures with a frozen proton position are typical of the strongest hydrogen bonds, which is in agreement with the geometry of the hydrogen bridge in potassium chloromaleate.

Because the electron density at the OH BCPs is very sensitive to the strength of the hydrogen bond, the difference in electron densities can be used as a measure of hydrogen bond strength. For the strongest hydrogen bonds, the two values are identical and the difference is zero. This measure of hydrogen bond strength is used in correlations of the potential and kinetic energy of electrons at OH BCPs. Similarly to the electron density, for optimized proton positions both energies change in a broad range. If the proton cannot be moved, the presence of the cation changes the electron energies in a narrow range that is characteristic of the strongest hydrogen bonds (Fig. 6). If, the difference of the OH bond lengths used as the measure of the hydrogen bond strength is replaced by the difference between the electron densities at OH critical points, the potential and kinetic energy changes along a curve common for the optimized hydrogen bond, as well as for the optimized location of the proton.

Strong hydrogen bonds can be characterized by similar OH bond lengths, but a more sensitive characteristic of the strongest hydrogen bonds is equalization of the electron densities, and of the kinetic and potential energies of the electrons at the BCPs in the hydrogen bridge.

When the proton is kept in a constant position, the presence of cations in the vicinity of the hydrogen bond does not influence the ellipticity of the electrons at the two BCPs in the hydrogen bridge. Similarly, the distance of the BCP from the bond center for both OH bonds, which is a measure of the bond's polarization, does not change and equals about 0.09 Å.

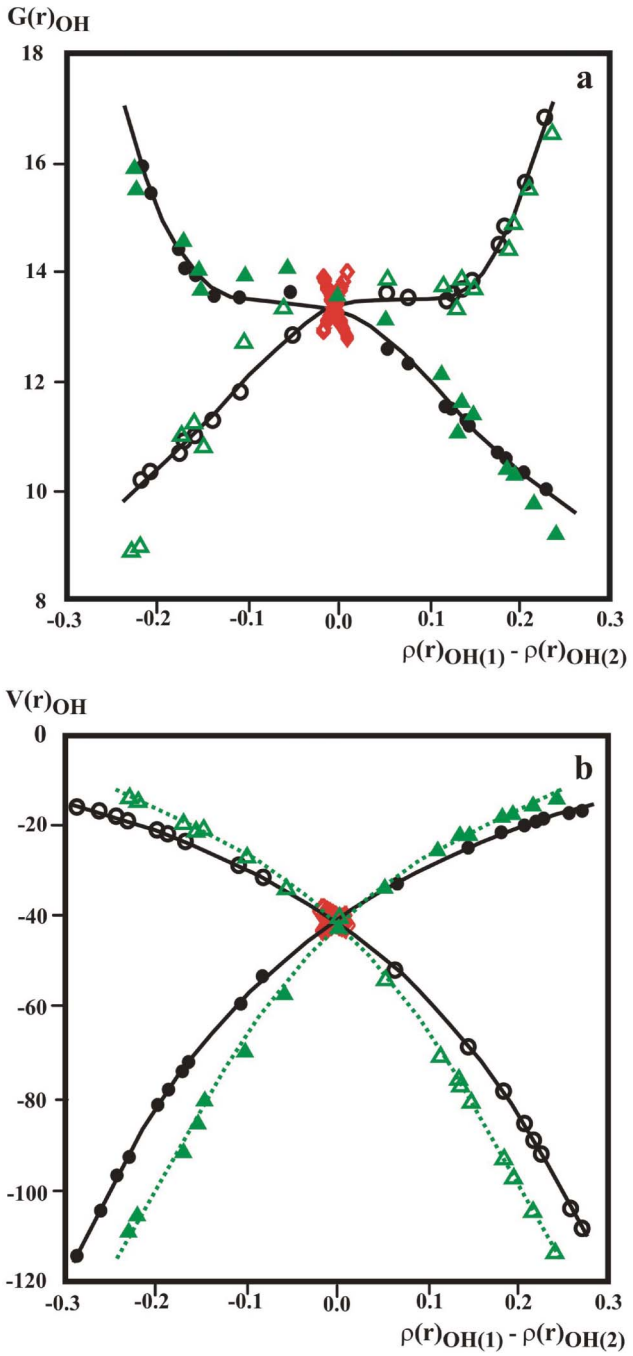

Fig. 6 (a) Kinetic and (b) potential energies of electrons at the BCPs of OH bonds as a function of the difference in the electron densities at the BCP of OH bonds. Points marked as in Fig. 5.

All the correlations of the AIM parameters discussed above are typical of systems with a systematic change in hydrogen bond strength and can be compared with results for hydrogen bonds in which the proton is moved from the donor to the acceptor. In the case of the compound under study, the shifting of the proton is forced by the presence of the cations around the chloromaleate anion instead of a direct changing of the OH distance.

Potential energy curve for proton motion in the hydrogen bridge. The best method to characterize the strength of a hydrogen bond, as well as the location of the proton in the hydrogen bridge, is to investigate the potential energy curve for proton motion from donor to acceptor. The model of the potential energy curve proposed by Lippincot and Schroeder[17] is commonly used to describe the properties of hydrogen bonds. Depending on the type of hydrogen bond, *i.e.* molecular, proton transfer or very strong bond, the potential energy curve is characterized by different shapes.[18] The location of the minimum of the curve suggests the coordinate of the proton in the hydrogen bridge.

It is very well known that the potential energy curve for strong hydrogen bonds is the most sensitive to a change in hydrogen bond geometry, as well as the environment of the compound with the hydrogen bond. For this reason, it is expected that the potential energy curve for proton motion in the strong hydrogen bond in potassium chloromaleate will be sensitive to the environment and thus to the presence of potassium cations. In Fig. 7 are shown the potential energy curves for the separate chloromaleate anion, examples of the curves that are the most shifted from the curve for the anion, and the curve calculated by including the surroundings of the chloromaleate anion, as in the crystal cell. The curve for the separate chloromaleate anion is typical of a strong hydrogen bond. A broad minimum without any barrier is located at the center of the bridge, so both OH distances are equal. The analogous curve including the cations and anions, as in the crystal cell, is an example of a curve for a strong low-barrier hydrogen bond. The two other curves suggest that the hydrogen bond is less strong. Although they are characterized by one minimum, the shape suggests the presence of a second minimum connected with a decreasing hydrogen bond strength. Also, the minima of these curves are shifted from a central location.

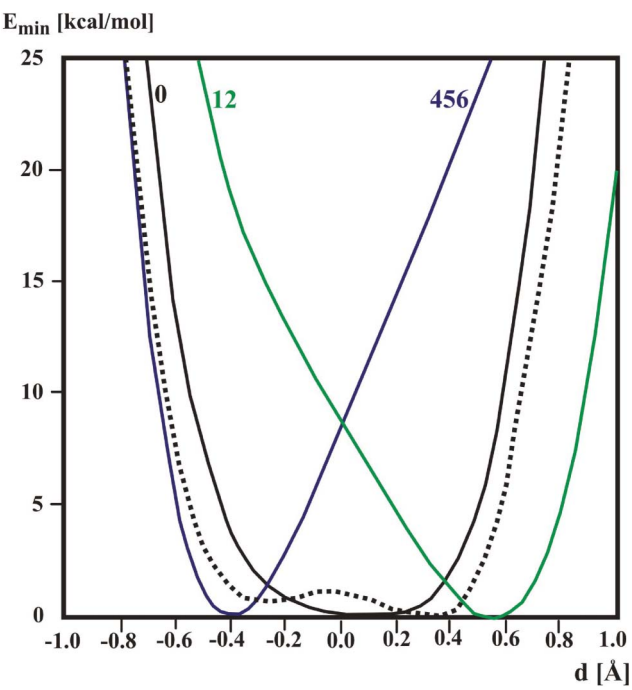

Fig. 7 Potential energy curves for proton motion in the OHO hydrogen bridge as a function of the difference in OH distances. Potassium cations marked according to Tables 1–3 (ESI†). Dotted line: curve for the chloromaleate anion surrounded by cations and anions as in the unit cell of the crystal.

The position of the minimum on the potential energy curve is very well correlated with the optimized position of the proton in the fixed structure. The correlation of the value of OH(1)–OH(2), at which the energy minimum is located, with the OH(1)–OH(2) obtained as the result of optimization is a straight line described as: $y = 0.5289x + 0.0401$ ($R^2 = 0.9799$). Fig. 7 illustrates the influence of the potassium cations located in the vicinity of the hydrogen bond. Whether the surroundings of the hydrogen bond are taken into account or not, the shape of the potential energy curve suggests significantly different strengths of the hydrogen bond. This problem is especially important because of the role of low-barrier hydrogen bonds in biological systems.[19] The first step in the classification of a hydrogen bond as low-barrier is to calculate the potential energy curve. The results for potassium chloromaleate exhibit the problem of including the surrounding cations. In the case of a strong hydrogen bond, neglecting the environment significantly influences the shape of the potential energy curve.

Potential energy surface. Because shifting the proton from donor to acceptor is connected with changes in both OH distances, information about the hydrogen bond is contained in the diagram of the potential energy calculated as a function of the two OH bond lengths. The proton is moved along the quantum mechanical reaction coordinate (QMRC) curve, which for an intermolecular hydrogen bond is identical to the bond order reaction coordinate (BORC), the line of proton movement that conserves its valency as 1.[20] For an intramolecular hydrogen bond, the BORC and QMRC curves are usually different,[13] and the reasons for this difference are not fully investigated. In the case of the chloromaleate anion, it is interesting to check if the presence of the potassium cations in the vicinity of the strong OHO hydrogen bond is reflected in the shape of the potential energy surface.

The potential energy surface for the chloromaleate anion, shown in Fig. 8, is typical of intramolecular hydrogen bonds. The QMRC curve is not identical to the BORC curve, and only in the central part of the diagram where the energy minimum is located are the two curves close to each other. The QMRC curve is located in the region of lower OH values compared with the BORC curve, which is characteristic of intramolecular hydrogen bonds with OHO angles characteristic of linear hydrogen bridges.[21]

The introduction of potassium cations influences the shape of the potential energy surfaces and the QMRC curve, so it can be concluded that the proton motion in the chloromaleate anion can be modified by the presence of potassium cations in the distance limit, as in the investigated compound. The most characteristic feature of the potential energy surface is the energy minimum. Fig. 8 illustrates how the cations surrounding the anion with a strong OHO bond can change the shape of the energy minimum and its location against the BORC curve. It is characteristic that for all the investigated combinations of cations listed in Tables 1–3 (ESI†), the BORC and QMRC curves are different. For the separate anion, the energy minimum is elongated close to the centre of the diagram, and is thus very close to the BORC curve. The presence of cations shifts the energy minimum to the region in which both OH bonds are different, and changes the shape of the minimum by making it narrower. If cations are present, shifting the proton in the chloromaleate anion is more difficult than for the separate anion, and if the shifting of the proton is forced, the proton must change its valency. The distance between the energy minimum and the minimum calculated for the separate anion illustrates the influence of the particular cation.

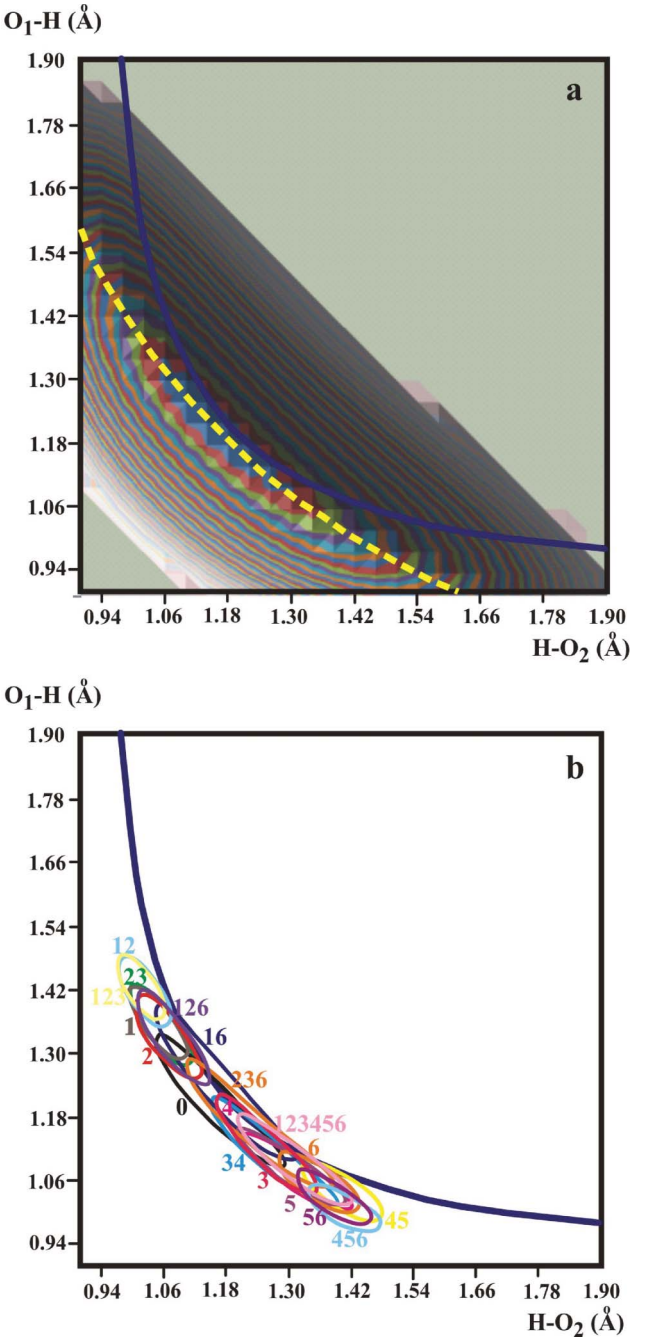

Fig. 8 a: Potential energy surface for the chloromaleate anion. b: Comparison of the potential energy levels at 1 kcal mol^{-1} for different combinations of potassium cations around the chloromaleate anion. Blue curve: BORC, yellow curve: QMRC.

Conclusion

The most popular theoretical method for hydrogen bond investigations used in this study show that a very strong OHO hydrogen bond is sensitive to the presence of potassium cations. The changes of the proton location in the hydrogen bridge are significant, and

follow general theoretical and experimental correlations obtained for a hydrogen bond when its strength is changed. Even a cation located about 6.4 Å from the proton can influence the proton moving between the donor and acceptor, as well as the electron density at the OH BCP. The next step of this investigation should be to check how long the distance between the cation and the proton should be so that it cannot influence the hydrogen bond.

Acknowledgements

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