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Intramolecular Hydrogen Bonding in Guanidinium and Potassium Hydrogen Malonates — an Infrared and X-Ray Diffraction Study

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A new modification of potassium hydrogen malonate was obtained by crystallization from dimethylsulphoxide (DMSO) solution. Its infrared spectrum differs in its essential features from the spectra of the known modification crystallizing from water^{1,9} but resemble those of guanidinium hydrogen malonate. Both spectra are interpreted in terms of strong, intramolecular hydrogen bonding. This is supported by the fact that the main features (CO and OH stretching) remain essentially unchanged on dissolution in DMSO and by the X-ray diffraction on guanidinium hydrogen malonate. The structure of its crystals was solved by the direct method and refined by full matrix least squares to R value of 0.044 for 453 observed reflections. The structure consists of planar guanidinium ions and hydrogen maleate residues containing short intramolecular, but asymmetric bonds of 2.407(3) Å.

INTRODUCTION

The hydrogen malonate ion assumes in its crystallized acid salts various conformations and engages in different types of hydrogen bonds. In potassium hydrogen malonate, it assumes C_{2v} symmetry and is nearly planar,¹ in the ammonium salt the carboxylate planes are perpendicular to each other² and in the sodium salt the carboxylate groups of two unequal malonate entities assume different angles of twist.³ In all these salts the hydrogen malonates form infinite hydrogen bonded chains. In the potassium salt the hydrogen bonds are of Speakmans type A_2 ,⁴ in the ammonium salt they are of pseudo- A_2 type, and in the sodium salt of type B_2 . In the »super-acid« salts of potassium⁵ and lithium⁶ the planar hydrogen malonate appears with short, intramolecular hydrogen bonds whereas in dirubidium-tetrahydrogen trimalonate⁷ the carboxylate groups are perpendicular and hydrogen bonding is again intermolecular.

Infrared spectra of several alkali hydrogen malonates have been investigated in the polycrystalline form and classified with respect to the apparent symmetry of hydrogen bonding.⁸ A more detailed study of infrared dichroism and Raman spectra of potassium hydrogen malonate single crystals has also been published.⁹ The spectra of the hydrogen malonates resemble in gross features those of acid salts of monocarboxylic acids,¹⁰ particularly by the presence of the very broad and strong absorption in the region between

1600 cm^{-1} and 600 cm^{-1} . This most prominent absorption is attributed to the ν OH mode and its deuteration behaviour is indicative of the type of the hydrogen bond potential function.¹⁰ However, this feature does not appear in the infrared spectrum of potassium hydrogen maleate which is the best known representative of symmetrical intramolecular hydrogen bonding. In fact, the assignment of the asymmetric OHO stretching mode in hydrogen maleates has been for a long time controversial. The relative weakness of the band carrying most of the ν_{as} OHO character in the hydrogen maleate spectra¹¹ and the lack of comparative data on strong, intramolecular hydrogen bonds induced us to look for further examples. Hydrogen malonates appeared to be attractive in this respect in view of the existing salts with intramolecular bonding^{5,6} and of the theoretical result concerning the conformational energy of the free ion which shows that the form with intramolecular bonding is the most stable one.¹² The variety of conformations and hydrogen bonding schemes observed in the different solid hydrogen malonates is also inviting for investigations on factors influencing the actual structure of hydrogen malonates. In this respect, the combination of vibrational spectroscopy and X-ray structure determination yields results with proper weight.

In this paper we report the infrared spectra of guanidinium hydrogen malonate (GHM) and of a new form of potassium hydrogen malonate (KHM), obtained by evaporation of its solution in dimethylsulphoxide (DMSO). We shall designate this form KHM(s) to differ from the previously known one, KHM(w), which crystallizes from water.¹ The infrared spectra of these two forms are essentially different whereas the spectra of GHM and KHM(s) are similar and are interpreted in terms of intramolecular hydrogen bonding. This is confirmed for GHM by X-ray diffractions and the evidence can be applied to KHM(s) too. Intramolecular hydrogen bonding in both GHM and KHM persists in DMSO solution in contrast to water solution.

EXPERIMENTAL

Transparent prismatic crystals of GHM were obtained by slow crystallization from either aqueous solution or from water — ethanol 1:1 mixture containing equimolar proportions of malonic acid and guanidinium carbonate.

KHM(s) was obtained in microcrystalline form from a saturated solution in DMSO by removing the solvent under vacuum or by slow evaporation at 60° under normal pressure. This modification spontaneously changes (on standing for few days) to the one obtainable from aqueous solution. The conversion also occurs with longer grinding. The infrared spectra were recorded as nujol and hexachlorobutadiene mulls on a Digilab FTS 15/80 spectrometer. Cells with 0.01 mm spacers were used for recording the spectra of saturated solutions in DMSO.

Crystals of GHM ($F_w = 163.1$ g/mol) used for diffraction work were prepared from water solution by slow evaporation. The crystals are orthorhombic: $C_{\text{cc}2}$, $a = 12.232(6)$ Å, $b = 5.082(2)$ Å, $c = 12.247(5)$ Å, $V = 761(3)$ Å³, $D_x = 1.432$ g/cm³, $Z = 4$, $\mu = 1.184$ cm⁻¹. A prismatic crystal of $0.55 \times 0.46 \times 0.34$ mm was used for intensity collection with graphite — monochromatized MoK $_{\alpha}$ radiation on an Enraf-Nonius CAD-4 diffractometer. The space group was determined from Weissenberg photographs and successful refinement.

The structure was solved by direct methods using MULTAN80.¹³ E map with the highest combined figure of merit resulted in initial positions for all the non-hydrogen atoms. Hydrogen atoms were located from the difference Fourier map. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were refined with isotropic thermal parameters. The methylenic hydrogen atoms with the isotropic thermal parameters of the attached heavier

atoms were not refined. The final R factor was 0.044. All calculations were performed on the DEC-10 computer at RCU-Ljubljana with the XRAY76 system of crystallographic programs.¹⁴

RESULTS

1. Infrared Spectra

The main features of the GHM and KHM(s) spectra are similar except for the guanidinium bands of the former (Figures 1 and 2). There is no

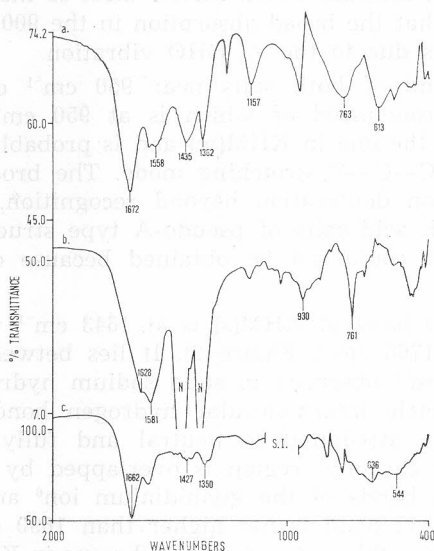


Figure 1. FTIR spectra of guanidinium hydrogen malonate. a — KBr pellet; b — deuterated in Nujol (N); c — solution in DMSO- d_6 (s.i. — solvent interference).

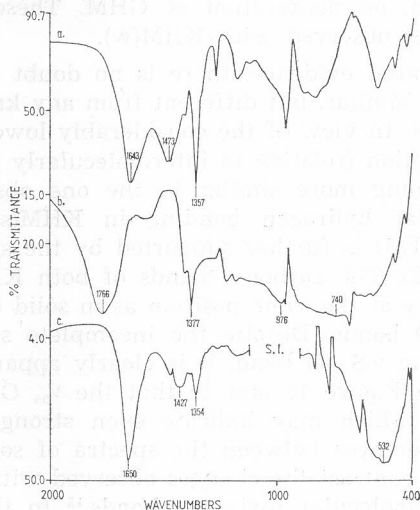


Figure 2. FTIR spectra of potassium hydrogen malonate. a — crystallized from DMSO; KBr pellet, b — crystallized from water, KBr pellet, c — solution in DMSO.

absorption above 1800 cm^{-1} attributable to hydroxyl stretching; a single carbonyl band near 1650 cm^{-1} appears and in both spectra a broad absorption marks the region of 900 cm^{-1} . Relative to the carbonyl band peak, its intensity is lower. In this respect as well as in its smaller width it remarkably differs from the very broad and strong $\nu_{\text{as}}\text{ OHO}$ absorption of KHM(w) and of other intermolecularly hydrogen bonded acid salts. However, the band in KHM(s) is at somewhat higher frequency and stronger than the band at 540 cm^{-1} of potassium hydrogen maleate which carries most of the $\nu_{\text{as}}\text{ OHO}$ character.¹¹ There is little doubt that the broad absorption in the 900 cm^{-1} region of GHM and KHM(s) spectra is due to the $\nu_{\text{as}}\text{ OHO}$ vibration.

The $\nu_{\text{as}}\text{ OHO}$ band of both salts near 950 cm^{-1} contains transmission windows the most pronounced of which is at 950 cm^{-1} . This transmission nearly coincides with the one in KHM(w) and is probably due to a resonance interaction with the C—C—C stretching mode. The broad $\nu\text{ OHO}$ absorption of GHM is reduced on deuteration beyond recognition, a phenomenon frequently observed with acid salts of pseudo-A type structure.¹⁰ The spectrum of deuterated KHM(s) could not be obtained because of unfavourable crystallization conditions.

The single $\nu\text{ C=O}$ band of KHM(s) is at 1643 cm^{-1} which is much lower than with KHM(w) (1766 cm^{-1} , Figure 2). It lies between the two bands at 1695 cm^{-1} and 1585 cm^{-1} observed in solid sodium hydrogen malonate.⁸ This salt contains asymmetric intermolecular hydrogen bonds and the two frequencies are properly attributed to neutral and fully ionized carboxylate groups. In GHM, the carbonyl region is overlapped by the C—N stretching and NH_2 deformation bands of the guanidinium ion⁶ and so it can only be stated that the carbonyl band is not higher than 1690 cm^{-1} , nor lower than 1650 cm^{-1} and thus it roughly corresponds to the one in KHM(s). The composite band in GHM moves on deuteration to 1600 cm^{-1} . The peaks near 1350 cm^{-1} are likely to be due to C—O stretching because they are only slightly displaced, but not removed, on deuteration of GHM. These frequencies roughly correspond to the ones observed with KHM(w).

According to infrared evidence, there is no doubt that the structures of KHM(s) and GHM are similar, but different from any known crystal structure of hydrogen malonates. In view of the considerably lower intensity and width of the $\nu_{\text{as}}\text{ OHO}$ absorption (relative to intermolecularly hydrogen bonded acid salts) and thus becoming more similar to the one observed with hydrogen maleate, intramolecular hydrogen bonding in KHM(s) and GHM is most likely to be present. This is further supported by the spectra of DMSO solutions (Figures 1 and 2). The carbonyl bands of both KHM modifications and of GHM are practically at the same position as in solid (KHM(s) and the same is true of the $\nu\text{ C=O}$ bands. Despite the incomplete solvent subtraction in the region of its strong $\nu\text{ S—O}$ band, it is clearly apparent from the solution spectra reproduced in Figure 1c and 2c that the $\nu_{\text{as}}\text{ OHO}$ absorption moved to lower frequencies which may indicate even stronger hydrogen bonding. The rather small differences between the spectra of solid GHM and KHM(s) and of their solutions contrast the changes observed with monocarboxylic acid salts, containing intermolecular hydrogen bonds.¹⁵ In the latter, the spectral changes occurring on dissolution clearly indicate a weakening of the hydrogen bonds and loss of symmetry if this was the case in the crystal state. Final

confirmation of intramolecular hydrogen bonding as well as more structural detail are offered by the X-ray structure determination.

2. X-Ray Diffraction

We report here only the essential results of the structure determination of GHM. Detailed data can be obtained upon request from one of the authors (L. G.).

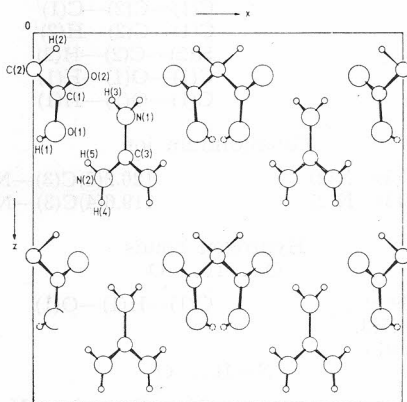


Figure 3. View of the unit cell of guanidinium hydrogen malonate crystal along the 010 axis.

The structure consists of planar guanidinium ions and nearly planar hydrogen malonate residues which contain short, asymmetrical hydrogen bonds of 2.407(3) Å. Figure 3 shows the general features of molecular packing in the unit cell of the crystal as viewed along [010]. The important interatomic distances and angles are presented in Table I. The comparison of C—O distances of the carboxylate groups with those of typical single C—OH, double C=O and C—O bonds in neutral and ionic carboxyl groups, respectively, shows that the situation in the hydrogen malonate is intermediate. The intramolecular hydrogen bond is bent; the O(1)—H—O(1) angle is 153(6)^o which is very close to the one observed with lithium and potassium »super-acid« salts (153^o, 155^o). In these salts the hydrogen bond is, however, slightly longer than in GHM. The latter is, on the other hand, comparable in length to the probably asymmetrical hydrogen bond in guanidinium hydrogen maleate which is 2.40(1) Å long.¹⁶

Owing to steric hindrance from the oxygens of one carboxyl group to the proximal oxygen of the other, the two groups cannot be in the same plane through the carbon atoms, but must twist with respect to this plane. In malonic acid one carboxyl group is twisted nearly at right angles relative to the plane through the central carbon atoms¹⁷ while in KHM(w) the carboxyl groups are twisted by approx. 5^o in opposite directions.¹ In GHM the carboxyl groups are twisted approximately by 2.8^o with respect to the plane defined by the three carbon atoms (Table I).

TABLE I
Interatomic Distances (Å) and Angles (°)

Hydrogen malonate ion				
C(1)—O(1)	1.282(5)	O(1)—C(1)—O(2)		123.4(3)
C(1)—O(2)	1.224(4)	C(2)—C(1)—O(2)		119.7(3)
C(1)—C(2)	1.524(3)	C(2)—C(1)—O(1)		116.9(2)
		C(1)—C(2)—H(2)		107.7(1)
		C(1)—C(2)—C(1) ^I		117.3(2)
		C(1)—C(2)—H(2) ^I		107.3(1)
		H(2)—C(2)—H(2) ^I		109.4
		C(1)—O(1)—H(1)		111(4)
		C(1)—O(1)—H(1) ^I		104(2)
Guanidinium ion				
N(1)—C(3)—N(2)		120.2(2)C(3)—N(1)		1.328(7)
N(2)—C(3)—N(2)		119.6(4)C(3)—N(2)		1.322(4)
Hydrogen bonds				
O...H...O				
O(1)—H(1)	0.89(5)	O(1)—H(1)—O(1) ^I		153(6)
O(1)—O(1)	2.407(3)			
O(1)—H(1) ^I	1.57(5)			
N—H...O				
		N...O	N—H	H...O
N(1)—H(3)—O(2)		2.875(4)	0.83(5)	2.07(5)
N(2)—H(5)—O(1)		2.963(4)	0.83(4)	2.15(5)
N(2)—H(4)—O(2) ^{II}		2.881(5)	0.82(4)	2.09(4)

Symmetry code: (I) X, — Y, Z; (II) X, 1 — Y, Z + 1/2

Guanidinium ions are planar within the limit of the experimental error. A similar situation was observed in several crystal structures of guanidinium salts.^{18,19,20} The C—N distances are 1.328(7) Å and 1.322(4) Å.

DISCUSSION

The infrared spectra of solid GHM and KHM(s) are different from the spectra displayed by intermolecularly hydrogen bonded acid salts of carboxylic acids. The difference becomes particularly evident when comparing the spectra of both modifications of KHM and it indicates intramolecular hydrogen bonding in the modification of KHM obtained by crystallization from DMSO. A further evidence of such bonding is the fact that the essential spectral features of the solids are retained in DMSO solution and, moreover, these features appear also with KHM(w) when dissolved in this solvent. The deuteration behaviour of the ν OHO band, *i. e.* remarkable weakening which prevents the location of the ν ODO analog indicate that the hydrogen bond is not of a symmetrical, single minimum type.

Further details of the structure of the hydrogen malonate entity and hydrogen bonding in GHM crystals have been obtained from the X-ray diffraction determination of GHM. These results support the conclusions of the spectroscopic investigation. Although the microcrystallinity of KHM(s)

crystals did not allow for diffraction work the similarity between the GHM and KHM(s) infrared spectra leaves no doubts about the structural analogy of the respective hydrogen malonate residues particularly as far as the character of hydrogen bonding is concerned.

The very existence of two KHM crystal modifications of KHM, one obtained from aqueous solution and the other from DMSO, induces one to reflections concerning the tendency of the hydrogen malonate to undergo inter- or intramolecular hydrogen bonding. Theoretical calculations on isolated hydrogen malonate¹² show that intramolecular hydrogen bonding is energetically favoured. However, in most of the crystallized hydrogen malonates and in water solution,²¹ intermolecular bonding appears to predominate. With KHM, the modification with the intermolecular hydrogen bond is more stable, which indicates that packing forces in this and in most of the other hydrogen malonates override the higher stability imparted to the free hydrogen malonate by the intramolecular bond. For the case of water solution it is easy to visualize that the open conformation of the hydrogen malonate entity offers more possibilities for solvation by both the proton donating and accepting solvent than the closed, intramolecularly hydrogen bonded form. In contrast, the aprotic DMSO does not provide for additional solvation of carbonyl groups of the open conformation and thus the inherent higher stabilization with intramolecular bonding prevails. Apparently, it is this form that is kinetically favoured in crystallization.

The final question concerns the stability of the intramolecularly bonded form of hydrogen malonate in the guanidinium salt. One explanation can be seen in the planar shape of guanidinium ion which allows for packing into layers with the nearly planar hydrogen malonate entities. Intermolecular hydrogen malonates which are currently explored should demonstrate the validity of the hypothesis.

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SAŽETAK

Intramolekulska vodikova veza u gvanidini- i kalij-hidrogenmalonatu — studij infracrvenih spektara i rendgenske difrakcije

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Nova modifikacija kalij-hidrogenmalonata dobivena je kristalizacijom iz otopine dimetilsulfoksida (DMSO). Njegov infracrveni spektar razlikuje se u bitnim obilježjima od spektara poznate modifikacije iskristalizirane iz vode, ali je sličan onome za gvanidini- i hidrogenmalonat. Oba spektra interpretiraju se u smislu jake intramolekulske vodikove veze. To je potkrijepljeno činjenicom da glavna obilježja (rastezanje veza CO i OH) ostaju u biti nepromijenjena otapanjem u DMSO, te podacima rendgenske difrakcije na gvanidini- i hidrogenmalonatu. Struktura njegova kristala riješena je direktnom metodom i utočnjena punom matricom najmanjih kvadrata do vrijednosti R od 0,044 za 453 opažene refleksije. Struktura se sastoji od planarnih gvanidinijevih iona i ostataka hidrogenmaleata koji sadrže kratke intramolekulske, ali nesimetrične veze duljine 2,407(3) Å.