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Determination of the Structure of H-Bonded Complexes of Some Anomalous Acid Salts of Dibasic Acids by Means of Solid-Phase Carbon-13 Nuclear Magnetic Resonance Spectroscopy and X-ray Diffraction

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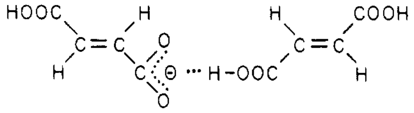
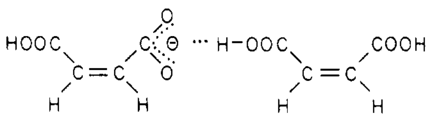
Carbon-13 high-resolution, solid-state NMR with magic angle spinning has been used to study the structures of the three anomalous acid salts tetramethylammonium dimaleate, tetramethylammonium difumarate, and tetramethylammonium diphthalate. The NMR spectrum of the difumarate indicates greater symmetry than that found for the dimaleate and diphthalate. Either the two fumaric acid molecules are crystallographically equivalent or each of them has to be centrosymmetric. In either case, a symmetrical hydrogen bond is required, or a rapid reversible migration of a proton in a double-well potential. An X-ray diffraction study of the difumarate confirms that the molecules are equivalent, with an intermolecular hydrogen bond that is close to symmetric, O···O 2.450 (3) Å, at a pseudo inversion center.

In a previous study[1] we have shown that the dibasic acids, H_2Y, form the expected neutral salt, R_2Y, the normal acid salt, RHY, and in some instances, two series of anomalous acid salts, RH_3Y_2 and $R_2H_4Y_3$, where R is the cation formed from the neutralizing base.

The stoichiometries of these anomalous acid salts are certain, but the determination of the detailed structures is complicated by the fact that only measurements made in the solid state are valid. On the basis of infrared spectroscopy data, it was concluded that the acid moieties in these anomalous salts are held together by hydrogen bonds. It was further assumed that (1) the carboxyl hydrogen will hydrogen bond preferentially to a carboxylate anion rather than to the neutral carboxyl group and (2) the unit structures will be terminated in carboxyl groups, which will undergo hydrogen bonding typical of carboxylic acids. On the basis of the foregoing considerations, we proposed structures I and II for the anomalous difumarate and the anomalous dimaleate anions, $H_3Y_2^-$.



I



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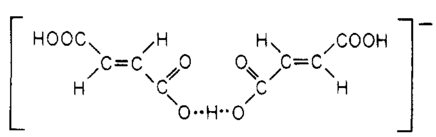

III

In this work we report the results of a solid-state ^{13}C NMR study of the structure of the anomalous acid salts of the type RH_3Y_2. To facilitate interpretation, we have focused on the salts of those acids which have the two carboxyl groups potentially coplanar and either cis or trans to one another, e.g., maleic acid, fumaric acid, and phthalic acid. Either potassium or tetramethylammonium counterions were used in order to simplify the infrared spectra by eliminating the bands that result from hydrogen-bonding interactions that involve the N–H of the unsubstituted ammonium cation.

The spectra and structures of the normal acid salts, RHY, are used as references. Potassium hydrogen maleate is especially useful for this purpose. In the anion the two carboxylate groups are equivalent and linked by a short, symmetrical hydrogen bond; this structure is supported by evidence from infrared spectroscopy,[2] neutron diffraction,[3] and X-ray diffraction.[4] Using ^1H and ^{13}C high-resolution solid-state NMR with magic angle spinning, Schroter, Rosenberger, and Hadzi[5] demonstrated that this technique permits determination of both the strength and symmetry of the O–H···O bonds in the normal acid salts, RHY, of dibasic acids and that the most important information provided by the ^{13}C solid-state NMR is the number of different signals, particularly those of the carboxylic carbon atoms. We will compare and contrast the CO region in the infrared spectra and the ^{13}C solid-state NMR spectra for four different normal acid salts, RHY, and three different anomalous acid salts of the type RH_3Y_2. As will be apparent from the results, ^{13}C NMR spectroscopy is a much more discriminating probe than infrared spectroscopy and reveals structural subtleties not accessible with infrared alone. As a further check on the interpretations, the X-ray structure of the tetramethylammonium difumarate was determined.

Results and Discussion

The carbonyl absorptions in the infrared for all of the salts of present interest are listed in Table I. Both potassium hydrogen maleate and tetramethylammonium

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Table I. Infrared Spectra of Normal Acid Salts, RHY, and Anomalous Acid Salts, RH_3Y_2, of Dibasic Acids

salt	carbonyl absorption, cm^{-1} COOH	carbonyl absorption, cm^{-1} COO^-
potassium hydrogen maleate		1575
tetramethylammonium hydrogen maleate		1585
potassium hydrogen fumarate	1675	1610
tetramethylammonium hydrogen phthalate	1700	1570
tetramethylammonium dimaleate	1725	1630
tetramethylammonium difumarate	1740	1640
tetramethylammonium diphthalate	1720	1640

hydrogen maleate show only a single absorption in the carbonyl region, at 1575 and 1585 cm^{-1}, respectively. These bands are characteristic of the carboxylate ion, and the absence of any absorption due to the carboxyl group is consistent with the proposed structures,[2,6] in which the two carboxylate groups have been made equivalent by the symmetrical hydrogen bond that links them.

Potassium hydrogen fumarate shows two carbonyl absorptions, one for the carboxyl group at 1675 cm^{-1} and the other for the carboxylate anion at 1610 cm^{-1}. The trans configuration prevents intramolecular interaction of the carboxyl and carboxylate groups, and the two carbonyl groups retain their separate identities. The X-ray structure determination[7] indeed shows two different ends of the fumarate ion. The planes of the carbonyl and carboxylate groups are rotated about 25° out of the plane of the C4 skeleton, in opposite directions. The molecules are linked, head to tail, to infinite chains by short, probably unsymmetrical, hydrogen bonds. The rubidium salt seems to be isostructural.[8]

In tetramethylammonium hydrogen phthalate, the carboxyl and carboxylate groups are again cis to one another; a strong, symmetrical hydrogen bond is not formed. The two carbonyls are distinguishable, with the carboxyl group absorbing at 1700 cm^{-1} and the carboxylate ion at 1570 cm^{-1}. The intramolecular hydrogen bond seems to be rare in the acid phthalates.[9] All of the potassium,[10] rubidium,[11] and ammonium[12] hydrogen phthalates have only intermolecular hydrogen bonds with the carboxylic groups rotated out of the plane of the benzene ring. However, the lithium hydrogen phthalate dihydrate does show a short symmetrical hydrogen bond, but still the acid molecule is not planar.[13]

The last three entries in Table I are for three anomalous acid salts of the type RH_3Y_2. The three salts, the dimaleate, the difumarate, and the diphthalate, all give similar infrared spectra. They show broad, multiband absorption due to hydrogen-bonded OH, no absorption due to free OH, and the carbonyl absorptions, one for COOH and one for COO^-, shown in Table I. The proposed structures, I and II, are consistent with these infrared spectra, if it is in fact true that infrared spectroscopy permits a distinction between the carbonyls in COOH and COO^- but does not allow the more subtle differentiation between a carbonyl in a carboxyl group whose OH is hydrogen bonded to a carboxylate anion, and the carbonyl in a carboxyl group whose OH is hydrogen bonded to another carboxyl, i.e., where the hydrogen bonding is typical of that in a carboxylic acid dimer.

Table II. Solid-State ^{13}C NMR Spectra of Normal Acid Salts, RHY, and Anomalous Acid Salts, RH_3Y_2, of Dibasic Acids

salt	measured chemical shifts (ppm) CO	measured chemical shifts (ppm) C=C	measured chemical shifts (ppm) CH_3
potassium hydrogen maleate	173.1	137.6	
tetramethylammonium hydrogen maleate	168.7	135.8	54.4
potassium hydrogen fumarate	174.0	137.3	
	172.9	132.9	
tetramethylammonium hydrogen phthalate	176.8	146.0	54.9
	170.2	133.0	
		129.7*[a]	
		127.0*	
tetramethylammonium dimaleate	175.7	138.9	56.4
	167.0	136.5	
	165.7	134.0	
tetramethylammonium difumarate	173.3	138.1	55.7
	166.8	133.8	
tetramethylammonium diphthalate	177.7	142.7	55.7
	170.2	136.1	
	167.2	130.6*	

[a] (*) overlapping aromatic absorptions.

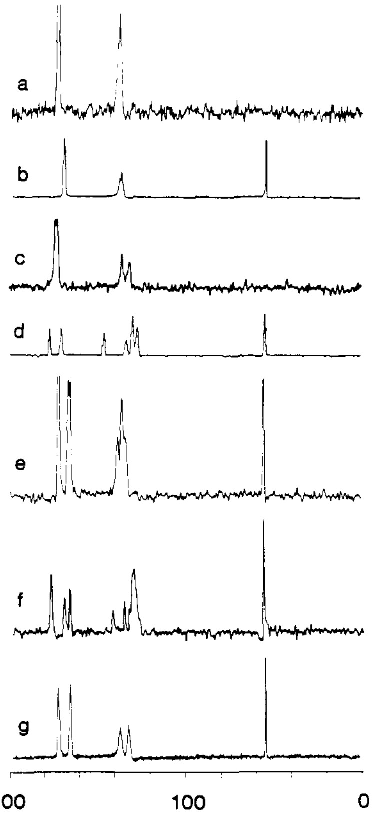

Figure 1. Solid-state ^{13}C NMR spectra of normal acid salts, RHY, and anomalous acid salts, RH_3Y_2, of dibasic acids. The chemical shifts are referred to TMS. Adamantane was used as a secondary standard. (a) Potassium hydrogen maleate, (b) tetramethylammonium hydrogen maleate, (c) potassium hydrogen fumarate, (d) tetramethylammonium hydrogen phthalate, (e) tetramethylammonium dimaleate, (f) tetramethylammonium diphthalate, (g) tetramethylammonium difumarate.

Solid-state ^{13}C NMR spectroscopy yields the more subtle kind of distinctions which we have indicated above. In Table II we have assembled the results obtained for the compounds of interest. Tabulated are the chemical shifts observed for carbonyl groups, for carbon–carbon double bonds, and for methyl groups.

For potassium hydrogen maleate, previous results[2,3,4] indicate that the two carbonyl groups have been made

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equivalent by the hydrogen bond and that the carbon–carbon double bond is, therefore, symmetrically substituted. The NMR spectrum (Figure 1 (a)) is consistent with the above interpretation. The spectrum has a single resonance for the carbonyl group and a single resonance for the carbon–carbon double bond. The spectrum for tetramethylammonium hydrogen maleate (Figure 1 (b)) provides further confirmation. Here again there is only one signal for the carbonyls and only one for the carbon–carbon double bond. The third peak is clearly assigned to the methyl groups in the tetramethylammonium cation.

The NMR spectra of both potassium hydrogen fumarate (Figure 1 (c)) and tetramethylammonium hydrogen phthalate (Figure 1 (d)) are consistent with the crystal structure data and with the conclusions reached with infrared spectroscopy. This leads to an NMR spectrum with two carbonyl and two carbon–carbon double bond resonances. In the aromatic region the NMR spectrum of the phthalate reflects the asymmetry induced by the carboxylate ion, with four of the six carbon signals overlapping in two major absorptions between 125 and 130 ppm. The absence of a strong, symmetrical hydrogen bond between the carboxyl group and the carboxylate ion is confirmed, as in the fumarate case, by distinct absorptions of the carbonyl groups.

Turning now to tetramethylammonium dimaleate, we will discuss its ^{13}C NMR spectrum (Figure 1 (e)) using the proposed structure of the anion, II, as our point of reference. The spectrum shows three absorption signals in the carbonyl region, three in the C=C region, and only one for the methyl groups. These findings are consistent with structure II. The two terminal carboxyl groups in II are in similar environments and result in a single carbonyl resonance, assuming that they engage in similar hydrogen bonding. The central portion of II, on the other hand, has the OH of a carboxyl group hydrogen bonded to a carboxylate anion. Here the two carbonyl groups are in different environments and yield two peaks, thus giving three carbonyl chemical shifts overall. Similarly, the carbon–carbon double bonds result in three peaks. The two outer CH groups in structure II are in similar environments and give a single absorption. The two inner CH groups, one bonded to a carboxyl group and the other to a carboxylate anion, are distinguishable, and a total of three carbon–carbon double bond shifts are observed. However, a number of other interpretations, leading to the correct number of chemical shifts, can be given.

Another example of a similar spectrum is provided by tetramethylammonium diphthalate (Figure 1 (f)), whose anion would be expected to have a structure very similar to that of the dimaleate. For this salt we observe a single CH$_3$ peak, three CO peaks, and several C=C peaks due to the aromatic ring.

On the basis of the proposed structure, I, tetramethylammonium difumarate (Figure 1 (g)) would be expected to provide a ^{13}C NMR spectrum very similar to the one obtained for the dimaleate. However, a much simpler spectrum, one with two CO peaks, two C=C peaks, and one CH$_3$ peak, was obtained. This surprising result was verified by repeated synthesis, analysis, and NMR measurements on all three disalts.

The spectra of the dimaleate and the diphthalate provide assurance that NMR can differentiate three kinds of carbonyl groups in the dimaleate and the diphthalate. If the difumarate gives a simpler spectrum, the proposed structure, I, must be incorrect and a structure having greater symmetry is required. The two fumaric acid molecules must be crystallographically equivalent or each of them has to be centrosymmetric. In either case a symmetrical hydrogen bond is required, or a rapid reversible migration of the proton in a double-well potential. The most straightforward suggestion is to make the hydrogen bond in I strong and symmetrical. This spreads the negative charge equally over two oxygen atoms, and the resulting structure is III. The outer carboxyl groups would generate one of the two observed carbonyl peaks, and the central groups would generate the other. The same reasoning would apply to the two C=C chemical shifts.

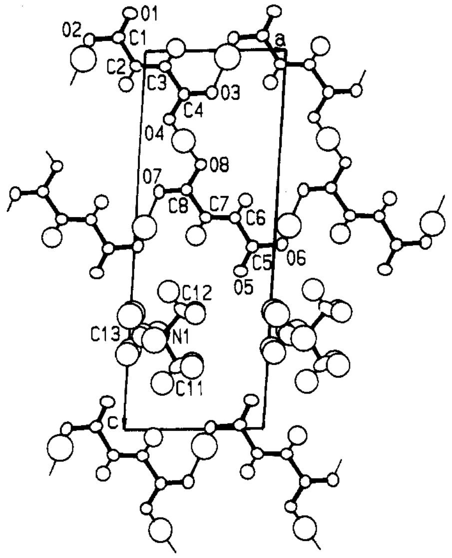

Figure 2. Projection along [010] of the atoms around $y = {}^1/_4$ in tetramethylammonium difumarate. A perspective view is used to reveal the otherwise hidden methyl group below the mirror plane. The 50% probability ellipsoid is plotted for each atom; therefore the hydrogen atoms appear larger. Hydrogen bonds are shown by thin lines.

As a check on the interpretation of the tetramethylammonium difumarate spectra, an X-ray structural study was undertaken.

The structure is shown in Figure 2. There are two independent fumarate units. Both these and the tetramethylammonium ion are situated in the mirror planes. There is also some noncrystallographic symmetry: If the tetramethylammonium ion is ignored, there is approximate $2/m$ symmetry on a lattice displaced $\simeq ({}^1/_3, {}^1/_4, {}^1/_4)$ from that of the space group symmetry. Additionally, the combination of these symmetry elements gives rise to a pseudo n glide in the [100] projection, resulting in $0kl$ reflections with $k + l$ odd either being unobserved or weak.

The two fumarate ions are de facto equivalent. They are connected by a very short, close to symmetrical, hydrogen bond over one of the pseudo $2/m$ centers mentioned above. The O(4)···O(8) distance is 2.450 (3) Å with O–H distances of 1.15 (4) Å and 1.30 (4) Å and an O(4)–H···O(8) angle of 177 (4)°. Furthermore, each of the ions is also connected to two of its kin by identical strong hydrogen bonds at each end: the O···O distances and O–H···O angles are 2.600 (3) Å and 174 (5)°, and 2.584 (3) Å and 178 (4)°, respectively. One of the carbonyl groups of each ion is not engaged in any hydrogen bonding, viz., O(1) and O(5). Infinite strands, two molecules wide, of hydrogen-bonded fumarate ions are formed along a. The distance between planes of molecules is only $b/2 = 3.388$ Å. The geometry of the tetramethylammonium ion is quite normal.

This shows clearly that the fumaric acid molecules are equivalent, with a short symmetric hydrogen bond, O···O distance of 2.450 (3) Å, over a pseudo inversion center in

Table III. Some Interatomic Distances[a] and Angles[b] in Tetramethylammonium Difumarate

C1–O1	1.203 (3)	C5–O5	1.196 (3)
C1–O2	1.313 (3)	C5–O6	1.318 (3)
C1–C2	1.485 (4)	C5–C6	1.486 (4)
C2–C3	1.298 (4)	C6–C7	1.304 (4)
C3–C4	1.483 (4)	C7–C8	1.486 (4)
C4–O3	1.240 (3)	C8–O7	1.233 (3)
C4–O4	1.279 (4)	C8–O8	1.280 (3)
O1–C1–O2	120.0 (2)	O5–C5–O6	120.6 (3)
O1–C1–C2	123.8 (3)	O5–C5–C6	123.1 (3)
O2–C1–C2	116.1 (2)	O6–C5–C6	116.3 (2)
C1–C2–C3	122.3 (2)	C5–C6–C7	122.0 (2)
C2–C3–C4	124.8 (2)	C6–C7–C8	125.3 (2)
C3–C4–O3	120.3 (2)	C7–C8–O7	119.6 (2)
C3–C4–O4	116.3 (2)	C7–C8–O8	116.1 (2)
O3–C4–O4	123.5 (2)	O7–C8–O8	124.3 (2)
O2–HO2	0.87 (4)	O2···O3	2.600 (3)
O3–HO2	1.73 (4)	O2–HO2–O3	174 (4)
O4–HO4	1.15 (4)	O4···O8	2.450 (3)
O8–HO4	1.30 (4)	O4–HO4–O8	177 (4)
O6–HO6	0.88 (4)	O6···O7	2.584 (3)
O7–HO6	1.71 (4)	O6–HO6–O7	178 (4)

[a] In angstroms. [b] In degrees.

the structure. Thus, the proposal above is confirmed. However, an extended interpretation of the dimaleate and diphthalate spectra must await quantification of the structural effects on chemical shifts in this class of compounds. Interestingly, both the cesium diphthalate[14] and the rubidium diphthalate dihydrate[15] have structures with a hydrogen-bonding scheme very much resemblant of that in the tetramethylammonium difumarate.

Experimental Section

All salts were prepared and analyzed as previously described.[1] The NMR measurements were performed on a Varian XL-200 spectrometer equipped with a probe for CP/MAS (cross-polarization/magic angle spinning) experiments with specimens in the solid state.[16-18] Typically 256 single 0.7-ms cross-polarizations from protons were accumulated with recycle and acquisition times of 2 and 0.1 s, respectively. Spinning rates were 1.9–2.0 kHz. Sideband suppression[9] was applied in all measurements.

X-ray data for tetramethylammonium difumarate were collected on a Huber four-circle diffractometer with monochromated Mo Kα (Mo Kα_1 = 0.70930 Å) radiation under the control of locally written software.[20] The monoclinic unit cell, space group $P2_1/m$ with $a = 6.399$ (1) Å, $b = 6.776$ (2) Å, $c = 17.290$ (3) Å, and $\beta = 94.22$ (2)°, holds two formula units. A hemisphere of reciprocal space was sampled by the $\omega - 2\theta$ scan technique and $\Delta\omega = 0.7° + 0.4° \tan\theta$ to a maximum $(\sin\theta)/\lambda = 0.60$ Å^{-1}. Three standards measured every 2 h showed no systematic variation. The 2898 reflections were corrected for Lp and absorption effects ($\mu = 1.1$ cm^{-1}). The structure solution was carried out with SHELXS;[21] 1555 reflections with $I > 5\sigma_c(I)$ were used in the refinement with unit weights. Secondary extinction correction[22] gave $q = 3.56 (7) \times 10^3$. The final structural model with all non-hydrogens anisotropic and hydrogens isotropic (171 parameters) resulted in $R = 0.032$, $R_w = 0.030$, and $S = 0.48$. Some interatomic distances and angles are given in Table III.

Acknowledgment. The nuclear magnetic resonance spectra were taken at the Major Analytical Instruments Facility of the Department of Chemistry, Case Western Reserve University.

Supplementary Material Available: Table of atomic coordinates and thermal parameters and table of anisotropic thermal parameters (2 pages); structure factor table (10 pages). Ordering information is given on any current masthead page.

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An AM1 Theoretical Study of the Structure and Electronic Properties of Porphyrin

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AM1 calculations are reported for the parent free base porphyrin. These calculations show that the predicted structure for this molecule is qualitatively different depending on the type of wave function employed. A RHF wave function leads to a relatively low-symmetry bond-alternating structure for porphyrin whereas a UHF wave function leads to the expected D_{2h} nearly bond-equivalent structure. The UHF energy is on the order of 1 eV lower than the RHF energy, a condition that is normally found only for biradicals. These results are interpreted in terms of electron-pair correlation effects and a π system for porphyrin isoelectronic with 18-annulene.

Introduction

The structure and electronic properties of porphyrin have been subjects of considerable interest for many years,[1] due to the importance of this molecule as the simplest example of a class of biologically significant ligands. Numerous X-ray[2,3] and NMR[4] studies of variously substituted porphyrins have been reported in the literature, and they all indicate a highly symmetric structure for porphyrin with nearly equivalent C–C bonds. Theoretical studies have also been undertaken,[5-17] but because of the large size

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