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Proton Magnetic Resonance Study of Piezoelectric Lithium Formate Monohydrate*

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Proton magnetic resonance (p.m.r.) in a single crystal of piezoelectric lithium formate monohydrate was investigated and two inequivalent p–p vectors were observed, each of length 1·63 Å. By suitable H-bonding schemes, the positions of the water protons were fixed. Also, the effect of vibrational and torsional motions on the observed length of the p–p vectors was discussed. The temperature dependence of the second moment in a powder sample showed a small transition at about 320°K and an abrupt and steep transition at about 370°K. The p.m.r. was investigated in a single crystal at 335°K and the Pake curve showed no change in the angular dependence but the length of the p–p vectors increased to 1·68 A.

Introduction

The investigation of hydrated crystals using proton magnetic resonance (p.m.r.) was pioneered by Pake (1948) and was advanced by several others (McGrath & Silvidi, 1963; Pedersen, 1964). Proton pairs in the water molecules of hydrated crystals form typical two spin systems and the intramolecular dipole–dipole interaction results in a splitting of the p.m.r. spectrum. The separation between the two lines for such a two-proton system, with reference to the crystallographic axes, is given by the Pake equation (Pake, 1948)

$$\Delta H=2\alpha[3\cos^2(\varphi-\varphi_0)\cos^2\delta-1]$$

where ΔH is the line separation in gauss, $2\alpha=3\mu/r3$ (μ is the proton magnetic moment, r is the proton–proton (p–p) separation), φ is the angle between H_0 and a reference axis in the plane of crystal rotation, φ_0 is the angle between the projection of the p–p line on to the above plane and the reference axis and δ is the angle between the p–p line and the plane of crystal rotation.

By studying the angular dependence of the p.m.r. spectrum in a single crystal it is possible to determine the parameters α, φ_0 and δ which completely specify the length and orientation of the p–p vector in the unit cell. This information, along with the heavy-atom structure and possible hydrogen bonding schemes, helps in fixing the positions of the water protons in the crystal.

As part of a general programme of study of hydrated crystals, we have investigated the p.m.r. in piezoelectric lithium formate monohydrate (LFMH) and the results are reported in this paper. Piezoelectricity in this compound was first reported by Chumakov & Koptsik (1961). Recently Singh, Bonner, Potopowicz and Van Uitert (1970) reported that, of all the solution-grown crystals, LFMH has the highest second harmonic conversion efficiency. Tiwary & Narayanan (1971) from their studies concluded that this crystal is also pyroelectric. The X-ray analysis of the crystal structure was carried out recently by Mohana Rao & Viswamitra (1971) and also by Torre, Abrahams & Bernstein (1971). Torre *et al.* suggest that this crystal is potentially ferroelectric. The infrared study was carried out by two different groups of workers (Harvey, Morrow & Shurvell, 1963; Donaldson, Knifton & Ross, 1964) and recently Ramanujam (1969) and Cadene (1970) independently recorded the Raman spectrum. All these investigations support the existence of H-bonding in this crystal.

The independent X-ray studies of Mohana Rao & Viswamitra (1971) and of Torre *et al.* (1971) gave the same results and confirmed the conclusions drawn by Cadene (1970) from his Raman effect studies. LFMH crystallizes (Mohana Rao & Viswamitra, 1971) in the orthorhombic system with a tetramolecular unit cell of dimensions $a=6{\cdot}504$, $b=9{\cdot}989$ and $c=4{\cdot}856$ Å. The space group is $Pbn2_1$. The crystallographically equivalent positions are given by (x,y,z), $(\frac{1}{2}-x,\frac{1}{2}+y,z)$, $(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2})$ and $(-x,-y,\frac{1}{2}+z)$. The formate ion, the water oxygen atom and the lithium ion lie in a plane approximately parallel to the (100) plane. The lithium ion is tetrahedrally coordinated by the oxygen atoms with a mean Li–O distance of 1·95 Å. Neighbouring tetrahedra related by the 2_1 screw share a corner and this results in an infinite chain of water molecules along the **c** axis. By difference Fourier synthesis the X-ray workers were able to locate the formate hydrogen atom and one of the water hydrogen atoms. However, the other water hydrogen atom along the c axis could not be located in this manner. Torre's structure analysis showed that the spontaneous polarization is largely determined by the contribution from the water dipole moment. Hence the present study was undertaken with a view to fixing the positions of the protons of the water molecules in this crystal and also to study any possible phase transitions.

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* A brief summary of this work was presented in the Nuclear Physics and Solid State Physics Symposium, February 1972, Bombay.

Experimental details

An aqueous solution of lithium formate was prepared by the addition of concentrated Analar grade formic acid to lithium carbonate in stoichiometric proportions. After the reaction was over, the solution was slightly acidified and allowed to evaporate slowly. The crystals obtained were elongated along the [001] direction. Since the signal-to-noise ratio was found to be rather poor in this substance, it became necessary to grow large single crystals. Two crystals, one suitable for rotation about the *a* axis and the other suitable for rotation about the *c* axis, were cut from a big single crystal. The crystals used in our experiments had rectangular cross sections with dimensions $2 \times 1{\cdot}5 \times 1$ cm. The edges of the crystals were rounded off to give the best filling factor in the r.f. coil.

The p.m.r. spectra were recorded using a home-made PKW type n.m.r. spectrometer (Pound, 1952) working at 13·5 MHz. The modulation width was about 1 gauss at 330 Hz and the magnetic field was swept at a rate of 0·05 gauss $\sec^{-1}$. The first derivative of the resonance line was recorded on a chart recorder.

The crystal was rotated about the *a* axis and the signals were recorded for 18 orientations at intervals of 10° each. The *c* axis was taken as the reference direction and the initial alignment ($\varphi = 0$) was with the *c* axis parallel to the static magnetic field H_0. The crystals had well developed faces parallel to the crystallographic axes and so the axis of rotation (*viz. a* axis) could be fixed without any difficulty. Also, when the magnetic field is parallel to the *b* axis ($\varphi = 90°$) the two inequivalent p–p vectors become equivalent and the spectrum should have only two components (only one value for ΔH). This condition was used to check the crystal setting and the accuracy is of the order of ±1°.

All the experimental curves had a central peak due to the protons of the formate group. In addition, there were two pairs of doublet lines due to two non-equivalent p–p vectors of the water molecules. The two pairs of doublet lines coalesce into a single pair when the *c* axis is making an angle of 90° with H_0. The intensities of the spectra due to the two pairs are equal indicating that the two p–p vectors lie in equal magnetic surroundings. A standard water-proton derivative curve was prepared from the best resolved spectrum and two such pairs of derivative curves were used in conjunction with the central signal to resolve the experimental curves. A ΔH value was measured for each pair and the values of ΔH were assigned to the two vectors in the following way.

Since there are two non-equivalent vectors there are two sets of $\Delta H_{\max}$ and $\Delta H_{\min}$. These values were substituted in the equations,

$$\Delta H_{\min} = -2\alpha \text{ when } (\varphi - \varphi_0) = 90°$$

and

$$\Delta H_{\max} = 2\alpha(3\cos^2\delta - 1) \text{ when } \varphi = \varphi_0,$$

to obtain approximate values of α, φ_0 and δ for each vector. With these values the theoretical Pake curves were plotted and the values of ΔH lying close to each curve were assigned to one p–p vector. Through suitable small variations in these values of α, δ and φ_0, a satisfactory visual fit of the experimental points with the theoretical curves was accomplished. This fit was further improved by the method of least-squares and this gave the final set of values of α, δ and φ_0.

A second crystal was rotated about the *c* axis and the spectra were recorded at intervals of 10°. The spectral intensities were unusually poor in this case and the spectra were not well resolved, making the complete analysis very difficult. However, the spectra, at a few favourable orientations where they could be analysed, gave results that agreed well with the *a* axis results.

It is known that CG–CG splittings (and not max–max splittings) give the correct Pake splittings when interpair interactions are strong and anisotropic giving rise to asymmetric signals. In this case the standard derivatives are asymmetric and depend on orientation. In our experiments, the spectra appeared to be symmetric and could be resolved using symmetric standard derivatives. Also except in favourable cases, it is difficult to apply the CG–CG method and so, to date, most authors have used the 'max–max' method only. In view of the symmetric nature of the spectra and in view of the fact that the spectra were not well resolved in many orientations, we used the 'max–max' method only.

Results and discussion

1. *Location of water protons*

The theoretical Pake curves along with the experimental points for rotation about the *a* axis are shown in Fig. 1. A value of 9·69 gauss for 2α was obtained for both the p–p vectors, thus giving an interproton distance of $1{\cdot}63 \pm 0{\cdot}02$ Å. The φ_0 and δ values for the two p–p vectors are given in Table 1.

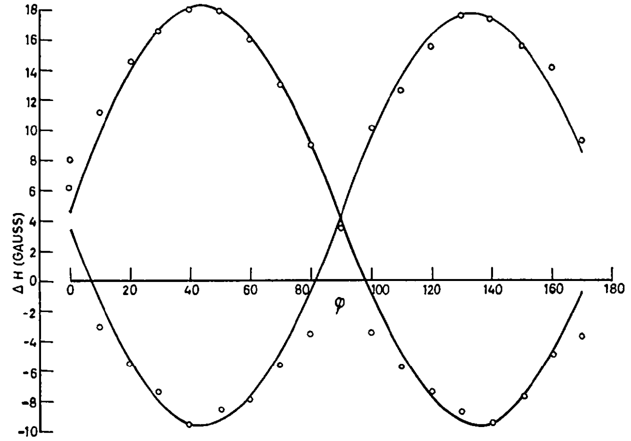

Fig. 1. Theoretical Pake curves and experimental points for rotation about the *a* axis in LFMH.

Table 1. *Orientation of the two* (p–p) *vectors in LFMH*

φ was taken to be 0° when H_0 was parallel to the *c* axis.

	φ_0	δ
$(\text{p–p})_1$	45°	11°
$(\text{p–p})_2$	134	13

The crystal structure of LFMH projected on the *bc* plane is shown in Fig. 2. The possible H-bonding schemes in LFMH were pointed out by X-ray workers and the bond lengths and angles were found to be

O_W–O(1)	2·732 Å ,
$O_W-O_W(-x,-y+1,\frac{1}{2}+z)$	2·900 Å ,
$O(1)-O_W-O_W(-x,-y+1,\frac{1}{2}+z-1)$	86°24′,
$O(1)-O_W-O_W(-x,-y+1,\frac{1}{2}+z)$	118°48′.

The hydrogen on the O(1)–O_W bond was located from the difference Fourier synthesis but the position of the second hydrogen atom on the O_W-O_W bond could not be located by the X-ray workers. They suggested that this hydrogen can either occupy a single potential minimum and be closer to one of the two water oxygens, O_W or $O_W(-x,-y+1,\frac{1}{2}+z)$, or be disordered, occupying two potential minima between these two.

The H bonds in the structure between O_W atoms related by the 2_1 screw result in the formation of an infinite chain of water oxygen atoms. It may be noted that a similar chain exists in piezoelectric lithium sulphate monohydrate (Larson & Helmholz, 1959).

In a p.m.r. experiment only the length and the orientation of the p–p vector are determined. But since the H atoms participate in hydrogen bonding, the p–p vector and the line joining the two acceptor atoms are expected to be approximately parallel, especially when the bonds are linear and of normal length. Therefore, the angles φ_0 and δ were calculated for the various O–O lines from the X-ray data and these values are given in Table 2.

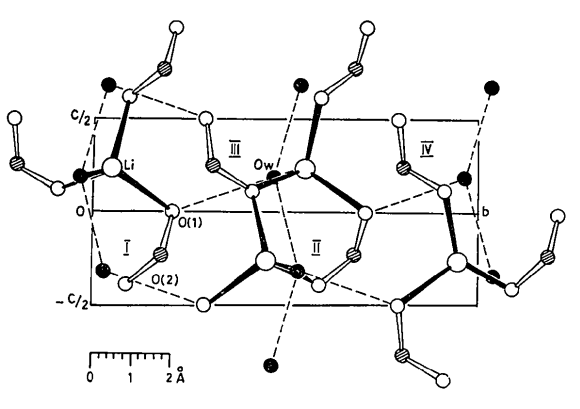

Fig. 2. Projection of the structure of LFMH along the *bc* plane (Mohana Rao *et al.*, 1971).

Table 2. *Orientations of the* O–O *lines which involve the acceptor oxygen atoms suggested by X-ray study* (*Mohana Rao et al.*, 1971)

H-bonding scheme	φ_0	δ
1· $O(1)\ O_W(-x,\ -y+1,\ \frac{1}{2}+z-1)$	64°42′	20°56′
2· $O(1)\ (-x,\ -y+1,\ \frac{1}{2}+z-1)$ $-O_W(x,\ y,\ z-1)$	115°18′	20°56′
3· $O_W-O(1)\ (-x,\ -y+1,\ \frac{1}{2}+z-1)$	44°30′	16°30′
4· $O(1)-O_W(-x,\ -y+1,\ \frac{1}{2}+z)$	135°30′	16°30′

A comparison of Tables 1 and 2 shows that the p–p vectors are parallel to the O–O directions 3 and 4. The H–O–H angle for this arrangement in the crystal was calculated using the values of the O–H distances given by the correlation diagram (Hamilton & Ibers, 1968) and this was found to be 114°47′. The O(1)–O_W–$O_W(-x,-y+1,\frac{1}{2}+z)$ angle given by the X-ray workers is 118·8°.

2. *Effect of vibrational motions*

The value of 1·63 Å obtained for *r* in our experiment is a little on the high side and indicates the presence of significant vibrational motions of the water molecule. The mean square amplitude of the vibration and the potential barrier V_0 hindering the vibration are calculated using the equations given by Pedersen (1964).

A reasonable value for V_0 is 6·5 kcal/mole when the water molecule is bound to two oxygen atoms (Pedersen, 1964). Using this value we obtain r_e, the equilibrium p–p distance, as 1·55 Å. But it is reasonable to assume that this value of r_e should be very nearly equal to the vapour-phase value of 1·518 Å. Assuming this to be the case, we get the mean square amplitude $\langle\theta_z^2\rangle$ to be 0·082 and the height of the potential barrier as 4 kcal/mole in the case of LFMH compared with about 6·5 kcal/mole encountered in other hydrated solids. This low value of the potential barrier explains the slightly higher value of 1·63 Å for the p–p distance in LFMH at room temperature as compared to the *r* value of 1·58 to 1·60 Å usually encountered in hydrated solids.

In the above derivation it has been assumed that the potential energy function is axially symmetric about the hydrogen bond, in which case $\langle\theta_x^2\rangle=0{\cdot}68\langle\theta_z^2\rangle$. However, depending on the form of the potential energy function, the mean square amplitudes $\langle\theta_x^2\rangle$ and $\langle\theta_z^2\rangle$ may be nearly equal (Pedersen, 1964). Assuming $\langle\theta_x^2\rangle=\langle\theta_z^2\rangle$ and $\langle\theta_z^2\rangle=0{\cdot}056$ (Pedersen, 1964) we get a value of 1·52 Å for r_e, the equilibrium p–p distance which agrees well with the vapour-phase value.

3. *Temperature dependence of the p.m.r. spectra*

The proton positions in the crystal having been located, the temperature variation of the powder spectrum was next studied. The probe used for this purpose was a modified version of the one described by Gutowsky, Meyer & McClure (1953). The room temperature signal was broad and poor in intensity. As the temperature was lowered below room temperature, the signal became undetectable. However, as the temperature was raised there was considerable improvement in the signal to noise ratio of the spectrum. The spectra were recorded up to about 380°K. Fig. 3 shows the plot of second moment *vs.* temperature in this range. It can be seen that as the temperature is raised the second moment starts falling in the temperature range of 315–330°K and then remains constant up to 370°K. Again, at 370°K the second moment falls abruptly to a very low value. On cooling the substance, the wings started appearing very slowly, though the intensity of the wings remained much smaller. Since lithium sulphate monohydrate has a similar H-bonding scheme, a powder sample of that substance was heated up to about 410°K and the spectra recorded but no noticeable effect on the spectrum was observed.

Though the Pake equation has been derived on the assumption of a rigid lattice, a more careful consideration shows that such an assumption is not necessary. For example a 180° flip motion of the two protons about the twofold axis of the water molecule does not produce any physical change in the system and the Pake doublet remains unaffected, assuming that interpair interactions are not too strong to introduce second-order effects. (This is usually a good assumption and 180° flip motion is best studied using deuteron magnetic resonance.) The other possible types of motion are classical free rotation and hindered rotation about an n-fold axis or quantum-mechanical tunnelling through a periodic n-fold potential barrier when $n \geq 3$. In this case the Pake splitting is given by

$$\Delta H = \tfrac{3}{2}\mu r^{-3}(3\cos^2\gamma - 1)\,(3\cos^2\theta' - 1)$$

where γ is the angle between the axis of reorientation and the p–p vector, while θ' is the angle between the axis of reorientation and the magnetic field. Thus the Pake treatment of the dipole interaction remains valid even in the presence of motion of the spins but now the line splittings and the observed second moments decrease.

In a powder sample γ can be calculated using the expression,

$$\frac{\text{second moment for rotating proton pairs}}{\text{second moment for rigid proton pairs}} = (\tfrac{1}{4})\,(3\cos^2\gamma - 1)^2\,.$$

In the present case γ was calculated to be 17° for the first transition. However, we could not find any suitable axis in the crystal making this angle of 17° with the p–p vector.

To obtain a better idea of the type of change taking place in the spectrum, a single crystal was rotated about the a axis at 335°K and the spectra were recorded for various orientations. The spectra remained the same as those at room temperature except for the narrowing of the resonance lines. The spectra were resolved and the Pake curves were drawn. The values of r, φ_0 and δ are shown in Table 3. It can be seen that the values of φ_0 and δ remained almost the same as at room temperature but the value of r increased from 1·63 to 1·68 Å. Thus, as the temperature of the substance is increased, there is an increase in the interproton distance of the water molecules. This increase in r also accounts for the small drop in the second moment of the powder sample because of the r^{-6} dependence of the moment. A similar observation was made by Pietrzak (1965) on a single crystal of beryllium sulphate tetrahydrate where the value of r was found to be 1·68 Å at room temperature and decreased to 1·63 Å as the temperature was lowered. However, no explanation was offered for this change in the value of r.

Table 3. *Orientation of the two* (p–p) *vectors in LFMH at* 335°K

φ was taken to be 0° when H_0 was parallel to the c axis.

	φ_0	δ	r
$(\text{p–p})_1$	44°	12°	1·68 ± 0·02 Å
$(\text{p–p})_2$	135	11	1·68 ± 0·02

As we have seen before, the O(1)–O_W–O_W angle determined from X-ray studies is 118°48′ while the H–O–H angle obtained is 114°47′. This may mean slightly bent hydrogen bonds. Chidambaram (1962) has shown from energy considerations that bent H bonds are more probable.

The X-ray workers were able to locate one of the hydrogen atoms of the water molecule but could not locate the other at room temperature. It is possible that this H atom has a large thermal parameter. As the temperature is raised this hydrogen atom becomes freer and this extra thermal energy may increase the H–O–H angle leading to the formation of linear hydrogen bonds. This would mean an increase in the

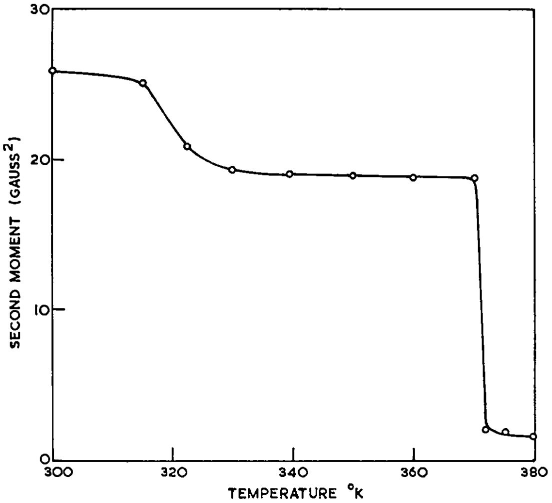

Fig. 3. Variation of second moment with temperature in a powder sample of LFMH.

p–p length also. Assuming that the H–O–H angle increases to 118°48′ as in the case when linear H bonds are formed in LFMH, the p–p length increases to 1·67 Å. As this is in fair agreement with our experimental value it is possible that the H bonds which are slightly bent at room temperature become linear as the temperature is raised.

At 370°K the second moment abruptly drops to a very low value. After the experiment, it was noticed that crystals had regrown on the walls of the sample tube from the powder. On heating the sample outside in an open tube we found that the sample first loses its water and then decomposes. But if we heat the sample in a closed tube the sample first gives out water and then dissolves in it becoming a colourless liquid. On slow cooling crystals started growing slowly. An infrared spectrum of the crystal grown in 'melt' showed no change from that grown from solution. In our n.m.r. experiment, since the powder was well packed in the sample tube the sample inside must have 'melted' because of the protective cover of the upper layer, thus accounting for the abrupt transition in the spectrum. This opens up possibilities of growing large crystals of this optically important substance by the melt technique.

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The Crystal and Molecular Structure of 8-[3-(*p*-Fluorobenzoyl)propyl]-1-phenyl-1,3,8-triazaspiro[4,5]decan-4-one, $C_{23}H_{26}N_3O_2F$

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Crystals of the title compound, $C_{23}H_{26}N_3O_2F$, are monoclinic, space group $P2_1/c$ with $a=18\cdot571$, $b=6\cdot072$, $c=20\cdot681$ Å, $\beta=118\cdot69°$ and $Z=4$. The structure was solved by direct methods and refined by block-diagonal least-squares calculations to an R value of 0·09. The results are compared with those obtained previously on butyrophenone derivatives and the observed differences are explained on the basis of conformational energy calculations.

The title compound, usually called spiroperidol, is one of the most potent neuroleptic drugs known to date. It is 3500 times more potent than chlorpromazine in dogs. It seemed interesting to determine this structure and to compare it with the other known compounds in the butyrophenone series (Koch & Germain, 1972).

Experimental

The single crystals used were obtained as colourless needles by evaporation from a 60:40 mixture of 2-propanol and dimethylformamide. Their quality was rather poor (high mosaicity). The crystal data and