

Effects of Temperature on some Hydrogen-Bond Networks in Crystals

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Observations on acetylene dicarboxylic acid dihydrate show that the crystal form (α) ordinarily obtained is stable from the melting point (about $+40^\circ\text{C}$.) down to about $+3^\circ\text{C}$. Below this range, X-ray reflexions reveal a continuous transformation to a new (β) polymorph. Intensity measurements show marked hysteresis in a thermal cycle including this change. At around -40°C . there is a further discontinuous transformation to a third (γ) polymorph. Dielectric measurements on the powders do not indicate the onset of ferro-electric properties at either transition.

The dihydrates of oxalic acid and of α acetylene dicarboxylic acid contain a structurally similar network of hydrogen bonds. In order to compare the thermal behaviour of these two networks, thermal expansions have been measured for the two crystals in all directions for which they were not previously known. In spite of the differences in the acid residues, the thermal expansions of the two crystals are closely similar.

One dominant effect in both crystals appears to be the sensitiveness of short hydrogen bonds to their vibrational energy content. In both crystals, directions of maximum thermal expansions in the sections of the expansion ellipsoid by the (010) plane and directions of the maximum isotope effects in this plane lie near to directions of the short hydrogen bonds. At right angles to these maximum expansions, in the (010) plane, expansions are much smaller. Both crystals also show marked thermal expansion along the symmetry (b) axis. This appears to be a property of the helices of hydrogen bonds joining the molecules in the crystals.

Introduction

Crystals whose structures are predominantly maintained by hydrogen bonds can be particularly sensitive to changes in thermal vibrations. One method of study is to compare hydrogen and deuterium crystals at the same temperature. On substituting hydrogen by deuterium, changes of lattice spacing are observed (e.g. Robertson & Ubbelohde, 1939*a*; Dickson & Ubbelohde, 1950) which can generally be attributed to changes in bond length, particularly of the shortest hydrogen bonds. There may also be concurrent changes in the molecular packing, especially when there are cooperative systems of hydrogen bonds in the lattice, such as networks of helices. Occasionally, these changes on substituting D for H are sufficiently large to result in the spontaneous crystallization of a polymorph of different structure, as in the case of KH_2PO_4 (Ubbelohde & Woodward, 1942) or resorcinol (Robertson & Ubbelohde, 1938).

Isotope substitution appears to change primarily the bond length and bond strength of the shorter $\text{O}\cdots\text{HO}$ bonds. Information about the more general influence of thermal vibrations on crystal structure can be obtained by comparing isotope effects with the overall thermal expansion. One object of the present research was to measure the overall thermal expansions of acetylene dicarboxylic acid dihydrate (hereafter re-

ferred to as ADAD) and to compare the magnitudes $\theta\alpha_{jj}$ and the directions of the principal axes of the ellipsoid of thermal expansion, with related values of $\rho\alpha_{jj}$, the isotope effect (Gallagher, Ubbelohde & Woodward, 1954). It has been found that, as the temperature is lowered, ADAD undergoes polymorphic transitions from the previously described α form to a β form at about $+3^\circ\text{C}$. and from the β form to a γ form at about -40°C . Persistence of crystal axes has been observed in single crystals taken through thermal cycles including the $\alpha \rightleftharpoons \beta$ transition. Pending measurements on the specific volume and specific heat of the crystals, the X-ray findings suggest that the transition may be added to the class of thermodynamically continuous (second order) transformations (cf. Kennedy, Ubbelohde & Woodward, 1953). On the other hand, the transition $\beta \rightarrow \gamma$ at about -40°C . involves a break-up into powder and is discontinuous (first order). These findings limited the range of temperatures over which the thermal expansion of the α crystal could be measured, for comparison with the isotope effect. Within the range $+35^\circ\text{C}$. to about $+3^\circ\text{C}$. the anisotropy of thermal expansion was found to be closely related to, though not identical in direction with, the isotope effect. Both sets of observations indicate that hydrogen bonds are markedly sensitive to thermal vibrations, particularly when they are short.

Oxalic acid dihydrate and ADAD contain closely

similar networks of hydrogen bonds. The main differences lie in the masses (molecular weights 88 and 112) of the acid residues, in the fraction of the crystal volume they occupy and in the acidity of the groups. Interesting correlations are possible between the effects of thermal vibrations on the pair of substances. For this purpose, the thermal expansion of oxalic acid dihydrate was measured along the b axis, under the same conditions as were used for the previously reported thermal expansions (Robertson & Ubbelohde, 1939*b*) normal to this axis. The effects of thermal vibrations on the two structures show close analogies. Such peculiarities as are observed indicate that torsional oscillations of the acid molecules strongly influence the dimensions of molecular helices in which the links are formed by hydrogen bonds.

Experimental

Crystals of acetylene dicarboxylic acid dihydrate (H and D) were prepared and mounted in thin pyrex envelopes as previously described (Gallagher, Ubbelohde & Woodward, 1954).

Microthermostat

For thermal studies on ADAD it was necessary to modify the low-temperature microthermostat previously described (Ubbelohde & Woodward, 1946),

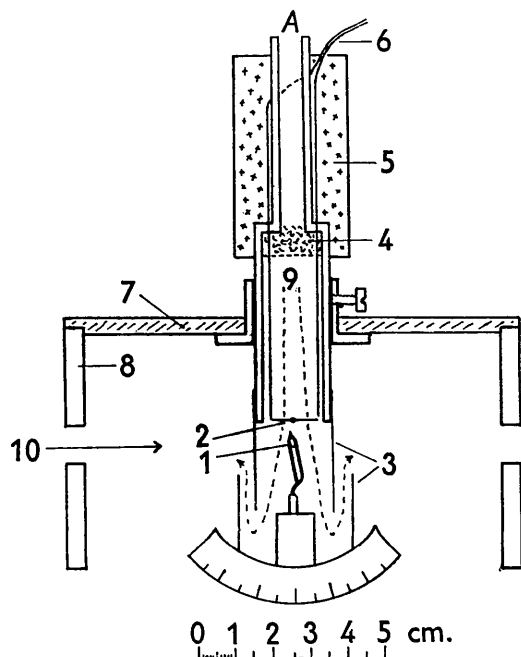


Fig. 1. Diagram to illustrate thermal chamber and support on multiple-exposure camera.

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|---------------------|------------------------|
| 1. Crystal. | 6. Thermocouple leads. |
| 2. Thermocouple. | 7. Perspex. |
| 3. Cellophane. | 8. Collimator holder. |
| 4. Copper turnings. | 9. Air stream. |
| 5. Insulation. | 10. X-ray beam. |

because of the need to traverse room temperature in covering the range from $+35^{\circ}\text{C.}$ to $+3^{\circ}\text{C.}$

A strong steady stream of air was blown over the crystal in its pyrex envelope and escaped between overlapping cellophane baffles (Fig. 1). This stream was previously brought to any desired temperature between $+100^{\circ}\text{C.}$ to -40°C. by passing through an adjustable heater unit and when necessary by the admixture of cold gas obtained by boiling liquid oxygen at a controlled rate. The temperature inside the cellophane chamber was measured by a fixed thermocouple about 2 mm. above the crystal. Temperature gradients in this chamber at 0°C. (room temperature 20°C.) as measured by an auxiliary exploring thermocouple were found to be:

Vertical temperature gradient $\approx 0.1^{\circ}\text{C. mm.}^{-1}$.

Horizontal temperature gradient within 3 mm. of centre of chamber $\sim 0.01^{\circ}\text{C. mm.}^{-1}$.

During use over 30-min. periods, the average deviation from the mean temperature was found to range from $\pm 0.25^{\circ}\text{C.}$ at 0°C. to $\pm 0.1^{\circ}\text{C.}$ at 70°C.

For oxalic acid dihydrate it was necessary to obtain measurements of the thermal expansion along the b axis over the same temperature range as used previously for other directions in this crystal. The crystals grown from an aqueous solution were sealed in thin pyrex tubes (Ubbelohde, 1950). When necessary they were cooled by a liquid drip to the boiling point of oxygen (Robertson & Ubbelohde, 1939*b*).

For all the thermal-expansion measurements, oscillation photographs on an Ubbelohde multiple-exposure camera were taken with unfiltered $\text{Cu } K\alpha$ radiation.

Thermal expansion results

In both compounds the monoclinic symmetry of the crystal requires that one axis ($\theta\alpha_{22}$) of the expansion ellipsoid should be in the direction of the symmetry (b) axis and that the $\theta\alpha_{11}$ and $\theta\alpha_{33}$ axes lie in the (010) plane. At least three measurements must be made in the ($h0l$) zone in order to determine their directions as well as their magnitudes; one further measurement in a direction near the b axis will then determine $\theta\alpha_{22}$.

Acetylene dicarboxylic acid

By analogy with oxalic acid dihydrate (Robertson & Ubbelohde, 1939*b*) it was expected that the principal axes of the thermal expansion ellipsoid would lie near those for the isotope effect. This influenced the choice of planes, which are recorded in Table 1 together with the values of the coefficients of expansion obtained. The general procedure has been detailed in a previous paper (Gallagher *et al.*, 1954). Mean errors for $\theta\alpha_{11}$, $\theta\alpha_{33}$ and the angle $\theta\psi$ between $\theta\alpha_{11}$ and the normal to the (100) plane were estimated from the results for those planes which are most sensitive to the parameter in question. For $\theta\alpha_{22}$ the

Table 1. *Thermal expansion of acetylene dicarboxylic acid dihydrate*

Plane	Bragg angle	No. of independent observations	Temperature range (°C.)	Expansion, $\Delta d/d \times 10^5 / ^\circ\text{C.}$	
<i>h</i> 0 <i>l</i> zone	77° 48.8' (Cu $K\alpha_1$)	12	+ 6 to + 35	3.05 } 3.13 }	
	4,0, $\bar{1}0$	78° 30.1' (Cu $K\alpha_2$)			12
80 $\bar{9}$	77° 35.2' (Cu $K\alpha_1$)	12		2.40 } 2.29 }	
	78° 15.9' (Cu $K\alpha_2$)	12			
14,0, $\bar{3}$	81° 22.0' (Cu $K\alpha_1$)	12		1.35 } 1.20 }	
	82° 19.2' (Cu $K\alpha_2$)	12			
10,0,6	76° 40.9' (Cu $K\alpha_1$)	12		1.19 } 1.19 }	
	77° 17.6' (Cu $K\alpha_2$)	12			
<i>o</i> <i>k</i> <i>l</i> zone	81° 40.1' (Cu $K\alpha_1$)	6		+ 5.4 to + 18.7	17.0 } 19.3 }
	046	82° 4.12' (Cu $K\alpha_2$)			
046	81° 40.1' (Cu $K\alpha_1$)	2		+ 18.7 to + 31.6	17.0 } 18.8 }
	046	82° 41.2' (Cu $K\alpha_2$)			

mean error was derived from the mean deviation of $\Delta d/d$ for the different observations on the 046 reflexion. The thermal expansion in the (010) plane, as calculated from these values of $\theta\alpha_{11}$, $\theta\alpha_{33}$ and $\theta\psi$, can be conveniently related to the crystal structure by a vectorial plot (Fig. 2(a)). The directions of the isotope expansion and the projection of the short hydrogen bond (2.56 Å) are shown for comparison in Fig. 7(a). In this plane, the maximum thermal expansion $\theta\alpha_{11}$ makes an angle of 26° 35' with the projection of the short hydrogen bonds and an angle of 21° 50' with the direction of maximum isotope effect ${}_1\alpha_{11}$, which lies much closer to the directions of the short hydrogen bonds.

In order to determine whether $\theta\alpha_{22}$ suffered any change on approaching the upper transition at +3° C. (see discussion) the expansion was measured in two ranges of temperature (Table 2).

Table 2. *Thermal expansion ellipsoid of acetylene dicarboxylic acid dihydrate*

<i>jj</i>	Temperature range (°C.)	$\theta\alpha_{jj}$, expansion $\Delta d/d \times 10^5 / ^\circ\text{C.}$
11	+ 6 to + 35	+ 3.06 ± 0.30
22	+ 5.4 to + 18.7	+ 25.7 ± 2.1
	+ 18.7 to + 31.6	+ 25.0 ± 1.8
33	+ 6 to + 35	+ 0.73 ± 0.26
$\theta\psi$	+ 6 to + 35	+ 96° 49' ± 6°

A polar diagram of the thermal expansion in the (201) plane is shown in Fig. 2(b). This is based on the mean of the values of $\theta\alpha_{22}$ for the two ranges of temperature, since no significant change was found on approaching the $\alpha \rightarrow \beta$ transition temperature.

Oxalic acid dihydrate

Few planes nearly normal to the *b* axis have high Bragg angles when Cu $K\alpha$ radiation is used. The

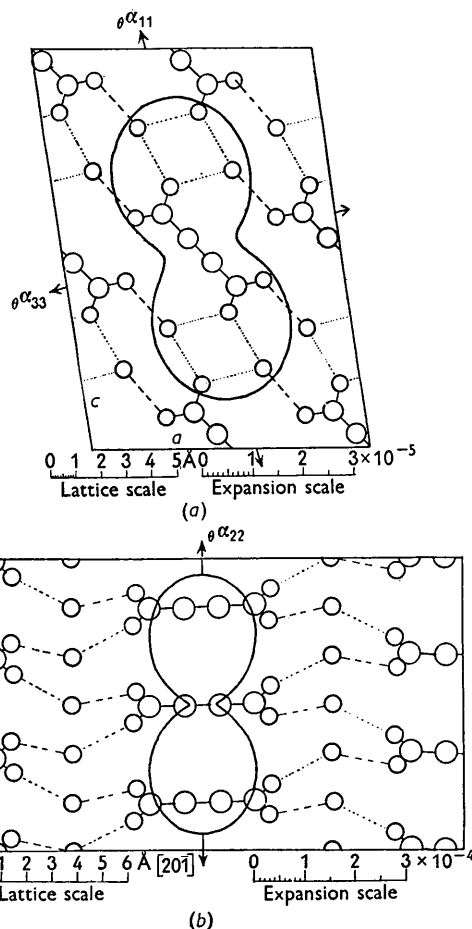


Fig. 2. Thermal expansion of acetylene dicarboxylic acid dihydrate (a) in (010) plane, (b) in (201) plane. Short hydrogen bonds shown by broken lines.

reflexions selected were given by the $53\bar{5}$ and $14\bar{1}$, with Bragg angles 65° 53' and 60° 10'. The normals

to these planes make angles of $45^{\circ} 16'$ and $8^{\circ} 32'$ respectively with the b axis.

The expansion normal to the $(10\bar{1})$ plane was calculated from the results of Robertson & Ubbelohde (1939b) to be 6.430×10^{-3} for the temperature range 90° K. to 290° K. In conjunction with the observed expansions normal to $53\bar{5}$ and $14\bar{1}$ this gives

$$[\epsilon_{\alpha_{22}}]_{90^{\circ} \text{ K.}}^{290^{\circ} \text{ K.}} = 31.1 \times 10^{-3} \text{ from } 53\bar{5} \text{ and } 30.4 \times 10^{-3} \text{ from } 14\bar{1}.$$

The mean value adopted, 30.7×10^{-3} , is considered to be probably correct to within 1%. A polar diagram of the thermal expansion in the (101) plane is shown in Fig. 3. The parameters for the thermal ellipsoid are collected in Table 3.

Table 3. *Thermal expansion ellipsoid of oxalic acid dihydrate (temperature range -183° C. to $+17^{\circ}$ C.)*

jj	Source	$\epsilon_{\alpha_{jj}}$, expansion $\Delta d/d \times 10^6/^{\circ}\text{C.}$
11	Robertson & Ubbelohde, 1939b	+ 5.5
22	Present work	+15.4
33	Robertson & Ubbelohde, 1939b	+ 0.00
ϵ_{ψ}		$110^{\circ} 30'$

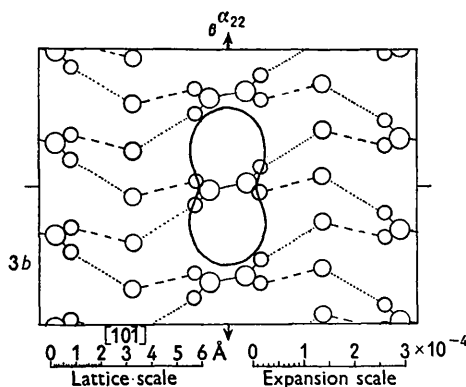


Fig. 3. Thermal expansion of oxalic acid dihydrate in (101) plane. Short hydrogen bonds shown by broken lines.

Eye estimations of intensity of the $14\bar{1}$ reflexions were used as previously described (Ubbelohde & Woodward, 1943) to calculate the increase of amplitude of thermal vibration normal to the (010) plane, corresponding with the observed thermal expansions.

From the results, $\sqrt{\{u_x^2(+16^{\circ} \text{ C.}) - u_x^2(-183^{\circ} \text{ C.})\}}$ was found to be 0.14 ± 0.01 Å. On the films available, the $53\bar{5}$ reflexion was unsuitable for making comparisons of intensities at different temperatures.

Observations on the $\alpha \rightleftharpoons \beta$ and the $\beta \rightarrow \gamma$ transitions in acetylene dicarboxylic acid dihydrate

Three methods were used to study these transitions.

(i) On lowering the temperature of the micro-

thermostat by small steps, and taking a series of rotation or oscillation photographs of the $(h0l)$ zone with the multiple-exposure X-ray camera, many of the reflexions were found to disappear below the $(\alpha \rightarrow \beta)$ transition point. The temperature at which this disappearance was observed varied somewhat with different specimens, presumably because thermodynamic equilibrium in single crystals is subject to hysteresis and 'smearing' (Ubbelohde, 1954). The β crystal obtained on cooling changed back again to the α crystal, generally with marked persistence of axes, when the temperature was sufficiently raised; because of hysteresis, the transition temperatures on cooling and on heating do not coincide (Table 4).

Table 4. *Transition temperatures in single crystals of ADAD showing hysteresis*

Specimen	Cooling ($^{\circ}\text{C.}$)	Heating ($^{\circ}\text{C.}$)
1	-1.0	—
2	+0.5	+8.0
3	+3.0	—
4	+3.5	—
5	-6.0	+8.0

Additional photographic studies are required to give the complete geometrical information about persistence of axes (cf. Kennedy *et al.*, 1953). In one instance the crystal broke up into one large and several small fragments. This large fragment was then taken through many thermal cycles without further break-up, and with recurrence of the axes of the α crystal in each cycle. In view of the persistence of axes observed in the crystal after each completed thermal cycle $\alpha \rightleftharpoons \beta$, the crystal axes of the β form must bear a definite geometrical relationship to those of the α form. Pending more detailed crystallographic studies on the β form, the full relationship cannot be worked out.

When the β crystal was cooled below about -40° C. it shattered irreversibly to a white powder of the γ form.

(ii) Because of the time required, certain features of transitions in single crystals are difficult to follow by X-ray photographs. Much more rapid observations were possible using a single-crystal Geiger-counter spectrometer (McKeown & Ubbelohde, 1954) which became available towards the close of this research. For example, a deuterium crystal was mounted for the $(h0l)$ zone, and the intensity of the 202 reflexion was recorded automatically so as to obtain one complete traverse of the reflected beam every minute. The integrated intensities reached a constant value, characteristic of the temperature of the crystal, within 1 min. of any change of temperature. But marked hysteresis was observed according to the direction of the temperature change. A typical plot of integrated intensity against temperature is shown in Fig. 4. In another set of observations there was break-up of a single crystal into sub-crystalline units, with persistence of the mean crystal

axis. The 202 reflexion from a freshly prepared crystal spread over about 7 min. of arc, but after a thermal cycle $\alpha \rightleftharpoons \beta$ 'wings' to the reflexion extended over as much as 6 deg. of arc. Sub-units responsible for these 'wings' would be embedded in the 'single crystal' in a state of considerable strain, and would possess internal surface energy over the surface of internal

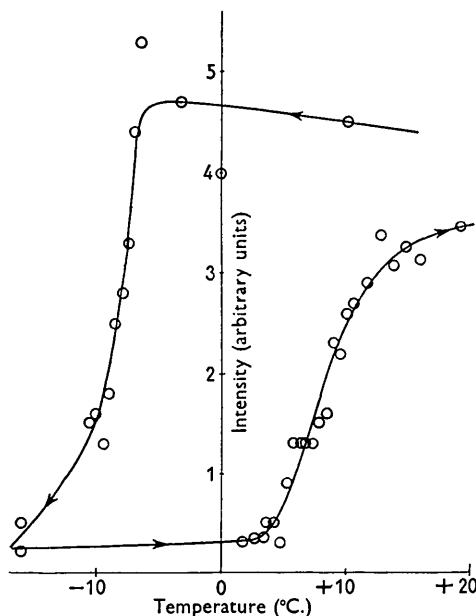


Fig. 4. Intensity of 202 reflexion from single crystal of acetylene dicarboxylic acid dihydrate on passing through the $\alpha \rightleftharpoons \beta$ transition, showing hysteresis.

misfit. As explained elsewhere (Ubbelohde, 1954) contributions to the free energy from such strain- and surface-energy terms lead to the 'continuous' nature of the transition, and to the hysteresis.

(iii) In order to test whether either the transition $\alpha \rightarrow \beta$ or $\beta \rightarrow \gamma$ leads to ferro-electricity, which has been observed on cooling other crystals containing cooperative assemblies of hydrogen bonds, possible changes in the dielectric constant of powdered ADAD

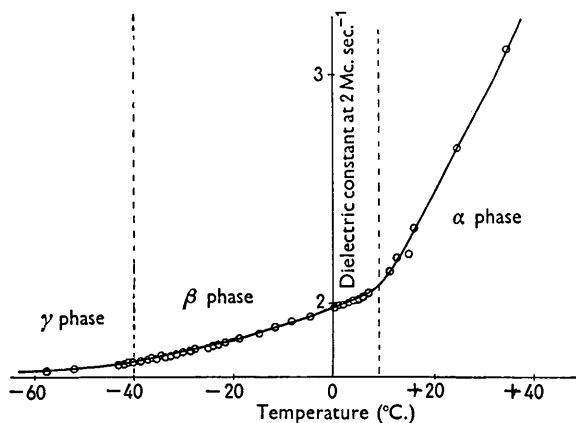


Fig. 5. Dielectric constant of acetylene dicarboxylic acid dihydrate plotted against temperature.

were investigated over a range of temperatures. The dry powder was tapped into the annular space between a glass cylinder, silvered on the inside, and a metal cylindrical core, silvered on its outside. This dielectric cell was submerged in a bath which could be maintained at various temperatures between -50°C . and $+30^{\circ}\text{C}$. Measurements of the dielectric capacity were made with at 2 Mc. sec.^{-1} and at 1 kc. sec.^{-1} .

Plots of the dielectric constant are shown in Fig. 5. They are given in arbitrary units since only a polycrystalline powder was available for these measurements. No ferro-electricity could be detected on cooling through either of the transitions.

Discussion

From the results, comparisons may be made between isotope effects ${}_{I}\alpha_{ij}$ and thermal expansions ${}_{\theta}\alpha_{ij}$ in each structure. Comparisons may also be made between corresponding effects in the two crystals. It appears that the crystal behaviour is predominantly controlled by the network of hydrogen bonds, and only depends in a subsidiary way on the acid molecule.

As is well known (e.g. Shaw, 1953; Gallagher *et al.*, 1954), certain assumptions must be made in order to infer bond-length alterations from measured changes in unit-cell dimensions. These assumptions might be avoided if a complete structure determination of sufficient accuracy were possible for the two states of the crystal, but generally this accuracy is much inferior to that with which changes in unit-cell dimensions can be measured. The following considerations may be used as a guide:

(i) Covalent C-C and C-O bonds are unlikely to suffer appreciable changes in length, in either oxalic acid or ADAD, due merely to changes in the vibrational energy content of the molecule.

(ii) On the present evidence, intramolecular twisting oscillations (Fig. 6) can probably be neglected around room temperature. The potential barriers opposing such oscillations are considerably larger than kT , particularly if the bond orders are greater than unity (McCoubrey & Ubbelohde, 1951).

(iii) Whilst factors (i) and (ii) explain why the nature of the acid molecule has only a subsidiary influence on the thermal behaviour of the crystals, differences may arise from the fact that both acid residues as a whole can probably change their orientations some-

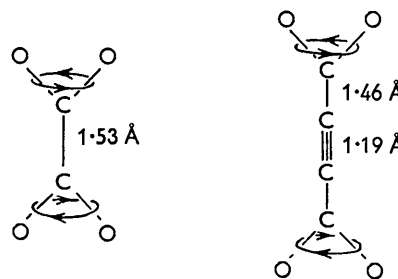


Fig. 6. Intramolecular twisting oscillations.

what in the crystal lattice, without requiring large increases in potential energy. Anharmonic oscillations involving changes of orientation of these molecules in the crystal lattice may consequently influence the thermal expansion, and may determine the onset of thermal transitions to related structures.

(iv) In both structures, a predominant influence on thermal behaviour is that of the hydrogen-bond helices. As in a number of previously studied cases (e.g. Robertson & Ubbelohde, 1939*b*; Ubbelohde & Woodward, 1947) the lengths of these bonds are likely to be sensitive to temperature, particularly when shorter than about 2.65 Å.

The behaviour of the present structures may be examined in the light of the above considerations.

Directions of expansion.—It can at once be noted that the smallest axes of the thermal expansion ellipsoids $\theta\alpha_{33}$ lie in the direction of sets of long hydrogen bonds (2.82–2.88 Å). The isotope effect in this direction shows a considerable contraction for ADAD and zero change for oxalic acid dihydrate. Thus these long hydrogen bonds do not appear to be sensitive to their content of vibrational energy. In the same (010) plane the maxima of thermal expansion lie near to the directions of the short hydrogen bonds (2.49 Å and 2.56 Å). Directions of these maxima differ somewhat for isotope effect and thermal expansion (Fig. 7), as might be expected if thermal expansion brings other vibrational contributions into play.

Both structures show a large $\theta\alpha_{22}$ thermal expansion along the axes of the helices formed by acid molecules linked by hydrogen bonds. ADAD likewise exhibits a marked isotope effect $\iota\alpha_{22}$ in this direction. (For oxalic acid dihydrate $\iota\alpha_{22}$ has not yet been measured.) One factor in this expansion can originate from an increase in the mean tilt of the acid molecules as the hydrogen bonds expand. Such a tilt brings with it a contraction in the α_{33} direction which could largely account for the negative value of $\iota\alpha_{33}$ in ADAD. In

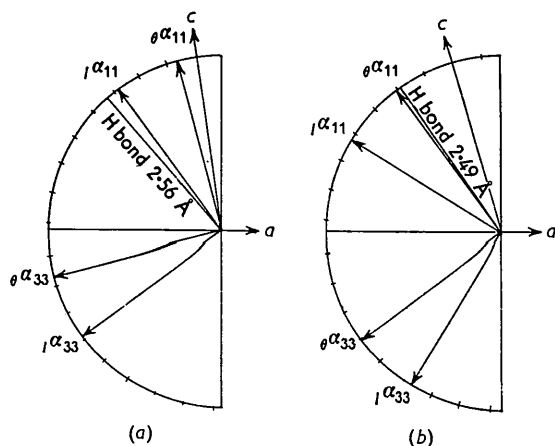


Fig. 7. Directions of principal axes of expansion ellipsoid in (010) plane and projections of short hydrogen bonds: (a) acetylene dicarboxylic acid dihydrate; (b) oxalic acid dihydrate.

ADAD the ratio $\theta\alpha_{22}/\theta\alpha_{11}$ to $\iota\alpha_{22}/\iota\alpha_{11}$ is approximately 8 to 1. The much larger value of $\theta\alpha_{22}/\theta\alpha_{11}$ is accompanied by a positive $\theta\alpha_{33}$. Torsional oscillations (factor (iii) above) of the acid molecules about their long axes would involve expansions normal to these axes which lie near the direction of $\theta\alpha_{11}$. Such oscillations, combined with an increase in mean tilt, could account for the observed values of the thermal expansions.

Finally, brief mention may be made of the interesting continuous transition in ADAD around +3° C. So far as present observations go, this shows features suggestive of continuous transitions which arise from a smearing of the free energies of the two forms, by the contribution of strain and internal surface energy terms (Ubbelohde, 1954). The large hysteresis covers the region of the free-energy/temperature curves over which smearing makes a significant contribution. In this instance, the spread of angles over which the 202 reflexions can be observed after a thermal cycle has been completed indicates that comparatively large geometrical distortions need not lead to disruption of the 'single crystal'. No doubt this explains why additional terms arise in the free-energy functions, thus permitting a smeared transition.

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