7

X-RAY THERMAL DIFFUSE SCATTERING IN AZELAIC AND PIMELIC ACIDS*

R. L. BANERJEE, M. L. CANUT AND J. L. AMOROS

Sección de Termodinámica Cristalina

DEPARTAMENTO DE CRISTALOGRAFIA. C.S.I.C. MADRID

(*Received, November* 9, 1960)

Plate II

ABSTRACT. Thermal diffuse scattering of azelaic and pimelic acids is studied by X-ray diffraction methods and compared with the observed diffuse scattering in other dycarboxilic acids. The interpretation of such diffuse scattering is done both by considering the propagation of thermal elastic waves accordingly with the crystal structure and by using the difference Fourier transform approach which gives account of the extended continuous regions of diffuse scattering. Also, the dynamic symmetry of the crystals is studied as deduced from the consideration of the observed diffuse scattering.

The study of X-ray thermal diffuse scattering is interesting because it gives the unique insight of the dynamics of the crystal. The treatment of this problem is complicated and the thermal wave theory is perhaps the best approach to the question in simple (ionic) crystals. In molecular crystals, however, where there is evidently a far complicated atomic pattern, the problem can be reduced greatly by considering the fact that the molecules can be treated as rigid bodies and therefore most of its dynamical picture is given by the movement of big structural units, the molecules. A long term programme of research was developed in the Departamento de Cristalografia, Madrid, with the aim of elucidating the status of the molecular crystals. Many types of such crystals were studied (hexamine Canut and Amorós, 1958), pentaerythritol (Alonso *et al.*, 1958), naphthalene (Acha *et al.*, 1958), anthracene (Annaka and Amorós, 1960, etc.) and a general theory was given to explain the continuous thermal diffuse scattering discovered in such crystals (Amorós *et al.*, 1960). It is therefore of interest to check the theory in another group of molecular crystals for which no previous computations were made. The group of molecular substances chosen is that of the dicarboxylic acids with odd number of carbon atoms.

The interest of the present research lies in the fact that the dicarboxylic acids with even number of carbon atoms have already been studied (Canut and

---

*This research was in part supported by the Directorate of Solid-State Sciences, Air Force Office of Scientific Research, through the European Office of Air Research and Development Command, under Contract AF 61(052)—193.

Amorós, 1957) and therefore a direct comparison of the two groups can easily be done and thereby a general picture of the lattice dynamics of long-chain compounds can be drawn.

ANTECEDENTS

The structure of pimelic acid COOH-$(CH_2)_5$-COOH has been determined by MacGillavry and his coworkers (1948). The crystal belongs to the monoclinic system and space group I $2/a$ and contains four molecules per unit cell.

The unit cell dimensions are :

$$a = 9.84\,\text{Å},\quad b = 4.89\,\text{Å},\quad c = 22.43\,\text{Å} \quad \text{and} \quad \beta = 130^\circ\,46'$$

The crystal structure of azelaic acid COOH-$(CH_2)_7$-COOH has not been determined as yet. According to Caspari (1928) the crystal belongs to the monoclinic system and contains four molecules per unit cell.

The unit cell dimensions are :

$$a = 9.72\,\text{Å},\quad b = 4.83\,\text{Å},\quad c = 27.14\,\text{Å} \quad \text{and} \quad \beta = 129^\circ 30'$$

The space group of azelaic acid has not been determined, but a careful observation of the distribution of the diffuse scattering of azelaic acid studied in the present work reveals that the distribution of the diffuse maxima obeys the same extinction condition as those of pimelic acid, i.e., $h+k+l$ = even. Therefore, the space group of azelaic acid should be the same as that of pimelic acid, i.e., I $2/a$, and the crystal structures of the two acids should also be the same, except for the difference in length of the molecules.

While obtaining azelaic acid crystals at room temperature from a slightly warm acetone solution, we happened to obtain azelaic acid crystals of another modification stable at room temperature. Much earlier Caspari (1929) obtained a high temperature modification of azelaic acid by slowly cooling down a hot solution of the acid.

Later, Dupré La Tour (1935) obtained this modification by slowly cooling down the azelaic acid melt.

The lattice constants of the modification that we have obtained along with those of the modification obtained by Caspari are given below:

	a	b	c	β
Azelaic acid (II)	5.69 Å	9.57 Å	27.78 Å	136°39′
α-azelaic acid (9)	5.61 Å	9.58 Å	25.35 Å	136°10′

EXPERIMENTAL METHOD

Single crystals were obtained from an acetone solution. The crystal used in the experiment had the dimensions of about 1.5×1.0×1.0 mm^3. It was mounted with its [010] axis vertical and considering its monoclinic symmetry, Laue photographs were taken at each 5° of a zone of 180°. Ilford industrial G films, filtered Cu $k\alpha$ radiation at 40KV., 20mA, and a Unicam camera with cylindrical film holder was used. The exposure time was 2 hours. In order to register the thermal diffuse scattering on the reciprocal lattice level $[010]_n$, the reciprocal co-ordinates ζ and ξ were measured for each diffuse spot with the help of the Bernal Chart after substracting the size of the corresponding Laue spot to correct for the crystal size and the divergence of the x-ray beam effects. We plotted the diffuse reflections on each reciprocal lattice level by using transparent paper and Martin's Chart (1956). This method saves much time in the tedious task of passing the photographic record of the diffuse scattering to the diffraction space (i.e. the reciprocal space). The crystal, x-ray beam orientation becomes unequivocally fixed when the diffuse scattering domains of each level of the reciprocal lattice are compared with the corresponding reciprocal lattice net, due to the fact that the thermal diffuse scattering maxima are always to be on the reciprocal lattice points.

Diffuse scattering domains in $[010]_n$ of azelaic acid

Laue patterns of dicarboxylic acids show two types of diffuse spots:

a) Streaks, characteristic of the molecules in chains, extended between the reciprocal lattice points when plotted in it.

b) Independent, round and definite spots, some of them very strong, giving a diffuse cloud around non-forbidden reciprocal lattice points.

With the [010] mounting of the crystals, the streaks always appear in the photograph cutting the equator at right angles and extending across the higher levels (Fig. 1, Plate II).

$[010]_0$ *level* :

The diffuse domains of this level are shown in the *Fig.* 2. The strongest round diffuse spot is associated with the reciprocal lattice point 200. The planes corresponding to this point contain the layers of the chains. Other round spots appear at the reciprocal lattice points with $h = 2n$ and $l = 2n$, that is, at the non-forbidden ones. The most prominent of them being those associated with 200, $40\bar{2}$, $60\bar{2}$, $\bar{4}08$, $\bar{4}010$, $\bar{4}022$, $\bar{6}012$, $\bar{6}010$, lattice points. Continuous diffuse scattering domains appear in the rows of the reciprocal lattice points having l = const = even.

The strongest continuous domains are extended along the rows with

$$l = 10.\ 18.\ 20.\ 22.\ 23$$

$[010]_1$ *level* :

The round diffuse spots of this level (Fig. 3) follow the extinction condition [illegible] = odd.

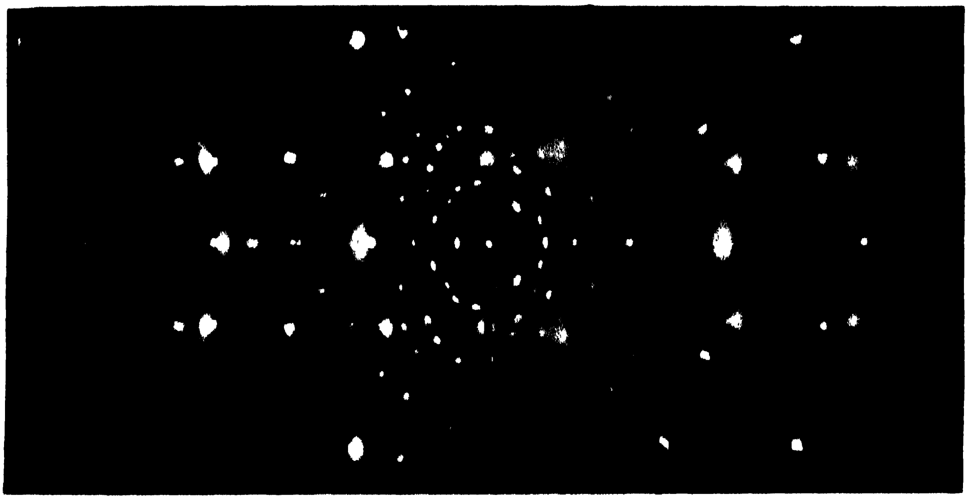

Fig. 1. Laue photograph. Azelaic acid. Vertical axis [010].

The streaks of this level unlike those of the zero level, do not appear in the very well defined continuous zones of $l =$ const.

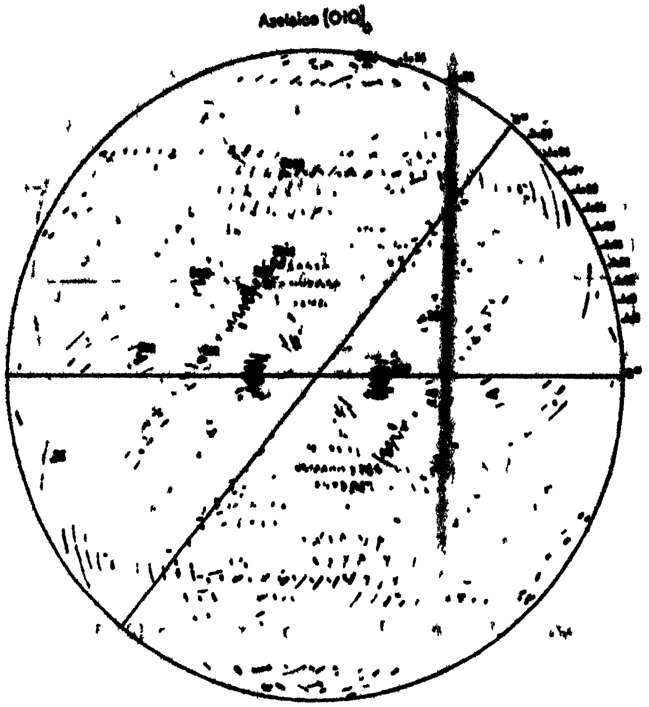

Fig. 2. Azelaic acid. Diffuse domains in $[010]_0$.

The strongest diffuse spots are associated with the following reciprocal lattice points: 110, $21\bar{1}$, 011, 310, $11\bar{8}$, $11\overline{10}$, $11\bar{6}$, $21\overline{21}$.

$[010]_{\frac{1}{2}}$ *level*:

The plotting of the diffuse reflections in this inter-layer (Fig. 4) was done only for those which extend across the zero and the first levels.

Moderately strong continuous domains of diffuse scattering appear in this level extended along the rows of the reciprocal lattice points having $l = 10, 22, 32$.

Apart from this there appears a strong diffuse domain at $2\,\frac{1}{2}\,0$ which is the section of the very strong round diffuse spot 200 of the zero level.

THREE DIMENSIONAL ANALYSIS OF THE DIFFUSE SCATTERING

From the analysis of the domains of the continuous diffuse scattering, it is clear that these domains, which appear along the rows of reciprocal lattice points with $l =$ const, that is, perpendicular to the chain direction (c axis), in all the levels $[010]_0$, $[010]_{\frac{1}{2}}$ and $[010]_1$, are actually sheets perpendicular to c axis of the crystal

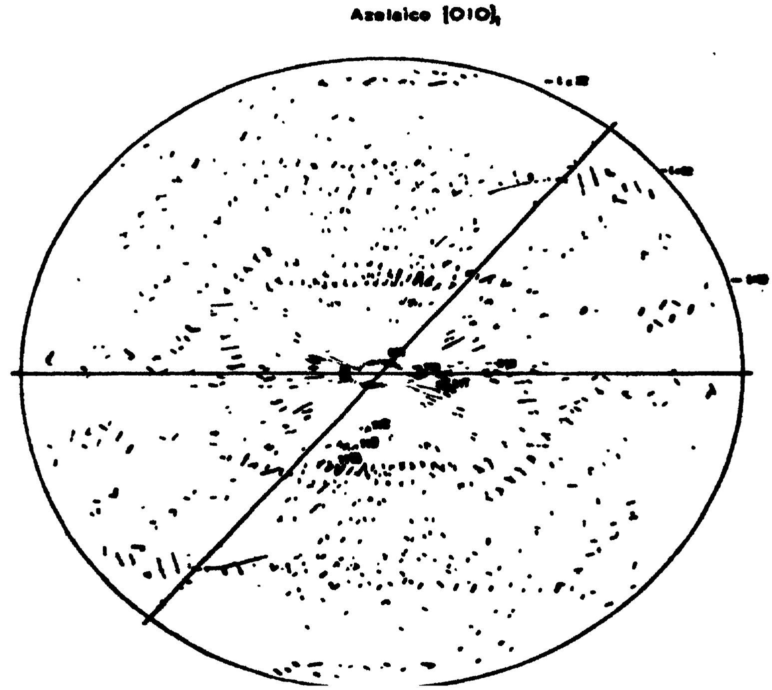

Fig. 3. Azelaic acid. Diffuse domains in $[010]_1$.

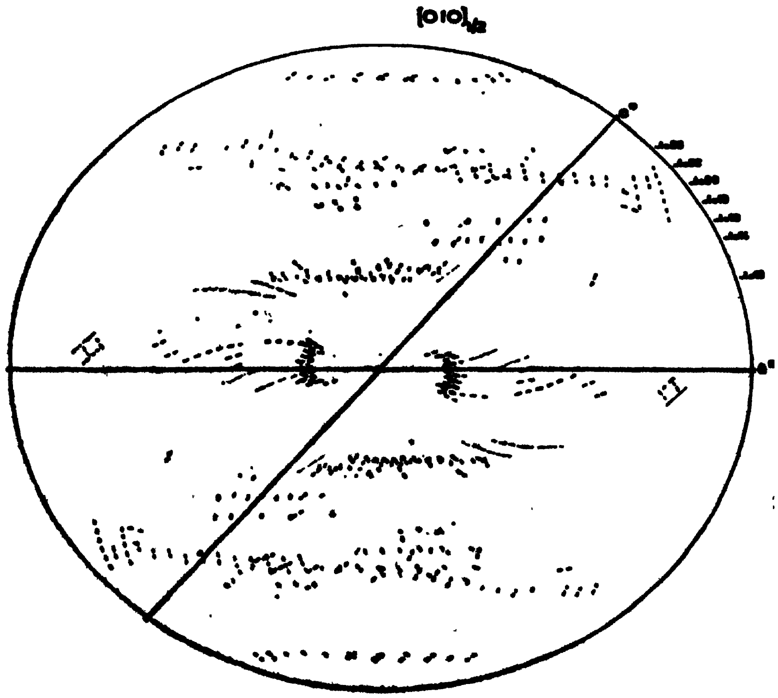

Fig. 4. Azelaic acid. Diffuse domains in $[010]_{\frac{1}{2}}$.

in three dimensions. The sheets passing through the reciprocal lattice planes with $l = 10$, 22 and 32 are the most prominent ones. These sheets are confined within a zone of 90° about the chain direction extending 45° on either side of it.

COMPARISON BETWEEN THERMAL DIFFUSE SCATTERING OF AZELAIC AND PIMELIC ACIDS

The morphology of the thermal diffuse scattering of pimelic acid has previously been studied by Canut and Amorós (1957). Fig. 5 shows the diffuse scattering domains of pimelic acid in the $[010]_0$ level.

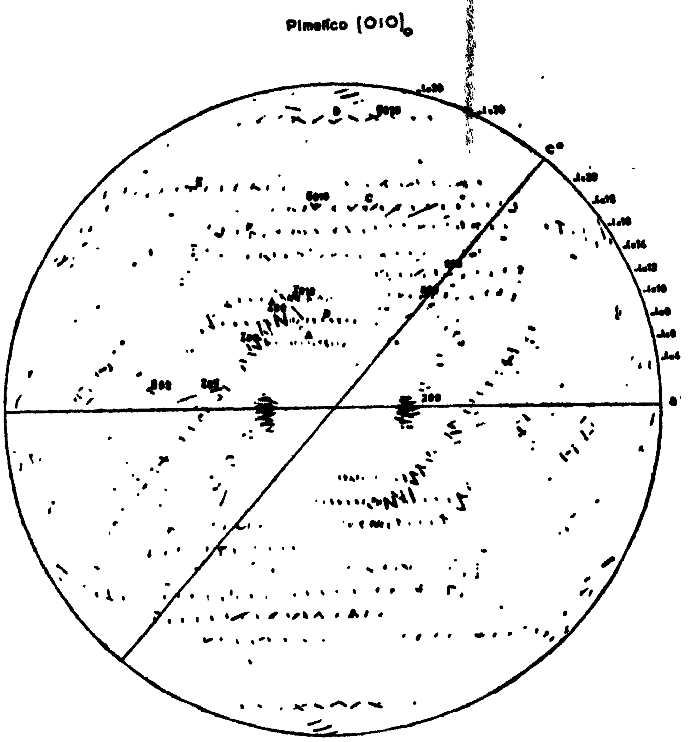

Fig. 5. Pimelic acid. Diffuse domains in $[010]_0$.

Comparison of the diffuse scattering domains of azelaic acid in $[010]_0$ level (Fig. 2) with that of pimelic acid (Fig. 5) reveals the fact these two acids, belonging to the odd series of dicarboxylic acids, give extremely similar diffuse scattering patterns. The only difference is that whereas in pimelic acid the strongest continuous diffuse scattering domains appear extended along the reciprocal lattice planes having l = const = 6, 8, 10, etc., those of azelaic acid appear in the planes having l = const = 10, 18, 20, 22 and 32.

But this is only an apparent difference. In fact the spatial distribution of these domains is the same in both the cases. The differences in the values of l are due to the fact that the lattice constants of the two acids are different.

INTERPRETATION

The interpretation of the diffuse scattering of pimelic and azelaic acids will be done together in order to have a correlated idea about the dynamics of the odd-dycarboxylic acids, and to be able to relate the results of this series with those of the even-series already studied in this laboratory.

PROPAGATION OF WAVES

It is well known that thermal waves in the crystals affect the form and extension of the diffuse scattering domains in the reciprocal space. This has been shown by Londsdale (1948) and others.

The theory of crystal dynamics shows that the diffuse scattering domains always extend in the reciprocal space in the direction of the propagation of the waves, either longitudinal or transverse.

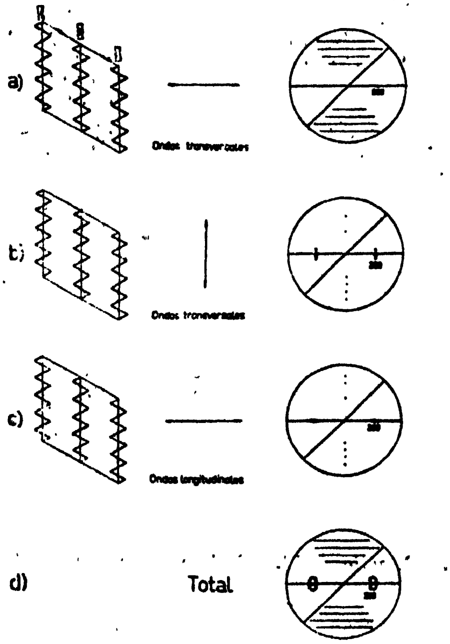

Fig. 6. Scheme of the effect of wave propagation in reciprocal space of a 'chain-like' crystal.
a) Transverse waves travelling at right angles to the chains.
b) Transverse waves travelling along the chains.
c) Longitudinal waves travelling at right angles to the chains.
d) Total effect.

Fig. 6 (Amorós and Canut, 1958) shows the effects of different types of wave on the distribution of diffuse scattering in the reciprocal lattice. Thus

Fig. 6 (a) shows the effect of the transverse waves propagating perpendicular to the chain direction which affect the relative chain-chain positions but not those of the atoms within the chains, in the distribution of diffuse scattering in the reciprocal lattice level $[010]_0$. Figs. 6 (b) and 6 (c) show the effects of transverse waves which propagate parallel to the chains affecting the relative positions of the atoms in the chains, and longitudinal waves which propagate perpendicular to the chains affecting the chain-chain interspace, respectively in the same reciprocal lattice level. Fig. 6 (d) shows the combined effect of the three types of waves mentioned above, on the form of the diffuse scattering domains in the said reciprocal lattice level.

The effect of the longitudinal waves in the direction of the chain has not been observed in either cases of the dicarboxylic acids studied.

In the dicarboxylic acids the molecular chains are parallel to [001] axis of the crystal therefore, the streaks that we have observed in the Laue photographs and are represented by the diffuse domains extended at right angles to the chain direction in the reciprocal lattice, are due to the waves of the first kind, i.e., the transverse vibrations of the chains propagating in the direction perpendicular to them. This we suppose to be the most important movement in these acids. As this kind of movement does not affect the relative positions of the atoms within the chain it is not easily detectable by normal structural method.

The second and the third kind of waves mentioned above determine the form of the diffuse domain around the reciprocal lattice point 200. This is the second feature of these crystals and is explicable with the help of the Figs. 6(b) and 6(c).

EXTENDED CONTINUOUS DOMAINS OF DIFFUSE SCATTERING

As we have stated above, the effect of the transverse wave propagating perpendicular to the chain direction on the shape of the diffuse scattering domains is to make them elongated along the direction perpendicular to that of the chain. Fig. 6(a) schematically represents this effect. While this figure explains the presence of the continuous domains of diffuse scattering extended along the rows of reciprocal lattice points having l = constant, it does not say anything about the extent of the elongation of these domains. On the other hand, the presence of continuous diffuse scattering regions has been observed in the cases of hexamine, anthracene, pentaerythritol, naphthalene, etc, studied in this laboratory; where the presence of the kind of transverse wave represented by fig. 6(a) might not be very important.

Moreover this kind of diffuse scattering is more clearly observed in a zone of 90° about the chain direction extending 45° on either side of it and these diffuse domains extend even across the forbidden reciprocal lattice points.

Therefore in order to explain this kind of diffuse scattering we have undertaken the "difference Fourier transform" (DFT) approach (Amorós *et al*; 1960) which assumes the presence of independent molecular vibrations in the crystal. The theory of this approach is given in the following paragraph.

DIFFERENCE FOURIER TRANSFORM

The Fourier transform of a molecule "at rest" is given by

$$G_R = \sum_{n=1}^{N} f_n \exp\,(2\pi i\, r_n.\, \bar{S}), \qquad \dots \quad (1)$$

where f_n is the atomic scattering factor without temperature correction. The effect of a harmonic movement in the molecule is the correction of the atomic scattering factor by the well known Debye factor,

$$f \exp\,(-M). \qquad \dots \quad (2)$$

The Fourier transform of a molecule under thermal agitation is given by

$$G_T = \sum_{n=1}^{N} f_n \exp\,(-M) \exp\,(2\pi i\, \bar{r}_n.\, \bar{S}). \qquad \dots \quad (3)$$

Since the molecular Fourier transform is the scattered radiation of the molecule, the difference

$$G_R - G_T \qquad \dots \quad (4)$$

corresponds to the modification of the scattering space by the thermal motion of the molecule.

Thermal diffuse scattering is due to the x-ray diffraction of crystals under thermal agitation. Therefore relation (4) can be a direct clue to the interpretation of such diffuse scattering. In order to compare directly the observed values of the thermal diffuse scattering (intensities) with the molecular-transform functions, we must multiply G by its complex conjugate $G*$.

A general way to compute molecular Fourier transforms is to use

$$G = \Sigma\, f_n \exp 2\pi i\, (hx_n + ky_n + lz_n) \qquad \dots \quad (5)$$

where h, k, l can be fractional numbers. The expression (5) corresponds to the molecular structure factor at the point (hkl) of reciprocal space. In the case of a unit cell with four molecules, the x-ray scattered intensity of the four independent molecules (neglecting phase relationship) will be given by

$$\sum_{1}^{4} I_j^2 = \sum_{1}^{4} (A_j^2 + B_j^2) \qquad \dots \quad (6)$$

corresponding to the molecules at rest. When subject to thermal motion, the intensity of the four independent molecules will be given by

$$I_{mot} = \sum_{1}^{4} (A_j^2+B_j^3) \; 1-\exp\left(-2B\frac{\sin^2\theta}{\lambda^2} \right) \qquad \ldots \quad (7)$$

and the effect of the independent motion of the 4 molecules will be given by

$$DFT = I_{rest}-I_{mot} = \sum_{1}^{4}(A_j^2+B_j^2) \left\{ 1-\exp\left(-2B\frac{\sin^2\theta}{\lambda^2} \right)\right\} \qquad \ldots \quad (8)$$

Expression (8) is just the difference in scattered intensities of the four molecules at rest and at motion. This expression gives in a direct way the effect, in diffraction space of the independent molecular motion in crystals. It has, for simplicity, been named the "difference Fourier transform" (*DFT*) of the molecules.

COMPUTATION OF THE MOLECULAR FOURIER TRANSFORMS OF PIMELIC ACID

For the computation of the molecular transform of pimelic acid we have utilised the atomic co-ordinates given by Mac-Gillavry and others (1948).

Scattering amplitudes for the individual molecules are calculated and hence we have got the difference of the intensities of scattering ($I_{rest}-I_{mot}$) by the individual molecules at rest and on vibration, by multiplying the squares of the scattering amplitudes by a factor $1-\exp\,(-2B\,\sin^2\theta/\lambda^2)$, where B is the temperature factor. In our case of pimelic acid, owing to the unavailability of the value of B, we have used $B = 2\,\text{Å}^2$. This value of B has been found to be that for succinic acid in the direction of the carbon chain. But as we are making the calculation of a limited zone of the reciprocal lattice about the direction of the chain, where the effect of the independent movement is more important, we have adopted this value of B (i.e. $B = 2$) as an approximate one for pimelic acid.

Because of the two-fold axis of symmetry of the molecules, scattering amplitude corresponding to $h = 2n$ (where n is any integer), comprises of only A and those corresponding to $h = 2n+1$, of only B, where

$$A = \sum_{n} f_n \cos 2\pi(hx + hy + lz)$$

and

$$B = \sum_{n} f_n \sin 2\pi(hx + ky + lz)$$

Now, we have to calculate the $\Sigma(I_{rest}-I_{mot})$ i.e., the DFT for all the four molecules of the unit cell.

But due to the symmetry of the crystal we have the following relations among the A's and B's of the different molecules of the cell:

$$
\begin{aligned}
&B_1 = B_2 = B_3 = B_4 = 0 \quad \text{when } h = 2n \\
&A_1 = A_2 = A_3 = A_4 = 0 \quad \text{when } h = 2n+1 \\
&A_1 = A_3 \ \text{when } h = 2n \text{ and } l = 2n \\
&A_1 = -A_3 \ \text{when } h = 2n \text{ and } l = 2n+1 \\
&A_1 = A_4 \ \text{when } h = 2n \text{ and } l = 2n \\
&A_1 = -A_4 \ \text{when } h = 2n \text{ and } l = 2n+1 \\
&B_1 = B_3 \ \text{when } h = 2n+1 \text{ and } l = 2n \\
&B_1 = -B_3 \ \text{when } h = 2n+1 \text{ and } l = 2n+1 \\
&B_1 = B_4 \ \text{when } h = 2n+1 \text{ and } l = 2n \\
&B_1 = -B_4 \ \text{when } h = 2n+1 \text{ and } l = 2n+1
\end{aligned}
\qquad \text{(R)}
$$

Thus we see that the absolute values of A's and B's for a particular reflection are the same for all the four molecules of the unit cell.

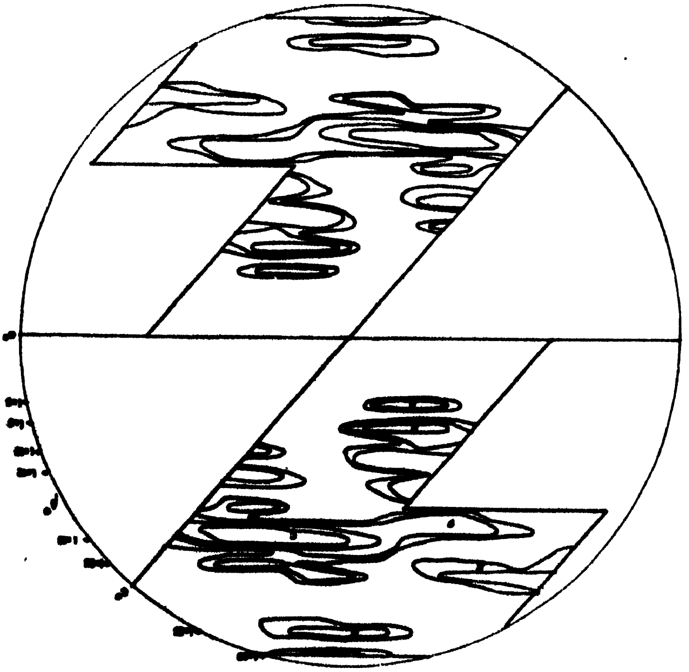

Fig. 7. Pimelic acid. Theoretical isodiffusion lines computed with DFT in the region where the effect of independent motion can be considered.

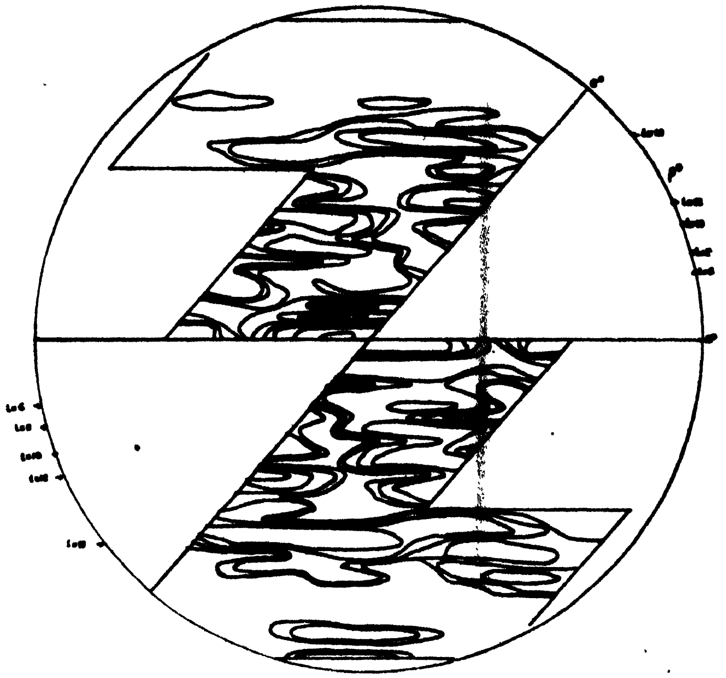

Fig. 8. Pimelic acid. $[010]_0$.
Upper part: Molecular FT_{rest}. Lower part: Molecular FT_{mot}.

Now by definition,

$$\mathrm{DFT} = \sum_{1}^{4} (I_{rest}-I_{mot})_j \qquad \text{where } j = 1, 2, 3, 4$$

$$= \sum_{1}^{4} (A_j^2 + B_j^2) \quad \{1-\exp\,(-2\mathrm{B}\,\sin^2\theta/\lambda^2)\}$$

where j is the number of molecule of the unit cell.

So, in our case, applying the relations (8), we get

$$\mathrm{DFT} = \sum^{4}(I_{rest}-I_{mot})_j$$

$$= 4A_1^2\{1-\exp\,(-2B\sin^2\theta/\lambda^2)\} \quad \text{for } h = 2n$$

and

$$= 4B_1^2\{1-\exp\,(-2B\sin^2\theta/\lambda^2)\} \quad \text{for } h = 2n+1$$

The difference of intensity $(I_{rest}-I_{mot})$ thus calculated have then been plotted on the reciprocal lattice net and the lines of equal $(I_{rest}-I_{mot})$ values of 20, 35, 70 and 140 have been drawn.

Figs. 5 and 7 are the experimental diffuse scattering pattern and the corresponding DFT map, respectively. The strong continuous diffuse scattering domains

A, B, C and D as also the comparatively weaker ones E and F in Fig. 5 are represented by strong A, B, C, D, and weak E and F of Fig. 7.

The agreement between the experimental and theoretical patterns (Figs. 5 and 7) amply justifies the validity of the DFT approach of interpreting the observed distribution of the extended continuous diffuse scattering and their origin. Fig. 8 shows the molecular Fourier transform maps of the molecules at rest and on motion. Comparison of the Fig. 8 with Fig. 7 shows the superiority of the DFT approach over that of molecular Fourier transform as expected theoretically.

THERMAL MOTION AND CRYSTAL SYMMETRY

We have observed in our present work as also in the previous work in this laboratory that the streaks which appear in the Laue photographs do not always follow the space group extinctions; in the sense that they extend even across the forbidden points of the reciprocal lattice.

This we explain to be due to the fact that the space group symmetry at some instantaneous positions of the molecules of the crystal undergoing thermal vibration (dynamic space group) is different from that of the crystal considered at rest (static space group) (Amorós and Canut, 1960).

Normal methods of structure analysis determine only the static space group. This procedure cannot detect the existence of the dynamic space group because of the fact that the instantaneous change of symmetry due to thermal motion does not change the positions of the Bragg reflections which depend only on the average central positions of the atoms. The thermal motion has got no effect on the Bragg reflections other than diminishing their intensities. Thus, this change of symmetry due to thermal vibrations cannot be detected by normal Fourier methods of Structure analysis.

Fig. 9 shows one complete unit cell containing the molecules in their respective positions and another containing the elements of symmetry corresponding to the space group $I2/a$ of the azelaic acid crystal.

The antiphase vibration represented by the arrow (1) is that due to a transverse wave propagating along the normal to the chain direction. Due to this kind of vibration of the glide plane *a*, the two fold axes in the centres of the molecules and the centres of symmetry within the hydrogen bonds vanish, giving the space group $P2_{1/n}$ to the crystal at some instantaneous state of the molecules undergoing vibrations.

The symmetry elements that vanish as a result of the vibration represented by the arrow (1) in the Fig. 9 also vanish as a result of that represented by the arrow (3). Therefore, the space group (dynamic) due to the latter kind of vibration is also $P2_{1/n}$.

The arrow (2) represents the antiphase libration of the chains about the axes along their direction. The screw axes lying in between the chains vanish at some instantaneous state of the molecules undergoing libration giving the space group (dynamic) $P_{2/n}$ to the crystal.

The systematic extinctions in $[010]_0$ levelowing to n are the same as those for I and, therefore, the extinction condition $h+l$ = even, in the $[010]_0$ level is maintained.

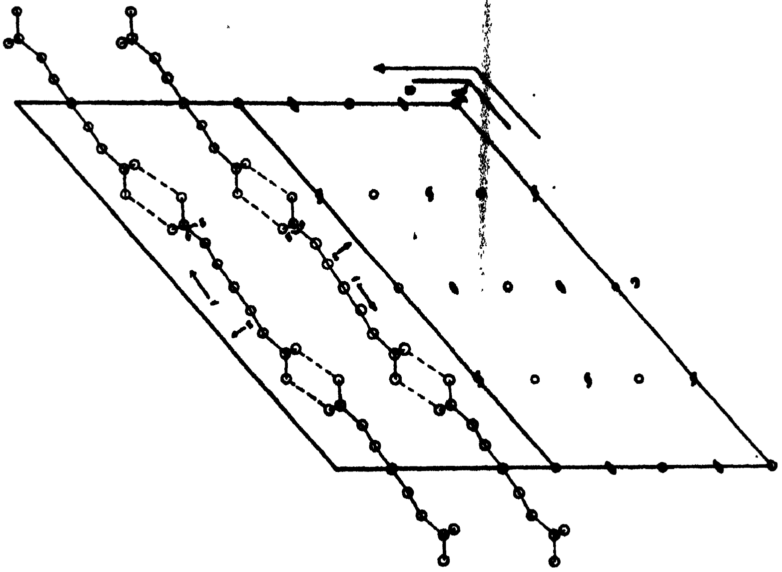

Fig. 9. Pimelic acid. Projection of the structure on (010).

COMPARISON BETWEEN THERMAL DIFFUSE SCATTERING OF THE DICARBOXYLIC ACIDS OF EVEN AND ODD SERIES

The difference between the distributions of the diffuse scattering zones in the reciprocal lattice of the acids belonging to the two series is not very great. The general features of these distributions are essentially the same. In the case of the acids belonging to the even series the extended continuous zones of diffuse scattering appear as well defined, even by spaced sheets perpendicular to the chain direction in the reciprocal space. The spacing of these sheets is reciprocal to 2.5Å. This distance 2.5Å corresponds to the zig-zag distance of the carbon atoms of the molecular chain and the length of the hydrogen bond binding the molecules of the same chain. That means the periodicity in the distribution of the continuous diffuse zones along the direction of the chain in the reciprocal space shows a well marked reciprocal relation to that of the chains. This reciprocal relation is also clearly exhibited by the DFT maps of the acids of the even series (Amorós and Canut, 1958).

But it is less clearly exhibited by the distribution of the continuous diffuse zones and their DFT representations of the acids of the odd series. A probable reason of the observed difference between the distributions of the continuous diffuse zones of the acids belonging to the two series is that in the case of the even series acids the chains are well defined but those in the case of the odd series are distorted. In the case of even series the carbon atoms of a chain are coplanar and the long axes of the molecules in the same chain are colinear whereas in the case of odd series neither the carbon atoms are coplanar nor the molecular axes are colinear.

REFERENCES

Acha A., Canut M. L. and Amoros, J. L., 1958, *Bol. R. Soc. Esp. Hist. Natt.*, (G) **56**, 405.

Alonso, P., Canut, M. L. and Amoros, J. L., 1958, *Bol. R. Soc. Esp. Hist. Nat.*, **56**, 379.

Annaka, S. and Amoros, J. L., *Z. Kristallog.*, (In press).

Amoros, J. L. and Canut, M. L., 1958, *Bol. R. Soc. Esp. Hist. Nat.*, (G) **56**, 25.

Amoros, J. L. and Canut, M. L., 1958, *Bol. R. Soc. Esp. Hist. Nat.* (G)**56**, 305.

Amoros, J. L., Canut, M. L. and Acha, A., 1960, *Z. Kristallog*, **114**, 39.

Amoros, J. L. and Canut, M. L., 1960, *Bol. R. Cos. Esp. Hist. Nat.*, (G) 57,

Canut, M. L. and Amoros, J. L., 1957, *P. Dep. Crist. Min.*, **3**, 15.

Canut, M. L. and Amoros, J. L., 1957, *P. Dep. Christ. Min.*, **3**, 27.

Canut, M. L. and Amoros, J. L., 1958, *Bul. R. Soc. Esp. Hist. Nat.*, (G) **56**, 323.

Caspari, W. A., 1928, *J. Chem. Soc. London*, **30**, 3235.

Caspari, W. A., 1929, *J. Chem. Soc. London*, **30**, 2709.

Dupre la Tour F., 1935, *Compt. Rendus*, 479.

Lonsdale, K., 1948, Crystals and X-rays, London, Bell, Sons.

Mac Gillavry, C. H., Hoodohagen G. and Sixma, F. L. J., 1948, *Rec. trav. Chem. Pays. Bas.*, **67**, 869.

Martin, W. G., 1956, *J. Appl. Phys.* **27**, 514.