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Growth, Crystallography, Anisotropy and Initial Conductivity Measurements of Single Crystals of the Nucleic Acid Components Thymine and Thymidine

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Growth, Crystallography, Anisotropy and Initial Conductivity Measurements of Single Crystals of the Nucleic Acid Components Thymine and Thymidine

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A considerable amount of quantum mechanical calculations on nucleic acid components has been reported.[1] Experimental solid state investigations have been carried out mostly on non-single crystal materials.[2,3,4] Forbidden band gap determinations, based on activation energy of electrical conductivity of powder compacts,[5] are at odds with doubts that in such experiments intrinsic conductivity is measured[6] and with questions regarding the applicability of the band model.[7,6] Discrepancies between conductivity activation energy determinations on powders and calculated energy values, based on molecular ionization potentials and electron affinities, have been reported.[8] The present report describes some ground work towards crystal physical studies on nucleic acid components.

CRYSTAL GROWTH

Crystal growth of the bases and nucleosides, from the melt, seems precluded by decomposition at the melting point (thymine), by marked supercooling of the melt (uridine) or by both of these phenomena (adenosine, thymidine). In attempting to grow anhydrous crystals from organic solvents, one may make use of the marked solubility of thymidine and uridine in absolute ethanol, of cytidine, thymidine and uridine in methanol, of adenosine, cytidine, thymine, thymidine, uracil and uridine in pyridine and of thymidine in dioxane. Crystal habit, using such solutions, was found to depend primarily on the substance being crystallized. The solubility of thymidine (Calbiochem A Grade) in absolute ethanol (Merck pro analysi), as a function of temperature, is given in Figure 1. Seeded growth from ethanol, dropping the temperature at the rate of 0.12°C/h, resulted in relatively perfect thymidine needles, as yet, only several millimeters long and 0.04 mm thick. Crystals of thymine were grown from the gas-phase, at temperatures below the melting point. In a typical experiment, a fore-pump evacuated glass tube with pressed thymine (Calbiochem A Grade) tablets at the left end, was placed in a two temperature-zone furnace. After 95 h, with the left half of the tube heated to about 169°C and the right zone at about 159°C, copious white needles, up to 5mm long, had grown in the right zone. The platelet-like needles readily cleave in the platelet-plane and the cleaved platelets further cleave, in the needle direction, into fibers.

CRYSTALLOGRAPHY

A plate-like needle of thymine, from a gas-phase crystallization, gave, on the optical goniometer, several reflections, within a prismatic zone, which, using the published monoclinic lattice constants of thymine,[9,10] could be provisionally indexed as (100), ($\bar{1}$00), (001) and (10$\bar{1}$), with {100} being prominent. Multiple reflections of the {100} may be due to imperfections, perhaps associated with the ready cleavage in this plane. On this basis, the <010> direction coincides with the needle axis, in agreement with the findings of Furberg *et al.*[9] on thymine needles grown from alcohol; these authors also found the {100} prominent. Our observations also confirm those of Ozeki *et al.*[10] on easy cleavage in (001) and (100). These authors showed molecular chains, formed by hydrogen-bonded thymine molecules, to run in the *b*-direction. An X-ray rotation photograph, using Cu-K_α radiation, was taken of the optically studied thymine crystal. The uncorrected period of identity along the needle (=rotation) axis was found to be 6.82Å. Furberg *et al.* determined thymine as monoclinic with lattice constants $a = 12.87$, $b = 6.83$, $c = 6.72$Å and $\beta = 105°$, and with space group

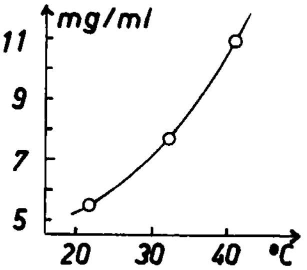

FIGURE 1 Solubility of thymidine in absolute ethanol at different temperatures.

$P2_1/c$. The needle axis was therefore unequivocally identified as the b-axis, in agreement also with the optical work.

A stereographic projection of the results of optical measurements on a needle of thymidine, grown from ethanol by the temperaturedrop method, is shown in Figure 2. The apparent positions of the three 2-fold axes are indicated. Using the lattice constants of Furberg *et al.* (determined on orthorhombic prisms, alongated along the c-direction; solvent not mentioned), the pair of prismatic pinacoids could be indexed as $\{310\}$; in addition, what appears to be a sphenoid could be detected. The needle gave uniform extinction between crossed polarizers. An X-ray rotation photograph (Cu-K_α radiation) of a similarly grown thymidine needle yielded an uncorrected period of identity, along the needle (=rotation) axis, of 4.84Å. Furberg *et al.* determined thymidine as orthorhombic with $a = 16.27$, $b = 13.86$ and $c = 4.86$Å and with a space group of probably $P2_1 2_1 2_1$. The needle axis was therefore identified as the crystallographic c-direction. This needle also gave uniform extinction between crossed polarizers.

ANISOTROPY OF SECOND–RANK TENSOR PHYSICAL PROPERTIES

$\bar{1}$ and 2_{x_2} suffice to describe crystal class 2/m of thymine and 2_{x_2} and 2_{x_1}, for example, suffice to describe class 222 of thymidine, where $\bar{1}$ is an inversion center and 2_{x_1} and 2_{x_2} are two-fold rotation axes, along cartesian coordinate axes x_1 and x_2. Using the corresponding transformation matrices, the relationship $j_k = \sigma_{kl}E_l$ between the components j_k of, for example, the current density vector and the components E_l of the electric field vector, the internal symmetry

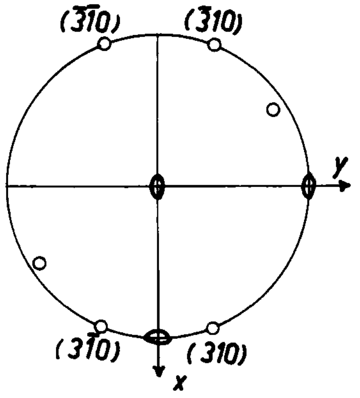

FIGURE 2 Stereographic projection of optical-goniometric measurements on a needle of thymidine, grown from a seeded saturated absolute ethanol solution, by lowering its temperature.

of the electrical conductivity tensor σ_{kl}, and the transformation law for a second-rank tensor, derived, for example, by Nye,[11] one obtains for thymine the conductivity tensor $\sigma_{ij} = \begin{bmatrix} \sigma_{11} & 0 & \sigma_{31} \\ 0 & \sigma_{22} & 0 \\ \sigma_{31} & 0 & \sigma_{33} \end{bmatrix}$, so that the following four equations will be necessary to completely describe ohmic conductivity in a crystal of thymine:

$$\begin{aligned} j_1 &= \sigma_{11}E_1 \\ j_1 &= \sigma_{31}E_3 \text{ or } j_3 = \sigma_{31}E_1 \\ j_2 &= \sigma_{22}E_2 \\ j_3 &= \sigma_{33}E_3 \end{aligned}$$

For example, applying the field along the needle axis of the thymine crystals and measuring the current density in the same direction permits determination of σ_{22}. Similarly, applying the symmetry element transformation matrices for thymidine, one obtains $\sigma_{ij} = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$ Experimentally, the three tensor components can be determined from the following three equations:

$$\begin{aligned} j_1 &= \sigma_{11}E_1 \\ j_2 &= \sigma_{22}E_2 \\ j_3 &= \sigma_{33}E_3 \end{aligned}$$

Applying the field in the thymidine needle direction and measuring the current density in the same direction allows determination of σ_{33}. For details regarding the effect of crystal symmetry on a second-rank tensor, Kleber *et al.*[12] can be consulted.

INITIAL CONDUCTIVITY MEASUREMENTS†

The crystal currents measured, of the order of 10^{-14} A, were so small, that the best available insulating material, Teflon, permitted, at the same voltage, considerably larger currents to flow. It was therefore necessary to construct a crystal holder with guard ring and appropriate circuit, eliminating stray currents through the Teflon base, holding two fine wires, which made contact to the crystal by means of silver paint. The Teflon base was also provided with means of manipulating the small crystals under the microscope. Crystal, electrometer (P.A.R. model 135) and battery were essentially in series, with the voltmeter measuring the iR-drop across crystal and electrometer. All equipment, including connecting leads, was shielded and grounded, leading to stable measurements.

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† Surface and bulk effects not yet differentiated between.

Initial experiments showed that, at voltages up to 90V, no currents were measurable through thymine crystals, while currents of the order of 10^{-14} A were measured through thymidine, at room temperature. Current values were reached instantaneously and reversing the polarity had no effect on the measured currents. A crystal of thymine, from the 95 hgas-phase crystallization, with effective conducting path length of 2.8 mm and a cross section of 0.35×0.10 mm^2 was shown to have $\sigma_{22} < 2.6 \times 10^{-14}$ Ω^{-1} cm^{-1}. An appreciable increase in conductivity, due to a possibly greater impurity content, associated with crystal growth from solution, could not be demonstrated. A crystal of thymine, grown from methanol solution, with a conductive path length of 1.89 mm and a cross section of 0.15×0.15 mm^2 could be shown to have $\sigma_{22} < 2.8 \times 10^{-15}$ Ω^{-1} cm^{-1}. A crystal of thymidine, obtained by room temperature evaporation of a saturated ethanol solution, had, after mounting, a conductive path length of 0.714 mm and a cross section of 0.193×0.135 mm^2. In the voltage range studied, the currents showed ohmic behavior, as seen in Figure 3. Similar results were obtained on other thymidine crystals. The room temperature conductivity of the above thymidine crystal, in the c-direction, was found to be $\sigma_{33} = 2.3 \times 10^{-13} \Omega^{-1}$ cm^{-1}.

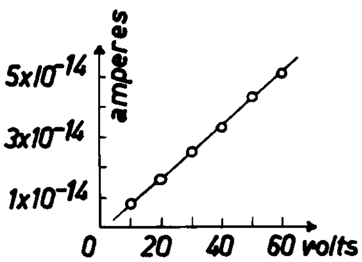

FIGURE 3 Voltage dependence of currents through a crystal of thymidine, obtained by room-temperature evaporation of a saturated ethanol solution. Currents measured by charge integration method.

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References

1. Snyder, L.C., Shulman, R.G. and Neumann, D.B., *J. Chem. Phys.* **53**, 256 (1970).
2. Basu, S. and Moore, W.J., *J. Phys. Chem.* **67**, 1563 (1963).
3. Liang, C.Y. and Scalco, E.G., *Nature* **200**, 1319 (1963).
4. Mesnard, G. and Vasilescu, D., *Compt. Rend.* **259**, 1451 (1964).
5. Mesnard, G. and Vasilescu, D., *Compt. Rend.* **255**, 1081 (1962).
6. LeBlanc, O.H., in *Phisics and Chemistry of the Organic Solid State*, Fox, D., Labes, M.M. and Weissberger, A., Eds, Vol. III, Interscience, 1967, p. 170.
7. Sharp, J.H. and Smith, M. in *Physical Chemistry*, Eyring, H., Henderson, D. and Jost, W., Eds, Vol. X, Academic Press, 1970, p. 435.
8. Mesnard, G., Vasilescu, D. and Mathon, Y., *phys. stat. sol.* **11**, K137 (1965).
9. Furberg, S., Hordvik, A. and Taugbøl, K., *Acta Chem. Scand.* **10**, 135 (1956).
10. Ozeki, K., Sakabe, N. and Tanaka, J., *Acta Crystallogr.* **B25**, 1038 (1969).
11. Nye, J.F., *Physical Properites of Crystals*, Oxford University Press, 1967, p. 11.
12. Kleber, W., Meyer, K. and Schoenborn, W., *Einführung in die Kristallphysik*, Akademie-Verlag, Berlin 1968.