

dependence than the DNA curve obtained by Berendsen and Migchelsen, but agrees in its general appearance with the collagen curve,<sup>9</sup> having a minimum at an angle of about 55° and a maximum at 0°. This result indicates a hydration structure in the DNA sample studied which is similar to that occurring in wet collagen. For any discussion concerning the disagreement between the two investigations, it is necessary to know details of the fibre drawing method used by Berendsen and Migchelsen.

The present work will be extended to wide line NMR measurements on oriented Na- and LiDNA samples at various relative humidities and temperatures. The spectra will be subjected to a complete band shape analysis to elucidate the coupling between the water and the adsorbant. The influence of electrolyte content will also be investigated.

Other nuclei than hydrogen might give valuable information.<sup>10</sup> Preliminary measurements of the <sup>31</sup>P NMR signal, however, gave a broad weak line which showed no angular dependence.

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## Semiconductivity of Dried Oriented DNA

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Szent-Györgyi's idea of comparing the gigantic macromolecules of biology with semiconductors has inspired many investigations.<sup>1</sup> In the case of DNA quantum-mechanical calculations by Hoffmann and Ladik<sup>2</sup> have shown that in the B form of DNA, with the base-pairs stacked perpendicular to the axis of the helix, the orbital overlap of the bases along the axis is sufficient to promote conductivity, and on this basis a mechanism for DNA duplication and cancer was proposed.

The experimental *d.c.* conductivity measurements have mainly been performed on dried DNA.<sup>3-5</sup> It has been found that the conductivity  $\sigma$  as a function of absolute temperature  $T$  follows the standard equation for a semiconductor  $\sigma = \sigma_0 \exp(-\Delta E/kT)$ . The activation energy  $\Delta E$  and the pre-exponential factor  $\sigma_0$  have been found to depend on the degree of dryness.

Samples of molecularly oriented DNA should be of great value for electrical measurements, a fact which has not passed unnoticed by others.<sup>4</sup> This inspired the development of a new wet spinning method whereby films of oriented DNA can be prepared in large amounts.<sup>9</sup>

In this communication some preliminary results concerning *d.c.* conductivity measurements on a dried film of oriented LiDNA are reported. The conductivity cell consisted of a piece of Teflon with two sprung-clips, 1 mm apart, serving both as holders for the film and as electrodes. Platinum was used as electrode material. The device was enclosed in a thermostatically controlled brass container. The DNA film was dried under vacuum at about 70°C and its conductivity was measured, still under vacuum, as a function of the temperature at various times using an EKCO N 616 B electrometer. The conductivity was ohmic. Measurements were also performed after drying in vacuum at about 125°C. The results for conduction perpendicular to the direction of molecular orientation are

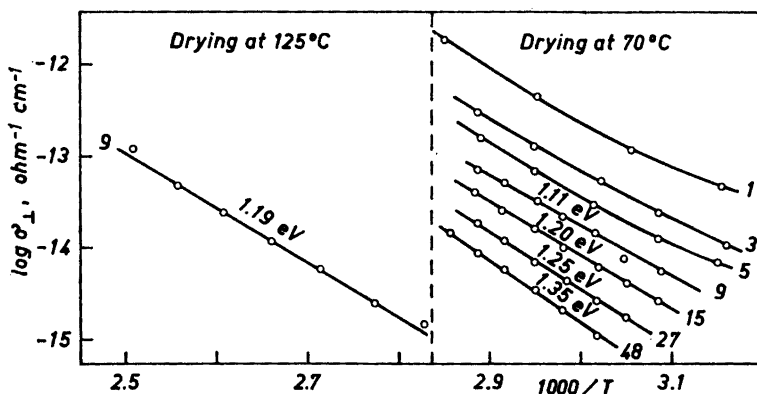


Fig. 1. Conductivity under vacuum of dried oriented LiDNA measured in the direction perpendicular to the helices. The drying time in days,  $t$ , is given as parameter. The activation energies  $\Delta E$  are indicated above the straight lines.

shown in Fig. 1, where  $\log \sigma_{\perp}$  has been plotted as a function of  $1/T$ , the time of drying in days,  $t$ , being given as a parameter. The activation energies  $\Delta E$  as calculated from the slope of the curves are in agreement with results obtained by others on dried unoriented DNA. They were not influenced by the presence of dry oxygen.<sup>8</sup> It has been found that  $\log \sigma_{\perp}$ , measured at constant temperature, decreased approximately linearly with  $\log t$  in the 70°C drying experiment.

Preliminary measurements of the conductivity along the direction of molecular orientation in the same film have not given evidence of a marked anisotropy<sup>4</sup> in the conductivity of LiDNA dried as described above. However, dichroism measurements on oriented NaDNA films<sup>10</sup> have indicated that even slight drying would cause a distortion of the DNA helices, possibly involving breakage of the inter-base hydrogen bonds and loss of base-stacking. X-Ray diffraction studies of wet-spun LiDNA films dried to the levels used in the semiconductivity measurements will therefore be performed. Preliminary results indicate that conspicuous structure changes do indeed occur. The present work will also be extended to oriented NaDNA films and a full report will be given later.

The recent discussion concerning the possibility of superconductivity in DNA<sup>11</sup> and NMR evidence for an anisotropy in the water of hydration of DNA,<sup>12</sup> suggesting anisotropy in the proton mobility,<sup>13</sup> has further emphasized the need for reliable

experimental information about the electrical properties of DNA. Access to samples of oriented DNA offers excellent opportunities to fulfil this need. Studies are now being undertaken to determine the *a.c.* and *d.c.* conductivities of oriented Li- and NaDNA samples, equilibrated at various relative humidities.<sup>14,15</sup>

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## A New Synthesis of Tri- and Tetrachloroethylene from Acetylene and Copper Chlorides

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It is a well known fact that the chlorination of acetylene in a solution containing copper chlorides and hydrogen chloride yields *trans*-1,2-dichloroethylene and 1,1-dichloroethylene.<sup>1</sup> The ratio  $\text{Cu}^{2+}:\text{Cu}^+$  to be used in this reaction is 1:4 to 1:9. It is also known that vinyl chloride, monovinylacetylene and other derivatives can be synthesized from acetylene, hydrogen chloride, and cuprous chloride. In all these methods a strongly acidic solution is used.

Surprisingly, it was found that by using a less acidic solution and a high  $\text{Cu}^{2+}:\text{Cu}^+$  ratio, tri- and tetrachloroethylenes could be synthesized directly from acetylene in very high yields.

In the first experiments acetylene was pumped through a vertical tube containing a nearly boiling aqueous solution of cupric chloride and lithium chloride. After a few minutes a reaction started and the deep

green solution darkened due to the formation of cuprous chloride complexes. At the same time, tri- and tetrachloroethylene distilled from the top of the tube. The highest reaction rate with respect to trichloroethylene was reached when one fourth to one fifth of the cupric ions were reduced.

In the following experiments the copper chloride solution ( $\text{Cu}^{2+}:\text{Cu}^+ = 80:20$ ) was pumped in from the bottom at the same level as the acetylene and at such a rate that only 1–2 % of the  $\text{Cu}^{2+}$  was reduced before the solution left the column in the upper part. The conversion of acetylene to chloride compounds was about 90 %, 85 % of which was a mixture of trichloroethylene and tetrachloroethylene.

The factors influencing these reactions have been evaluated and the most important are:

1.  $\text{Cu}^{2+}:\text{Cu}^+$ -ratio
2. pH of the solution
3. The total chloride concentration of the solution. More than 10 moles/liter has to be used in order to obtain good complexing of the cuprous chloride. It is well known that alkali chlorides are good agents for these purposes. It was found that chlorides of Li, Mg, Ca, and  $\text{NH}_4$  were better than those of Na and K.
4. The copper concentration has to be high in order to get a small reaction tube.

Nothing is exactly known about the mechanism of this reaction, but Bodländer

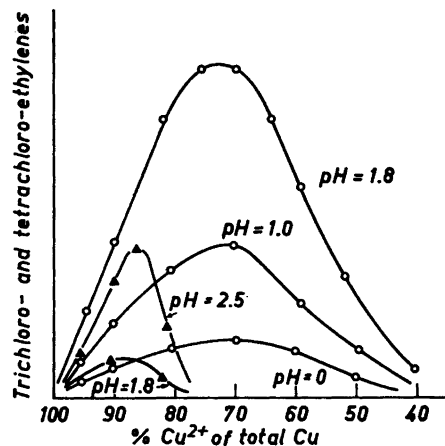


Fig. 1. Effect of  $\text{Cu}^{2+}:\text{Cu}^+$ -ratio and pH on the formation of chloroacetylene. O, trichloroacetylene; ▲, tetrachloroacetylene.

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