axis will be halved for the structures with the chain running in the same directions. The angular part of the screw operation of the helix was found to depend largely upon radial co-ordinates of the \( N_{\text{base}} - C_{\text{sugar}} \) bond: for example, for the pairing 4 and 17, in which \( N_{\text{base}} \) has a radial co-ordinate of 4.5 A, an angular co-ordinate of about 45° gives a satisfactory structure, as contrasted with the Watson-Crick pairing (5 and 15), which has 6.7 A for the \( N_{\text{base}} \) radius and an angular co-ordinate of 36°, the larger radius requiring the shorter angular separation.

In the absence of more precise information on the bond lengths, bond angles, and particularly the favored orientations to be expected about the numerous single bonds in the polynucleotide chain, it does not seem appropriate to determine exact atomic co-ordinates, especially since there is latitude of ±10° or more in the angular separation of the bases.

We conclude from this study that polynucleotides may assume two-chain structures other than the one proposed by Watson and Crick.

This investigation was aided by a grant from the National Science Foundation.


6 J. Donohue, L. R. Lavine, and J. S. Rollett, to be published in Acta Cryst.
9 It has been pointed out by Professor Pauling that it is possible with only small distortion for guanine and cytosine to pair by formation of three hydrogen bonds (d1—a2, a1—to d2, d2—a1), combining pairings 15 and 16. The formation of this additional hydrogen bond may confer extra stability on the Watson-Crick Structure.

PHASE RELATIONS IN SYSTEMS COMPRISING BROMINE AND QUATERNARY AND TERNARY ALKYL AMMONIUM BROMIDES OR CHLORIDES

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The quaternary and ternary alkyl ammonium chlorides and bromides are highly soluble in bromine at 25°. Bowen and Barus1 have shown that salts of this type complex with bromine molecules to form compounds melting below 60°. However, they did not investigate the phase relations in these systems in a systematic manner. In carrying out measurements of the conductance, viscosity, and vapor pressure of these systems, we found it desirable to determine the phase relations in some detail, in order to establish the nature of the compounds formed.
To establish the phase relation, solubilities were determined by noting the temperature at which the last traces of solid disappeared. A weighed quantity of salt was introduced into a tube which was provided with a stopcock and could be connected to a pump and to a source of bromine. Bromine was distilled into the tube, and the contents were heated until they were homogeneous. The amount of bromine was determined by weighing the tube. The solution was cooled off until crystals appeared. Thereafter, it was slowly heated in a bath, the contents of the tube being mixed by shaking. From time to time the tube was removed briefly from the bath and the solution was examined under a strong light to determine to what extent solid particles remained. Concentrated solutions are transparent, and particles are readily seen if present. The temperature at which the solid particles just disappeared was noted. Thereafter, more bromine was distilled into the tube, and the solubility was again determined.

Phase relations were determined for tetra-\( n \)-butylammonium bromide, trimethylammonium bromide, trimethylammonium chloride, and tri-\( iso \)-amylammonium chloride. With the last-named compound the existence of only the complex with one molecule of bromine, \((C_6H_{11})_3NHCl·Br_2\), was established, because the viscosity of the solutions was so high that other compounds could not well be found by the method employed.

Bromine was purified by the method described by Moessen and Kraus.\(^2\) Salts were prepared and purified according to conventional methods. The ternary salts decompose at higher temperatures; \(Bu_4NB\) melted at 117.3–117.7\(^\circ\). In Figure 1 are shown phase diagrams of three salts, mole fractions of the solutions being plotted against the temperature at which solid particles just disappeared. The plot for \(Me_3NHCl\) is displaced with respect to that for the other salts. In Table 1 are given the composition and the melting points for the solid phases that have been identified.

<table>
<thead>
<tr>
<th>Mole Per Cent</th>
<th>Formula</th>
<th>M.P., ° C.</th>
<th>Mole Per Cent</th>
<th>Formula</th>
<th>M.P., ° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Br)</td>
<td>(Bu_4NB)-(Br_2)</td>
<td>76 (app.)</td>
<td>(Br)</td>
<td>(Me_4NHBr)-(Br_2)</td>
<td>34</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
<td>50</td>
<td>(Me_4NHBr)-(2Br_2)</td>
<td>6</td>
</tr>
<tr>
<td>75</td>
<td>(Bu_4NB)-(3Br_2)</td>
<td>37</td>
<td>66</td>
<td>(Me_4NHBr)-(3Br_2)</td>
<td>1.5</td>
</tr>
<tr>
<td>50</td>
<td>(Me_3NHCl)-(2Br_2)</td>
<td>37</td>
<td>75</td>
<td>(Me_4NHBr)-(3Br_2)</td>
<td>1.5</td>
</tr>
<tr>
<td>66</td>
<td>(Me_4NHCl)-(2Br_2)</td>
<td>11.5</td>
<td>50</td>
<td>(Am_4NHCl)-(Br_2)</td>
<td>33</td>
</tr>
<tr>
<td>80</td>
<td>(Me_4NHCl)-(4Br_2)</td>
<td>11.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The complexes formed by the bromide and chloride ions depend on the alkyl groups of the positive ions. Thus \(Bu_4NB\) forms complexes with one and three molecules of bromine, while \(Me_3NHBr\) forms complexes with one, two, and three molecules of bromine. On the other hand, \(Me_4NHCl\) forms compounds with one, two, and four, but not with three, molecules of bromine.

All the compounds exhibit maximum melting points, and successive phases form eutectics, with the possible exception of \(Me_3NHBr\)-\(Br_2\). The uncomplexed salt in this case is practically insoluble in the melt. \(Bu_4NB\) is quite soluble in the resulting melt, forming a eutectic with \(Bu_4NB\)-\(Br_2\) at 40 mole per cent bromine. \(Me_4NHCl\) forms a eutectic with \(Me_4NHCl\)-\(Br_2\) at about 45 mole per cent bromine. The low solubility of \(Me_4NHBr\)-\(Br_2\) in the melt is somewhat surprising.
No evidence was found indicating exchange between chloride ions and bromine.

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2 G. W. Moessen and C. A. Kraus, these *PROCEEDINGS*, 38, 1023, 1952.