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THE INFLUENCE OF TERMINAL SUBSTITUENTS UPON THE NEMATIC-ISOTROPIC TRANSITION TEMPERATURE

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1. Introduction. — In an earlier paper [1] the nematic-isotropic transition temperatures \( T_c \) of homologous series were reviewed and interpreted qualitatively. It is of importance both from a theoretical and from a practical point of view to get a more quantitative insight into the factors that influence this transition temperature. Maier and Saupe [2] considered the difference in free energy between the nematic and the isotropic phase, taking into account the attractive dispersion forces. This leads to

\[ T_c = A/(4.54kV^2) \]  

where \( k \) is Boltzman's constant and \( V \) is the molar volume. The molecular properties are incorporated in the factor \( A \) which is approximately proportional to the square of the anisotropy of the molecular polarizability

\[ A \sim (\Delta \alpha)^2 \]  

where \( \Delta \alpha = \alpha_{||} - \alpha_{\perp} \), \( \alpha_{||} \) is the polarizability along the long axis of the molecule and \( \alpha_{\perp} \) the polarizability perpendicular to this axis. In this paper the relation between \( T_c \) and \( (\Delta \alpha)^2 \) as given by eq. (1) and (2) will be investigated. This will be done by varying the terminal substituent in some liquid crystalline series.

Up to now any relation between terminal substituents \( X \) (\( X = \text{CH}_3, \text{Cl}, \text{CN}, \text{etc.} \)) and \( T_c \) was purely empirical [3, 4, 5]. We suggest that within a series the influence of the terminal substituents upon \( T_c \) can be determined by considering the anisotropy in the polarizability of the \( C_{Ar} - X \) bond. It is then supposed that the anisotropy of the polarizability of a molecule can be obtained by addition of the anisotropies of the polarizabilities of the various groups [6]:

\[ \Delta \alpha = \Delta \alpha_M + \Delta \alpha_X \]  

where \( \Delta \alpha_M \) is constant within a series. Using eq. (1) and (2) the relation between \( T_c \) and these molecular properties is then given by

\[ T_c \sim (\Delta \alpha_M)^2 + 2 \Delta \alpha_M \Delta \alpha_X + (\Delta \alpha_X)^2 \]  

and since \( \Delta \alpha_M \gg \Delta \alpha_X \), eq. (4) gives approximately a linear dependence of \( T_c \) on \( \Delta \alpha_X \). We shall now check whether this linear relation holds for two series of compounds.

2. Results and discussion. — In Table I the values for the anisotropy of the polarizability of the \( C_{Ar} - X \) bonds for a number of substituents \( X \) is given. These values were calculated from the Kerr constant of the different monosubstituted benzenes in solution [7]. Unfortunately no values can be given for \( X = \text{alkoxy} \).

<table>
<thead>
<tr>
<th>( X )</th>
<th>( \Delta \alpha ) (Å³) of ( C_{Ar} - X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.5</td>
</tr>
<tr>
<td>\text{CH}_3</td>
<td>1.2</td>
</tr>
<tr>
<td>Cl</td>
<td>2.5</td>
</tr>
<tr>
<td>Br</td>
<td>3.9</td>
</tr>
<tr>
<td>NO₂</td>
<td>4.0</td>
</tr>
<tr>
<td>CN</td>
<td>4.4</td>
</tr>
</tbody>
</table>
Two series of nematic compounds were considered. The first is a series of Schiff bases we prepared:

\[
\text{CH}_3\text{O}-\text{CH}=\text{N}-\text{X} \quad \text{(I)}
\]

It has not been recognized that all these compounds show nematic behaviour. The data are given in table II.

**Table II**  
*p-methoxybenzylidene-p-X-anilines*

<table>
<thead>
<tr>
<th>X</th>
<th>mp (°C)</th>
<th>(T_c) (°C)</th>
<th>mp lit (°C)</th>
<th>(T_c) lit (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>62</td>
<td>26</td>
<td>62</td>
<td>—</td>
<td>[8]</td>
</tr>
<tr>
<td>CH₃</td>
<td>92</td>
<td>38</td>
<td>93</td>
<td>38</td>
<td>[9]</td>
</tr>
<tr>
<td>Cl</td>
<td>92-93</td>
<td>47</td>
<td>92</td>
<td>—</td>
<td>[10]</td>
</tr>
<tr>
<td>OCH₃</td>
<td>146</td>
<td>102</td>
<td>146</td>
<td>99</td>
<td>[5]</td>
</tr>
<tr>
<td>Br</td>
<td>118</td>
<td>34</td>
<td>120</td>
<td>—</td>
<td>[10]</td>
</tr>
<tr>
<td>NO₂</td>
<td>124.5</td>
<td>82.5</td>
<td>124.5</td>
<td>—</td>
<td>[11]</td>
</tr>
<tr>
<td>CN</td>
<td>107</td>
<td>119</td>
<td>105</td>
<td>118</td>
<td>[12]</td>
</tr>
</tbody>
</table>

A plot of \(T_c\) against \(\Delta \alpha_x\) is given in curve A of figure 1, and shows a linear relationship. The line was calculated with the method of the least squares. Only bromine as substituent does not fit and is not included in the calculations.

As a second example we used a series of phenyl-p-benzoyleoxybenzoates

\[
\text{C}_6\text{H}_{11}-\text{O}-\text{C}-\text{O}-\text{C}-\text{X} \quad \text{(II)}
\]

prepared by Van Meter and Klanderman [13]. The results are given as curve B in figure 1. In this case also a linear relationship was observed.

The value of \(\Delta \alpha_M\) which gives the lowest deviation between the experimental data and the calculated data is for series (I) 27.0 (Å)³ and for series (II) 53.6 (Å)³. If values could be given for other series of compounds it would be possible to give a classification of the influence on \(T_c\) not only of the terminal substituents but also of the rest of the molecular systems.

It is known that besides dispersion forces, excluded volume effects can be important within a series for the behaviour of \(T_c\) [14, 15]. Apparently these effects play a minor role for the substituents studied here. For larger substituents (like oxyhexyl, nonyl) it is probably not true anymore and such a simple relationship as eq. (4) cannot be expected to apply. This cannot be tested at the moment since for these substituents polarizability data are not available.

We conclude that consideration of the anisotropy of the \(C\&\text{---X}\) bond for terminal substituents \(X\) is a valuable tool in predicting \(T_c\).
3. Experimental. — The Schiff bases were prepared by condensing equimolecular amounts of p-methoxybenzaldehyde with the appropriate anilines. They were recrystallized till they showed sharp melting points. The melting and clearing temperatures were determined with a Reichert Thermopan polarizing microscope and a Mettler FP 52 heating stage.

References