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Physical properties of nematic Schiff’s bases

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Abstract. — The anisotropy of the diamagnetic susceptibility, the density and the entropy change at the nematic-isotropic transition of a number of structurally related Schiff’s bases are reported. Order parameters have been calculated from the anisotropies of the susceptibility. The results indicate that there is a close correspondence between the order parameter and the relative volume change at the nematic-isotropic transition. The experimental data suggest that there exists considerable flexibility of the alkylene chains both in the nematic and isotropic phases. The experimentally observed trends can be understood within the framework of theoretical models, which take account of molecular flexibility.

1. Introduction. — In the nematic liquid crystalline phase the long axes of the elongated molecules tend to align along a preferred direction, represented by a unit vector \( \mathbf{n} \), the director. The molecular centres of mass on the other hand are distributed at random. The nematic phase is uniaxial, which implies that various macroscopic physical quantities are anisotropic in nature. In this paper the anisotropy of the diamagnetic susceptibility of a number of structurally related Schiff’s bases is considered. The diamagnetic susceptibility relates the magnetic moment \( \mathbf{M} \), induced by an applied field \( \mathbf{H} \), to the field according to

\[
M_\alpha = \chi_{\alpha\beta} H_\beta \quad \alpha, \beta = x, y, z
\]

where \( \chi_{\alpha\beta} \) denotes an element of the susceptibility tensor \( \chi \). Choosing the \( z \)-axis along the director, the tensor in the nematic phase is given by

\[
\chi = \begin{bmatrix}
\chi_{\perp} & 0 & 0 \\
0 & \chi_{\perp} & 0 \\
0 & 0 & \chi_{||}
\end{bmatrix}
\]

where \( \chi_{\perp} \) and \( \chi_{||} \) denote the volume susceptibilities parallel and perpendicular to the director, respectively.

Since magnetic interactions between the molecules are small, the anisotropy \( \Delta \chi = \chi_{||} - \chi_{\perp} \) is related in a simple way to the degree of orientational order of the molecules (see section 4). In order to obtain additional information with regard to the nematic-isotropic transition, we have also measured the entropy change at this transition. Moreover the densities have been determined as a function of temperature, from which the relative volume changes at the transition and the packing fractions have been calculated. The observed trends will be related to differences between the molecular structures and properties of the various compounds.

The compounds studied are \( o \)-hydroxy-\( p \)-methoxybenzylidene-\( p' \)-butylaniline (OHMBBA), \( p \)-methoxybenzylidene-\( p' \)-cyanoaniline (MBCA), anisylidene-\( p \)-aminophenylacetate (APAPA) and a number of homologues of APAPA. The molecular structure of these materials can be represented by the formula

\[ \text{CH}_3\text{O} \underset{R_1}{\text{---}} \text{CH} \overset{N}{\underset{R_2}{\equiv}} \text{CH} \]

where \( R_1 \) and \( R_2 \) are side and end groups, respectively. A list of abbreviations and nematic ranges of these materials is given in table I. The side group \( R_1 \) is

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Table I. — List of liquid crystals studied. $T_m$ and $T_c$ are the transition temperatures crystal-nematic and nematic-isotropic. The anisotropy of the mass susceptibility can be calculated according to eq. (5) with the parameters $\Delta \chi^a(0)$, $\beta$ and $\gamma$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta \chi^a(0)$ ($10^{-7} \text{ cm}^3 \text{ g}^{-1}$)</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBBA</td>
<td>18</td>
<td>45.0</td>
<td>1.911 5</td>
<td>0.998 4</td>
<td>0.173 7</td>
</tr>
<tr>
<td>OHMBBA</td>
<td>44</td>
<td>64.6</td>
<td>2.075 8</td>
<td>0.998 1</td>
<td>0.198 1</td>
</tr>
<tr>
<td>MBCA</td>
<td>106</td>
<td>118.0</td>
<td>2.000 6</td>
<td>0.998 5</td>
<td>0.134 3</td>
</tr>
<tr>
<td>APAPA</td>
<td>82</td>
<td>111.0</td>
<td>2.118 5</td>
<td>0.994 1</td>
<td>0.185 3</td>
</tr>
<tr>
<td>APAPA2</td>
<td>72</td>
<td>110.6</td>
<td>2.053 8</td>
<td>0.996 5</td>
<td>0.194 4</td>
</tr>
<tr>
<td>APAPA3</td>
<td>53</td>
<td>112.8</td>
<td>2.010 1</td>
<td>0.998 1</td>
<td>0.181 3</td>
</tr>
<tr>
<td>APAPA4</td>
<td>61</td>
<td>100.0</td>
<td>2.126 1</td>
<td>0.996 8</td>
<td>0.217 3</td>
</tr>
<tr>
<td>APAPA5</td>
<td>83</td>
<td>103.2</td>
<td>1.966 4</td>
<td>0.996 7</td>
<td>0.198 3</td>
</tr>
<tr>
<td>APAPA6</td>
<td>64</td>
<td>97.1</td>
<td>1.738 8</td>
<td>0.997 0</td>
<td>0.192 8</td>
</tr>
<tr>
<td>APAPA7</td>
<td>67</td>
<td>98.8</td>
<td>1.773 1</td>
<td>0.997 3</td>
<td>0.196 9</td>
</tr>
<tr>
<td>APAPA8</td>
<td>72</td>
<td>93.7</td>
<td>1.812 6</td>
<td>0.998 8</td>
<td>0.201 8</td>
</tr>
<tr>
<td>APAPA9</td>
<td>76</td>
<td>96.5</td>
<td>1.659 1</td>
<td>0.998 8</td>
<td>0.187 8</td>
</tr>
</tbody>
</table>

is a hydrogen for all compounds except OHMBBA, where $R_1$ represents a hydroxy group (OH). The end group $R_2$ is a butyl ($\text{C}_4\text{H}_9$), cyanide (CN) and acetate ($\text{OCOCH}_3$) group for OHMBBA, MBCA and APAPA respectively. The homologues of APAPA have been denoted for simplicity as APAPAn. For these materials $R_2$ stands for the ester group $\text{OCOC}_2\text{H}_{2n+1}$.

The compounds studied have no smectic phases. Consequently we can exclude smectic-like short range order, which could influence the trends in various physical properties observed in the nematic phase.

2. Experimental. — The compounds studied were purchased from various factories and purified before use by several recrystallizations from methanol. The transition temperatures were determined using a Mettler FP5 hot stage. After several recrystallizations the nematic-isotropic melting ranges appeared to be of the order of 0.1 °C.

The magnetic susceptibilities have been measured at the Philips’ Research Laboratories (Eindhoven) using the Faraday-Curie method. We have used the same equipment as employed by de Jeu and Claessen [1], who have investigated the diamagnetic susceptibility of two homologous series of azoxybenzenes. For a description of the experimental set-up and possible errors connected with this method we therefore refer to these authors. The Faraday-Curie method allows a determination of the mass susceptibility $\chi = \chi / \rho$, where $\rho$ is the density. Since for the compounds studied, $\chi$ is less negative than $\chi^a$, the director $n$ is aligned parallel to the magnetic field direction. As a consequence one can measure in the nematic phase only $\chi^a$. However, since $\chi^a$, the susceptibility in the isotropic phase, is independent of temperature, $\Delta \chi^a = \chi^a - \chi^a_{\text{iso}}$ can be obtained from the expression

$$\Delta \chi^a = \frac{3}{2} (\chi^a - \chi^a_{\text{iso}}). \quad (3)$$

We have measured the densities, using an apparatus built in this laboratory. The central part is a hollow V-shaped glass tube, which can be filled with a liquid. The tube is cemented tightly at the ends in a copper block. The principle of operation is based on the variation of the natural oscillation frequency of the tube, due to changes in its mass [2]. If the tube contains a liquid with density $\rho$, the oscillation period is given by

$$\tau = (A\rho + B)^{1/2} \quad (4)$$

where $A$ and $B$ are constants, depending on the properties of the tube. We have calibrated the tube using two organic fluids with known densities, viz. acetonaphene and meta-xylene. The accuracy of the calibration has been checked by measuring the density of double distilled water. The measured density of this liquid appeared to deviate less than 0.1 % from tabulated values. The oscillator was mounted in a massive copper block, which was heated electrically. The estimated accuracy of the measurements is about 0.1 %.

The entropy change $\Delta \Sigma$, associated with the nematic-isotropic transition, has been determined for the series APAPAn by means of differential scanning calorimetry, using a Perkin Elmer DSC meter (type 1B). The values of $\Delta \Sigma$ were derived from the transition heats, using pure In as a standard.

3. Results. — As an example of the susceptibility measurements figure 1 shows the anisotropy of the mass susceptibility as a function of reduced temperature for OHMBBA. The solid curve through the points is a least squares fit according to the formula

$$\Delta \chi^a(T/T_c) = \Delta \chi^a(0) (1 - \beta T/T_c)^\gamma \quad (5)$$

where $\Delta \chi^a(0)$, $\beta$ and $\gamma$ are fitting parameters, $T$ is the temperature and $T_c$ the nematic-isotropic transi-

![Fig. 1. — Anisotropy of the mass susceptibility as a function of reduced temperature for OHMBBA. The open and filled circles represent two independent measurements.](image-url)
The entropy change $\Delta \Sigma$ has been determined for the homologous series APAPAn. We emphasize that we did not take into account the pretransitional effects in calculating $\Delta \Sigma$. As far as we know, APAPA is the only compound of the series for which $\Delta \Sigma$ has been measured [5]. For this material the reported value is considerably higher than the value found by us (0.34 cal. K$^{-1}$ mole$^{-1}$). The results of the entropy measurements will be given in section 4.3.

4. Discussion. — 4.1 Molecular Flexibility. — The trends in various physical properties, observed in homologous series, are closely related to the properties of the alkyl chains. An important question in this respect is how flexible the chains of nematicogenic molecules are, as compared with, for example, n-alkanes in the liquid state. Raman [6] and DMR [7] measurements indicate that the chains indeed are rather flexible. X-ray measurements [8] on the other hand yield a somewhat more rigid picture. In the liquid state n-alkanes are not rigid, i.e. are not exclusively in the extended trans configuration, but can adopt a great number of conformations. The bonds occur in three possible states, i.e. the energetically favourable trans state (t) and the two symmetrical gauche states ($g^+$, $g^-$), obtained by rotations around the carbon-carbon bonds of about $\pm 120^\circ$. The gauche/trans energy difference per mole, $E_{gt}$, is a measure of the flexibility; the statistical weight of a gauche state is equal to $\exp(-E_{gt}/RT)$, where $R$ is the gas constant. For n-alkanes $E_{gt} = 500$ cal/mole [9].

It is conceivable that in the nematic phase the formation of gauche conformers will be suppressed to some extent as a result of the presence of the ordering field originating from the neighbouring molecules. These external conformational constraints can equivalently be interpreted in terms of an effective gauche/trans energy difference $E_{gt}$, which is higher compared with the n-alkane value. At the clearing point $T_c$, the conformational constraints disappear and it may be expected that the chains have conformational freedom comparable to that of the n-alkanes. Possibly $E_{gt}$ is somewhat higher than 500 cal/mole as a result of short range correlations in the isotropic phase. The difference in population of chain conformations between the nematic and isotropic phase, due to a different value of $E_{gt}$, will be reflected in the entropy change at the nematic-isotropic transition. This idea has led Martire [10] to calculate $E_{gt}$ in the various mesophases of the dialkoxyazoxybenzenes from the increments in $\Delta \Sigma$ per methylene group, by analogy to the melting of n-alkanes. Assuming that $E_{gt} = 500$ cal/mole in the isotropic phase, he obtained a value of 1 050 cal/mole in the nematic state. However, assuming that in the smectic phase the chains are in the extended trans configuration, as suggested by X-ray work, the result was 3 150 cal/mole for $E_{gt}$.
in the nematic and 2 600 cal/mole for \( E_{\text{gt}} \) in the isotropic phase. The majority of experimental studies suggest a value of \( E_{\text{gt}} \) in the isotropic phase close to 500 cal/mole.

Although the nematic-isotropic transition has been studied in a variety of papers, only a few of them deal with molecular flexibility. In this respect we should mention the models developed by Dowell and Martire [11] and Marëelja [12]. Dowell and Martire have studied the effect of chain flexibility and chain length on the transition properties, using a steric mean field cubic lattice model. The molecules are thought to be composed of a number of flexible and rigid segments, which can occupy only a finite number of orientations. Both attractive and repulsive forces are taken into account. In Marëelja's theory on the other hand, steric repulsions have been neglected. Starting point is the mean field theory of Maier and Sauge [13]. The van der Waals forces between the anisotropically polarizable molecules are described in terms of a number of coupling constants, which take account of the interaction between the rigid cores and flexible chains. Our results can be interpreted reasonably well within the framework of these models, as will be shown in the next sections.

4.2 Order parameters and density. — If \( \xi, \eta \) and \( \zeta \) are the axes of a coordinate system, fixed to the molecules, the degree of orientational order can be described by the tensor \( S \) with elements [14]

\[
S_{ij} = \frac{1}{2} \left\langle 3 \, i_x j_x - \delta_{ij} \right\rangle, \quad i, j = \xi, \eta, \zeta. \quad (8)
\]

Here \( z \) denotes the preferred direction. By a proper choice of \( \xi, \eta, \) and \( \zeta \) the tensor \( S \) can be diagonalized. Since \( S \) has zero trace, there are two independent order parameters. Taking the \( \zeta \)-axis as the long molecular axis, we choose \( S = S_{\xi\xi} + D = S_{\eta\eta} - S_{\eta\eta} \). The relation between \( \Delta \chi \), the components of \( S \) and the diagonal components of the molecular diamagnetic polarizability tensor \( \kappa \) can be expressed as [15]

\[
\Delta \chi = N \left\{ \frac{1}{2} \left( \kappa_{\xi\xi} + \kappa_{\eta\eta} \right) S + \frac{1}{2} \left( \kappa_{\eta\eta} - \kappa_{\xi\xi} \right) D \right\} . \quad (9)
\]

Here the number density \( N = N_A \rho / M \), where \( N_A \), \( \rho \) and \( M \) are Avogadro's number, the density and the mass number, respectively. The order parameter \( D \) describes the difference between the tendencies of the two transverse molecular axes to align along the preferred direction. \( D \) is related to the deviation from axial symmetry around the long molecular axis. For cylindrically symmetric molecules \( D = 0 \) and eq. (9) reduces to

\[
\Delta \chi = N \left[ \kappa_{\eta\eta} - \frac{1}{2} \left( \kappa_{\xi\xi} + \kappa_{\eta\eta} \right) \right] S. \quad (10)
\]

In order to calculate \( S \), we shall use eq. (10), which is only justified if the term \( (\kappa_{\xi\xi} - \kappa_{\eta\eta}) D/2 \) in eq. (9) is small. Information about \( D \) is scarce. Nuclear magnetic resonance on deuterated \( p \)-cyano \( p' \)-pentyl-biphenyl [16] indicates that \( D \) is about 0.05 while for PAA a value of about 0.04 has been reported [17]. However these results depend strongly on the choice of various molecular parameters, as has been demonstrated by Höhener et al. [18] for MBBA. These authors were able to fit their spectra assuming \( D = 0 \), indicating that the value found for \( D \) strongly depends on the experimental technique used, as de Jeu suggested previously [1]. Assuming nevertheless \( D = 0.05 \) and a twist angle of 45° between the aniline and benzylidene ring [19] and using the benzene values for \( \kappa_{\xi\xi} \) and \( \kappa_{\eta\eta} \) [10], the term \( N_A (\kappa_{\xi\xi} - \kappa_{\eta\eta}) D/2 \) is calculated to be

\[
2.1 \times 10^{-6} \text{ cm}^2/\text{mole},
\]

which is about 7% of the measured anisotropy of the molar susceptibility of MBBA [3]. We conclude therefore that, irrespective of the uncertainty about \( D \), disregarding the \( D \)-term will not lead to substantial errors.

Eq. (10) shows that \( S \) can be calculated provided the factor \( \Delta \chi^M = N_A (\kappa_{\xi\xi} - (\kappa_{\xi\xi} + \kappa_{\eta\eta})/2 \) is known. In order to obtain \( \Delta \chi^M \), Haller [21] applied an extrapolation of \( \ln \Delta \chi \) vs. \( \ln (1 - T/T_c) \) to zero temperature, where \( S \) was assumed to be unity. However this procedure can only give a rough estimate, since the extrapolation covers a very broad temperature interval. A better approach is to derive \( \Delta \chi^M \) from susceptibility measurements on solid single crystals. Unfortunately, no data of \( \kappa_{\eta\eta} \) have been reported for the materials considered. Sherrel and Creliln [22] have calculated \( \Delta \chi^M \) for MBBA, applying Pascal's additivity rules [23] and using tabulated bond susceptibilities [20] and obtained the value

\[
54.0 \times 10^{-6} \text{ cm}^2/\text{mole}.
\]

Using this value and de Jeu's [3] susceptibility data for MBBA, the values of \( S \) calculated from eq. (10) appeared to agree excellently with \( S \)-values obtained from various different techniques [24]. With this value of \( \Delta \chi^M \) for MBBA as a starting point, we have calculated this quantity for the other compounds, using tabulated magnetic bond polarizabilities [20]. The magnetic anisotropy of the chains has been calculated assuming that only the trans configuration gives a contribution. We have used the molecular model, drawn in figure 3, taking for \( \beta \) the value 6.5⁰,

Fig. 3. — The molecular structure of the homologues of APAPA.
Table III. — Order parameters $S_c$, densities $\rho_c$, relative density changes $\Delta \rho/\rho_c$ and packing fractions $\eta_c$ at the nematic-isotropic transition. $V$ is the molecular volume and $\Delta \chi'$ the calculated anisotropy of the molar susceptibility for $S = 1$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta \chi'$ $(10^{-6} \text{ cm}^3/\text{mole})$</th>
<th>$S_c$</th>
<th>$\rho_c$ $(\text{g/cm}^3)$</th>
<th>$\Delta \rho/\rho_c$</th>
<th>$V$ $(\text{Å}^3)$</th>
<th>$\eta_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OHMBBA</td>
<td>54.0</td>
<td>0.31</td>
<td>1.0637</td>
<td>0.15</td>
<td>287</td>
<td>0.649</td>
</tr>
<tr>
<td>MBCA</td>
<td>45.6</td>
<td>0.34</td>
<td>1.0749</td>
<td>0.38</td>
<td>233</td>
<td>0.638</td>
</tr>
<tr>
<td>APAPA</td>
<td>56.1</td>
<td>0.39</td>
<td>1.0987</td>
<td>0.35</td>
<td>258</td>
<td>0.634</td>
</tr>
<tr>
<td>APAPA2</td>
<td>58.8</td>
<td>0.33</td>
<td>1.0758</td>
<td>0.23</td>
<td>275</td>
<td>0.629</td>
</tr>
<tr>
<td>APAPA3</td>
<td>55.5</td>
<td>0.35</td>
<td>1.0544</td>
<td>0.28</td>
<td>292</td>
<td>0.624</td>
</tr>
<tr>
<td>APAPA4</td>
<td>57.2</td>
<td>0.33</td>
<td>1.0505</td>
<td>0.22</td>
<td>309</td>
<td>0.628</td>
</tr>
<tr>
<td>APAPA5</td>
<td>55.3</td>
<td>0.37</td>
<td>1.0333</td>
<td>0.22</td>
<td>326</td>
<td>0.624</td>
</tr>
<tr>
<td>APAPA6</td>
<td>56.6</td>
<td>0.34</td>
<td>1.0260</td>
<td>0.19</td>
<td>343</td>
<td>0.625</td>
</tr>
<tr>
<td>APAPA7</td>
<td>55.2</td>
<td>0.35</td>
<td>1.0138</td>
<td>0.25</td>
<td>360</td>
<td>0.622</td>
</tr>
<tr>
<td>APAPA8</td>
<td>56.2</td>
<td>0.30</td>
<td>1.0086</td>
<td>0.23</td>
<td>377</td>
<td>0.623</td>
</tr>
<tr>
<td>APAPA9</td>
<td>55.1</td>
<td>0.32</td>
<td>0.9960</td>
<td>0.22</td>
<td>395</td>
<td>0.621</td>
</tr>
</tbody>
</table>

The probability that the chain is in the trans configuration has been calculated using $E_{gt} = 1050 \text{ cal/mole}$ (see section 4.1). The values of $\Delta \chi'$ calculated in this way have been collected in table III.

Within the homologous series, the well known odd-even effect is observable, which levels off with increasing chain length.

Knowing the factors $\Delta \chi'$, the parameters $S$ can be calculated. These parameters represent in fact some average, since the ordering of the rigid cores differs from the ordering of the flexible tail segments, as has been shown experimentally [7]. However, since the magnetic anisotropy of the chains is small compared with the anisotropy of the cores, the calculated order parameters reflect to a high approximation the ordering of the cores. In figures 4 and 5 we have displayed $S$ as a function of temperature for a number of compounds. A remarkable feature is that within the series APAPA$n$ the temperature dependence of $S$ seems to become stronger with increasing chain length. This behaviour could be attributed to the assumption of zero $D$, which is increasingly less justified if $D$ increases within the series. An increase of $D$ is plausible, since with increasing chain length the molecular shape is determined more and more by the shape of the chain, which is somewhat flat because the planar trans state is energetically favourable.

In molecular statistical theories dealing with the nematic-isotropic transition, the values of various physical properties at $T_c$ are important parameters. We have listed in table III the order parameters $S_c$, the nematic densities $\rho_c$ and the relative density changes $\Delta \rho/\rho_c$ at $T_c$. Besides, we have included in the table the molecular volumes $V$ (calculated from tabulated bond lengths and intermolecular radii [27] and the packing fractions $\eta_c = N_A \rho_c V/M$. The errors in $S_c$ and $\Delta \rho/\rho_c$ are estimated to be approximately 7 and 10 percent, respectively, since these parameters are obtained from an extrapolation procedure. The table shows clearly that there is a close correspondence between $S_c$ and $\Delta \rho/\rho_c$. As we would expect intuitively a high value of $S_c$ is observed for compounds with a high relative volume change. In addition a gradual decrease of $\Delta \rho/\rho_c$ and, consequently, of $S_c$, with increasing chain length is noticeable in the series APAPA$n$. The trends in $S_c$ and $\Delta \rho/\rho_c$ observed within the homologous series are qualitatively in agreement with the predictions of the Dowell-Martire model [11]. The decrease of the
packing fractions can only be explained within the framework of this model if the chains are assumed to be somewhat less flexible (e.g. \( E_{gt} \approx 800 \text{ cal/mole} \)) than the n-alkanes (\( E_{gt} = 500 \text{ cal/mole} \)). Accepting a value of 800 cal/mole for \( E_{gt} \), a decrease of \( T_c \) is predicted in the lattice model if the attractive forces are assumed to be somewhat anisotropic, which certainly holds for the compounds studied. A decrease of \( T_c \) can also be understood within the framework of the theory of Marčelja [12].

One might wonder whether the experimentally observed trends can also be explained in terms of theories which do not take account of molecular flexibility. For this purpose the molecular statistical theory of Ypma and Vertogen [28] provides a suitable starting point. In this theory an equation of state was derived for the nematic phase, based on both anisotropic attractive forces and the anisotropic shape dependent steric repulsions. The theory predicts an increase of \( S_c \) and \( \Delta p / \rho_0 \) with increasing molecular length to width ratio. The experimentally observed trends in \( S_c \) and \( \Delta p / \rho_0 \) within the series APAPA\( n \) can only be reconciled with the predictions of this model, if the length to width ratio is assumed to decrease with increasing chain length. This possibility has been suggested in a previous paper [26], in which we presented calculations of the length to width ratio of the chains, statistically averaged over all conformations, using the n-alkane value for \( E_{gt} \). Although we found that the chains tend towards a more spherical shape with increasing length, a decrease of the overall molecular length to width ratio could only be found, if unrealistically low values of \( E_{gt} \) were used (less than 400 cal/mole). We conclude that the effect of molecular flexibility must be incorporated in theories of the nematic-isotropic phase in order to understand the trends observed in homologous series.

4.3 Entropy Change. — A simple Landau theory [29] predicts that the entropy change at the nematic-isotropic transition is proportional to \( S_c^2 \). The observed alternation in \( \Delta \Sigma \) (see Fig. 6) can be attributed indeed largely to the alternation in \( S_c \). However it is clear that this simple relationship fails to explain the increase in \( \Delta \Sigma \) with increasing chain length, since \( S_c \) decreases somewhat.

An increase of \( \Delta \Sigma \) with increasing chain length is usually observed within homologous series [30]. However, in the majority of cases these series exhibit both nematic and smectic phases. In these series, therefore, part of the increase of \( \Delta \Sigma \) is possibly due to an increase of smectic short range order, as has been suggested by Arnold [31]. This possibility can be ruled out in our case, since the compounds studied in this paper only show nematic liquid crystalline behaviour.

An increase of \( \Delta \Sigma \) is predicted both by the lattice model of Dowell and Martire [11] and the mean field theory of Marčelja [12]. In Marčelja's theory packing effects, associated with hard core repulsions, have not been taken into account. Part of the entropy change in this model results from the difference in conformational freedom of the chains between the nematic and isotropic phase. Evidently this effect plays a role in the present series. This is supported by the observation that if the length of APAPA is increased using relatively rigid substituents, no increase of \( \Delta \Sigma \) is observed. The increase of \( \Delta \Sigma \) for APAPA\( n \), attributed to an increasing population difference of gauche conformers, allows an estimate of the effective gauche/trans energy difference \( E_{gt} \) in the nematic phase, as has been discussed in section 4.1. Again taking the liquid n-alkane value of 500 cal/mole for the isotropic phase, this means for the present series a value \( E_{gt} \approx 1000 \text{ cal/mole} \). This indicates that the flexibility of the chains is still considerable.

5. Conclusions. — In this paper, we have investigated a number of structurally related Schiff's bases. Since the materials only show nematic liquid crystalline behaviour, the experimentally observed trends are probably not obscured by possible influences of short range smectic order. The present study has shown that,

1) there is a close correspondence between the order parameters \( S_c \) and the relative volume change at the nematic-isotropic transition;
2) the trends observed in the homologous series can only be understood in terms of theories which take account of molecular flexibility;
3) the increase of the entropy change \( \Delta \Sigma \) at \( T_c \) with increasing chain length cannot be explained in terms of a simple Landau theory. Part of \( \Delta \Sigma \) results from a difference in conformational freedom of the alkylene chains between the nematic and isotropic phase. Nevertheless there is considerable chain flexibility in both phases.
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