

DEPENDENCE OF THE CLEARING TEMPERATURE ON  
ALKYL CHAIN LENGTH IN NEMATIC HOMOLOGOUS SERIES

W.H. de Jeu, J. van der Veen and W.J.A. Goossens

Philips Research Laboratories, Eindhoven, Netherlands

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In homologous series of nematic compounds with relatively high clearing temperatures, these temperatures are known to decrease with increasing chain length. Recently, however, series with relatively low clearing temperatures have been synthesized in which these temperatures increase with increasing chain length. In both cases the clearing temperatures alternate within a series. A qualitative explanation is given for these facts. The discussion is based on an expression for the free energy in which both the attractive dispersion forces and the excluded volume affects are taken into account.

TWO RECENT letters discussed the dependence of the clearing temperature  $T_c$  on the length  $n$  of the alkyl chain in nematic homologous series.<sup>1,2</sup> In both letters the experimental situation was evaluated as giving a decrease of  $T_c$  with increasing  $n$ , while the alternation of  $T_c$  within a series was not considered. However, in recent years many new homologous series of liquid crystals have been synthesized with relatively low melting and clearing points,<sup>3</sup> where  $T_c$  hardly changes or (for the lowest  $T_c$  values) even increases with increasing  $n$ . This is illustrated in Fig. 1 for some azobenzenes; further examples can be found in reference 3. Therefore a possible explanation of the variations in  $T_c$  has to account for:

- (1) the alternation of  $T_c$  within a homologous series,
- (2) an increase of  $T_c$  with  $n$  at relatively low temperatures,
- (3) a decrease of  $T_c$  with  $n$  at higher temperatures.

Most discussions of  $T_c$ <sup>1–3</sup> have been within the framework of the theory of Maier and Saupe.<sup>4</sup> They considered the difference in free energy between the nematic and the isotropic phase, taking into account the attractive dispersion forces only. However, from order parameter measurements at various pressures<sup>5</sup> and at constant volume<sup>6</sup> it is known that the entropy

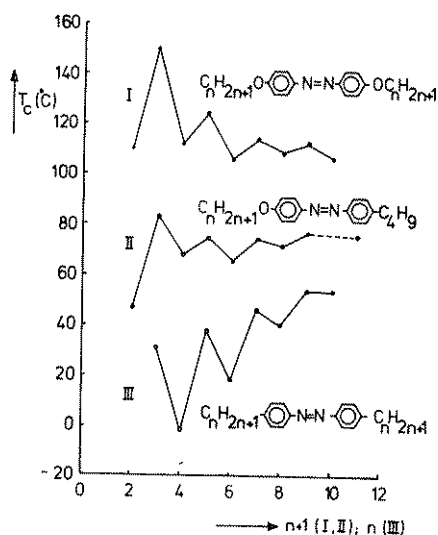


FIG. 1. Clearing temperatures of some homologous series of para substituted azobenzenes. I: WEYGAND C. and GABLER R., *Ber.* 71B, 2399 (1938); GABLER R., dissertation, Leipzig (1939). II,  $n = 1-6$ : STEINSTRASSER R. and POHL L., *Z. Naturforsch.* 26b, 577 (1971). II,  $n = 7-10$ ; III,  $n = 3, 4$ : VAN DER VEEN J., unpublished results. III,  $n = 5-10$ : VAN DER VEEN J., DE JEU W.H., GROBBEN A.H. and BOVEN J., *Mol. Cryst. Liq. Cryst.* 17, 291 (1972).

contribution to the free energy due to steric intermolecular interactions (repulsive forces) is equally important. The simplest form of the free energy per molecule accounting for both contributions is<sup>5</sup>

$$\Delta F = -AS^2 - BTS^2 - T \Sigma(S), \quad (1)$$

where  $S$  is the order parameter.  $-AS^2$  is the internal energy due to the dispersion forces,  $A$  being approximately proportional to the anisotropies of the molecular polarizabilities;  $BS^2$  represents the packing entropy due to excluded volume effects that favour molecular alignment.  $\Sigma$  is the orientational entropy given by  $-k \int P \ln P d\Omega$  where  $P$  is the probability for one molecule to have its orientation in the solid angle  $d\Omega$ . The equilibrium value for  $S$  can be calculated from the self-consistency equation for  $S$  together with the requirement  $\partial\Delta F/\partial S = 0$ . The condition  $\Delta F = 0$  for a phase transition at constant volume leads analogously to the result of Maier and Saupe<sup>4</sup> to

$$T_c = \frac{2A}{4.54k - 2B}, \quad (2)$$

together with a value  $S_c = 0.43$  at  $T_c$ .

The relative values of  $T_c$  for different homologous series have been correlated qualitatively with variations in  $A$  due to different anisotropic polarizabilities.<sup>3</sup> The alternation of  $T_c$  within a series can also be understood in this way: On increasing  $n$  for a rigid zig-zag conformation the increment in the polarizability along the molecular axis is about twice the increment in the polarizability perpendicular to the axis starting from an even number of chain atoms, while they are about

equal when starting with an odd number.<sup>7</sup> This zig-zag conformation can be expected to be favoured somewhat. These arguments on the increments in the anisotropy of the polarizability also predict an overall increase of  $T_c$ . This is what is observed for lower temperatures (see Fig. 1). The diminishing alternation with increasing  $n$  can be attributed to the increased flexibility of longer alkyl chains. That the alternation in  $T_c$  (for equal chain length) is less at higher temperatures (see Fig. 1) is also in agreement with this view.

An expression for  $B$  cannot easily be given, but it seems plausible that  $B$  is in some way proportional to the effective length/breadth ratio of the molecule.<sup>8</sup> According to Stenschke<sup>2</sup> the reduction in the effective length/breadth ratio of a molecule due to the bending of the alkyl chains is proportional to the length and to the temperature. Therefore the increased flexibility of the alkyl chain on increasing  $n$  could lead to a smaller value of  $B$ . This effect will be relatively small at lower temperatures, and the variations in  $A$  determine the dependence of  $T_c$  on  $n$ . When the temperature is increased the flexibility of the alkyl chains will become more pronounced and finally the decrease in  $B$  might dominate, leading to a decrease of  $T_c$  with  $n$ . This qualitative reasoning is in agreement with the fact that the decrease in  $T_c$  with increasing  $n$ , if present, is in general the stronger the higher  $T_c$ .<sup>9</sup>

Finally we note that a decrease in  $T_c$  can also be attributed to the increase in the molar volume  $V$  with  $n$ .<sup>1</sup> However, this would give a uniform reduction of  $T_c$  with  $n$  independent of the temperature, which does not seem to be in agreement with the experimental data.

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