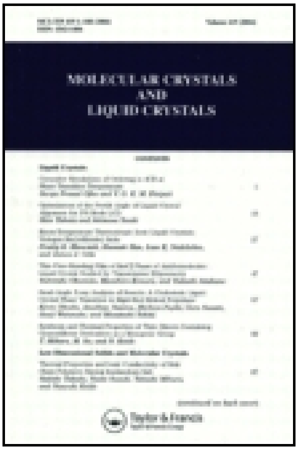

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ODD-EVEN EFFECT IN THE HOMOLOGOUS SERIES OF THIOESTERS

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Abstract Transition temperatures, both principal relaxation times and respective activation energies have been found for the first five members of the pentylphenyl-alkoxythiobenzoate homologous series. It has been found that the transition temperatures exhibit a weakly descending odd-even effect whereas all dynamic quantities increase almost continuously with the number of carbon atoms in the alkoxy chain.

INTRODUCTION

Odd-even effect is observed for clearing temperatures (T_{NI}) of thermotropic liquid crystals for many a homologous series. However, for a homologous series with high transition temperatures a characteristic descending odd-even effect (type I) shows up whereas for substances with low T_{NI} a descending odd-even alternation (type II) is observed. The odd-even effect has been found for many other physical quantities taken at a reduced temperature below the N-I transition. It has been experimentally proved that such dielectric parameters as: 1. the dielectric increments[1-3], 2. the dielectric anisotropy both in the radio[1,3] and microwave frequency ranges[2], 3. the dielectric relaxation time, connected with the reorientation around the short axis ($\tau_{\parallel}$)[1] as well as respective critical frequencies[3], show this effect.

It was also established that for some quantities[3] the odd-even effect is like the one observed for the T_{NI} temperatures. In the case of both principal relaxation times ($\tau_{\parallel}$ and $\tau_{\perp}$) acquired for the first seven members of the di-alkoxyazoxybenzene homologous series[4,5] there is only a weak alternation at the beginning and for higher members both quantities increase almost continuously. This may be due to the fact that the dielectric relaxation times are measured with a small accuracy (± 15%), especially the shorter one ($\tau_{\perp}$) coming from the fast molecular reorientations about the long axis. When one chooses experimental points taken with help of the same apparatus the evidence seems to be better[5].

Thiol esters have been studied in our group by different methods including dielectric relaxation[4-10] and up to now the five members of the 4-n-pentylphenyl-4'-n-alkoxythiobenzoate ($\overline{m}$ S 5) homologous series, viz. $\overline{5}$S5, $\overline{6}$S5, $\overline{7}$S5, $\overline{8}$S5, $\overline{9}$S5 and $\overline{10}$S5, have been investigated by this method. In this paper we would like to sum up the studies in view of possible odd-even effect for the dynamic quantities acquired.

RESULTS AND DISCUSSION

Fig. 1 presents transition temperatures obtained for the five members of the tioesters homologous series. As is seen there is a weakly descending odd-even effect for the T_{NI} transition temperatures. The amplitude of the alternations is also small as one has to here with the chain segments being far away from the phenyl ring. Our diagram is in a good agreement with that presented in[11], however, we have also included the experimental points for $\overline{5}$S5.

The dielectric and optical anisotropies measured by us for all members metioned behave quantitatvely the same way as the T_{NI} temperatures do and such a behaviour has been discussed in earlier papers[1-3]. In this paper we shall pay our attention to molecular

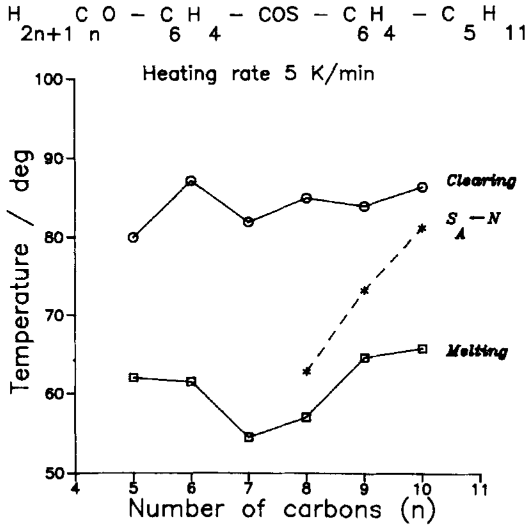

FIGURE 1. Transition temperatures as functions of the number of carbon atoms in the alkoxy chain for $\bar{n}S5$ homologous series.

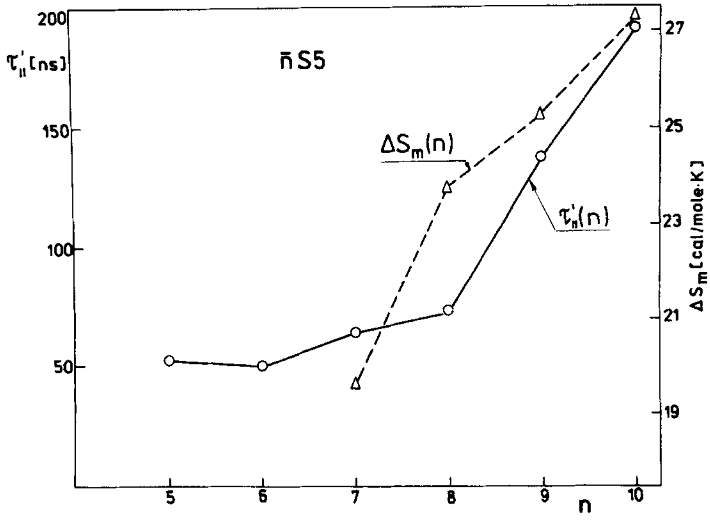

FIGURE 2. Odd-even effect for the relaxation time connected with the reorientation about the short molecular axis. The ΔS_m entropy values (Δ) have been taken from[11].

dynamics sensitivity to the alkoxy chain length. In Fig. 2 the dependence of the dielectric relaxation time ($\tau_{\parallel}$), connected with the reorientation about the short axis, on the alkoxy chain length is seen for the series of the thioesters. The length of the alkyl group was kept constant. As one can see for the first three members of this homologous series ($\overline{5}$S5, $\overline{6}$ S5 and $\overline{7}$S5) there is a weakly ascending odd-even effect. One should notice that if we had plotted the critical frequency ($\nu_c = 1/(2\pi\tau_{\parallel})$) we would, however, have obtained a weakly descending odd-even effect.

Fig. 3 presents the activation energies (ΔH) originating from the reorientation of molecules around their short axes (180°-jumps). In this case there also is a weak odd-even effect at the beginning and for higher members a strong increase of ΔH takes place. The same kind of behaviour we have found for the energy barriers connected with the reorientations about the long molecular axis.

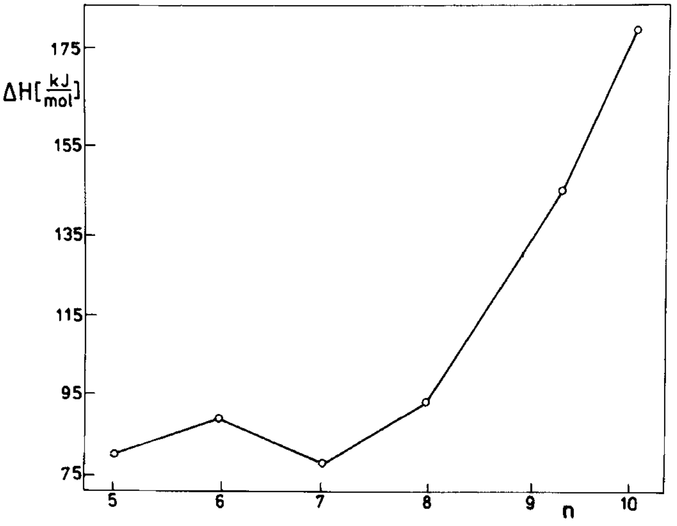

FIGURE 3. Activation energies for the rotation about the short axis as a function of carbon atoms in the alkoxy chain.

It would be interesting now to discuss how increasing of the number of chain segments influences the dynamic quantities. Marcelja[12] has for the first time considered the effect of ordering of molecular end chains on the thermodynamic parameters. Marcelja' s theory explains the following:
1. The odd-even effect of T_{NI} within a homologous series and its decrease with "n" for substances with higher transition temperatures;
2. The odd-even effect for transition entropies (ΔS_{NI}) and its strong increase with "n".
According to the theory the entropy values calculated were too high but they show an odd-even effect and, at the same time, they strongly increase with the chain length. The pronouced changes between the odd and even members of a series are caused by strong variations of the order parameter at transition temperatures what has also been shown by means of a chain model calculations[13].

The dynamic quantities show the odd-even effect similar to that observed experimentally and proved thoretically for transition entropies, however, the former exhibit much weaker amplitude of alternations. It means that the dielectric relaxation times and activation energies are not so strongly related to the order parameter. Yet the alternations seen for the first three substances suggest that the alkoxybenzoate part of the molecule is "rigid" in the sence of the Marcelja's theory. It would be interesting to study this effect for the alkylphenyl-moiety as to check how elongation of the alkyl group affects the physical quantities. The classical odd-even effect is in this case rather weak[11].

From the physical standpoint one should explain that lengthening of the alkoxy group changes the principal molecular axes frame, and at the same time, the angles between the molecular axes and the net dipole moment are also varied[1,4]. It is a reason for changing of the static quantities as well as the dynamic ones.

In conclusion we can say that either the molecule as a whole or its moiety bearing the dipole moment is rigid in the sense of Marcelja' s model and that the molecular dynamics parameters behave the same way as the transitions entropies.

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