

$$(T_{2.23})^{-1} = \left\{ \frac{3mK_1[\text{Cl}^-] + 2}{1 + K_1[\text{Cl}^-]} \right\} \frac{[\text{Cl}_2]_0}{[\text{Cl}^-]} \left(\frac{1}{T_{22}} \right) \quad (26)$$

The first term in brackets is not very sensitive to the temperature dependence of K_1 because the latter appears in both the numerator and denominator. It may be noted that if $m = 0.67$, close to our experimental value of 0.76, then $(T_{2.23})^{-1}$ becomes independent of K_1 . This is consistent with our observation that E_b values are within ± 1 kcal mol⁻¹ of E_d values from the blank solutions, as would be expected if both are controlled by the temperature dependence of the viscosity of the solution. Finally calculations with m ranging from 0.1 to 10 and K_1 changing by a factor of 10 either greater or less than its value at 25° indicate that the temperature dependence of K_1 cannot explain the bendover in $(T_{2P})^{-1}$ at low temperatures.

In conclusion, it appears that the observations of the present work raise more questions than are answered. The results are in qualitative disagreement with those of Hall, *et al.*,⁶ in that they indicate that there is no chemical exchange control of the line broadening at 25°. In addition, the chemical exchange controlled line broadening which is observed below about -35° does not appear to be consistent with the value of k_4 implied from recent electrochemical measurements. It is hoped that these problems will be resolved by further independent studies.

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Transition Entropies and Mesomorphic Behavior of Para-Disubstituted Azoxybenzenes

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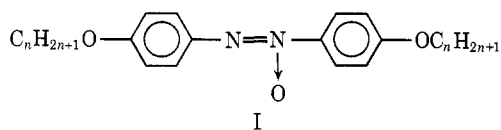
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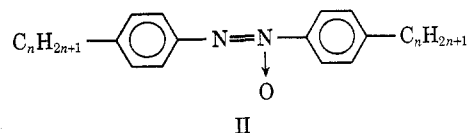
Calorimetric data are presented for the mesomorphic homologous series of the *p,p'*-di-*n*-alkylazoxybenzenes. Analysis of the change in the entropy ΔS_{NI} at the nematic-isotropic transition shows for the lower members of this and other series an alternation of ΔS_{NI} with the number of carbon atoms in the alkyl substituent similar to the alternation of the clearing temperature T_c . This variation is probably due to an alternation of the nematic order at the clearing temperature. For the higher members of the series ΔS_{NI} increases strongly due to a contribution to the entropy of short-range smectic order. Both first- and second-order smectic-nematic phase changes are observed.

1. Introduction

Calorimetric studies of homologous mesomorphic series are relatively scarce.¹⁻⁴ Fortunately, one of the most classical series of liquid crystals, the *p,p'*-di-*n*-alkoxyazoxybenzenes⁵ (I)



has been very carefully studied calorimetrically by Arnold.^{6,7} However, a comparison with other related series has not been made. The *p,p'*-di-*n*-alkylazoxybenzenes⁸ (II)



seem very suitable for such a comparison. In this paper we

TABLE I: Transition Temperatures $T(^{\circ}\text{C})$, Enthalpy Changes $\Delta H(\text{kJ mol}^{-1})$, and Entropy Changes $\Delta S(\text{J K}^{-1} \text{mol}^{-1})$ of Series II

n	Solid-solid			Melting point			Smectic-nematic			Nematic-isotropic		
	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS
3				65	20.0	59				60.5	0.57	1.70
4	13 ^a	2.1 ^a	7.4 ^a	22	12.4	42				32	0.27	0.89
5	-14	1.7	6.6	24	12.6	42				67.5	0.69	2.04
6				24	11.7	39	17	0.02	0.07	54.5	0.57	1.73
7				34	12.6	41	54.5	0.16	0.50	71	1.12	3.26
8				39	19.4	62	64.5	2.30	6.80	67	2.30	6.75
9				45	24.0	76				76.5 ^b	6.97 ^b	19.9 ^b
10	35	19.7	64	50	28.0	87				76 ^b	7.90 ^b	22.6 ^b

^a Sometimes this transformation does not occur; instead the solid melts into nematic at 19° ($\Delta H = 13.1$; $\Delta S = 45$). ^b Smectic-isotropic.

shall first present calorimetric data for the latter series. Then the entropy changes ΔS_{NI} at the nematic-isotropic transition of both series will be discussed on the basis of the molecular-statistic theory of the nematic phase.

2. Experimental Section

The synthesis of the *p,p'*-di-*n*-alkylazoxybenzenes has been described in ref 8 where the purity is also discussed. The compounds were recrystallized several times from methanol until the nematic-isotropic transition occurred within 0.2°. This transition was determined using a Reichert polarizing microscope and a Mettler FP52 heating stage at a heating rate of 0.2°/min.

The enthalpy changes were determined with a DTA apparatus built at the Component Parts Development Centre. Calibration in the relevant temperature range was performed using the tabulated heats of fusion and melting points of α -naphthylamine, *p*-bromophenol, pyrocatechol, and benzoic acid.⁹ The heating rate was 1.2°/min. For compound II ($n = 5$), the results were checked using a Perkin-Elmer DSC II and found to be consistent within about 5%.

3. Results

The calorimetric results for series II are given in Table I. Compound II ($n = 4$) exists in two crystalline forms that melt at slightly different temperatures. In general the transition temperatures differ somewhat from the values reported earlier.⁸ The values given here are more accurate. In Figures 1 and 2 the transition temperatures and ΔS_{NI} are plotted against $n + 1$ (series I) and n (series II), respectively. In this way the variations with increasing chain length are very similar.

The transition temperatures show the following well-known trends. (1) T_c alternates with n , while the amplitude of the alternation diminishes with increasing n . (2) The smectic-nematic transition temperature T_{SN} increases with n until T_c is reached.

It should be emphasized that the trend in T_c does not change where the nematic-isotropic is replaced by the smectic-isotropic transition. Apart from the alternation T_c decreases with n for series I and increases with n for series II.

The trends in ΔS_{NI} can be summarized as follows. (1) Up to $n = 6$ ΔS_{NI} alternates in a way similar to T_c . This alternation is rather strong (a factor of 2). (2) From $n = 7$ ΔS_{NI} increases strongly with n . However, ΔS_{NI} remains smaller than ΔS_{SI} (smectic-isotropic).

For $n = 6$ the smectic-nematic transition is practically second order, almost no heat of transition being detectable.

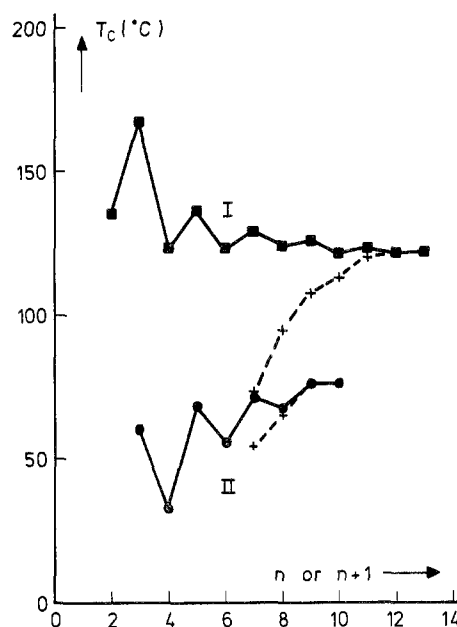


Figure 1. Clearing point and smectic-nematic transition temperature (+) for series I ($n + 1$) and II (n).

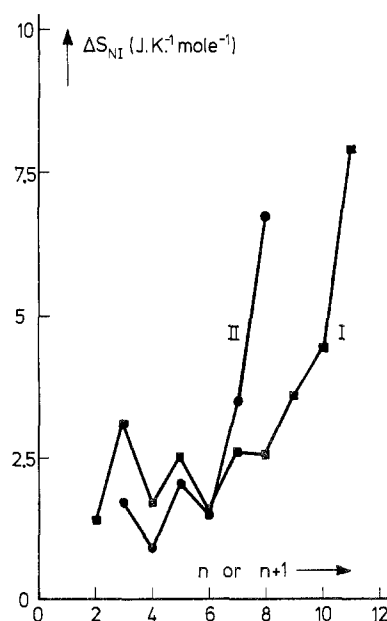


Figure 2. ΔS_{NI} as a function of the substituent chain length for I, di-*n*-alkoxyazoxybenzenes ($n + 1$), from ref 6, and II, di-*n*-alkylazoxybenzenes (n).

For $n = 7$ the heat of transition is still small and for $n = 8$ the transition is clearly first order.

4. Discussion

In the molecular-statistic theory of Maier and Saupe¹⁰ the difference in free energy between the nematic phase and the isotropic phase is considered, taking into account the attractive dispersion forces. In a mean field approximation this free energy difference per molecule is

$$\Delta F = - (A\eta^2/V^2) - T\Delta S(\eta) \quad (1)$$

where $\eta = (1 - (3/2)\overline{\sin^2 \theta})$ is the order parameter, A is a factor approximately proportional to the anisotropies in the molecular polarizabilities, V is the molar volume, and $\Delta S(\eta)$ is the difference in orientational entropy. The theory predicts a first-order nematic-isotropic transition at

$$T_c = A/4.54kV^2 \quad (2)$$

together with a constant value $\eta_c = 0.43$ at T_c .

The relative variations of T_c for different homologous series can be correlated qualitatively with variations in A due to different anisotropic polarizabilities.¹¹ Moreover within a homologous series the anisotropy in the polarizability is different for an even and an odd number of chain atoms. Using eq 2 this explains the alternation in T_c .¹¹ However, to account for the general decrease of T_c with n , for example, in series I, it is necessary to extend eq 1 by a factor representing "excluded volume" effects that favor molecular alignment.¹²

There is ample evidence of considerable short-range nematic order in the isotropic phase, even at several degrees above T_c .¹³ Therefore it seems plausible that ΔS_{NI} depends mainly on the long-range order as given by η . Because of the constancy of η_c in the theory of Maier and Saupe this leads to a constant value of ΔS_{NI} at T_c . The constancy of η_c is due to the mean field approximation and is independent of the specific form of the interaction potential.¹⁴ Nevertheless, variations in ΔS_{NI} are possible if not one molecule but a cybotactic group of molecules is taken as the statistical entity in the theory.¹⁰ However, this would lead to an alternation of the size of these cybotactic groups with increasing n in a homologous series,⁷ which does not seem very probable. We conclude that within this framework the alternation of ΔS_{NI} cannot be understood.

Experimentally the order parameter is usually measured at constant pressure. This does not affect a comparison with a free energy expression because η_c was found to be independent of the pressure.¹⁴ Unfortunately not many measurements of η_c values of a homologous series are available. Weber¹⁵ found that η_c was almost constant within series I, but his results are not very accurate. Later measurements for $n = 1$ and $n = 2$ indicate (extrapolated) values for η_c of 0.3 and 0.4, respectively.¹⁶ If this is repre-

sentative of the general trend it would be consistent with the alternation in ΔS_{NI} up to $n = 6$. In a similar way the smaller values of ΔS_{NI} for the lower members of series II could be due to an overall lower order parameter in this series. Consistent and accurate order parameter measurements on the homologous series are necessary to settle the question of the dependence of ΔS_{NI} on η_c more definitely.

Looking at the higher members of the series we notice that in both series the strong increase in ΔS_{NI} above $n = 6$ coincides with the occurrence of a smectic phase at lower temperatures. In a first approximation it seems that the closer T_{SN} is to T_c , the higher ΔS_{NI} . As already suggested by Arnold⁷ this could well be an additional contribution to ΔS_{NI} of short-range smectic order within the nematic phase. The existence of such cybotactic groups has been established by X-ray diffraction.¹⁷ Recently several other physical phenomena have been reported to indicate that pretransitional smectic ordering is not restricted to a narrow temperature range above T_{SN} , but indeed can exist right up to the clearing temperature. Of course this contribution can be expected to become more pronounced when T_{SN} is closer to T_c .

The occurrence of the first- and second-order smectic-nematic phase transitions in series II is very interesting. A further discussion will be given elsewhere.¹⁸

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