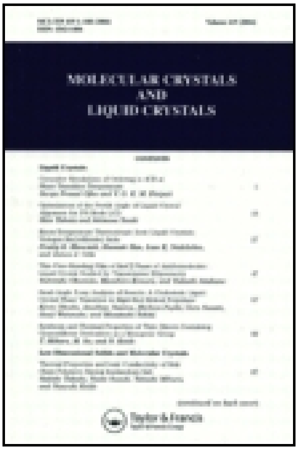

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Determination to 2 kbar of the Nematic-Isotropic and Melting Transitions in p-Azoxyanisole

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Determination to 2 kbar of the Nematic-Isotropic and Melting Transitions in p-Azoxyanisole

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Differential thermal analysis to 2 kbar of zone-refined *p*-azoxyanisole in hydrostatic apparatus has corroborated the results of Hulett and of Robberecht at lower pressures–initial slopes $\lesssim 48$ deg kbar^{-1} for the nematic-isotropic transition and $\lesssim 31$-32 deg kbar^{-1} for the melting curve–and also established that the curvatures, $-d^2 T_{\mathrm{trans}}/dp^2$, are ~ 5 deg kbar^{-2} for the liquid transition and >O for the melting curve. At transition temperatures above ~ 2 kbar, irreversible effects are encountered. A self-consistent discussion, using 1 bar data, is given for the thermodynamics of the nematic-isotropic transition in *p*-azoxyanisole and the implications of this discussion have been pursued for *p*-azoxyphenetole and other di-*n*-azoxy-benzenes.

INTRODUCTION

P-azoxyanisole (PAA) is the most extensively studied of liquid crystals and hence should seemingly be the one for which an accurate and self-consistent thermodynamic description might be made. Alben has demonstrated the difficulties of various microscopic models[1] in accounting for the macroscopic data and

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also has shown how a "theory independent" approach[2] can yield useful results. However, there might be some question as to how much of published data on PAA are "reliable" as a consequence of the demonstration,[3-4] by small angle X-ray scattering, of significant effects of impurities near the nematic-isotropic transition.

This work presents new experimental results, using the purest material[5] apparently available, for the effects of pressure on the temperature of the nematic-isotropic transition and on the melting temperature. Previous data for these phase boundaries from Hulett[6] in 1897 were essentially corroborated and extended by Robberecht[7] in 1938. Puschin and Grebenschtschikow[8] reported data in some disagreement in 1926 and very recently Deloche *et al.*[9] published results in severe disagreement with the earlier work and also claimed that PAA decomposed above ~ 3 kbar.

The present experiments to 2 kbar strongly corroborate the results of Hulett[6] and of Robberecht[7] for the trajectory of the nematic-isotropic transition and also tend to favor their results for the melting curve, as compared to the other data.[8-9] No trustworthy data above 2 kbar were obtained because of irreversible effects–"decomposition"–encountered. Self-consistent and accurate descriptions of the variations in volume and in entropy near the nematic-isotropic transition are proposed and better agreement than hitherto is achieved between prediction and experiment for the slope of the phase boundary. The suitability of similar descriptions for data near the mesophase transitions in the other di-*n*-azoxy-benzenes is explored in the appendices.

EXPERIMENTS AND RESULTS

The PAA used in the experiments was zone-refined and from the same supplier as the material used by Gravatt and Brady in experiments[4] which demonstrated the great effect of impurities in PAA from other sources. For the high pressure differential thermal analysis (dta) runs, 3-10 mg of the sample material was packed into a platinum tube which was then sealed in an oxyacetylene flame. For the first run, the PAA was freshly powered and loaded into the tube in air whereas, for the second and third runs, the PAA was freshly powdered under argon and loaded in a glove box, with P_2O_5 present, and the tube then crimped shut before being brought out into air for the welding. The arrangement of sample and chromel-alumel thermocouples and the high pressure apparatus, using argon as the pressure medium, is described elsewhere.[10]

Pressures were read to ±5 bar from a Heise Bourdon tube pressure gage. Under approximately isobaric conditions, temperature was varied at rates from 0.1 to 1 deg $\sec^{-1}$ and both sample temperature and differential temperature were recorded with a 2-pen strip chart recorder. The maximum differential temperature before traversing the nematic-isotropic transition was always less than 1°. Upon approaching the nematic-isotropic transition on both heating and cooling, abrupt shifts in the differential pen were observed and taken as indicative of the transition, with the temperature so obtained on heating and cooling always agreeing to within 2°.

In the first, exploratory, run data were taken at sizeable increments of pressure and upon increasing pressure to about 3 kbar, the signals disappeared and did not reappear upon decrease of pressure. In the second run, data were taken at smaller increments of pressure. The pressure was occasionally decreased and a corroborative point taken until, above ~ 2 kbar, corroboration could not be achieved in this way, the signals falling lower in temperature and thus indicating some irreversible effects, presumably decomposition. Tactics for the third run were similar to those for the second and again corroboration of previous points became impossible after the excursion to above ~ 2 kbar.

Temperatures for the solid-liquid transition could not be determined as precisely as for the mesophase transition because the onset of melting was not as sharp as the signal for the mesophase transition, possibly because of the much larger thermal effect which often resulted in a differential temperature of ~ 3°. After traverses above 2 kbar, the melting signals also fell lower in temperature as compared with the data obtained before the onset of "decomposition".

Data for the nematic-isotropic transition and for melting are shown in Figure 1. The data from other workers[6-9] are not shown in order to avoid confu-

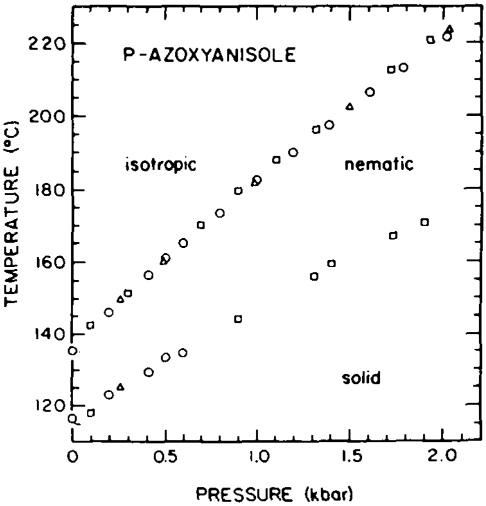

FIGURE 1 Temperatures of solid-nematic and nematic-isotropic transitions in *p*-azoxyanisole as a function of pressure. Triangles represent data from the first run, circles the second, and squares the third.

sion. Agreement among the data from several runs is within 3°. The initial slopes from the present data are $\lesssim 48$ deg kbar^{-1} for the nematic-isotropic transition and $\lesssim 31$ deg kbar^{-1} for melting. For the nematic-isotropic transition the initial curvature $-d^2T_{ni}/dp^2$ is ~ 5 deg kbar^{-2} and it also appears that $d^2T_{mp}/dp^2 < 0$ for the melting curve (Figure 1). At 1 bar, direct measurement of the temperature of the nematic-isotropic transition, $T_{ni} \approx 135° - 136°C$, and the melting temperature $T_{mp} \approx 116° - 117°C$.

DISCUSSION

The present data for the nematic-isotropic phase boundary strongly corroborate the results of Hulett[6] and of Robberecht.[7] The present data for the melting curve also tend to favor the results of Hulett[6] and Robberecht[7] over those of other investigators.[8-9] A possible explanation for the discrepancy between the Puschin-Grebenschtschikow data[8] and the preferred data is that the former erred in their pressure calibration, since the ratio of slopes of the phase boundaries is about the same for all of these data. No explanation can be offered for the disagreement of the results of Deloche *et al.*[9]

Two other recent investigators also lend some support to the present data. McColl[11] suggests a slope of 46.3 deg kbar^{-1} from NMR measurements to 2 kbar on material of unspecified source or purity. The uncertainty in slope may be $\sim 5\%$, as estimated from the data plotted in his Figure 1. Johnson and Miller[12] report that 900 psi increased the nematic-isotropic transition temperature 2.5° above that obtained at ambient pressure, yielding an initial dT/dp of ~ 41 deg kbar^{-1}.

At 1 bar, Gravatt and Brady[4] report $T_{ni} = 136°C$ which is comparable with the present results and with the value of 135.9°C reported by Hulett[6] and by Robberecht.[7] At 1 bar, Hulett[6] reported 118.3o°C and Robberecht 117.8°C. Assuming that the present material[5] is purer than the PAA used by these earlier workers, it is difficult to detect any significant differences due to impurities on the trajectories of the phase boundaries.

The "decomposition" encountered above ~ 2 kbar and above $\sim 220°C$ is not understood. In contrast to the speculation[9] of Deloche *et al.* it does not appear to be due to reaction with "unevacuated air". Whether there is a significant time dependence involved in the degradation is unknown. Deloche *et al.*[9] do not state how long their material was kept at the higher temperatures and pressures. In these experiments, temperatures did not exceed those of the nematic-isotropic transition by more than 10-15° at each pressure and $\sim$ 5-10 min were usually necessary for the cycles in temperature at each pressure. No attempt was made to analyze the material after "decomposition".

For the solid-liquid transition, the Clausius-Clapeyron equation

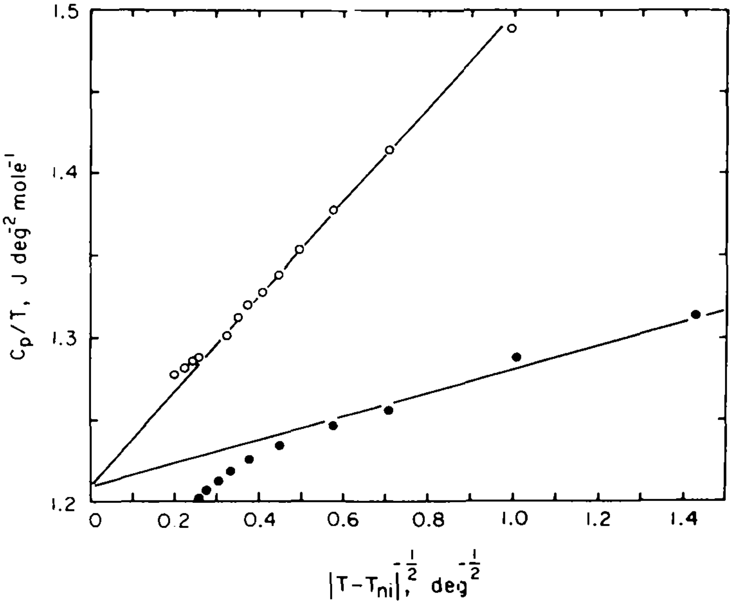

FIGURE 2 Plot of Arnold's c_p/T data for *p*-azoxyanisole vs. $|T - T_{ni}|^{-1/2}$. Open circles denote data for $T < T_{ni}$, filled circles for $T > T_{ni}$. The slopes differ by a factor of ~4.

$dT_{mp}/dp = \Delta V/\Delta S$ relates thermodynamic data at 1 bar with the initial melting slope. Agreement of data[13-15] for the discontinuities with the preferred high pressure data is within 10%, which is usually considered good agreement.

For the nematic-isotropic transition, most thermodynamic estimates thus far have been for discontinuities in volume and in entropy or enthalpy. Such data may then be interrelated and compared with dT_{ni}/dp by the Clausius-Clapeyron equation. Measurements at the transition are hampered by the rapid and sizeable variations in the thermodynamic properties near T_{ni}. Current estimates[13-16] for ΔV and ΔS can be combined to yield a range of values for dT_{ni}/dp which bracket the preferred value.

Among those theories which attempt to interrelate the rapidly varying thermophysical properties near the transition, that of Torgalkar *et al.*[17] yields an erroneous value for the slope. Alben's analysis[2] involves arbitrarily subtracting out backgrounds for the cusp-like variations of C_p/TV, $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and $-\left(\frac{\partial V}{\partial p}\right)_T$ with temperature and results in equations[4] much like Ehrenfest's equations which relate discontinuities in specific heat, thermal expansion and isothermal compressibility at a second order transition. Alben's results for the slope scatter considerably about the preferred value and part of the problem may be the lack

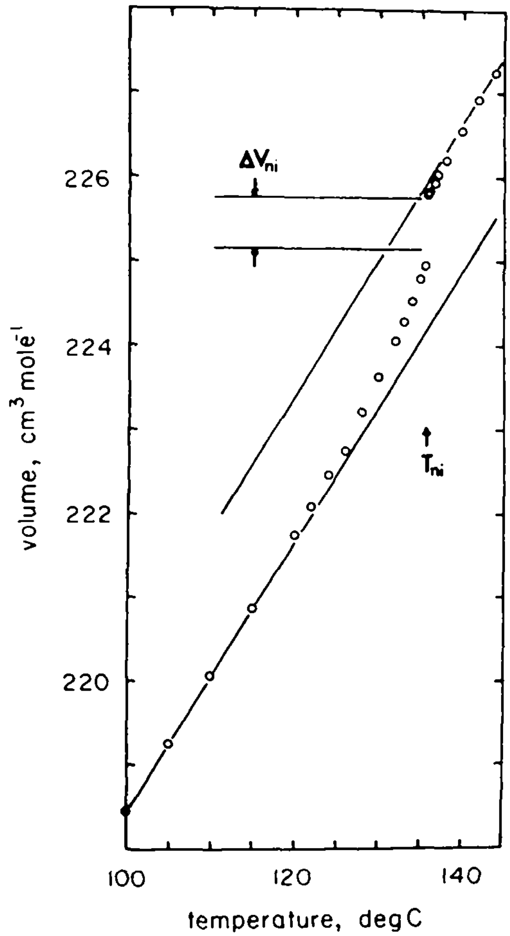

FIGURE 3 Plot vs. temperature of molar volumes derived from density data quoted by Maier and Saupe. The regions of similar thermal expansion are shown.

of good interpolation functions for the rapidly varying quantities near the transition temperature. In the following section there are presented simple and accurate representations for some of the generally preferred data near the transition which self-consistently interrelate the rapid variations and discontinuities in the data with the preferred slope.

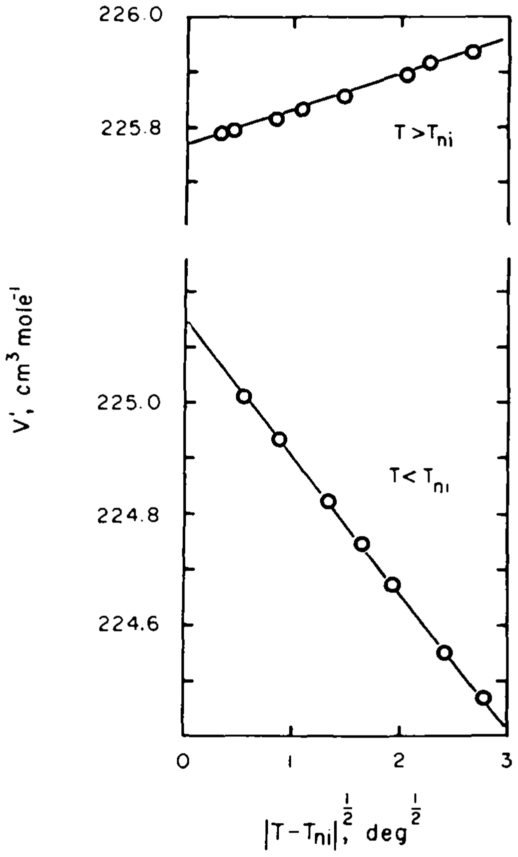

FIGURE 4 Plot of $V' \equiv V - B(T - T_{ni})$ vs. $|T - T_{ni}|^{-1/2}$ as a test of Eq. (2). The slopes of the drawn lines are $-C_n$ for $T < T_{ni}$ and $+ C_i$ for $T > T_{ni}$, where $C_n/C_i \sim 4$. The difference between the intercepts at $T - T_{ni}$ is the discontinuous volume change ΔV_{ni}

REPRESENTATIONS FOR THE THERMODYNAMIC DATA

As chosen by Alben,[2] for example, the preferred thermodynamic data are here also taken to be the specific heat and latent heat data[14] of Arnold and the density measurements[16] quoted by Maier and Saupe. These appear to be the most careful and extensive measurements relating to the entropy and volume, have been approximately corroborated by others[15 18 19] and are conveniently tabulated together with the T_{ni} for the respective samples and laboratory temperature scales. As done by Alben,[2] for example, the data are here intercompared at temperatures relative to the nematic-isotropic transition temperature for the particular measurements, i.e., as a function of $(T-T_{ni})$.

In contrast to other efforts [2, 17] though, analytical representations are sought for the specific heat [14] and volume [16] data in order to avoid errors in estimating quantities by interpolation. The impetus for the present approach is the recent macroscopic description [20] for the transition in sodium nitrate, for which there are also many excellent data and only an unclear microscopic understanding. The physical assumption here is that the nematic-isotropic transition in PAA may be considered as a first-order transition at T_{ni} superimposed on a lambda transition at the same temperature. The slope, dT_{ni}/dp, obtained via the Clausius-Clapeyron equation for the discontinuities at T_{ni} must be consistent with both the preferred experimental value and the slope obtained from the Pippard equations, [21] which interrelate the rapidly varying quantities near a lambda transition. The superposition of a first-order transition on a lambda transition does not seem to invalidate the thermodynamical treatment of the latter, as shown by the treatment [22] of the high-low quartz inversion, for example.

Arnold's superior specific heat data[14] may be represented by

$$C_p/T = (C_p/T)_0 + A\,|T - T_{ni}|^{-1/2} \qquad (1)$$

where $(C_p/T)_0$ and A are constants, the latter differing below and above T_{ni}.

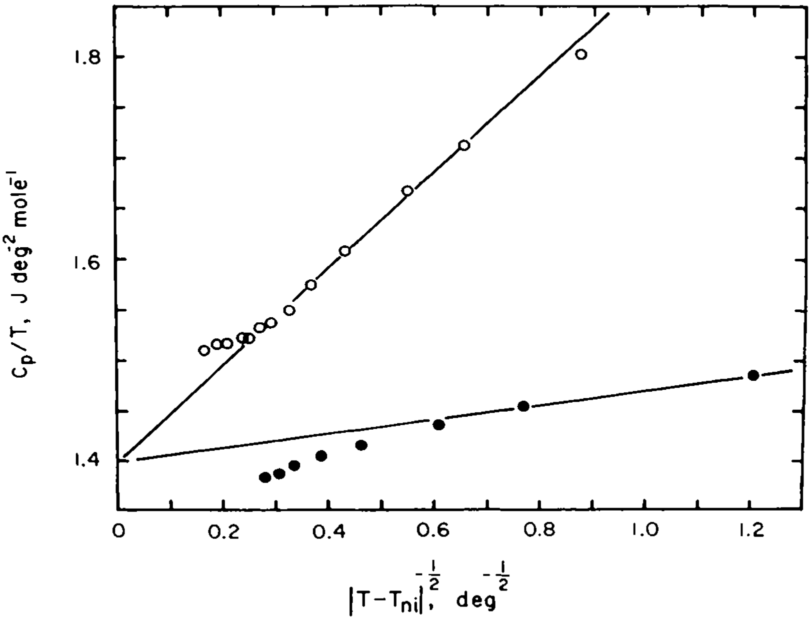

FIGURE 5 Plot of Arnold's c_p/T data for p-azoxyphenetole vs. $|T - T_{ni}|^{-1/2}$. Open circles denote data for $T < T_{ni}$, filled circles for $T > T_{ni}$. The slopes differ by a factor of ~ 6.7.

For $T_{ni} = 135.01°\mathrm{C}$,[14] Eq. (1) appears valid (Figure 2) down to $T \approx T_{ni}{}^{-16^\circ}$, up to $T \sim T_{ni} + 3°$ and within less than a degree of T_{ni}. The intercept $(C_p/T)_0$ is ≈ 1.21 J deg^{-1} mole^{-1}; $A \approx 0.29$ J deg$^{-3/2}$ mole^{-1} for $T < T_{ni}$ and $\sim 1/4$ as great for $T > T_{ni}$ (Figure 2).

Plotting the molar volumes obtained from the Maier-Saupe density measurements[16] (mol.wt. = 258.3) vs. temperature shows that the thermal expansions are about the same far enough below and above T_{ni}. Within the "transition region", the Maier-Saupe data[16] may be represented by

$$V = V_n + B\,(T - T_{ni}) - C_n\,(T_{ni} - T)^{1/2} \quad \text{for} \quad T < T_{ni} \tag{2a}$$

and

$$V = V_i + B\,(T - T_{ni}) + C_i\,(T - T_{ni})^{1/2} \quad \text{for} \quad T > T_{ni}, \tag{2b}$$

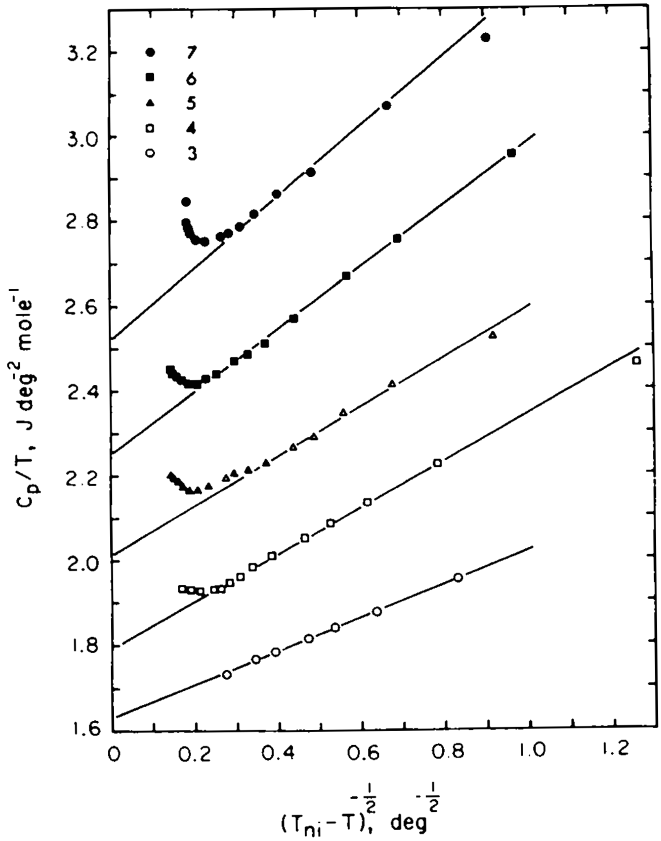

FIGURE 6 Plots of c_p/T vs. $(T_{ni} - T)^{-1/2}$ for n = 3, 4, 5, 6 and 7, for $T < T_{ni}$.

where B, C_n and C_i are constants, as are V_n and V_i, which are related to the discountinuous volume change ΔV_{ni} as $\Delta V_{ni} = V_i - V_n$. Also as shown in Figure 2, $B \approx 0.16_1$ cm^3 deg^{-1} mole^{-1}. Figure 4 shows the plots of $V' \equiv V\text{-}B\,(T\text{-}T_{ni})$ vs. $|T\text{-}T_{ni}|^{1/2}$ (Eq. (2)) for $T_{ni} = 135.8$°C.[16] By modest extrapolation to $T = T_{ni}$ (Figure 4), ΔV_{ni} is estimated as 0.62 cm^3 mole^{-1}; $C_n \approx 0.24_6$ cm^3 deg$^{-1/2}$ mole^{-1} and $C_n/C_i \sim 4$; Eq. (2) appears valid over the same temperature range as Eq. (1).

To relate these results consistently to the experimental $\mathrm{d}T_{ni}/\mathrm{d}p$, one must consider: the Clausius-Clapeyron relation for the first-order component of the transition–with $\Delta S_{ni} \approx 1.40_6$ J deg^{-1} mole^{-1},[14] $\Delta V_{ni}/\Delta S_{ni} \approx 44$ deg kbar^{-1}; the Pippard equation,[21]

$$(C_p/TV)(\mathrm{d}\,T_{ni}/\mathrm{d}\,p) - \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \approx \text{constant, as } T \to T_{ni}, \qquad (3)$$

for the λ-like component of the transition–via which a comparison of the constants A, C_n and C_i (Eqs. (1) and (2)) yields $\mathrm{d}T_{ni}/\mathrm{d}p \approx 43$ deg kbar^{-1}. Thus reasonably self-consistent agreement is achieved.

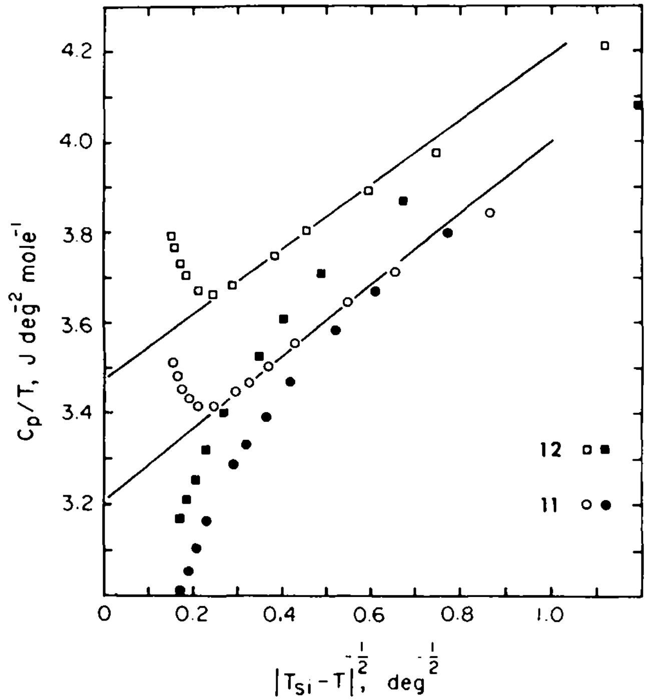

FIGURE 7 Plots of c_p/T vs. $|T_{ni} - T|^{-1/2}$ for n = 11 (circles) and 12 (squares). Open symbols denote data for $T < T_{si}$, filled symbols data for $T > T_{si}$.

Another Pippard equation[21] involves the isothermal compressibilities, for which direct measurements are lacking. Isothermal compressibilities calculated from adiabatic compressibilities obtained from sound velocity data[23, 24] do not result in conclusions as to the slope in contradiction to the above although the accumulated uncertainties are such that these data cannot be used here.

Only rarely (e.g., the sound velocity data[25] of Gabrielli and Verdini) is it obvious that impurities have drastically altered the thermophysical properties of PAA in the transition region. It is hoped that current speculation concerning the gross effects of impurities on thermophysical properties near the nematic-isotropic transition will result in accurate and extensive remeasurement of those properties in purer PAA.

To demonstrate that the representations offered above are useful for substances other than PAA, Appendix 1 examines the extensive data for *p*-azoxyphenetole and Appendix 2 examines Arnold's specific heat data[14] about the mesophase transitions in other di-*n*-azoxybenzenes.

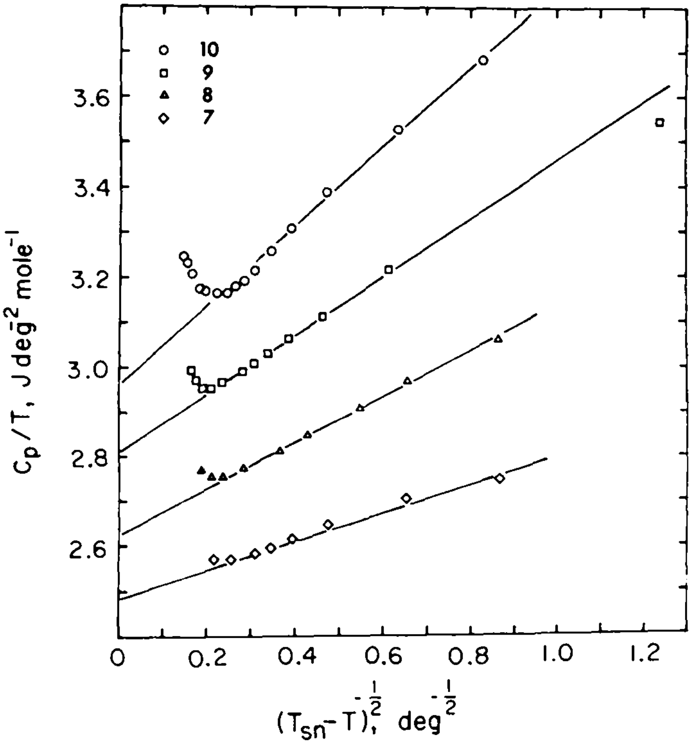

FIGURE 8 Plots of c_p/T vs. $(T_{sn} - T)^{-1/2}$ for n = 7, 8, 9, and 10, for $T < T_{sn}$.

Acknowledgements

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Appendix

p-Azoxyphenetole

Figure 5 shows the plot of Arnold's c_p/T data [14] for *p*-azoxyphenetole according to Eq. (1). For T_{ni} = 167.31°C,[14] $(c_p/T)_0 \approx 1.40$ J deg^{-2} mole^{-1} and $A \approx 0.48$ J

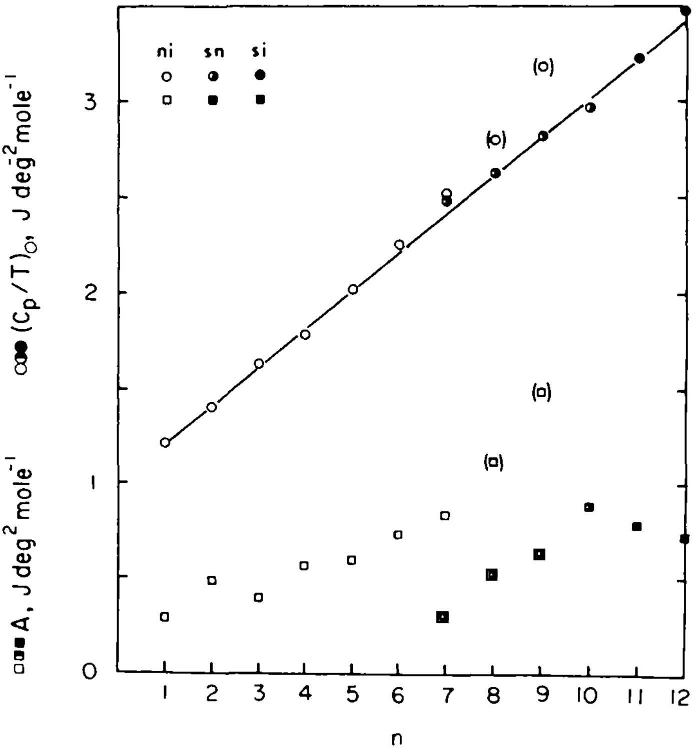

FIGURE 9 Intercepts $(c_p/T)_n$ (circles) and slopes A (squares), according to Eq. (1), plotted vs. *n*, the number of carbon atoms in the alkyl chains. Open symbols pertain to data for nematic-isotropic transitions (Figure 6), half-filled symbols to data for smectic-nematic transitions (Figure 8) and filled symbols to data for smectic-isotropic transitions (Figure 7). Open symbols enclosed in parentheses derive from fits of Figure 10, which are also discussed in text.

deg $^{-3/2}$ mole^{-1} for $T < T_{ni}$; A is ~$6._7$ times as great below T_{ni} as above. Equation (1) appears valid down to $(T_{ni}\text{-}T)^{-1/2}$ ~ 0.25 or $T \approx T_{ni}$-16°. Bauer and Bernamont[26] have made precise relative volume measurements from 145° to 180°C, where T_{ni} = 167.7°C. For volume measured in "divisions" of their apparatus,[26] analyses as above suggest $\Delta V_{iCC} \approx 1.19$ div. and $(\partial V/\partial T)_p \approx$ constant + 0.085 $(T_{ni} - T)^{-1/2}$ div. For ΔS_{ni} = 3.10 J deg^{-1} mole^{-1} [14] and A from above, the slope dT_{ni}/dp is self-consistently estimated as ~0.18 div. deg mole J^{-1}. If Schenck's density data[27] are converted to molar volumes (mol. wt. = 286.3) and analyzed according to Eq. (2), there results $B \approx 0.24_0$ cm^3 deg^{-1} mole^{-1}. Comparison of this slope for $T > T_{ni}$ with the Bauer-Bernamont data[26] then suggests that 1 div. $\approx 2.6_1$ cm^3 mole^{-1}. Hence dT_{ni}/d$p \approx 47$ deg kbar^{-1}, which compares very well with Hulett's value[6] of ≈ 46 deg kbar^{-1}.

Appendix

Some Other 4,4′ - Di-n-Alkoxy-Azoxybenzenes

Arnold's careful calorimetric measurements[14] on the 4,4′-di-*n*-alkoxy-azoxybenzenes (for n = 3-12 carbon atoms in the alkyl chains) may be analyzed similarly to the above for n = 1 and 2. In addition to the nematic and isotropic phases, smectic phases also occur in these compounds, with increasing n; the transition temperatures T_{ni}, T_{sn} and T_{si} in the following representations are always taken to be the values given by Arnold.[14]

Figure 6 shows the plots of the c_p/T data[14] according to Eq. (1) for the *n-i* transitions of n = 3, 4, 5, 6 and 7; Eq. (1) appears valid down to $(T_{ni}\text{-}T)^{-1/2}$ ~ 0.25 or over about the same temperature range as for n = 1 and 2. To avoid cluttering Figure 6 unduly, the data for $T > T_{ni}$ are not shown but the approximate symmetries appear to be: n(ratio of A from Eq. (1) below T_{ni} to that above) - 3(~$4._4$); 4(~$3._8$); 5(~$3._2$); 6(~$3._7$); 7(~4). For n = 11 and 12, the smectic phase transforms directly to the isotropic liquid and Figure 7 shows that Eq. (1) also accurately represents the data and appears valid down to $(T_{si} - T)^{-1/2}$ ~ 0.25; A appears to be the same below and above T_{si} (for n = 11, especially). Figure 8 shows that Eq. (1) is also valid down to $(T_{sn} - T)^{-1/2}$ ~ 0.25 for the data for the *s-n* transitions of n = 7, 8, 9 and 10.

The results for the intercepts $(c_p/T)_0$ and the slopes A (below the transition temperatures) of Eq. (1) are plotted vs. n, for the various transitions, in Figure 9. To a very good approximation, $(c_p/T)_0$ varies linearly with n as $(c_p/T)_0 \approx 1.0_0 + 0.20\,n$ J deg^{-2} mole^{-1}. No such simple relation seems to be apparent for the slopes A vs. n (Figure 9).

There is increasing difficulty, however, in representing the specific heat da-

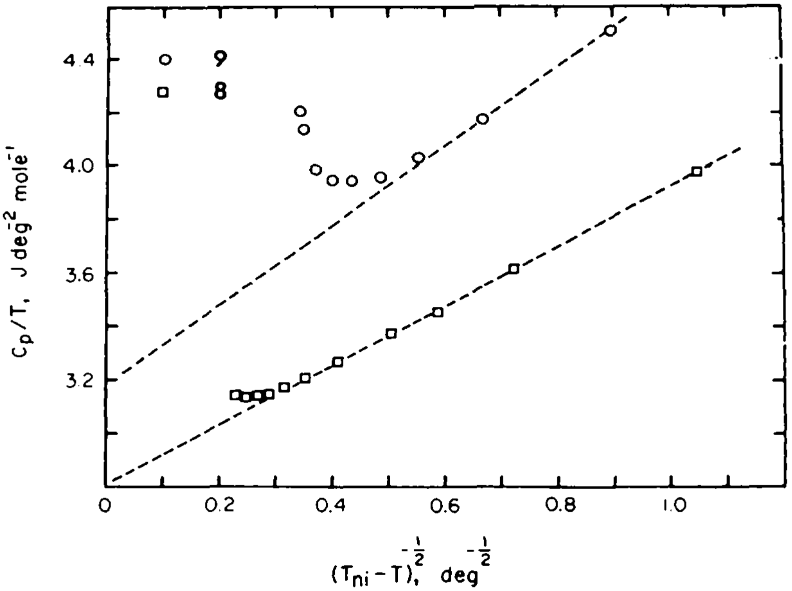

FIGURE 10 Plots of c_p/T vs. $(T_{ni} - T)^{-1/2}$ for n = 8 and 9, for $T < T_{ni}$. The *apparent* fits of Eq. (1) represented by the drawn lines are discussed in the text.

ta[14] for those nematic phases which exist over increasingly limited temperature ranges, i.e., for $n = 7$, 8, 9 or 10, $T_{ni} - T_{sn}$ is,[14] respectively, 28.89°, 18.57°, 8.59° or 2.89°. Figures 6 and 8 show that, for $n = 7$, Eq. (1) is an adequate representation for both the $n - i$ and $s - n$ transitions, with about the same $(c_p/T)_0$. Figure 10 shows the plots of Eq. (1) for $n = 8$ and 9 for $T < T_{ni}$, which seemingly give approximate fits; the temperature ranges are much less than the usual $(T_{ni} - T)^{-1/2} \sim 0.25$, however, and the intercepts do not follow the established pattern (Figure 9). It seems clear that the lambda-like contributions to c_p/T from the $s-n$ and $n-i$ transitions are "overlapping" for these nematic phases. If one attempts to subtract the contributions of the $s-n$ transition to c_p/T in the nematic field (Figure 10) so that $(c_p/T)_0$ and the temperature range for the validity of Eq. (1) conform with the above hypothesis, the slopes A for the n–i transitions in n=8 and 9 would be even higher than the values deduced from Figure 10 (and shown in parentheses in Figure 9). Thus, extrapolations of A vs. n, to higher n, for the n-i transition are uncertain (Figure 9) and the lack of understanding of the slopes and symmetries for the transitions, and their variation with n, thwart the attempts to represent c_p/T analytically in these narrow nematic fields.

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