

melting points of usual compounds are on the order of a few °C/kbar only. The slopes of these transition lines differ slightly<sup>(6)</sup> from those found by other authors,<sup>(7-9)</sup> especially for the nematic-isotropic transition; all these slopes are summarized in Table 1. The temperature range, and consequently also the pressure range, are severely limited by thermal degradation of the sample; in fact, above 3 kbar, we observed a strong decrease of the transition temperature values: the azoxy groups probably react with the unevacuated air, and some molecules break; the nematic state then disappears. For that reason, the experimental points above 3 kbar do not represent states of thermodynamic equilibrium, and do not have any physical meaning.

The latent heats at both transitions, and the corresponding changes in specific volume are respectively in the same ratio, which is about 30: this explains why the two slopes are so similar. The weakness of the volume change and of the increase in entropy at the nematic-isotropic transition suggests that a substantial short range order is preserved in the isotropic phase: this is commonly mentioned as characterizing the weak first order character of this transition. There is some dispersion in the latent heat data found in the literature<sup>(12-16,29)</sup>; we assume that volumetric data<sup>(11,18)</sup> are more reliable, and apply the Clausius-Clapeyron equation:

$$\Delta H = T \left( \frac{dP}{dT} \right) \Delta V$$

to estimate the latent heats from our  $dP/dT$  data. The resulting values of  $\Delta H$  are listed in Table 2; they are in almost reasonable agreement with the most recent measurements of  $\Delta H$ .

#### 4. Order Parameter

The NMR CW spectrum of PAA in the nematic phase is characterized by a doublet which is produced by unaveraged dipolar interactions of the benzene ring protons. The separation between the peaks of that doublet is proportional to the order parameter

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle, \quad (17)$$

$\theta$  being the angle between the long axis of the molecule and the

optical axis of the nematic. This allows a direct determination of the order parameter in the nematic phase at various temperatures and pressures.

For most thermotropic nematics, the order parameter  $S_c$ , at the nematic-isotropic transition, is about 0.42, although their transition temperatures show substantial variations.<sup>(18)</sup> On the other hand,  $S_c$  appears to be smaller than 0.4 in the *p*-methoxybenzylidene-*p,n*-butylaniline (MBBA),<sup>(19)</sup> anisaldazine<sup>(20)</sup> and in some Schiff bases,<sup>(21)</sup> but significantly higher in the 4,4'-azoxydiphenetole (PAP), the 4-(*n*-hexyloxy) benzoic acid (PHBA),<sup>(22)</sup> and a few more exotic nematic mixtures.<sup>(23)</sup> Of course, in some of these systems, the molecules may well be more or less flexible than the usual azoxy-molecules, and the respective importance of attractive potentials and excluded volume effects is probably not at all the same as in PAA.

It is tempting to speculate that attractive anisotropic potentials and hard core effects will perhaps not have the same dependence on intermolecular distances: going to higher pressures would enhance one of these effects with respect to the other, and might result in a change in the value of  $S$  close to the transition. We have been looking for such an effect, changing the absolute temperature of the transition by 17% and the specific volume by 15% (the isothermal compressibility is  $\beta = 5 \times 10^{-11}$  cm<sup>2</sup>/dyne<sup>(24)</sup>). In fact, we find that the order parameter  $S_c$  at the nematic-isotropic transition is *constant* within experimental errors from 0 to 3 kbar (Fig. 2):

$$S_c = 0.40 \pm 0.015.$$

The same is true for the solid-nematic transition:

$$S_M = 0.55 \pm 0.015.$$

Maier-Saupe's theory of the nematic to isotropic phase transition<sup>(18)</sup> does indeed predict that the value of  $S$  should not change along the transition line. In this respect our result agrees with Maier-Saupe's theory, but it is not yet clear that it is a proof of it. We shall now try to find what is the minimum set of assumptions which can lead to our result.

The equilibrium value of  $S$ , at given  $P$  and  $T$ , is the one which minimizes the free enthalpy (or Gibbs energy) of the nematic phase. We write it for one molecule (chemical potential), try to show up the