Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Birefringence of N-(p-propoxybenzylidene) - p - pentylaniline and N - (p - butoxybenzylidene) - p - pentylaniline

D. Revannasiddaiah [a] & D. Krishnamurti [a]
[a] Department of Physics, University of Mysore, Mysore, 570 006, India

To cite this article: D. Revannasiddaiah & D. Krishnamurti (1979): Birefringence of N-(p-propoxybenzylidene) - p - pentylaniline and N - (p - butoxybenzylidene) - p - pentylaniline, Molecular Crystals and Liquid Crystals, 53:1-2, 63-68

To link to this article: http://dx.doi.org/10.1080/00268947908083984

Mol. Cryst. Liq. Cryst., 1979, Vol. 53, pp. 63–68
© Gordon and Breach Science Publishers, Ltd., 1979
Printed in Holland

Birefringence of *N*-(*p*-propoxybenzylidene)-*p*-pentylaniline and *N*-(*p*-butoxybenzylidene)-*p*-pentylaniline

D. REVANNASIDDAIAH and D. KRISHNAMURTI
Department of Physics, University of Mysore, Mysore 570 006, India

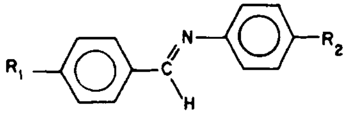
(*Received October 4, 1978; in final form January 8, 1979*)

The paper reports the refractive index and density data of *N*-(*p*-propoxybenzylidene)*p*-pentylaniline and *N*-(*p*-butoxybenzylidene)*p*-pentylaniline in the nematic and liquid phases. The orientational order parameters for these two compounds are discussed.

INTRODUCTION

The compounds *N*-(*p*-propoxybenzylidene)*p*-pentylaniline) (PBPA) and *N*-(*p*-butoxybenzylidene)*p*-pentylaniline (BBPA) exhibit the nematic phase near room temperature and hence the study of their birefringence is comparatively easy. Their molecular structure (shown in Figure 1) may be seen to be similar to that of (*p*-methoxybenzylidene)*p*-*n*-butylaniline (MBBA). The present paper reports the results of experimental measurements of the densities and the refractive indices of the above two compounds at different temperatures. The densities were measured by using a capillary tube and corrections were made for the thermal expansion of glass. The refractive indices were measured using a small angle hollow-prism and the techniques of measurements were the same as adopted earlier.[1,2]

The chemicals used in this investigation are from M/s Eastman Organic Chemicals, USA, with a given purity of 98% *minimum* (by nonaqueous titration). The nematic–isotropic transition temperature for PBPA and BBPA are determined using the polarizing microscope. The observed values of 69.1 and 80.5°C respectively are in good agreement with the values



	R_1	R_2
PBPA	$O(CH_2)_2CH_3$	$(CH_2)_4CH_3$
BBPA	$O(CH_2)_3CH_3$	$(CH_2)_4CH_3$
MBBA	OCH_3	$(CH_2)_3CH_3$

FIGURE 1 Structural formula of the compounds PBPA, BBPA and MBBA.

of 69 and 80°C for the nematic–isotropic transition temperatures listed for these compounds by M/s Eastman Organic Chemicals and Atomergic Chemetals, USA. We have determined the refractive indices at different temperatures starting from the nematic–isotropic transition point, downwards to 45.5°C in the case of BBPA and 26.8°C in the case of PBPA. In the case of BBPA three different enantiotropic phases are reported by Smith *et al.*[3] at temperatures below 44.4°C. The solid–nematic transition in the case of PBPA as reported by Smith *et al.* occurs at 32.7°C; however, the nematic phase of PBPA persists in a supercooled state and hence it is possible to make measurements up to 26.8°C. The nematic–isotropic transition temperatures reported by Smith *et al.* are higher than our values by 2°C in the case of PBPA and by 4.1°C in the case of BBPA. Such differences arise from the samples being of different purities. This is not uncommon; for example, in the case of MBBA different values of the nematic–isotropic transition temperature (ranging over 5°C) are found in the literature.[4–7] Under these circumstances, the data here are all presented as a function of the relative temperature $(t_c - t)$, t_c being the nematic–isotropic transition point.

RESULTS AND DISCUSSION

The refractive index and density data are shown in Tables I and II. The measurements of the temperatures, refractive indices and densities are estimated to be correct to within ±0.2°C, 0.001 and 0.001 gm/cm^3 respectively.

As is well-known, the orientational order parameter S is given by the relation

$$S = \frac{(\alpha_e - \alpha_0)}{(\alpha_{\parallel} - \alpha_{\perp})}, \tag{1}$$

TABLE I

Densities and refractive indices of *N*-(*p*-propoxybenzylidene)*p*-pentylaniline (t_c = 69.1°C)

	ρ in	4358 Å		5461 Å		5780 Å		5893 Å	
$(t_c - t)$°C	gm/cm^3	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
−0.1	0.992 (liquid)	1.630 (liquid)		1.585 (liquid)		1.578 (liquid)		1.576 (liquid)	
4.6	1.001	—	—	1.692	1.542	1.677	1.537	1.676	1.536
6.8	1.004	1.788	1.568	1.707	1.538	1.693	1.534	1.691	1.532
10.2	1.007	1.807	1.562	1.722	1.533	1.710	1.529	1.706	1.528
13.1	1.009	1.818	1.558	1.730	1.530	1.719	1.526	1.715	1.525
15.6	1.011	1.826	1.556	1.736	1.529	1.725	1.524	1.721	1.523
20.1	1.014	1.837	1.553	1.743	1.527	1.734	1.522	1.730	1.521
22.6	1.016	1.842	1.552	1.749	1.526	1.738	1.521	1.734	1.520
27.3	1.019	1.851	1.550	1.757	1.524	1.745	1.520	1.742	1.519
30.6	1.022	1.856	1.549	1.761	1.524	1.749	1.519	1.746	1.518
31.8	1.023	1.858	1.549	1.763	1.524	1.751	1.519	1.748	1.518
34.6	1.025	1.863	1.548	1.767	1.523	1.755	1.519	1.751	1.518
37.6	1.027	1.867	1.547	1.771	1.523	1.758	1.518	1.755	1.517
42.3	1.030	1.875	1.546	1.778	1.523	1.764	1.518	1.761	1.517

TABLE II

Desnsities and refractive indices of *N*-(*p*-butoxybenzylidene)*p*-pentylaniline (t_c = 80.5°C)

	ρ in	4358 Å		5461 Å		5780 Å		5893 Å	
$(t_c - t)$°C	gm/cm^3	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
−0.2	0.981 (liquid)	1.622 (liquid)		1.578 (liquid)		1.571 (liquid)		1.569 (liquid)	
3.2	0.985	—	—	—	—	1.665	1.528	1.663	1.526
6.0	0.988	1.769	1.555	1.691	1.527	1.680	1.522	1.678	1.520
7.9	0.990	1.781	1.550	1.701	1.523	1.689	1.518	1.686	1.517
10.9	0.993	1.793	1.546	1.712	1.520	1.700	1.515	1.695	1.514
13.5	0.996	1.802	1.542	1.720	1.517	1.708	1.513	1.703	1.512
18.0	0.999	1.815	1.539	1.730	1.514	1.718	1.510	1.713	1.509
22.5	1.003	1.825	1.537	1.737	1.513	1.726	1.509	1.721	1.508
25.9	1.005	1.832	1.536	1.742	1.512	1.731	1.508	1.726	1.507
31.4	1.010	1.841	1.533	1.749	1.511	1.737	1.507	1.734	1.506
35.0	1.013	1.847	1.532	1.753	1.511	1.741	1.507	1.738	1.506

where α_e and α_o are respectively the average effective polarizabilities for the extraordinary and ordinary rays, and $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizabilities respectively parallel and transverse to the long axis of the molecule. $(\alpha_{\parallel} - \alpha_{\perp})$ is the optical anisotropy of the molecule and shall hereafter be referred to as $\Delta\alpha$. The calculation of α_e and α_o involve assumptions with regard to the nature of the local field in the medium and two methods, viz., (i) the use of Vuks formulae and (ii) the use of Neugebauer relations, have been adopted by the earlier workers.[8-12] However, for the reasons stated in our earlier paper[2] we prefer to use the Neugebauer relations for calculating the values of α_e and α_o.

In order to estimate the value of $\Delta\alpha$, the following procedure was adopted. Data on the orientational order parameter of MBBA are available from NMR studies made by Lee *et al.*[13] The refractive index and density data, for the nematic phase of MBBA have also been reported.[14,15] Using the refractive index data (for 5893 Å) and density data, the values of α_e and α_o for MBBA in the nematic phase at different temperatures are calculated. Using the values of S from the NMR data and the values of $(\alpha_e - \alpha_o)$ at different temperatures it is possible to calculate the values of $\Delta\alpha$ in the case of MBBA using Eq. (1). The values of $\Delta\alpha$ calculated from the S factors in the range of $(t_c - t)$ 10 to 20°C are practically constant and the average value of $\Delta\alpha$ in the case of MBBA is found to be 22.34×10^{-24} cm^3. The structures of the molecules under discussion are similar to that of MBBA, except for the fact that there are differences with regard to the number of end methylene groups. It may be assumed that the contribution of the central rigid portion of the molecules (in Figure 1), to the optical anisotropy is the same in the cases of MBBA, PBPA and BBPA. However, the actual value of the optical anisotropy in each case would be different owing to the contributions from the relevant end groups being different for the three cases. From the known values of the optical anisotropy of bond polarizabilities[16] (for 5893 Å), it is possible to calculate the contributions due to the end groups in the cases of MBBA, PBPA and BBPA by assuming the all-trans conformation for the molecules. By taking into account the difference between the contributions, the corrected values of the optical anisotropy of the molecules of *N*-(*p*-propoxybenzylidene) *p*-pentylaniline and *N*-(*p*-butoxybenzylidene)*p*-pentylaniline are found to be 23.57 and 24.14×10^{-24} cm^3 respectively. Using these values of $\Delta\alpha$, the orientational order parameters at different temperatures are calculated and shown in Figure 2. It is also possible to calculate the values of $\Delta\alpha$ of these two compounds for the other wavelengths by assuming the values of S factor calculated for 5893 Å at any one temperature. Using these values of $\Delta\alpha$, the orientational order parameters at each temperature could be obtained from the index data for different wavelengths. It may be mentioned that in both the compounds such calculations lead to consistent values of S at each temperature.

It may be seen from Figure 2 that the trends of the variation of the order parameter S with temperature are similar for the two compounds, the butoxy compound (the molecular length of which is longer) having the higher value of the order parameter at the same reduced temperature. Similarly, the difference between the values of the internal field constants i.e., the value of $(\gamma_o - \gamma_e)$ at the same reduced temperature $(t_c - t)$ is found to be greater

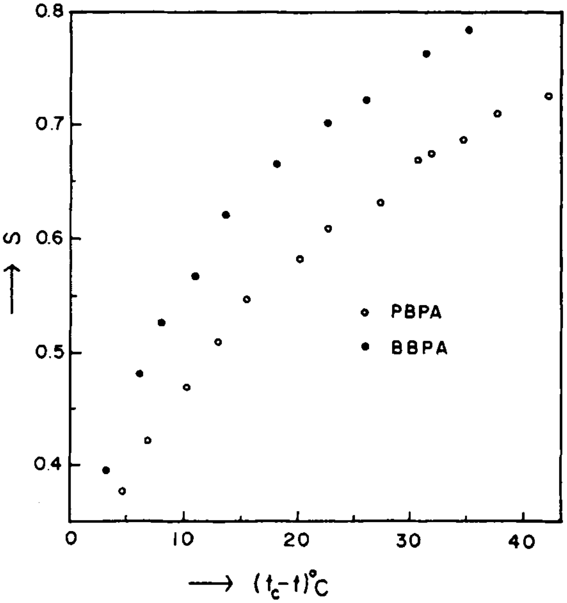


FIGURE 2 Orientational order parameter S versus $(t_c - t)$ for the compounds PBPA and BBPA.

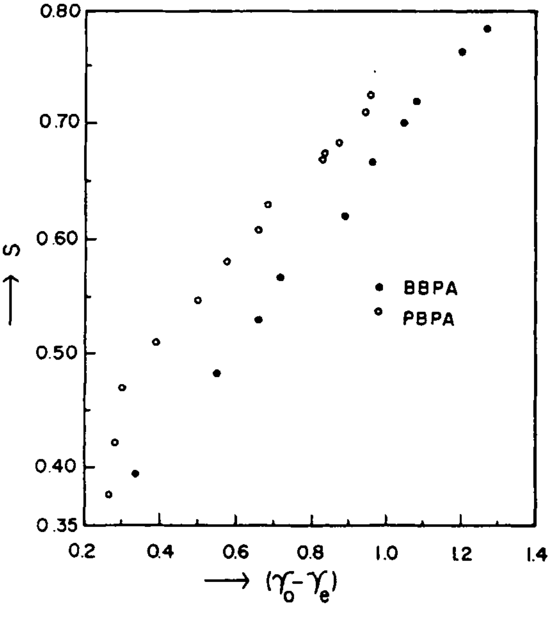


FIGURE 3 Orientational order parameter versus $(\gamma_o - \gamma_e)$ for the compounds PBPA and BBPA, calculated from the index data for 5893 Å.

in the case of the butoxy compound than in the case of the propoxy compound. Further, in the case of each compound a graphical plot of the values of S versus $(\gamma_o - \gamma_e)$ exhibits an approximately linear variation as shown in Figure 3 indicating that the anisotropy of the internal field increases with increasing molecular order i.e. order parameter S.

Acknowledgement

The authors are thankful to the University Grants Commission (India) for the research grant provided for the project on liquid crystals. One of us (DR) wishes to express his thanks to the University Grants Commission (India) for the award of a Junior Research Fellowship.

References

1. N. V. Madhusudana, R. Shashidhar, and S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.*, **13**, 61 (1971).
2. R. Somashekar, D. Revannasiddaiah, M. S. Madhava, H. S. Subramhanyam, and D. Krishnamurti, *Mol. Cryst. Liq. Cryst.*, **45**, 243 (1978).
3. G. W. Smith, Z. G. Gardlund, and R. J. Curtis, *Mol. Cryst. Liq. Cryst.*, **19**. 327 (1973).
4. I. Haller, H. A. Huggins, and M. J. Freiser, *Mol. Cryst. Liq. Cryst.*, **16**, 53 (1972).
5. G. Vergoten and G. Fleury, *Mol. Cryst. Liq. Cryst.*, **30**, 213 (1975).
6. R. T. Thompson, D. W. Kydon, and M. M. Pintar, *Mol. Cryst. Liq. Cryst.*, **39**, 123 (1977).
7. K. Hirakawa and S. Kai, *Mol. Cryst. Liq. Cryst.*, **40**, 261 (1977).
8. S. Chandrasekhar and N. V. Madhusudana, *J. Phys.*, **30**, C4-24 (1969).
9. A. Saupe and W. Maier, *Z. Naturforsch*, **16a**, 816 (1961).
10. A. Axmann, *Mol. Cryst. Liq. Cryst.*, **3**, 471 (1968).
11. H. S. Subramhanyam, C. S. Prabha, and D. Krishnamurti, *Mol. Cryst. Liq. Cryst.*, **28**, 201 (1975).
12. G. R. Van Hecke, B. D. Santarsiero, and L. J. Theodore, *Mol. Cryst. Liq. Cryst.*, **45** (1 and 2), 1 (1978).
13. Y. S. Lee, Y. Y. Hsu, and D. Dolphin, *Liquid Crystals and Ordered Fluids*, (ed. J. F. Johnson and R. S. Porter), Plenum Press, New York, Vol. 2, p. 357.
14. M. Brunet-Germain and P. Chatelain, *C.R. Acad. Sci. Paris*. **B271**, 1075 (1970).
15. P. I. Rose, presented at the Fourth International Liquid Crystal Conference, Kent, Ohio, USA, August 1972.
16. C. G. Le Fevre and R. J. W. Le Fevre, *Physical Methods of Chemistry* (ed. A. Weissberger and B. W. Rossiter), Wiley-Interscience, New York, 1972, Part IIIC, p. 437.