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A comparison of experimental order parameters of nematogens with different theories

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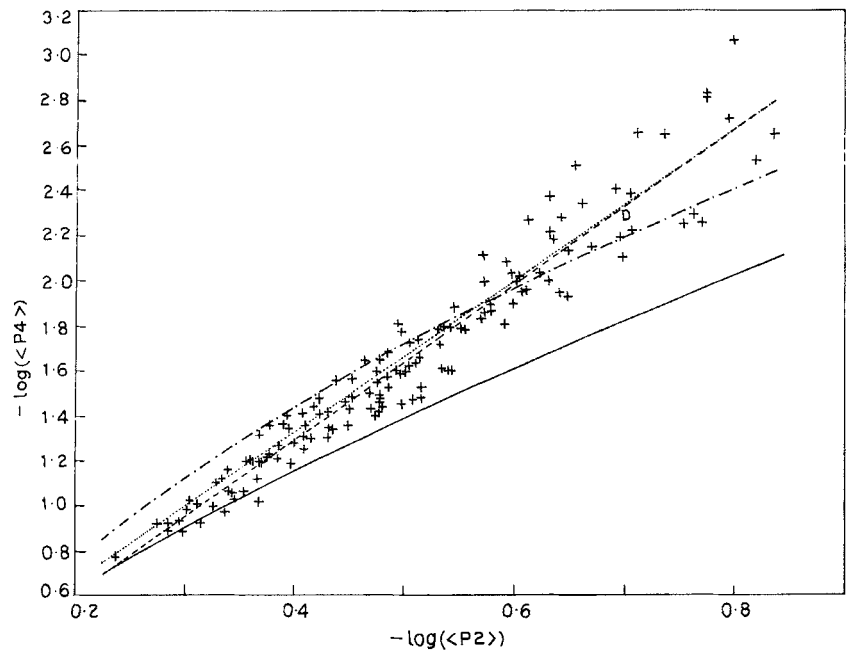
Orientational order parameters, $\bar{P}_2$ and $\bar{P}_4$, as calculated from our X-ray diffraction studies, have been compared with the predictions of mean-field and continuum theories. It is observed that the agreement with Faber's continuum theory is surprisingly good.

During the past 12 years we have extensively studied aligned samples of nematogens using an X-ray diffraction technique [1–12]. We have determined the orientational distribution function for a large number of liquid-crystalline substances in the nematic mesophase and hence calculated the orientational order parameters $\bar{P}_2$ and $\bar{P}_4$. In trying to fit our experimental results to the well-known Maier–Saupe (MS) mean-field theory, we have consistently found that our $\bar{P}_2$ values are in fair agreement



Comparison of experimental $\bar{P}_2$ and $\bar{P}_4$ values with different theories, +, experimental values; ——, Maier–Saupe mean-field theory; —·—·—, HJL theory ($\delta = -0{\cdot}8$); ....., Faber's theory; – – – –, linear least square fit (equation (2)).

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Details of the nematogens studied.

Compound name (short name)	T_{NI}/°C	Temperature range studied/°C	Number of observations	Mean $m \pm$ s.d.	Reference
(1) *p*-Methoxyphenyl trans-4-pentyl cyclohexane carboxylate (MPPCC)	71·1	20–70	12	0·295 ± 0·018	[8]
(2) *p*-Propoxyphenyl trans-4-pentyl cyclohexane carboxylate (PPPCC)	71·1	40–68	8	0·315 ± 0·017	[8]
(3) *p*-Ethoxyphenyl trans-4-butyl cyclohexane carboxylate (EPBCC)	74·6	20–73·5	13	0·307 ± 0·019	[8]
(4) *p*-Cyanophenyl trans-4-pentyl cyclohexane carboxylate (CPPCC)	78·7	25–77·4	13	0·295 ± 0·019	[8]
(5) Para azoxyanisole (PAA)	136	110–128	4	0·289 ± 0·021	[11]
(6) Bis-(4′-*n*-hexyloxybenzal)-2-chloro-1,4-phenylene diamine (BHeCP)	198	94–180	7	0·316 ± 0·011	[5]
(7) Bis-(4′-*n*-octyloxybenzal)-2-chloro-1,4-phenylenediamine (BOCP)	178·5	58–148	8	0·333 ± 0·010	[5]
(8) Bis-(4′-*n*-decyloxybenzal)-2-chloro-1,4-phenylenediamine (BDeCP)	166	112–155	6	0·321 ± 0·013	[5]
(9) Cyanobenzylidene-*p*-octyloxy aniline (CBOOA)	107	86–103	3	0·310 ± 0·022	[3]
(10) 5-(4-*n*-Butylphenyl)-2-(4-cyanophenyl)-pyrimidine (BPCPP)	244·7	90–240	13	0·303 ± 0·013	[4]

(11) 4′-Pentyloxy-4-cyanobiphenyl (5OCB)	67·5	35–66	6	0·301 ± 0·017	[2]
(12) 4-Octyloxy-4-cyanobiphenyl (8OCB)	79·5	67–79	3	0·305 ± 0·023	[2]
(13) 4′-Cyanophenyl-4′-heptylbenzoate (CPHB)	56	34–55·5	6	0·297 ± 0·020	[1]
(14) Bis-(4,4′-*n*-octyloxybenzylidene)-1-4-phenylenediamine (OOBPD)	231	207–227	4	0·327 ± 0·013	[6]
(15) Anisylidene-*p*-aminophenyl acetate (APAPA)	108·5	80–102	5	0·295 ± 0·010	[7]
(16) *p*-*n*-Butoxybenzylidene-*p*′-*n*-butylaniline (BBBA)	74	50–70	5	0·321 ± 0·029	[9]
(17) *p*-Ethoxybenzylidene-*p*-*n*-butylaniline (EBBA)	79	29–75	8	0·324 ± 0·020	[10]
(18) *p*-*n*-Propoxybenzylidene-*p*-*n*-butylaniline (PBBA)	58·5	25–55	7	0·313 ± 0·020	[10]
(19) 5-(4′-*n*-Pentylcyclohexyl)-2-(4-cyclophenyl)-pyrimidine (PCCPP)	235	97·5–175	10	0·295 ± 0·015	[12]
(20) 4-*n*-Pentyl-4-cyano-*p*-terphenyl (PCTP)	239·5	134·3–201·3	11	0·326 ± 0·020	[12]
Total	20 compounds		152	0·308 ± 0·018	

with the theory, whereas our $\bar{P}_4$ values are much smaller than the theoretical expectations. Similar results have also been obtained by other research workers [13, 14]. Moreover, it has not been possible to fit our experimental $\bar{P}_2$ and $\bar{P}_4$ values simultaneously with the modified mean-field theory of Humphries, James and Luckhurst (HJL) [15]. Faber [16] has derived a simple expression relating the order parameters, viz. $\ln \bar{P}_4/\ln \bar{P}_2 = 10/3$, from a continuum theory of disorder in nematic liquid crystals. In the figure we have plotted $\ln \bar{P}_4$ against $\ln \bar{P}_2$ and have compared our 152 experimental order parameter values obtained from 20 nematic compounds with the theoretical predictions from MS, HJL and Faber's theories. It is surprising that, in spite of the crudity of the various assumptions made in Faber's theory, the agreement of this theory with our experimental results is impressive. It is clearly seen in the figure that the Maier–Saupe curve does not at all follow the trend of the experimental points. The Humphries, James and Luckhurst theory, which assumes a mean-field potential of the form

$$V(\theta) = -A[\bar{P}_2 P_2(\cos\theta) + \delta \bar{P}_4 P_4(\cos\theta)], \tag{1}$$

can be used to calculate $\bar{P}_2$ and $\bar{P}_4$ values for different values of δ. Since the HJL curve shifts almost parallel to the MS curve upwards or downwards depending upon the sign and value of δ, the HJL theory cannot reproduce the general trend of the experimental data points for any of the δ values. However, we have drawn the HJL curve for $\delta = -0{\cdot}8$ in the figure to show the discrepancy. Such a value of δ is unrealistic, since it implies $\bar{P}_2$ to be less than 0·3 at the nematic–isotropic transition temperature and we have never observed such low values of $\bar{P}_2$ in our X-ray diffraction experiments.

We have fitted our data by least squares method to a straight line given by the equation

$$\ln \bar{P}_4 = 3{\cdot}427 \ln \bar{P}_2 + 0{\cdot}0756, \tag{2}$$

which is also shown in the figure. We have also tried to fit a cubic polynomial to our experimental data with only marginal improvement in the fitting with respect to the linear form given by equation (2). It may be noted that the slope of the best fit straight line is within 3 per cent of the value predicted by Faber's theory.

The table gives the names of the compounds studied, their nematic–isotropic transition temperatures, temperature range of the X-ray diffraction measurements, number of observations at different temperatures and the mean value of m ($\equiv \ln \bar{P}_2/\ln \bar{P}_4$) along with its standard deviation. It is seen that the mean values of m are almost always equal to Faber's value of 0·3 within experimental uncertainties. It may be of interest to note that of six (BHeCP, BOCP, BDeCP, BPCPP, OOBPD and PCTP) nematogens with rather long rigid parts (consisting of three phenyl or pyrimidine rings), five give large m values. We are unable to explain why it is so, but we feel that more experimental results with such nematogens are needed to check this trend. The continuum theory of Faber may have to be modified if this trend is confirmed by other researchers.

It is also necessary that Faber's theory be tested more rigorously by measuring the elastic constants along with the order parameters, since the agreement of our experimental results with this theory may be fortuitous. With this aim in mind we are at present setting up an apparatus for measuring elastic constants of the nematogens we have studied by X-ray diffraction. Also, we feel that very slow neutron scattering may be used to obtain information regarding collective modes in liquid crystals, which may be used to test and if necessary modify the continuum theory as presented by Faber.

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References

[1] BHATTACHARJEE, B., PAUL, S., and PAUL, R., 1981, *Molec. Phys.*, **44,** 1391.
[2] BHATTACHARJEE, B., PAUL, S., and PAUL, R., 1982, *Molec. Crystals liq. Crystals*, **89,** 181.
[3] JHA, B., BHATTACHARJEE, B., PAUL, S., and PAUL, R., 1983, *Phys. Stat. Sol.* (*a*), **72,** 461.
[4] JHA, B., NANDI, A., PAUL, S., and PAUL, R., 1984, *Molec. Crystals. liq. Crystals*, **104,** 289.
[5] JHA, B., MANDAL, P., PAUL, S., and PAUL, R., 1989, *Phase Transitions*, **15,** 39.
[6] MANDAL, P., PAUL, R., and PAUL, S., 1985, *Molec. Crystals liq. Crystals*, **131,** 299.
[7] MANDAL, P., MITRA, M., BHATTACHARJEE, K., PAUL, S., and PAUL, R., 1987, *Molec. Crystals liq. Crystals*, **149,** 203.
[8] MITRA, M., PAUL, R., and PAUL, S., 1989, *Molec. Crystals liq. Crystals*, **177,** 71.
[9] MANDAL, P., MITRA, M., PAUL, S., and PAUL, R., 1987, *Liq. Crystals*, **2,** 183.
[10] MITRA, M., MAJUMDAR, B., PAUL, R., and PAUL, S., 1990, *Molec. Crystals liq. Crystals* B, **180,** 187.
[11] JHA, B., ZEMINDER, A., PAUL, S., and PAUL, R., 1980, *North Bengal Univ. Rev.*, **1,** 123.
[12] MAJUMDAR, B., 1988, Ph.D. Thesis, University of North Bengal (unpublished data).
[13] JEN, S., CLARK, N. A., PERSHAN, P. S., and PRIESTLEY, E. B., 1973, *Phys. Rev. Lett.*, **31,** 1552.
[14] HEAGEN, H. J. P., 1975, *J. Phys. Lett., Paris*, **36,** 209.
[15] HUMPHRIES, R. L., JAMES, P. G., and LUCKHURST, G. R., 1972, *J. chem. Soc. Faraday Trans. II*, **68,** 1031.
[16] FABER, T. E., 1977, *Proc. R. Soc.* A, **35,** 247.