

Pressure studies on phase transitions in 4-alkoxyphenyl-4'-nitrobenzoyloxybenzoates

V. N. Raja

Raman Research Institute, Bangalore 560 080, India

B. R. Ratna and R. Shashidhar*

Bio/Molecular Engineering Branch, Code 6190, Naval Research Laboratory, Washington, D.C. 20375-5000

G. Heppke and Ch. Bahr

Iwan-N.-Stranski Institut, ER11, Technische Universität Berlin, Strasse des 17 Juni 135, D-1000 Berlin 12, Germany

J. F. Marko, J. O. Indekeu,[†] and A. Nihat Berker

Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 12 January 1989)

We have studied the effect of high pressure on the phase transitions in the seventh to tenth homologs of 4-alkoxyphenyl-4'-nitrobenzoyloxybenzoates (DB.*k*O.NO₂). While pressure does not induce any new phases in *k*=7 or 8, it has a dramatic effect on *k*=10: triply reentrant behavior is seen over a narrow range of pressure, the sequence of transitions being the same as that observed in *k*=9 or DB.9O.NO₂ at atmospheric pressure. This is the first instance of pressure-induced multiply reentrant behavior in a single-component system. The observed sensitivity of the multiply reentrant behavior to molecular chain length and pressure is according to the predictions of the frustrated spin-gas model of polar liquid crystals.

Reentrant nematic behavior is generally exhibited by compounds whose molecules possess a strongly polar cyano or nitro end group.¹ Among such materials 4-nonyloxyphenyl-4'-nitrobenzoyloxybenzoate (DB.9O.NO₂) is unique: it exhibits multiply reentrant behavior²⁻⁴ involving three nematic and four smectic-*A* phases. Interestingly, the lower as well as higher homologs of DB.9O.NO₂ do not exhibit any reentrant behavior, showing thereby that this rich polymorphism is extremely sensitive to changes in chain length.

On the theoretical side, the frustrated spin-gas model⁵⁻¹² has suggested that *microscopic frustration of dipoles* together with *competing short-range antiferroelectric and ferroelectric orders* can account for the observed polymorphism of reentrance in polar compounds.¹¹ An important step has been the discovery in this model of quadruple reentrance,⁶ which is exactly equivalent to the experimentally observed multiply reentrant behavior in DB.9O.NO₂.²⁻⁴ Another significant achievement has been the qualitative agreement between calculated and measured reentrant transition enthalpies.^{7,13}

This Communication presents our high-pressure studies on the seventh to tenth members of DB.*k*O.NO₂, and reports the observation of pressure-induced multiple reentrance in a single-component liquid crystal. Good agreement is found with the predictions of the spin-gas model.

The materials have been synthesized at the Technische Universität, Berlin. Knowing the sensitivity of the phase sequence to impurities,³ special care was taken to ensure the purity of the samples. The transition temperatures were in good agreement with those reported in the literature.² The pressure studies were conducted using an optical high-pressure cell with sapphire windows. The transitions were detected by an optical transmission technique.

The details of the pressure setup¹⁴ will not be repeated here. The accuracies in the determination of the pressure and temperature were ± 1 bar and ± 25 mK, respectively.

The pressure-temperature (*P-T*) diagrams of DB.7O.NO₂ and DB.8O.NO₂ are shown in Figs. 1 and 2. Both compounds show essentially the same features. At atmospheric pressure or 1 bar, nematic (*N*), monolayer smectic-*A* (*Sm-A*₁) and the ribbon (or *Sm-C*_̄) phases are

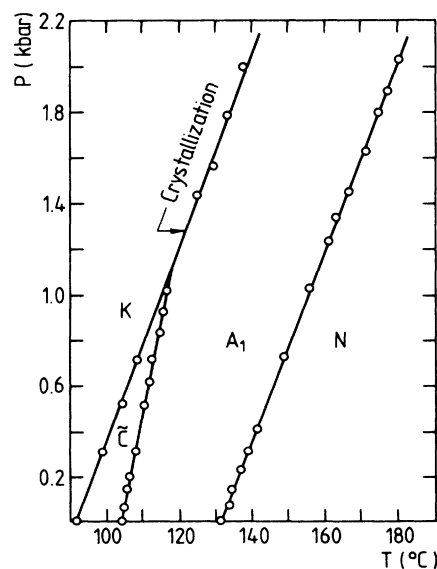
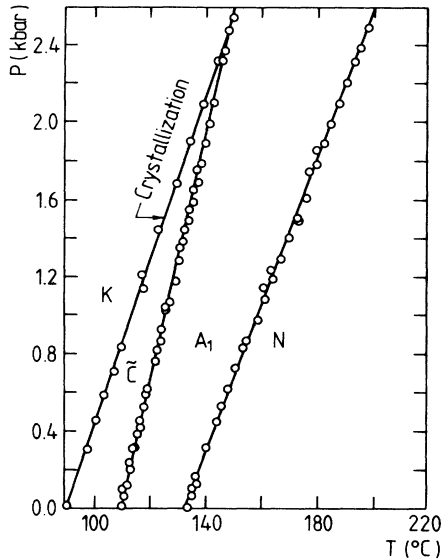


FIG. 1. Experimental pressure-temperature (*P-T*) diagram of DB.7O.NO₂.


 FIG. 2. Experimental P - T diagram of DB.80.NO₂.

seen. With increasing pressure the temperature range of the Sm- A_1 phase increases. The increased stability at high pressures appears to be a general feature of the monolayer (Sm- A_1) phase (see, e.g., Refs. 15 and 16). In the spin-gas model this characteristic is seen from the increasing stability of local-ferroelectric (Sm- A_1 -like) fluctuations with increasing pressure. Also, no pressure-induced phases are seen and instead, the Sm- C phase is suppressed at high pressures.

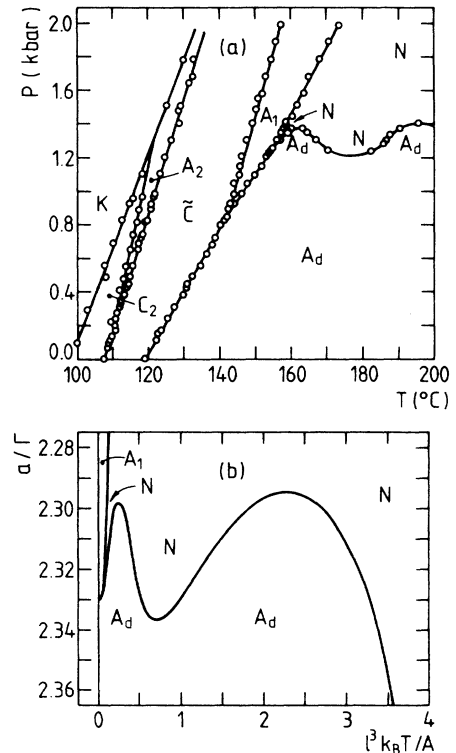
By contrast, the P - T diagram of DB.100.NO₂ [Fig. 3(a)] shows several pressure-induced phases. The Sm- A_2 phase is induced beyond 0.2 kbar and the Sm- A_1 phase beyond 0.8 kbar. Perhaps the most important feature of the phase diagram of DB.100.NO₂ is that the Sm- A_d - N phase boundary *curls twice*, leading to the appearance of the reentrant nematic (N) phase twice in the pressure region 1.2–1.38 kbar. These reentrant nematic phases show pronounced fluctuations when observed under pressure using a polarizing microscope and hence are easily identified.

The theoretical counterpart of this phase diagram, in the spin-gas model, is shown in Fig. 3(b). The sequence obtained is the “quadruple reentrance,”⁶

$$N\text{-Sm-}A_d\text{-}N\text{-Sm-}A_d\text{-}N\text{-Sm-}A_1,$$

where the higher-temperature Sm- A_d phase is characterized by short-range antiferroelectric order stabilized by atomic permeation, the subsequent N phase arises from dipolar frustration, the lower-temperature Sm- A_d phase features short-range antiferroelectric order sustained by librational permeation, the subsequent N phase is caused by the competition and mutual cancellation of local ferroelectric and antiferroelectric orders, and finally, the Sm- A_1 phase has dominant short-range ferroelectric order.^{6,11}

The basic elements in the model are the n discrete positions (“notches”) for mutual atomic permeation of nearest-neighbor molecules. In addition, there are m


 FIG. 3. (a) Experimental P - T diagram of DB.100.NO₂. (b) Theoretical P - T diagram for $n=5$, $B/A=1.451$, $m=3$, and $\delta=0.015l/n$, as in Ref. 6.

“subnotches” for librational permeations on a subscale $\delta \ll l/n$, where l is an effective molecular length. The distance between the notches, l/n , is denoted by Γ and corresponds to the distance between next-nearest-neighbor carbon atoms in an all-*trans* tail configuration. In other words, $k \approx 2n$, where k is the number of carbons in the tail. The average lateral separation between nearest-neighbor molecules is a , and a/Γ serves as a measure of (inverse) pressure. The temperature variable is given by $l^3 k_B T/A$, where A is the strength of the dipole-dipole interaction potential V between the molecules,

$$V_{12} = A[\hat{s}_1 \cdot \hat{s}_2 - 3(B/A)(\hat{s}_1 \cdot \hat{r}_{12})(\hat{s}_2 \cdot \hat{r}_{12})]/|\mathbf{r}_{12}|^3,$$

where \mathbf{r}_i is the position of the dipole of molecule i , \hat{s}_i is the unit vector describing the dipolar orientation, $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, and $\hat{r}_{12} = \mathbf{r}_{12}/|\mathbf{r}_{12}|$. $B < A$ for net tail-tail steric hindrance and $B > A$ for net tail-tail entanglement.

The temperature scale in the model does not correspond directly to the experimental scale, since the complex degrees of freedom of the molecules are ignored. Also, fluctuations into isotropic, smectic- C or crystalline phase are ignored to date.

The experimental identification of the Sm- A phases [as given in Fig. 3(a)] proceeds by comparing the P - T diagram of DB.100.NO₂ with that of DB.90.NO₂ (Fig. 4) reproduced from Ref. 3. It is clear that the basic features of the P - T diagram of DB.90.NO₂ are qualitatively similar to those exhibited by the P - T diagram of DB.100.NO₂ in the pressure range of 1.2–1.38 kbar. It

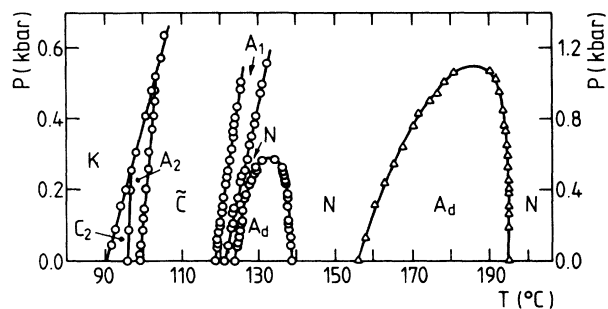


FIG. 4. Experimental P - T diagram of DB.90.NO₂, from Ref. 3.

can therefore be assumed that the smectic- A phase which appears beyond pressures of 0.2 kbar is the Sm- A_2 phase, while that which is seen for pressures higher than about 0.85 kbar is the Sm- A_1 phase. (The bilayer and the monolayer nature of these phases are of course to be verified by x-ray studies at high pressure.) Since we also know from the x-ray results at 1 bar (Ref. 17) that the two Sm- C phases of DB.100.NO₂ are Sm- \tilde{C} and Sm- C_2 , the sequence of transitions exhibited by this material in the P range of 1.2–1.38 kbar can be written as N -Sm- A_d - N -Sm- A_d - N -Sm- A_1 -Sm- \tilde{C} -Sm- A_2 .

Thus we have observed the first instance of *pressure-induced triply reentrant behavior* in a single-component system. It also appears that pressure induces a lower homologlike behavior in DB.100.NO₂. It would be of interest to see if the pressure range over which triply reentrant behavior is seen can be brought closer to atmospheric pressure by adding a lower homolog to DB.100.NO₂. With this in mind we have studied a 57.3 mol% mixture of DB.100.NO₂ in DB.80.NO₂ which exhibits the sequence N -Sm- A_d -Sm- A_1 -Sm- \tilde{C} at 1 bar. (For a complete description of the transitions exhibited by this binary system, see Ref. 18.) The P - T diagram of this mixture is shown in Fig. 5. It is seen that again pressure induces a triply reentrant behavior, but the range of pressure over which this occurs is now between 0.1–0.2 kbar, i.e., the mixture just misses being a triply reentrant system at 1 bar.

On the theoretical side we have also performed calculations for mixtures and found that if small concentrations (e.g., 2%) of $n=4$ molecules are present in an $n=5$ compound, the quadruple reentrance is shifted towards lower pressures with respect to pure $n=5$. In these calculations the value of B/A is taken to be the same for molecules of different notch number n , and equal to

$$B/A = x(B/A)_4 + (1-x)(B/A)_5,$$

where x is the concentration of $n=4$ molecules and $(B/A)_i$ is a typical value of B/A for which quadruple

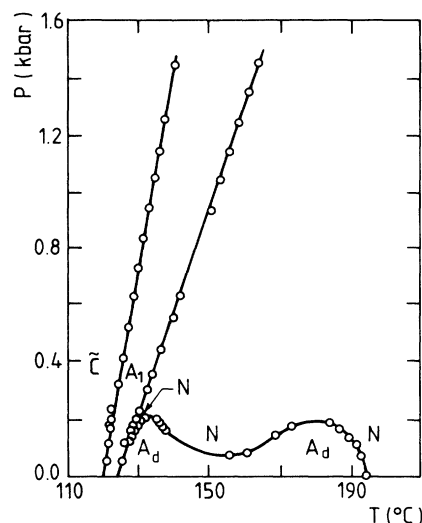


FIG. 5. Experimental P - T diagram of 57 mol% of DB.100.NO₂ in DB.80.NO₂.

reentrance is found in the pure $n=i$ compound.

The spin-gas model predicts that quadruple reentrance is very sensitive to changes in chain length.⁶ The phenomenon is not found for $n < 4$ or $n > 6$ (i.e., $k < 8$ or $k > 12$). For $n=4, 5$, or 6 , it occurs within narrow ranges of the model parameter B/A .⁶ The pressure ranges are $2.43 < a/\Gamma < 2.49$ for $n=4$, $2.28 < a/\Gamma < 2.39$ for $n=5$, and $2.44 < a/\Gamma < 2.47$ for $n=6$. These ranges are very similar for $n=4$ and $n=6$, corresponding to relatively low pressures, but the range is significantly different for $n=5$, corresponding to relatively high pressures. The theory thus clearly predicts that there is both a *maximal pressure* and a *maximal pressure range* for quadruple reentrance around $n=5$ ($k \approx 10$). The experimental data thus far confirm half of this prediction: when k is decreased from 10 the quadruple reentrance shifts from high pressures ($k=10$) to 1 bar ($k=9$), and then disappears ($k=8$ or 7). For $k=7$ and 8 , only the sequence N -Sm- A_1 is seen, precisely as in the theoretical phase diagrams for $n=4$ at pressures *above* the low pressures to which quadruple reentrance is pushed away.

It would be very interesting to test the other half of the theoretical prediction by studying mixtures of $k=10$ compounds with *longer* homologs.

We thank Professor S. Chandrasekhar and Professor C. W. Garland for useful discussions. J.F.M. and A.N.B. acknowledge support by the National Science Foundation under Grant No. DMR-87-19217. J.O.I. acknowledges support by the Belgian National Fund for Scientific Research.

*Also at the Department of Chemistry, Georgetown University, Washington, D.C. 20057; and on leave of absence from the Raman Research Institute, Bangalore 560 080, India.

†Permanent address: Laboratorium voor Molekulfysika,

Katholieke Universiteit Leuven, B 3030 Leuven, Belgium.

¹See, e.g., F. Hardouin, A. M. Levelut, M. F. Achard, and G. Sigaud, *J. Chim. Phys.* **80**, 53 (1983).

²Nguyen Huu Tinh, F. Hardouin, and C. Destrade, *J. Phys.*

- (Paris) **43**, 1127 (1982).
- ³R. Shashidhar, B. R. Ratna, V. Surendranath, V. N. Raja, S. K. Prasad, and C. Nagabhushan, *J. Phys. (Paris) Lett.* **46**, L445 (1985).
- ⁴E. Fontes, P. A. Heiney, J. L. Haseltine, and A. B. Smith III, *J. Phys. (Paris)* **47**, 1533 (1986).
- ⁵A. N. Berker and J. S. Walker, *Phys. Rev. Lett.* **47**, 1469 (1981).
- ⁶J. O. Indekeu and A. N. Berker, *Phys. Rev. A* **33**, 1158 (1986).
- ⁷J. O. Indekeu, A. N. Berker, C. Chiang, and C. W. Garland, *Phys. Rev. A* **35**, 1371 (1987).
- ⁸J. O. Indekeu and A. N. Berker, *Physica A* **140**, 368 (1986).
- ⁹A. N. Berker and J. O. Indekeu, in *Incommensurate Crystals, Liquid Crystals and Quasi-Crystals*, edited by J. F. Scott and N. A. Clark (Plenum, New York, 1987), p. 205.
- ¹⁰J. O. Indekeu, *Phys. Rev. A* **37**, 288 (1988).
- ¹¹J. O. Indekeu and A. N. Berker, *J. Phys. (Paris)* **49**, 353 (1988).
- ¹²J. F. Marko, J. O. Indekeu, and A. N. Berker, this issue, *Phys. Rev. A* **39**, 4201 (1989).
- ¹³K. Ema, G. Nounesis, C. W. Garland, and R. Shashidhar, *Phys. Rev. A* **39**, 2599 (1989).
- ¹⁴A. N. Kalkura, R. Shashidhar, and M. S. Urs, *J. Phys. (Paris)* **44**, 51 (1983).
- ¹⁵R. Shashidhar, *Mol. Cryst. Liq. Cryst.* **98**, 13 (1983).
- ¹⁶S. K. Prasad, R. Shashidhar, K. A. Suresh, A. N. Kalkura, G. Heppke, and R. Hopf, *Mol. Cryst. Liq. Cryst.* **99**, 185 (1983).
- ¹⁷V. N. Raja (unpublished).
- ¹⁸V. N. Raja, R. Shashidhar, B. R. Ratna, G. Heppke, and Ch. Bahr, *Phys. Rev. A* **37**, 303 (1988).