

High-pressure volumetric measurements near a smectic-nematic-isotropic triple point

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High-pressure volumetric measurements were used to investigate the importance of short-range smectic fluctuations in the nematic-isotropic transition. Three members of the homologous series of di-alkylazoxybenzenes were chosen as samples, since the nematic range varies considerably in these compounds. The investigation was aided by the discovery of a smectic-*A*–nematic–isotropic triple point at elevated pressure in the ninth member of the series. Theoretical work on pretransitional effects in the isotropic phase is not very useful in describing the effect of large smectic fluctuations on the nematic-isotropic transition itself. However, one recent theoretical proposal argues that the volume change at this transition should increase due to the presence of short-range smectic order, and our experimental results confirm this prediction.

INTRODUCTION

Although the nematic phase possesses no long-range smecticlike order, the influence of short-range smectic fluctuations on the properties of the nematic phase has been evident for a number of years. Perhaps the best example occurs in cholesteric rather than nematic liquid crystals, where the divergence of the pitch just before the transition to the smectic phase has supported the view that smecticlike fluctuations occur in the cholesteric phase.¹ Evidence that the nematic-isotropic transition is also affected by these smectic fluctuations was contained in the work of many authors, whose data demonstrated that transition entropies or volume changes were dependent on either the nearness of a smectic phase or some property of a nearby smectic phase.^{2–5} More recently, both theorists and experimentalists have shown interest in the effect of these smectic fluctuations on pretransitional properties in the isotropic phase just above the transition to the nematic phase.^{6–10} In addition, one theoretical discussion of the nematic–smectic-*A* transition included a calculation for the entropy change of the nematic-isotropic transition, indicating that it should increase as the width of the nematic phase decreases.¹¹

To properly investigate the influence of these smectic fluctuations on the nematic-isotropic phase transition, one needs a system where the smectic phase is extremely close to the nematic-isotropic transition. A system with a smectic-*A*–nematic–isotropic triple point would be ideal for such an experiment, since the width of the nematic phase becomes vanishingly small as the triple point is ap-

proached. Such triple points have been found in mixtures,^{9,12} but more appropriate for high-pressure volumetric measurements would be a single compound possessing a triple point at elevated pressure. We therefore chose to investigate the homologous series of di-alkylazoxybenzenes (*n*AB), since the nematic phase grows narrow as the alkyl chains are lengthened, disappearing completely in the ninth member of the series. Table I lists the transition temperatures at atmospheric pressure for the seventh (7AB), eighth (8AB), and ninth (9AB) members of the series. Even if a triple point could not be found, the high-pressure volumetric data generated along the smectic-nematic and nematic-isotropic transitions would provide a systematic indication of the importance of these smectic fluctuations in the nematic-isotropic transition. In addition, the nonreentrant smectic-*A*–nematic transition such as the one found in these compounds as well as the smectic-isotropic transition have not been studied under pressure, so the data would also be valuable in this regard.

This paper contains the results of such high-pressure volumetric experiments. A smectic-nematic-isotropic triple point was found in 9AB, and the volume change at the nematic-isotropic transition in these three compounds confirms the prediction that it should increase due to the presence of large smectic fluctuations. In addition, comparison of the data along these transitions with the data for other transitions yields interesting results.

THEORY

Since a Landau–de Gennes free-energy framework is successful in understanding the effect of smectic fluctuations on pretransitional properties in the isotropic phase, it is appropriate to see what this formulation has to say about the nematic-isotropic transition itself. The free energy must include the free energies of the nematic-isotropic and smectic-nematic transitions, together with coupling terms between smectic and nematic order parameters.^{6–8} The usual nematic free energy is given by

$$F_N = F_I + \frac{1}{2} A_N S^2 - \frac{1}{3} B_N S^3 + \frac{1}{4} C_N S^4, \quad (1)$$

TABLE I. Transition temperatures at atmospheric pressure (in °C) for the seventh through ninth members of the homologous series of di-alkylazoxybenzenes.

| Compound | Solid | Smectic <i>A</i> | Nematic | Isotropic |
|----------|-------|------------------|---------|-----------|
| 7AB | 34.1 | 53.8 | 70.5 | |
| 8AB | 38.7 | 64.4 | 66.5 | |
| 9AB | 44.4 | | 76.0 | |

where F_I is the free energy of the isotropic phase, S is the nematic order parameter, and A_N , B_N , and C_N are expansion coefficients. A_N is assumed to have a temperature dependence given by

$$A_N = a_N(T - T_{NI}^*), \quad (2)$$

where T_{NI}^* is the fictitious second-order transition temperature. a_N , B_N and C_N are assumed to be constant with temperature. The free energy for the nematic-smectic- A transition involves an expansion in even powers of the Fourier component of the density, $|\psi|$, and its spatial derivatives. For isotropic phase calculations, only the coefficient of the $|\psi|^2$ term, A_S , is important. It is assumed to have a temperature dependence given by

$$A_S = a_S(T - T_{NA}^*), \quad (3)$$

where T_{NA}^* is the second-order smectic-nematic transition temperature. Coupling terms of the form $S|\psi|^2$ and $S^2|\psi|^2$ are also included in the free energy.

The procedure is as follows: smectic fluctuations are integrated out first, renormalizing the free energy of the nematic phase. This effective nematic free energy is then worked out in the mean-field approximation. The temperature dependence of the new coefficient of the S^2 term, \tilde{A}_N , is

$$\tilde{A}_N = a_0(T - T_{NI}^*) + \frac{\chi}{(T - T_{NA}^*)^{1/2}} - \frac{\lambda^2}{(T - T_{NA}^*)^{3/2}}, \quad (4)$$

where χ and λ^2 are constants which depend on the coefficients in front of the $S^2|\psi|^2$ and $S|\psi|^2$ terms, respectively. With this change, the authors are able to explain anomalies in the behavior of several pretransitional properties of the isotropic phase, including light scattering, optical Kerr effect, flexoelectricity, and heat capacity. It can easily be seen from Eq. (4) that the largest deviation from mean-field behavior comes when T_{NI} is close to T_{NA}^* , which agrees nicely with experimental results.

It is not difficult to extend this result to show that the transition entropy and volume change at the nematic-isotropic transition are also affected by this renormalization. The transition entropy is given by the temperature derivative of Eq. (1), except that A_N , B_N , and C_N are now the renormalized coefficients, \tilde{A}_N , \tilde{B}_N , and \tilde{C}_N . Whereas the expression for \tilde{A}_N contains three temperature-dependent terms, the expressions for \tilde{B}_N and \tilde{C}_N contain many more terms leading to an extremely complicated expression for the transition entropy. Even if only the $S|\psi|^2$ coupling term is used, the expression for \tilde{A}_N , \tilde{B}_N , and \tilde{C}_N contain two, three, and six terms, respectively. Since the relative sizes of all the free-energy terms are not known, approximation of the resulting transition entropy expression is not possible.

Anisimov has suggested another way to investigate the nematic-isotropic transition entropy theoretically.¹¹ Short-range smectic order in the nematic phase causes the free energy near the nematic-smectic- A transition to have a singular part. This implies that smectic fluctuations increase the entropy of the nematic phase, with the largest increase near the nematic-smectic- A transition. If one assumes that the short-range smectic order vanishes

in the isotropic phase, then the nematic-isotropic transition must include the entropy change due to these smectic fluctuations. The closer this transition is to the nematic-smectic- A transition, the larger this entropy change due to short-range smectic order. Anisimov calculates this entropy contribution by integrating the singular part of the heat capacity from the nematic-isotropic transition temperature to a temperature well into the isotropic phase,

$$\Delta\Sigma = \int_{\Delta}^{t_0} \delta c_p dt = \int_{\Delta}^{t_0} A(t^{-\alpha} - 1) dt, \quad (5)$$

where $t = (T - T_{NA})/T_{NA}$, $\Delta = (T_{NI} - T_{NA})/T_{NI}$, and t_0 represents a reduced temperature well into the isotropic phase ($t_0 \approx 0.1$). A and α are the coefficient and exponent, respectively, of the singular part of the heat capacity. The volume change at the transition shows the same dependence as the transition entropy, since they are related by the Clausius-Clapeyron equation,

$$\Delta V = \left[\frac{dP}{dT} \right]_{\text{coex}}^{-1} \Delta\Sigma = \left[\frac{dP}{dT} \right]_{\text{coex}}^{-1} \int_{\Delta}^{t_0} A(t^{-\alpha} - 1) dt. \quad (6)$$

According to this relation, ΔV should increase as the nematic range, Δ , decreases, with the dependence growing stronger the smaller the nematic range.

EXPERIMENTAL METHOD

The samples of 7AB, 8AB, and 9AB were obtained from Frinton Laboratories. The transition temperatures for the 7AB and 9AB compounds agreed with the highest literature values, so these were used without additional purification. The 8AB transition temperatures were a degree or so below the majority of temperatures reported in the literature, so it was recrystallized from ethanol. This procedure brought its transition temperature up to a value consistent with the literature values.

The experimental apparatus allowed simultaneous measurement of the pressure, volume, and temperature of the sample and has been described previously.¹³ The liquid crystal sample was contained in a 4.5-cm³ stainless-steel bellows, the specific volume of which could be measured to an accuracy of 0.00015 cm³/g. The smectic-nematic, nematic-isotropic, and smectic-isotropic transitions were investigated by starting at a temperature and pressure in the less-ordered phase, and then increasing the pressure in steps of 100 psi, recording the volume each time. This process was performed slowly enough to keep the sample at the equilibrium temperature, and was continued until the sample was well into the more-ordered phase. The entire procedure was repeated at several points along each of the coexistence curves.

Figure 1 contains data for typical constant temperature runs for 9AB. The volume change at the smectic- A -isotropic transition was by far the largest observed; the smectic- A -nematic and nematic-isotropic volume changes in 9AB were larger than in the other two compounds. On the other hand, the smectic- A -nematic transition in 7AB was so small that we could not detect it with our apparatus. The existence of a triple point is shown nicely by the data in Fig. 1, in that only one transition is seen just above the transition temperature at atmos-

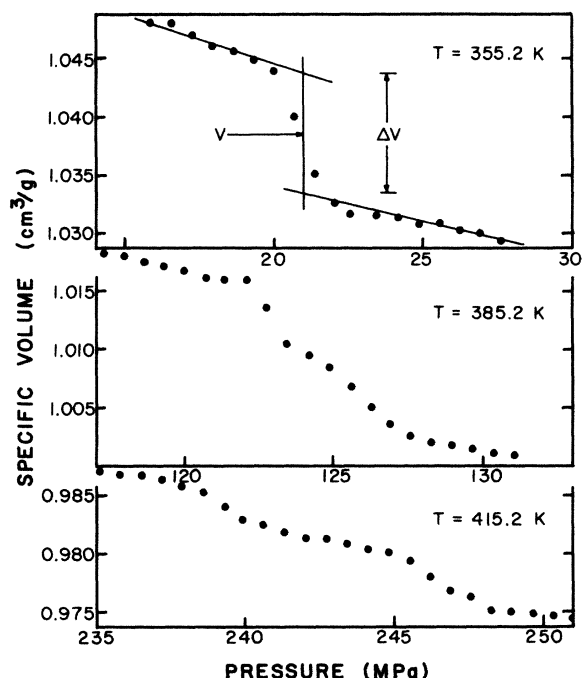


FIG. 1. Isotherms in 9AB. The upper figure shows a single isotropic–smectic-*A* transition whereas the lower two figures show two transitions (isotropic–nematic and nematic–smectic-*A*). The straight lines in the upper figure are least-squares linear fits to the data away from the transition; V , specific volume at the transition; ΔV , specific volume change at the transition.

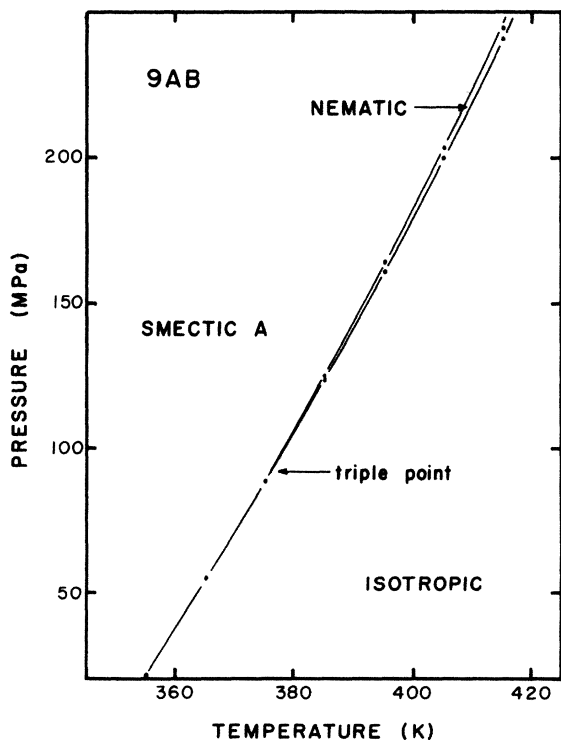


FIG. 2. Phase diagram for 9AB. The intersection of the phase boundaries indicates an isotropic–nematic–smectic-*A* triple point at 376 ± 2 K and 92 ± 6 MPa.

TABLE II. Slopes of the coexistence curves (in MPa/K) for the seventh through ninth members of the homologous series of di-alkylazoxybenzenes.

| Compound | $(dP/dT)_{NI}$ | $(dP/dT)_{SN}$ | $(dP/dT)_{SI}$ |
|----------|----------------|----------------|----------------|
| 7AB | 3.07 | | |
| 8AB | 3.17 | 3.62 | |
| 9AB | 3.83 | 3.93 | 3.39 |

pheric pressure, followed by two closely spaced transitions at higher temperature, and ending with two distinct transitions at even higher temperature. Seven separate constant-temperature runs were performed with this sample, from which we generated the phase diagram shown in Fig. 2. Extrapolation of the coexistence curves to their intersection allows us to determine that the triple point is at 376 ± 2 K and 92 ± 6 MPa. Similar measurements in 7AB and 8AB produced the phase diagrams for these compounds. The slopes of the measured coexistence curves for all three compounds are given in Table II.

The specific volume V and the specific volume change ΔV were determined for each transition by fitting straight lines to the data on either side of the transition. A vertical line at the center of the transition which intersected these two lines was then drawn; the point midway between these two intersections served to determine the specific volume of the transition while the vertical distance between the intersections was used as a measure of the specific volume change. This procedure is illustrated in Fig. 1. The results are shown in Figs. 3 and 4, where the relative volume change $\Delta V/V$ is displayed for the three different types of transitions. In just about all cases, the relative volume change decreases as one moves up the coexistence curve, a property characteristic of liquid-crystal transitions in general.^{4,13}

One other property which is important theoretically is the ratio of the temperature change to volume change along the coexistence curve. This ratio is usually expressed as

$$\gamma = \frac{\partial \ln(T/T_0)}{\partial \ln(V/V_0)}, \quad (7)$$

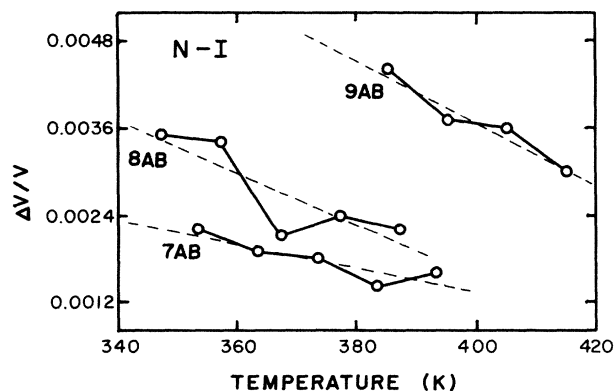


FIG. 3. Relative volume change at the nematic–isotropic transition. The straight lines are least-squares linear fits to the data.

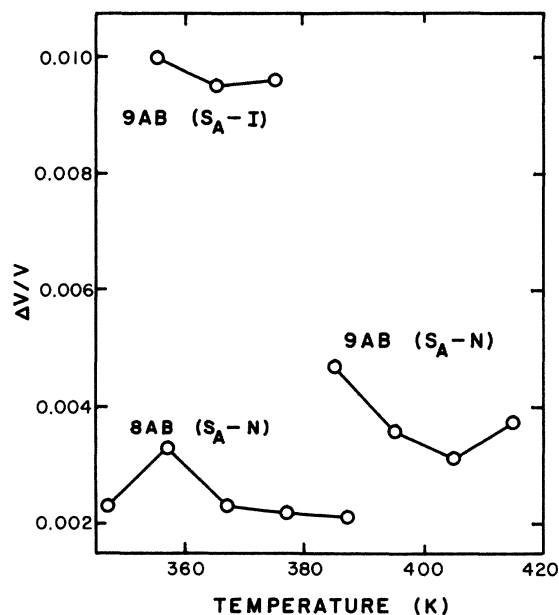


FIG. 4. Relative volume change at the smectic-*A*–nematic and smectic-*A*–isotropic transitions. The volume change at the smectic-*A*–nematic transition in 7AB was too small to be observed using this technique.

where T_0 and V_0 represent a point on the coexistence curve. γ is sensitive to the relative strength of steric repulsions as compared to attractive interactions¹⁴ and has been measured for other liquid-crystal phase transitions. The data from our measurements for the nematic–isotropic and smectic-*A*–nematic transitions are shown in Figs. 5 and 6. The γ values for the nematic–isotropic transitions are virtually the same for all three compounds and typical of work done in the past. The smectic-*A*–nematic value is higher than values found for both smectic-*A*–nematic transitions in reentrant systems and smectic-*C*–nematic transitions.⁴ The measurement of this parameter for the smectic-*A*–isotropic transition represents the first data of this kind.

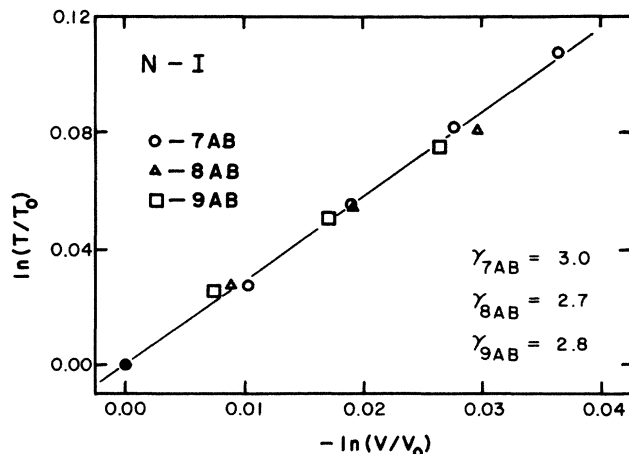


FIG. 5. Volume and temperature dependence along the nematic–isotropic coexistence curve. The γ values represent the slope of least-squares linear fits to the data.

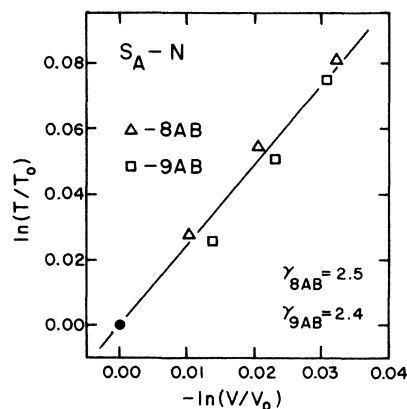


FIG. 6. Volume and temperature dependence along the smectic-*A*–nematic coexistence curve. The γ values represent the slope of least-squares linear fits to the data. The γ value for the smectic-*A*–isotropic transition (data not shown) is 3.0.

DISCUSSION

The existence of a triple point in 9AB, although not a striking finding, does have some general implications. Many homologous series follow the pattern of the dialkylazoxybenzenes in that the nematic phase disappears in the higher homologs at atmospheric pressure. It could very well be that many of these series contain a member with a triple point at higher pressure. Therefore, it would seem to be the case that in 9AB, and perhaps more generally, the nematic phase is favored over the smectic phase at elevated pressure. This is exactly what happens in reentrant systems due to the difficulty of packing dimers with bulky central cores into smectic layers. Perhaps the steric interactions associated with packing compounds with aromatic cores and hydrocarbon endchains are somewhat similar to the packing of dimers. It should be pointed out that at least one theoretical investigation into such a question yields a reentrant nematic phase, i.e., enhancement of the nematic phase under pressure, for molecules comprised of a rigid central core and semiflexible endchains.¹⁵

Figure 3 is direct confirmation of the theoretical prediction that the volume change at the nematic–isotropic transition increases when a smectic-*A*–nematic transition gets closer. Data taken at atmospheric pressure for this series indicates a strong odd-even effect, with volume changes for the even members being much less than the odd members.² This would seem to imply that 8AB should have a volume change smaller than 7AB. The closeness of the smectic-*A*–nematic transition in 8AB (2.1 K), however, completely masks the odd-even effect, producing a transition with a larger volume change. The smectic-*A*–nematic transition is even closer in 9AB, resulting in an even larger volume change. In all three of these compounds, the nematic phase widens as the pressure and temperature are increased. This can be seen for 9AB in Fig. 2. The theory would predict that this will cause the volume change to decrease as the temperature or pressure is increased, but more important, the form of Eq. (6) indicates that the decrease should be faster the closer the smectic-*A*–nematic transition. Such an effect is evi-

dent in Fig. 3, where straight line fits to the data have been drawn to illustrate this trend.

The decrease in the volume change at the smectic-*A*–nematic transition as the nematic temperature interval increases as shown in Fig. 4 (recall that the volume change in 7AB was too small to be seen) is a well-known effect. It was first explained theoretically by the same coupling of order parameters discussed earlier,¹⁶ but recent work has shown that it is the singular part of a continuous transition which actually decreases as the width of the nematic phase increases.¹¹ Investigation of the smectic-*A*–isotropic transition under pressure, however, is a new endeavor. The data in Fig. 4 compares favorably with data for this compound taken at atmospheric pressure.

The measured γ values invite comparison to previous work. The similarity of the γ values for the nematic-isotropic transition of all three compounds indicates that the smectic fluctuations have little effect on this property. The values are higher than the values found in the dialkoxyazoxybenzene series,^{4,13} providing evidence that either steric repulsions play a larger role or attractive interactions play a smaller role in the series lacking the oxygen atom at the linkage between aromatic core and hydrocarbon endchain. Note that the smectic-*A*–isotropic transition is also similar in this regard. Also of interest is the fact that the smectic-*A*–nematic γ values are higher than those measured either the smectic-*A*–nematic transition of a reentrant compound or the smectic-*C*–nematic transition.⁴

CONCLUSION

Measurements in the neighborhood of a smectic-nematic-isotropic triple point are useful in elucidating the role of smectic fluctuations in the transition from the nematic to isotropic phase. The results presented here confirm the validity of one theoretical idea which has been proposed to explain the nematic–smectic-*A* transition.

Such a triple point should be most useful for experimentalists investigating pretransitional behavior in the isotropic phase, since the width of the nematic phase can be varied at will. Rather than perform the experiments under pressure, investigations can utilize mixtures, varying the composition of the system instead of the pressure. Such triple points have already been reported in the literature;^{9,12} our data demonstrates that the 8AB/9AB system should possess a triple point at atmospheric pressure for some intermediate composition. We hope the work presented in this paper will encourage others to utilize these triple points in their investigations.

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¹P. E. Sokol and J. T. Ho, *Appl. Phys. Lett.* **31**, 487 (1977).

²W. H. deJeu and W. A. P. Claasen, *J. Chem. Phys.* **68**, 102 (1978).

³M. F. Achard, G. Sigaud, and F. Hardouin, in *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer-Verlag, Berlin, 1980), p. 149.

⁴C. S. Johnson and P. J. Collings, *J. Chem. Phys.* **79**, 4056 (1983).

⁵Y. Guichard, G. Sigaud, and F. Hardouin, *Mol. Cryst. Liq. Cryst. Lett.* **102**, 325 (1984).

⁶B. Pouligny, J. P. Marcerou, J. R. Lalanne, and H. J. Coles, *Mol. Phys.* **49**, 583 (1983).

⁷A. Gohin, C. Destrade, H. Gasparoux, and J. Prost, *J. Phys. (Paris)* **44**, 427 (1983).

⁸M. A. Anisimov, E. E. Gorodetskii, and V. E. Podnek, *Pis'ma*

Zh. Eksp. Teor. Fiz. **37**, 352 (1983) [*JETP Lett.* **37**, 414 (1983)].

⁹M. A. Anisimov, V. I. Labko, G. L. Nikolaenka, and I. K. Yudin, *Mol. Cryst. Liq. Cryst. Lett.* **2**, 77 (1985).

¹⁰G. S. Attard and G. R. Luckhurst, *Chem. Phys. Lett.* **117**, 523 (1985).

¹¹M. A. Anisimov, *Pis'ma Zh. Eksp. Teor. Fiz.* **37**, 11 (1983) [*JETP Lett.* **37**, 11 (1983)].

¹²J. W. Goodby and G. W. Gray, *J. Phys. (Paris) Colloq.* **40**, C3-363 (1979).

¹³R. V. Tranfield and P. J. Collings, *Phys. Rev. A* **25**, 2744 (1982).

¹⁴R. Alben, *Mol. Cryst. Liq. Cryst.* **13**, 193 (1971).

¹⁵F. Dowell, *Phys. Rev. A* **28**, 3520 (1983); **28**, 3526 (1983).

¹⁶W. L. McMillan, *Phys. Rev. A* **4**, 1238 (1971); **6**, 936 (1972).