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Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Velasco, E. , Mederos, L. and Sluckin, T. J.(1996) 'Molecular theory of smectic C liquid crystals', Liquid Crystals, 20: 4, 399 — 409

To link to this Article: DOI: 10.1080/02678299608032053

URL: http://dx.doi.org/10.1080/02678299608032053

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LIQUID CRYSTALS, 1996, VOL. 20, NO. 4, 399-409

Molecular theory of smectic C liquid crystals

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(*Received 14 August 1995; accepted 13 October 1995*)

We generalize an earlier density functional theory of liquid crystals by Mederos and Sullivan. The original theory took account of anisotropic hard core interactions, and for suitable intermolecular interactions predicted nematic and smectic A phases as well as isotropic liquid and vapour phases. In this generalization we also take into account quadrupolar or dipole-induced dipole interactions. The modified theory now also predicts the existence of a smectic C phase.

1. Introduction

The molecules from which the liquid crystalline phases are built are sometimes complex, sometimes flexible, but always extremely anisotropic. A qualitative understanding of the phase progression for particular liquid crystals can sometimes be obtained from a consideration of the nature of the anisotropic interactions between the molecules. Nevertheless, a detailed description of the thermodynamics of particular liquid crystals remains a challenging problem.

Much progress in liquid crystal physics has been obtained using simple models. These models do not represent molecules in a realistic way, but nevertheless permit simple ideas about the interplay between different forms of interaction potential to be explored. The Maier–Saupe [1] and Onsager [2] theories of thermotropic and lyotropic nematic liquid crystals are well known examples. The density functional theories of liquid crystals which have been widely employed over the last decade put these ideas on a firmer footing [3–10].

In this paper we construct a density functional theory of thermotropic smectic C (S_C) liquid crystals. In so doing we combine ideas from a number of areas, most notably, earlier theories of our own of lyotropic smectic C liquid crystals [11] and of thermotropic smectic A (S_A) liquid crystals [7]. The crucial problem is how to combine effects of shape and longer range dispersion forces self-consistently. For suitable interaction parameters, as temperature is reduced, our theory predicts isotropic fluid, then a nematic or smectic A phase, and finally a smectic C phase. Varying the interaction parameters can eliminate some or all of the liquid crystal phases. We also obtain a vapour phase. At this stage, the phase transitions between the phases are more first order than is observed experimentally, however, and we shall return to this feature of our results at the end of the paper.

The paper is constructed as follows. In § 2 we give a brief background to previous attempts at modelling smectic phases. In § 3 we present the model and theory. In § 4 we present results on the phase diagrams predicted by our theory. Finally in § 5 we give a brief discussion.

2. Theories of smectic phases

The smectic phases are layered phases. In the smectic A phase the molecules are more or less oriented in a direction perpendicular to the layers, whereas in the smectic C phase the director is tilted with respect to the layer normal.

It was long the folklore of the liquid crystal community that an essential ingredient of the physics of the smectic phases was a degree of flexibility in the liquid crystal molecules. That this was not the case was shown by Stroobants *et al.* [12] in a classic set of simulations. These simulations showed that a smectic A phase could be induced in hard spherocylinders at sufficiently high packing fractions. A subsequent density functional theory by Mulder [13] explained easily why this was the case, albeit in an idealized case of perfectly aligned molecules. The transition to a layered phase can be thought of as coming from an effective interaction whose

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0267-8292/96 $12·00

origin is the (entropic) volume exclusion, and whose effect is more marked at high packing fractions.

In small molecule liquid crystals, of course, the S_A phase appears with decreasing temperature rather than increasing density. Nevertheless it is an appealing idea that the essential cause remains a balance between some short range repulsion, whose origin is the molecular shape, and longer range attraction. Somehow the attraction can dominate at lower temperatures. Mederos and Sullivan [7] were able to construct an explicit scheme within which this was the case.

The crucial innovation of Mederos and Sullivan was to use a non-local density functional of the form made popular by Tarazona [14] in his studies of the freezing transition. Density functional theories predict that temperature-driven phase transitions follow from a balance of short range steric repulsion and longer range dispersive attraction. The reference system, with only short range repulsive interactions, was taken to be a system of *parallel* hard ellipsoids, whose interaction could then be extrapolated from a stretched hard sphere fluid. This scheme predicted a sensible phase diagram, with isotropic fluid, nematic and S_A phases in the right places. The scheme gives no insight into more complex smectic phases, however.

Speculation into the molecular origins of the S_C phase go back at least two decades. One idea posits a direct connection between molecular biaxiality and the phase biaxiality implicit in the S_C phase [8, 15]. Alternatively, transverse dipoles can break the uniaxial symmetry of a hard rod [16–18]. The problem with this idea is that a resulting S_C phase would be extremely biaxial and rotations around the molecular long axis would be essentially frozen, which seems not to be the case experimentally [19].

From a different perspective, Barbero and Durand [20] have argued, using essentially macroscopic arguments, that electric quadrupole interactions are a basic physical mechanism underlying not only tilted phases, but also tilted textures at the surface of a nematic phase. Now, the electric quadrupole interaction comes from the V_{224} term in a spherical harmonic expansion of the intermolecular potential. Using more microscopic arguments, a number of authors, including ourselves [21–23] have shown that indeed tilted surface textures arise from just this contribution to the intermolecular potential.

In fact, as shown in detail by van der Meer [24], the effect of the induced dipole potential caused by the presence of off-centre transverse dipoles is rather similar to that of point electric quadrupoles placed at the molecular centres. Both of these potentials have a V_{224} component, although the induced dipole interaction has a r^{-6} behaviour, whereas the quadrupole term has r^{-5} behaviour at long distances. A few years ago Poniewierski and one of the present authors [11] investigated the properties of a fluid of parallel hard cylinders with a superimposed long range V_{224}/r^6 potential. This study showed that a smectic C phase was indeed produced, although some anomalous features of the phase diagram remained. The most striking of these was that, as temperature was decreased, in an intermediate density regime, the phase progression could be from a smectic to a nematic phase, rather than the expected converse.

The results of this study were nevertheless encouraging, given the simplicity of the model, especially in view of the unphysical restriction of perfect orientational order. The present study attempts to combine the attractive features of the model of Poniewierski and Sluckin [11]—which does contain a S_C phase—and that of Mederos and Sullivan [7]—which deals rather more realistically with the thermal onset of smectic behaviour.

3. Model

In this section we shall give a brief account of the model and the numerical techniques used to solve it. We use density-functional theory to calculate the equilibrium structure and thermodynamics of the liquid crystal material. We suppose rigid rod-like molecules whose orientation is uniquely defined by a direction $\hat{\mathbf{\Omega}}$. In the density-functional formalism, the molecular liquid is then characterized by the one-particle distribution function $\rho(\mathbf{r}, \hat{\mathbf{\Omega}})$, where $\mathbf{r}$ is the position of a point in the material. An approximate free-energy functional is then constructed and minimized with respect to the density distribution. For systems with realistic intermolecular interaction potentials, the conventional perturbation theory of liquids gives the free energy as

$$F = F_{\text{ref}} + F_{\text{att}}, \tag{1}$$

where F_{ref} and F_{att} represent the contributions from a reference fluid of purely repulsive molecules, and the perturbation due to attractive forces, respectively. Let us consider the two contributions separately.

3.1. *The attractive contribution to the free energy*

The contribution of the attractive interactions is given in the mean-field approximation

$$F_{\text{att}} = \frac{1}{2} \int\int \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'\, \mathrm{d}\hat{\mathbf{\Omega}}\, \mathrm{d}\hat{\mathbf{\Omega}}' \rho(\mathbf{r}, \hat{\mathbf{\Omega}}) V_{\text{att}}(\mathbf{r} - \mathbf{r}', \hat{\mathbf{\Omega}}, \hat{\mathbf{\Omega}}') \rho(\mathbf{r}', \hat{\mathbf{\Omega}}'). \tag{2}$$

This approximation is in the original spirit of van der Waals' theories of liquids. This approximation has been successfully used in related theories of liquid crystals [5, 7, 8, 11, 13]. More sophisticated theories of simple liquids, such as the Weeks–Chandler–Andersen theory [25], also involve the pair distribution functions in the hard core fluid. We adopt the simplest approximation, namely that $g_{\mathrm{HC}}(\mathbf{r}) = 1$ for allowable configurations. Using a more sophisticated $g_{\mathrm{HC}}(\mathbf{r})$ would considerably complicate the theory, and would almost certainly have little qualitative effect on the form of the results. The principal effect would be to introduce an effective temperature dependence in the parameters A, B, C, D, which we shall introduce below, which characterize the intermolecular potential.

The attractive intermolecular potential between a pair of molecules, V_{att}, can be expanded in spherical harmonics:

$$V_{\mathrm{att}}(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}') = \sum_{ll_1l_2} V_{ll_1l_2}(r) \sum_{m_1m_2m} C(ll_1l_2; m_2m_2m) \times Y_{l_1m_1}(\hat{\mathbf{\Omega}})Y_{l_2m_2}(\hat{\mathbf{\Omega}}')Y^*_{lm}(\hat{\mathbf{r}}). \tag{3}$$

Here all coordinates are referred to a laboratory-fixed reference frame. We truncate the expansion at $l = 2$. We have modelled the components $V_{l_1l_2l}(r)$ by the following Lennard–Jones forms, suggested by the WCA perturbation theory [25]:

$$V_{l_1l_2l}(r) = \varepsilon_{l_1l_2l}\,v(r), \tag{4}$$

where

$$v(r) = \begin{cases} \left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right], & r > 2^{1/6}\sigma \\ -1/4, & r < 2^{1/6}\sigma. \end{cases} \tag{5}$$

Clearly these are arbitrary choices, although they have been used with success in earlier analogous studies [7]. Note that we have chosen the range parameters of all the components to be equal. σ will be identified below as the average diameter of the anisotropic hard core, σ_{eq}.

Using the addition theorem for spherical harmonics, we obtain the following physically more transparent expression for the intermolecular potential:

$$\begin{aligned} V_{\mathrm{att}}&(\mathbf{r},\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}') \\ &= v(r)\{A + BP_2(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') + C[P_2(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{r}}) + P_2(\hat{\mathbf{\Omega}}'\cdot\hat{\mathbf{r}})] \\ &\quad + D[1 - 5(\hat{\mathbf{\Omega}}'\cdot\hat{\mathbf{r}})^2 - 5(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{r}})^2 + 2(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')^2 \\ &\quad + 35(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{r}})^2(\hat{\mathbf{\Omega}}'\cdot\hat{\mathbf{r}})^2 - 20(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{r}})(\hat{\mathbf{\Omega}}'\cdot\hat{\mathbf{r}})(\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')]\}. \end{aligned}$$

The parameters A, B, C, and D are related to the $\varepsilon_{l_1l_2l}$ in the following way:

$$A = \frac{\varepsilon_{000}}{(4\pi)^{3/2}} \quad B = \frac{\surd(5)\varepsilon_{220}}{(4\pi)^{3/2}}$$
$$C = \frac{5\varepsilon_{202}}{(4\pi)^{3/2}} \quad D = \frac{15\varepsilon_{224}}{(4\pi)^{3/2}\surd(70)}. \tag{7}$$

The first term in equation (7) is independent of angular orientation and sets the temperature scale of the liquid–vapour critical point. The B term, which only depends on the relative angle θ between the symmetry axes of the two molecules $\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}'$, promotes nematic formation and is the usual Maier–Saupe term. The C term couples the molecular orientation to the intermolecular vector $\mathbf{r}$ and favours configurations in which the molecules arrange in layers. The D term, which has a quadrupolar symmetry, and which we have discussed in the last section, is expcted to drive the molecules to a tilted configuration. An additional contribution V_{222}, appearing in the expansion (3), will not be considered in the present study.

The one-particle distribution function can be factorized, without loss of generality, as

$$\rho(\mathbf{r},\hat{\mathbf{\Omega}}) = \rho(\mathbf{r})f(\mathbf{r},\hat{\mathbf{\Omega}}), \tag{8}$$

where $f(\mathbf{r},\hat{\mathbf{\Omega}})$ is the orientational distribution function. The latter can also be expressed in a spherical harmonic representation,

$$f(\mathbf{r},\hat{\mathbf{\Omega}}) = \sum_{i=0}^{\infty}\sum_{m=-l}^{l}\left(\frac{2l+1}{4\pi}\right)^{1/2} f_{lm}(\mathbf{r})Y^*_{lm}(\hat{\mathbf{\Omega}}), \tag{9}$$

where $f_{lm}(\mathbf{r})$ are orientational order parameters. In the case of smectic phases these functions depend only on z, which is along the layer normal. At the present level of truncation of the expansion (3), the biaxial smectic C phase can be represented by the density wave $\rho(z)$ and the five coefficients $f_{lm}(z)$ $(m = -2,\ldots,2)$ generated within the subspace $l = 2$. In the undistorted smectic phase, the director will always have the same orientation irrespective of the spatial location of a molecule [26]. We can thus arbitrarily choose the x axis as lying along the projection of the director onto the smectic layers. Mirror symmetry across the xz plane then implies the relation $f_{l,-m} = (-1)^m f_{lm}$, which reduces the number of order parameters to three. It is convenient to redefine these parameters as follows [5]:

$$\eta(z) = f_{20}(z) = \int \mathrm{d}\hat{\mathbf{\Omega}}P_2(\cos\theta)f(z,\hat{\mathbf{\Omega}}), \tag{10a}$$

$$\mu(z) = -\left(\frac{3}{8}\right)^{1/2} f_{22}(z) = \int \mathrm{d}\hat{\mathbf{\Omega}}\sin^2\theta\cos 2\phi f(z,\hat{\mathbf{\Omega}}), \tag{10b}$$

$$\nu(z) = \left(\frac{3}{8}\right)^{1/2} f_{21}(z) = \int \mathrm{d}\hat{\mathbf{\Omega}}\sin 2\theta\cos\phi f(z,\hat{\mathbf{\Omega}}). \tag{10c}$$

The biaxial state of the phase is characterized by nonzero values of μ and ν. The final expression for the attractive free energy per unit volume in terms of the orientational order parameters is

$$\frac{F_{\mathrm{att}}}{V}=\frac{1}{2d}\int_0^d \mathrm{d}z\rho(z)\int \mathrm{d}z'\rho(z')$$
$$\times [A\tilde{v}_{000}(z-z')+B\tilde{v}_{220}(z-z')$$
$$\times (\eta(z)\eta(z')+\tfrac{3}{4}\mu(z)\mu(z')+\tfrac{3}{4}v(z)v(z'))$$
$$+C\tilde{v}_{202}(z-z')(\eta(z)+\eta(z'))+D\tilde{v}_{224}(z-z')$$
$$\times (6\eta(z)\eta(z')+\tfrac{3}{4}\mu(z)\mu(z')-3v(z)v(z'))], \qquad (11)$$

where $\tilde{v}_{l_1l_2l}(z)$ are appropriate projections of the coefficients $v_{l_1l_2l}(r)$ along the z direction,

$$\tilde{v}_{l_1l_2l}(z)=\int \mathrm{d}\mathbf{R}v(r)P_l(z/r), \qquad (12)$$

where $\mathbf{r}=(\mathbf{R},z)$ and $r=|\mathbf{r}|$.

3.2. *The reference free energy*

Let us turn to the contribution from the reference fluid, F_{ref}. A full account of our model for F_{ref} is given by Mederos and Sullivan [7]. There is a contribution from the ideal gas F_{id}:

$$F_{\mathrm{rep}}=F_{\mathrm{id}}+\Delta F_{\mathrm{rep}}$$
$$=k_{\mathrm{B}}T\int \mathrm{d}\mathbf{r}\,\mathrm{d}\hat{\mathbf{\Omega}}\rho(\mathbf{r},\hat{\mathbf{\Omega}})(\log\rho(\mathbf{r},\hat{\mathbf{\Omega}})-1)+\Delta F_{\mathrm{rep}}. \qquad (13)$$

The contribution from the purely repulsive forces ΔF_{rep} is usually described by a reference hard-interaction model with temperature-independent hard-core. This contribution is simply neglected in the McMillan and Kobayashi [27] treatment. However, it is now clear that these hard core effects are crucial in determining liquid crystalline behaviour and must be included at liquid densities. Different models have been proposed to improve on the old treatments, using both isotropic and anisotropic hard interactions. In her studies of nematic ordering at fluid interfaces, Telo da Gama [5] used simple hard-sphere interactions (in a local-density approximation),

$$\Delta F_{\mathrm{rep}}=\Delta F_{\mathrm{HS}}[\rho(\mathbf{r})]=\int \mathrm{d}\mathbf{r}\rho(\mathbf{r})\Delta\Psi_{\mathrm{HS}}(\rho(\mathbf{r})), \qquad (14)$$

where $\Delta\Psi_{\mathrm{HS}}(\rho)$ is the excess of free energy per particle of a hard-sphere fluid of density ρ.

By an appropriate scaling, this approximation also applies to a system of *perfectly aligned hard ellipsoids* of major and minor diameters $\sigma_{\parallel}$ and $\sigma_{\perp}$, respectively. Now, since we would like to describe smectic phases, which exhibit density oscillations over molecular length scales, we have to go beyond the local approximation of equation (14) and use a non-local theory, the simplest of which is due to Tarazona [14].

In this theory

$$\Delta F_{\mathrm{rep}}=\int \mathrm{d}\mathbf{r}\rho(\mathbf{r})\Delta\Psi_{\mathrm{HS}}(\bar{\rho}(\mathbf{r})), \qquad (15)$$

where $\bar{\rho}(\mathbf{r})$ is an averaged local density which takes account of local interactions. The mapping between hard spheres and perfectly aligned ellipsoids is taken care of by defining

$$\bar{\rho}(\mathbf{r})=\int \mathrm{d}\mathbf{s}w(s;\bar{\rho}(\mathbf{r})\sigma_{\mathrm{eq}}^3)\rho(\mathbf{r}+\tilde{\sigma}\cdot\mathbf{s}), \qquad (16)$$

where σ_{eq} is an equivalent hard-sphere diameter satisfying $\sigma_{\mathrm{eq}}^3=\sigma_{\parallel}\sigma_{\perp}^2$, w is a weight function, and $\tilde{\sigma}$ is a diagonal tensor with components $\sigma_{\perp}$, $\sigma_{\perp}$ and $\sigma_{\parallel}$ in the x, y and z directions, respectively.

The weight function plays an important role in defining the region over which densities must be averaged in order to calculate the effective local density in equation (16). This density is then used to calculate a local free energy density in equation (15). The criteria for a sensible choice of weight function in a non-local density functional theory have been extensively discussed in the literature [7], and our particular choice has been discussed in more detail elsewhere [14]. We remark here only that our weight function involves averaging over a direction perpendicular to the layers; the length scale of this averaging is given by the average diameter of the reference hard core molecules, and the criterion for the averaging is designed by scaling these molecules in one direction to hard sphere fluids whose properties are well understood.

The free energy per unit volume is then written as

$$\frac{\beta F}{V}=\frac{\beta F_{\mathrm{att}}}{V}\times\frac{1}{d}\int_0^d \mathrm{d}z\rho(z)$$
$$\times[\log\rho(z)-1+\beta\Delta\Psi(\bar{\rho}(z))-S_{\mathrm{rot}}(z)], \qquad (17)$$

where d is the layer spacing. In the above equation, the ideal-gas free energy has been split into translational and rotational parts,

$$\frac{\beta F_{\mathrm{id}}}{V}=\frac{1}{d}\int_0^d \mathrm{d}z\rho(z)[\log\rho(z)-1]-\frac{1}{d}\int_0^d \mathrm{d}z\rho(z)S_{\mathrm{rot}}(z), \qquad (18)$$

where the local rotational entropy per particle is

$$S_{\mathrm{rot}}(z)=-\int \mathrm{d}\hat{\mathbf{\Omega}}f(z,\hat{\mathbf{\Omega}})\log 4\pi f(z,\hat{\mathbf{\Omega}}), \qquad (19)$$

and $\beta=1/k_{\mathrm{B}}T$.

3.3. *The rotational entropy*

The evaluation of the rotational entropy has posed problems in a variety of liquid crystal theories. The early truncation of the potential function eliminates order parameter components with indices higher than $l=2$ from the mean-field term. It is not, however, permissible to truncate the expansion of the orientational distribution function in evaluating the rotational entropy. To do so would destroy the Boltzmann form of the distribution function in terms of an effective potential. Nevertheless, a functional dependence of the rotational entropy on the order parameters is absolutely necessary; this expansion must remain valid when the system is out of equilibrium. In the case of the nematic liquid crystal, a detailed analysis of this problem has been carried out by Katriel *et al.* [28]. The analysis which follows is a more sophisticated version of their argument.

We shall show that the exact rotational entropy can be expressed as a functional of the three $l=2$-order parameter components when the mean field does not couple to higher order components. Demanding that the free-energy functional (1) be stationary with respect to $f(z,\hat{\mathbf{\Omega}})$ leads to the integral equation

$$f(z,\hat{\mathbf{\Omega}})=\frac{e^{-\beta V_{\mathrm{eff}}(z,\hat{\mathbf{\Omega}})}}{\int \mathrm{d}\hat{\mathbf{\Omega}}\, e^{-\beta V_{\mathrm{eff}}(z,\hat{\mathbf{\Omega}})}}. \tag{20}$$

The effective potential V_{eff} is defined by

$$V_{\mathrm{eff}}(z,\hat{\mathbf{\Omega}})=\int \mathrm{d}\mathbf{r}'\,\mathrm{d}\hat{\mathbf{\Omega}}'\rho(z')f(z',\hat{\mathbf{\Omega}}')V_{\mathrm{att}}(\mathbf{r}-\mathbf{r}',\hat{\mathbf{\Omega}},\hat{\mathbf{\Omega}}'), \tag{21}$$

and can be written in terms of functions $I_i(z)$, $i=0,\ldots,3$ (whose explicit expressions are not given) as

$$V_{\mathrm{eff}}(z,\theta,\phi)=I_0(z)+I_1(z)P_2(\cos\theta)+I_2(z)\sin 2\theta\cos\phi + I_3(z)\sin^2\theta\cos 2\phi. \tag{22}$$

The functions $I_i(z)$ are given as convolutions of the coefficients $\tilde{V}_{l_1 l_2 l}(z)$ and the order parameters $\rho(z)$, $\eta(z)$, $\sigma(z)$ and $\nu(z)$. Equation (20) can be written in terms of only $I_1(z)$, $I_2(z)$ and $I_3(z)$,

$$f(z,\hat{\mathbf{\Omega}})=\frac{e^{-[I_1(z)P_2(\cos\theta)+I_2(z)\sin 2\theta\cos\phi+I_3(z)\sin^2\theta\cos 2\phi]}}{\int \mathrm{d}\hat{\mathbf{\Omega}}\, e^{-[I_1(z)P_2(\cos\theta)+I_2(z)\sin 2\theta\cos\phi+I_3(z)\sin^2\theta\cos 2\phi]}} \tag{23}$$

We stress that this equation is a condition for equilibrium and therefore is only satisfied *at equilibrium*: we cannot use it to compute the entropy since it defines f self-consistently. Now for a non-equilibrium $f(z,\hat{\mathbf{\Omega}})$ we can use the functional form (23) to write, without loss of generality,

$$f(z,\hat{\mathbf{\Omega}})=\frac{e^{A_1(z)P_2(\cos\theta)+A_2(z)\sin 2\theta\cos\phi+A_3(z)\sin^2\theta\cos 2\phi}}{\int \mathrm{d}\hat{\mathbf{\Omega}}\, e^{A_1(z)P_2(\cos\theta)+A_2(z)\sin 2\theta\cos\phi+A_3(z)\sin^2\theta\cos 2\phi}}, \tag{24}$$

where $A_i(z)$ are undetermined functions of z, which can be thought of as external one-body potentials which set up a predetermined orientational structure in the system (given by η, σ and ν). Using equations (10) and (19), the rotational entropy can be shown to be given in terms of these functions as

$$S_{\mathrm{rot}}(z)=A_1(z)\eta(z)+A_2(z)\nu(z)+A_3(z)\sigma(z) - \log\int\frac{\mathrm{d}\hat{\mathbf{\Omega}}}{4\pi} \times e^{A_1(z)P_2(\cos\theta)+A_2(z)\sin 2\theta\cos\phi+A_3(z)\sin^2\theta\cos 2\phi} \tag{25}$$

Now for given order parameters $\eta(z),\sigma(z),\nu(z)$, the entropy can be computed from (25) by inverting equations (10), with $f(z,\hat{\mathbf{\Omega}})$ given by (24), thus obtaining the parameters $A_i(z)$. Note that z merely plays the role of a label in this procedure.

3.4. *Theoretical procedure and numerical method*

It has been shown by Mederos and Sullivan [7] that this model, without the quadrupolar term ($D=0$), contains the essential physics to describe nematic and $\mathrm{S_A}$ phases, as well as liquid–vapour coexistence. Poniewierski and Sluckin [11] have also shown that in a simplified model with perfect orientational order a non-zero quadrupolar term ($D\neq 0$) induces tilted smectic phases. In a tilted smectic phase, molecules adopt a layered configuration in which their symmetry axes tilt away from the layer normal. The tilt is described by an angle ψ. If d_{A} is the layer spacing in the smectic A phase, the corresponding quantity in the tilted or smectic C phase will be given approximately by $d_{\mathrm{C}}=d_{\mathrm{A}}\cos\psi$. In our extended theory, the tilt angle is automatically incorporated into the description of the mean field through the orientational order parameters.

The tendency of the system towards tilting which arises from the effect of the quadrupole is opposed by the C term and the hard core. The hard-core contribution is difficult to model. We have tried, therefore, to simplify this portion of the problem as much as possible. The physical intuition is that for non-zero tilt, the molecules have less free volume at their disposal to move within the layer, leading to an increase of steric energy in the layer. We now describe the way in which this effect is incorporated into the theory.

In our model, the hard core consists of parallel ellipsoids of diameters $\sigma_\perp$ and $\sigma_\parallel$. The ellipsoids are in turn parallel to the layer normal or z direction. The local energy per particle is given by the hard-sphere free energy evaluated at the average density $\bar{\rho}(z)$, which is a weighted average of the density wave over an ellipsoidal volume related to the molecular volume; the weight function w is isotropic and has the range of the direct correlation function.

A crucial part of the modelling process concerns the way in which tilting the director with respect to the layer normal affects the reference hard core system. We modify the hard-core major diameter according to $\sigma_\parallel(\psi) = \sigma_\parallel \cos\psi$; the ellipsoids do not tilt, but the molecular volume remains constant. There is then an increase in the local average density of the layer and a corresponding increase in the energy. This is because $\sigma_\perp$ will be larger and the contribution from the maximum of the density wave to the weighted average over the modified molecular volume will be more important. This effect is compensated by the relaxation of the layer spacing to fill the interlayer free volume. The coupling between the layer spacing favoured by the hard core and the tilt angle means that, in a constrained minimization of the free energy (at constant tilt angle), the hard-core sets up an underlying structure. The balance between the different mean-field terms determines the final stability of the smectic C phase.

The treatment of the reference hard core system, although it clearly contains some of the important physics of the problem, is not entirely satisfactory. The reference system, for example, has a different symmetry from the real smectic C liquid crystal. We shall briefly return to this question in the final section.

The free energy (18) has been written as a functional of the spatially-varying order parameters ρ, η, μ and v. These functions are periodic along z, with period d, the interlayer spacing. In order to find the equilibrium state of the system, the free energy has to be minimized with respect to all these functions. This is an exceedingly complicated numerical problem, which can be solved only by using sophisticated numerical techniques.

The methodology is as follows. First, the order parameters are discretised on a mesh along the z axis, $\rho_i = \rho(z_i)$, $\eta_i = \eta(z_i)$, etc., $z_i = hi$. Using $h = 0{\cdot}05\sigma_{\mathrm{eq}}$ the number of independent variables exceeds 100 for the values of $\sigma_\parallel$ (around 2) considered. The period d is also an independent variable. We have implemented an efficient conjugate gradient minimization method to deal with such a large number of variables. However, the calculation of phase diagrams entails an unreasonable amount of computer time. A simplification can be introduced by assuming that the distribution function is uniaxial in the reference frame of the director (i.e. neglecting molecular biaxiality). This permits the elimination of one further order parameter. It turns out to be more transparent in this case to take the remaining two independent order parameters as the tilt angle ψ, and the degree of orientational order around the director, $\eta_p(z)$. We assume that the tilt angle remains constant throughout the material and does not depend on z. The relation between the order parameters in the laboratory and director reference frames is, in the uniaxial case,

$$\begin{aligned}\eta(z) &= \eta_p(z)P_2(\cos\psi),\\ \mu(z) &= \eta_p(z)\sin^2\psi,\\ v(z) &= \eta_p(z)\sin 2\psi.\end{aligned} \tag{26}$$

Another practical problem involves the minimization with respect to the period. This requires an extremely fine mesh and consequently an unreasonably large amount of computer time. We thus choose to use a parameterization scheme for the order parameter profiles. The latter can be expanded in a Fourier series along the z direction (normal to the layers), and the free energy minimized with respect to the expansion coefficients. But for highly structured smectics many terms in the series are needed. Because of this, and also to avoid problems with negative densities, we use an exponential parameterization for $\rho(z)$ and $\eta_p(z)$:

$$\begin{aligned}\rho(z) &= \rho_0 N_\lambda \mathrm{e}^{\lambda\cos(2\pi z)/d}\\ \eta_p(z) &= \eta_0 N_{\lambda_1} \mathrm{e}^{\lambda_1\cos(2\pi z)/d},\end{aligned} \tag{27}$$

where N_λ, N_{λ_1} are normalization constants, ρ_0 is the mean density and η_0 gives the nematic order.

It eventually became clear that the free energy and thermodynamic behaviour of the system are not severely influenced by the simplifying assumption of taking the orientational profile $\eta_p(z)$ as a constant, $\eta_p(z) = \eta_0$. This is equivalent to making a decoupling approximation at the level of the one-particle distribution function,

$$\rho(z, \hat{\mathbf{\Omega}}) \approx \rho(z) f(\hat{\mathbf{\Omega}}), \tag{28}$$

which, for highly ordered smectics, works very well.

It therefore finally turned out to be sufficient to consider the free energy as a variational function of the parameters λ, η_0, ψ and d for fixed density ρ_0 and temperature T. In our later runs, a standard Newton–Raphson minimization algorithm was used. A set of selected checks were carried out using the full minimization conjugate gradient scheme. In this way, we were able to conclude that the two approximations introduced above do not play any significant role as far as the determination of the phase diagram is concerned.

In the calculations, a non-dimensional temperature scale is set by defining $T^* = k_{\mathrm{B}}T/A$, making it convenient to rescale B, C and D by $B^* = B/A$, $C^* = C/A$ and $D^* = D/A$. The non-dimensional densities are defined by

$\rho_0^* = \rho_0\sigma^3$. In what follows we may without ambiguity drop the asterisks.

4. Results

In their model for smectic C phases, Poniewierski and Sluckin (PS) [11] used a hard-cylinder core in Onsager approximation and a quadrupolar interaction considered in a mean field approximation. It is important to note that in this model the molecular orientations are frozen, i.e., the nematic order parameter is set to one. PS found nematic, S_A and S_C phases, with second order phase transitions between all pairs of phases, and also a NAC point. In the quadrupole (or temperature)–density plane an interesting feature was observed consisting of the smectic phases being less stable with respect to the nematic as quadrupole (temperature) was increased (decreased). It was argued that this result could be an artifact of the approximation for the hard core, or alternatively a real feature resulting from the tendency of the quadrupole to stabilize the nematic relative to the smectic phases.

We first make contact with the work of PS by studying, within our model, the limit of perfect order. This enables us to check whether some of the global features of the two models, such as the phase diagram and the order of the phase transitions separating the phases, were comparable. For typical values of other parameters, the results for the temperature–quadrupole (T–D) phase diagram are shown in figure 1. We find that indeed the same three phases occur as in PS.

We observe that, by contrast with the PS model, where the only mean-field term is a quadrupole, in our model there are three attractive terms. As a result T and D can no longer be combined into a single universal parameter. The values of $\sigma_\parallel$, B and C determine the regions of stability of the isotropic, nematic and S_A phases. The D-term favours a S_C and affects only the smectic phases. It thus controls the location of the N–S_A, N–S_C and S_A–S_C phase boundaries. From figure 1 it is clear that an increasing quadrupole decreases the stability of the S_A with respect to both nematic and S_C. The quadrupole thus discourages the formation of a layered phase in which all the molecules point at directions perpendicular to the layer. We shall present additional evidence of this below.

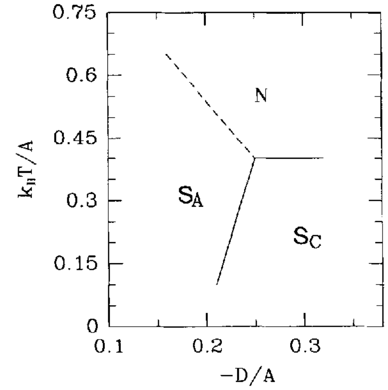

Figure 1. The $T-D$ phase diagram in the limit of perfect nematic order, with $\sigma_\parallel = 2{\cdot}25$, $B = 0{\cdot}3$, $C = 0{\cdot}34$ and $\rho_0 = 1$.

Of some significance is the fact that the S_A–S_C and N–S_C transitions are first order whereas in the PS model they are second order. We do find that the N–S_A transition is almost certainly second order all the way down to $D = 0$, as in the PS model. It is possible that the order of these transitions changes for longer molecules, but we have not been able to carry out calculations to check this point. It is, however, important to bear in mind that the PS calculations were done with a molecular length-over-width ratio of 5; increasingly longer molecules should favour second order transitions. However, our $\sigma_\parallel/\sigma_\perp$ is not directly comparable to their L/D since they do not play similar roles in their respective theories [7].

When the constraint of perfect nematic alignment is relaxed, the question is whether the S_C phase appears at all. The quadrupolar interaction favours a tilted configuration in a layer when the molecules are forced to stay parallel to each other. However, when molecules are free to rotate around axes perpendicular to their symmetry axes, the minimum energy of a pair of molecules with linear quadrupoles corresponds to a 'T' configuration, which is incompatible with a layered structure. This may destroy the nematic order, and hence with it the smectic C order. The stability of the S_C phase will depend on a delicate balance between the hard core and C term, which prevent the layer from tilting, and the quadrupole or D term, which favours the tilt, if only nematic order can be maintained.

Using the full (free orientations) model, we first equilibrated a S_A phase with $\sigma_\parallel = 2{\cdot}25$, $B = 0{\cdot}3$ and $C = -0{\cdot}34$. In the results which follow, the B and C parameters will take these values. This choice was motivated by the work of Mederos and Sullivan [7] who calculated the complete phase diagrams in the $T - \rho_0$ and $P - T$ planes. For these parameters, the phase diagram exhibits nematic and S_A phases, with I–N–S_A and V–I–S_A triple points and the nematic phase is only moderately stable. At $T = 0{\cdot}15$, with mean density of $\rho_0 = 0{\cdot}9$, the system is well inside the region of S_A stability. The quadrupole was then switched on, and we performed constrained minimisations with fixed tilt. In figure 2 we present results for the free energy of the constrained S_C, relative to the S_A, for different values of the quadrupole parameter.

As the quadrupole strength is increased, the system finds it increasingly favourable to tilt. For $D = -0{\cdot}32$,

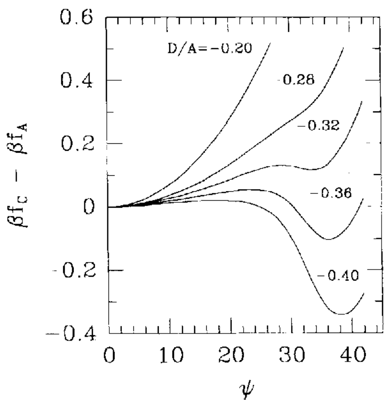

Figure 2. Helmholtz free energy as a function of angular tilt in a smectic phase, showing increasing stability of the S_C phase as quadrupolar strength D is increased. Phase and molecular parameters as discussed in the text.

the tilted structure is mechanically metastable with respect to the S_A, and for still larger D it becomes more stable. It is interesting to note that the minimum of the free energy occurs at $\psi \approx 37°$, and that the transition is first order since the free energy exhibits a barrier. The quadrupolar energy of a layered arrangement of parallel molecules is a minimum for an angle of $\approx 49°$. The occurrence of tilt angles less than that reflects the competition between quadrupole and the other molecular forces. The results embodied in figure 2 demonstrate the possibility of having a tilted smectic phase in a model with quadrupolar forces when the latter compete with other smectic-forming interactions.

Figure 3 shows the behaviour of the parameter λ, related to the smectic order parameter, as a function of tilt angle. As can be seen from the figure, the layers become more structured as the system tilts and the smectic order parameter peaks precisely at the tilt angle where the free energy presents its minimum. This shows the strong coupling between the structural parameters of the theory. Likewise, the nematic order parameter, depicted in figure 4, increases with the tilt angle, which reflects the increasing difficulty found by the molecules to disorder orientationally as the packing in the layers becomes higher. Figures 3 and 4 show that for a tilt angle of $\approx 30{\cdot}6°$, the effect of the quadrupole essentially vanishes. At this tilt angle, the energy of two parallel molecules interacting via a quadrupole is precisely zero. This effect remains even when the nematic order is not perfect so long as the distribution around the director is symmetric.

We now discuss the phase behaviour of the model. We set the quadrupole parameter $D = -0{\cdot}36$, and consider two values of $\sigma_{\|} = 2{\cdot}00$ and $\sigma_{\|} = 2{\cdot}25$. For shorter ellipsoids, no stable S_C phase was found. The corresponding phase diagrams are presented in figures 5 and 6. For $\sigma_{\|} = 2{\cdot}00$, the S_A phase is not stable and the phase diagram shows (apart from the vapour phase) isotropic, nematic and S_C phases separated by first order phase boundaries. Increasing the molecular elongation to $\sigma_{\|} = 2{\cdot}25$ favours the S_A phase which, however, supersedes the nematic. In figure 7 we show how the tilt angle behaves as a function of temperature at constant density. The tilt angle reduces very slightly as temperature is increased, but this change is essentially insignificant.

An unphysical feature of the model appears at higher temperatures when trying to locate the I–S_A transition; this seems to be second order, rather than first order as expected. We have extended the calculations to include a periodic wave in η_p according to (27) and looked for possible effects arising from couplings with the density wave. This does not appear to change the behaviour. We are presently investigating this anomaly in more detail.

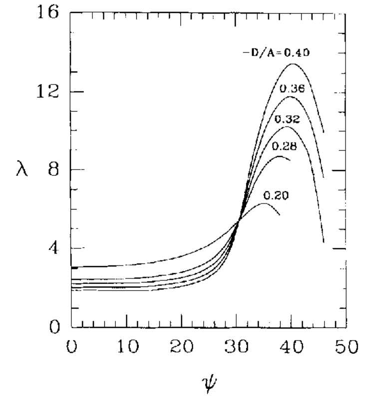

Figure 3. The quantity λ as a function of tilt angle ψ for the same phase parameters as in figure 2. The ratio $r = \rho_{\max}/\rho_{\min} = e^{2\lambda}$. Thus $\lambda = 3$ corresponds to $r \approx 300$, and $\lambda = 14$ corresponds to $r \approx 10^{12}$.

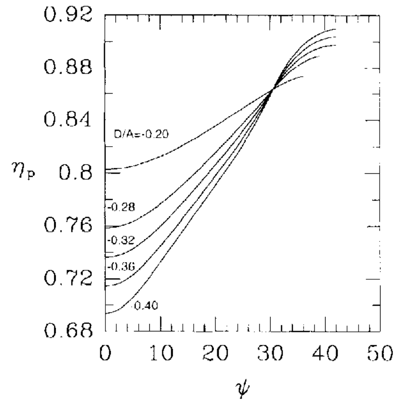

Figure 4. The nematic order parameter η_p as a function of tilt angle, for the system of figures 2 and 3.

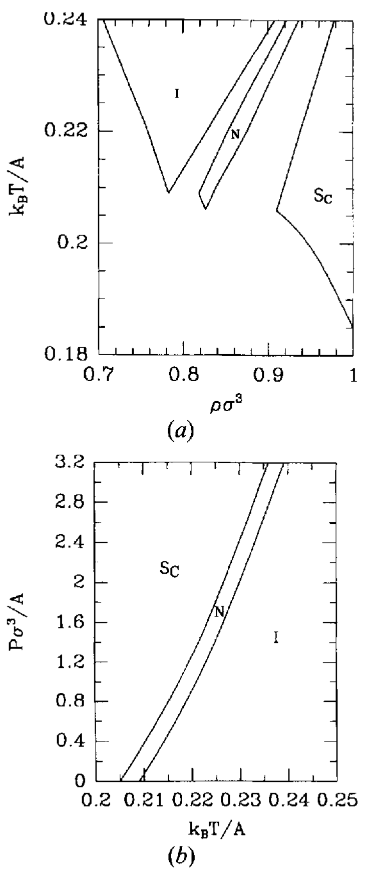

Figure 5. (*a*) Phase diagram in ρ–T plane for the system discussed in the text with $\sigma_\parallel = 2{\cdot}00$ showing I, N and S_A phases. (*b*) Same phase diagrams in P–T plane.

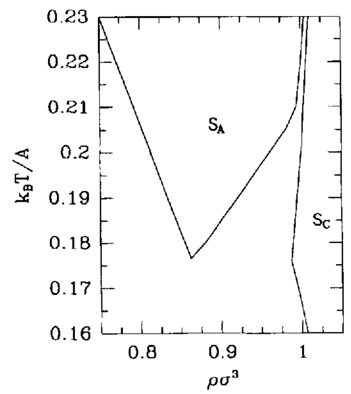

Figure 6. Phase diagram in ρ–T plane for system discussed in text with $\sigma_\parallel = 2{\cdot}25$ showing I, N and S_A phases.

5. Discussion and conclusions

In the model without a quadrupole, the parameters of the model, B, C and $\sigma_\parallel$ can be varied, and quantitatively different phase diagrams are obtained [7]. The region of S_A stability on the phase diagram depends crucially on the value of C. However, the nematic phase is not affected by either C or D since the effect of terms $V_{l_1 l_2 l}$ on uniform phases vanishes unless $l = 0$. For a high enough value of C, the smectic phase dominates at the temperatures of interest, in the sense that along liquid–vapour coexistence, the sequence of phases is isotropic–S_A. The nematic phase is pushed to high temperatures and the region of nematic stability reduced. For low values of C, the smectic A phase is stable only at very low temperature.

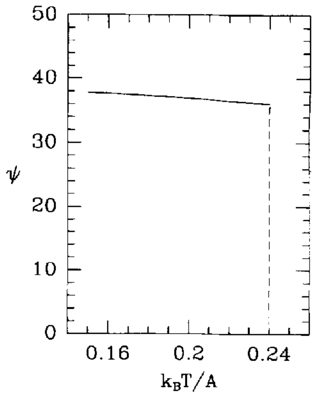

Figure 7. Temperature dependence of the tile angle ψ, as discussed in the text; $\sigma_\parallel = 2{\cdot}25$, $\rho_0 = 0{\cdot}9$.

Mederos and Sullivan [7] have shown that in the present theory the formation of the smectic A phase results from coupling of repulsive and attractive interactions. For weakly anisotropic cores, the stability of the smectic phase induced by the C term is pre-empted by solid formation, whereas only when both $\sigma_\parallel$ and C are simultaneously large do genuine smectic phases occur. The mechanism underlying the formation of smectic phases in this theory has been extensively discussed in [7]. The stability of the system against density fluctuations in one dimension can be understood by examining the q-vector dependence of the free-energy Fourier transform. The hard-sphere contribution favours ordering at a weakly density-dependent wavelength which is roughly equal to $\sigma_\parallel$ (see figure 2 of Mederos and Sullivan). On the other hand, the A and B contributions discourage order at any finite wavelength, whereas the C contribution presents a minimum at some wave number which competes with the hard core minimum. This is demonstrated in figure 8. It is from this competition that a periodic density wave settles at some period $d \approx \sigma_\parallel$.

With the addition of the quadrupole, the S_A phase becomes less stable with respect to both nematic and S_C phases. We show in figure 9 how the smectic and nematic order parameters λ, η of a constrained smectic A vary as a function of increasing quadrupole. Both order parameters are dramatically reduced. A large quadrupole is

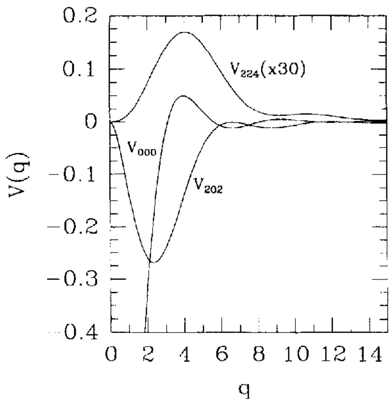

Figure 8. *B*, *C* and *D* contributions to the Fourier components $V_n(q)$ of the mean field potentials $I_n(z)$ defined in equation (22).

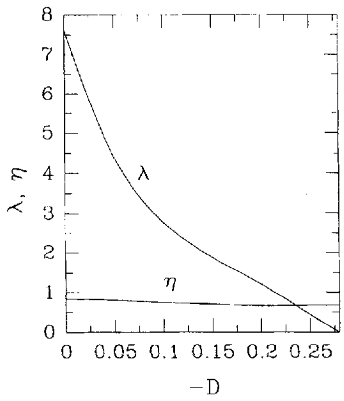

Figure 9. The effect of adding quadrupolar potential interaction terms onto the nematic and smectic order parameters in the S_A phase. Same phase parameters as in figure 4.

required to overcome the free energy barrier opposing tilt exerted by both the hard core and the *C* term.

The mechanism for this effect can also be discussed in the light of the *q*-vector behaviour of the free energy. One feels intuitively that reducing the value of *C* should favour the formation of a S_C phase. Now, however, the S_A phase simply cannot occur. Herein lies the most obvious defect of the model: the hard core by itself cannot produce a layered structure. As a result, in order to have stable S_A and S_C phases, we need, simultaneously, large values of *C* and *D*. But a large value of *D* has the effect of destroying the stability of the S_A structure, whereas a large *C* kills the nematic. Which of these two phases shares the phase diagram with the S_C will depend on the value of $\sigma_\parallel$. For high $\sigma_\parallel$, the S_A phase is favoured whereas for low $\sigma_\parallel$, the nematic is favoured because the S_A phase now has reduced stability, as compared to the nematic phase whose stability is unaffected by the value of $\sigma_\parallel$. The relative stability of the nematic and S_A phases depends very sensitively on $\sigma_\parallel$.

It thus turned out to be difficult to construct a phase diagram in which all three phases were present at the temperatures of interest. It seems likely that more sophisticated treatment of the basic physics of the hard core is required in order to obtain phase diagrams which more satisfactorily describe the possibility of a continuous transition between the S_A and S_C phases, and thus the possibility of a correct phase progression with decreasing temperature. Work on such a model is in progress.

We gratefully acknowledge the influence of Professor Don Sullivan. This work was partly supported by the 'Acciones Integradas' Grant No. HB141 jointly financed by the British Council and the Ministerio de Educación y Ciencia of Spain. During the initial stages of this work, EV was supported by EPSRC(UK), under Grant No. GR/H68352. Two of us (EV and LM) would also like to acknowledge financial support from DGICYT(Spain) under grant PB91-0090.

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[26] Strictly speaking, we need to establish explicitly that the director orientation is constant as one moves through the smectic medium. However, this seems a harmless starting assumption that is unlikely to be violated.

[27] See, for example, MCMILLAN, W. L., 1971, *Phys. Rev. A*, **4**, 1238; *ibid.*, 1972, **6**, 936; KOBAYASHI, K., 1970, *J. phys. Soc. Japan*, **29**, 101; 1971, *Mol. Cryst. liq. Cryst.*, **13**, 137.

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