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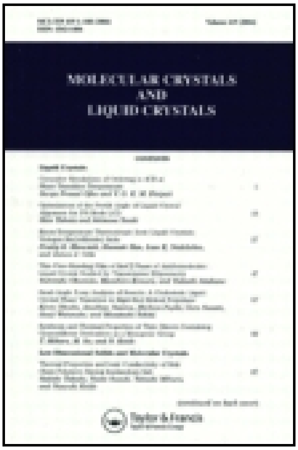

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Electrooptically Switchable Columnar Liquid Crystals: Modeling and Conjectures

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Electrooptically Switchable Columnar Liquid Crystals: Modeling and Conjectures

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Elements of a theory of electrooptically switchable columnar liquid crystals are developed. Assuming spontaneously polarized columns of circular cross section, we consider their dipolar interaction, a special van der Waals interaction of the aromatic molecular cores, and a mean-field theory of a ferroelectric phase transition. Available X-ray data are tentatively assigned to column lattices of low dipolar energy. The agreement between theory and experiments seems satisfactory, especially when the columnar dipole moments per unit length are split and placed at a distance from the column center. However, a dependence of molecular side-chain packing energies on dipolar orientations, so far unmanageable, may intervene and determine which of the low-energy states is the ground state.

Keywords: discotic liquid crystals; electrooptical switchable columnar phases; ferroelectrical liquid crystals; mean-field theory

1. INTRODUCTION

Discotic liquid crystals, also called columnar, were discovered in 1977 by Chandrasekhar et al. [1]. In these materials, each column is typically a stack of dislike molecules consisting of a rigid core and four to eight equal side chains attached to it. It was pointed out early on

This work is dedicated to the late Prof. S. Chandrasekhar. He had invited me to give a talk at a conference celebrating the 25th anniversary of his discovery of discotic liquid crystals. It was an honor to attend, but finishing the manuscript he requested took much longer than anticipated and I missed by far the deadline of the conference proceedings [27].

Special thanks go to my former graduate students, Harald Bock and Gabriela Bagordo, who did many of the experiments that are so difficult to understand. Harald Bock got much support from G. Heppke and advice from G. Scherowsky, as well as from their groups. In turn, he inspired them to extend our studies to other materials so that many of the data that I try to explain were obtained by them. I owe additional thanks to G. Heppke for supplying me over the past years with information related to the subject whenever I turned to him.

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by Prost [2] that the columns can be spontaneously polarized and electrooptically switchable in analogy to smectic C* liquid crystals. As a requirement for spontaneous polarization, the cores have to be collectively tilted while the chains remain more or less normal to the column axis. The core tilt is likely to result from pressure in the region of the side chains, as noted by de Gennes [3]. In addition, the side chains have to possess chiral and polar groups. The molecular contributions to the spontaneous dipole moment are due to the angles between side chains and core. The columnar dipole moment per unit length is perpendicular to the column and parallel to the tilt axis. In the following, switching means reorienting the spontaneous dipole moments of the columns. Electroclinic effects are regarded as negligible. The limiting values of the optical tilt angle (i.e., the angle of rotation of the optical axes) are typically in the range from $\pm 20^\circ$ to $\pm 40^\circ$.

First attempts by Levelut et al. [4] to switch a columnar liquid crystal, which by structure should be ferroelectric, did not succeed. The material studied was a triphenylene derivative with six symmetrically grafted side chains of the type $-O-CO-CH_2-C(CH_3)^*\ H-C_6H_{13}$. The optical tilt angle of its columnar phase with a column lattice of symmetry $P2_1/a$ or $/b$ and two columns per unit cell did not change in electric fields. This was confirmed later on by others applying fields up to electric breakdown near $10^6\,\mathrm{Vcm}^{-1}$ [5,6]. The absence of switching was attributed to the elliptic cross section of the columns, which arises from the core tilt and suppresses their rotation and other mechanisms of reversing their polarity.

Several switchable columnar liquid crystals were found in the 1990s. The first to be discovered was a dibenzopyrene derivative, which exhibits bistable switching [5]. The aromatic core carries eight side chains of the type $-O-CO-C(CH_3)^*\ H-O-C_mH_{2m+1}$ with $m = 6$. Chains of this kind were chosen because their chiral groups are particularly close to the aromatic core. The homolog with $m = 7$, studied in much detail, undergoes a transition between a low-field and a high-field phase at $10\,\mathrm{V}\,\mu\mathrm{m}^{-1}$, with the ferroelectric polarizations being 60 and $180\,\mathrm{nCcm}^{-2}$, respectively [7]. The complete chemical structure of this compound is shown in Fig. 1. Altogether, the four homologous compounds with $m = 4$ to 7 were synthesized and examined [5,7–9]. Their columnar mesophases occur near 100°C and assume large optical tilt angles either overnight or, in an electric field, instantaneously. In the cases $m = 7$ and $m = 5$, the column lattices were analyzed by X-ray scattering. They turned out to be rectangular with six columns per unit cell [10]. In the Debye–Scherrer spectrum, the main peak indicated a basically hexagonal lattice but was split, just resolvably, by little less than 1%. The second strongest peak,

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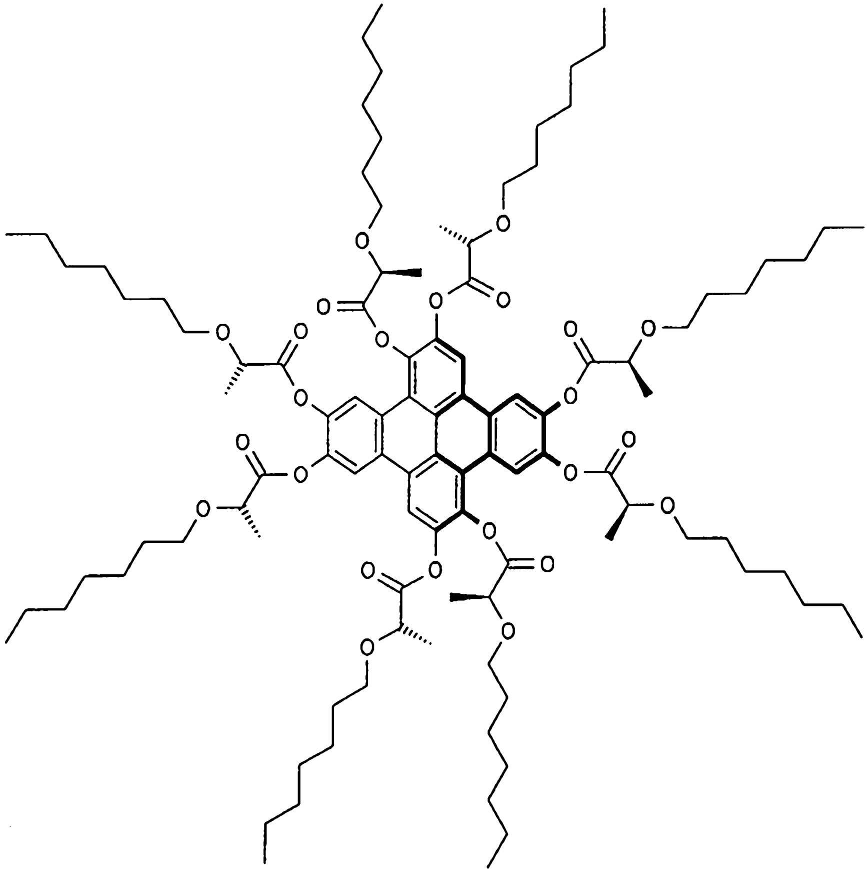

FIGURE 1 Molecule of a switchable dibenzopyrene derivative (with $m = 7$, see main text).

about 1% in intensity of the first, was characteristic of a triplet superstructure. X-ray scattering was done only in the fieldless ground state, as in all further cases.

Phenanthrene derivatives with a variety of side chains equal or similar to those already mentioned were synthesized in another search for switchable columnar liquid crystals [11–14]. Some of the pure chiral compounds and their binary mixtures could be switched. Most of them changed rather steeply (i.e., within $\pm 2\,\mathrm{V\mu m^{-1}}$) from one limiting optical tilt angle to its opposite. Because they were also stable at zero electric field with zero angle, they were called tristable [12,13]. Depending on sample preparation, they sometimes behaved in a bistable manner. The polarization reached values up to $70\,\mathrm{nCcm^{-2}}$, but

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it was not generally measured. Temperatures were between room temperature and 100°C. With a mixture of two phenanthrene derivatives, one with achiral side chains, electrooptical switching progressed gradually at a rate of ±1 degree per $\pm 1\,\mathrm{V\mu m^{-1}}$ [11]. Polarization and column lattice were unknown in this case. The structures of three steeply switching phenanthrene derivatives, a pure one and binary mixtures, were investigated by X-ray scattering [13,14]. In two cases, there was a triplet superstructure of the hexagonal lattice, again with a relative signal strength of roughly 1%. It was absent in one of the binary mixtures and in a racemic mixture prepared of the pure compound.

Gradual switching was also observed, near room temperature, with a pyrene derivative having four symmetrically attached side chains of the type grafted on dibenzopyrene with $m = 7$ [15]. A more or less linear increase of the optical tilt angle reaching 10° at $25\,\mathrm{V}\mu m^{-1}$ is followed by a rather steep rise to about 20° at $35\,\mathrm{V}\mu m^{-1}$ before leveling off. X-ray scattering revealed an apparently hexagonal lattice with a triplet superstructure having once more a relative signal strength of about 1% [10].

There are additional columnar liquid crystals with chiral side chains that have been found to be electrooptically switchable. They are less well explored than those introduced so far; polarizations and usually X-ray data are not available for them nor for closely related homologs. Interestingly, a triphenylene derivative forming a columnar liquid crystal between 120 and 237°C displays bistable switching up to 200°C and gradual switching beyond this temperature [16,17]. Its column lattices have not yet been determined. The chemical structure of its six side chains, each containing a benzene ring, is depicted in Fig. 2. Gradually switching metalloorganic compounds [18,19] and an indenoisochinoline derivative displaying steep switching and a hexagonal column lattice [20] have also been discovered. A brief review of ferroelectrically switchable columnar liquid crystals that addresses some of their physical properties is given in Ref. [21].

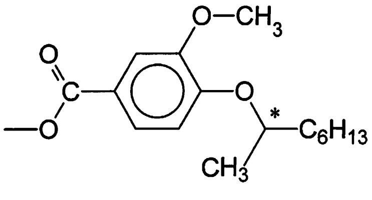

FIGURE 2 One of six equal side chains of a switchable triphenylene derivative.

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The aim of the present article is twofold. We first develop elements of a theory of switchable columnar liquid crystals. The general results are then used in an attempt to understand those examples for which enough data are available, in particular X-ray data, of their column lattices. Unless otherwise stated, the cross sections of the columns are assumed to be circular. The assumption facilitates calculations and seems to be supported by the experiments. Switching by itself speaks for easy rotation of the columns, and the column lattices, where known, are hexagonal or almost so, apart from weakly expressed superstructures. Actually, to avoid empty space the cross sections of the columns would have to be hexagonal rather than circular. The associated increase in the area of 10% is taken into account by a correction factor.

In the case of dibenzopyrene, phenanthrene, and pyrene derivatives, a circular columnar cross section could result from the tilt of the elongated aromatic core if it is in the right direction. On the other hand, triphenylene derivatives with symmetrically attached side chains should always give rise to an elliptic cross section when tilted because of the threefold symmetry axis of the aromatic core. This may explain why the triphenylene derivative of Levelut et al. [4] does not switch but the derivatives of the other three aromatics do. However, the switchable triphenylene derivative with six side chains containing a benzene ring fails to obey such a rule [16,17]. In the absence of X-ray data for it, we do not try to explain the failure. Torsional fluctuations of the columns, which are treated in the context of a ferroelectric phase transition, could provide another mechanism rounding off the columns. They might transform (slightly) elliptic cross sections into almost circular ones, if a collective transformation increases sufficiently the fluctuation amplitudes and, thereby, entropy to make up for the deformational energy.

How circular the cross sections really are is a delicate question. Elliptic cross sections, if suitably arranged in a column lattice, can scatter like a strictly hexagonal lattice with a superstructure, even though their centers may deviate from the ideal lattice sites. Moreover, unlike hard bodies, adjacent columns will interpenetrate with their side chains to an unknown extent. We return to these problems later.

Our treatment of some aspects of switchable mesophases begins with the dipolar interaction of the columns. Uniform dipole moments per unit length are thought to be located at the centers of stiff columns. We are interested in finding energetically favorable column lattices. The total dipolar energy comprises the direct dipolar interactions and the contribution of a remarkable self-stabilization of ferroelectric states. The two column lattices of theoretically lowest total energy, having one or two columns per unit cell, do not agree with any of the

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X-ray data. Looking for the next-best solutions, we find two lattices of surprisingly low energy with six columns per unit cell, which could be compatible with the data.

A special van der Waals interaction between the aromatic core regions of adjacent columns is considered next. We calculate its strength and find its aligning effect to be insignificant as compared to dipolar interaction, despite the large aromatic cores of the molecules in question. However, special van der Waals interaction may come into play when elliptic cross sections are taken into consideration.

The aligning power of dipolar and other interactions is counteracted by torsional fluctuations of the columns. To examine the stability of dipolar order we propose a mean-field theory of a ferroelectric phase transition leading from disordered to uniformly oriented columnar dipoles. In addition to the dipole moment per unit length, the theory involves the twist modulus of the columns. Each column is exposed to the electric field of ferroelectric self-stabilization, zero in the disordered state, but otherwise assumed to rotate freely. The critical temperature estimated from this theory seems sufficiently high to permit ordering by dipolar interaction.

Based on the theoretical results we finally make some tentative assignments of X-ray spectra to column lattices for the switchable columnar liquid crystals. The focus is on the dibenzopyrene, phenanthrene, and pyrene derivatives for which relatively complete data are available. A rather consistent picture emerges when it is taken into account, in a qualitative way, that the molecular dipoles are not at the molecular centers but in the wings of the molecules, roughly halfway between center and radius of the column. Remaining inconsistencies are attributed to a dependence of entropic side-chain packing energies on dipolar orientations.

2. DIPOLAR INTERACTION

The dipolar interaction of spontaneously polarized columns is treated in terms of two-dimensional electrostatics. Omitting torsional fluctuations and any spontaneous twist, we first write down a generic formula for the dipolar interaction energy w per unit length of two parallel columns. Assuming the dipole moments to be uniformly spread over the central axes of the columns, we have

$$w = -w_0 \cos\,(\varphi_2 + \varphi_2)\; d_0^2/d^2 \tag{1}$$

with $w_0 > 0$. Here d is the center-to-center distance of the columns, d_0 being its miminum. The angles φ_1 and φ_2 are made by the directions of

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the dipole moments and a vector connecting the column centers in the plane orthogonal to the columns. In a hexagonal lattice each column has six nearest neighbors, twelve next-nearest neighbors on the second hexagon around it (at $d = \sqrt{3}d_0$ and $d = 2d_0$), eighteen neighbors on the third, and so on. The sum of the contributions of the hexagons will converge, logarithmic divergence being ruled out for periodic patterns.

To obtain an explicit formula for the direct dipolar interaction of two columns, we express the spontaneous polarization of the single column by the maximum ferroelectric polarization of the columnar liquid crystal, $P = P_{\rm sp}^{\rm max}$. The dipole moment per unit length of column may then be written as the product of $P_{\rm sp}^{\rm max}$ and the area of the columnar cross section,

$$P_{\rm sp}^{\rm max}\frac{\pi}{4}d_0^2\lambda, \tag{2}$$

where the factor $\lambda = 2\sqrt{3}/\pi \simeq 1.10$ corrects for replacing the circular cross section by the hexagon. Accordingly, the interaction energy per unit length of two columns becomes

$$w = -\frac{1}{2\pi\varepsilon\varepsilon_0 d^2}\left(P_{\rm sp}^{\rm max}\frac{\pi}{4}d_0^2\lambda\right)^2\cos(\varphi_1 + \varphi_2) \tag{3}$$

where ε is the dielectric constant. Comparison with Eq. (1) leads to

$$w_0 = \frac{\pi d_0^2}{32\varepsilon\varepsilon_0}\left(P_{\rm sp}^{\rm max}\lambda\right)^2, \tag{4}$$

which may be regarded as the standard value of dipolar interaction energy per unit length of column.

In a ferroelectric columnar liquid crystal with spontaneous polarization $\mathrm{P_{sp}} \neq 0$, there will be an electric field in a (fictitious) cylindrical cavity even when the averaged, macroscopic field vanishes. As a rule, the macroscopic field is zero unless a field is applied because the polarization charges on the surface of a ferroelectric tend to be neutralized by real charges. The calculation of the cavity field $E_{\rm cav}$ in the absence of (or minus) a macroscopic field requires a model. We adopt for this purpose the Clausius–Mosotti approach with two modifications. The spherical cavity is replaced by a cylindrical cavity of circular cross section parallel to the columns. And the vacuum dielectric constant ($\varepsilon = 1$) is substituted with the background dielectric constant $\varepsilon > 1$ of an organic liquid devoid of the spontaneous dipole moments of the columns. The cavity field results from the polarization charges lining the

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surface of the fictitious cavity, which are not neutralized by real charges. For circular cylinders one has

$$E_{\text{cav}} = \frac{1}{2\varepsilon\varepsilon_0} P_{\text{sp}}. \tag{5}$$

The cavity field acts on the column(s) positioned in the cavity. Because it has same sign as P_{sp}, it will stabilize the ferroelectric polarization. The energy of self-stabilization per unit volume is

$$W_{\text{self}} = -\frac{1}{2} E_{\text{cav}} P_{\text{sp}}, \tag{6}$$

with the factor 1/2 taking into account that E_{cav} increases in proportion to P_{sp}. Insertion of Eq. (5) in Eq. (6) yields

$$W_{\text{self}} = -\frac{1}{4\varepsilon\varepsilon_0} (P_{\text{sp}})^2. \tag{7}$$

Multiplying this by the area of the columnar cross section gives the energy per unit length of column,

$$w_{\text{self}} = -\frac{\pi d_0^2}{16\varepsilon\varepsilon_0} P_{\text{sp}}^2 \lambda. \tag{8}$$

These energies reach their extrema at maximum polarization $P_{\text{sp}} = P_{\text{sp}}^{\max}$. Comparison with Eq. (4) yields in particular

$$w_{\text{self}}^{\text{extr}} = -2w_0 \frac{1}{\lambda}. \tag{9}$$

For arbitrary column lattices, the total dipolar energy is the sum of the energies of direct dipolar interaction and self-stabilization. The radius of the cylindrical cavity can be chosen such as to accommodate hexagons up to the desired order.

With uniformly oriented columnar dipoles (i.e., for $P_{\text{sp}} = P_{\text{sp}}^{\max}$), the direct dipolar interactions offset one another for each hexagon, regardless of its order. Nevertheless, the total dipolar energy of this state, $-10.88w_0$ for a sextet of columns according to Eq. (9), appears to be lower than the total dipolar energy of any other column lattice. The next most favorable array is made of inline head-to-tail dipole chains alternating in sign, as sketched in Fig. 3.

Because it is antiferroelectric, its total dipolar interaction is the sum of direct interactions. Considering only nearest neighbors (i.e., first hexagons), one finds $-2w_0$ for its energy per unit length of column, which is in very close agreement with Eq. (9). Inclusion of the next hexagons, the second and the third, changes this into $-(4/3)w_0$ and $-1.415w_0$, respectively. Hence, for a sextet of columns the numbers are $-8w_0$ and $-8.49w_0$.

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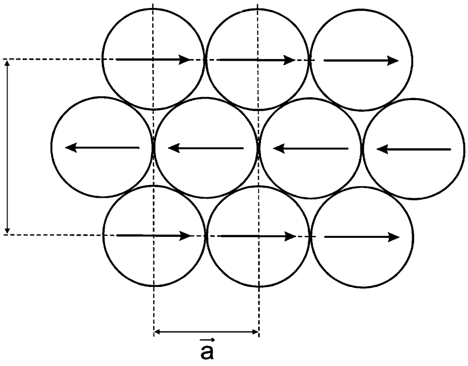

FIGURE 3 Antiferroelectric column lattice made of inline head-to-tail dipole chains alternating in sign. The basic lattice vectors $\vec{a}$ and $\vec{b}$ define a rectangular two-column unit cell. As in the following figures, the columnar cross sections are circles, and the orientations of the columnar dipoles are indicated by arrows.

Curiously, neither maximum ferroelectric polarization nor alternating chains of inline head-to-tail dipoles, with one or two columns per unit cell, turned up in the X-ray studies of switchable columnar liquid crystals. Searching for the two next-best solutions from the energy point of view, we selected the following two column lattices. One of them is a lattice of tiny dipole loops consisting of three columns each, as sketched in Fig. 4. Its dipolar energy per unit length of six-column

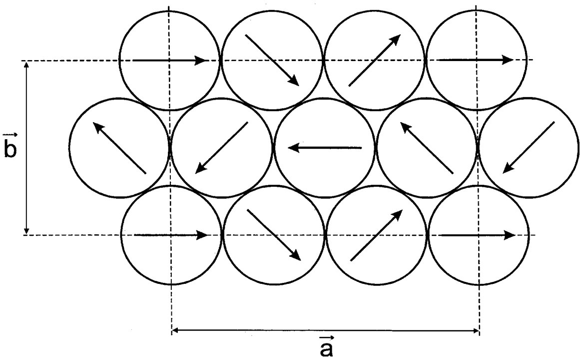

FIGURE 4 Antiferroelectric column lattice consisting of left- and right-handed triangular dipole loops arranged in alternating vertical series of either type. The basic lattice vectors $\vec{a}$ and $\vec{b}$ define a rectangular six-column unit cell. (See also Fig. 3.)

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unit cell is $-8w_0$ up to first as well as second hexagons and $-8.082w_0$ up to third hexagons. The oblique dipoles feel small torques turning them toward the flat configuration of Fig. 3, which apparently represents an energy miminum. Although it is not quite stable in our idealized model of dipolar interaction, the column lattice of Fig. 4 is adopted here as a separate solution because of its triplets with threefold symmetry axis. Note that the dipole loops alternate between left-handed and right-handed in the horizontal direction of Fig. 4. The dipolar energy of a lattice of equally handed loops would be much higher, being $-4w_0$ up to first as well as second hexagons for the six-column unit cell. The other particularly favorable lattice, shown in Fig. 5, appears to be stable and again has a six-column unit cell. Apart from horizontal parallel dipoles (one in three), it consists of staggered head-to-tail dipole chains in the vertical direction, which alternate in sign. The lattice is ferroelectric, but its polarization is only one third of the full value, $P=(1/3)P_{\mathrm{sp}}^{\max}$. The energy per unit cell of unit length, including a self-stabilization term of $-(4/3)w_0$, is $-5.33w_0$, $-8w_0$, and $-7.275w_0$ up to first, second, and third hexagons, respectively. The exact self-stabilization term containing λ in the denominator leads to the additive correction $+0.124w_0$ per unit cell for all orders. The horizontal dipoles producing the polarization are decoupled from the vertical ones. In principle, they can rotate together without change in dipolar energy, which would give rise to additional column lattices of the same energy. Reasons why the column lattices of Figs. 4 and 5 could be preferred over uniform polarization and the alternating inline chains of head-to-tail dipoles are discussed when we come to the conjectures.

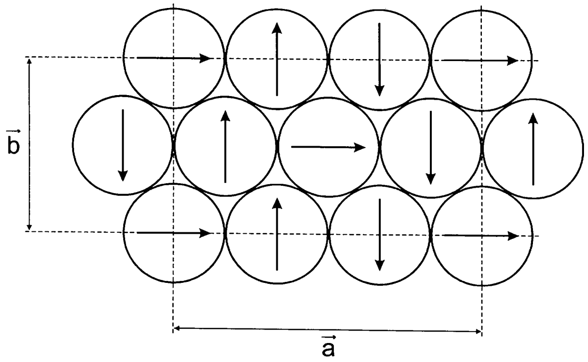

FIGURE 5 Partially ferroelectric column lattice made of staggered head-to-tail dipole chains alternating in sign and uniformly oriented dipoles forming a hexagonal lattice. The basic lattice vectors $\vec{a}$ and $\vec{b}$ define a rectangular six-column unit cell. (See also Fig. 3.)

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For later use, let us estimate a few numbers characteristic of dipolar interaction. Inserting into Eq. (7) $P_{\mathrm{sp}}^{\max} = 180\,\mathrm{nCcm}^{-2}$, the rather large value measured in the high-field phase of the dibenzopyrene derivative with chain length $m = 7$ [7], the known distance $d_0 = 2.5\,\mathrm{nm}$ of the columns [10] and $\varepsilon = 2$, the standard value of apolar organic material, one has

$$w_0 = 1.3 \cdot 10^{-13}\mathrm{Jm}^{-1}. \tag{10}$$

Therefore, with a molecular repeat distance of 5 Å along the column, nearly 100 molecules are needed to reach kT which at $T = 100^\circ\mathrm{C}$ is $5{\cdot}10^{-21}\,\mathrm{J}$. Another interesting number is the maximum electric field E_0, which adjacent columns produce at each other's centers. From Eq. (7) and the above value of $P_{\mathrm{sp}}^{\max}$ one obtains

$$E_0 = \frac{1}{8\varepsilon\varepsilon_0} P_{\mathrm{sp}}^{\max}\lambda = 14\,\mathrm{V}\mu\mathrm{m}^{-1}. \tag{11}$$

This is less than an order of magnitude below the field strength of electric breakdown.

3. SPECIAL VAN DER WAALS INTERACTION

Van der Waals interaction is the main reason for cohesion of organic matter. In columnar liquid crystals with regions of aromatic cores in the columns, a special van der Waals interaction may be expected to act between (and within) those regions on top of a practically homogeneous cohesion. It is due to the π-electrons of the molecular aromatic cores. An estimate of the special interaction between columns is desirable mostly to check whether it competes with dipolar interaction in aligning the columns. The following calculation starts from pairs of molecules. The molecular cores are assumed to be at the centers of the columns. Quantum-mechanical second-order perturbation theory is used to compute van der Waals interaction between the π-electrons of two molecules in a medium of dielectric constant $\varepsilon = 2$, a value that still applies to aromatics of the size considered. This treatment seems possible because the lowest π-electron excitation energies are about 5 eV for benzene and less for aromatics with two or more contiguous benzene rings. Therefore, they are much below the ca. 10 eV required to optically excite saturated organic material. At large enough distances, the energy of van der Waals interaction is governed by the interaction energies of the transition dipole moments of the interacting molecules [22]. The virtual transitions of the π-electrons lead from a filled delocalized orbit to an empty one, where we ignore deformations of the molecular frame by the electronic excitation. Only the two singlet transitions of lowest energy are taken into account, whose transition dipole moments should be orthogonal.

Let us denote the transition dipole moments by $\vec{p}_{1\alpha}$ and $\vec{p}_{2\beta}$, where the first subscript refers to the molecule (1 or 2) and the second to its principal axis (α, $\beta = 1$, 2). The van der Waals energy may be expressed by

$$\gamma = -\sum_{\alpha,\beta}^{1,2} \frac{4I^2_{1\alpha,2\beta}}{\Delta E_{1\alpha} + \Delta E_{2\beta}}. \tag{12}$$

Here $\Delta E_{1\alpha}$ and $\Delta E_{2\beta}$ are the molecular excitation energies, whereas

$$I_{1\alpha,2\beta} = \frac{1}{4\pi\varepsilon\varepsilon_0}\left[\frac{p_{1\alpha}\cdot\vec{p}_{2\beta}}{r^3} - \frac{(3\vec{r}\cdot\vec{p}_{1\alpha})(\vec{r}\cdot\vec{p}_{2\beta})}{r^5}\right] \tag{13}$$

is the interaction energy of the transition dipole moments, $\vec{r} = \vec{r}_2 - \vec{r}_1$ being the vector connecting the molecular centers at $\vec{r}_2$ and $\vec{r}_1$. The factor 4 in Eq. (12) takes into account that the transitions in the two molecules can be accomplished by either a spin-up or a spin-down electron.

For a numerical estimate of special van der Waals interaction, we start from a pair of molecules at equal height in adjacent columns. We consider first a columnar liquid crystal without tilt of the aromatic cores. The π-electrons are assumed to move in circular orbits, so the two transition dipole moments are of equal size (i.e., $p_{1\alpha} = p_{1\beta} = p$) and can be chosen parallel and perpendicular to $\vec{r}$. This choice leaves only two nonvanishing terms in Eq. (12), the transition dipole moments of both molecules being either in line or side by side. Because of Eq. (13), the larger term is from the inline case. The interaction energy of its transition dipole moments may be written as

$$I = -\frac{1}{4\pi\varepsilon\varepsilon_0}\frac{2p^2}{r^3}.$$

In the model of circular orbits, the transition dipole moment is $p = 0.25 d_c e_0$ where d_c is the diameter of the aromatic core and $e_0 = 1.6\cdot 10^{-19}$C the elementary charge. Taking $d_c = 1\,$nm (for dibenzopyrene), $\varepsilon = 2$, and $r = d_0 = 2.5\,$nm (the column diameter of the $m = 7$ dibenzopyrene derivative [10]) to compute I, and subsequently inserting I^2 and $\Delta E_1 = \Delta E_2 = 3\text{eV} = 5\cdot 10^{-19}\,$J (estimated for dibenzopyrene) into Eq. (12), one arrives at

$$\gamma_0 = -3.4 \cdot 10^{-24}\,\text{J} \tag{14}$$

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where the subscript zero indicates that this single term serves as a reference. No error bars can be given for γ_0, which is the basis for all further estimates. The pair interaction has to be multiplied by an enhancement factor f to obtain the interaction of molecule 1 with the column of molecule 2 instead of molecule 2 alone. One finds $f \simeq 4$ when a molecular period of 5 Å is assumed along the column. (The pair interaction energy decreases with increasing difference in height not only through an increase in distance but also by a gradual loss of inline ordering. The enhancement factor can be evaluated from a plot of molecular interaction vs. relative height.) Accordingly, the contribution of the transition dipole moments pointing to the other column to the special van der Waals interaction is $4\gamma_0$ per molecule and, with the effective molecular thickness of 5 Å,

$$v_0 = -2.7 \cdot 10^{-14}\,\mathrm{Jm}^{-1} \tag{15}$$

per unit length of column. We regard this as our “standard value” of special van der Waals interaction energy per unit length of a pair of columns. Its absolute value is 20% of w_0, the corresponding dipolar interaction energy, Eq. (10). The second term of van der Waals interaction, due to the side-by-side transition dipole moments normal to $\vec{r}$, is precisely 1/4 of Eq. (14) for a pair of molecules at equal height. The enhancement factor in this case is $f \simeq 6$ so that the additional interaction energy per unit length of a pair of columns becomes $-(3/8)v_0$.

Special van der Waals interaction can produce an aligning effect only when the aromatic cores of the molecules are tilted by an angle ϑ. The effect is particularly weak because the energy of van der Waals interaction does not change sign, being negative for all orientations of the transition dipole moments. A crude estimate is made for a special case that can be conveniently handled because cross terms ($\alpha \neq \beta$) vanish in Eq. (12) at all relative heights. Considering side-by-side tilt axes and columnar dipoles in adjacent columns, we first note that reversing one of the dipoles does not change the part of special van der Waals interaction mediated by the transition dipole moments perpendicular to $\vec{r}$. The part originating from the tilted transition dipole moments pointing obliquely to the other column does change but only very little. Going from parallel to antiparallel side-by-side tilt-induced dipoles, we find this energy to increase by $0.1|v_0| \simeq 0.02w_0$ for the tilt angle $\vartheta = 45^\circ$. There is no energy difference for $\vartheta = 90^\circ$ and, of course, $\vartheta = 0^\circ$. An estimated strength of about $0.01w_0$ probably means that the directing effect of special van der Waals interaction is generally too weak to compete with dipolar interaction in switchable columnar liquid crystals.

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All these numbers apply to adjacent columns. Special van der Waals interaction is totally irrelevant at larger distances of the columns because it drops off with $1/d^5$, unlike the $1/d^2$ law of dipolar interaction. The extreme increase of (the absolute value of) special van der Waals interaction at very small distances may, however, play a role when the columnar cross sections are sufficiently elliptic, a case which is not be investigated but touched on later.

4. FERROELECTRIC PHASE TRANSITION

Induced polarization in isotropic liquids reinforces itself by the cavity field that it produces in a fictitious spherical cavity in addition to the applied field. The Clausius–Mosotti formula relating susceptibility to molecular polarizability is based on this idea. The formula is also used to understand the ferroelectric phase transition of certain crystals in terms of a polarization catastrophe taking place when the temperature is lowered beyond a critical value [23]. The spontaneously polarized columns of switchable columnar liquid crystals may be viewed as single molecules of infinite extension and dipole moment in a cylindrical cavity. In this picture the fully ferroelectric state would be beyond the catastrophe and stable at all temperatures.

However, torsional fluctuations along the columns, until now omitted, will weaken and finally destroy a dipolar order of the column lattice as the temperature is raised. In the following, we propose a mean-field theory for the phase transition from the uniformly polarized state to that without any long range order of the dipoles, the mean-field being the cavity field E_{cav}. We are interested mainly in deriving a formula predicting the transition temperature.

The theory of torsional fluctuations of a single column is similar to that of normal displacement fluctuations of a stretched polymer, which has been treated extensively in the literature [24]. Considering the end of a semi-infinite column, we first ask for the distribution function $\psi(\varphi)$ of the twist angle φ at the end. If in statistical equilibrium one more molecule is added to the column, this normalized probability density should obey a balance equation of density changes; that is

$$\frac{1}{2}\langle(\Delta\varphi)^2\rangle\frac{\partial^2\psi(\varphi)}{\partial\varphi^2}+\frac{a}{kT}(E_0-U(\varphi))\psi(\varphi)=0. \tag{16}$$

Here a is the effective thickness of a molecule, $U(\varphi)$ the potential energy, and E_0 the so-called ground state eigenenergy, both per unit

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length of column, whereas $\Delta\varphi$ is the twist angle difference between subsequent molecules. Making use of

$$\langle(\Delta\varphi)^2\rangle = \left\langle\left(\frac{\partial\varphi}{\varphi z}\right)^2\right\rangle a^2$$

and the equipartition theorem

$$\frac{1}{2}\kappa\left\langle\left(\frac{\partial\varphi}{\partial z}\right)^2\right\rangle a = \frac{1}{2}kT$$

where κ is the torsional stiffness (of dimension Nm), one can convert this into

$$-\frac{1}{2}\frac{(kT)^2}{\kappa}\frac{\partial^2\psi(\varphi)}{\partial\varphi^2} + U(\varphi)\psi(\varphi) = E_0\psi(\varphi), \tag{17}$$

which has the form of a Schrödinger equation. The probability of a molecule within an infinite chain to assume the angle φ is then $\psi^2(\varphi)$. The present model omits any spontaneous torsion τ_0 of the column, but it should be possible to incorporate τ_0 by substituting $(-i(\partial/\partial\varphi)- \tau_0)^2$ for $-(\partial/\partial\varphi)^2$ in Eq. (17) and allowing $\psi(\varphi)$ to be a complex function. The spontaneous twist τ_0 would play the role of a vector potential.

Torsional diffusion is unrestricted if $U(\varphi) \equiv 0$. The ground state of $\psi(\varphi)$ in this case has the normalized eigenfunction

$$\psi_0(\varphi) = \frac{1}{\sqrt{2\pi}},$$

with eigenenergy $E_0 = 0$. The first two "excited" states may be defined by the normalized eigenfunctions

$$\psi_1(\varphi) = \frac{1}{\sqrt{\pi}}\cos\varphi$$

and the same with sin φ replacing $\cos\varphi$.The eigenenergy per unit length of column of these excited states is

$$E_1 = \frac{1}{2}\frac{(kT)^2}{\kappa}$$

because their wave number on the closed orbit of length 2π is $q = 1$. A (small) electric field E in the direction $\varphi = 0$ produces the perturbation

$$H'(\varphi) = -EP_{\mathrm{sp}}^{\max}\lambda\frac{\pi}{4}d_0^2\cos\varphi,$$

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which is a potential energy per unit length of column. To the first order this perturbation has no effect on $\psi(\varphi)$ and its eigenenergy. The second-order correction of the eigenenergy per unit length of column is

$$w_2 = \frac{\langle \psi_0 | H' | \psi_1 \rangle^2}{E_0 - E_1}.$$

Straightforward integration yields

$$w_2 = -\frac{\pi^2 \kappa d_0^4 \lambda^2}{16(kT)^2} (P_{\mathrm{sp}}^{\max})^2 E^2$$

for a single column. Because of

$$P(E) = -\frac{\partial w_2}{\partial E} \frac{4}{\pi d_0^2 \lambda},$$

the corresponding polarization is

$$P(E) = \frac{\pi \kappa d_0^2 \lambda}{2(kT)^2} (P_{\mathrm{sp}}^{\max})^2 E. \tag{18}$$

A formula for the critical temperature T_c of a second-order phase transition can now be obtained by equating the perturbation field E to the cavity field $E_{\mathrm{cav}} = (1/2\varepsilon\varepsilon_0)P_{\mathrm{sp}}$ of the polarization induced by it. For a cylindrical cavity of circular cross section, the self-consistency relation takes the form

$$\frac{1}{2\varepsilon\varepsilon_0} P(E) = E.$$

Inserting Eq. (18) and $\varepsilon = 2$ and solving for kT results in

$$(kT_c)^2 = \frac{\pi \kappa d_0^2 \lambda}{8\varepsilon_0} (P_{\mathrm{sp}}^{\max}). \tag{19}$$

We insert $P = 180\,\mathrm{nCcm}^2$, as measured for the high-field phase of the $m = 7$ dibenzopyrene derivative, and $d_0 = 2.5 \cdot 10^{-9}$cm, as obtained for the same material from X-ray scattering. After introducing

$$\kappa = K_{22} \frac{\pi}{4} d_0^2 \lambda, \tag{20}$$

where K_{22} is a nematic twist modulus, one arrives, with the typical value $K_{22} = 3 \cdot 10^{-12}$ N, at

$$kT_c = 4.1 \cdot 10^{-21}\,\mathrm{J}, \tag{21}$$

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which is equivalent to $T_c = 300\,\mathrm{K}$. This theoretical value is somewhat lower than the temperature of the experiments of ca. 370 K. It should be higher than that if the ferroelectric order is due solely to dipolar interaction. The ferroelectric phase transition is peculiar because polarization charge densities in the bulk due to fluctuations of the column lattice will be compensated by real charges, which are discrete and perform their own fluctuations. Despite its complex nature, we discuss it like a second-order ferromagnetic phase transition. In those transitions the mean-field value of the transition temperature is often ca. 30% below the actual value. On the other hand, there is reason to believe that the torsional stiffness κ is larger than the value used in this estimate. It may be a few times larger than the value derived from the nematic twist modulus as the tilted cores make the column resemble a stack of chairs, with the tilted parts offering an additional resistance to twist. For the material in question, the $m = 7$ dibenzopyrene derivative, T_c may thus be expected to be higher instead of lower than 370 K. It cannot be measured as the isotropic phase intervenes below T_c. Interestingly, the otherwise poorly specified triphenylene derivative with a benzene ring in the side chains undergoes an apparently second-order ferroelectric phase transition at 470 K, as has been mentioned above.

The two values of the critical temperature, crudely estimated for one material and measured for the other, independently suggest that dipolar interaction is indeed of the right size to explain ordered column lattices. At the moment, there seems to be no need for invoking other packing energies. The discussion of conjectured column lattices of switchable columnar liquid crystals will, therefore, be based as far as possible on the dipolar interaction of columns with circular cross section.

5. ASSIGNMENTS AND OTHER CONJECTURES

The column lattice of Fig. 4, an array of triangular dipole loops of both senses, seems suitable to represent the antiferroelectric triplet superstructure of phenanthrene and pyrene derivatives. Because of its much lower dipolar energy, the rectangular six-column unit cell is preferred over a hexagonal superlattice of dipole loops of one sense only, which would have a three-column hexagonal unit cell. It seems plausible to assume that the resolution of X-ray scattering, somewhat better than 1%, was not enough to distinguish the mixed from the pure case. The model of dipole loops is supported by the fact, mentioned previously, that the triplet superstructure was absent when a racemate was prepared of one of the compounds. Generally, a single

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Debye–Scherrer signal at $(hk) = (11)$ or (20) of the six-column rectangular unit cell revealed the triplets, its intensity being roughly 1% of that of the basic hexagonal lattice at $(hk) = (02)$ or (31). The basic lattice vectors $\vec{a}$ and $\vec{b}$ of the two-dimensional column lattice are defined in Figs. 4 and 5. The switching process leading from the antiferroelectric triplet superstructure to a final, presumably fully prolarized, ferroelectric state varied considerably among the columnar liquid crystals investigated. The transition was possibly abrupt when it took place at low fields such as $\pm 2\,\mathrm{V\mu m^{-1}}$ but passed through (unknown) intermediate column lattices when it was finished only at high fields (e.g., $\pm 35\,\mathrm{V\mu m^{-1}}$).

Unlike the derivatives of phenanthrene and pyrene, the four dibenzopyrene derivatives are partially ferroelectric in the fieldless state. Two of them, with side chains $m = 7$ and $m = 5$, were examined by X-ray scattering and found to have a quasi-hexagonal rectangular six-column unit cell. Its column lattice seems to be well represented by the staggered vertical head-to-tail dipole chains of Fig. 5. By far the strongest signal was the slightly split (by less than 1%) main peak at $(hk) = (02)$ and (31) of the almost hexagonal lattice. The weaker part originates from the smaller Bragg spacing and should therefore be (02). The second-strongest peak, ca. 1% in height of the main peak, was that of a triplet superstructure at $(hk) = (11)$ or (02). It agrees in indexing and, approximately, relative strength with the triplet peak of the phenanthrene and pyrene derivatives. Two still weaker reflections at $(hk) = (42)$ or (51) and $(hk) = (22)$ or (40), observed only in the case $m = 7$, can also be ascribed to the triplets.

A further peak with a relative strength of about $\left(\frac{1}{3}\right)\%$ at $(hk) = (32)$ and one or two even weaker ones at $(hk) = (21)$ and (12) indicate that the two triplets composing the sextet are not identical. All this seems to conform with the column lattice of Fig. 5. It should be noted, however, that the X-ray spectra depended somewhat on the glass of the capillary and may not have reached their final shapes while the samples were kept for a few days at the temperature of the columnar phase. Very weak signals at $(hk) = (10)$ and (30) for $m = 7$ and $(hk) = (01)$ for $m = 5$ were also observed. They should not exist in a precisely centered rectangular column lattice of the type of Fig. 5 and are discussed later. The column lattice of Fig. 5 is also compatible with results obtained on the $m = 7$ derivative by atomic force microscopy. Such experiments done after freeze fracture of electrically aligned samples showed the partial ferroelectric polarization to be parallel to one of the directions connecting adjacent columns [10].

Let us now try to understand why the antiferroelectric double triplets of Fig. 4 and the partially ferroelectric staggered dipole chains

TABLE 1 Dipolar Energies of Sextets of Columns in Units of w_0, an Energy per Length, of Four Different Column Lattices

	Hexagons counted	Fully ferroel.		Antiferroel. in line (Fig. 3)	Antiferroel. loops (Fig. 4)	Partly ferroel. staggered (Fig. 5)
Unsplit dipoles	none	–10.88		n.a.	n.a.	n.a.
	1st	n.a.		−12	−8	−5.33 +0.12
	up to 2nd	n.a.		−8	−8	−8 +0.12
	up to 3rd	n.a.		−8.49	−8.33	−7.27 +0.12
Corrections for splitting		Dipoles in line	Dipoles side by side			
Simply	1st	−2.7	+2.9	+5.8	−1.9	−1.5
Doubly	1st	+2.5	−2.5	−2.1	c. 0 (est.)	−0.7

Note: The dipoles are central, simply split, or doubly split (see main text for details). The total values are given in the case of unsplit dipole moments, but only the corrections due to splitting are shown in the two cases of splitting. When the dipoles are split, the numbers for the fully ferroelectric state depend on whether the unsplit dipoles are in line or side by side.

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of Fig. 5 can be preferred over the antiferroelectric inline dipole chains of Fig. 3 and, especially, the fully ferroelectric state. For this purpose we begin with refining the calculation of the dipolar interaction energies. Until now the dipoles were placed at the column centers, while actually the molecular dipolar groups are in the wings of the molecules (i.e., at about half the column radius). To achieve a better approximation, the columnar dipole moments per unit length are now split into two equal parts, which are shifted by $d_0/4$ in opposite directions normal to the tilt axis and the column. It seems sufficient to consider the effect of splitting on nearest-neighbor interactions. The resulting corrections of the dipolar energy per sextet of columns are listed in Table 1, which also compiles some of the results obtained for unsplit dipoles. As soon as the dipoles are split, the direct dipolar interactions do not offset each other in the fully ferroelectric state whose energy now depends on the common direction of the dipoles. There are two principal axes of dipolar orientation, which dipole splitting affects differently. In one case, the dipoles are in line and point to nearest neighbors. In the other case, they are side by side and point to next-nearest neighbors. The two cases are distinguished in the table.

For a check, we then quarter the dipole moments per unit length, dividing the halves into two equal parts, which are shifted again by $d_0/4$ in opposite directions, this time parallel to the tilt axis. The corrections associated with such an extreme placement of four dipoles, whose distance from the center line of the column is $\sqrt{2}d_0/4$, are also listed in Table 1. Inspection of the corrections due to simple and double splitting shows that they are quite different including changes of sign. This points to a strong dependence of dipolar interaction on the structure and stacking of the disklike molecules. It seems reasonable to give more weight to the calculated effects of simple splitting than those of double splitting. Accordingly, we may expect a realistic distribution of the dipole moments to lower the dipolar interaction energies of the double triplets (Fig. 4) and the staggered dipole chains (Fig. 5) but to raise that of the antiferroelectric inline dipole chains (Fig. 3) from the values obtained without splitting. With these corrections, the column lattices agreeing with the X-ray data (Figs. 4 and 5) could be of lower dipolar energy than the antiferroelectric inline lattice of Fig. 3, which contrary to expectation has not been found. Which of the two is more favorable and how accurate the assignments are depends presumably on molecular details. However, one of the fully ferroelectric substates, probably inline dipoles, seems to remain at the minimum of dipolar energy. The persistence of this wrong prediction may be taken as a sign that something is missing in a model presupposing nothing but circular cross sections and dipolar interactions of the columns.

Do the small deviations of the column lattice from hexagonality offer a solution of this problem? We recall that the relative strength of the triplet signals and, in the dibenzopyrene derivatives, the split of the Bragg spacings of the hexagonal lattice were about 1%. These findings suggest that the aromatic core regions of the columns are shifted from their ideal positions by no more than a few percent of the column spacing d_0. The effect on dipolar interaction energies through their $1/d^2$ dependence would be twice as large, which is probably too little to destabilize the fully ferroelectric state. Similar arguments apply to special van der Waals interaction, which comes into play when d is variable. Its $1/d^5$ law cannot quite compensate for its estimated reduced strength of $|v_0| = 0.2w_0$ if d varies by only a few percent. Incidentally, a predominant special van der Waals interaction would tend to align the dipoles uniformly, either side by side or in line, depending on whether the columnar dipole moment is parallel or perpendicular to the major axis of an elliptic cross section of the columns.

There is a more likely solution of the present problem. So far, any packing energies except dipolar and special van der Waals interaction have been disregarded. However, even if the columnar cross sections would be precise circles (or hexagons), the energies of side-chain packing may depend on the dipolar orientations of adjacent columns. The entropic free energy of chain packing in a transition from single

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columns (e.g., in an organic solvent) to a columnar liquid crystal could amount to several kT per molecule. Its variation with the type of column lattice will be a small fraction of it. Only this part competes with the dipolar interaction energy of the columns. It can still be significant because the energy of dipolar interaction is no more than $2 \cdot 10^{-2} kT$ per molecule according to the estimate made above.

In a column with collectively tilted molecular cores one may expect a crowding of side-chain attachment points on the sides of the core region that are normal to the tilt axis. The crowding could result in an elevated packing free energy in the case of inline dipoles to counter an increased overlap of side chains from adjacent columns. We suspect that this is the reason for the absence of ferroelectric inline ordering. It is not attempted here to resolve the conceptual conflict between hard columns and side-chain packing energies depending on dipolar orientations.

The faint signals of the partially ferroelectric dibenzopyrene derivatives indicating deviations from centeredness cannot be readily explained by the difference between the two kinds of triplets. For scattering vectors parallel to the axes $\vec{a}$ and $\vec{b}$ of the rectangular lattice, the difference should be unnoticeable as long as the columnar dipoles retain their positions and directions. As an especially speculative conjecture, it is proposed that all columnar dipole moments are slightly rotated from their ideal directions in Fig. 5. The rotation is thought to be in a single sense for $m = 7$ and alternating in sense from line to line of the figure for $m = 5$. The horizontal dipoles take part in the rotations. This could explain why the center of the rectangular unit cell is shifted along the a-axis for $m = 7$ and the b-axis for $m = 5$. The advantage of such a rotation by a few or several degrees would be to prevent crowding of side chains of adjacent columns. This is, in a milder form, the same effect as the avoidance of inline dipoles to keep down the chain packing energies.

6. CONCLUSION

Although it does not correctly identify the ground state, the simple model in terms of circular columnar cross sections and dipolar interaction appears to be useful, even without dipole splitting. It provides the basis for a mean-field theory of a ferroelectric phase transition in the column lattice, in particular a formula for the critical temperature, which seems in reasonable agreement with experimental results. Also, in a search for the energetically most favorable states next to the nonexistent predicted ground state the model brings forth two column lattices matching two different types of X-ray data. The model can be improved by splitting the columnar dipoles. However, it disregards the unknown dependence of side-chain packing energies on dipolar orientations, which may intervene in a nonnegligible manner.

Besides the length of column needed to reach a dipolar interaction energy of kT, there is another interesting length definable along the column. It is the angular persistence length $l_p = \kappa/kT$ of dipolar orientation in the absence of aligning interactions. The theory of the ferroelectric phase transition can be valid only if l_p is much larger than the molecular repeat distance of ca. 5 Å in the column. Otherwise, torsional stiffness is not a good concept because the angle differences between subsequent molecules in the stack are likely to exceed the range of validity of Hookean elasticity. Inserting $K_{22} = (3 \times 10^{-12}$ to $1 \times 10^{-11})$ N and $d_0 = 2.5\,\mathrm{nm}$ into Eq. (19) as well as putting $kT = 5 \cdot 10^{-21}\,\mathrm{J}$ (100°C), one finds $l_p = (30$ to $100)$ Å, which seems large enough, at least at the upper limit.

Electrooptically switchable columnar liquid crystals have been synthesized and studied with a view to discovering new types of electrooptical devices. Especially interesting in this respect are the lyomesophases [25,26] in which up to 50% by weight of dodecane are mixed with the bistable triphenylene derivative having a benzene ring in each of its six side chains [8,9]. One of these phases displays bistable switching down to room temperature. Generally, lyomesophases should be good candidates for near perfect validity of our model because the presence of a diluent reduces the packing energies due to the side chains. Even the pure bistable triphenylene derivative, displaying no high-field phase, is likely to be fully ferroelectric, in agreement with our model. It would be highly desirable to find out the structure of this columnar phase, as yet known neither without nor with dodecane admixture.

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