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Various columnar phases formed by bent-core mesogens

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Two new compounds containing bent-core mesogens are presented in which a flexible central methyleneoxycarbonyl unit acts as the bent fragment. The compounds form different two-dimensional columnar ('B₁') phases both with a rectangular lattice but different in the angle of the director of the molecules with respect to the *a*-axis of the lattice. Based on X-ray diffraction measurements structural models are proposed which cannot be described with the common model of *p2mg* symmetry for B₁ phases of bent-shaped molecules. The new models are of layer group symmetry (*p11n* and *pm2₁n*) and are discussed as a new common model for two-dimensional columnar phases of bent-shaped mesogens.

1. Introduction

'Banana' phases are liquid crystalline phases composed of bent molecules. They represent one of the hottest topics in liquid crystalline research in recent years [1–3]. Aside from the main group of phases designated using B₁ up to B₇, more and more subgroups have been discovered, e.g. ferro- and antiferro-electric subphases [4, 5]. This multitude of phases is caused by the special shape of the molecules and consequently by their steric requirements, by a possible polar order and by the chance to arrange the non-chiral molecules in chiral phases.

So far the B₁ phase appears to be a uniform class. The B₁ phase has been described as a two-dimensional columnar phase with a rectangular lattice in which the molecules are organized in small layer fragments with their bent direction (two-fold axis) parallel to the *b*-axis of the lattice (perpendicular to the layer normal) [3, 6, 7]. The derived packing (see later figure 9) corresponds to the steric requirements and has been related to the symmetry of the two-dimensional space group *p2mg*, No. 7 according to [8]. The existence of a tilt has been proved by X-ray patterns of oriented samples. By comparison of the molecular length with the corresponding cell parameters, however, a non-tilted variant is also indicated [9].

In the following sections the investigation of well developed monodomains of two compounds is reported, clearly proving the existence of a tilted and a non-tilted variant. Considering the symmetry conditions, a new packing model must be discussed, which could also be

applied to columnar phases of other bent-core mesogens. The same model has been used to explain the optical observations obtained by applying an electric field to a liquid crystalline phase for an odd-spacer twin [10, 11].

2. Experimental

The transition temperatures and corresponding enthalpies were determined using a differential scanning calorimeter (Perkin Elmer, DSC Pyris1). The mesophases were assigned using a polarizing microscope (Leitz Orthoplan) equipped with a Linkam hot stage (THM 600/S) and by XRD techniques. Non-oriented powder samples were studied using the Guinier method (Huber Diffraktionstechnik GmbH), while measurements on oriented samples were performed using a diffractometer with a 2D detector (HI-STAR, Siemens AG). Well developed monodomains of the mesophases were obtained by slowly cooling a drop of the isotropic melt below the clearing point on a thin and cleaned glass plate situated on an aluminium hot plate. The incident X-ray beam was nearly parallel to the glass plate; therefore only the upper half of the reciprocal space could be observed very well. The lower part was shadowed by the glass plate and in particular by the hot plate.

3. Materials

The substances are members of a homologous series of new bent-core molecules. The structure of the compounds, the transition temperatures and the corresponding enthalpies are given in figure 1. They were determined during a cooling run at a rate of 5 K min⁻¹.

Compound **I** was prepared by the esterification of

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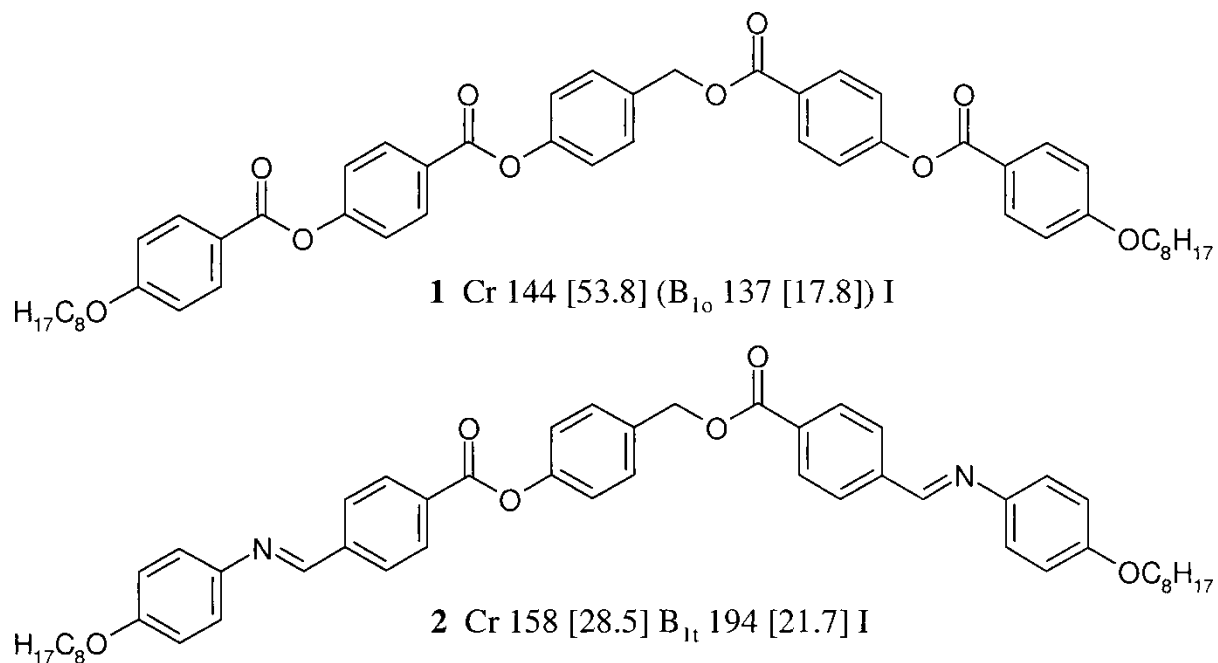


Figure 1. Chemical structure, transition temperatures ($^{\circ}\text{C}$) and transition enthalpies (kJ mol^{-1}) in square brackets of the investigated substances. DSC heating rate was 5 K min^{-1} ; the round brackets denote a monotropic phase. The additional indices o or t indicate an orthogonal or a tilted phase, respectively.

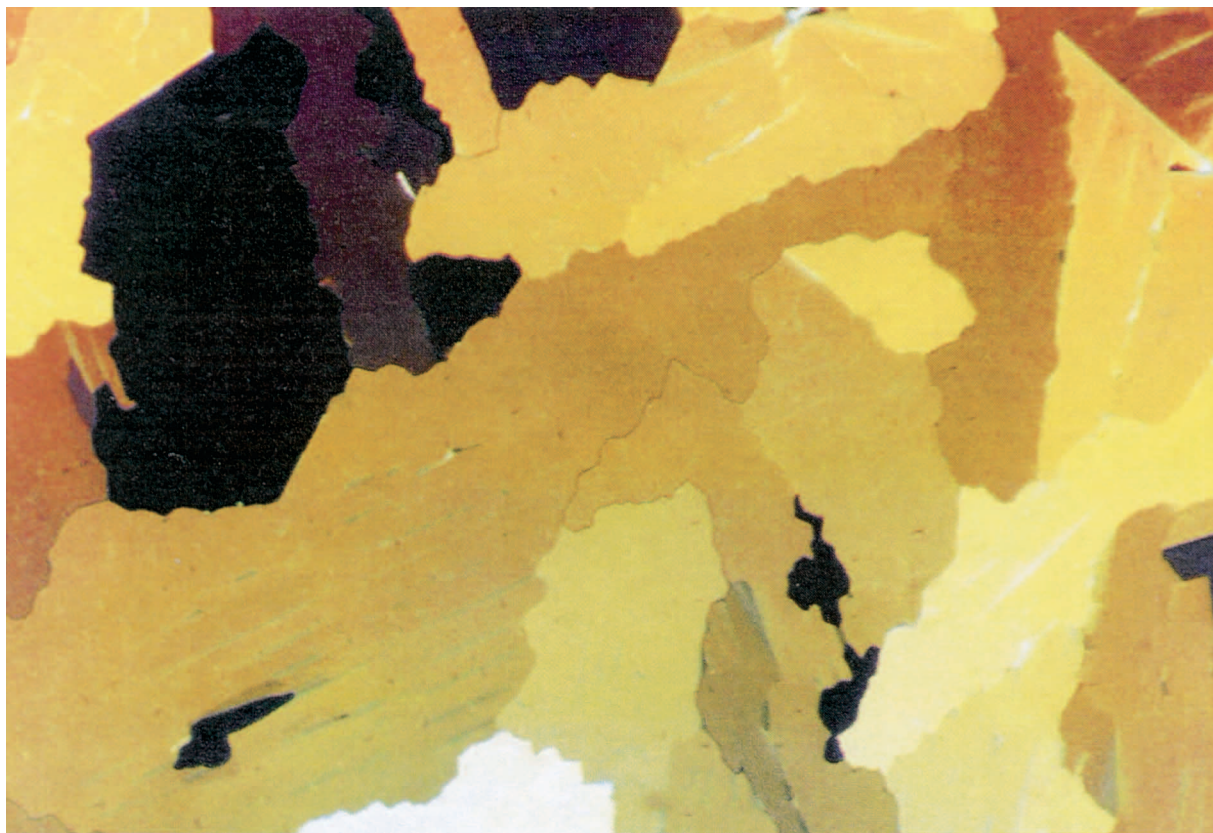


Figure 2. Mosaic texture of the B₁₀ phase of compound **1** (132°C).

one part 4-hydroxybenzylalcohol and two parts 4-(4-*n*-octyloxybenzoyloxy)benzoic acid with dicyclohexylcarbodiimide and catalytic amounts of *N,N*-dimethylaminopyridine in dichloromethane. For compound **2**, 4-(4-*n*-octyloxyphenyliminomethyl)benzoic acid was used. The compounds were recrystallized several times from ethanol with some DMF.

Compound **1**: ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 0.88–0.90 (m, 6H, CH_3), 1.28–1.50 (m, 18H, $(\text{CH}_2)_5$), 1.77–1.84 (m, 4H, OCH_2CH_2), 4.03 (t, 4H, OCH_2 , $J=6.4$ Hz), 5.38 (s, 2H, CH_2OOC), 6.96 (m, 2H, Ar-H), 6.97 (d, 2H, Ar-H, $J=8.8$ Hz), 7.25 (m, 2H, Ar-H), 7.29 (d, 2H, Ar-H, $J=8.8$ Hz), 7.36 (d, 2H, Ar-H, $J=8.8$ Hz), 7.52 (m, 2H, Ar-H), 8.12 (m, 2H, Ar-H), 8.13 (d, 2H, Ar-H, $J=8.8$ Hz), 8.14 (d, 2H, Ar-H, $J=8.8$ Hz), 8.26 (d, 2H, Ar-H, $J=8.8$ Hz).

Compound **2**: ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 0.86–0.89 (m, 6H, CH_3), 1.28–1.50 (m, 18H, $(\text{CH}_2)_5$), 1.74–1.82 (m, 4H, OCH_2CH_2), 3.97 (t, 4H, OCH_2 , $J=6.4$ Hz), 5.40 (s, 2H, CH_2OOC), 6.92 (d, 2H, Ar-H, $J=9.0$ Hz), 6.93 (d, 2H, Ar-H, $J=9.0$ Hz), 7.25 (d, 2H, Ar-H, $J=9.0$ Hz), 7.26 (d, 2H, Ar-H, $J=8.6$ Hz), 7.27 (d, 2H, Ar-H, $J=9.0$ Hz), 7.53 (d, 2H, Ar-H, $J=8.6$ Hz), 7.94 (d, 2H, Ar-H, $J=8.4$ Hz), 8.01 (d, 2H, Ar-H, $J=8.4$ Hz), 8.15 (d, 2H, Ar-H, $J=8.4$ Hz), 8.27

(d, 2H, Ar-H, $J=8.4$ Hz), 8.52 (s, 1H, CH-N), 8.56 (s, 1H, CH-N).

4. Results

4.1. Polarizing microscopy

On slow cooling the isotropic melt of compound **1**, the columnar phase appears as a typical mosaic texture with large domains of uniform birefringence growing dendritically from rhomboid nuclei (figure 2). On faster cooling, spherulitic defects occur. On shearing the sample, a fan-like texture develops (figure 3). The phase is monotropic, so in thin layers crystallization takes place after a few minutes. The texture of the mesophase of compound **2** (figure 4) is dominated by circular defects growing from spherulitic nuclei into a form which looks like liverwort. Sometimes banana-leaf or lancet-like defects occur which can be spirally furled. The mesophase is highly viscous.

4.2. X-ray investigations

The powder-like pattern of compound **1** has two reflections in the small angle region (figure 5) and a diffuse scattering in the wide angle region pointing to a liquid-like behaviour of the lateral distances. It was



Figure 3. Fan-shaped texture after shearing the mosaic texture of compound **1** (132°C).



Figure 4. Texture of the B_{II} phase of compound **2** (170°C).

possible to obtain large and very well oriented monodomains of this compound. In contrast to the strong tendency of crystallization in thin layers or in capillaries, respectively, these monodomains stay in liquid crystalline state over a period of many hours. The X-ray pattern of such domains is shown in figure 6. The positions of the reflections are symmetrical to an axis

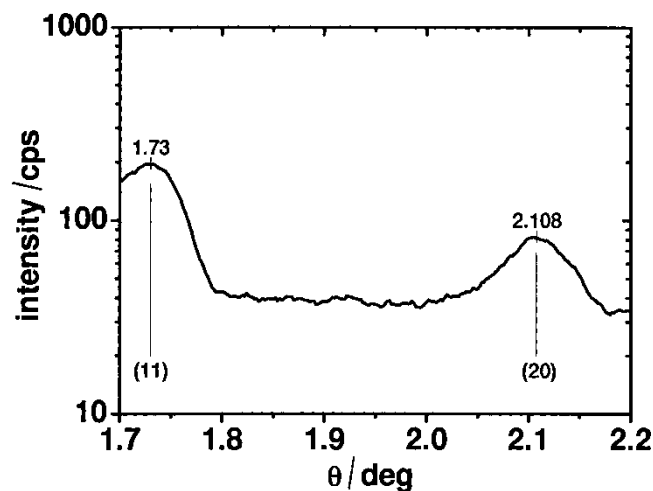


Figure 5. Intensity scans with indexing of the SAXS pattern of a non-oriented sample of compound **1** at 132°C.

inclined with respect to the meridian. This axis is assumed to be the a^* axis in reciprocal space. The pattern can be indexed on the base of a rectangular lattice where the $1\bar{1}$ reflection is on the meridian of the pattern. This means that the mesophase grows along a direction parallel to the normal of the $(1\bar{1})$ net planes from the surface into the bulk. The lattice parameters are $a=42.5\text{ \AA}$ and $b=32.0\text{ \AA}$. A rough estimation of the number of molecules per unit cell according to $z = \rho \times V_{\text{cell}} \times N_A \times M^{-1}$ (ρ = density, assumed to be about 1.1 g cm^{-3} ; V_{cell} = volume of a slice $a \times b \times 4.8\text{ \AA}^3$; N_A = Avogadro's number; M = molar mass) results in about six molecules per unit cell or three per building group.

The $[20]$ direction is orthogonal with respect to the direction of the outer diffuse scattering, so there is no tilt of the molecules. It can be concluded that the averaged long axis of the molecules is parallel to the a -axis of the lattice and the length is equal to the a -value. This offers the possibility of estimating a bending angle. Assuming an all-*trans* conformation of the alkyl chains, the legs of the molecule are about 27.8 and 23.7 \AA long (based on semiempirical calculations with mopac, pm3 Hamiltonian; measured from the methyl group to

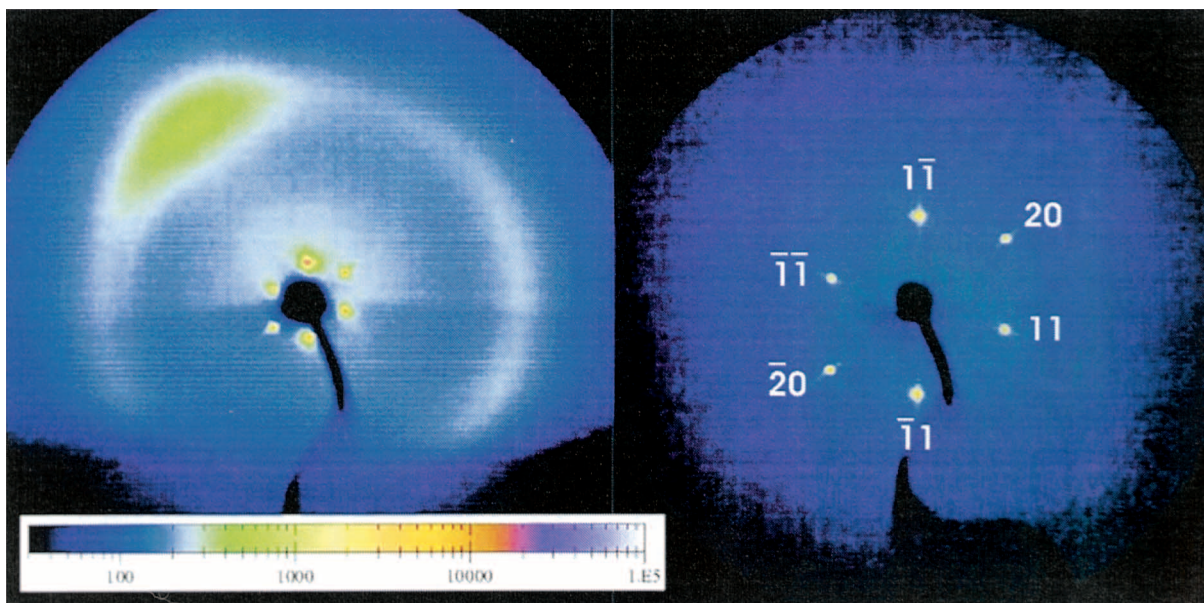


Figure 6. X-ray pattern of an oriented sample of compound **1**: (a) WAXS; (b) SAXS with indexing. Intensities are given in counts over an exposure time of 3 600 s.

the methylene carbon of the hydroxybenzyl alcohol). Thus the bend angle of the molecules is about 111° .

The powder-like pattern of compound **2** exhibits more reflections in the small angle region as shown in figure 7. It was possible to obtain well oriented samples again, but the domains were much smaller. In contrast to compound **1** the $[h0]$ direction is orthogonal to the surface of the drop, or parallel to the meridian. The diffuse outer scattering is clearly positioned off the equator indicating a tilt of the molecules (figure 8). The molecules are tilted by about 20° . The resulting unit cell is comparatively large ($a=42.6 \text{ \AA}$, $b=139.1 \text{ \AA}$) and contains many more molecules (about 24 per unit

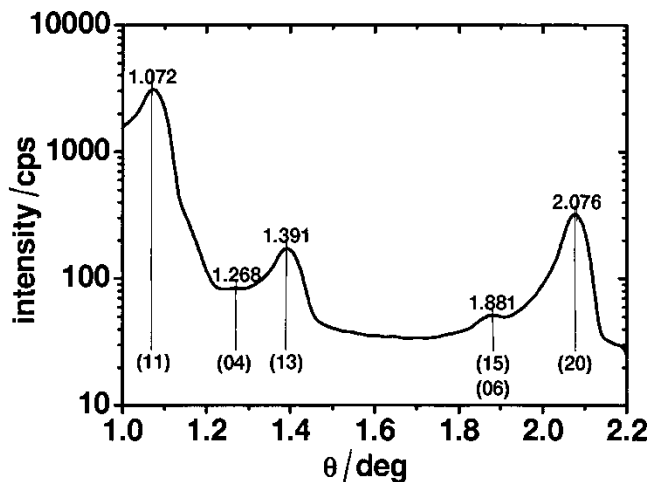


Figure 7. Intensity scan with indexing of a powder-like SAXS pattern of compound **2** at 160°C .

cell, about 12 per building unit). Assuming an all-*trans* conformation of the alkyl chains again, the legs of the molecule are about 28.2 and 24.0 \AA long (see compound **1** for conditions). The bend angle of the molecules is about 120° .

5. Discussion

Both compounds studied are unusual bent mesogens as they contain a methyleneoxycarbonyl link instead of the typical 1,3-disubstituted phenyl ring. Because of the flexible linking group the compounds under discussion are intermediate between rigid bent core mesogens and flexible twins. The flexibility of the bent link is restricted, however, in an assembly of molecules in the mesophase. On the other hand the typical tetrahedron angle of 109.5° of the substituents at the methylene group is increased because of the steric requirements of both the phenyl and the oxycarbonyl substituents. Another unusual feature of these compounds is their low molecular symmetry. They consist of two different legs of different lengths. Therefore the following explanation involves a simplification: specifically it neglects the molecular symmetry. The molecules stack without a special order in the columns and so the average molecule should be considered as a bent rod of C_{2v} symmetry. This assumption is necessary for the modelling.

The structural model of the B₁ phase reported to date (figure 9) consists of a packing, where the C_2 axes of the molecules are parallel to the b -axis of the lattice [3, 6, 7, 9]. The model would fulfil the symmetry of the plane

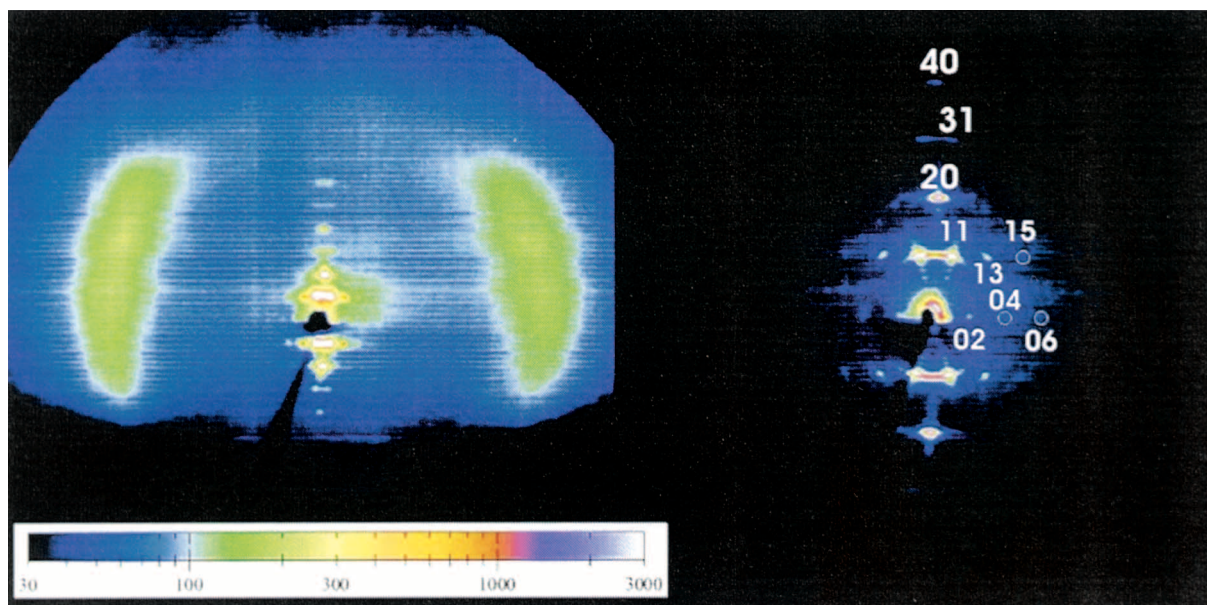


Figure 8. X-ray pattern of an oriented sample of compound **2**: (a) WAXS; (b) SAXS with indexing. Intensities are given in counts over an exposure time of 7 200 s for the WAXS and 3 600 s for the SAXS.

group No. 7 ($p2mg$) and would lead to the reflection condition $h=2n$ for the $h0$ reflections. Our X-ray pattern proved the existence of a non-tilted structure (compound **1**) and a tilted one (compound **2**). The first one could also be described by the plane group No. 7 ($p2mg$). The pattern of the second compound clearly displays additional reflection conditions ($0k: k=2n; hk: h+k=2n$), which are not compatible with the cited

plane group. There are two other plane groups ($p2gg$ and $c2mm$) with reflection conditions fulfilling the experimental findings, but the symmetry cannot be realized with the model shown in figure 9. In addition, the tilt angle, which is usually assumed to be between the averaged molecular long axis and the ab -plane, violates the symmetry of the plane groups discussed up to now.

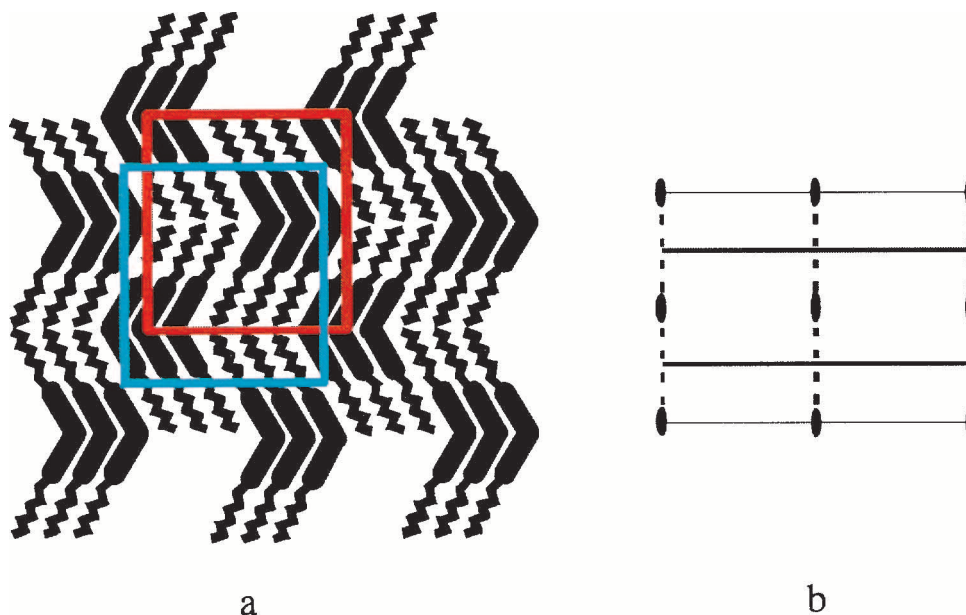


Figure 9. (a) Model of the B_1 phase used to date; the red rectangle represents the common view of the lattice unit, the blue rectangle represents the real lattice unit of $p2mg$ symmetry. (b) Symmetry conditions of the plain group $p2mg$; an oval represents two-fold rotation axis perpendicular to the ab -plane, a solid line represents a mirror line and a broken line represents a glide line.

To overcome these problems, the C_2 axes of the molecules have been assumed to be perpendicular to the ab -plane. But because of this assumption, the top and the bottom of the drawing plane will be different. Therefore, we have to pass over to the 80 layer groups. The layer groups can be derived from the 230 space groups neglecting the third direction [8, 12, 13, and 14].

The derived models are sketched in figures 10(a), and 10(b). The two-dimensional lattice is formed by columns (or layer fragments) in which the molecules are stacked with their C_2 axes along the column and orthogonal to the ab -plane. Such a packing leads to a spontaneous polarization along the column axes, which will be compensated by an antiparallel packing of neighbouring columns. This antiparallel packing is a stringent requirement for the symmetry conditions of the cells and

demands a screw axis or a glide plane parallel to the ab -plane. These symmetry elements of the lattices and the appropriate layer groups are sketched in figure 11. Accordingly, the structure of the B₁ phase of compound 1 is characterized by the layer group $pm2_1n$ (No. 32), which can be derived from the space group No. 31 [8]. The structure of the B₁ phase of compound 2 can be described by the monoclinic/oblique layer group $p11n$ (No. 21, cell choice 2) [14], derived from the space group No. 7. In the case under discussion the lattice vectors a and b make an angle of about 90° leading to a rectangular columnar phase.

6. Conclusion

The results described in the previous section clearly indicate the existence of two different B₁ phases. They

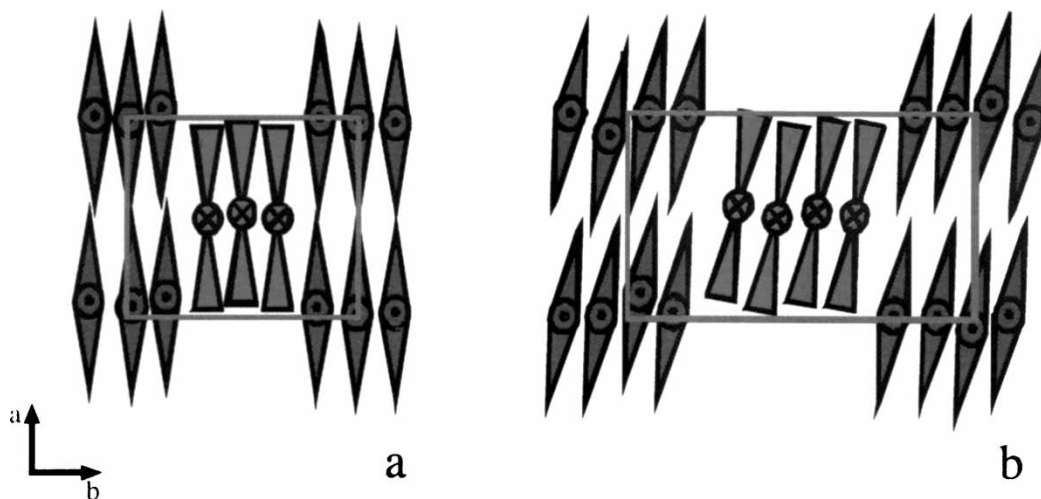


Figure 10. Sketches of the models for (a) the B_{1o} phase and (b) the B_{1t} phase.

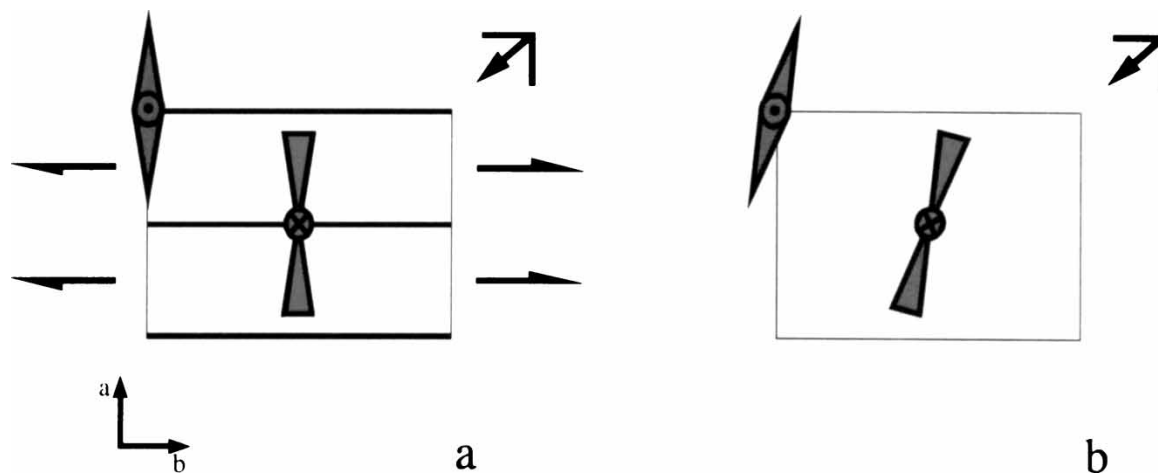


Figure 11. Symmetry conditions in layer groups $pm2_1n$ (a) and $p11n$ (b), with the exemplary placement of two molecules into them; a solid line represents a mirror plane, and an arrow represents a two-fold screw axis. The glide plane parallel to the ab -plane is represented by a corner line with an arrow denoting the glide direction.

are different in the alignment of the molecules (and therefore different with respect to the lattice symmetry) within the rectangular lattice and have been preliminary designated by B_{10} and B_{1t} —non-tilted and tilted. A more precise nomenclature would be $Col_{rect}(pm2_1n)$ and $Col_{rect}(p11n)$, including the symmetry of the layer group. The observed symmetry, based on X-ray patterns of well developed monodomains, demands—at least for the B_{1t} phase—a new packing model for the bent-shaped molecules. In this packing model the bent direction (C_2 axis of the molecules) is perpendicular to the ab -plane (or in direction of the columns)—a model which has been used earlier to explain the results found by optical observations [8, 9]. It is expected that this model can be applied also to other examples reported in the literature. The two compounds reported in this paper are members of two homologous series which are under investigation.

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