PHYSICAL REVIEW E **72**, 041709 (2005)

Structure of mesogens possessing *B*7 textures: The case of the bent-core mesogen 8-OPIMB-NO_2

C. L. Folcia and J. Etxebarria
Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

J. Ortega
Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

M. B. Ros
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain

(Received 8 February 2005; revised manuscript received 27 April 2005; published 24 October 2005)

A structural investigation of the compound 8-OPIMB-NO_2 is carried out. This material is a mesogen formed by bent-core molecules where the so-called *B*7 phase was originally proposed. X-ray data are successfully indexed in terms of a oblique two-dimensional lattice. Using additional information from optical second harmonic generation several possible structural models are proposed. The models are based on molecular packing considerations. All these structures are clearly different from those of other materials previously classified as *B*7. The necessity of a revised nomenclature for classifying the structures of these compounds is pointed out.

DOI: 10.1103/PhysRevE.72.041709 PACS number(s): 61.30.Eb, 42.65.Ky, 61.30.Cz, 61.10.Eq

Among the mesogens formed by bent-core molecules [1–3], the so-called *B*7 phase is special due to the spectacular textures it presents, which are remarkable even for the liquid crystals standards. On cooling from the isotropic phase, the *B*7 phase nucleates as spiral domains, oval domains with stripes, telephone wires, checker board textures, etc. The compound where these textures were first observed is called 8-OPIMB-NO_2 and *B*7 was the name proposed for this phase [4]. The molecular structure and phase sequence are shown in Fig. 1.

Subsequently, many other materials with similar textures have appeared in the literature [5–14]. However, it is not clear that all the materials with *B*7 textures have really the same structure. For example Bedel *et al.* found that materials studied in Ref. [5] are not miscible with the *B*7 reference compound 14-OPIMB-NO_2. Ortega *et al.* [15] observed *B*7-like textures in a compound classified in principle as *B*1 [16] after a prolonged electric-field treatment. Other contradictory reports on the features of the *B*7 phase are also pointed out in Ref. [11]. In view of all these facts we can conclude there is no clear rule of what really constitutes the *B*7 phase.

Recently Pelzl *et al.* [14] have proposed to distinguish between compounds such as MHOBOW [13] or PBCOB [9,13] and the materials studied in Refs. [4–8,10–12,14]. The distinction is made on the basis of some characteristics of the x-ray diffraction patterns observed for powder samples. In the first group of materials there are strong commensurate reflections (which indicate a layer structure) and small incommensurate satellites (indicating a one-dimensional undulation of the smectic layers with a relatively long wavelength). The compounds of the second category, however, should have different structures since the x-ray diagrams have strong incommensurate reflections. It seems that in all cases the structures can be constructed in terms of an underlying two-dimensional (2D) lattice, though a complete structural model has only been presented for compounds of the first type [13,17].

In this paper we present a structural investigation of the material 8-OPIMB-NO_2. The study is essentially based on x-ray measurements. Different indexing schemes will be discussed in detail. On the basis of such measurements and additional information from nonlinear optical data we will conclude with some structural models for the phase.

For the x-ray measurements we used a small-angle goniometer with a high-temperature attachment and a linear position-sensitive detector (PSD) of 4° of angular range. Monochromatic Cu $K\alpha$ radiation was used. The material cannot be aligned so the measurements were made on a powder sample in a Lindemann capillary of diameter 0.5 mm.

Figure 2 shows the observed reflections for Bragg angles $\theta < 2°$. Eight peaks (numbered in the figure) can be appreci-

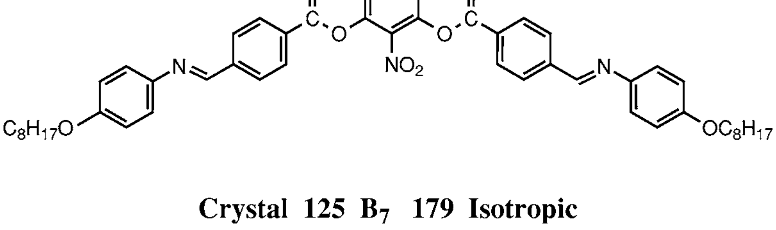

FIG. 1. Chemical structure and phase sequence of the studied material.

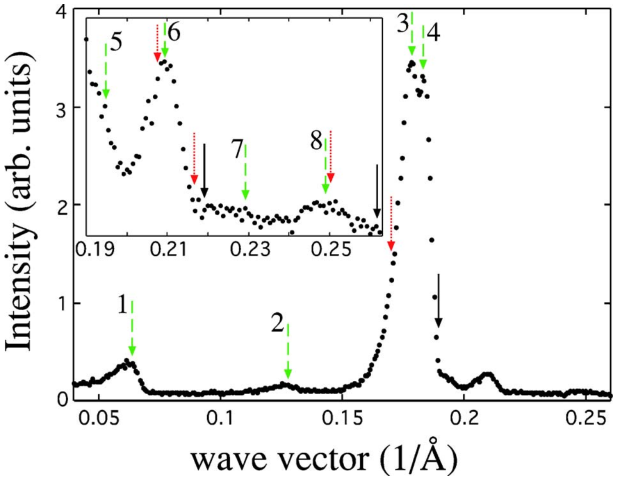

FIG. 2. (Color online) X-ray diffraction intensities as a function of the wave vector $q=4\pi/\lambda \sin\theta$, where λ is the x-ray wavelength. Eight peaks are observed for Bragg angles $\theta<2°$. The different types of arrows indicate the calculated peak positions according to several indexing schemes. The best agreement is found for an oblique 2D cell [dashed (green) arrows]. The resulting Miller indices are 1:(20), 2: (40), 3: (11), 4: $(\bar{1}1)$, 5: (31), 6: $(\bar{3}1)$, 7: (51), 8: $(\bar{5}1)$. Only reflections (hl) with $h+l$ even are observed.

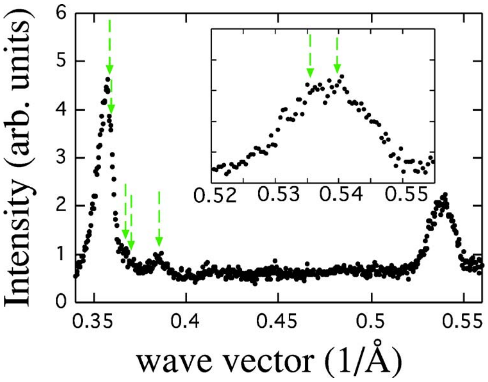

FIG. 3. (Color online) Intensities of the (hl) reflections with $l=2$ and 3. The arrows indicate the calculated positions of the peaks (from left to right) (02), (22), $(\bar{2}2)$, (42), $(\bar{4}2)$. Small $(h2)$ satellites $(h\neq 0)$ are only visible at low temperatures and using long exposure times. In the inset reflections (13) and $(\bar{1}3)$ are also indicated. The data correspond to 130 °C.

ated. The measurement corresponds to a temperature of 170 °C. Additional sharp peaks at larger angles as well as a broad diffuse reflection at about $\theta=10°$ were observed when the PSD was conveniently positioned. All data are consistent with previously made measurements [4,17].

The diagram is mainly characterized by a high double peak together with other low-intensity reflections. The peaks with the smallest angles (1 and 2 in Fig. 2) correspond to the first and second order of a given periodicity which is incommensurate with any other in the diagram. It results therefore that the structure of the material can only be described by a 2D lattice.

We turn now to the indexing of the peaks. The simplest hypothesis is a 2D orthogonal lattice, as in the case of MHOBOW [13]. It then seems reasonable to take peak 1 as (10) [or peak 2 as (20)], and the highest peak 3 as (01), which corresponds to the smectic periodicity. As a result of this assignment the cell parameters are $a=98.5$ Å, $c=35.2$ Å. However, this simple model does not work. As can be seen in Fig. 2 the calculated peak positions for (11), (21), and (31) reflections (see black arrows) give rise to poor indexing for the peaks 4, 6, and 8, respectively. In addition, peaks 5 and 7 do not exist in this model. Therefore we have to resort to a oblique cell.

Under the assumption of a 2D oblique lattice we will now begin with the same indices assignment for peaks 1 (or 2) and 3. Taking peak 4 as (11) we obtain the same values of a and c as before, and an angle $\beta=84.5°$ between the a and c directions. Within this model peaks 5, 6, 7, and 8 become $(\bar{1}1)$, (21), $(\bar{2}1)$, and (31), respectively. The agreement [see dashed (green) arrows in Fig. 2] is very good. However, there is a problem. Since we are close to an orthogonal lattice (β is not so far from 90°), reflections (hl) and $(\bar{h}l)$ should be similar in intensity. This occurs by continuity reasons, since both reflections are symmetry equivalent in the orthogonal model, which is described by an orthorhombic layer group. Then, it is difficult to explain why peaks (11) and $(\bar{1}1)$ (4 and 5) are so different. The same happens between (21) and $(\bar{2}1)$ (peaks 6 and 7), and between (31) (peak 8) and $(\bar{3}1)$, which is absent in the diagram. A third possibility consists in considering that peaks 3 and 4 correspond to (11) and $(\bar{1}1)$, together with (10) and (20) to peaks 1 and 2 as above. Now, by construction, (11) and $(\bar{1}1)$ reflections have similar size. A nearly orthogonal lattice ($a=98.5$ Å, $c=37.1$ Å, $\beta=87.5°$) is obtained again but, apart from the absence of the (01) reflection (which could be included within the left side of the double peak), the different diffraction angles do not match the experimental ones [dotted (red) arrows in Fig. 2].

Finally we again assume that peaks 3 and 4 are (11) and $(\bar{1}1)$, but now assign the indices (20) and (40) to peaks 1 and 2. The agreement between observed and calculated peak positions is excellent [see again dashed (green) arrows in Fig. 2, whose positions exactly coincide with those of the second hypothesis though the indices assignment is different]. The indices for peaks 5, 6, 7, and 8 are now (31), $(\bar{3}1)$, (51), and $(\bar{5}1)$, respectively. The cell parameters result $a=197$ Å, $c=35.2$ Å, $\beta=85.2°$. In this model the intensities of reflections $(h1)$ and $(\bar{h}1)$ are well correlated. Remarkably, the (01) peak is absent and, more in general, only (hl) reflections satisfying $h+l=2n$ are observed. This fact is nothing but a systematic extinction rule that implies we have a centered lattice. At larger Bragg angles other reflections with $l>1$ have also been found. These are compatible with the above cell parameters and selection rule (see Fig. 3). Therefore we unambiguously conclude we have a 2D oblique centered lattice [18].

In Table I the experimental wave vectors q of the different peaks are summarized together with their fitting errors δq and Miller indices corresponding to each indexing scheme. The cell parameters present a slight variation as a function of temperature. This is especially the case with a (which changes between 190 and 197 Å from 130 to 170 °C) and β

TABLE I. Experimental wave vectors q of the eight peaks observed for Bragg angles below 2° and their fitting errors δq (in units of 10^{-3} Å^{-1}) for the four indexing models considered in the text. For each peak the Miller indices are given in parenthesis. The experimental error in q is about 10^{-3} Å^{-1} in all cases.

	q (Å^{-1}) (expt)	δq Model 1		δq Model 2		δq Model 3		δq Model 4	
Peak No. 1	0.064	0	(10)	0	(10)	0	(10)	0	(20)
Peak No. 2	0.127	1	(20)	1	(20)	1	(20)	1	(40)
Peak No. 3	0.178	1	(01)	1	(01)	0	(11)	1	(11)
Peak No. 4	0.183	7	(11)	0	(11)	0	$(\bar{1}1)$	0	$(\bar{1}1)$
Peak No. 5	0.194	—		1	$(\bar{1}1)$	—		1	(31)
Peak No. 6	0.209	10	(21)	0	(21)	2	(21)	0	$(\bar{3}1)$
Peak No. 7	0.229	—		0	$(\bar{2}1)$	13	$(\bar{2}1)$	0	(51)
Peak No. 8	0.249	13	(31)	0	(31)	1	(31)	0	$(\bar{5}1)$

(which decreases from 86.0° to 85.2° in the same temperature interval).

Apart from the data deduced from the x-ray measurements, we have complementary information on the structure deduced from optical observations. First, optical textures under the polarizing microscope reveal that the structure is anticlinic because texture colors are dark, indicating low birefringence, and the extinction directions are parallel to the polarizers directions in the circular domains. In addition, we have found that the material is second-harmonic generation (SHG) active even in the absence of any electric field. This last experiment was carried out with a Nd:YAG laser and the sample was inside a Lindemann capillary. While no SHG is detected in the isotropic phase, a surprisingly strong signal appears on cooling at the transition into the mesophase. This effect is quite reproducible on different runs. The SHG signal decreases somewhat on further cooling, but remains non-null in spite of the strong light scattering that the sample presents in all the range of stability of the mesophase. Consequently we conclude that the structure cannot have an inversion center.

On the basis of the above experimental results a structural model can now be proposed. Let us first consider the fact that the lattice is 2D and centered. These characteristics already invalidate for our material the *B*7 model proposed by Coleman *et al.* [13] because it is based on a noncentered lattice. In fact, a better approach seems to be constituted by some columnar models proposed for the *B*1 (instead of *B*7) phase, where there is molecular interdigitation often leading to centered lattices. Evidently, nontilted or synclinic models [19,20] must be put aside, since we clearly have an anticlinic structure. Moreover, any anticlinic variant of the two latter structures implies very unfavorable molecular packing at the edge of the columns and, therefore, must also be discarded [21].

We now consider the model proposed by Coleman *et al.* for the *B*1 phase (Fig. 1H of Ref. [13]). The molecular organization is schematized in Fig. 4. The structure is anticlinic and centered (for nonresonant x-ray scattering) [24]. In addition, the splay of the polarization that the structure exhibits permits a much more effective molecular packing at the defects. Unfortunately, the structure is centrosymmetric (layer group $p2_1/c11$ [25]) and the inversion centers remain even if the lattice is forced to be oblique. However, inspired by Coleman's model we present in Fig. 5 four different structures compatible with our experimental results. As can be seen, all of them are anticlinic, oblique, and noncentrosymmetric. On the other hand, although these structures are not truly centered, they are indistinguishable from a centered one for nonresonant x-ray measurements, especially in this material in which the parameter a is very large [24]. The structures depicted in Figs. 5(a) and 5(b) are antiferroelectric and homochiral while the ones in Figs. 5(c) and 5(d) are ferroelectric and racemic. It is important to remark that there is no experimental evidence to conclude that the studied phase has ferroelectric or antiferroelectric ordering since the material is not switchable.

From the position of the diffuse scattering maximum in the wide-angle region ($\theta = 10°$) and the a-value we deduced that approximately 20 molecules conform each fragment in Fig. 5. On the other hand, a molecular tilt angle of about 40° was obtained from the experimental c-value and the calculated molecular length of the most stable conformation of the central core and the most extended side chains.

It should be noted that among the four models, two of them [Figs. 5(a) and 5(c)] represent a frustration of the smectic layer formation of the well-known structures SmC_AP_A

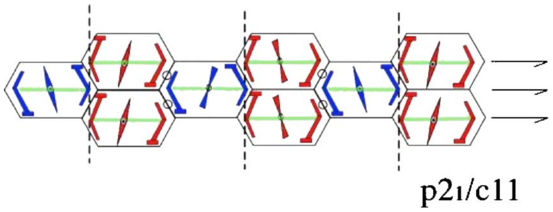

FIG. 4. (Color online) Structure proposed in Ref. [13] for the *B*1 phase. Polarization splay within the columns improves the molecular packing at the edges. The layer group of the structure is $p2_1/c11$ and the lattice is orthogonal. The symmetry elements (inversion centers, glide planes, and screw axes) are indicated. For nonresonant x-ray scattering all columns are equivalent (due to the liquid disorder inside them) and, therefore, the lattice is orthogonal centered. In this case the symmetry is higher and the layer group becomes *cmmm*.

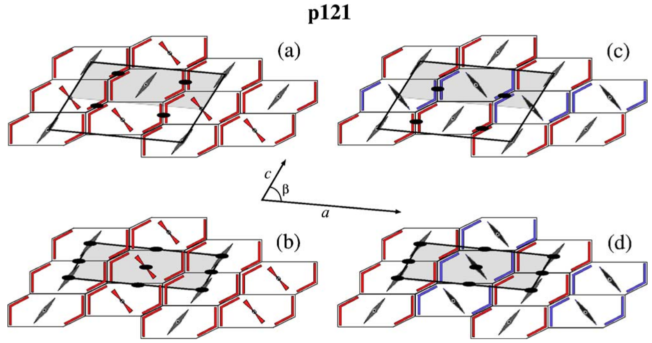

FIG. 5. (Color online) The four structures proposed for the *B*7 phase of the studied material. The layer group is the monoclinic-oblique *p*121 in all cases. The centered unit cell determined from the (nonresonant) x-ray experiment is shadowed. It is not the true unit cell, but the cell of the lattice of columns with liquid disorder inside. The true crystallographic cell and the symmetry elements are also indicated. The molecular tilt decreases as we approach the edge of the columns. This effect induces a molecular leaning to maintain constant the smectic layer thickness. For simplicity at the edge of the columns the molecules have been drawn contained on the plane of the figure.

and SmC_AP_F, which are very often found in bent-core mesogens. The origin of the layer fracture can be understood in terms of defects of the polarization splay which would produce half-layer displacement in order to obtain more effective molecular packing.

A final point must be raised regarding the oblique character of the structure. As can be seen in Fig. 5, packing requirements imply a molecular leaning at the edge of the columns. The origin of this effect is due to a decrease of the tilt angle at the defects of the polarization splay [13]. This fact, in its turn, gives rise to a small molecular leaning to keep the layer thickness constant everywhere. This molecular organization then forces the structure to be slightly oblique as depicted in Fig. 5. It should be noticed that the alternation of the dipole moment components along the layer normal results in a null polarization in this direction.

In summary, we have presented several possible structural models for the compound where the name "*B*7 phase" was originally coined. None of these structures corresponds to what currently is understood by a *B*7 phase. Surprisingly, the deduced structures are closer to some columnar models proposed for the *B*1 phase. The lack of smectic planes explains why free-standing films are not stable in this material [4] (in contrast, e.g., to MHOBOW [13]) and, however, the formation of freely suspended filaments is favored. Probably other *B*7-like materials cannot be classified as *B*7 either. More structural work is necessary to find out if other compounds with *B*7 optical textures also have structures similar to a *B*1 phase. In any case, it seems evident that the present classification scheme for bent-core mesogens is confusing and must be revised.

We are grateful to Professor G. Madariaga for his help with the x-ray measurements. This work was supported by the CICYT of Spain (Project No. MAT2003-07806-C02) and the University of the Basque Country (Project No. 9/UPV 00060.310-13562/2001).

---

[1] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, J. Mater. Chem. **6**, 1231 (1996).

[2] D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Kórblova, and D. M. Walba, Science **278**, 1924 (1997).

[3] G. Pelzl, S. Diele, and W. Weissflog, Adv. Mater. (Weinheim, Ger.) **11**, 707 (1999).

[4] G. Pelzl, S. Diele, A. Jakli, Ch. Lischka, I. Wirth, and W. Weissflog, Liq. Cryst. **26**, 135 (1999).

[5] J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen, and M. F. Achard, Liq. Cryst. **27**, 1411 (2000).

[6] G. Heppke, D. D. Parghi, and H. Sawade, Liq. Cryst. **27**, 313 (2000).

[7] D. S. S. Rao, G. G. Nair, S. K. Prasad, S. A. Nagamani, and C. V. Yelamaggad, Liq. Cryst. **28**, 1239 (2001).

[8] V. Prasad, Liq. Cryst. **28**, 1115 (2001).

[9] C. K. Lee, A. Primak, A. Jakli, E. J. Choi, W. C. Cinand, and L. C. Chien, Liq. Cryst. **28**, 1293 (2001).

[10] R. A. Reddy and B. K. Sadashiva, Liq. Cryst. **29**, 1365 (2002).

[11] J. Mieczkowski, J. Szydlowska, J. Matraszek, D. Pociecha, E. Gorecka, B. Donnio, and D. Guillon, J. Mater. Chem. **12**, 3392 (2002).

[12] H. N. S. Murthy and B. K. Sadashiva, Liq. Cryst. **30**, 1051 (2003).

[13] D. A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Y. Takanishi, E. Körblova, D. R. Link, R. F. Shao, W. G. Jang, J. E. Maclennan, O. Mondainn-Mova, C. Boyer, W. Weissflog, G. Pelzl, L. C. Chien, J. Zasadzinski, J. Watanabe, D. M. Walba, H. Takezoe, and N. A. Clark, Science **301**, 1204 (2003).

[14] G. Pelzl, M. A. Schröder, U. Dunemann, S. Diele, W. Weissflog, C. Jones, D. Coleman, N. A. Clark, R. Stannarius, J. Li, B. Das, and S. Grande, J. Mater. Chem. **14**, 2492 (2004).

[15] J. Ortega, J. Etxebarria, C. L. Folcia, J. A. Gallastegui, N. Gimeno, and M. B. Ros, Poster STR-P075 presented at the *20th International Liquid Crystal Conference, Ljubljana, Slovenia, 2004*.

[16] J. Ortega, M. R. de la Fuente, J. Etxebarria, C. L. Folcia, S. Díez, J. A. Gallastegui, N. Gimeno, M. B. Ros, and M. A. Pérez-Jubindo, Phys. Rev. E **69**, 011703 (2004).

[17] D. A. Coleman, Ph.D. thesis, University of Colorado, 2003.

[18] Strictly speaking, a 2D oblique centered lattice must be described in terms of a primitive oblique unit cell. This is the international convention. However, we have preferred to maintain the centered oblique lattice because the structure is close to a rectangular centered lattice and, in this way, the lattice parameters keep a clearer physical meaning.

[19] J. Szydlowska, J. Mieczkowski, J. Matraszek, D. W. Bruce, E. Gorecka, D. Pociecha, and D. Guillon, Phys. Rev. E **67**, 031702 (2003).

[20] K. Pelz, W. Weissflog, U. Baumeister, and S. Diele, Liq. Cryst. **30**, 1151 (2003).

[21] An anticlinic modification of the $B1$ structure proposed by Watanabe *et al.* in Ref. [22] could present acceptable molecular packing at the edge of the columns, but must not be considered since it is not strictly centered. On the other hand the anticlinic columnar structure reported in Fig. 20b of Ref. [23] is not centered either.

[22] J. Watanabe, T. Niori, T. Sekine, and H. Takezoe, Jpn. J. Appl. Phys., Part 2 **37**, L139 (1998).

[23] C. Tschierske and G. Dantlgraber, Pramana **61**, 455 (2003).

[24] This structure is not strictly centered even for nonresonant x-ray scattering due to its anticlinicity. Therefore $2n+1=h+l$ reflections are not rigorously forbidden. However, some considerations can be done regarding the structure factor of the building units. In liquid crystals exhibiting 2D periodicity the tilt direction of the different units could, in principle, be detected. The difference between tilt signs is manifested mainly at the edge of the building units. However, this effect is highly weakened by the splay of the polarization. On the other hand, it is evident that the deviation from the centered character must be less important the larger the length of the smectic fragments.

[25] *International Tables for Crystallography, Vol. E, Subperiodic Groups*, edited by V. Kopsky and D. B. Litvin (Kluwer Academic, Dordrecht, 2002).