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Evidence of a tilted columnar structure for mesomorphic phases of benzene-hexa-n-alkanoates

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Résumé. — Des mesures optiques sur les phases mésomorphes de n-hexa-alkanoates de benzène et leurs mélanges avec du benzène montrent que les plans de ces molécules discoïdes ne sont pas, comme on le croyait jusqu'ici, perpendiculaires à l'axe des colonnes où elles sont empilées. Cette constatation provient essentiellement de l'existence, dans les domaines de texture de courbure circulaire, de pinceaux d'extinction obliques obtenus entre polariseur et analyseur croisés. En effet ces pinceaux ne sont ni parallèles ni perpendiculaires aux directions de l'analyseur et du polariseur, l'inclinaison peut varier d'un spécimen à l'autre jusqu'à un angle maximum de l'ordre de 35°. L'empilement des disques inclinés à un angle d'environ 35° (par rapport à l'axe optique de la molécule) rend compte de toutes les observations. Quatre modèles différents d'une telle structure sont discutés ici : Deux où toutes les molécules ont le même axe d'inclinaison et deux où une succession en *arête de poisson* des orientations de ces axes est considérée. Tous ces modèles conduisent à un réseau pseudo-hexagonal rectangulaire. Il est montré que la déviation par rapport à la configuration de symétrie axiale ainsi obtenue est suffisamment faible pour ne pas être incompatible avec les résultats de diffraction de R.X. interprétés jusqu'ici par une symétrie hexagonale. Ces structures permettent plusieurs modes de jumelage des molécules qui expliquent les images optiques complexes obtenues dans quelques domaines de courbure circulaire.

Abstract. — Optical observations on the mesomorphs of benzene-hexa-n-alkanoates, and their admixtures with benzene, show that the planes of these discotic molecules are not perpendicular to the columns in which they are stacked, as was supposed originally. This evidence comes principally from the occurrence in texture domains of circular bending, between crossed polarizer and analyser, of oblique extinction brushes (i.e., brushes not parallel or perpendicular to polarizer and analyser directions). The obliquity varies from specimen to specimen up to a maximum of about 35°. A tilted stacking, with a tilt angle (for the optic axes of the molecules) of about 35°, will fit all the observations. Four alternative variants of such structures, two with the same tilt axes for all molecules, two with a *herring-bone* alternation between two orientations of tilt axis, all of which give rectangular pseudo-hexagonal lattices, are discussed. It is shown that the departure from hexagonal axial ratio required by these tilted structures is small enough not to be incompatible with the X-ray diffraction evidence previously interpreted as indicating hexagonal symmetry. These structures allow several different twinning modes, and complex optical features in some domains of circular bending are explicable in terms of these twinings.

The canonic or columnar phases of benzene-hexa-n-alkanoates ⁽¹⁾ discovered in 1977 [1] were originally considered to have hexagonal symmetry. It is difficult, however, to obtain well-aligned samples of these substances, and the quality of the X-ray diffraction pictures obtained would not suffice to exclude the alternative of a pseudo-hexagonal structure, e.g., one with the columns comprising aperiodic

stackings of discs, arranged in a centred rectangular lattice having an axial ratio b/a differing by up to about 10 % from the ideal hexagonal value of $\sqrt{3}$.

Evidence since acquired, inviting a reconsideration of this symmetry assignment, particularly concerns the birefringence. This was earlier observed to be negative, i.e., having a smaller refractive index for the electric vector parallel to the columnar axis than transversely : consistently with the model according to which the columns are stacks of the *discotic* molecules with their planes normal to the axis. In subsequent observations, both with the pure substances and with admixtures of benzene to them (which lowers the temperature range of existence of the

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⁽¹⁾ We employ the word *discotic* for description of such molecules as these, not of the type of mesomorphic phases of which they provide examples.

mesomorphs, apparently without phase change) textures have not infrequently been obtained in which the columnar axes (or, more objectively, certain parallel striations thought to be parallel to the columnar axes) are curved in circles or in spirals (Fig. 1, and Fig. 7 of ref. [2]). Between crossed polarizer and analyser these may give well-defined extinction brushes, 90° apart, but not in the *standard* directions



Fig. 1. — Texture domains of circular bending showing oblique extinction brushes. (a) Top : pure benzene-hexa-n-heptanoate (BH7), (b) Bottom : BH7 + benzene. Polarizer-analyser directions \oplus .

parallel to polarizer and analyser : rather, when well-defined and accurately radial they are inclined at angles up to about 35° to right or left of the polarizer and analyser directions. Some relatively narrow fans, with extinction in the *standard* directions along the central radius of the fan, are indeed seen, particularly in the pure substances : and curved brushes, transitional brushes connecting a radial brush at $+\sim 35^\circ$ in one zone to one at $-\sim 35^\circ$ in a zone of larger radius, and zig-zag brushes alternating between those extreme orientations, are also seen. The birefringence appears to be weaker, but not zero, at the centre of a transitional brush, or of the « zig » or « zag » of a zig-zag, i.e., when it is at a position angle of 0° relative to polarizer or analyser directions.

The obvious implication is that the direction of minimum polarizability is not parallel to the columns, but rather inclined to it by an angle of about 35° .

This implies a *tilted columnar* structure, in which the columns comprise stacked discotic molecules with their planes non-orthogonal to the axes of the columns. Such a structure has been reported by Destrade *et al.* [3] as occurring as a second mesomorphic phase for the hexa-n-alkoxybenzoate of triphenylene ($R = C_6H_{13}O$). Their paper does not report the evidence from which this structure was deduced.

A small deflection of the brushes can be attributed to a spiral rather than a circular configuration in these textures (see Fig. 7 of ref. [2]). However, for an equi-spaced spiral whose radius r increases by p for each turn, the spiral deviates from orthogonality to the radius by an angle $p/2\pi r$, less than 1° after 10 turns, and less than 10° after only a single turn of the spiral, quite incapable of explaining the brush-deflections actually observed.

If the molecules are regarded as thin rigid discs, all tilted by 35° in the same direction, the right sections of the columns they form become ellipses of axial ratio $\cos 35^\circ \sim 0.82$. A corresponding distortion of the hexagonal lattice would certainly be more than could escape notice. However, the molecule is not rigid : it should rather be regarded as having a rigid core comprising the benzene ring and its directly attached oxygen atoms, and a flexible aliphatic fringe. The diameter of the rigid core is only about a third of that of the whole molecule. The anisotropy of polarizability resides mainly in the rigid aromatic core : if this tilts more than the molecule as a whole we can account for the birefringence observations without asking for an unacceptably large lattice distortion. Such a configuration allows the fringing aliphatic chains more space in which to gain entropy from their flexibility.

Figure 2 shows the four rectangular lattices of columns with tilted molecules, having uniform tilt in each column, which in principle are compatible with the existing limited evidence, Ia and Ib being centred rectangular lattices, having one column per primitive unit cell, and IIa and IIb having two columns per unit cell, which is rectangular. Other pseudo-hexagonal structures, e.g., monoclinic, or with more columns per unit cell, are not excluded by the limited evidence, but may reasonably be disregarded till there is evidence requiring their consideration.

In IIa the two classes of molecules (fictitiously represented as rigid discs) are tilted through angles φ (from orientations orthogonal to the column axis c) about axes with rectangular indices $[uv.]$ and $[\bar{u}\bar{v}.]$, making angles respectively $\pm \theta$ with \mathbf{a} . IIa reduces to Ia when $\theta = 0$. For both Ia and IIa the mean rotation axis for the tilt is \mathbf{a} .

In IIb the corresponding rotation axes for the two classes of molecules are $[uv.]$ and $[\bar{u}\bar{v}.]$, making angles θ and $\pi - \theta$ respectively with \mathbf{a} . The mean rotation axis is \mathbf{b} , and IIb reduces to Ib when $\theta = \pi/2$.

Calculating mean polarizabilities by crude approximation, treating the molecules as circular discs and

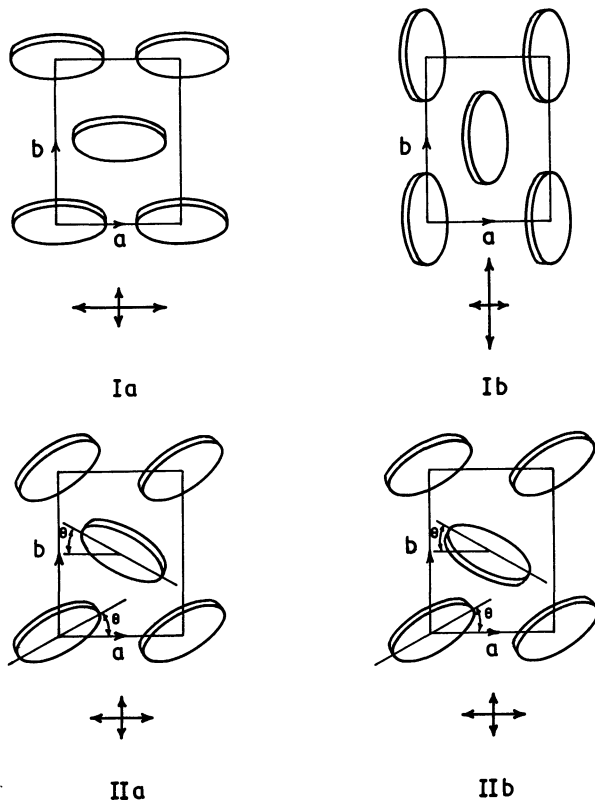


Fig. 2a. — Rectangular pseudo-hexagonal columnar structures with tilted discotic molecules : viewed in projection along the columnar axis *c* : pseudo-principal polarizabilities in the *ab* plane indicated for each.

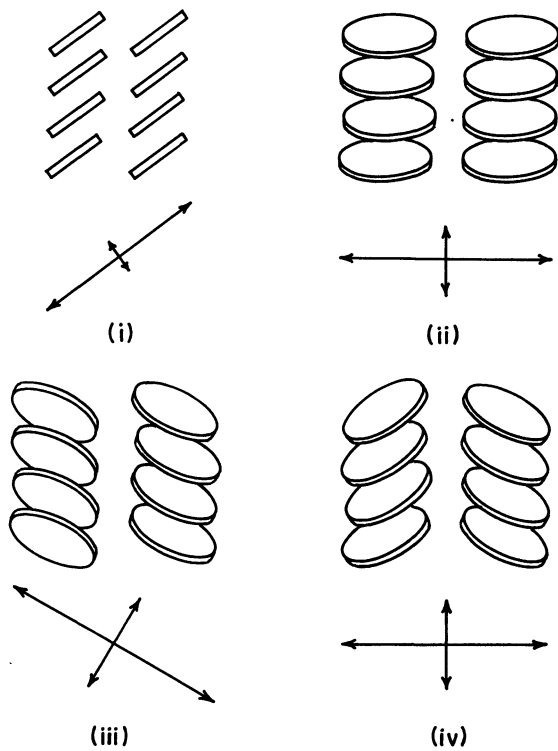


Fig. 2b. — Columns with tilted discotic molecules : viewed in projections perpendicular to *c*. (i) Ia seen along *a* or Ib seen along *b*, (ii) Ia seen along *b* or Ib seen along *a*, (iii) IIa seen along *a* or IIb seen along *b*, (iv) IIa seen along *b* or IIb seen along *a* : pseudo-principal polarizabilities indicated for each.

ignoring internal field interactions, effective tilt angles φ_{eff} are given by

$$\tan \varphi_{eff} = \tan \varphi \cos \theta \quad \text{in case IIa}$$

$$\tan \varphi_{eff} = \tan \varphi \sin \theta \quad \text{in case IIb .}$$

φ_{eff} denotes the angle which the principal axis of minimum polarizability (provided that $\sin^2 \varphi \sin^2 \theta < 1/2$) makes with the column axis *c*. Denoting by $\alpha_{||}$ the polarizability of the molecule along its symmetry axis (normal to its plane) and α_{\perp} ($> \alpha_{||}$) the polarizability in any direction perpendicular to its symmetry axis (parallel to its plane) we have principal polarizabilities, for case IIa :

$$\alpha_1 = \alpha_{\perp} - (\alpha_{\perp} - \alpha_{||}) (1 - \sin^2 \varphi \sin^2 \theta) ,$$

$$\alpha_2 = \alpha_{\perp} - (\alpha_{\perp} - \alpha_{||}) \sin^2 \varphi \sin^2 \theta ,$$

$$\alpha_3 = \alpha_{\perp} ,$$

the directions for α_1 and α_3 being normal to *a* and at angles respectively $\varphi_{eff} = \arctan (\tan \varphi \cos \theta)$ and $\varphi_{eff} \pm \pi/2$ from *c*, while that for α_2 is parallel to *a*. The direction for α_3 is parallel to the planes of both classes of molecule.

For light incident along *a* the directions of electric vector for greatest and least refractive index are principal axes of mean molecular polarizability, inclined to the crystallographic axes *c* and *b*, and the difference between these polarizabilities is :

$$\alpha_3 - \alpha_1 = (\alpha_{\perp} - \alpha_{||}) (1 - \sin^2 \varphi \sin^2 \theta) .$$

For light incident along *b* or *c* the corresponding directions are parallel to the crystallographic axes (*a* and *c* or *a* and *b* respectively) and the effective polarizability differences are :

$$(\alpha_{\perp} - \alpha_{||}) (\cos^2 \varphi - \sin^2 \varphi \sin^2 \theta) ,$$

$$\text{and } (\alpha_{\perp} - \alpha_{||}) (\sin^2 \varphi \cos^2 \theta - \sin^2 \varphi \sin^2 \theta) ,$$

respectively. These are successively smaller values, and even possibly zero or reversed in sign.

For case IIb one may apply the same formulae, exchanging *b* for *a* throughout. Cases Ia and Ib are obtained by setting $\theta = 0$, without and with this interchange respectively.

Expected lattice distortions from hexagonality are such as to make $b/a < \sqrt{3}$ in case Ia, $> \sqrt{3}$ in case Ib. No such simple correlation between tilt and lattice distortion can be inferred for cases IIa and IIb. For either of these, molecular tilt axes close to $\pm a$ should make $b/a < \sqrt{3}$ and tilt axes closer to $\pm b$ make $b/a > \sqrt{3}$. With tilt axis inclinations $\theta = 45^\circ$ an elementary argument suggests no departure from $b/a = \sqrt{3}$, though there is significant optical tilt and birefringence (but birefringence disappears for viewing along *c*). This is without invoking the considerations of molecular flexibility discussed above. However, type II structures require rather large

actual tilts (larger than the effective tilt optically observed) and are perhaps on this account less probable. A strictly zero departure from hexagonal lattice symmetry when true hexagonal symmetry is broken by the tilt is of course a highly improbable accident.

If it is assumed that in domains of circular bending the axis about which columns are bent can be any direction in the **ab** plane, then the extinction brush obliquity, when viewing between crossed polarizer and analyser looking along the axis of bend (i.e., the axis about which the columns are bent) can take any value between extremes to right or left equal to the full value of optical tilt (or effective optical tilt for case II structures). Various values of obliquity are in fact observed, for straight radial brushes, with one and the same substance. A few measured values for the pure heptanoate are $\sim 15^\circ$, 20° , 35° and for its admixtures with benzene $\sim 15^\circ$, 30° , but zero obliquity, though sometimes seen in narrow fans has never been seen for a straight radial brush in a circularly bent sector of substantial width (say, 90° or more). This avoidance of zero or near-zero obliquities suggests the existence of a tilt-bend coupling leading to the avoidance of tilt axes near to orthogonality with the axis of bend. The existence of such a coupling is to be expected from general symmetry principles, and a plausible argument to show that its sign should be such as to favour this avoidance follows from the consideration that an elastic rod of elliptical cross-section bends more easily about the longer than the shorter axis of the cross-section. The same argument suggests a weaker bend modulus for bending about the **a**-axis when $b/a < \sqrt{3}$, or the **b**-axis when $b/a > \sqrt{3}$ (and must be an inadequate argument for decision for type II structures with $\theta \sim 45^\circ$).

When, as is frequently observed (e.g., in Fig. 1b, and Fig. 7 of ref. [2]) one and the same brush orientation (and therefore the same liquid crystal lattice orientation) recurs after one or more intervening zones in which it is different, it must be inferred that these zones are in some twin-relationship to each other.

Cooperative rotation of columns about **c**, inducing a twinning of the rectangular lattice (whereby any of the $\langle 2\bar{1}\bar{1} \rangle$ hexagonal directions becomes the **a** direction of the rectangular lattice and its orthogonal

$\langle 01\bar{1} \rangle$ becomes **b**) is likely to be an easy process. If the lattice is not otherwise allowed to rotate, and the bend axis can take any direction orthogonal to **c**, then by utilization of this twinning the **a**, or **b**, axis, as appropriate, need never be further than 30° from the axis of bend : and if polymorphism between Ia and Ib, or between IIa and IIb, structures is also permissible, the departure need not exceed 15° .

Regions seen in a planar texture (i.e., one in which the viewing direction is always perpendicular to **c**), having less than the maximal deflection of extinction direction from **c**, and less than the maximal birefringence seen under this condition (the two appear to go together) may have two possible interpretations : one, that the lattice is rotated so that the viewing direction is some other than **a**, for cases Ia and IIa, or **b** for cases Ib and IIb ; or that the thickness of the specimen contains domains with opposite direction of tilt. When this occurs as a transition zone, where the brush passes through zero deflection to connect two zones in which there are equal and opposite constant deflections, the latter is probably the correct explanation : the boundary (across which the lattice can be continuous : only the sign of tilt changing) is in this case conical.

Thin dark striations with circular curvature, believed to follow the **c** direction, are probably to be interpreted as boundaries across which there is a change of orientation of the rectangular lattice, by rotation about **c**. The pure substance (rather than its admixtures with benzene) shows greater complexities of texture which cannot be unambiguously interpreted : these include both circular and radial boundaries separating regions with different extinction setting, some of which may be boundaries separating regions of opposite tilt in a continuous lattice, others having also a change of lattice orientation.

With the possibility of twinning and other processes occurring in the structure, and the experimental difficulty of preparing well-aligned specimens, a precise X-ray determination of the departure of the axial ratio **b/a** from the ideal hexagonal value of $\sqrt{3}$ may not be an easy task. However, it may be possible to distinguish between a face-centred rectangular lattice and a herring-bone pattern. Such an investigation is now in progress.

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