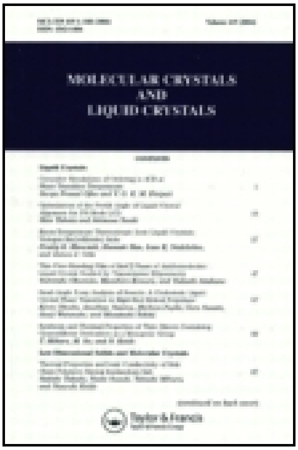

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Dissymmetric Hexasubstitued Triphenylenes†

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Version of record first published: 20 Apr 2011.

To cite this article: Nguyen Huu Tinh , M. C. Bernaud , G. Sigaud & C. Destrade (1981): Dissymmetric Hexasubstitued Triphenylenes† , Molecular Crystals and Liquid Crystals, 65:3-4, 307-316

To link to this article: http://dx.doi.org/10.1080/00268948108082140

Mol. Cryst. Liq. Cryst., 1981, Vol. 65, pp. 307–316
0026-8941/81/6504-0307$06.50/0

Dissymmetric Hexasubstituted Triphenylenes†

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(*Received June 9, 1980*)

Several dissymmetrical hexasubstituted triphenylenes have been prepared. They exhibit a low temperature thermotropic mesophase. It is shown that it corresponds to a columnar mesophase (an hexagonal arrangement of columns of discs). The magnetic properties of these new disc-like liquid crystals are compared with those of the corresponding symmetrical ones.

INTRODUCTION

Up to now disc-like mesogens provide two different thermotropic mesophases: a highly ordered columnar arrangement of discs, columnar mesophase D^1, and a fluid phase very similar to a classic nematic one (called N_D^2). This last one can be assimilated to a nematic phase in which the director vector is perpendicular to the plane of the flat disc-like molecules.[2] All the other phases correspond to a structure in which the molecules are stacked in infinite columns[3–6] with respect to a regular (o = ordered discs in a column) or irregular (d = disordered discs in a column) and considering the symmetry of the two dimensional lattice of columns: hexagonal (h) or rectangular (r) we have proposed a classification of these columnar phases[6] and shown the existence of four different arrangements: D_{ho}, D_{hd}, D_{rd} and D_t^1 this last phase has been very recently identified as a tilted (t) columnar phase.[1,4]

The disc-like molecules exhibit a six-fold axis (hexa-n-alkanoates of benzene[3]) or a three fold one (hexa-n-alkoxy[7,8] alkanoyloxy[7] or benzoyloxy triphenylenes.)[1,2,8]

Our purpose was to lower the symmetry of the disc-like molecules, for example, by putting dissymetric alkyl chains on a three-fold central rigid core in order to obtain a two-fold symmetry molecules and to examine the

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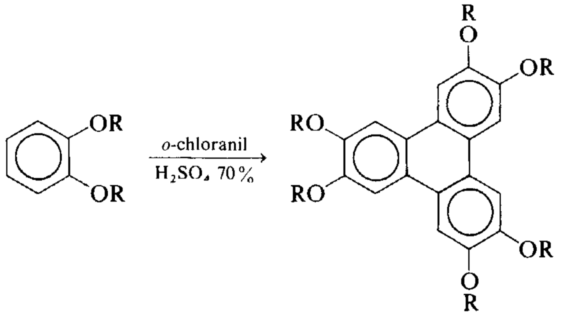
† This work was presented in the third Liquid Crystals Conference of Socialist Countries, Budapest, August 1979.

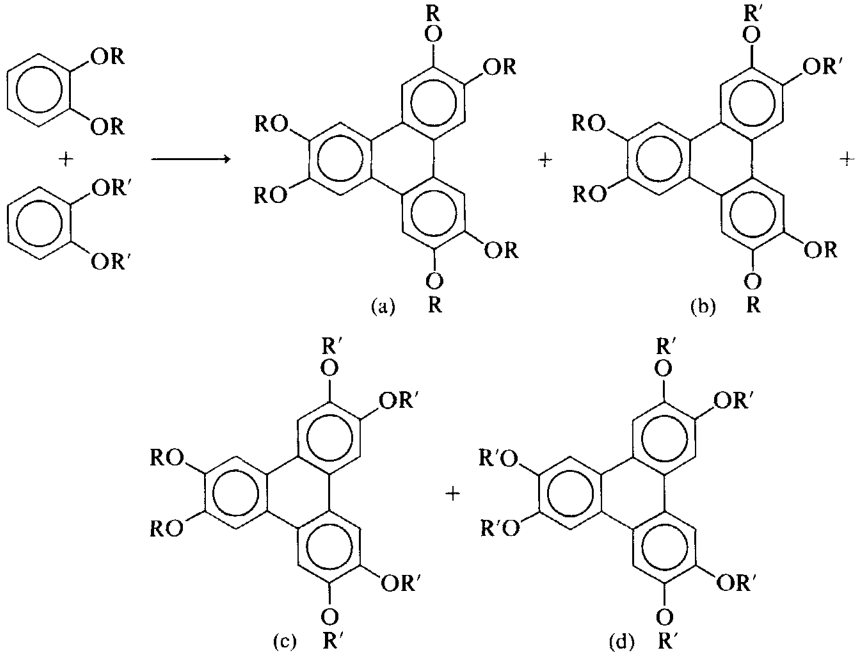
effect of this dissymetry on the mesophase. In keeping with this idea, we have built up several dissymmetrical hexa-*n*-alkoxy triphenylenes.

SYNTHESIS METHOD

We have adapted a method previously described for the preparation of symmetric hexa alkoxy triphenylenes:[9] the action of chloranil on an *o*-dialkoxy benzene in sulfuric acid to give the corresponding symmetric



hexa alkoxy triphenylene. But if we use a mixture (1/1) of two *o*-dialkoxy benzenes with $R > R'$ in the same condition we can obtain a mixture of four different hexalkoxy triphenylenes:



Two |(a) and (d)| are symmetric corresponding compounds and the other two |(b) and (c)| are dissymmetric ones. With respect to the general shape of the molecule due to the different alkyl chain length, we call these last compounds "*V*" (four long chains) and "*Y*" (two long chains). For instance, a mixture of dioctyloxybenzene and dihexyloxybenzene provides the V_{6-8} and Y_{6-8} hexaalkoxy triphenylenes.

In any case, it is possible to separate the four different compounds by repeated chromatographs on silica gel using a mixture of benzene and hexane (50/50). The purification is perfected at last by several recrystallizations in a mixture of absolute ethanol and diethyl ether.

The purity of the different samples has been checked by Mass and NMR spectroscopy and thin layer chromatography.

MESOMORPHIC PROPERTIES

The transitions were studied by differential scanning calorimetry using a DUPONT 990 thermal analyzer and optical textures were observed with a polarizing microscope equipped with a heating stage (METTLER FP5). The results are listed in Table I: they are compared with the corresponding symmetric derivatives. In most cases a stable thermotropic mesophase is observed at a relatively low temperature. In fact the same behaviour (lowering of fusion temperature) is observed also with "rod-like" liquid crystals. The

TABLE I

Transition temperature and enthalpy values (Kcal/mole) for the different dissymmetrical prepared compounds. The notation C_5, C_6, C_8, C_9, C_{10} corresponds to the symmetrical derivatives: for instance C_5 = hexapentyloxytriphenylene. | | indicates that the temperature was obtained on cooling, *K* = crystalline phase, *I* – isotropic, *D* = columnar phase

	K		*D*		*I*
C_6	·	68(8.7)	·	97(0.86)	·
V_{6-8}	·	47(17.6)	·	84(2.8)	·
Y_{6-8}	·	47(11.1)	·	84(0.9)	·
C_8	·	67(19.9)	·	86(1.0)	·
C_5	·	69(7.8)	·	122(2.0)	·
V_{5-9}	·	53(12.4)	·	71(1.4)	·
Y_{5-9}	·	54(14.3)	·	74(1.3)	·
C_9	·	57(17.0)	·	78(0.64)	·
V_{5-10}	·	57(14.0)	·	|56|(0.50)	·
Y_{5-10}	·	61(14.7)	·	63(0.67)	·
C_{10}	·	58(17.0)	·	69(0.46)	·

most important feature of these phases is the complete analogy of their optical textures with the corresponding symmetrical derivatives: see, for instance, Figures 1a, 1b.

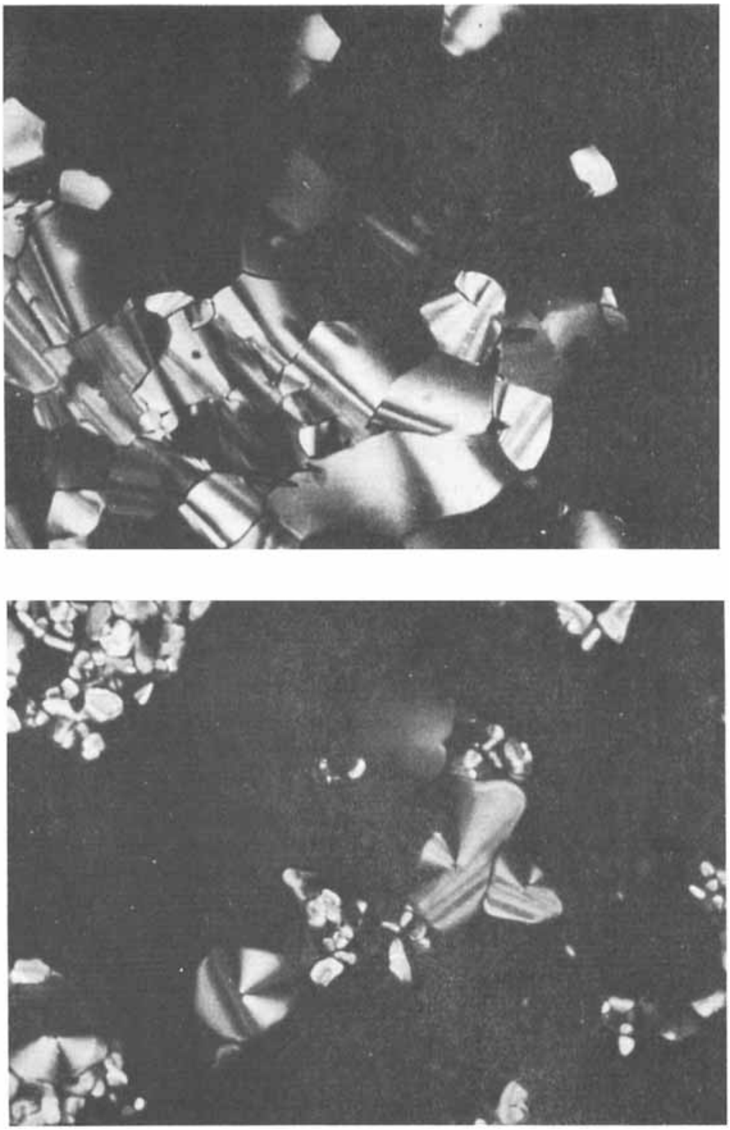


FIGURE 1 Optical texture of dissymmetric Y_{5-9} hexasubstituted triphenylene (a) and of a symmetric one, hexapentyloxy triphenylene (b).

In both cases, large homeotropic domains are observed with uniform extinction between crossed polars and some birefringent domains very similar to focal conics, one can observe with S_B phase. Several binary phase diagrams studies between symmetrical and dissymmetrical derivatives confirm these observations. The phases are in any case totally miscible (see for instance Figure 2) and confirm the presence of a columnar hexagonal ordered phase we call D_{ho} in our classification. So the analogy of this mesophase with a S_B is very great in an optical texture and molecular structure point of view: in both cases, an hexagonal ordered arrangement of molecules.

If one would like to use with columnar phases the same nomenclature than with smectic phases it could be said that the D_{ho} phase is a D_B phase

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Magnetic susceptibility measurements have been performed on these dissymmetric molecules. Thus the orientating effect of the field can be compared to what is observed with the D_{ho} phases of symmetric disc-like molecules.[10] The thermal evolution of the susceptibility $\chi_{//}$ measured in a direction

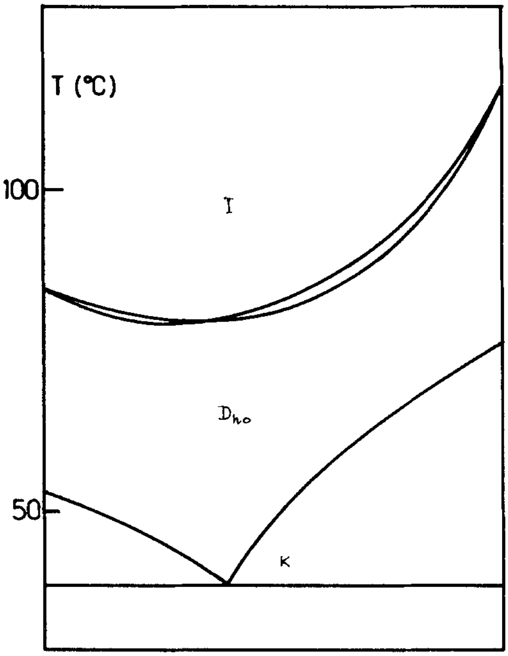


FIGURE 2 Diagram of isobaric state for the mixture Y_{5-9} (on left) and hexapentyloxytriphenylene on right).

parallel to the field for the Y_{5-9} compound is represented on the Figure 3a. We have besides reported the curve corresponding to the $n = 5$ symmetric hexaalokoxy triphenylene (Figure 3b). The two compounds behave similarly with a clear decrease of the magnetic susceptibility at the isotropic-columnar transition which is indicative of an orientating effect of the field as described in a previous paper[10] (the aromatic cores tend to orientate in directions parallel to the magnetic field).

DISCUSSION

In spite of the molecular dissymmetry, we have pointed out that these compounds exhibit a perfectly hexagonal ordered columnar phase D_{ho}[1,5,8] The most realistic hypothesis which can be made to explain this fact is that the molecules in the column adapt an helicoidal repartition, so that on an average the diameter of the column is constant.

We show also that the steric hindrance of the dissymmetrical alkyl chain is very weak and is not able to induce a nematic disc-like phase N_D;[1,2] up to now a carboxylate group is only able to destroy or deforms the order of the discs in a column.

On a more general point of view on disc-like mesogens, it is very surprising that dissymmetrical molecules are able to lead to perfectly cylindrical columns, while symmetrical ones can lead to heliptic deformed columns![1,5,6]

At last the magnetic properties of the D_{ho} phase are not affected by the dissymmetry of the molecules. This result is interesting since the field keeps an orientating effect when at the same time the transition temperatures are lowered.

Acknowledgements

The authors are indebted to Dr M. F. Achard for magnetic susceptibility measurements.

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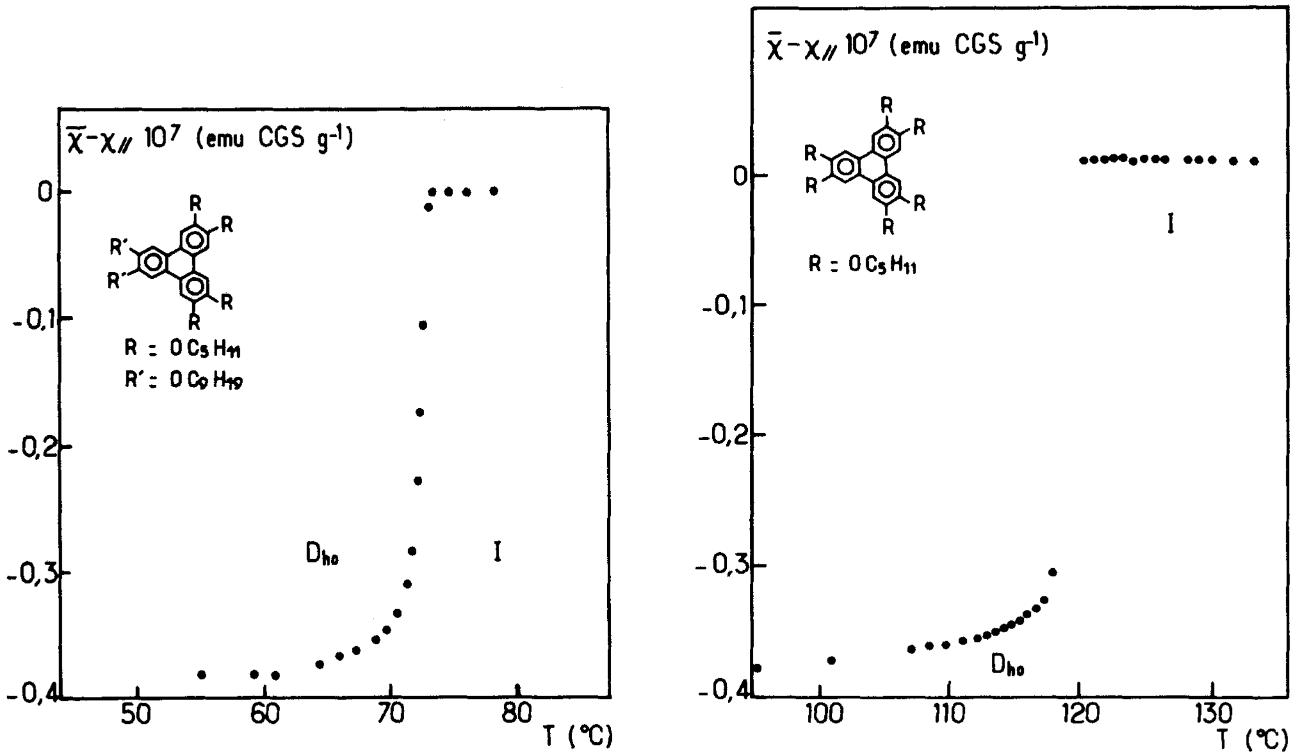

FIGURE 3 Thermal evolutions of the diamagnetic susceptibility for a disymmetric (a) and a symmetric (b) hexasubstituted triphenylene $\bar{\chi}$ = average susceptibility in the isotropic phase, $\chi_{//}$ = susceptibility measured in a direction parallel to the magnetic field.

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Mol. Cryst. Liq. Cryst., 1981, Vol. 65, pp. 315–316
0026-8941/81/6504-0315$06.50/0

Printed in the U.S.A.

Announcement

GORDON RESEARCH CONFERENCE
Liquid Crystals

Colby-Sawyer College
New London, New Hampshire

July 6–10, 1981

For further information contact:

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Kingston, Rhode Island 02881
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Gordon Research Conference, Liquid Crystals
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Program

6 July. Michael Clark, "Dual frequency addressing in liquid crystal devices"; William Heffner, "Bistable cholesteric twist cells: Operating characteristics"; Noel Clark, "Electro-optic effects in ferro-electric liquid crystals"; Shunsuke Kobayashi, "Critical surface tension and optical properties of substrates and their aligning properties for liquid crystal molecules". Poster session on device-related subjects.

7 July. David Johnson, "The nematic-smectic-A-smectic-C multicritical point"; David Nelson, "Smectic and cholesteric order in 2 dimensions"; Tom Lubensky, "Theory of nematic to smectic phase transitions"; Robert Pelkovits, "Smectic C to A transition in 3 dimensions"; Alfred

Saupe, "Nematic-nematic transitions and biaxial nematic phases in amphiphilic systems"; Ken Miyano, "Molecular interactions in monolayer films manifester in mechanical properties".

8 July. Horst Stegemeyer, "Physical properties of blue phases"; Paul Keyes, "The cholesteric blue phase; theory and experiment"; Saul Meiboom, "Observations on three blue phases"; Hans Gruler, "Monomolecular films in biophysics". Poster session on academic subjects.

9 July. Georges Durand, "Plastic behavior of smectic phases under shear and compression"; Alan Leadbetter, "Modulations in liquid crystal structures"; John Goodby, "The hexatic and crystal B phases and the accompanying problems of phase classification"; David Litster, "X-ray scattering studies of smectic phases"; Modeleine Veyssie, "Macromolecular solutes in nematic solvents"; H. Finkelmann, "Optical and thermodynamic investigations on linear and cross-linked liquid crystalline polymers"; Andy Griffin, "Chemical structure of thermotropic liquid crystalline polymers".

10 July. S. Chandrasekhar, "Defects in discotic phases"; Jean Charvolin, "Structural study of the calamitic-discotic transition in lyotropic nematics"; H. Gasparoux, "New experimental aspects of liquid crystal polymorphism: Disc-like phases and frustrated polar smectic-A systems".

Persons wishing to contribute to one of the poster sessions should send abstracts of 20 lines or less for consideration to Dwight W. Berreman, Room 1D-435, Bell Laboratories, Murray Hill, New Jersey 07974 to arrive by April 1. Notification of acceptance of abstracts will be mailed by April 15. A few posters with astounding new information may be accepted later if space permits.