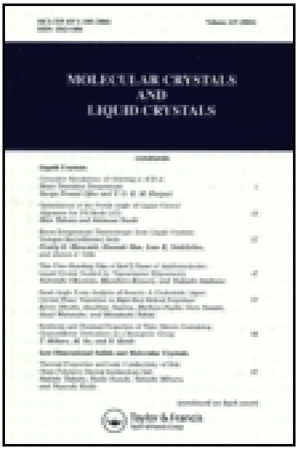


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Columnar Mesomorphism of the Mixed Substituted Apolar Triphenylenes: Prognosis and Experimental Data

Ol'Ga Zemtsova [a] , Ol'Ga Akopova [a] , Nadejda Usol'Tseva [a] & Christian Erdelen [b]

[a] Laboratory of Liquid Crystals, Ivanovo State University, 153025, Ivanovo, Russia

[b] University Bayreuth, D-95440, Bayreuth, Germany

Version of record first published: 24 Sep 2006

To cite this article: Ol'Ga Zemtsova, Ol'Ga Akopova, Nadejda Usol'Tseva & Christian Erdelen (2001): Columnar Mesomorphism of the Mixed Substituted Apolar Triphenylenes: Prognosis and Experimental Data, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 364:1, 625-634

To link to this article: http://dx.doi.org/10.1080/10587250108025032

Mol. Cryst. and Liq. Cryst., 2001, Vol. 364, pp. 625-634
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Columnar Mesomorphism of the Mixed Substituted Apolar Triphenylenes: Prognosis and Experimental Data

OL'GA ZEMTSOVA[a], OL'GA AKOPOVA[a], NADEJDA USOL'TSEVA[a] and CHRISTIAN ERDELEN[b]

[a]*Laboratory of Liquid Crystals, Ivanovo State University, 153025 Ivanovo, Russia and* [b]*University Bayreuth, D-95440 Bayreuth, Germany*

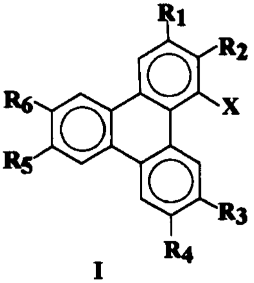
The calculations of molecular parameters (MP) of triphenylene derivatives with the mixed substituents were carried out here. The prognosis of columnar mesomorphism (CM) for this series of compounds was made on the basis of the value of MP. The compounds **Ia-If** are synthesized, their thermotropic and lyotropic mesomorphism have been studied. The good agreement of calculation and experimental data has been found for a new series of triphenylenes.

Keywords: columnar mesomorphism; lyomesophase; mesogenic compounds; molecular parameters; triphenylene derivatives

INTRODICTION

The triphenylene derivatives have been studied intensively with respect to their liquid crystal properties. The new samples of *asymmetrically shaped triphenylenes* (**Ia-If**) are represented in this report. The special molecular parameters (MP) are calculated for all these substances. The mesomorphic values of these parameters were obtained earlier [1,2] on large series of discotic mesogenic compounds [3]. Hence, in all probability it is possible to predict the formation of columnar mesophase for *symmetrically substituted* discotic compounds.

With the purpose of further study of influence of a molecular structure of triphenylene derivatives on their mesomorphic properties the calculated data about the CM prognosis of *asymmetrically shaped* compounds series I were compared with experimental results. Besides, the binary mixtures composed of non-mesogenic compounds series I with various organic solvents have been studied. The main purpose of this investigation was to discover the lyomesophase formation in the case of non-mesogenic compounds.



I

a: $R_1=R_4=R_5=R_6=-OC_5H_{11}$;
$R_2=R_3=-OCH_3$
b: $R_1=R_3=R_4=R_6=-OC_5H_{11}$;
$R_2=R_5=-OCH_3$
c: $R_1=R_3=R_4=R_6=-OC_5H_{11}$;
$R_2=R_5=-OCH_3$
and
$R_1=R_3=R_4=R_5=-OC_5H_{11}$;
$R_2=R_6=-OCH_3$ **(mixture of isomers)**
d: $R_1=R_3=R_4=R_6=-OC_5H_{11}$;
$R_2=R_5=-OC(O)-CH_3$
e: $R_1=R_2=R_4=R_5=R_6=-OC_5H_{11}$;
$R_3=-OCH_2CH(CH_2-CH_3)_2$
f: $R_1=R_2=R_3=R_4=R_5=R_6=-OC_4H_9$;
$X=-NH-C(O)-CH_3$

MATERIALS AND METHODS

The basic method of this work was the calculation and the analysis of molecular parameters value. The technique of calculation does not differ from the proposed in [2]. The molecular structures were optimized with the help of molecular technique method (force field of MM^+). Optimization has finished at a gradient 0.01 Kcal/mol. Three types of MP have been calculated: the geometrical parameters ($K = L_{max}/S$; $K_c = l_c/b_c$; $K_p = l_c/2l_p$); the molecular-mass parameters ($M_m = M_c/M_p$; $M_r = M_m \cdot K_s$); the parameter of substitution ($K_s = N/N_{max}$). For discotic *mesogenic* compounds the MP varies in the followings limits: $K = 2.0\text{-}8.5$, $K_p = 0.25\text{-}0.70$, $K_c = 1.00\text{-}2.60$, $K_s = 0.25\text{-}1.0$, $M_m = 0.3\text{-}0.8$, $M_r = 0.15\text{-}0.80$. The compounds are able to form CM, if the molecular parameters are situated within the above-mentioned limits. Also it is necessary to note, that the probability of the mesophase formation of such compounds is very small in the case of falling of MP outside the above-mentioned limits. The synthesis of compounds **Ia-If** includes several stages: alkylation of 1,2-dioxybenzene by alkylbromide or alkyliodide in alcohol-alkaline medium, trimerization in conditions of interface catalysis [4], nitration hexaalkoxytriphenylene by the concentrated nitric acid in the presence of glacial acetic acid and diethyl ether [5], reduction of nitrogenic compound up to amino-triphenylene derivative using fine-dyspersated tin in medium of a boiling glacial acetic acid [6], acylation of amino-triphenylene derivative by acetic anhydride in pyridine medium [6]. The optical microscopy studies of pure compounds **Ia-If** and their binary compositions with organic solvents were made with the help of polarizing microscope " Leitz Laborlux 12 Pol " with a heating stage " Mettler FP 82 ". The heating rate was 2°C/min. Linear and cyclic alkanes, benzene, chloroform, tetraline or *trans*-decaline were used as organic solvents. The solvents were obtained from Merck Ltd., Darmstadt, Germany, and employed without further purification.

The structure and the purity of compounds **Ia-If** were controlled by the data of UV-spectroscopy (See Table 1) and by the data of the elemental analysis (See Table 2). The spectra were made with the help of Spectrometer UV-VIS Lambda 20 (Perkin).

TABLE 1 UV-spectra of compounds **Ia-If**

Compounds	Λ_1/lgε_1	λ_2/ lgε_2	λ_3/ lgε_3	λ_4/ lgε_4
Ia	262.69/5.83	271.74/5.93	303.37/5.39	-
Ib	258.09/5.82	266.57/5.96	275.89/6.12	304.33/5.49
Ic	258.11/5.87	266.60/6.02	275.89/6.18	304.6/5.54
Id	258.10/5.75	266.56/5.89	275.89/6.05	304.41/5.42
Ie	260.0_{infl}/5.74	267.17/5.87	276.24/6.02	304.65/5.43
If	270.0_{infl}/6.09	279.61/6.22	306.44/5.69	-

TABLE 2 Data of the elemental analysis of compounds **Ia-If**

Compounds	Brutto-formula	M.m.	C,%	H,%	N,%
Ia	$C_{42}H_{56}O_8$	688.90	70.45 (73.23)	8.11 (8.19)	
Ib	$C_{40}H_{56}O_6$	632.88	74.95 (75.91)	8.84 (8.92)	
Ic	$C_{40}H_{56}O_6$	632.88	74.89 (75.91)	8.90 (8.92)	
Id	$C_{40}H_{56}O_6$	632.88	74.79 (75.91)	8.88 (8.92)	
Ie	$C_{49}H_{74}O_6$	759.13	77.03 (77.53)	9.45 (9.83)	
If	$C_{44}H_{63}NO_7$	718.00	72.46 (73.61)	8.61 (8.84)	1.55 (1.95)

Note: M.m.-molecular mass, ( )-theoretical data

RESULTS AND DISCUSSION

While analyzing the MP value (See Table 1) it is possible to assume, that the compounds **Ia-Ic** will not form CM, because the value of Mm parameter falls outside the limits of above established series of discotic mesogenic compounds [1]. In contrast, each parameter is stacked in above-mentioned limits for substance **Ie** that is able to form CM. By preliminary results of the prognosis the probability of formation of CM for each of compounds **Id-If** is equal: the compounds **Id-If** can be as mesogenic, as non-mesogenic. We controlled the preliminary prognosis of CM of this series of compounds by synthesizing of them and by studying of compounds **Ia-If** with the help of polarizing microscopy. The transition temperatures are presented in the table 3 (See Table3).

TABLE 3 Molecular parameters of compounds of series I and transition temperature

Compounds	K	K_P	M_m	M_r	P	Cr Col I
Ia	5.43	0.68	1.01'	0.51	-	• - 166 •
Ib	3.90	0.68	1.01'	0.51	-	• - 110 •
Ic	6.64	0.65	1.01'	0.51	-	• - 108 •
Id	4.87	0.70	0.86'	0.43	±	• - 108 •
Ie	3.59	0.62	0.72	0.36	+	• 45 • 105 • (• 43 • 105 •)
If	4.50	0.75'	0.86'	0.50	±	• 144 • 170 • (• 147 • 163 •)

Note: '- value, which fall outside the intervals limits of MP; P- the prognosis of CM; K_s = 0.50 (for **Ia-Ie**), K_s = 0.583 (for **If**); K_c = 1.00-2.60 (for the entire series); ( ) -on the cooling.

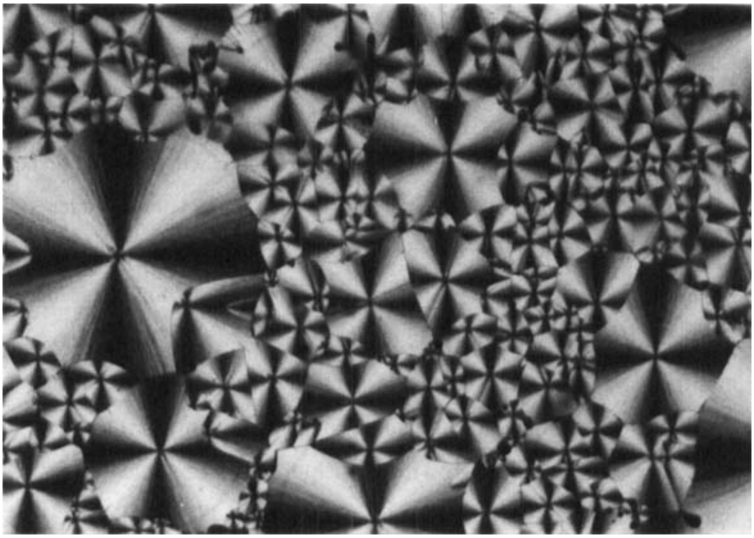


FIGURE 1. Optical texture of the crystallization of **Ib** at 75^{0}C, on cooling, crossed polarizers, x 100.
See Color Plate XXIII at the back of this issue.

The research of mesomorphic state of compounds **Ia-Id** has shown that the columnar mesophase is not observed either on heating, or on cooling. It is well coordinated with the above-mentioned prognosis (See Table 1). It was stated that these compounds undergo only phase transition from a crystal condition to an isotropic liquid. The appearance of large spherulites is seen while cooling the sample in crystal phase (Figure 1 illustrates).

Our microscopy supervision proved the formation of CM of compound **Ie** what is in accordance with our prognosis (See Table 1). On heating the sample transforms to a liquid crystal condition with flower-like texture, which is characteristic for compounds with hexagonal columnar packing.

Large hexagonal domains with branches dendrite form appear from isotropic liquid on cooling.

FIGURE 2. Optical texture of the lyotropic mesophase of **Ie**/chloroform mixture at 53°C, on heating, crossed polarizers, x100. See Color Plate XXIV at the back of this issue.

It was revealed also, that the compound **If** is monotropic liquid crystal. Transition of a solid crystal phase to an other crystal phase with larger crystals takes place on heating a sample at temperature 144,4°C. At temperature 170,2°C the phase transition to isotropic liquid has been observed.

Mesophase with mosaic texture, which is kept up to complete crystallization of a sample, takes place on cooling of a preparation with small hysteresis (at temperature 162,8°C).

According to our investigation the compound **Id** is non-mesogenic. But in accordance with the prognosis the probability of formation of CM is high. Perhaps it possesses a latent mesophase, which can be revealed by other methods.

In this work we also turn to studies of lyotropic mesomorphism of the above-mentioned compounds in binary systems with the non-aqueous solvents: linear and cyclic alkanes, benzene, chloroform, tetraline or *trans*-decaline. Using this series of the solvents, we did not manage to form lyomesophase of non-mesogenic samples of triphenylene.

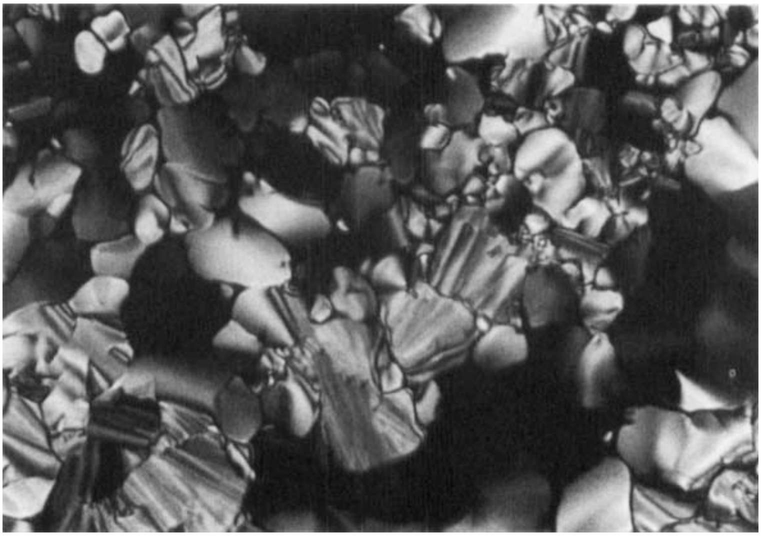


FIGURE 3. Optical texture of the lyotropic mesophase of **Ie**/ cyclohexene mixture at 69°C, on heating, crossed polarizers, x 100. See Color Plate XXV at the back of this issue.

The mesogenic compound **Ie** forms the lyomesophase with some of the solvents. It depends on the nature of the solvent: the lyomesophase is formed in mixture only with cyclooctane, cyclohexene, chloroform, dimetylformamide or *trans*-decaline. For example, in the process of adding of chloroform the **Ie** forms herringbone texture (Figure 2 illustrates), with cyclohexene **Ie** forms flower-like domains of lyomesophase (Figure 3 illustrates).

In binary systems the compound **If** with the above-mentioned solvents has lost its monotropic mesophase during the process of adding of the solvents. As have been stated previously for mesogenic scyllitol derivatives [7] in this very case a transition to columnar thermotropic mesophase with ***disordered*** arrangement of molecules in columns takes place.

CONCLUSION

1. A series of new triphenylene derivatives with asymmetrical substitution is synthesized.
2. It is possible to use the MP calculation for ***asymmetrical hetero-substituted triphenylenes*** similar to MP calculation for discotic compounds with symmetrical homo-substuents.
3. Non-mesogenic compounds **Ia-Id** and monotropic sample **If** do not show any lyotropic mesophase.
4. The lyomesophase is received only for a thermomesomorphic sample **Ie** in binary mixtures with cyclooctane, cyclohexene, chloroform, dimetylformamide or *trans*-decaline.

Acknowledgments

We thank The Competition Center of Fundamental Natural Science at St. Petersburg State University for financial support (Grant 97-0-9.3-385).

References

[1] O.B. Akopova, A.A. Bronnikova, A. Krowchynski, L.N. Kotovich, L.S. Shabyshev, L.A. Val'kova, *Zhurn. Strukturnoj Khimii* **39**, (3), 464–472, (1998). Rus.

[2] Ol'ga Akopova, Sergey Zdanovich, Ol'ga Zemtsova, Nadejda Usol'tseva, *Mol. Cryst. Liq. Cryst.* (2000). Will be published.

[3] O.B. Akopova, V.I. Bobrov, Yu. G. Erykalov, *J. Phys. Khimii* **64**, (6), 1460–1471, (1990). Rus.

[4] O.B. Akopova, A.M. Shabysheva Sertifical USSR Patient N1622363, (1991). Rus.

[5] N. Boden, R. J. Bushby, A. N. Cammidge, *Liq. Cryst.* **18**, (4), 673–676, (1995).

[6] S. Kumar, M. Manickam, V. S. K. Balagurusamy, H. Schonherr, *Liq. Cryst.* **26**, (10), 1455–1466, (1999).

[7] N. Usol'tseva, K. Praefcke, A. Smirnova and D. Blunk, *Liq. Cryst.* **26**, (12), 1723, (1999).