SYNTHESIS AND INVESTIGATION
OF POLYSUBSTITUTED TRIPHENYLENES
WITH A PREDICTABLE TYPE OF MESOMORPHISM

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This paper reports on synthesis and investigation of columnar mesophases of the new members of the homologous series of nitro and amino derivatives of hexaalkoxytriphenylenes, whose mesomorphism was predicted earlier. The forecast is in good agreement with the experimental data. The effect of the introduction of the donor and acceptor groups into the central fragment of triphenylene on the phase transition temperature, texture, and range of existence of columnar mesophases is examined. The predicting ability of the molecular parameters suggested previously for the series under analysis is discussed. It is found that introduction of a nitro group, which is a strong electron acceptor, into the central fragment of triphenylene lowers the melting temperature of the compound versus its analog and does not promote columnar mesomorphism in the lower nonmesomorphous homologs. At the same time, this slightly expands the range of existence of the mesophase in higher homologs.

INTRODUCTION

Liquid crystals consisting of discoid molecules were synthesized about twenty years ago [1]. Currently, more than 1000 compounds forming columnar mesophases and discoid nematics are known. The compounds with columnar mesophases based on the triphenylene nucleus with polar groups such as NO_2, NH_2 have recently stirred the growing interest [2, 3]. These compounds are essential for creating new substances with liquid-crystal and other properties, including Langmuir films [4] and discoid nematics, which became an area of active efforts over the past five years [5-8].

Previously [4], molecular parameters K, K_c, K_s, K_p, M_m, and M_r were calculated for hypothetical structures I and used to predict columnar mesomorphism (CM); some of these compounds were synthesized and their mesomorphous properties were determined. Here we deal with a wider range of synthesized compounds with a predictable type of mesomorphism. We have also carried out texture studies and investigated the effect of the modification of the triphenylene molecule on the phase transition temperatures; some new triphenylene structures are considered. Our major task here is experimental verification of the prognostic ability of the parameters given in [4].

a: $R = -OC_nH_{2n+1}$, $X = -NO_2$, $n = 1-5$, 7-16;

b: $R = -OC_nH_{2n+1}$, $X = -NH_2$, $n = 1-5$, 7-16;

c: $R = -OC_nH_{2n+1}$, $X = -NH-CH=CH-(O)CR'$,

1c: $R' = -OC_mH_{2m+1}$, $n = 1-5$, 7-16, $m = 1-16$;

2c: $R' = -C_6H_4-OC_mH_{2m+1}$, $n = 1-16$, $m = 1-16$;

d: $R = -OC_nH_{2n+1}$, $X = -N=HC-R'$, $n = 1-16$;

1d: $R' = -C_6H_4-Br$, 2d: $R' = -C_6H_4-CN$,

3d: $R' = -C_6H_4-NO_2$, 4d: $R' = -C_6H_4-C(O)H$,

5d: $R' = -C_6H_4-O(O)-C-C_6H_4OR''$, $R'' = -C_mH_{2m+1}$, $m = 1-16$;

e: $R = -OC_nH_{2n+1}$, $n = 7$, 11, $X = -N=N-C_6H_4-C(O)OR'$, $m = 1-12$;

f: $X=T-N=HC-C_6H_4-CH=N-T$, $T = I$, $R = -OC_nH_{2n+1}$, $n = 1-7$.

I
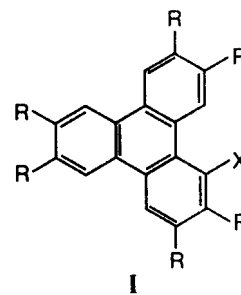
RESULTS AND DISCUSSION

Compounds **I**a, b were synthesized according to a previously suggested scheme [4], which included the following stages: alkylation of 1,2-dioxybenzene by alkyl bromides or alkyl iodides in alcohol-alkaline media; trimerization of 1,2-dialkoxybenzenes under phase transfer catalysis conditions [9]; nitration with concentrated nitric acid ($d = 1.52$ g/cm^3) in a mixture of glacial acetic acid and absolute diethyl ether [2] for homologs 5-12 or in a mixture of glacial acetic acid and chloroform for lower homologs with varied reaction time; reduction by finely disperse tin in boiling glacial acetic acid [2]. Compounds **I**-1d, 3d, If were synthesized by reaction of the amino derivative of triphenylene with a corresponding aldehyde in dry benzene, or azomethines were obtained by fusion. We did not manage to obtain compound **I**-1d, since *p*-bromobenzaldehyde sublimes under the reaction conditions (fusion), and at lower temperatures in benzene no synthesis takes place because of steric hindrances. The compounds were purified chromatographically on aluminum oxide or silica gel from organic solvents (hexane, benzene, carbon tetrachloride, and chloroform) taken in different ratios, and further recrystallized from alcohol, alcohol-benzene mixture, or hexane (amino derivatives) to constant physicochemical characteristics.

The structure of the synthesized compounds was confirmed by element analysis (Table 1) and also by UV and IR spectroscopy data (Tables 2 and 3). The presence of one nitro group in the triphenylene ring was proven by NMR data [2, 4]. The electronic spectra are broad-band (Table 2). The highest absorption intensity is observed at a wavelength of 280 nm, which refers to the $\pi-\pi*$ transition in the conjugate system of the triphenylene ring. The other 5 or 6 maxima are shaped as shoulders. Introduction of a nitro group into the central fragment gives rise to a new absorption band, 368 nm, in the visible part of the spectrum, which is missing in the spectrum of the starting (unsubstituted) compound and is most likely to be due to $n-\pi*$ in the nitro group (Table 2, compare lines 4 and 11). The molar absorption coefficients also increase due to the hyperchromic effect, resulting from the introduction of an auxochrome nitro group. Compounds from this series have a deep yellow coloring, also indicating that the nitro group is included in the conjugate system of the triphenylene ring. The amino derivatives are colored light beige and, accordingly, have lower absorption coefficients. For the azomethine derivative of terephthalic aldehyde, the spectra differ in the absorption intensity, which is doubled compared to the amino derivative; the position and the number of bands in the spectrum do not change, indicating the absence of full conjugation in the whole molecule because of the deviation of the triphenylene rings from the plane. This is clearly illustrated by the model of the molecule optimized by the MM method with the HyperChem program, version 5.02 (Fig. 1).

For the nitro derivatives of triphenylene, the IR spectra contain the absorption bands of the asymmetric and symmetric stretching vibrations of the nitro group around 1524 and 1268 cm^{-1}, respectively. In the range 3400-3100 cm^{-1}, the IR spectrum of the amino derivative of triphenylene exhibits absorption bands of the symmetric and asymmetric stretching vibrations of the NH$_2$ group (3385 and 3280 cm^{-1}, respectively); the deformation vibration bands are observed in the regions 1600-1400 and 900-800 cm^{-1}. In the range 800-900 cm^{-1} for the azomethine derivative If, the spectrum contains the bands of the deformation vibrations of the disubstituted and pentasubstituted benzene, 796 and 870 cm^{-1}, respectively.

Studies on the mesomorphous properties of the synthesized compounds have shown that all of them, except the former two, form liquid crystals (Table 3). In all homologs, the nitro group considerably decreases the melting temperature but increases the bleaching temperature of the liquid crystal homologs compared to their unsubstituted analogs. However, the nitro group introduction effect, decreasing the melting point of the compound, does not promote columnar mesomorphism in the lower homologs. Thus the nitro group substantially expands the range of existence of the mesophase in those homologs which formed columnar structures prior to NO$_2$ introduction. This experimental fact clearly correlates with the results of the prediction and suggests that the M_m parameter is the critical factor governing the appearance of CM in this series (Table 3). The introduction of the amino group instead of the nitro group produces minor effect on the values of the parameters used to predict the existence of columnar mesophases. Again, the experiment gives good agreement with the prediction. The range of existence of the mesophase in the amino derivatives of triphenylene is much narrower than that in the nitro derivatives; this is explained in [4]. We have managed to prepare amino derivative samples with higher purity compared to [4], due to the additional low-temperature crystallization from hexane (Table 3). This has made it possible to record (on cooling) characteristic texture of homolog 7, which is an amino derivative of triphenylene (Fig. 2*a*). Figure 2*b* shows the texture of homolog 10 of the nitro derivative of triphenylene. The photograph was taken near the phase transition of isotropic liquid to the mesophase; one can see distorted finger-like domains, indicating hexagonal packing of columns. For nearly all homologs of series Ia, quick cooling of samples leads to mosaic striped texture, which under shear deformation

TABLE 1. Element Analysis Data for Polysubstituted Triphenylenes

Com-pound	Mol. formula	MM	Calculated, %%			Found, %		
			C	H	N	C	H	N
Ia-1	$C_{24}H_{23}NO_8$	453.45	63.56	5.12	3.09	63.81	5.45	3.50
Ia-2	$C_{30}H_{35}NO_8$	537.61	67.02	7.36	2.61	67.22	7.03	2.72
Ia-5	$C_{48}H_{71}NO_8$	789.99	72.97	9.08	1.77	72.80	8.88	1.70
Ia-7	$C_{60}H_{95}NO_8$	957.55	75.25	10.02	1.46	75.00	9.69	1.40
Ia-9	$C_{72}H_{119}NO_8$	1126.92	76.73	10.66	1.24	76.29	10.33	1.38
Ia-10	$C_{78}H_{131}NO_8$	1211.10	77.35	10.92	1.16	77.58	10.55	1.30
Ia-11	$C_{84}H_{143}NO_8$	1295.28	77.88	11.50	1.08	77.31	11.15	1.19
Ib-7	$C_{60}H_{97}NO_6$	928.58	77.60	10.55	1.51	77.01	10.11	1.44
Ib-10	$C_{78}H_{113}NO_6$	1192.92	78.53	9.57	1.17	78.22	9.01	1.23
If	$C_{128}H_{196}N_2O_{12}$	1955.26	78.62	10.12	1.43	78.11	10.49	1.57

TABLE 2. Electronic Absorption Spectra of Polysubstituted Triphenylenes

No.	Compound	$\lambda_1/\log\varepsilon_1$	$\lambda_2/\log\varepsilon_2$	$\lambda_3/\log\varepsilon_3$	$\lambda_4/\log\varepsilon_4$	$\lambda_5/\log\varepsilon_5$	$\lambda_6/\log\varepsilon_6$	$\lambda_7/\log\varepsilon_7$
1	Ia-1	369_{sh} /3.23	350_{sh} /3.70	308_{sh} /4.55	279/5.23	273_{sh} /5.19	263_{sh} /4.80	244_{sh} /4.50
2	Ia-2	268_{sh} /3.33	350_{sh} /3.69	308_{sh} /4.50	279/5.15	273_{sh} /5.11	265_{sh} /4.75	243_{sh} /4.45
3	Ia-5	368_{sh} /3.33	352_{sh} /3.79	308_{sh} /4.60	279/5.13	273_{sh} /5.01	265_{sh} /4.85	242_{sh} /4.57
4	Ia-7	370_{sh} /3.40	347_{sh} /3.98	306_{sh} /4.90	279/5.45	272_{sh} /5.35	261_{sh} /5.16	244_{sh} /4.82
5	Ia-9	368_{sh} /3.30	350_{sh} /3.70	309_{sh} /4.50	280/5.06	275_{sh} /4.91	263_{sh} /4.74	—
6	Ia-10	368_{sh} /3.25	346_{sh} /3.65	310_{sh} /4.48	279/5.00	272_{sh} /4.88	265_{sh} /4.72	245_{sh} /4.44
7	Ia-11	368_{sh} /3.45	348_{sh} /3.99	307_{sh} /4.98	279/5.59	272_{sh} /5.45	262_{sh} /5.20	244_{sh} /4.92
8	Ib-7	370/3.04	355/3.17	308_{sh} /4.36	282/4.80	274_{sh} /4.69	254_{sh} /4.37	—
9	Ib-10	369/3.68	348/3.14	311_{sh} /3.83	282/4.69	276_{sh} /4.51	263_{sh} /4.18	—
10	If	372_{sh} /3.11	350/3.44	312_{sh} /4.76	282/5.65	272/5.22	—	—
11	Ia-7′	—	345/3.58	307/4.33	278/4.98	270/4.80	260/4.65	250_{sh} /4.37

Note. Petroleum ether as a solvent; Ia-7′ is triphenylene not containing a nitro group.

TABLE 3. Molecular Parameters of Hypothetical Structures Ia, Their Known Unsubstituted Analogs II, and Phase Transition Temperatures, $K = 1.00$

No.	n	M_m	M_r	K	K_p	ΔT_{col}, °C	CM prediction
1	2	3	4	5	6	7	8
				Ia			
1	1	3.88	2.27	3.51	2.41	0(220)	—
2	2	2.09	1.22	3.57	1.85	0(177)	—
3	3	1.41	0.82	2.29	1.08	—	—
4	4	1.07	0.63	4.60	0.75	—	+, −
5	5	0.85	0.50	3.33	0.69	>132(<0-132)	+
6	6	0.72	0.42	3.39	0.52	>116(<20-136)	+
7	7	0.61	0.36	2.57	0.51	>134(<0-134)	+
8	8	0.54	0.31	3.06	0.40	—	+
9	9	0.48	0.28	2.69	0.36	>108(<15-123)	+
10	10	0.43	0.25	2.66	0.33	>100(<15-115)	+

TABLE 3 (Continued)

1	2	3	4	5	6	7	8
11	11	0.39	0.23	2.01	0.33	>90(<20-110)	+
12	12	0.36	0.21	2.51	0.31	—	+
				Ib			
	7	0.56	0.33	2.54	0.51	(60) 85-145	+
	10	0.39	0.23	2.76	0.33	(69) 74-143	+
				If			
	7	0.70	0.41	3.00	0.51	97 (53-150)	+
				II			
13	1	3.50	1.75	1.86	2.06	0(317)	–
14	2	1.80	0.90	2.20	1.30	0(247)	–
15	3	1.20	0.60	2.50	1.01	0(177)	–
16	4	0.93	0.46	2.80	0.80	57(89-146)	+
17	5	0.75	0.38	3.10	0.66	53(69-122)	+
18	6	0.62	0.31	3.40	0.57	29(68-97)	+
19	7	0.54	0.27	3.80	0.49	24(69-93)	+
20	8	0.47	0.24	4.10	0.44	19(67-86)	+
21	9	0.42	0.21	4.40	0.39	21(57-78)	+
22	10	0.38	0.19	4.70	0.36	11(58-69)	+
23	11	0.34	0.17	5.10	0.33	12(54-66)	+
24	12	0.31	0.16	5.40	0.30	0	–, +

Note. ΔT_{col} is the range of existence of the columnar phase; the values in parentheses are phase transition temperatures (for compounds II, ΔT and phase transition temperatures are taken from [10]).
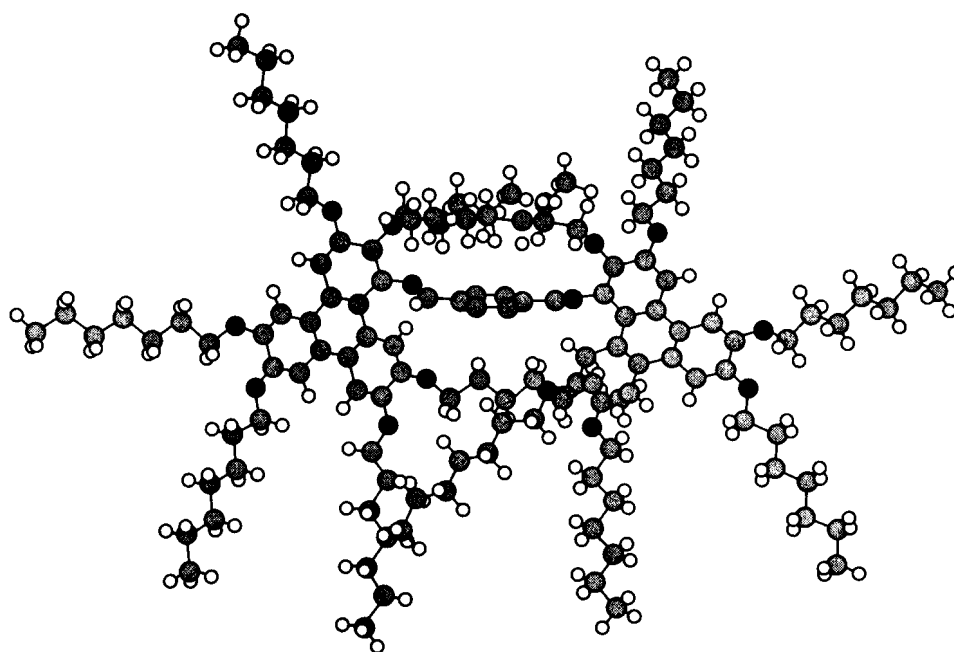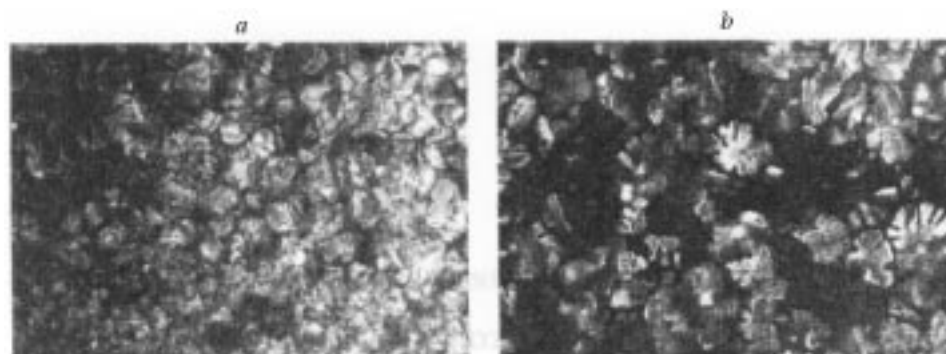

Fig. 1. Model of compound If.

Fig. 2. Textures of compounds Ib-7 (*a*) and Ia-10 (*b*) on cooling (nicols intersected, magnification ×200).

becomes ribbon texture. In the temperature range 53-150 ℃, the spatially distorted dimeric compound If has a mosaic small-domain texture.

Thus there is a good correlation between the prediction and experiment for this series of molecular structures. It has been shown that the M_m parameter is critical to the formation of a mesophase in the nitro derivatives of triphenylene. Dimerization of triphenylene derivatives via the bridging azomethine group of terephthalic aldehyde does not lead to a considerable rearrangement in the supramolecular structure, and expands the range of existence of the mesophase from 60℃ in Ib to 97℃ in dimer If. The lengthening of the bridging group will probably considerably affect the packing type of such molecules.

EXPERIMENTAL

The UV spectra were measured on a ''Specord UV VIS'' spectrophotometer. The IR spectra were measured on an M-80 spectrometer for thin films or KBr pellets. Thermopolarization measurements were carried out with a MIN-8 polarization microscope. The parameters were calculated using the procedure suggested in [11, 12].

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