POLYSUBSTITUTED TRIPHENYLENES WITH ACTIVE GROUPS. MOLECULAR PARAMETERS, SYNTHESIS, STRUCTURE, AND MESOMORPHISM

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Molecular parameters of hexaalkoxytriphenylenes with different substituents on the periphery of the triphenylene nucleus of known and hypothetical structures are calculated. The probability of a discophase for compounds of this series is estimated from molecular parameters. Several compounds of this series having polar groups (NO_2, NH_2) in the 1 position of the triphenylene nucleus have been synthesized. The compounds synthesized were investigated by thermopolarizing microscopy and X-ray diffraction analysis. The data on the mesomorphism of the new compounds are in good agreement with our prediction that alkoxytriphenylenes with polar groups have a discophase. It is established that introduction of an electron-accepting group at position 1 of the triphenylene nucleus expands the temperature range of existence of the discophase to room temperature. On the contrary, introduction of an electron-donating group narrows this interval. Compounds of this series presumably have a hexagonal columnar structure.

INTRODUCTION

New liquid crystals with specific properties may be obtained by combining different structural elements in a molecule. Thus combining lath-shaped and discoidal fragments gives rise to cubic, nematic, and smectic mesophases along with the columnar mesophase [1-3]. Recently, these composite structures were found to have a biaxial nematic phase [4].

It was interesting to study the effect of modification of hexasubstituted liquid crystal triphenylenes, especially by introducing chemically active polar groups, on discoidal mesomorphism. Introduction of chemically active groups is promising for future design of molecular structures with various useful properties (charge transfer complexes, polymer liquid crystal films, sensory systems, metal complexes, etc.). It was predicted by computer simulation [7] that introduction of electron-accepting groups at position 1 of the triphenylene nucleus creates conditions for molecular chirality due to distortion of the rigid structure of the central fragment of the molecule. This gave further impetus to this research.

RESULTS AND DISCUSSION

For investigation we chose compounds I and II. Known structures:

a: $R = R' = OC_n H_{2n+1}$,X = H,n = 1-12[10];b: $R = R' = OC_n H_{2n+1}$, $X = NO_2$,n = 6[5, 6];c: $R = R' = OC_n H_{2n+1}$, $X = NH_2$,n = 6[5, 6];

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The compounds of the triphenylene series were synthesized by the following scheme:



Synthetic conditions were as follows: a: RI, KOH, C₂H₅OH, 80°C; b: *p*-chloranil, 70% v/v H₂SO₄, phase transfer catalysis [11];

No.	Radicals	M _m	M _r	K	K _c	Kp	Discophase (present or not)
Ia	n						
1	1	3.50	1.75	1.86	1.0	2.06	-
2	2	1.80	0.90	2.20	1.0	1.30	-
3	3	1.20	0.60	2.50	1.0	1.01	-
4	4	0.93	0.46	2.80	1.0	0.80	+
5	5	0.75	0.38	3.10	1.0	0.66	+
6	6	0.62	0.31	3.40	1.0	0.57	+
7	7	0.54	0.27	3.80	1.0	0.49	+
8	8	0.47	0.24	4.10	1.0	0.44	+
9	9	0.42	0.21	4.40	1.0	0.39	+
10	10	0.38	0.19	4.70	1.0	0.36	+
11	11	0.34	0.17	5.10	1.0	0.33	+
12	12	0.31	0.16	5.40	1.0	0.30	+
Ъ	m/n						
13	9/5	0.49	0.24	4.40	1.0	0.39	+
14	10/5	0.45	0.22	4.70	1.0	0.36	+
15	8/6	0.51	0.26	4.10	1.0	0.44	+
16	6/8	0.56	0.28	4.10	1.0	0.44	+
17	5/9	0.59	0.30	4.40	1.0	0.39	+
18	5/10	0.56	0.28	4.70	1.0	0.36	+
Ic	n = 6	0.71	0.41	2.90	1.1	0.57	+
Id	6	0.65	0.38	3.00	1.1	0.57	+
Ie	6	0.60	0.35	2.80	1.1	0.57	+
If	6	0.71	0.41	3.10	1.1	0.57	+
lg	6	0.69	0.40	3.00	1.1	0.57	+
Ih	6	0.78	0.45	2.50	1.1	0.57	+

TABLE 1. Molecular Parameters of Known Structures of Polysubstituted Triphenylenes

TABLE 2. Molecular Parameters of Hypothetical Structures of Polysubstituted Triphenylenes

Compound	Radicals	M _m	M _r	K	Kp	Discophase (prediction)
1	2	3	4	5	6	7
IIa	n					
1	4	1.06	0.61	2.4	0.80	±
2	5	0.85	0.49	2.7	0.66	+
3	7	0.61	0.35	3.2	0.49	+
4	8	0.58	0.34	3.5	0.44	+
5	9	0.48	0.28	3.8	0.39	+
6	10	0.43	0.25	4.0	0.36	+
7	11	0.39	0.23	4.3	0.33	+
8	12	0.36	0.21	4.6	0.30	+
9	16	0.27	0.16	5.7	0.29	±
IIb			ļ.			
10	4	0.98	0.57	2.4	0.80	± ±
11	5	0.78	0.45	2.7	0.66	+

1	2	3	4	5	6	7
12	7	0.56	0.33	3.2	0.49	+
13	8	0.49	0.28	3.5	0.44	+
14	9	0.44	0.25	3.8	0.39	+
15	10	0.39	0.23	4.1	0.36	+
16	16	0.25	0.14	5.7	0.23	
IIc	n/m					
17	4/4	0.81	0.47	2.4	0.56	±
18	7/7	0.50	0.29	3.1	0.39	+
19	15/15	0.25	0.14	4.8	0.22	±
20	16/16	0.23	0.13	5.0	0.20	±
21	7/1	0.50	0.29	2.3	0.56	+
22	7/4	0.47	0.27	2.6	0.46	+
23	7/5	0.46	0.27	2.8	0.43	+
24	7/11	0.41	0.24	3.4	0.32	+
25	7/12	0.41	0.24	3.5	0.31	+
IId						
26	2/2	0.98	0.57	2.4	0.59	±
27	3/3	0.78	0.45	2.7	0.52	±
28	13/13	0.25	0.15	4.9	0.23	±
29	7/1	0.47	0.28	2.9	0.46	+
30	7/6	0.43	0.25	3.5	0.35	+
31	7/8	0.42	0.24	3.7	0.32	+
32	7/15	0.37	0.21	4.5	0.25	+
33	7/16	0.37	0.21	4.7	0.24	+
II, 1 <i>e</i>						
34	7/7	0.47	0.27	3.1	0.37	+
35	14/14	0.26	0.15	4.6	0.22	-
36	7/1	0.54	0.31	2.4	0.52	+
37	7/2	0.52	0.30	2.6	0.48	+
38	7/5	0.49	0.28	2.9	0.41	+
39	7/11	0.44	0.25	3.5	0.31	+
40	7/12	0.43	0.25	3.6	0.30	+
II, 2e	n	0.70				
41	4	0.79	0.46	2.1	0.80	±
42		0.50	0.29	2.8	0.49	+
43	14	0.27	0.16	4.5	0.26	±
44	16	0.24	0.14	4.9	0.23	_
II, 3e		1.02	0.60		0.07	
45	5	1.03	0.60	2.1	0.96	
40	4	0.82	0.48	2.3	0.80	± .
47	12	0.51	0.30	3.1	0.49	+
48 40	14	0.32	0.20	4.4	0.30	+
49 II 4-	10	0.24	0.14	5.4	0.23	-
11, 4e 50	2	1 20	0.67	1.4	0.02	
JU 51		0.74	0.07	1.4	0.92	-
52	4	0.74	0.45	1.0	0.74	+
52	/	0.48	0.28	2.1	U.49	+

TABLE 2 (Continued)

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1	2	3	4	5	6	7
53	12	0.30	0.18	2.9	0.30	+
54	13	0.28	0.16	3.0	0.29	+
55	16	0.23	0.13	3.6	0.23	_
II, 5e						
56	3	0.90	0.52	2.2	0.90	±
57	4	0.74	0.43	2.3	0.80	+
58	7	0.48	0.29	3.2	0.49	+
59	13	0.28	0.16	4.6	0.29	+
60	16	0.23	0.13	4.8	0.23	-
II, 6e						
61	3	0.90	0.52	2.0	0.81	±
62	4	0.74	0.43	2.1	0.73	+
63	7	0.48	0.29	2.7	0.49	+
64	13	0.28	0.16	4.0	0.29	+
65	16	0.23	0.13	4.8	0.23	-
II, 7e		ļ				
66	3	0.95	0.55	1.9	0.81	±
67	7	0.49	0.28	2.6	0.49	+
68	12	0.31	0.18	3.7	0.30	+
69	15	0.25	0.14	4.4	0.24	-
IIf						
70	4	0.75	0.44	2.3	0.48	+
71	5	0.64	0.37	2.5	0.43	+
72	13	0.29	0.17	4.0	0.23	±
73	16	0.24	0.14	4.7	0.19	

TABLE 2 (Continued)

Note.  $K_c = 1.1$  for all structures given here.

c: HNO₃, d = 1.5, CH₃COOH, diethyl ether,  $T = 20^{\circ}$ C, 0.2 h [5];

d: 80%  $N_2H_4$ , ethylene glycol + triethylene glycol, 250°C, 2 h;

e: Na, ethylformate, diethyl ether [12];

f: (7) in  $CH_3OH + (5)$  in  $C_2H_5OH$  [12].

Previously, molecular parameters (MP) of known structures I (a-h) and new hypothetical structures II (a-f) of the triphenylene series were calculated, and the probability of a discophase was estimated for the latter (Tables 1, 2).

MP were calculated based on the principles stated in [8]. As shown by the data of Table 1 for known mesogenic structures, molecular parameters are within the following ranges:  $K_c = 1-1.1$ , K = 2.8-5.1,  $K_s = 0.50-0.58$ ,  $K_p = 0.33-0.80$ ,  $M_m = 0.34-0.93$ ,  $M_r = 0.17-0.46$ . The limiting values do not go beyond the limits established earlier [8, 9] for other discoidal liquid crystals. Then MP of hypothetical structures II (*a-f*) were estimated. The choice of structures was dictated by our desire to study the effect of polar substituents (both donors and acceptors) introduced at position 1 of the triphenylene nucleus on MP and discoidal mesomorphism. It follows from the data of Table 2 that the  $K_c$  parameter is very weakly affected, its value being 1.1 (varying by only several hundredths) for all structures under analysis, including known triphenylene compounds (Table 1). The substitution parameter  $K_s$  increases slightly (0.58 for all compounds in Table 2). We analyzed 256 hypothetical structures but selected (Table 2) only those structures which either show the maximal probability of a discophase or the probability is indefinite and requires synthetic verification.

We synthesized structures Ia (5, 7, 9, 10), IIa (5, 7, 10), and IIb (7) (Scheme I). Compound 2 was obtained by alkylation of pyrocatechol with alkyl iodide or alkyl bromide. Oxidative trimerization of 2 was performed under phase transfer catalysis conditions according to procedure [11]. The nitro and amino derivatives were prepared by

the second s						
Compound	K		М		Ι	Prediction
II, 5a	٠	< 25	٠	132	•	+
II, 7 <i>a</i>	٠	$< T_{\rm room}$	•	134	•	+
II, 10a	٠	<28	•	115	•	+
II, 7b	٠	81	•	92	•	+
II, 7/1 <i>c</i>	•	45	٠	110	•	+

 TABLE 3. Transition Temperatures of Polysubstituted Triphenylenes

 with Polar Groups

procedures [5], with synthetic conditions partly modified for compound 5 (see the procedures in EXPERIMENTAL). The enaminoketone derivative of triphenylene 8 was obtained according to [12].

Detailed procedures are given below. The compounds were identified by elemental analyses and by UV, IR, and NMR spectroscopies. The electronic absorption spectrum of IIa7 differs slightly from that of intermediate Ia7; the molar absorption coefficients, however, increase significantly due to the introduction of an electron-accepting group  $NO_2$  into the nucleus. The NMR spectra show five signals of unsubstituted protons in the triphenylene nucleus, proving that only one nitro group is introduced (see NMR data in the synthetic procedures).

Table 3 lists the phase transition temperatures obtained using thermal polarizing microscopy. They reveal a correlation between the theoretical and experimental mesomorphism data for compounds IIa (5, 7, 10) and IIb (7). The introduction of an electron-accepting nitro group or an electron-donating amino group into the triphenylene nucleus substantially affects the range of existence of a discophase due to redistribution of electron density over the molecular skeleton. In the case of the nitro group, electron density is shifted to it from the triphenylene nucleus, decreasing the  $\pi$ - $\pi$  interaction across the triphenylene nucleus and thus expanding the range of existence of a discophase. The shift is also favored by a steric factor: the bulky nitro group loosens the supermolecular structure. The amino group, on the contrary, shifts electron density toward the triphenylene nucleus, narrowing the range of existence of the discophase.

Thermal polarizing microscopy studies for compound IIa7 showed that at room temperature the compound is in a gel-like anisotropic state and, when pressed, undergoes an elastic shear deformation or spreads above 110°C. The microstructure is noncharacteristic and finely domain, as can be seen on heating. The domains are oriented and enlarged during spreading. A transition to an isotropic liquid occurs at 130-134°C and takes place throughout the entire region visible in the microscope. When the compound is quickly cooled in polarized light, one can see mosaic striated texture, which easily gives way to ribbon texture upon shear deformation in the temperature range from 120 to 110°C. When the sample is very slowly cooled, the texture becomes partly oriented (with large extinct regions seen in a microscope), but we failed to obtain a wholly oriented sample. When the compound is slowly cooled below 133°C, domains appear which have finger-like protrusions characteristic of columnar mesophases with hexagonal packing of columns [13]. The domains later draw together, forming a "flower" microstructure. For the fifth and sixth homologs, the clarification temperatures are almost the same but differ considerably from the clarification temperature of the analog without a nitro group, for which the temperature of transition to an isotropic liquid is below 100°C [10]. This indicates that the mesomorphic properties of polysubstituted triphenylenes are more strongly affected by introduction of the nitro group into the central ring than by variation of the length of the six hydrocarbon radicals on the periphery of the molecule. The X-ray diffractogram of a bulky sample IIa7 measured at room temperature in the region of large angles contains a distinct ring corresponding to a lattice parameter of 3.5 Å and a diffuse ring corresponding to a lattice parameter of 4.5 Å. In the region of small angles, there are two distinct rings corresponding to lattice parameters of 18.1 and 20.9 Å. Thus the results of polarizing microscopy and X-ray diffraction analyses indicate that compound IIa7 involves two similar structures, which we failed to separate by two chromatographic procedures and several recrystallizations from ethanol.

Recently, we started to investigate formation of Langmuir films of compounds of this series. The behavior of IIa7 on the water-air interface was studied. The  $\pi$ -A isotherms contain two plateaus, one at  $\pi$  around 3 mN/m and another around 8 mN/m, indicating structural rearrangements in the layer.

### **EXPERIMENTAL**

UV spectra were recorded on a "Specord UV VIS" spectrophotometer. IR spectra were measured with an M-80 spectrometer for thin films or KBr pellets. Thermopolarizing studies were performed with a MIN-8 polarizing microscope. X-Ray diffractograms were measured on a DRON 2.0 diffractometer ( $CuK_{\alpha}$  radiation) with photographic recording of the diffraction pattern. Langmuir films were formed on a "Joyce Loeble" plant (England).

Below we give detailed procedures for syntheses of polysubstituted triphenylene homologs with polar groups (the scheme with designations is given above).

1-Nitro-2,3,6,7,10,11-hexaheptyloxytriphenylene (4) was obtained from (3) by dissolving the latter (0.467 g, 0.511 mmole) in a mixture of ether (15 ml) and glacial acetic acid (2 ml) and by adding concentrated nitric acid, d = 1.52 (0.15 ml), with stirring. The mixture was stirred at room temperature for several minutes. The solution was diluted with water and washed with a solution of potash and then again with water. The mixture was separated on a separating funnel, and the solvent was distilled off in vacuum. The residue was chromatographed on silica gel from hexane and then from a mixture of solvents: hexane, carbon tetrachloride, and benzene. After chromatographing, the first fraction was recrystallized in sequence from isopropanol and ethanol. The product is a yellowish brown substance readily soluble in hexane, methylene chloride, benzene, and ether. Molecular formula:  $C_{60}H_{96}NO_8$ , MM 959.57 (yield 90%). Calculated (%): C 75.10, H 10.10, N 1.46. Found: C 75.15, H 9.92, N 1.50.

UV spectrum (petroleum ether)  $\lambda$ , nm/log  $\epsilon$ : 262 sh/4.90, 270 sh/5.06, 279/5.18, 310/4.74.

IR spectrum, thin film cm⁻¹:  $\nu$ (NO₂) 1528,  $\nu$ (NO₂) 1268,  $\delta$ (NO₂) 680.

¹H NMR spectrum for (CDCl₃): 7.84 (s, 1H, Ar<u>H</u>), 7.75 (s, 2H, Ar<u>H</u>), 7.71 (s, 1H, Ar<u>H</u>), 7.70 (s, 1H, Ar<u>H</u>), 7.46 (s, 1H, Ar<u>H</u>).

1-Amino-2,3,6,7,10,11-hexaheptyloxytriphenylene (5): 0.378 mmole of (4) and ~1 ml of N₂H₄ (80%) were kept for 2 h in a (1:2) mixture of ethylene glycol and triethylene glycol. Then the reaction mixture was heated to  $T = 180-190^{\circ}$ C to dryness. The temperature was elevated to 250-260°C, and the mixture was maintained at that temperature for 2 h. The mixture was cooled and washed with water. The final product was extracted with diethyl ether (3×50 ml). The extracts were consolidated, washed with water and dried, and the solvent was removed in vacuum. The residue was recrystallized from ethanol. This finally gave 0.3 g of compound (5). Molecular formula: C₆₀H₉₈NO₆, MM 929.59, 0.42 g (yield 80%). Calculated (%): C 77.52, H 10.65, N 1.51. Found: C 77.10, H 10.54, N 1.49.

¹H NMR spectrum (CDCl₃): 8.82 (s, 1H, Ar<u>H</u>), 7.83 (s, 1H, Ar<u>H</u>), 7.80 (s, 1H, Ar<u>H</u>), 7.77 (s, 1H, Ar<u>H</u>), 7.37 (s, 1H, Ar<u>H</u>), 4.57 (brs, 2H, N<u>H</u>₂), 4.23-4.19 (m, 12H, OC<u>H</u>₂), 1.95-1.88 (m, 12H, OCH₂C<u>H</u>₂), 1.57-1.35 (m, 36H, C<u>H</u>₂), 0.91 ( $\tau$ , 18H, J = 7Hz, C<u>H</u>₃).

UV spectrum, petroleum ether,  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 352 (3.86), 308 sh (4.49), 279 (5.10), 270 sh (5.07), 263 sh (4.79), 253 sh (4.59).

IR spectrum, cm⁻¹, KBr pellets:  $\nu(NH_2)$  3400,  $\delta(NH)$  1680,  $\nu(CN)$  1340.

1(1'-Amino-2',3',6',7',10',11'-hexaheptyloxytriphenylene)-3-methylprop-1-en-3-one (8) (Scheme 1) was synthesized by reaction of the hydroxylmethylene derivative of acetone dissolved in methanol with 0.047 g of (8) dissolved in a mixture of methanol and ethanol with heating. The mixture was kept with heating for another 30 min, then cooled, and neutralized with acetic acid. A yellowish brown compound gradually precipitated from the solution. Yield 50%. Molecular formula C₆₄H₁₀₂NO₇, MM 997.67. Calculated (%): C 77.04, H 10.33, N 1.4. Found: C 77.00, H 10.50, N 1.45.

UV spectrum, petroleum ether,  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 370 (3.86), 355 (4.02), 306 (4.65), 279 (5.21), 273 nn (5.12), 264 nn (4.91).

IR spectrum, KBr pellets, cm⁻¹:  $\nu - s(N-H)$  3440,  $\nu - as(N-H)$  3360,  $\nu(C=O)$  1740,  $\nu(C=C)_{cis}$  1645,  $\nu_{\delta k}$  1515,  $\delta(N-H)$  1680,  $\nu(-C-N)$  1290.

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