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Synthesis and mesomorphic properties of 4-alkyl-3,4′-disubstituted biphenyls and terphenyls

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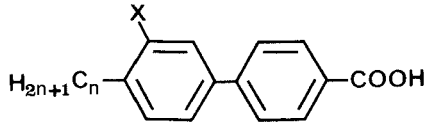
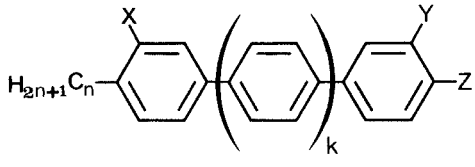
Liquid-crystalline 4-alkyl-3-chloro(methyl)-4′-substituted biphenyls and terphenyls have been synthesized. Investigation of the mesomorphic properties of these compounds shows that unlike their unsubstituted analogues they form a liquid-crystalline phase at a lower temperature and over a narrower temperature range.

1. Introduction

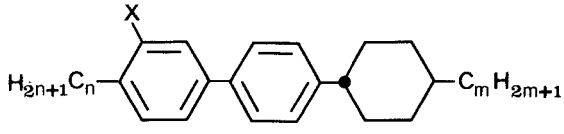
Incorporation of lateral substituents into mesogenic molecules is generally accompanied by a reduction in the mesophase formation temperature [1, 2]. We had supposed that substitution of hydrogen atoms in the molecules of 4,4′-disubstituted biphenyls and terphenyls by halogen atoms and a methyl group would correspond to the same regularity and allow us to obtain liquid-crystalline compounds which are promising for the production of mixtures with low transition temperatures. We have, therefore, synthesized 4-alkyl-3-chloro-(methyl)-4′-substituted biphenyls and terphenyls (**I–V**) and investigated their mesomorphic properties.



(Ia–e)

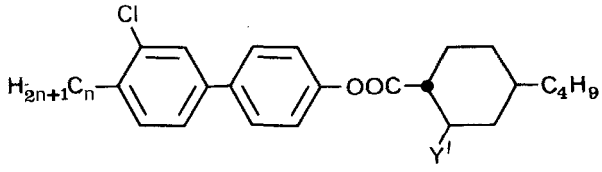


(IIa–j)

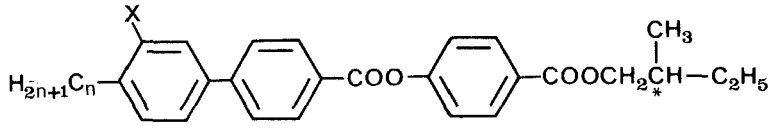


(IIIa–g)

* Author for correspondence.



(IVa, b)



(Va–c)

n, m = 4–7; X = Cl, CH_3; Y = H, Cl; Y' = H, CH_3; Z = OH, OC_2H_5, OC_3H_7, OC_4H_9, OC_5H_{11}, CN, C_6H_{13}; k = 0, 1.

2. Results and discussion

4-Alkyl-3-chloro-(methyl)-biphenyl-4′-carboxylic acids (**I**) were obtained by acetylation of 4-alkyl-3-chloro-(methyl)biphenyls and then by oxidation of the resulting ketones with alkali metal hypobromites. The phenols (**IIa, b**; Z = OH) were synthesized by nitration of the corresponding biphenyls, by reduction of the nitrocompounds, by conversion of the amines into diazonium salts and then by their decomposition. The corresponding alkyloxy derivatives (**IIc–h**; $Z = OC_mH_{2m+1}$) were obtained by further alkylation of the hydroxy compounds with alkylhalides in the presence of alkali. The biphenyls (**III**) were synthesized by hydrogenation of the reaction products of 4-alkyl-3-substituted-4′-magnesiumbromobiphenyls with 4-alkylcyclohexanones. The esters (**IV, V**) were synthesized by reaction of the acid chlorides with 4-substituted phenols in the presence of pyridine. The nitrile (**IIj**; Z = CN) was obtained by treatment of the acid chloride (**Ie**; n = 7; X = Cl) with aqueous ammonia and then by dehydration of the amide of the acid in the presence of thionyl chloride.

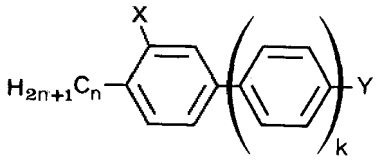
The composition and structure of the compounds (**I–V**) were confirmed by the results of elemental analysis and by infrared and proton NMR spectroscopy. Thus, in the proton NMR spectra, triplets at 2·58 ppm and at 3·43 ppm (J = 7 Hz) correspond to the signals from the hydrogen atoms in the α-methylene fragments of alkyl and alkyloxyl chains. The signals from the hydrogen atoms in the benzene rings are observed within the range 7·76–6·46 ppm. The infrared spectrum of compound (**IIj**) contains an intense band at 2230 cm^{-1} corresponding to the stretching vibrations of the nitrile group.

The correlation of the transition temperatures of the compounds with the corresponding parameters of the unsubstituted biphenyls and terphenyls [3] showed that

Table 1. Electrooptic parameters for 4-*n*-pentyl-4′-cyanobiphenyl (A) and mixtures containing 96 wt% of A and 4 wt% of one of the compounds (**IIe–g**).

Liquid-crystalline material	Threshold voltage V	Saturation voltage V
A	0·98	1·47
A + **IIe**	0·91	1·42
A + **IIf**	0·85	1·21
A + **IIg**	0·90	1·40

Table 2. Yields and transition temperatures of 4-alkyl-3-4′-disubstituted biphenyls and terphenyls (I–V).



Compound	*n*	*X*	*k*	*Y*	Yield/%	Transition temperatures							
						C		S		N		I	
Ia	5	Cl	1	COOH	37	•	152°C	•	178°C	•	219°C	•	(176°C–243°C)
Ib	5	CH_3	1	COOH	42	•	142°C			•	211°C	•	
Ic	6	Cl	1	COOH	41	•	155°C	•	186°C	•	213°C	•	(165°C–244°C)
Id	6	CH_3	1	COOH	32	•	144°C			•	200°C	•	
Ie	7	Cl	1	COOH	30	•	139°C	•	187°C	•	207°C	•	(156°C–262°C)
IIa	5	Cl	1	OH	25	•	60°C					•	
IIb	5	CH_3	1	OH	9	•	83°C					•	
IIc	5	CH_3	1	OC_2H_5	37	•	43°C					•	
IId	5	Cl	1	OC_2H_5	25	•	44°C					•	
IIe	5	Cl	1	OC_3H_7	27	•	22°C					•	
IIf	5	Cl	1	OC_4H_9	31	•	27°C					•	
IIg	5	Cl	1	OC_5H_{11}	20	•	6°C					•	
IIh	5	Cl	2	OC_3H_7	32	•	139°C	•			175°C	•	
IIi	4	Cl	1	$C_6H_3(3\text{-}Cl)C_6H_{13}$	27	•	78°C					•	
IIj	7	Cl	1	CN	28	•	43°C					•	(28·5°C–42·0°C)
IIIa	4	Cl	1	$C_6H_{10}C_3H_7$	68	•	20°C	•	67°C	•	81°C	•	
IIIb	5	Cl	1	$C_6H_{10}C_3H_7$	44	•	31°C	•	73°C	•	93°C	•	
IIIc	4	Cl	1	$C_6H_{10}C_5H_{11}$	56	•	10°C	•	80°C	•	83°C	•	
IIId	5	Cl	1	$C_6H_{10}C_5H_{11}$	67	•	10°C	•			79°C	•	
IIIe	5	CH_3	1	$C_6H_{10}C_5H_{11}$	42	•	38°C	•			79°C	•	
IVa	5	Cl	1	$OOCC_6H_{10}C_4H_9$	57	•	54°C	•	110°C	•	129°C	•	
IVb	5	Cl	1	$OOCC_6H_9(CH_3)C_4H_9$	52	•	50°C	•			68°C	•	
Va	5	Cl	1	$COOC_6H_4COO2\text{–}CH_3C_4H_9$	21	•	59°C	•	83°C	•	92°C	•	
Vb	5	CH_3	1	$COOC_6H_4COO2\text{–}CH_3C_4H_9$	27	•	66°C	•	80°C	•	88°C	•	
Vc	7	Cl	1	$COOC_6H_4COO2\text{–}CH_3C_4H_9$	34	•	34°C	•	91°C	•	101°C	•	

The transition temperatures of the unsubstituted analogues are given in brackets.

incorporation of a chloride or a methyl group into the aryl fragment is accompanied by a lowering of the clearing transition temperature and by a narrowing of the mesophase temperature range resulting in the disappearance of liquid-crystalline properties in 4-alkyl-3-chloro-4'-alkyloxybiphenyls and 4-heptyl-3-chloro-4'-cyanobiphenyl (**IIc–j**). However, the absence of liquid-crystalline properties for these compounds does not mean that they cannot be used as components of liquid-crystalline mixtures. The investigation of the electrooptic and dynamic parameters of the mixtures containing biphenyl derivatives showed that after they were added to a liquid crystal material the threshold voltages and saturation voltages drop (see table 1). This might result from a weakening of the anisotropic molecular interactions which are responsible for orientational ordering in the nematic phase of 4-*n*-pentyl-4'-cyanobiphenyl after the incorporation of these compounds. It should be noted that the liquid-crystalline mixtures have clearing temperatures 3–5°C lower and the viscosities do not strongly differ from the liquid crystal solvent.

3. Experimental

The infrared spectra of 0·1 M solutions of compounds in carbon tetrachloride were recorded with a SPECORD-IR 75 spectrophotometer. The proton NMR spectra of 10 per cent solutions in carbon tetrachloride and deuterochloroform with hexamethyldisiloxane as an internal standard were recorded with a TESLA BS-467 (60 MHz). The transition temperatures were determined with a polarizing microscope (preliminary investigations showed that the compounds form, in addition to the nematic phase, smectic A and C phases). The measurement of the electrooptic parameters of the materials was performed at room temperature in twisted nematic cells.

4-alkyl-3-chloro(methyl)biphenyls were synthesized by the reaction of 3-phenyl-6-alkylcyclohex-2-enones with phosphorus pentachloride or methylmagnezium iodide and the aromatization of the products prepared. 4-Alkyl-3-chloro(methyl)biphenyl-4'-carboxylic acids (**Ia–e**), 4-hydroxybiphenyls (**IIa, b**), *trans*-4-alkyl-cyclohexyl-biphenyls (**III**), 4-alkyl-3-chloro(methyl)-4'-alkyloxybiphenyls and terphenyls (**II**), the esters (**IV, V**) were obtained using the corresponding procedures. The yields and transition temperatures are presented in table 2.

References

[1] Deutscher, H.-J., Korber, M., Altmann, H., and Schubert, H., 1979, *J. prakt. Chem.*, **321**, 969.

[2] Van Meter, J. P., and Seidel, A. K., 1975, *J. org. Chem.*, **40**, 2998.

[3] Demus, D., Demus, H., and Zaschke, H., 1974, *Flüssige Kristalle in Tabellen* (Verlag für Grundstoffindustrie, Leipzig), p. 191.