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Paradoxes in Thermal Stability of the Liquid-Crystal Phase of Phenylpropargyl Phenyl Ethers: I. Synthesis and Mesogenic Properties of Phenylpropargyl Phenyl Ethers

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Abstract—The ethers $PhC{\equiv}CCH_2OC_6H_3RR'$ were prepared in 51–83% yields by reactions of phenylpropargyl tosylate in alkaline solution with appropriate *p*- and *o*-substituted phenols. Below are given R, R', and the ranges of existence of the nematic mesophase (°C): *p*-I, H, 104–137; *p*-Cl, H, 65–117; *p*-F, H, 33–53; *p*-OMe, H, 79–120; H, H, 44–115; *p*-$(Me)_3C$, H, 74–82; *p*-COOH, H; *p*-NO_2, H, 77–96; *o*-NO_2, H, 83–139; *o*-CHO, H, 75–115; *p*-Br, *o*-NO_2, 95–132; *p*-Cl, *o*-NO_2, 71–123; *p*-F, *o*-NO_2, 79–120; *o*-Cl, H, none; *p*-COOPr, H, none; and *p*-COOPh, H, 116–134. In contrast to the traditional views, the presence of the *o*-nitro group enhances, rather than distorts, the thermal stability of the mesophase. The stability increases in parallel with the –*R* effect of the *o*-substituent.

It was shown previously [1] that in hydroquinone bis(phenylpropargyl) diether the nematic phase exists in a relatively broad range (*C* 128 *N* 183 *I*). In going to shorter-chain analogs based on *p*-cresol (*C* 60 *N* 78 *I*) and *p*-bromophenol (*C* 84 *N* 120 *I*) the melting point, as expected, decreased, but the thermal stability of the mesophase decreased also [2].

In this work we continued a study of the thermal stability of the mesophase of phenylpropargyl phenyl ethers in relation to their structure. The ethers were prepared by the following scheme:

$$PhC{\equiv}CCH_2OTs + HOC_6H_3RR' \xrightarrow{K_2CO_3} PhC{\equiv}CCH_2OC_6H_3RR',$$

R' = H; R = *p*-I (**I**), *p*-Cl (**II**), *p*-F (**III**), *p*-OMe (**IV**), H (**V**), *p*-$(Me)_3C$ (**VI**), *p*-COOH (**VII**), *p*-NO_2 (**VIII**), *o*-NO_2 (**IX**), *o*-CHO (**X**). R' = *o*-NO_2; R = *p*-Br (**XI**), *p*-Cl (**XII**), *p*-F (**XIII**). R = *o*-Cl, R' = H (**XIV**).

With 2,4-dinitrophenol, there was no conversion even when the reaction was performed in high-boiling cyclohexanone, which is due to extremely low nucleophilicity of the corresponding phenolate.

Compound **VII** was subsequently treated with thionyl chloride, and the resulting acid chloride without isolation was converted to *n*-propyl (**XV**) and phenyl (**XVI**) esters.

The ranges of thermal stability of the mesophase of **I**–**VI** and **VIII**–**XVI** are listed in Table 1.

The results (compounds **I**–**VI**) follow the trends observed with other classes of liquid crystals: The thermal stability of the mesophase increases when the molecule contains polar substituents at the *para* positions; the ordering decreases with increasing branching of the radical and with replacement of heavier halogens by fluorine [3].

The results obtained with **VIII** and **IX** appeared to be rather unexpected: In contrast to common views, introduction of the nitro group into the *ortho* position enhanced, rather than distorted, the thermal stability of the mesophase as compared to the *p*-substituted analog.

Study of the liquid-crystal properties of **XI**–**XIII** showed that the effect of the *o*-nitro group tends to grow as the size of the *p*-substituent decreases. For example, the thermal stability of the mesophase of **XIII** sharply increases as compared to **III**.

We think that the observed paradoxes are due to the following factors.

(1) Possible formation of quasi-rings in phenylpropargyl *o*-nitrophenyl ethers through Coulombic interaction of the oxymethylene protons with the lone electron pairs of the oxygen atoms of the nitro group, favoring closer packing of molecules. Similar phe-

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nomena were observed to some extent previously [3] but formation of a quasi-ring was detected only in the case of a strong hydrogen bond (with the Schiff base derived from salicylaldehyde). Naturally, the strength of this Coulombic interaction should vary in parallel with the negative resonance effect of the substituent in the phenol ring, increasing the positive charge of the hydrogen atoms in the methylene bridge.

(2) Terminal interactions between the nitro group and the positively charged hydrogen atoms of the *o*-nitrophenol ring.

(3) Intermolecular interactions between the oxymethylene and nitro groups.

To check these assumptions, we prepared compounds **X** and **XIV**. We expected that the effects of substituents would decrease the thermal stability of the mesophase, with its total disappearance in the case of **XIV**. The relative contributions of hypothetically possible interactions to the thermal stability of the mesophase are refined by quantum-chemical calculations which are in progress.

The ^{1}H NMR spectra of **II, IV, V**, and **IX** contain a benzene multiplet in the range 6.9–7.7 ppm; the methylene protons give a singlet at 4.2–4.8 ppm. In the case of **IV**, the methoxyl protons give a singlet at 2.7 ppm. The IR spectra of all the compounds contain C≡C absorption bands at 2220–2230 cm^{-1}, stretching absorption bands of the benzene rings at 1580–1600 cm^{-1}, and stretching absorption bands of the ether moiety at 1240–1250 cm^{-1}. In the IR spectra of **VIII**, **IX**, and **XI**–**XIII** are also observed bands at 1500–1530 and 1320–1350 cm^{-1} belonging to stretching vibrations of the nitro group. The carbonyl group gives rise to a band at 1720–1750 cm^{-1} in the case of **VII**, **XV**, and **XVI** and at 1690 cm^{-1} in the case of **X**.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer (thin films or KBr pellets). The ^{1}H NMR spectra were taken on a Tesla BS-587 spectrometer (80 MHz, C_6D_6, internal reference TMS). The phase transition points were determined using a polarization microscope with a heating stage equipped with a VRT-3 temperature-control unit.

Table 1. Ranges[a] of thermal stability of the mesophase of the synthesized phenylpropargyl phenyl ethers

Comp. no.	Range, °C	Comp. no.	Range, °C
I	104–137	**X**	75–115
II	65–117	**XI**	95–132
III	33–53	**XII**	71–123
IV	79–120	**XIII**	79–120
V	44–115	**XIV**	–
VI	74–82	**XV**	–
VIII	77–96	**XVI**	116–134
IX	83–139		

[a] The lower boundary corresponds to the $C \rightarrow N$ transition, and the upper boundary, to the $N \rightarrow I$ transition.

***p*-Iodophenyl phenylpropargyl ether (I).** A mixture of 2.86 g of phenylpropargyl tosylate, 2.20 g of *p*-iodophenol, and 1.38 g of potassium carbonate in 20 ml of acetone was refluxed until the conversion was complete (monitored by TLC, Silufol plates, development with aqueous $KMnO_4$, eluent benzene). The mixture was decomposed with water, alkalized to pH 10, extracted with benzene, and dried with $CaCl_2$, after which low-boiling fractions were distilled off. The residue was recrystallized from ethanol; 2.54 g (76%) of phenylpropargyl *p*-iodophenyl ether was obtained. Compounds **II**–**XIV** were prepared similarly; their physicochemical constants and yields are given in Table 2.

***p*-(Phenylpropargyloxy)benzoic acid (VII).** To a suspension prepared from 70 ml of absolute ethanol, 0.46 g of sodium metal, and 1.38 g of *p*-hydroxybenzoic acid was added 2.86 g of phenylpropargyl tosylate. Then 20 ml of DMSO was added, and the mixture was allowed to stand at room temperarture for 48 h and then heated for 3 h at 80°C. The alcohol was distilled off, and the residue was acidified with 10% HCl. The precipitate was filtered off on a Schott filter and then recrystallized from ethanol. The yield and physicochemical constants are given in Table 2.

***n*-Propyl *p*-(phenylpropargyloxy)benzoate (XVI).** To 0.45 g of **VII** in 20 ml of benzene was added 0.43 g of $SOCl_2$, and the mixture was refluxed for 7 h. The solvent and unchanged thionyl chloride were distilled off in a vacuum. To the resulting solution, at cooling with ice-cold water, was added a solution of 0.17 g of phenol and 0.2 ml of triethylamine in 15 ml of benzene. The mixture was heated for 5 h at 80°C and broken down with water; the organic layer was separated and dried over $CaCl_2$. Low-boiling fractions were distilled off, and the residue was recrystallized from ethanol. Compound **XV** was prepared similarly. The yields and physicochemical constants are listed in Table 2.

Table 2. Physicochemical constants and elemental analyses of **I**–**XIV**

Comp. no.	Yield, %	mp, °C	Found, %		Formula	Calculated, %	
			C	H		C	H
I	76	104	54.01	3.37	$C_{15}H_{11}IO$	54.05	3.30
II	68	64–65	74.19	4.59	$C_{15}H_{11}ClO$	74.23	4.54
III	62	33	79.59	4.81	$C_{15}H_{11}FO$	79.65	4.87
IV	72	78–79	81.94	5.91	$C_{16}H_{14}O_2$	82.35	5.88
V	83	44	85.98	5.66	$C_{15}H_{12}O$	86.54	5.77
VI	68	74	86.25	7.76	$C_{19}H_{20}O$	86.36	7.58
VII	60	208–210	77.58	4.83	$C_{16}H_{12}O_3$	77.77	4.76
VIII	79	76–77	71.14	4.25	$C_{15}H_{11}NO_3$	71.15	4.35
IX	73	83	71.12	4.29	$C_{15}H_{11}NO_3$	71.15	4.35
X	69	75	81.28	5.10	$C_{16}H_{12}O_2$	81.36	5.08
XI	73	95	54.15	3.12	$C_{15}H_{10}BrNO_3$	54.22	3.01
XII	70	71	62.59	3.51	$C_{15}H_{10}ClNO_3$	62.61	3.48
XIII	60	78–79	66.54	3.67	$C_{15}H_{10}FNO_3$	66.42	3.69
XIV[a]	63	–	74.22	4.58	$C_{15}H_{11}ClO$	74.23	4.54
XV	52	37–38	77.48	6.10	$C_{19}H_{18}O_3$	77.55	6.12
XVI	55	116	80.34	4.82	$C_{22}H_{16}O_3$	80.49	4.88

[a] n_D^{20} 1.6120, d_4^{20} 1.1617.

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