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Synthesis and Mesomorphic Properties of 1,2-(4-Substituted Phenyl) Ethynes Containing Fluoro Atoms

Aldona Beganskienė [a] , Povilas Adomėms [a] , Romualdas Sirutkaitis [a] & Yasuyuki Goto [b]

[a] Vilnius University, Chemistry Department, Naugarduko 24, Vilnius, 2006, Lithuania

[b] Chisso Corporation, Research Center, 5-1 Goi Kaigan, Ichihara, Chiba, Japan, 290

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SYNTHESIS AND MESOMORPHIC PROPERTIES OF 1,2-(4-SUBSTITUTED PHENYL) ETHYNES CONTAINING FLUORO ATOMS

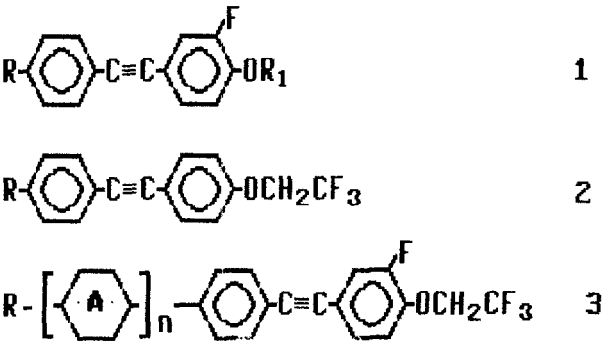
Aldona BEGANSKIENĖ, Povilas ADOMĖNAS, Romualdas SIRUTKAITIS
Vilnius University, Chemistry Department
Naugarduko 24, Vilnius 2006, Lithuania, and
Yasuyuki GOTO
Chisso Corporation, Research Center
5-1 Goi Kaigan, Ichihara, Chiba, Japan 290

ABSTRACT

It's important to evaluate an influence of different structural units on the mesomorphic and physical properties of mesogenic compounds. A number of 1,2-diphenylethynes containing fluorine atom in an aromatic ring (I, II) and several fluorine atoms in a terminal alkyl chain (II, III) were obtained in this work.

INTRODUCTION

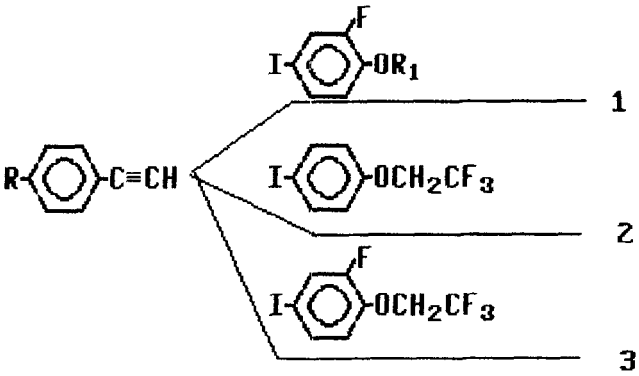
Tolane derivatives, due to the considerably high refractive index anisotropy (Δn), low viscosity and rather high stability, are useful components of liquid crystalline materials. In this work we examined an influence of number and position of fluorine atoms on the properties of tolane type compounds. The following types of compounds were synthesized:



R, R_1 = alkyl; n= 0,1; A- cyclohexylene, phenylene.

SYNTHESIS

The synthesis has been performed according to the following scheme.



The tolane derivatives have been obtained by a palladium-catalyzed coupling reaction of 4-substituted phenylacetylenes with fluoro-substituted iodobenzenes, either by a reaction of 4-alkyliodobenzenes with 4-substituted phenylacetylenes, containing polyfluoro-substituted alkoxy chain.

4-Alkoxy-2-fluoroiodobenzenes were obtained by a direct iodination of 2-fluoroalkoxybenzenes. 4-Trifluoroethoxy- and 3-fluoro-4-trifluoroethoxyiodobenzenes were prepared via nitration stage of appropriate trifluoroethoxybenzenes. The nitrobenzenes so obtained were reduced. The resulting anilines were diazotized and treated with sodium iodide solution in a usual way.

4-Substituted phenylacetylenes containing fluoro atoms were prepared from corresponding acetophenones. The acetophenones were treated with phosphorus pentachloride. The resulting phenyl-1,1-dichloroethanes were dehydrochlorinated with sodium hydroxide yielding the said compounds.

RESULTS AND DISCUSSION.

The phase transition temperatures of the new compounds obtained are given in Table 1.
The compound 1.3, containing fluoro-atom in benzene ring, forms monotropic nematic phase, while other homologues of this type are nonmesomorphic compounds. Differently from hydrogen analogs, fluoro-substituted compound 2 for ms smectic A mesophase. Two-ring compounds (3.1, 3.2), containing fluoro-atoms both in benzene ring and alkoxy-chain, are nonmesomorphic compounds. Three-ring compounds form only smectic mesophases, if all the rings are aromatic (3.3). When one cyclohexane ring is used instead of an end phenyl ring, nematic mesophase appears (compound 3.4) along with smectic.

Table 1. Phase transition temperatures of 3,4,4'-substituted diphenylethines

Comp.	R	X	R_1	K-I, K-N, K-S,	S_1-S_2	S_2-S_3,S-N	S-I, N-I
1.1	C_3H_7	F	C_4H_9	58.5			-
1.2	C_5H_{11}	F	CH_3	44.0			-
1.3	C_5H_{11}	F	C_2H_5	61.5			(47.5)
2	C_5H_{11}	H	CH_2CF_3	69.5			80.5
3.1	C_4H_9	F	CH_2CF_3	33.0			-
3.2	C_5H_{11}	F	CH_2CF_3	43.5			-
3.3	C_5H_{11}-C_6H_4	F	CH_2CF_3	118.0	129.0	154.5	208.0
3.4	C_5H_{11}-C_6H_{10}	F	CH_2CF_3	55.5		103.5	160.0

The melting enthalpies of compounds 1.3 and 3.1 are 5.78 kcal/mol and 4.95 kcal/mol, correspondingly. These values are close to that of nonfluorinated tolans.

Most of obtained compounds are non-mesomorphic either form mesophase at rather high temperatures. For this reason the

dielectric anisotropy of fluorinated tolans was evaluated by measuring the dielectric permittivity of the solutions, consisting of 10% compound upon investigation and 90% of almost non-polar alkyl-alkoxytolan. The measurements were carried out at 30°C, using measuring field with frequency 10 kHz and orienting magnetic field 5.3 kGs. The results are given below (Table 2).

Table 2. Dielectric permittivity of fluorinated tolans.

Compound	X	R_1	ε	ε	Δε
1.3	F	OC_2H_5	23.8	27.0	- 3.2
2	H	OCH_2CF_3	25.5	22.7	+2.7
3.2	F	OCH_2CF_3	22.7	19.6	+3.1

One can see, that an influence of trifluoroethoxy group to dielectric anisotropy is larger than that of lateral aromatic fluoro atom, as both the compounds (2) and (3.2) posses positive dielectric anisotropy.