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Roman Dąbrowski [a], Jerzy Dziaduszek [a], Witold Drzewiński [a], Krzysztof Czupryński [a] & Zofia Stolarz [a]

[a] Military Technical Academy, 01-489, Warsaw, Poland

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SYNTHESIS AND MESOMORPHIC CHARACTERISTIC OF BICYCLO-(2,2,2)OCTANE DERIVATIVES WITH THE -NCS TERMINAL GROUP

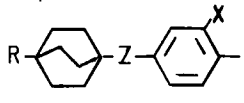
ROMAN DĄBROWSKI, JERZY DZIADUSZEK, WITOLD DRZEWIŃSKI, KRZYSZTOF CZUPRYŃSKI, ZOFIA STOLARZ

Military Technical Academy, 01-489 Warsaw, Poland

Abstract Compounds containing in their molecule an alkyl substituted bicyclo(2,2,2)octane ring and the phenylisothiocyanato group bonded to it directly or via bridging group such as -COO- , -OCO- , $-CH_2-CH_2-$ or $-CH_2O-$ have been synthesized. The phase transition temperatures, melting enthalpies and viscosities of these compounds have been determined and their suitability as components of nematic mixtures has been tested.

INTRODUCTION

Gray and Kelly[1,2] and Carr and Gray[3,4] have synthesized nematic mesogenes containing the bicyclo(2,2,2)octane ring and the phenylcyano group and have shown that these mesogenes exhibit much higher clearing points than the analogous compounds containing a benzene or cyclohexane ring. The bulk viscosity of the former is, however, very high, amounting at room temperature to 100 mPa·s and even more[5,6]. In order to check whether such properties are characteristic for other polar bicyclo(2,2,2)octane derivatives or specific only for cyano compounds we synthesized several homologous series of compounds of formula 1 :



(1)

in which Z is a single bond or a bridging group: -OCO- , -COO- , $-CH_2-CH_2-$ or $-CH_2O-$, R is an alkyl and X a hydrogen or fluorine atom.

SYNTHESIS

The compounds of formula (1) have been obtained by us according to scheme 1. More details on the preparative procedures may be found in our patent applications[7,8]. We found it useful that the main initial products: 4-alkylbicyclo(2,2,2)octanols and 4-alkylbicyclo(2,2,2)octanecarboxylic acids are obtained by the methods described by Gray[2] and Adomenas[9], respectively.

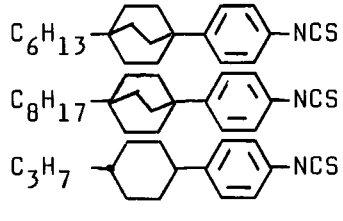
MESOMORPHIC PROPERTIES

The phase transition temperatures and melting enthalpies of compounds (1) determined by the DSC method are summarized in Table I.

The clearing points ($T_{N \rightarrow I}$) of all five series of investigated compounds were found to be very similar to those observed for the analogous series of cyano compounds. The substitution of the fluorine atom in position ortho with respect to the -NCS group (1c series) lowers but slightly the clearing point (by about 10°). Kelly observed for cyano compounds a much greater lowering of the clearing point (by about 45°)[10].

Many compounds(1)exhibit low or very low melting enthalpies and a nematic phase only which makes them highly useful for obtaining low-melting mixtures with a wide range of the nematic phase especially with CHBT compounds (4-(trans-4-alkylcyclohexyl)benzeneisothiocyanates).

For example, the simple ternary eutectic mixture:

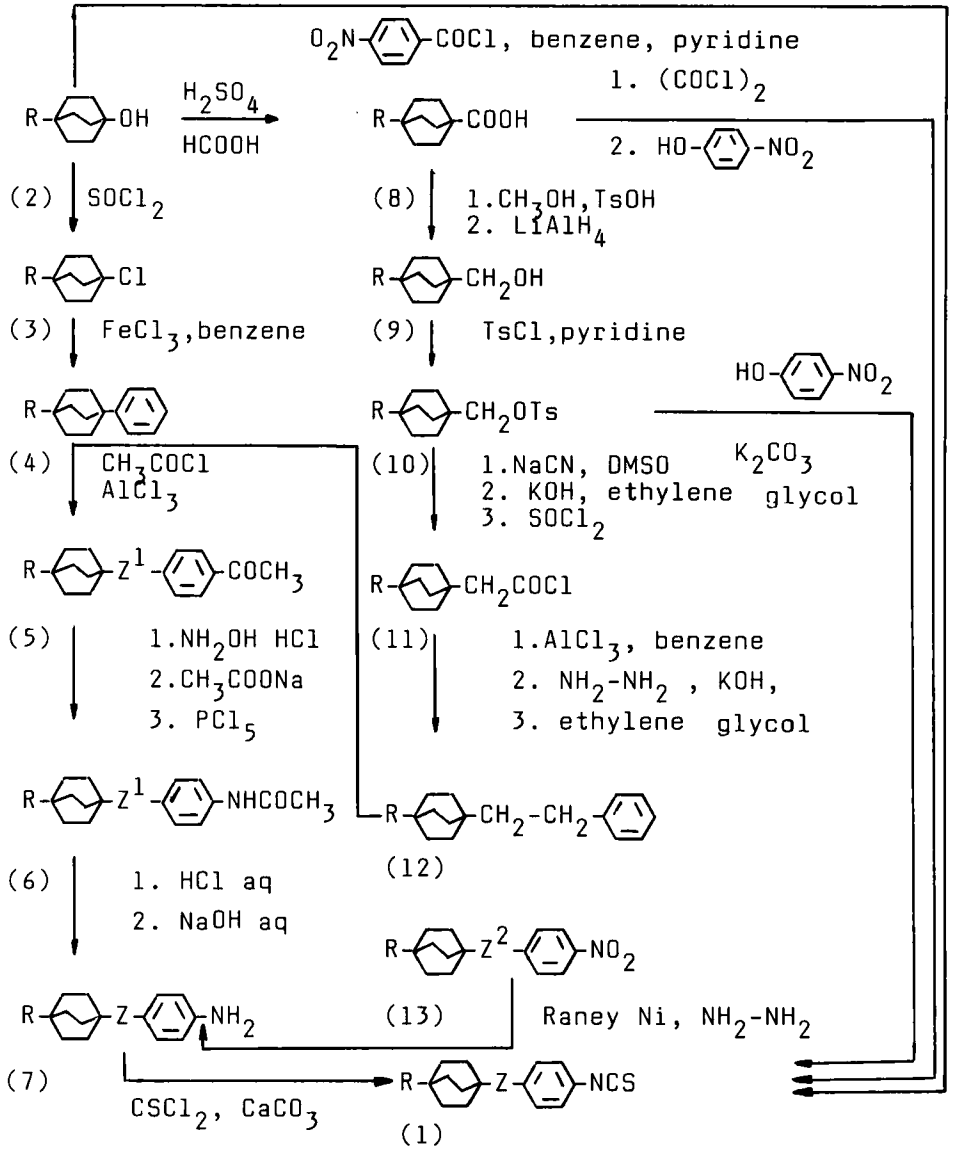


37.30 wt %

25.90 wt %

36.80 wt %

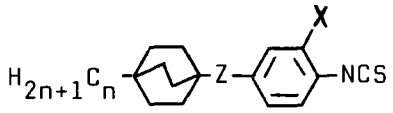
shows: T_m=-8°C, $T_{N \rightarrow I}$= 67.5°C and $\eta_{20°}$= 17.5 mPa·s .



Z = Z^1 (single bond, $-CH_2-CH_2-$) ; or Z = Z^2 (-OCO- , -COO- , $-CH_2O-$) ; R = $H_{2n+1}C_n$ -

SCHEME 1. The route of synthesis compound (1)

TABLE I. Phase transition temperature (°C) and melting enthalpy (kJ mole^{-1}) for the compounds



(1)

		Temperature transition								ΔH_m
n	X	C_1		C_2		N		I		
				Series 1a (Z=single bond)						
3	H		*	103	*	(88)	*			18.4
4	H		*	93	*	(82)	*			34.2
5	H	* 64.5	*	74	*	99.5	*	5.0	;	15.5
6	H		*	50.5	*	89	*			13.5
7	H	* 48	*	57[a]	*	95	*	8.1	;	13,6
8	H		*	50.5	*	87.5	*			19.2
				Series 1b (Z=-CH_2-CH_2-)						
4	H		*	64	*	105.5	*			10.5
6	H		*	61	*	105.5	*			15.5
				Series 1c (Z=-COO-)						
4	H		*	72.5	*	100	*			20.5
5	H		*	74.5	*	113.5	*			18.0
5	F		*	63.5	*	102.5	*			27.4
6	H	* 39.5	*	51.5	*	106	*	7.1	;	19.2
8	H	* 52.5	*	62.5[b]	*	103	*	2.3	;	22.2
8	F	* 59	*	68.5	*	92.5	*	5.0	;	33.8
				Series 1d (Z=-OCO-)						
5	H	* 62	*	97	*	115	*	3.1	;	30.2
				Series 1e (Z=-CH_2O-)						
5	H		*	77	*	(75)	*			28.8

a) compound melts at 51.5° and than crystallizes at 53° to the form having the metioned transition.

b) compound melts at 59° and than crystallizes at 61° to the form having the metioned transition.

A mixture composed of greater numbers of compounds (1) and CHBT reveals very low melting points.

BULK VISCOSITY

The viscosity of mixtures was determined by the cappillary viscosity meter. The binary eutectic mixture composed of compounds 1b (n=4, n=6) in a proportion of 57.94 wt% and 42.06 wt% exhibits: $\eta_{20°}$=36.7 mPa·s, viscosity activation energy E_a=0.383 eV, and T_{N-I} = 105°C.

The ternary mixture compounds (1a) with alkyl C_3H_7 ; C_6H_{13}; C_8H_{17} in proportion 1:3:3 reveals: $\eta_{20°}$ = 33 mPa·s, and E_a=0.286; for comparison the eutectic mixture A of three isothiocyanates with the same alkyls of the CHBT series (37.6;44.9;17.5 wt%) shows $\eta_{20°}$=10.9 mPa·s and E_a = 0.285 eV. The bulk viscosity of compounds (1a) is hence three time greater than that of CHBT compounds, but the same as in the nonpolar esters of bicyclo(2,2,2)octanecarboxylic acid [12].

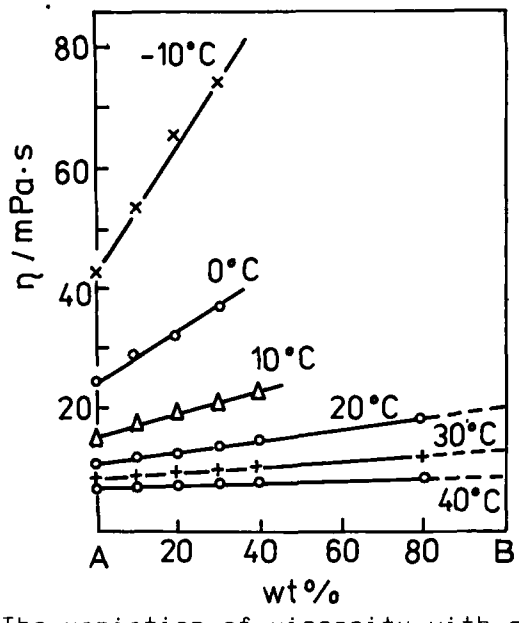


Figure 1. The variation of viscosity with concentration of compound B (1a, n=6) in the mixture A at different temperatures.

Up to the concentration of 80 wt% of B in A solutions were obtained from which at 20°C the solid phase does not precipitate and which show a linear dependence of viscosity on concentration. By extrapolating to the 100 wt% concentration of B we find $\eta_{20°}$ = 20 mPa·s which is 1.5 times smaller than that observed for a mixture containing solely compounds (1a).

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