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MESOPHASE PROPERTIES OF N-GLYCIDYL(ITYL)-AMIDES

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Abstract

Galactose, glucose, xylose and corresponding itol derivatives with the general formula Su–ZR in which *Z* is an amido group either NHCO (type I) or NR'CO (type II) were synthetized and their mesophasic behaviour studied. It was shown that the thermotropic and lyotropic phase transition temperatures are influenced by the following structural parameters: alkyl or perfluoroalkyl chain length, *Z* junction, free OH group number, cyclic or acyclic Su structure.

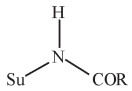
Keywords: DSC, glycoamides, glycoamphiphiles, liquid crystals, lyotropy, thermotropy

Introduction

Glycoderivatives with the general formula Su–ZR, in which a monosaccharidic or itolic unit Su, is linked by an atom or an atom group *Z*=O, S, OCO to R alkyl chains (R=n–C_nH_{2n+1}; n=6–18) constitute a large range of non-ionic amphiphilic compounds abundantly studied in the last years [1–16]. With regard to the mesophasic behaviour, it was shown that the thermotropic and lyotropic mesophase properties of these compounds are mainly dependent on the following structural parameters:

– alkyl chain length [7, 12–14] and its position in the Su group [8, 12–15],
– linkage *Z* [7, 14],
– free OH group number [11, 12],
– cyclic or acyclic structure of Su [16].

In this work, we described the synthesis of new analogous compounds in which *Z* is the amido group –NHCO– (type I) or –NR'CO– (type II), with a view to compare the phase transition temperatures to those of the corresponding glucidic derivatives with *Z*=OCO, O and S. Moreover, this series of compounds allows an examination of the mesophasic behaviour of compounds having the same cyclic or acyclic polar head and one (type I) or two (type II) hydrophobic tails.



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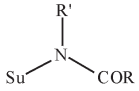

II

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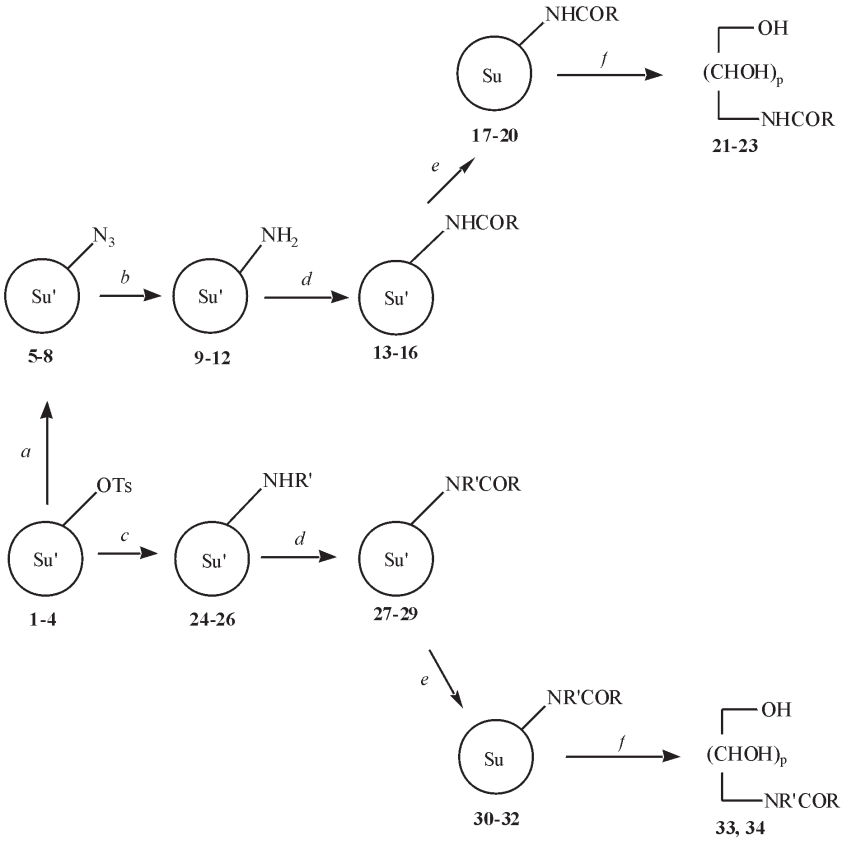
Materials and methods

General analytical methods

Optical rotations in MeOH solution were measured with a digital polarimeter DIP-370 (JASCO) at 25°C. NMR spectra were recorded with a Bruker WB spectrometer operating at 300 MHz using $CDCl_3$ or DMSO-d_6 as solvents. Chemical shifts are reported in δ units (ppm) relative to $SiMe_4$ used as internal standard. Column chromatography was performed using silica gel (60 mesh) with the appropriate gradient elution.

Phase transition temperatures were determined by DSC using a Mettler FP85 microfurnace and/or by thermal polarized light microscopy using Olympus BX50 po-



Su=5-Deoxy-*D*-xylofuranos-5-yl (17, 30), 1-Deoxy-*D,L*-xylit-1-yl (18, 31)
6-Deoxy-*D*-galacotpyranos-6-yl (19, 32), 6-Deoxy-*D*-glucopyranos-6-yl (20)
5-Deoxy-*D*-xylit-5-yl (21, 23), 6-Deoxy-*D*-galactit-6-yl (22, 34), 6-Deoxy-*D*-glucit-6-yl (23)
p=3, 4
Type **I** *R*=CH_3 (a), *n*-C_7H_{15} (b), *n*-C_8H_{17} (c), *n*-$C_{11}H_{23}$ (d), *n*-$C_{12}H_{25}$ (e), *n*-$C_2H_4C_6F_{13}$ (f)
Type **II** *R*=CH_3 with *R'*=*n*-C_8H_{17} (ac), *n*-$C_{12}H_{25}$ (ae), $C_2H_4C_6F_{13}$ (af)
R=C_7H_{11} with *R'*=*n*-C_8H_{17} (bc), *n*-$C_{12}H_{25}$ (be), $C_2H_4C_6F_{13}$ (bf)

Scheme 1 Synthesis of the N-glycidyl(ityl)amides

larizing transmitted light equiped with a Mettler FP82 microfurnace. Both Mettler apparatus were connected to a FP90 Central Processor. For thermotropic liquid crystals, transition temperatures, noted M_p (solid→liquid crystal) and C_p (liquid crystal→isotropic liquid) are T_{onset} measured by DSC in aluminium crucibles of 40 μL. The apparatus was calibrated with indium, benzophenone and benzoic acid. All the products were lyophilized before the study. For lyotropic liquid crystals, transition temperatures, noted T_1 (liquid crystal apparition) and T_2 (liquid crystal disappearence) are determined by simply allowing crystals of the test material to dissolve in water, thereby creating a concentration gradient which supports mesophase formation.

Synthesis

Type I and II compounds were prepared using Scheme 1.

Type I compounds

Step a. The activated precursors Su'–OTs: 1,2-*O*-isopropylidene-5-*O*-tosyl-α-*D*-xylofuranose (1), 2,3:4,5-di-*O*-isopropylidene-1-*O*-tosyl-*D,L*-xylitol (2), 1,2:3,4-di-*O*-isopropylidene-6-*O*-tosyl-α-*D*-galactopyranose (3) and 1,2-*O*-isopropylidene-6-*O*-tosyl-α-*D*-glucofuranose (4) are described in the literature [7, 13, 15, 17]. These compounds ($6 \cdot 10^{-2}$ mol) reacted with NaN_3 (7.8 g, 0.12 mol) in DMF (250 mL) for 3 h at 140°C to obtain the azido derivatives Su'–N_3 5–8 in 65 to 90% yields after toluene extraction and silica gel chromatography with petroleum ether–acetone gradient elution.

Step b. Azido derivatives 5–8 ($4.2 \cdot 10^{-2}$ mol) were reacted with triphenylphosphine (1 g, $4.2 \cdot 10^{-2}$ mol) in 1 M NH_3-pyridine (120 mL) for 30 min at room temperature to obtain the amino derivatives Su'–NH_2 9–12 in 96 to 98% yields after diethyl ether extraction and subsequent evaporation under reduced pressure.

Step c. It is for compounds Type II.

Step d. Amino derivatives 9–12 ($4.5 \cdot 10^{-2}$ mol) were reacted with acyl chlorides RCOCl ($5.4 \cdot 10^{-2}$ mol) in toluene (60 mL) in the presence of Na_2CO_3 (4.8 g, $4.5 \cdot 10^{-2}$ mol) for 15 min at room temperature (–10°C for the xylitol derivative 10 to preserve the 4,5-acetal group), to obtain the amido derivatives Su'–NHCOR 13–16 in 92 to 96% yields after water–toluene extraction and silica gel chromatography with petroleum ether–acetone gradient elution.

Step e. Amido derivatives 13–16 ($1.8 \cdot 10^{-2}$ mol) were reacted with a 9:1 CF_3CO_2H–H_2O mixture (20 mL) for 30 min at room temperature to obtain the unprotected compounds Su–NHCOR 17–20 in 75 to 85% yields after evaporation under reduced pressure and silica gel chromatography with 1:4 petroleum ether–acetone or acetone (Table 1).

Step f. The unprotected compounds 17–20 (10^{-2} mol) were reacted with $NaBH_4$ (2.6 g, $6.6 \cdot 10^{-2}$ mol) in methanol (100 mL) for 4 h at room temperature. 2.5 mL of formic acid was then added and the reaction mixture was stirred for 1 h before the itol derivatives 21–23 were extracted in 60 to 70% yields after silica gel chromatography with 1:4 methanol–acetone.

Table 1 Physicochemical and microanalytical (C, H, N) data of type I and type II compounds

Com.	$[\alpha]_D^{25}$ MeOH[a]	M_p/°C	Formula	Calcd.			Found		
				C	H	N	C	H	N
17d	8.9 (*c* 1.0)	103.4	$C_{17}H_{33}NO_5$	61.60	10.4	4.23	61.65	10.07	4.21
18b	–	69.2	$C_{13}H_{27}NO_5$	56.30	9.81	5.05	55.99	9.88	4.99
18d	–	73.5	$C_{17}H_{35}NO_5$	61.23	10.58	4.20	60.87	10.53	4.18
19d	110.5 (*c* 1.0)	95.6	$C_{18}H_{35}NO_6$	59.81	9.76	3.87	59.78	9.84	3.72
20d	180.4 (*c* 1.0)	69.5	$C_{18}H_{33}NO_6$	60.14	9.25	3.90	60.23	9.32	3.81
21d	5.4 (*c* 1.2)	53.9	$C_{17}H_{35}NO_5$	61.23	10.58	4.20	61.34	10.49	4.15
22d	2.8 (*c* 1.0)	110	$C_{18}H_{37}NO_6$	59.48	10.26	3.85	59.55	10.19	4.01
23d	–2.1 (*c* 0.7)	134	$C_{18}H_{37}NO_6$	59.48	10.26	3.85	59.22	10.09	3.75
30ac	19.9 (*c* 1.0)	<20	$C_{15}H_{29}NO_5$	59.38	9.63	4.62	59.47	9.58	4.56
30ae	19.1 (*c* 1.0)	55.3	$C_{19}H_{37}NO_5$	63.48	10.37	3.90	63.44	10.43	3.82
30bc	19.3 (*c* 1.1)	57	$C_{21}H_{41}NO_5$	65.08	10.66	3.61	65.15	10.62	3.75
30be	15.3 (*c* 1.0)	<20	$C_{25}H_{49}NO_5$	67.68	11.13	3.16	67.74	11.09	3.25
30bf	11.0 (*c* 2.0)	<20	$C_{21}H_{28}F_{13}NO_5$	40.59	4.54	2.25	40.51	4.62	2.31
31ac	–	80.2	$C_{15}H_{31}NO_5$	58.99	10.23	4.59	59.10	10.29	4.64
31be	–	77	$C_{25}H_{51}NO_5$	67.37	11.53	3.14	67.43	11.51	3.21
32ac	137.4 (*c* 0.9)	103.3	$C_{16}H_{31}NO_6$	57.64	9.37	4.20	57.49	9.57	4.14
32bc	121.6 (*c* 0.9)	138.9	$C_{22}H_{43}NO_6$	63.28	10.38	3.35	63.34	10.49	3.21
32af	123.2 (*c* 0.8)	152.1	$C_{16}H_{18}F_{13}NO_6$	33.87	3.20	2.47	33.78	3.29	2.39
32bf	98.6 (*c* 1.0)	142.4	$C_{22}H_{30}F_{13}NO_6$	40.56	4.64	2.15	40.67	4.67	2.09
33ac	6.1 (*c* 1.0)	67.8	$C_{15}H_{31}NO_5$	58.99	10.23	4.59	59.05	10.28	4.52
33ae	3.0 (*c* 1.0)	60.9	$C_{19}H_{39}NO_5$	63.12	10.87	3.87	63.08	10.92	3.82
33bc	13.6 (*c* 0.9)	57.0	$C_{21}H_{43}NO_5$	64.74	11.13	3.60	64.68	11.09	3.55
33bf	9.0 (*c* 1.3)	<20	$C_{21}H_{30}F_{13}NO_5$	40.46	4.85	2.25	40.51	4.91	2.17
34ac	8.4 (*c* 1.1)	106.9	$C_{16}H_{33}NO_6$	57.29	9.92	4.18	57.18	10.01	4.25
34bc	3.1 (*c* 1.1)	99.3	$C_{22}H_{45}NO_6$	62.97	10.81	3.34	63.05	10.78	3.39
34af	6.9 (*c* 0.9)	<20	$C_{16}H_{20}F_{13}NO_6$	33.75	3.54	2.46	33.81	3.62	2.39
34bf	5.1 (*c* 0.6)	77.7	$C_{22}H_{32}F_{13}NO_6$	40.44	4.94	2.14	40.50	5.00	2.08

[a]*c* concentration of the solution

Type II compounds

This synthesis required the preparation of N-alkyl amino derivatives Su'–NHR' 24–26 performed in *step c*, from *O*-tosyl derivatives 1–4 ($2.5 \cdot 10^{-2}$ mol) which were reacted with alkylamines R'NH_2 ($5.0 \cdot 10^{-2}$ mol) in xylene (50 mL) in the presence of Na_2CO_3 (2.7 g, $2.5 \cdot 10^{-2}$ mol) for 24 h at 140°C. The expected compounds were obtained in 75 to 85% yields after extraction and silica gel chromatography with petroleum ether–diethyl ether gradient. The conditions used in the above *steps d, e* were then successively applied to obtain the compounds 30–32 in 65 to 80% overall yields. $NaBH_4$ reduction of compounds Su–NR'–COR 30 and 32 using the conditions described above, *step f*, gave the corresponding itol derivatives 33 and 34 in 70% yield.

The structure of type I and type II compounds were verified by NMR. Physical and microanalytical data are recorded in Table 1.

Results and discusssion

Almost all the studied type I and type II compounds showed thermotropic liquid crystal behaviour (smectic A^*) and the majority of them also gave lyotropic mesophases

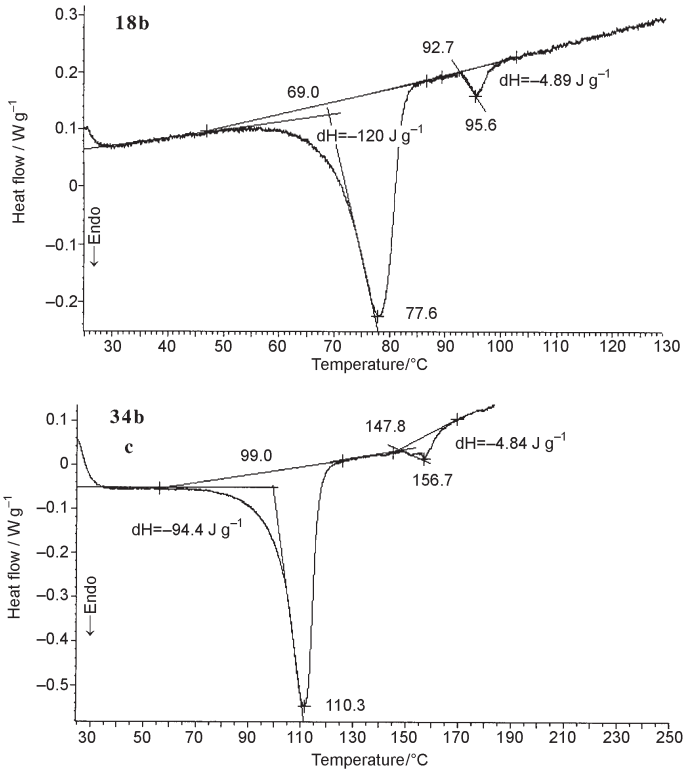


Fig. 1 DSC curves of compunds 18b and 34bc at 5°C min^{-1} heating rate, sample mass: 10 mg

(lamellar). The reported DSC phase transition temperatures were obtained at a 5°C min^{-1} heating rate (Fig. 1). A previous investigation of heading rate, from 1 to 10°C min^{-1} showed the best DSC data observed at a heading rate of 5°C min^{-1}).

Table 2 Phase transition temperatures (M_p, C_p) in °C and corresponding enthalpy changes (ΔH) in kJ mol^{-1} of type I and analogous compounds, measured at 5°C min^{-1}

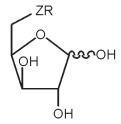
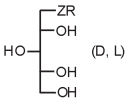
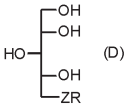
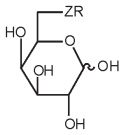
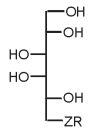
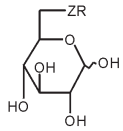
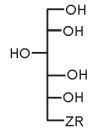
Su	α/β	*ZR*	Thermotropy		Lyotropy	
			M_p (ΔH)	C_p (ΔH)	T_1	T_2
	1:1	$NHCOC_{11}H_{23}$ (17d)	103.4 (28.4)	138.6 (0.60)	78	>96
	2:3	$OC_{12}H_{25}$ [15]	69.8 (34.1)	106.5 (1.07)	42	>96
	1:1	$SC_{12}H_{25}$ [15]	92.6 (17.0)	136.6 (1.56)	40	>96
		$NHCOC_7H_{15}$ (18b)	69.0 (33.3)	92.7 (1.36)	20	83.3
		$NHCOC_{11}H_{23}$ (18d)	73.5 (39.3)	175.5 (1.74)	35	47
		$OCOC_{11}H_{23}$	69.5 (52.3)	133.1 (1.57)	45.5	>96
		$OC_{12}H_{25}$ [7,12]	43.6 (17.6)	112.0 (1.41)	80	96
		$SC_{12}H_{25}$ [7]	66.7 (59.6)	139.3 (1.47)	56	95
		$NHCOC_{11}H_{23}$ (21d)	53.9 (21.1)	148.2 (3.40)	50	>96
		$OC_{12}H_{25}$	49.5 (36.3)	111.1 (1.25)	30	>96
	2:3	$NHCOC_{11}H_{23}$ (19d)	95.6 (9.87)	141.1 (0.55)	70	>96
	α	$OCOC_{11}H_{23}$	94 (22.8)	182 (4.02)	57.5	>96
	α	$OC_{12}H_{25}$ [14]	119 (44.5)	171 (1.29)	no	LLC[a]
	α	$SC_{12}H_{25}$ [14]	109 (44.1)	185 (2.84)	no	LLC[a]
		$NHCOC_{11}H_{23}$ (22d)	110 (15.0)	140 (0.88)	no	LLC
		$OC_{12}H_{25}$	142 (66.2)	171 (1.49)	no	LLC
		$SC_{12}H_{25}$	140.2 (44.0)	205 (0.5)	no	LLC
	2:3	$NHCOC_{11}H_{23}$ (20d)	59.2 (66.2)	123.2 (–)	55	>96
	α	$OC_{12}H_{25}$ [13]	95.5 (48.4)	137.3 (5.43)	91	>96
		$NHCOC_{11}H_{23}$ (23d)	134.0 (isotrope)	147.7 (1.8)	no	LLC
		$OC_{10}H_{21}$ [18]	78.8 (35.0)			

Table 2 presents the phase transition temperature data of type I compounds. It has previously been shown that with analogous glycidyl alkyl-linked compounds,

both the melting point (M_p) and the clearing point (C_p) increase with increasing the alkyl chain length from 6 to 10–12 carbon atoms [3, 7, 14, 15]. Similar effects were observed with type I compounds as illustrated with the *D,L*-xylit-1-yl derivatives 18a and 18b.

The data shown in Table 2 allow a comparison of the influence of the *Z* linkage. The phase transition temperatures study of the series 1-Z-*n*-alkyl-*D,L*-xylitols [7] (18b and 18d analogs) and 6-Z-*n*-alkyl-α-*D*-galactopyranose [14] (19d analogs) with *Z*=O, S or OCO showed that for thermotropic mesophases, the clearing point (C_p) decreased in the order

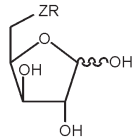
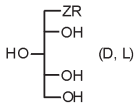
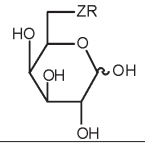
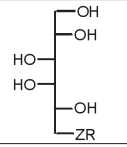
S>OCO>O

and that this order is inverted for lamellar liquid crystals [7]. This was interpreted as being due to the efficiency of the *Z* link in stabilizing liquid crystals. Moreover, molecular simulations showed [7] that the aliphatic chain in the thioether has more freedom of motion than that of the ether, due to the small size of the oxygen relative to sulphur. From this comparison, it appears that the thermotropic liquid crystal properties are stabilized when the motions of the aliphatic chain and the xylitol polar head substrate are decoupled. The increased decoupling between the sugar unit and the aliphatic chain facilitates intermolecular hydrogen bonding interactions between the sugar moieties, which, in turn, stabilizes mesophase formation, i.e. the thioethers have the higher isotropization temperatures. The ester linkage is more rigid than either the thioether or ether linkages, and because of this, the aliphatic chain has a more restricted environment which, from the above arguments, should lower mesophase stability. However, the more rigid nature of the linking group effectively extends the length of the '*quasi*-core' or polar head-group, thereby stabilizing thermotropic properties. In addition, the carbonyl group of the ester can act as an extra point for hydrogen bonding interactions. Thus, we might expect the esters to have properties intermediate between those of ethers and thioethers.

In lyotropic systems, the reversal of the thermotropic stability sequence may be related to a reversal in the relative roles of the dichotomus regions of the amphiphilic molecules. In the dry thermotropic state, the aliphatic chains can act as the liquid-like part of the phase while the sugar units are responsible for the mesophase structure and rigidity. In comparison, in the lyotropic phase, the roles are reversed. The sugar moieties have the fluid-like interactions with water and the rigidity in this case is provided by the aliphatic chains which are excluded from the 'aqueous medium'.

Following the above interpretations, we expected for type I compounds (*Z*=NHCO) results similar to the corresponding esters (*Z*=OCO) since in both series the carbonyl group can act as an extra point for hydrogen bonding interactions. As reported in Table 3, this is not generally verified: the *Z* influence varies with both the polar head structure and the alkyl chain length. We also observed that neither the free OH group number nor the cyclic or acyclic substrate structure directly affects the phase transition temperatures. Thus the *D*-xylose derivative 17d, with three OH groups has a higher M_p value than *D*-galactose 19d and *D*-glucose 20d derivative with four OH groups. Xylitol derivatives 18d and 21d, with acyclic polar heads, have

Table 3 Influence of the *Z* linkage on the phase transition temperatures

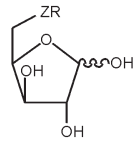
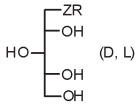
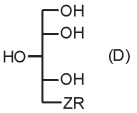
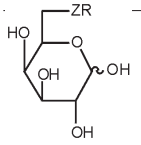
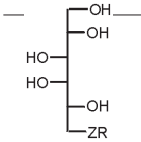
Compound	*R*	M_p	C_p	C_p–M_p	T_1
	C_8H_{17} [15] $C_{11}H_{23}$[a]	S>O NHCO>S>O	S>O S>NHCO≈O	S>O S>NHCO≈O	S>O NHCO>S≈O
	C_7H_{15}[b] $C_{11}H_{23}$[a]	NHCO≈OCO>S>O NHCO>OCO>S>O	S>O>OCO≈NHCO NHCO>S>OCO>O	S>O>OCO≈NHCO NHCO>S>O>OCO	O>S>OCO>NHCO
	C_7H_{15}[b] $C_{11}H_{23}$[a]	O>S>OCO O>S>OCO≈NHCO	S>O>OCO S>OCO>O>NHCO	S>O>OCO OCO>S>O>NHCO	NHCO>OCO
	$C_{11}H_{23}$[a]	S≈O>NHCO	S>O>NHCO	S>O≈NHCO	

[a]*R*=$C_{12}H_{25}$ for the analogs Su–OR and Su–SR [7, 14]
[b]*R*=C_8H_{17} for the analogs Su–OR and Su–SR [7, 14]

lower M_p values than *D*-xylose compound 17d, with cyclic polar head, but this order is inverted between *D*-galactitol 22d (acyclic) and *D*-galactose 19d (cyclic) derivatives, whereas they have close C_p values.

These results lead to the rationalization that the variations in the phase transition temperatures are influenced both by the alkyl chain length and the *Z* linkage and are associated with the intermolecular hydrogen bonding, which also contributes to the mesophase stability and which, for each compound, are dependent on the relative OH group orientations in the polar head.

Table 4 Phase transition temperatures (M_p, C_p) in °C and corresponding enthalpy changes (ΔH) in kJ mol^{-1} of type II compounds, measured at 5°C min^{-1}

Su	*ZR*	Thermotropy		Lyotropy	
		M_p (ΔH)	C_p (ΔH)	T_1	T_2
	$NHCOC_{11}H_{23}$ (17d)[a]	103.4 (28.4)	138.6 (0.60)	78	>96
	$NC_8H_{17}COCH_3$ (30ac)	<20 (isotrope)		no	LLC
	$NC_{12}H_{25}COCH_3$ (30ae)	55.3 (isotrope)		54	86.4
	$NC_8H_{17}COC_7H_{15}$ (30bc)	57.0[b]	63.0[b]	no	LLC
	$NC_{12}H_{25}COC_7H_{15}$ (30be)	<20	49.9	<20	61.4
	$NC_2H_4C_6F_{13}COC_7H_{15}$ (30 bf)	<20 (isotrope)		no	LLC
	$NHCOC_7H_{15}$ (18b)[a]	69.2 (23.0)	93.6 (1.34)	<20	83.5
	$NC_8H_{17}COCH_3$ (31ac)	80.2 (36.2)	175.5 (1.59)	35	>96
	$NC_{12}H_{25}COC_7H_3$ (31be)	77[b]	85[b]	<20	64.2
	$NHCOC_{11}H_{23}$ (21d)[a]	53.9 (21.1)	148.2 (3.40)	50	>96
	$NC_8H_{17}COCH_3$ (33ac)	67.8[b]	72.3[b]	<20	40.4
	$NC_{12}H_{25}COCH_3$ (33ae)	60.9 (33.7)	87.3 (1.23)	<20	>96
	$NC_8H_{17}COC_7H_{15}$ (33bc)	57.0[b]	63.0[b]	no	LLC
	$NC_2H_4C_6F_{13}COC_7H_{15}$ (33bf)	<20	28.3	no	LLC
	[A]$NHCOC_{11}H_{23}$ (19d)[a]	95.6 (9.87)	141.1 (0.55)	70	>96
	$NC_8H_{17}COCH_3$ (32ac)	103.3 (35.0)	175.1 (0.85)	<20	34.3
	$NC_8H_{17}COC_7H_{15}$ (32bc)	138.9 (40.9)	150.8 (0.87)	<20	46
	$NC_2H_4C_6F_{13}COCH_3$ (32af)	152.1		no	LLC
	$NC_2H_4C_6F_{13}COC_7H_{15}$ (32bf)	142.4 (4.3)	154.3 (0.27)	no	LLC
	$NHCOC_{11}H_{23}$ (22d)[a]	110 (15.0)	140 (0.88)	no	LLC
	$NC_8H_{17}COCH_3$ (34ac)	106.9[b]	112.2[b]	46.4	78.3
	$NC_8H_{17}COC_7H_{15}$ (34bc)	99.0 (39.6)	147.8 (2.03)	no	LLC
	$NC_2H_4C_6F_{13}COCH_3$ (34af)	<20	84.2	no	LLC
	$NC_2H_4C_6F_{13}COC_7H_{15}$ (34bf)	77.7 (13.1)	138 (1.37)	no	LLC

[a]corresponding type I compound
[b]polarized optic micrsoscopy

Table 4 reports the phase transition temperatures of type II compounds. With respect to the corresponding type I derivatives, the presence of a second hydrophobic tail generally increases the thermotropic phase transition temperatures (except xylose

30 and glucose 34 derivatives) and decreases the lyotropic ones. Moreover, any compound with the perfluoroalkyl chain (R'=$C_2H_4C_6F_{13}$) gives lyotropic liquid crystals.

As for type I compounds, the rationalization of these results needs to consider both the relative OH group orientation and the steric effects of the hydrophobic tails.

* * *

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