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Mesomorphic self-assembly of 1,3-Diacylaminobenzenes§

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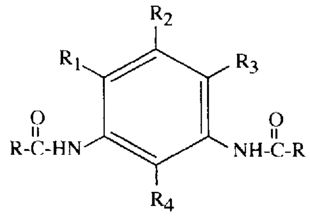
Some new examples of hydrogen-bonded 1,3-diacylaminobenzene mesogens are presented. This odd type of polymeric self-hydrogen bonded supramolecular association allows a nematic and/or a columnar order to be obtained. Such a *m*esogenic *h*ydrogen-*b*onded arrangement (MHB) should be able to stabilize diverse mesomorphic molecular edifices such as layers, columns and tubes.

Besides the peculiar case of the 3D cubic variant, thermotropic liquid crystals consist of parallel molecular stackings in uncorrelated lamellae (smectics) or columns (columnar mesophases); in nematics, parallelism between disc-like or rod-like mesogenic compounds forms the only extant order [1, 2].

The mesogenic molecule is rod-shaped, disc-shaped, or of hybrid architecture such as that of *phasmids* [3, 4] with a rod-like core ending in two disc-shaped portions. Additionally molecules of any shape may also be mesogenic when equipped with groups which induce mesomorphic dimeric or polymeric associations by establishing directed intermolecular bindings such as hydrogen bonds [5–10].

In previous work, two amide groups judiciously grafted onto alkylated benzenes **1a–g** [11–13] were shown to induce mesogenic infinite polymeric threads by hydrogen bonding; these threads arrange in nematic or lamello–columnar phases. The presence, close to an amide group (*ortho*-position), of at least one substituent more bulky than a hydrogen seems necessary in order to observe mesomorphic wires; in this way, the relative conformations of the two amide groups is favourable for intermolecular hydrogen bonding [14–18].

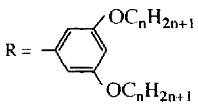
Mesogenic four-chain diamides **2a,b** were also investigated [13]. Therefore the functionalization of such diamides might allow their fixation to suitable molecular systems with interesting physico–chemical properties, so to obtain mesomorphic materials with selected properties, more likely to occur and to be amplified in an ordered medium such as a liquid crystalline phase. Moreover, this *m*esogenic *h*ydrogen-*b*onded arrangement (MHB) should be able to stabilize mesomorphic molecular edifices such as layers, columns and tubes.



$R = n\text{-}C_nH_{2n+1}$

1 **a** $R_1 = R_3 = R_4 = CH_3$, $R_2 = H$
b $R_1 = R_3 = H$, $R_2 =$ *tert*-butyl, $R_4 = CH_3$
c $R_1 = R_2 = R_3 = H$, $R_4 = CH_3$
d $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$
e $R_1 = R_4 = CH_3$, $R_2 = R_3 = H$
f $R_1 = R_3 = CH_3$, $R_2 = R_4 = H$
g $R_1 = R_2 = R_3 = R_4 = CH_3$

Scheme 1.



2 **a** $R_1 = R_3 = R_4 = CH_3$, $R_2 = H$
b $R_1 = R_3 = H$, $R_2 =$ *tert*-butyl, $R_4 = CH_3$

Scheme 2.

To this end, we first investigated 3,5-diamides **3a**, with an alkyl carboxylate group in position 1, as well as diamides **3b** bearing an ω-alkenyl ester moiety as a potential pendent group in a new type of mesogenic comb polymer. Also, polar substitutents such as NO_2 or CN incorporated into non-centrosymmetric polarizable mesogenic compounds are known to lead to materials with potentialities in non-linear optics. [19] In order to

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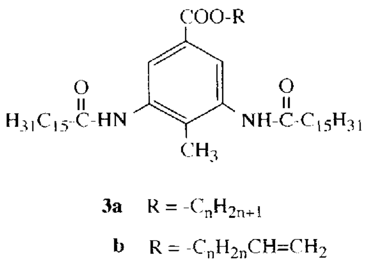
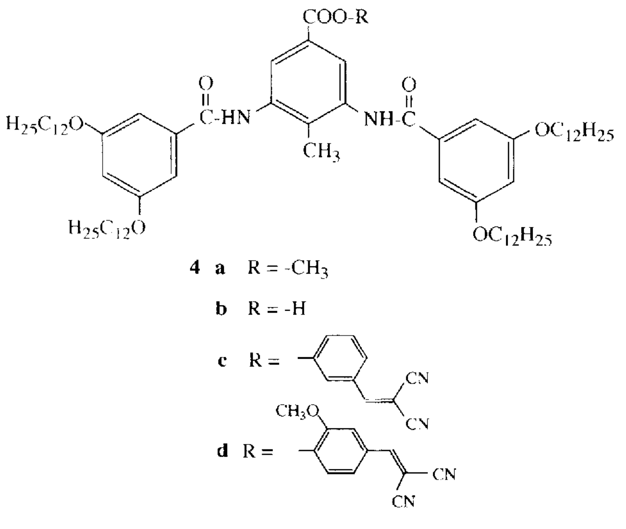


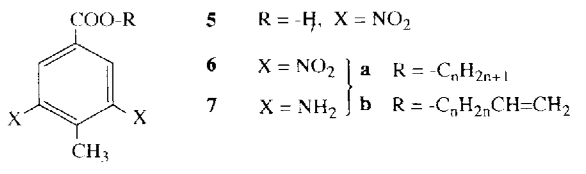
Scheme 3.

improve the mesogenic versatility of MHB, we explored the diamide ester series **4** with bulky and polar excrescences such as *meta*-substituted benzylidenemalononitrile (**4c**) and *para*-substituted 3-methoxybenzylidenemalononitrile (**4d**) moieties.

Diamides **3a** and **3b** were prepared by reaction (1·5 h heating at reflux with stirring) of the diamines **7a** and **7b**, respectively, with palmitoyl chloride (Aldrich, 2 equiv.) in dry acetone in the presence of Na_2CO_3. The white precipitate was separated, washed with warm $CHCl_3$ and the filtrate evaporated to give the crude diamide which was purified by crystallization from ethanol (60–80% yield). Diamines **7a** and **7b** were obtained by reduction of the corresponding dinitro derivatives **6a** and **6b** with tin (7 equiv.) and conc. HCl (17 equiv.) in ethanol (1·5 h at reflux). After cooling, $NaHCO_3$ was added and the extracts (CH_2Cl_2) were dried over $MgSO_4$; removal of the solvent afforded the crude diamine, which was crystallized from pentane giving a yellow solid which was used without further purification for the next step. Dinitro derivatives **6a** and **6b** were prepared by treating (25°C, 20 h with stirring) the appropriate alcohol with 1 equiv. of 3,5-dinitro-4-methylbenzoyl chloride (obtained from the corresponding acid **5**, Aldrich) in dry pyridine. After usual work-up, the residue was recrystallized from ethanol and used without further purification in the next step.



Scheme 4.



Scheme 5.

Diamides **4c** and **4d** were prepared by treating (25°C, 12 h) the appropriate hydroxybenzylidenemalononitrile [20, 21] (1 equiv.) with the acid **4b** in dry CH_2Cl_2 in the presence of dicyclohexylcarbodiimide (2 equiv.) and 4-*N*,*N*-dimethylaminopyridine (2 equiv.). After filtration, the mixture was chromatographed on silica gel using a CH_2Cl_2–MeOH (95:5) mixture as eluent and subsequently recrystallized from a CH_2Cl_2–ethanol mixture to afford a white solid (50% yield). The precursor phenols were both prepared according to Horner [20]. A mixture of the hydroxybenzaldehyde (20 mmol), malononitrile (20 mmol), $AcNH_2$ (300 mg) and ammonium acetate (300 mg) in AcOH (8 ml) was heated at reflux for 5 min. After cooling and adding an excess of water, the precipitate was separated and recrystallized from 50% aqueous ethanol (80–90% yield). Acid **4b** (m.p. 198°C) was obtained by saponification of the methyl ester **4a** in ethanolic KOH (6 h at reflux, 90% yield, recrystallized from ethanol). Methyl ester **4a** (columnar mesophase→isotropic liquid: 151°C) was prepared by reaction (3 h at reflux with stirring) of methyl 3,5-diamino-4-methylbenzoate **7a**, $n=1$ (obtained by tin reduction of the corresponding dinitro derivative **6a**, $n=1$) with 3,5-di-*n*-dodecyloxybenzoyl chloride (2·5 equiv. in the presence of Na_2CO_3. After the same work-up as for diamides **3a** and **3b**, the crude white solid was recrystallized from ethanol (60% yield).

^1H NMR and microanalytical data were in agreement with the assigned structures. The thermal and optical properties were studied by differential microcalorimetry and using a polarizing microscope equipped with a variable temperature stage. The X-ray powder diffraction patterns were obtained using a fixed film–fixed sample position with a point focusing X-ray beam ($\lambda CuK_\alpha = 1{\cdot}541$ Å) issuing from a doubly bent pyrolytic graphite monochromator. The phases, transition temperatures and enthalpies, and hexagonal lattice parameters are given in tables 1 and 2.

All the compounds displayed a hexagonal columnar phase consisting of parallel columns with one molecule per slice of column. In series **3a** and **3b**, an additional nematic phase occurs, but only for the shortest ester chain ($n=8$). Compound **3a** ($n=8$) was used in the

Table 1. Transition temperatures (°C), enthalpies (kJ mol^{-1}) (in italics) and hexagonal lattice parameters *a* (Å) for compounds **3a** and **3b**.

	n	Cr		Hex		N		I	*a*
3a	8	●	135 *25·7*	●	147 *0·3*	●	166 *1·6*	●	20·2
			[Cr$_1$→Cr$_2$: 102·5°C, 39·5 kJ mol^{-1}]						
	12	●	122 *30·5*	●	174 *2·7*	—		●	22·4
	16	●	121 *27·7*	●	166 *0·3*	—		●	23·0
3b	8	●	124 *27·8*	●	166	● *2·7*	168	●	20·9
			[Cr$_1$→Cr$_2$: 92°C, 38·1 kJ mol^{-1}]						
	9	●	120 *29·1*	●	172 *3·4*	—		●	21·1
			[Cr$_1$→Cr$_2$: 95°C, 48·2 kJ mol^{-1}]						

Cr = crystalline phase; Hex = hexagonal columnar phase; N = nematic phase; I = isotropic liquid; ● = the phase exists; — = the phase does not exist.

Table 2. Transition temperatures (°C), enthalpies (kJ mol^{-1}) (in italics) and hexagonal lattice parameters *a* (Å) for compounds **4c** and **4d**.

	Hex		I	*a*
4c	●	151·5 *5·4*	●	26·10
4d	●	193·5 *15·1*	●	26·85

structure study of wire shaped thermotropic mesogens [22]. In the hexagonal columnar phase, an increasing intercolumnar separation *a* is observed from C_8H_{17} to $C_{16}H_{33}$ (**3a**) and from $C_8H_{16}CH{=}CH_2$ to $C_9H_{18}CH{=}CH_2$ (**3b**) although all the ester chains are included in the disc containing the two $C_{15}H_{31}CONH$ chains. This behaviour may be related to a decrease of the space taken up by the hexadecanoylamino chains which are more confined by lengthening the ester chain.

The four-chain mesogens **4c** and **4d** exhibit a complicated columnar polymorphism, and table 2 gives data concerning only the last mesophase before the isotropic liquid is formed on heating. Such columnar mesomorphic materials are of interest because their high, permanent electric dipole perpendicular to the column axis could allow orientation of the mesophase and lead to large non-linear responses.

The synthesis and study of chiral MHB systems, covalent MHB polymers and MHB metal complexes are in progress.

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