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Preliminary communication

Heterocyclic 1,2,4-triazoles as calamitic mesogens

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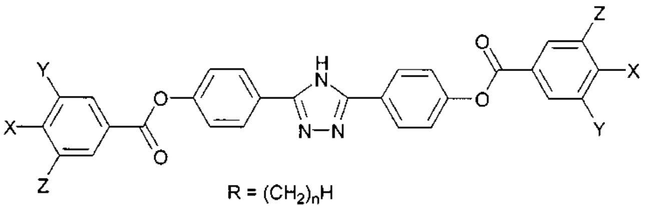
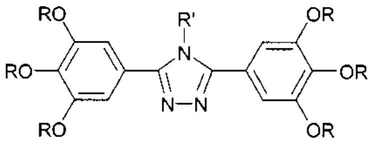
A new type of heterocyclic 1,2,4-triazole (**1–3**) derivatives prepared from their amino derivatives, and used as the mesogenic core to generate calamitic phases, is reported. These rod-like molecules formed nematic and/or smectic C mesophases, and the relatively higher clearing temperatures observed are probably attributable to intermolecular H-bonding formed by the ionizable proton at the N-4 position.

Studies on mesomorphic heterocyclic derivatives [1, 2] have increased recently due to improvements in their synthetic chemistry. The interest in this type of compound arises from the fact that the incorporation of heteroatoms can result in large changes in corresponding mesophases and/or in the physical properties of the phases observed, since most of the common heteroatoms (e.g. N, O, S) incorporated are chemically classified as more polarized than carbon. Five-membered heterocycles [3] have been considered less suitable for the formation of mesogenic materials than six-membered analogues, due to their unfavourable deviation from linearity or planarity. On the other hand, the formation of classical calamitic mesogens is more easily achieved with compounds having 1,4-disubstituted six-membered rings, than by compounds with 1,2- or 1,3-disubstituted five-membered rings. Although extensive research focused on biological activity has been reported [4], studies on mesogenic 1,2,4-triazoles as potential mesogenic materials are rarer than studies on other heterocyclic analogues. In a previous paper [5] we first reported a series of 1,2,4-triazole derivatives **4**, which exhibited hexagonal columnar phases (Col_h). No other example of similar 1,2,4-triazole compounds exhibiting mesomorphic properties has been reported since then. In this communication, as part of our research on mesomorphic heterocycles, a series of similar triazole compounds **1**–**3** used as core centre is reported. These triazole derivatives are structurally similar to the previously reported compounds **4**, except for the substituent attached at the N-4 position. The substituent (R′ = benzyl, dodecanoxyl, 4-methoxyphenyl, hexyl or phenyl) bonded to the N-4 atom in compounds **4** is replaced by an ionizable H-atom, leading to the possibility of H-bonding. These rod-like compounds are found to exhibit nematic (N) and/or smectic C (SmC) phases; the difference in mesomorphic properties observed between compound **1**–**3** and **4** is discussed. To the best of our knowledge this is the first example of calamitic mesogens formed by 1,2,4-triazole derivatives.



R = $(CH_2)_nH$
1 X = OR; Y = Z = H
2 Y = Z = $OC_{12}H_{25}$; X = H
3 X = Y = Z = OC_8H_{17}



4 R′ = benzyl, phenyl, 4-methoxyphenyl, hexyl, dodecanoxyl

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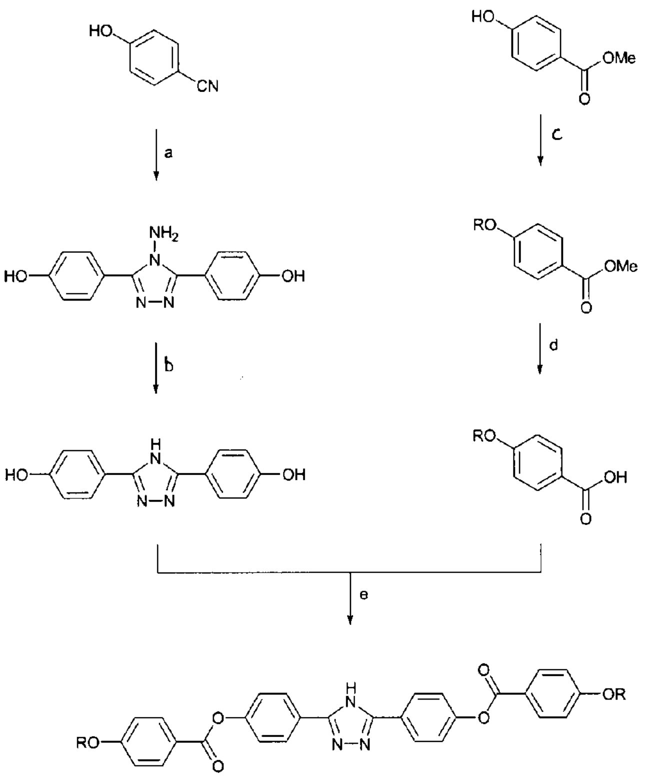

Scheme 1. Reactions and reagents. (a) Hydrazine monohydrate (3.0 eq), hydrazine dichloride (1.0 eq), stirred in $HOCH_2CH_2OH$ at 120°C, 85%; (b) $NaNO_2$ (1.3 eq), HCl (6.0N, 1.0 eq), stirred in H_2O, 12 h, 81%; (c) *R*Br (1.1 eq), K_2CO_3 (2.0 eq), KI (cat.), refluxed in CH_3COCH_3, 24 h. 85%; (d) KOH (1.0 eq), refluxed in C_2H_5OH/H_2O (1/1), 12 h, 94%; (e) DMAP (2.0 eq), DIC (5.0 eq), stirred in THF, at rt, 12 h, 45–67%.

A variety of general routes [6] has been applied to the preparation of both symmetric and unsymmetric 1,2,4-triazole derivatives. Symmetrical 3,5-disubstituted-4-amino-1,2,4-triazoles are easily accessible by several routes [7]. The synthetic pathways to compounds **1**–**3** used in this work are summarized in the scheme. The specific 3,5-bis(4-hydroxyphenyl)-4-amino-1,2,4-triazole [7] was first prepared by a hydrazine-induced cyclization reaction from 4-cyanophenol in the presence of hydrazine dichloride at 120°C. The yields were relatively high, in the range of 78–86%. The deaminated compound, 5-bis(4-hydroxyphenyl)-1,2,4-triazole [8] was prepared by treatment with $NaNO_2$ in 6.0 N aqueous hydrochloric acid and isolated as light pink solids. The yield was *c.* 80% after recrystallization from methanol. The final compounds **1**, 3,5-bis(4-alkoxybenzoic acid-4-phenylester)-1,2,4-triazoles, were obtained by the reaction of 3,5-bis(4-hydroxyphenyl)-1,2,4-triazole, 4-alkoxybenzoic acid, 4-dimethylaminopyridine (DMAP) and *N*,*N*′-diisopropylcarbodimide (DIC) in THF with stirring at room temperature. The products, isolated as white solids, were purified by silica gel chromatography, eluting with CH_3COCH_3/CH_2Cl_2 (1/9). The reaction yields were generally low, *c.* 48–67%. All derivatives were characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis. In the infrared spectrum the –NH stretching bands occurred at 3210–3318 cm^{-1}. Typical results are given below, and elemental analyses in table 1.

3,5-Bis(4-hydroxyphenyl)-1,2,4-triazole. Yield 81%. ^{1}H NMR (CD_3OD): δ6.88 (d, $J = 8.72$ Hz, $-C_6H_4$, 4H), 7.85 (d, $J = 8.68$ Hz, $-C_6H_4$, 4H). ^{13}C NMR (CD_3OD):δ111.18, 114.30, 127.24, 151.86, 160.15. IR (KBr): 3500, 3195, 1658, 1617, 1545, 1505, 1450, 1387, 1801, 1266, 1226, 1175, 1117, 1046, 984, 839, 741, 653, 603, 512 cm^{-1}. HRMS (*m*/*z*): calcd 253.0851, found 253.0846.

3,5-Bis(4-propoxybenzoic acid-4-phenyl ester)-1,2,4-triazole. Yield 48%. ^{1}H NMR ($CDCl_3$): δ1.07 (t, $-CH_3$, $J = 7.42$ Hz, 6H), 1.77–1.91 (m, $-CH_2$, 4H), 4.01 (t, $-OCH_2$, $J = 6.56$Hz, 4H), 6.96 (d, $-C_6H_4$, $J = 8.88$ Hz, 4H), 7.31 (s, $-C_6H_4$, 4H), 8.07 (d, $J = 8.55$ Hz, $-C_6H_4$, 4H), 8.14 (d, $J = 8.82$ Hz, $-C_6H_4$, 4H). ^{13}C NMR ($CDCl_3$): δ 10.33, 22.29, 69.63, 76.22, 76.86, 77.06, 77.49, 114.19, 114.40, 121.01, 122.19, 127.58, 132.25, 152.20, 163.54, 164.79. IR (KBr): 3211, 2965, 2938, 1728, 1606, 1578, 1510, 1498, 1459, 1422, 1380, 1313, 1261, 1214, 1166, 1131, 1072, 1018, 992, 975, 882, 846, 761, 691 cm^{-1}.

The mesomorphic behaviour of compounds **1**–**3** was characterized and studied by differential scanning calorimetry (DSC, Mettler DSC 821) and polarizing optical microscopy (Zeiss Axioplan 2). The phase transitions and thermodynamic data are summarized in table 2. All compounds **1** formed liquid crystalline phases regardless of the length of the alkoxy side chains, and the formation of calamitic mesophases was dependent on the carbon length of the terminal chains. The derivatives with shorter terminal chains ($n = 3$, 6) exhibited nematic phases only; compounds with longer chains ($n = 8$, 10, 12, 14) exhibited nematic/smectic C

Table 1. Elemental analysis data for compounds **1**–**3** with calculated values in parentheses.

Compound	*n*	C/%	H/%	N/%
1	3	70.42 (70.70)	5.56 (5.41)	7.02 (7.27)
	6	72.50 (72.60)	6.76 (6.55)	6.23 (6.35)
	8	73.59 (73.61)	7.20 (7.16)	5.86 (5.85)
	10	74.51 (74.49)	7.85 (7.68)	5.31 (5.43)
	12	74.92 (75.24)	8.12 (8.14)	5.04 (5.06)
	14	75.86 (75.90)	8.66 (8.53)	4.65 (4.74)
	16	76.06 (76.48)	8.80 (8.88)	4.36 (4.46)
2	12	74.14 (74.17)	9.42 (9.42)	3.31 (3.41)
3	8	76.60 (76.15)	9.94 (9.67)	3.37 (3.51)

Table 2. Phase behaviour of compounds 1. *n* represents the number of carbons in the alkoxy chain. Cr_1, Cr_2 = crystal phase; SmC = smectic C phase; N = nematic phase; I = isotropic. The transition temperature (°C) and enthalpies (in parentheses, $kJ\,mol^{-1}$) determined by DSC at a scan rate of $10.0°C\,min^{-1}$.

1; *n* = 3					Cr	$\xrightleftharpoons[196.3\ (23.0)]{231.8\ (38.5)}$	N	$\xrightleftharpoons[323.5\ (0.42)]{336.3\ (1.05)}$	I
6			Cr_1	$\xrightleftharpoons[65.1\ (16.1)]{115.7\ (23.8)}$	Cr_2	$\xrightleftharpoons[156.8\ (17.8)]{179.4\ (25.2)}$	N	$\xrightleftharpoons[289.0\ (0.84)]{304.6\ (0.98)}$	I
8	Cr_1	$\xrightleftharpoons[97.1\ (8.14)]{143.8\ (15.8)}$	Cr_2	$\xrightleftharpoons[150.3\ (17.1)]{166.7\ (21.1)}$	SmC	$\xrightleftharpoons[172.4\ (0.19)]{185.3\ (0.28)}$	N	$\xrightleftharpoons[266.6\ (0.76)]{272.6\ (0.83)}$	I
10	Cr_1	$\xrightleftharpoons[129.7\ (2.89)]{139.5\ (40.9)}$	Cr_2	$\xrightleftharpoons[148.0\ (19.1)]{161.5\ (24.2)}$	SmC	$\xrightleftharpoons[225.9\ (0.31)]{233.2\ (0.98)}$	N	$\xrightleftharpoons[258.7\ (0.88)]{272.1\ (0.98)}$	I
12	Cr_1	$\xrightleftharpoons[134.6\ (23.2)]{147.1\ (9.96)}$	Cr_2	$\xrightleftharpoons[144.2\ (16.5)]{152.5\ (4.32)}$	SmC	$\xrightleftharpoons[230.1\ (1.00)]{236.3\ (1.30)}$	N	$\xrightleftharpoons[249.7\ (1.03)]{256.1\ (0.86)}$	I
14	Cr_1	$\xrightleftharpoons[127.3\ (22.7)]{138.7\ (22.0)}$	Cr_2	$\xrightleftharpoons[139.6\ (19.1)]{146.9\ (19.1)}$	SmC	$\xrightleftharpoons[239.9\ (1.88)]{242.9\ (1.97)}$	N	$\xrightleftharpoons[248.8\ (1.11)]{251.1\ (1.10)}$	I
16			Cr_1	$\xrightleftharpoons[126.7\ (22.8)]{133.7\ (15.6)}$	Cr_2	$\xrightleftharpoons[130.6\ (12.3)]{139.9\ (8.95)}$	SmC	$\xrightleftharpoons[229.4\ (2.42)]{235.5\ (3.93)}$	I
2; *n* = 12							Cr	$\xrightleftharpoons[43.8\ (29.0)]{59.3\ (32.4)}$	I
3; *n* = 8							Cr	$\xrightleftharpoons[121.8\ (3.96)]{128.9\ (7.92)}$	I

phases. The compound with longest chains ($n = 16$) formed a smectic C phase only. This trend in mesomorphic properties is commonly observed with other rod-like molecules. An increase in terminal length often results in an enhanced dipole–dipole interaction between the terminal chains, leading to the formation of more ordered smectic C or other highly ordered smectic phases.

The temperature range of the nematic phases observed in compounds **1** was dramatically decreased with increasing chain length, ranging from 125.2°C ($n = 3$) to 8.2°C ($n = 14$) on heating, except for the compound 1 ($n = 3$). The N–I transition enthalpies were insensitive to the carbon length, in the range $\Delta H = 0.83$ ($n = 8$) to 1.10 ($n = 14$) $kJ\,mol^{-1}$. The nematic phase was identified by optical schlieren textures, as shown in the figure. However, for compounds **1** with longer chains ($n = 8$, 10, 12, 14) an additional smectic C phase was observed at lower temperatures. The common textures identified as smectic C phases (see the figure) were observed on cooling from the nematic phases of the compounds. In contrast to the nematic phases, the SmC→N temperature transitions were increased with increasing chain length, in the range 18.6°C ($n = 8$) to 96.0°C ($n = 14$) on heating cycle. The SmC-N transition enthalpies were also increased with increasing chain length; $\Delta H = 0.28$ ($n = 8$) to 1.97 ($n = 14$) $kJ\,mol^{-1}$. The overall range of the calamite mesophase did not parallel the carbon length, i.e. 95.6 to 125.2°C.

The clearing temperatures of compounds **1** decreased with chain length, 336.3°C ($n = 3$) to 235.5°C ($n = 16$). The clearing temperatures of compound **1** were all relatively high compared with the similar triazole compounds **4**, which in fact cleared at room temperature. The effect of increasing the terminal chain length on the formation of mesomorphic properties was also studied. Compounds **2** and **3** with four and six terminal chains Cr–I were also prepared. However, they were not truly mesogenic, and only Cr–I transitions at 59.3°C and 128.9°C, respectively, were observed for compounds **2** and **3**. Increasing the number of terminal alkoxy chains resulted in a dramatic lowering of melting points.

In summary, a new series of heterocyclics with 1,2,4-triazoles as core group has been prepared. The

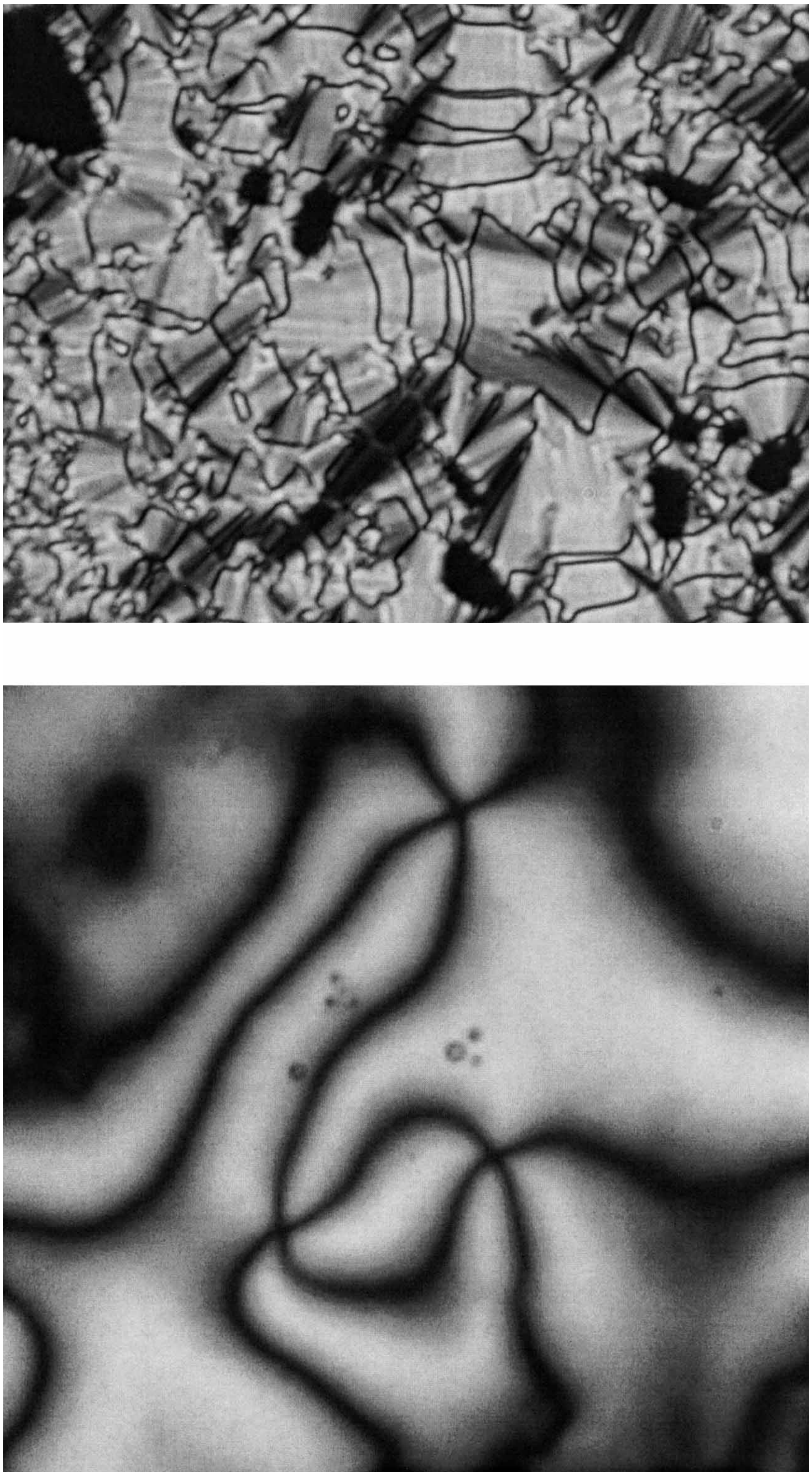

Figure 1. Optical textures (100 ×) of smectic C (top) and nematic (bottom) phases observed in compound 1 ($n = 14$).

rod-like molecules exhibit calamitic nematic and/or smectic C phases. The presence of an ionizable proton at the N-4 position and/or more polarized nitrogen atoms on the 1,2,4-triazole ring may be responsible for the mesomorphic properties and higher clearing temperature over similar analogues. Future studies will be focused on the mesomorphic investigation of corresponding ionic compounds isolated by deprotonation of the –NH group.

This paper is dedicated to Professor Kwang-Ting Liu of National Taiwan University on his 65th birthday. We also thank the National Science Council of Taiwan, ROC for funding (NSC-91-2113-M-027-003 & NSC-91-2113-M-008-017) in generous support of this work.

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