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Room temperature columnar 1,2,4-triazole core

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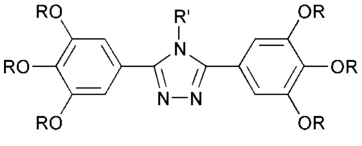
A new type of five-membered heterocyclic 1,2,4-triazoles (1–5) with various substituents on the N-4 position, such as benzyl, phenyl or *n*-alkyl groups, utilized as core group to generate room temperature columnar mesophases is reported. The presence of lone pair electrons on the nitrogen atoms and/or nonplanarity in this type of heterocyclic structure might be responsible for the formation of the columnar mesophases and the resulting lower melting and clearing temperatures.

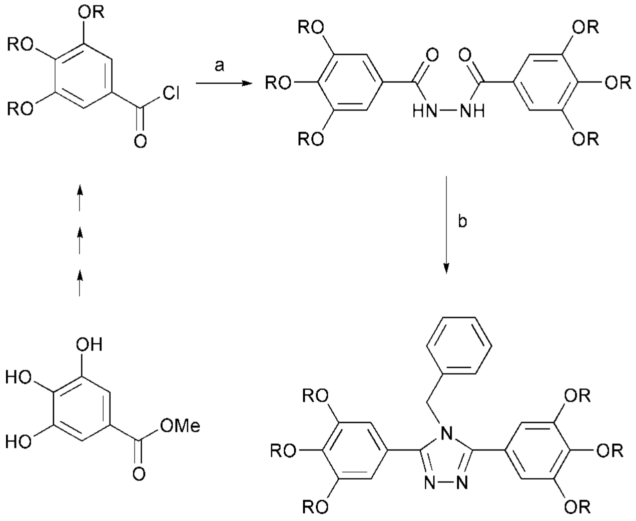
Whereas a variety of synthetic routes developed to prepare 1,2,4-triazole derivatives[1] have been well known for a long time, the majority of attention and studies devoted to compounds containing a 1,2,4-triazole moiety was exclusively focused on their important biological chemistry. Numerous triazole-based compounds have been studied and found to display a wide range of medicinal activities.[2] In contrast, other structurally similar heterocyclic molecules[3,4] have received much attention from materials chemists due to their diverse structural features and remarkable mesomorphic properties. The mesomorphic properties of five-membered heterocyclic derivatives[4] have been reviewed by Demus. Many heterocyclic five-membered rings, such as thiophenes, pyrazoles or isoxazoles, are all well known and better studied. Five-membered rings[5,6] have generally been considered less suitable for the formation of mesogenic materials than six-membered rings due to their relatively favorable deviation from linearity or planarity. In addition, the presence of lone-pair electrons on heteroatoms introduces[6] a transverse dipole moment, often resulting in a change of dielectric anisotropy. Compared to other heterocyclic molecules, the mesomorphic studies of 1,2,4-triazole derivatives as potential materials are very limited. No known example of 1,2,4-triazole-based compounds exhibiting mesomorphic properties has been reported. In this communication a series of compounds (**1**–**5**) containing triazole as the core group was prepared and studied. These compounds exhibited hexagonal columnar phases, and in fact, they are all room temperature liquid crystals.



1 R' = benzyl; R = $(CH_2)_nH$
2 R' = phenyl; R = $C_{10}H_{21}$
3 R' = 4-methoxyphenyl; R = $C_{10}H_{21}$
4 R' = hexyl; R = $C_{10}H_{21}$
5 R' = dodecyloxy; R = $C_{10}H_{21}$

The synthetic pathway is quite straightforward, as summarized in Scheme 1. The compounds were synthesized[7] as follows. 3,4,5-Trialkoxybenzoic acid *N*-(3,4,5-trialkoxybenzoyl)hydrazides (**6**) were obtained by reaction of 3,4,5-trialkoxybenzoic acid chlorides and hydrazine with yields ranging from 72–80%. Next a mixture of compounds **6** and phosphorus trichloride was first stirred at room temperature, and to this mixture *n*-alkylamine or benzylamine was then added and used also as solvent, and the neat reaction mixture was heated at 180 °C. The products, isolated as pale yellow oils, were purified by silica gel chromatography eluting with hexane–ethyl acetate (10 : 1). The reaction yields were generally low, *ca.* 25–35%. All derivatives were characterized by ^{1}H, ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H and ^{13}C NMR data in $CDCl_3$, for *e.g.*, 3,4,5-tris(octyloxy)benzoic acid *N*-[3,4,5-tris(octyloxy)benzoyl]-hydrazide (**6**) each showed one characteristic peak at δ 9.62 ppm and 171.90 ppm, respectively, and these peaks were assigned to amide-H (-NH) and amide-C (-CONH). In addition, the appearance of a singlet peak at 5.30 ppm shifted from free benzylamine (3.82 ppm) was assigned to $-NH_2$ and confirmed the formation[8] of the product (**1**). In the infrared spectrum the -CO stretching bands occurred at 1590–1739 cm^{-1} and the -NH stretching frequency at 3150–3235 cm^{-1}.

The mesomorphic behavior was studied by thermal analysis (DSC; Mettler DSC-821) and polarizing optical microscopy (Nikon Microphot-FXA, Mettler FP90/FP82HT). The transition temperatures and the enthalpies of **1**–**5** are summarized in Table 1. All the prepared compounds (**1**–**5**) are found to be room temperature liquid crystals. Compounds with a variety of different groups [benzyl (**1**), phenyl (**2**, **3**) or *n*-alkyl (**4**, **5**)] substituted at the N-4 position were prepared to study the effect of mesomorphic properties on structural features. All these substituents were all directly bonded to the central core group, and the difference in the mesomorphic properties observed might be correlated to the structural change.



Scheme 1 *Reagents and conditions*: a: N_2H_4 (3.0 equiv.), stirred in dried CH_2Cl_2, 2 h, 78–90%; b: PCl_3 (20.0 equiv.), stirred at 180 °C in benzylamine, 10 h, 25–35%.

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Table 1 Phase behavior[a] for the compounds **1**–**5**

Compound	n	Phase behaviour
1	6	Co$_{lhd}$ $\underset{55.2\ (3.13)}{\overset{61.6\ (3.25)}{\rightleftharpoons}}$ I
	7	Col$_{hd}$ $\underset{58.2\ (2.18)}{\overset{66.5\ (2.22)}{\rightleftharpoons}}$ I
	8	Col$_{hd}$ $\underset{66.7\ (4.84)}{\overset{69.1\ (4.18)}{\rightleftharpoons}}$ I
	10	Col$_{hd}$ $\underset{59.6\ (2.80)}{\overset{62.7\ (3.61)}{\rightleftharpoons}}$ I
	12	Col$_{hd}$ $\underset{64.6\ (5.07)}{\overset{67.1\ (5.21)}{\rightleftharpoons}}$ I
	14	Cr $\underset{41.3\ (91.4)}{\overset{74.8\ (61.0)}{\rightleftharpoons}}$ I
2		Col$_{hd}$ $\underset{75.3\ (5.17)}{\overset{80.1\ (5.72)}{\rightleftharpoons}}$ I
3		Col$_{hd}$ $\underset{95.0\ (2.85)}{\overset{99.9\ (3.02)}{\rightleftharpoons}}$ I
4		Col$_{hd}$ $\underset{52.9\ (7.05)}{\overset{62.8\ (6.00)}{\rightleftharpoons}}$ I
5		Col$_{hd}$ $\underset{66.4\ (9.22)}{\overset{71.2\ (9.05)}{\rightleftharpoons}}$ I

[a] n represents the number of carbons in the alkoxy chain. Cr = crystal phase; Col$_{hd}$ = disordered hexagonal columnar phase; I = isotropic. The transition temperatures (°C) and enthalpies (in parentheses, kJ mol^{-1}) are determined by DSC at a scan rate of 5.0 °C min^{-1}.

All compounds (**1**–**5**) formed columnar mesophases regardless of the structural substituents on the the N-4 position. The compounds **1** (n = 6, 7, 8, 10, 12) exhibited hexagonal columnar phases. DSC data indicated that all compounds gave only one enantiotropic transition, columnar-to-isotropic (Col→I), at temperatures higher than room temperature. The clearing temperatures of the compounds were observed in the range of 61.6–67.1 °C on heating, and this clearing temperature was not sensitive to the carbon length of alkoxy sidechains. The compound with longer carbon sidechains (n = 14) formed a crystalline phase. The transition temperatures of crystal-to-columnar were all below room temperature, and not measured. The mesophase was characteristically identified as hexagonal columnar (Col$_h$) based on optical texture observed.

Changing the substituent groups on the N-4 position from benzyl (**1**) to phenyl (**2**) increased the clearing temperature by *ca.* 18 °C. Consequently, this structural change also expanded the useful temperature range of the mesophase. The temperature range increase in this series of compounds was further observed, as expected, in compound **3**, in which the phenyl group was replaced by a 4-methoxyphenyl group. The effect on increasing clearing temperatures of structural modification in compounds **1**–**3** was attributed to the relatively higher rigidity of 4-methoxyphenyl (**3**) than a less rigid phenyl (**2**) or benzyl (**1**) group at the N-4 position. In contrast, a slight change in clearing temperatures was also observed in compounds **4** and **5**. These compounds, having more flexible aliphatic groups, such as n-hexyl (**4**) or n-dodecyloxy (**5**) exhibited similar mesomorphic properties to compound **2**. The identification of columnar phases was also characterized by polarized optical microscope. A typically pseudo focal-conic or fan texture with linear birefringent defects on slowly cooling from the isotropic liquid was clearly observed, which is often characteristic of hexagonal columnar phases. A relatively smaller enthalpy obtained (2.18–9.22 kJ mol^{-1}) for the columnar-to-isotropic transition was also evidence for the formation of hexagonal columnar phases. Fig. 1

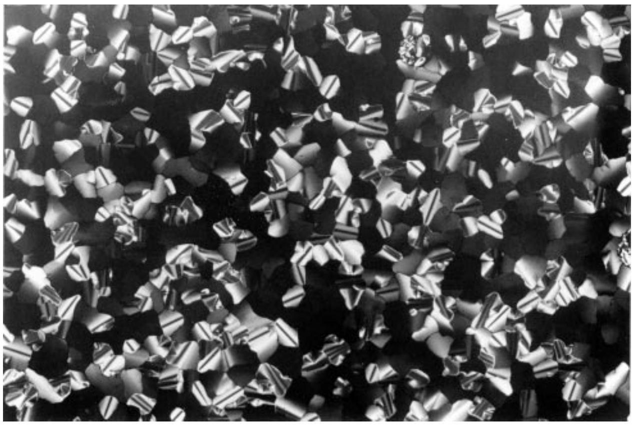

Fig. 1 Optical textures (100 ×) observed for compound **3** at 55 °C.

In summary, a new type of heterocyclic compounds derived from 1,2,4-triazole as core group was prepared. All derivatives exhibited room temperature columnar phases. The presence of more polarized nitrogen atoms on the 1,2,4-triazole ring might be responsible for the formation of better mesomorphic properties over other all five-membered-carbon ring analogues.

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Notes and references

1 *Progress in Heterocyclic Chemistry*, Vol. 10–11, ed. G. M. Gribble and T. L. Gilchrist, Pergamon, Elsevier Science Ltd., Oxford, 1998; 1999; Vol. 11.

2 L. Zirngibl, *Antifungal Azoles: A Comprehensive Survey of their Structures and Properties*, Wiley-VCH, New York, 1998; G. J. Tanoury, C. H. Senanayake, R. Hett, A. M. Kuhn, D. W. Kessler and S. A. Wald, *Tetrahedron Lett.*, 1998, **39**, 6845.

3 L. S. Konstantinova, O. A. Rakitin, C. W. Rees, L. I. Souvorova, T. Torroba, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1999, 73; A. Mallia, M. George and S. Das, *Chem. Mater.*, 1999, **11**, 207; E. Bialecka-Florjanczyk, A. Orzeszko, I. Sledzinska and E. Gorecka, *J. Mater. Chem.*, 1999, **9**, 381; H. C. Lin, C. W. Ko, K. Guo and T. W. Cheng, *Liq. Cryst.*, 1999, **26**, 613; J. Belmar, M. Parra, C. Zuniga, C. Perez, C. Munoz, A. Omenat and J. L. Serrano, *Liq. Cryst.*, 1999, **26**, 389.

4 D. Demus, J. Goodby, G. W. Gray, H. W. Spiess and V. Vill, *Handbook of Liquid Crystals*, Wiley-VCH, New York, 1998, Vol 2B.

5 W. R. Li, K. C. Kao, Y. C. Yo and C. K. Lai, *Helv. Chim. Acta*, 1999, **82**, 1400.

6 L. L. Lai, C. H. Wang, W. P. Hsieh and H. C. Lin, *Mol. Cryst. Liq. Cryst.*, 1996, **287**, 177.

7 O. R. Gautun and P. H. J. Carlsen, *Acta Chem. Scand.*, 1991, **45**, 609.

8 Spectroscopic data for compound **1** (n = 8): 4-benzyl-2,5-bis[3,4,5-tris(octyloxy)phenyl]-4*H*-1,2,4-triazole, pale yellow oil, yield 29%. ^{1}H NMR (ppm, CDCl$_3$): 0.88(m, -CH$_3$, 18H), 1.25–1.55(m, -CH$_2$, 60H), 1.64–1.76(m, -CH$_2$, 12H), 3.62(t, -OCH$_2$, 8H), 3.95(t, -OCH$_2$, 4H), 5.30(s, -CH$_2$, 2H), 6.80(s, -C$_6$H$_2$, 4H), 7.18–7.48 (m, -C$_6$H$_5$, 5H). ^{13}C NMR (ppm, CDCl$_3$): 13.95, 22.52, 25.76, 25.87, 28.96, 29.11, 29.19, 29.33, 30.08, 31.67, 31.72, 48.66, 68.45, 73.26, 106.41, 121.36, 125.41, 127.76, 129.20, 137.36, 139.16, 153.07, 156.31. IR (neat): 725, 841, 1116, 1255, 1328, 1381, 1428, 1469, 1487, 1587, 2855, 2925 cm^{-1}. Anal. Calcd for C$_{69}$H$_{113}$N$_3$O$_6$:

C 76.69, H 10.54, N 3.89. Found C 76.59, H 10.34, N 4.02%. Spectroscopic data for compound **4**: 4-hexyl-3,5-bis[3,4,5-tris(decyloxy)phenyl]-4*H*-1,2,4-triazole, off-white oil, yield 28%. ^{1}H NMR (ppm, $CDCl_3$): 0.75–0.88(m, $-CH_3$, 21H), 1.03–1.60(m, $-CH_2$, 90H), 1.70–1.81(m, $-CH_2$, 14H), 4.01(m, $-OCH_2$, 12H), 4.01(m, $-NCH_2$, 2H), 6.82(s, $-C_6H_2$, 4H). ^{13}C NMR(ppm, $CDCl_3$): 13.73, 14.02, 22.24, 22.62, 25.82, 26.05, 29.29, 29.35, 29.53, 29.58, 29.62, 29.69, 29.98, 30.30, 30.87, 31.86, 44.97, 69.42, 73.51, 107.82, 122.54, 139.87, 153.44, 155.52. IR (neat): 2924, 2854, 1584, 1487, 1467, 1431, 1380, 1332, 1240, 1116, 845, 722 cm^{-1}. Anal. Calcd for $C_{68}H_{119}N_3O_6$: C 77.30, H 11.60, N 3.38. Found C 77.13, H 11.49, N 3.39%.