Tristriazolotriazines: a core for luminescent discotic liquid crystals†

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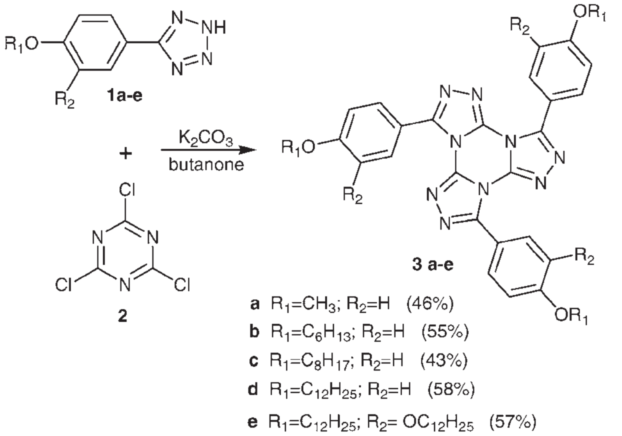
Received (in Cambridge, UK) 25th June 2008, Accepted 25th July 2008
First published as an Advance Article on the web 3rd September 2008
DOI: 10.1039/b810680k

The synthesis and structural, thermal, optical and theoretical characterization of new tris[1,2,4]triazolo[1,3,5]triazines were performed to support their application as liquid crystals and advanced materials.

Disc-like molecules comprising a rigid aromatic core and peripheral flexible chains are of great interest in molecular electronics due to their ability to self-assemble into columnar superstructures with one-dimensional conducting properties.[1,2] In addition, the insertion of an *N*-heterocycle core in a discotic molecule may enhance the electron-transport as well as the luminescence properties for electro-optical device applications.[3] The heterocycle tris[1,2,4]triazolo[1,3,5]triazine, synthesized by Huisgen *et al.*[4] by heating phenyltetrazole and cyanuric chloride in toluene, possesses an interesting disc-like shape and although it has the potential for application in advanced materials (discotic liquid crystals or film forming compounds), it has not yet been exploited. In addition, it has been poorly characterized, and only a ^{13}C NMR study was found in the literature.[5]

Herein, we describe the synthesis of disc-like molecules **3a–e** based on triphenyl substituted tris[1,2,4]triazolo[1,3,5]triazine containing peripheral aliphatic chains, their thermal and optical properties and the X-ray structure of the heterocycle. In order to investigate the thermal stability and film forming behavior in terms of the flexible chain sizes, different alkoxyl groups in **3b–d** were studied (6, 8 and 12 carbon atoms). The methoxyl group in **3a** was chosen to generate a more crystalline material for the X-ray structure characterization, as well as to simplify theoretical calculations.

The final compounds **3a–e** were synthesized as shown in Scheme 1. Aryltetrazoles **1a-e**[6] were reacted with cyanuric chloride **2** in a modified Huisgen protocol, using butanone as the solvent and potassium carbonate as the base to activate the tetrazole and also for uptake of the HCl generated in the reaction. Compounds **3a–e** were obtained in reaction yields from 43 to 58% (see ESI†). The structures of all compounds were characterized using IR, ^{1}H, and ^{13}C NMR spectra and elemental analysis, including an ^{15}N NMR and X-ray diffraction analysis of compound **3a**.



Scheme 1 Synthesis of tristriazolotriazines **3a–e** with yields in parentheses.

In order to examine the molecular structure of this heterocycle, as well as the organization in the solid state, attempts to obtain a single crystal of compound **3a** were carried out. From slow evaporation of the methanol solution crystals suitable for X-ray diffraction were obtained. The X-ray structure of compound **3a** confirms the isomeric form of the triazole rings in the final compounds (Fig. 1).‡ The peripheral phenyl rings are

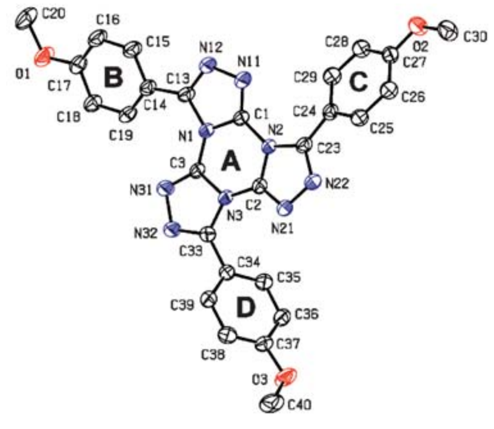


Fig. 1 X-ray structure of compound **3a**. Ellipsoids at 50% probability level.

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† Electronic supplementary information (ESI) available: Experimental details for the synthesis of the final compounds **3a–e**, characterization data, DSC and TGA. ^{15}N NMR, theoretical calculations, cyclic voltammogram and X-ray data (CIF) of compound **3a**. CCDC reference number 686712. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b810680k

Table 1 Thermal and optical properties of compounds **3a–e**

	Thermal properties			Optical properties					
				Abs. λ_{max}/nm		Fl. λ_{max}/nm			
Compounds	Transitions/°C[a]	T_g/°C[b]	$T_{dec.}$/°C[c]	Sol.[d]	Film	Sol.[d]	Film	Φ_{Fl}[e]	E_g/eV[f]
3a	C 278.0 I	—	400	290	290	360	363	0.25	3.9
3b	C 129.9 I	55.4	445	294	288	362	366	0.33	3.9
3c	C 93.8 I	46.7	437	294	287	362	368	0.33	3.9
3d	C 86.6 I	70.3	441	294	286	362	371	0.34	3.9
3e	C 92.2 (19.3) Col_h 207.6 (6.8) I	—	436	311	316	387	388	0.47	3.5

[a] First heating scan (DSC). C: crystal; Col_h: hexagonal columnar phase; I: isotropic liquid. (ΔH/kJ mol^{-1}). [b] Second heating scan (DSC). [c] Onset of decomposition under N_2 (TGA). [d] $CHCl_3$ solution (10^{-5} mol L^{-1}). [e] Relative to the PBD (Φ_{Fl} = 0.83)[7]. [f] Determined from absorption spectra of the films.

clearly in a non-planar conformation with respect to the triazine core. The mean plane angles for the twist of the rings B, C and D from the central ring A are 19.3(1), 28.7(1) and 61.8(1)°, respectively. Molecular packing is mainly due to van der Waals interactions, which is in agreement with the softness of the crystals, and also due to dipolar interactions (calculated dipole moment is 2.0 D, with a large component (1.8 D) perpendicular to the tristriazolotriazine core). Molecular π-stacking is sterically inhibited in the solid phase, which improves the potential for these materials to be applied as good solid state emitters, since the formation of excimers *via π-stacking is known to suppress the emission in solids.*[8]

B3LYP/6-311G(d,p) calculations[9] (see ESI†) for compound **3a** corroborated the observed non-planar conformations and the structural parameters were in excellent agreement with the crystallographic data. Conformational analysis of one phenyl group yielded 11.5 kJ mol^{-1} for the barrier to internal rotation of a single phenyl group. This value is quite small, thus allowing a conformational equilibrium to be attained quickly at room temperature and, thus, a symmetric structure can be expected in solution in the NMR time scale. In fact, symmetric structures in the ^{1}H, ^{13}C and ^{15}N NMR spectra of the final compounds were found.

The thermal and optical properties of compounds **3a–e** are summarized in Table 1. They are thermally stable compounds as shown by their high decomposition temperatures (> 400 °C) according to TGA measurements. Except for **3a**, these compounds do not show tendencies towards crystallization, which is further evidence of non-aggregation in the solid state. After melting, compounds **3a–d** do not crystallize upon cooling and the obtained transparent films remain stable for months without any crystallization. Upon heating, the second DSC scan of these compounds reveals only one glass transition temperature (see ESI†). It was observed that increasing the length of the aliphatic chains leads to a decrease in the melting point and improves the film forming behavior. Compound **3e**, with six peripheral aliphatic chains, is an interesting discotic liquid crystal exhibiting a very wide hexagonal columnar phase (Col_h) from 92.2 to 207.6 °C. The mesophase was assigned as Col_h on the basis of the typical pseudo focal conic textures observed by polarized optical microscopy on cooling (Fig. 2) and confirmed by X-ray diffraction (see ESI†). The cell parameter *a* was calculated to be 30.4 Å, smaller than the van der Waals diameter of the molecule (43.0 Å) in the most extended conformation. This indicates either interdigitation or partial folding of the chains. The core–core mean distance was found to be 3.5 Å, suitable for π-stacking. In addition, similarities in the optical textures were observed at temperatures above and below the melting point, indicating the retention of a columnar structure in the low temperature phase.

As a consequence of this amorphous behavior, stable spin-coated films are easily obtained on quartz plates from their respective $CHCl_3$ solutions. UV and fluorescence spectra were then measured in solution and in solid films (Fig. 3).

The maximum absorption wavelengths for compounds **3a–e** in solution and in the film are quite similar, peaking at around 290–311 nm ($\varepsilon \sim$ 50 000 L mol^{-1} cm^{-1}) and 286–316 nm, respectively. These are attributed to the π–π* transitions in the heteroaromatic portion of the molecule due to the high molar absorption coefficient.

The INDO/S-CIS calculated electronic spectrum[10] for a non-planar conformation of compound **3a** is in better agreement with the experimental data than that calculated for the planar conformation (see ESI†). The band at 290 nm involves two transitions (calculated at 295 nm), each one involving mainly HOMO–LUMO and HOMO–LUMO + 1 orbitals. The nearest transitions to this main band occur at ~ 280 nm with very low oscillator strength values and involve very high energy unoccupied molecular orbitals. Thus, the observed band has only two contributions whose molecular orbitals are illustrated in Fig. 4.

These compounds show strong blue fluorescence in solution with maximum emission wavelengths between 360 and 387 nm and fluorescence quantum yields (Φ_{Fl}) varying from 25 to 47% (Table 1). They also showed strong fluorescence in the solid phase, exhibiting emission maxima at wavelengths between 363 and 390 nm, with very small red-shifts compared to those in solution.

Fig. 2 Polarizing optical photomicrographs of pseudo focal conic texture of Col_h for **3e** obtained at 205 °C (left) and 202 °C (right) on cooling.

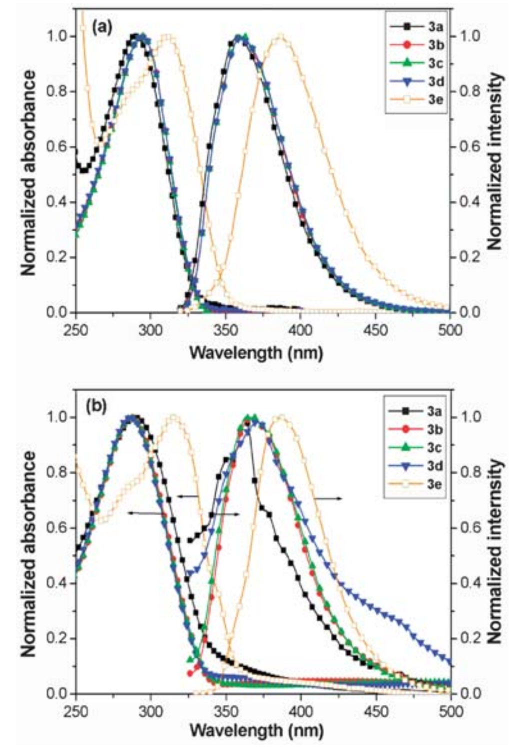

Fig. 3 Absorption and fluorescence spectra of **3a–e** in solution (a) and film (b).

Fig. 4 HOMO and LUMOs at the INDO/S level.

Fluorescence spectra of compound **3e** in the Col$_h$ phase showed the same maximum wavelength (388 nm) but with a significant decrease (about 25%) in the curve area, compared to the emission in the solid phase (see ESI†). This is indicative of a larger extent of self-quenching aggregates[2d] in the liquid crystal phase, consistent with the intracolumnar distance (3.5 Å) observed by XRD analysis. The energy gap between HOMO and LUMO (E_g) was obtained from solid phase absorption spectra according to the published method.[11] The optical E_g values were found to be as high as 3.5 eV in **3e** and around 3.9 eV in **3a–d**. Electrochemically, compound **3a**, used as a representative case, exhibited only an irreversible oxidation wave peaking at 1.6 V *vs.* SCE (see ESI†), suggesting that the tristriazolotriazine core potentially has electron-transporting characteristics. Thus, the HOMO energy was obtained from the oxidation potential[12] corresponding to −5.8 eV. The LUMO was found to be −1.9 eV, by subtracting its optical band gap from the HOMO value. These high band gap values characterize these compounds as wide gap, blue emitting materials, which is advantageous since it indicates that they can be applied as hosts in electroluminescent devices.[13]

In summary, we performed the synthesis and structural, thermal and optical characterization of new tris[1,2,4]triazolo[1,3,5]-triazines. Non-planar conformational structures led to good solid emitter and film forming behavior. In addition, a discotic liquid crystal was built with this center possessing a very stable Col$_h$ phase with a temperature range wider than 115 °C. Interestingly, these compounds present a high thermal stability associated with film forming behavior. The theoretical calculations were in good agreement with the experimental observations, corroborated spectral assignments and provided information on the structural and optical behavior at the electronic/molecular level.

Financial support from *Conselho Nacional de Desenvolvimento Científico e Tecnológico* (CNPq, PRONEX, FAPESC) is gratefully acknowledged. The authors are grateful to Mrs Marly Soldi (DSC and TGA measurements), Dr Fernando Halwass (^{15}N NMR measurements), Dr Gustavo A. Micke (MS spectra) and Dr Haidi Fiedler and Dr Edson Minatti for free access to the photophysical instruments. We also thank the reviewers for their helpful and interesting suggestions.

Notes and references

‡ Crystal data: formula $C_{27}H_{21}N_9O_3$; FW 519.53; crystal system: triclinic, space group $P\bar{1}$, T = 293 K, a = 6.418(3), b = 12.867(2), c = 14.500(9) Å, α = 80.73(2), β = 86.34(5), γ = 89.67(3)°, V = 1179.4(9) Å^3, Z = 2, D_{calc} = 1.463 Mg m^{-3}, μ = 0.101 mm^{-1}; unique reflections = 4194 (R_{int} = 0.0462); parameters = 353; GOOF (F^2) = 1.026; R_1 [$I > 2\sigma(I)$] = 0.0642, wR_2 (all data) = 0.1834.

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