

Communication

Synthesis and Crystal Structure of 9-(4,6-dichloro-1,3,5-triazin-2-yl)-9H-carbazole

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Abstract: A carbazole-triazine hybrid was prepared by addition-elimination between carbazole and 2,4,6-trichlorotriazine in the presence of base. The compound shows intensely blue fluorescence both in solution and solid state when irradiated with UV-radiation. The structure of (**3**) was supported by the spectroscopic data and unambiguously confirmed by the single crystal X-ray diffraction data. It was crystallized in the monoclinic space group C2/c with unit cell dimensions $a = 20.280(3)$, $b = 8.0726(14)$, $c = 16.005(3)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 98.947(3)^\circ$, $V = 2588.3(8)$ Å³, $Z = 8$.

Keywords: carbazole-triazine hybrid; fluorescence; crystal structure

1. Introduction

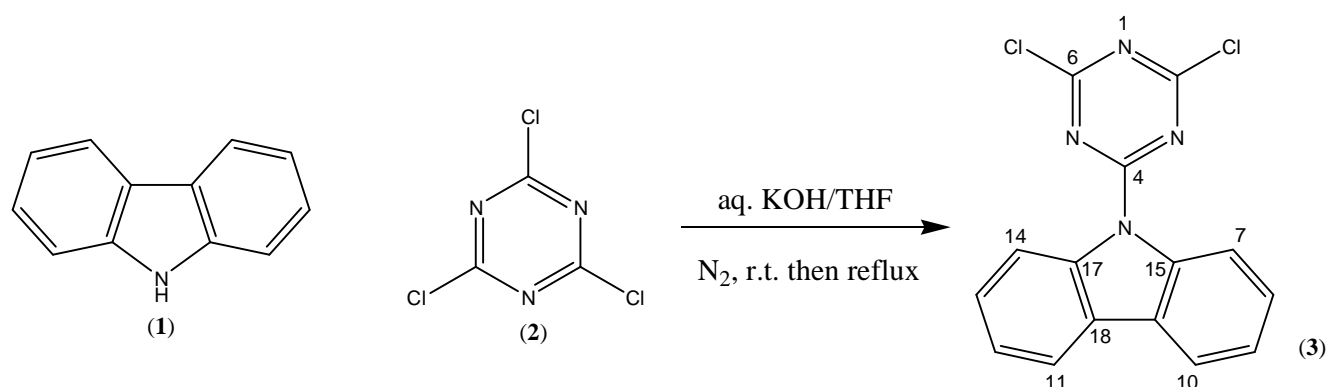
Extensively π -conjugated materials have attracted much interest in the recent past due to their excellent semiconducting properties [1,2]. In fact, such materials are responsible for the emergence of the new science of organic semiconductors and organic electronics that promises fulfilling the future electronics challenges with respect to the low cost, easy tenability of properties of the materials by functionalization of materials, ease of fabrication of devices due to solution phase processability of the

materials, large area flat panel displays, compressed memory devices, *etc.* Carbazole-based materials are important candidates in this respect due to their excellent redox and luminescent properties and good thermal and environmental stability. The carbazole nucleus can be functionalized at 3-, 6- and 9-positions [3]. A lot of literature is available on carbazole based materials for organic electronic applications and many of the materials have gained commercial utility in this respect [4]. On the other hand, 1,3,5-triazines are another important class of π -conjugated heterocycles with nitrogen atoms in the six-membered ring each with a lone-pair of electrons pointing outside the ring. 1,3,5-Triazine derivatives are of great interest due to their importance as drug precursors and additives for stabilizing light emission in OLEDs [5-8]. Carbazole-triazine hybrids have gained special importance in the field of organic electronics as electroluminescent materials [9,10].

2. Results and Discussion

The title compound was synthesized by modification of a reported method [11] according to the route depicted in Figure 1. Thus, carbazole (1) was converted into corresponding salt in the presence of aqueous KOH. Treatment of carbazole with cyanuric chloride (2) afforded 9-(4,6-dichloro-1,3,5-triazin-2-yl)-9H-carbazole (3) by addition elimination mechanism.

Figure 1. Synthesis of 9-(4,6-dichloro-1,3,5-triazin-2-yl)-9H-carbazole (3).



The compound (3) in solid state as well as in THF and chloroform solution exhibits intense blue fluorescence when irradiated with 253 nm UV-radiation.

The molecular structure (Figure 2) shows almost planar geometry. Aromatic rings C4 to C9 and C10 to C15 make a dihedral angle of 3.6(1)°, the relevant angles with the triazine ring are 3.5(1)° and 4.3(1)°, respectively. Corresponding torsion angles C4-N1-C1-N2 and C15-N1-C1-N4 are 0.4(2)° and -1.3(2)°. Bond lengths and angles lie in expected ranges.

The crystal packing exhibits no marked intermolecular D-H...A contacts, but orientation of mean planes of molecules may well be described as π -stacked columns along [010] (Figure 3). Stacking distance is about 3.4 Å and the molecule planes alternate in a head-to-tail manner.

Figure 2. Molecular structure of (3). Anisotropic displacement ellipsoids are drawn at the 50% probability level.

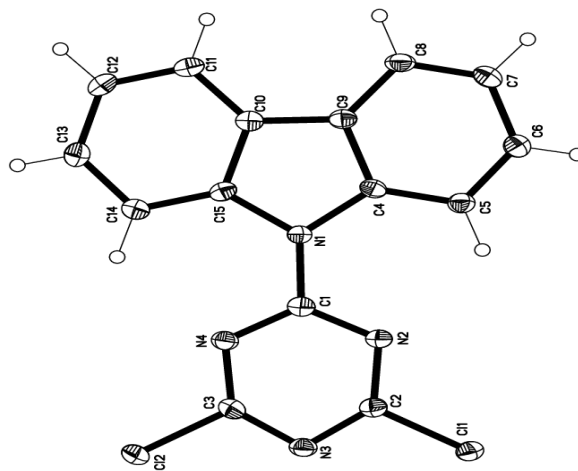
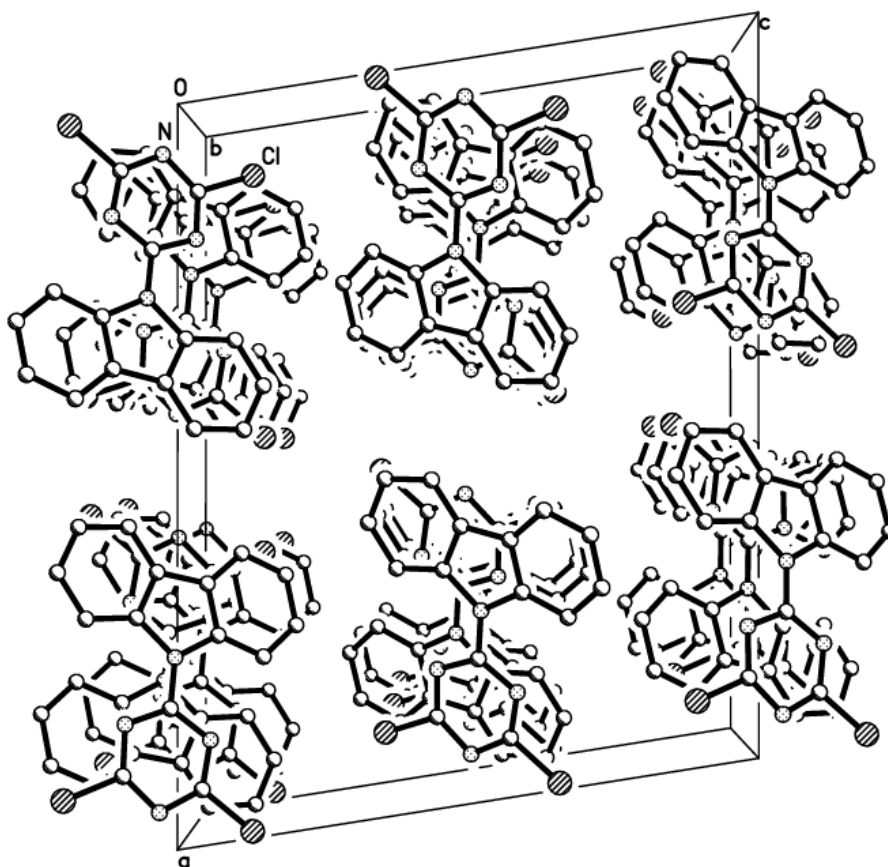


Figure 3. Crystal packing of (3) showing the π -stacking pattern of molecules along [010]. H-atoms are omitted.



Crystal Structure Determination

Data were collected at 120(2) K on a Bruker AXS SMART APEX CCD diffractometer using MoK α radiation. Multi-scan absorption correction was with SADABS [11]. The structure was solved by direct methods [12], full-matrix least-squares refinement [12] on F^2 and 190 parameters, all but H atoms

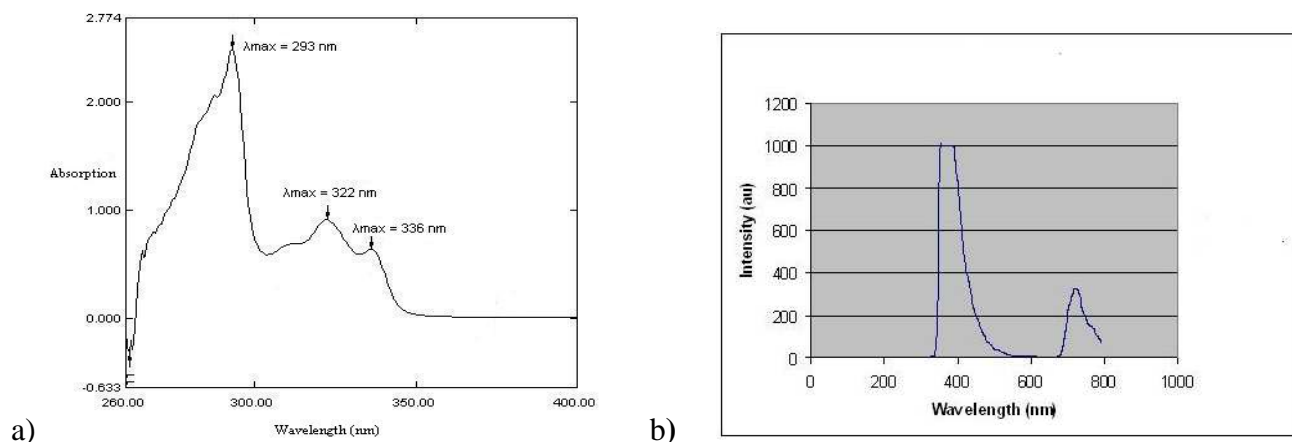
refined anisotropically, H atoms from difference Fourier maps refined with riding model on idealized positions with $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{C})$ and C-H distances of 0.95 Å. Experimental data are listed in Table 1.

Table 1. Crystal data and structure refinement for (3).

Empirical formula	$\text{C}_{15}\text{H}_8\text{Cl}_2\text{N}_4$	
Formula weight	315.15	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 20.280(3) Å b = 8.0726(14) Å c = 16.005(3) Å	$\alpha = 90^\circ$. $\beta = 98.947(3)^\circ$. $\gamma = 90^\circ$.
Volume	2588.3(8) Å ³	
Z	8	
Density (calculated)	1.618 mg/m ³	
Absorption coefficient	0.498 mm ⁻¹	
F(000)	1280	
Crystal size	0.49 × 0.18 × 0.15 mm ³	
Theta range for data collection	2.03 to 27.88°.	
Index ranges	-26 ≤ h ≤ 18, -10 ≤ k ≤ 10, -20 ≤ l ≤ 21	
Reflections collected	9398	
Independent reflections	3075 [R(int) = 0.0324]	
Completeness to theta = 27.88°	99.4%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9290 and 0.7923	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3075 / 0 / 190	
Goodness-of-fit on F ²	1.053	
Final R indices [I > 2sigma(I)]	R1 = 0.0367, wR2 = 0.0896	
R indices (all data)	R1 = 0.0476, wR2 = 0.0951	
Largest diff. peak and hole	0.410 and -0.286 e. Å ⁻³	

The UV spectrum of (3) in THF (Figure 4a) depicts the double band pattern characteristic of the fluorescent compounds at λ_{max} 322 nm and 336 nm, respectively. The higher λ_{max} at 293 nm is due to the nitrogen's influence on triazine functionality. The photoluminescence spectrum (Figure 4b) indicates fluorescence at 400 nm due to the presence of the carbazole moiety. The band at 750 nm is due to the solvent THF.

Figure 4. (a) The photoluminescence spectrum and (b) UV spectrum of compound (3) in dilute THF solution.



3. Experimental Section

Melting points were recorded using a digital Gallenkamp (SANYO) model MPD BM 3.5 apparatus and are uncorrected. ^1H NMR spectra were determined as CDCl_3 solutions at 300 MHz using a Bruker AM-300 spectrophotometer. FT IR spectra were recorded using an FTS 3000 MX spectrophotometer, Mass Spectra (EI, 70 eV) on a GC-MS instrument. UV-vis and fluorescence spectra were recorded on a Perkin Elmer Lambda 20 UV/Visible Spectrophotometer and a Perkin Elmer LS 55 Fluorescence Spectrophotometer, respectively.

Synthesis of 9-(4,6-dichloro-1,3,5-triazin-2-yl)-9H-carbazole (3)

1.67 g (1 mmol) of carbazole was dissolved in 10 mL of THF and to the clear solution was added 1 mL of 1M aq. KOH (1 mmol). The reaction mixture was stirred for 12 h at room temperature and the brown colored potassium salt of carbazole was obtained after removing the solvent which was dried *in vacuo*. The salt was dissolved in 10 mL of dry THF and 1.83 g (1 mmol) of cyanuric chloride was added in small portions under a nitrogen atmosphere. During the addition of cyanuric chloride the color of the salt solution gradually disappeared. The reaction mixture was stirred at room temperature for 1 h and then refluxed for 6 h. The solvent was removed to leave a solid. Single crystal of the title compound was grown by slow evaporation of a chloroform solution of the compound for 5 days. Yield 93%, m.p. 214 °C. ^1H NMR (300 MHz, DMSO-d_6), δ 8.12 (d, 2H_{Ar}), 7.51 (d, 2H_{Ar}), 7.40 (dd, 2H_{Ar}), 7.19 (d, 2H_{Ar}), ^{13}C NMR (75.4 MHz, DMSO-d_6), δ 140.09 (C-4), 125.53 (C-2), 123.06 (C-15), 120.00 (C-9), 118.7 (C-8), 110.82 (C-16).

4. Conclusions

A carbazole-triazine hybrid compound was synthesized which shows intensely blue fluorescence and is an intermediate towards a variety of carbazole-based heterocycles.

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