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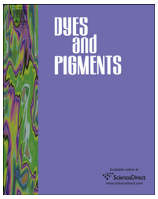

Bistriazine-based streptocyanines. Preparation, structural determination and optoelectronic properties

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ABSTRACT

A series of bistriazine-based streptocyanines has been selectively prepared. A variety of substituents has been introduced into the triazine ring with *p*-phenylenediamine as a conjugated spacer between the triazine and the streptocyanine moieties. Fukui indices have been used to explain the different sequential reactivity of the chlorine atoms in the triazine ring. 1D- and 2D-DNMR spectroscopy and computational calculations have been carried out to explain the dynamic behavior of these complex systems, which can be explained by the presence of a Cl … H bond. This method was used to build conjugated systems and to show the interaction between the triazine part, the spacer, and the streptocyanine moiety. A study of the optoelectronic properties has been performed by UV–vis and fluorescence spectroscopy. Streptocyanine-based bistriazines are violet-blue emitters and large Stokes shifts of more than 6000 cm^{-1} were observed. The title compounds showed interesting properties which have potential for use in optoelectronic devices.

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1. Introduction

π-Conjugated molecular structures are among the most investigated systems in the field of molecular materials due to their interesting optical and electronic properties [1]. However, the efficiency of optoelectronic devices based on π-conjugated systems is not only highly depended on the chemical structure but also on the supramolecular aggregation. Therefore, the construction of π-conjugated assemblies with controlled morphology and the desired properties is crucial for the fabrication of the aforementioned devices [2].

The choice of a good material for a specific application is hindered by the complex structure–property relationship. An interesting approach to tune the absorption in π-conjugated systems is the incorporation of electron donor (D) and electron acceptor (A) moieties in the molecular design [1,3,4]. Linear and star-shaped systems are among the most interesting π-conjugated materials that contain D and A groups.

Triazine derivatives have been used for the construction of star-shaped derivatives. Some examples of star-shaped triazine derivatives with a D–π–A [5] or D–π–A–π–D–π–A [6] electronic arrangement have found applications in solar cells [7], magnetic materials [8], and blue-luminescent OLEDs [9]. In particular, the later type of system has been shown to promote electron transport, and the derivatives synthesized according to this design exhibit large Stokes shifts, high thermal stability, and solvatochromism [10]. π-Conjugated systems that contain only one triazine ring have been investigated for many years [11,12] but bistriazines have received much less attention [13].

We recently described the preparation of mono- and bistriazines with phenylenediamine spacers with interesting optoelectronic properties. The electronic properties depend on the solvent and, in methanol, large bathochromic shifts and high quantum yields were observed [14].

According to the approach outlined above, we planned the preparation of bistriazines with a streptocyanine spacer. Streptocyanines are highly conjugated dyes with extended π-systems. These dyes show absorptions at long wavelengths and have high molar absorptivities. Streptocyanines with Donor and Acceptor

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groups have been used as Push-Pull systems [15]. These materials are classified as streptopolymethines, cationic hemicyanines, anionic streptopolymethine oxonols, neutral merocyanines, and cyanines based on zwitterionic squarines. Cyanines have found applications in Dye Sensitized Solar Cells (DSSC) [7] as donor-π bridge-acceptor systems and, in some cases, they show impressive efficiency [16]. Many of these compounds are either blue emitters or absorb in the NIR region [17].

Kawamura [11] synthesized a squarylium-triazine dyad as a photoradical generator that absorbs strongly in the red region and undergoes an intramolecular photodissociative electron-transfer reaction.

The aim of this research is the preparation of a new series of bistriazine-based streptocyanines in order to show the influence of this remarkable π-deficient heterocycle, that can show all possible supramolecular interactions, on the optoelectronic properties of streptocyanine dyes.

2. Results and discussion

2.1. Synthesis of streptocyanines **7**

The synthesis of the streptocyanines was planned in three steps, starting with cyanuric chloride (**1**), disubstitution with aliphatic and aromatic amines (**2**), reaction with *p*-phenylene diamine (**4**) to give the monofunctional product (**5**) and finally reaction with 3-chloro-*N*,*N*,*N*′,*N*′-tetramethyl-1,5-diaza-1,3-pentadienium hexafluorophosphate (**6**) (Scheme 1).

Starting with cyanuric chloride it is possible to replace sequentially the three chloro-substituents with nucleophiles [18]. The first substitution can be performed at 0 °C, the second one at room temperature while the third substitution requires higher temperatures, usually under reflux in an appropriate solvent.

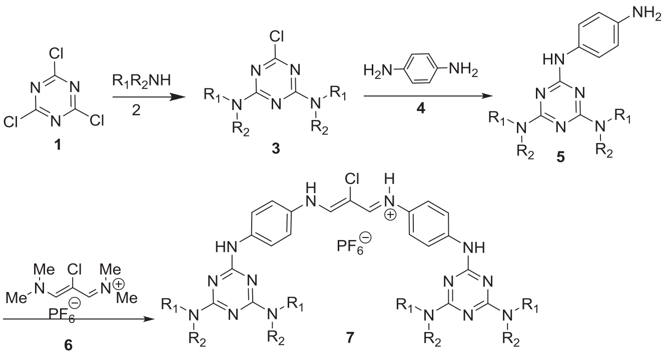
The Fukui indices in cyanuric chloride and the mono- and disubstituted compounds were determined computationally in order to explain the different reaction conditions in the sequential substitution of the chloro-substituents in cyanuric chloride. In brief, Fukui indices provide information about which atoms in a molecule have a higher tendency to either lose or accept an electron.

In chemistry this information is used to identify the positions that are more prone to undergo nucleophilic or electrophilic attack. Therefore, in an attempt to rationalize the different reactivities of the chloro-substituents in cyanuric chloride, the condensed Fukui function for the nucleophilic attack (f_A^+) [19] on monosubstituted and disubstituted derivatives was calculated at the reactive carbon atoms of the triazine ring within the framework of Density Functional Theory (DFT) [20], employing the functional B3LYP [21] and 6-311 + G(d,p) [22] as the basis set. The electrophilicity of an atom A in a molecule M (of N electrons) was calculated using the following equation:

$$f_A^+ = P_A(N+1) - P_A(N)$$

Where P stands for the population of atom A in a molecule M. The calculated values are collected in Table 1.

The Fukui indices confirm that increased substitution of the triazine ring results in a decrease in the electrophilic character that hinders nucleophilic substitution in the carbon atoms. For this reason, the calculated outcomes represent a straightforward method to interpret the selectivity observed.



Scheme 1. Synthesis of dimeric triazines with a streptocyanine spacer.

2.2. Disubstituted triazines

The synthesis of disubstituted triazines was performed by double substitution of cyanuric chloride according to the procedure of Kolmatov [23] for aromatic amines. The reaction conditions and yields were very dependent on the basicity of the amine. For strongly basic amines an acetic acid/sodium acetate buffer was used but for amines with low basicity only acetic acid was required (Table 2). *p*-Anisidine, 1-naphthylamine and diphenylamine were selected because they show interesting properties as fluorophores in fluorescence spectroscopy [24].

The reaction with diphenylamine (pKa = 0.79) required the use of acetic acid and 60 h to produce the monosubstituted product **3c'** in good yield (85%). The use of solvent-free conditions at high temperatures [25] enabled triple substitution to give **3c"** in 74% yield. Finally, preparation of the desired 6-chloro-4,6-bis(*N*,*N*-diphenylamino)-1,3,5-triazine (**3c**) could be performed in basic conditions (Disiopropylethylamine, DIPEA) under reflux in di(*n*-butyl)ether (Scheme 2).

2.3. Introduction of the spacer, p-phenylenediamine (**4**)

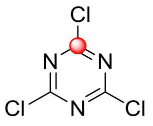
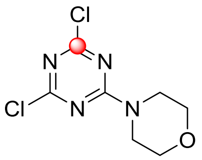
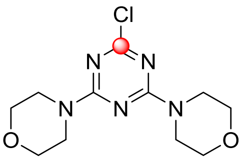
The third substitution, which required harsher conditions, was performed under microwave irradiation in the minimum amount of DMSO (Table 3), with simple purification procedures to give compounds **5** in excellent yields [14].

2.4. Preparation of streptocyanines **7**

Finally, the synthesis of the streptocyanines was performed by reaction of triazines **5** with 3-chloro-*N*,*N*,*N*′,*N*′-tetramethyl-1,5-diaza-1,3-pentadienium hexafluorophosphate (**6**) [26] in ethanol under reflux (Table 4).

The new compounds were characterized by spectroscopic methods, particularly MALDI-TOF mass spectrometry and NMR spectroscopy. The most characteristic signals in the ^{1}H- and ^{13}C-NMR spectra of compounds **7** are listed in Table 5. These dimeric systems show complex NMR spectra that are consistent with the structures and also with the wide range of dynamic processes that these compounds undergo. Some NMR spectra were recorded at 353 K because broad signals were observed for most compounds at

Table 1
Fukui indices (f_A^+) of the highlighted atom.

		
$f_A^+ = 0.065$	$f_A^+ = 0.048$	$f_A^+ = 0.039$

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