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Synthesis and Characterization of 1,3-Bis-(2-dialkylamino-5-thienyl)-substituted Squaraines—A Novel Class of Intensively Coloured Panchromatic Dyes

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ABSTRACT

By the reaction of N,N-*disubstituted 2-aminothiophenes with squaric acid in a 1-butanol–toluene mixture at reflux temperature, a novel heterocyclic type of deeply coloured squaraines is obtained in generally moderate yields. These sparingly soluble dyes exhibit narrow absorption bands at about 700 nm in organic solvents and, in a dispersed form, wide absorption bands ranging into the IR region at about 900 nm.*

INTRODUCTION

Due to the commercial availability of easily modulating near-IR laser diodes, several types of IR-absorbing dyes have become of interest.[1] Such dyes absorb the emitting light of the laser diode and convert it, by means of several photophysical processes, mainly into thermal energy which can initiate different physical or chemical processes in the direct neighbourhood of the light-absorbing specimen. Thus, near-IR-absorbing dyes can be used for manufacturing optical data-storaging media or information-recording systems.[2] An important criterion for the use of near-IR-absorbing dyes is, besides their ability to absorb light in the IR region with high intensity, an extreme photochemical stability which is related, to some extent, to their

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insolubility in most common solvents. It is known that photochemical stability cannot be attained, in general, with the classical representatives for IR-absorbing dyes, namely the long-chained polymethine dyes or the vinylogues of diaryl- and triarylmethane dyes.[3,4]

A class of organic dyes which do not seem to have this disadvantage is the squaraines, several representatives of which have been known for nearly three decades.[5,6] They are normally available by condensation of squaric acid, or of its derivatives, with electron-rich aromatic, heteroaromatic or olefinic compounds, such as *N,N*-dialkylanilines, azulenes, pyrroles, indoles or methylene bases of quarternary heterocyclic compounds,[7] and are sparingly soluble in most usual solvents.

Despite the relatively wide range of squaric compounds now known, with the exception of some hydroxy-substituted 1-benzothiophenes,[8] no thiophene-containing representatives have yet been reported. *N,N*-Dialkyl-substituted 2-aminothiophenes, which are iso-pi-electronic analogues of the *N,N*-dialkylanilines, have not hitherto been used for preparing appropriated squaraine derivatives. In view of this, and of the findings[9,10] that several aminothiophene-containing dyes frequently exhibit some modified physical and chemical properties compared to their carbocyclic analogues, some squaraines using *N,N*-disubstituted 2-aminothiophenes have now been prepared. These heterocyclic educts are relatively easy to synthesize by condensation of 2-mercapto- or 2-hydroxythiophenes with a secondary amine[11] or a secondary amine splitting reagent,[12] respectively, as well as by a ring-closure procedure starting from *N,N*-disubstituted thioacetamides and halogeno-ketones.[13] They are highly reactive toward dye-forming reagents, such as aryldiazonium salts,[14] aromatic aldehydes or formic acid derivatives and their vinylogues.[15,16]

RESULTS AND DISCUSSION

Preparation of 1,3-bis-(2-dialkylamino-5-thienyl)-substituted squaraines (3)

Condensation of *N,N*-disubstituted 2-aminothiophenes (**1**) with squaric acid (**2**) can be achieved by heating the components in a 1:1 mixture of toluene and 1-butanol at reflux temperature (Method A) or by heating squaric acid in the toluene–1-butanol mixture for a few hours and subsequently adding the required *N,N*-disubstituted 2-aminothiophene (**1**) to the hot solution, in which the formation of squaric acid 1-butyl esters has been effected (Method B). Whereas Method B is mostly useful for preparing the more soluble squarine dyes, Method A is more suited for the less soluble derivatives. Table 1 outlines the results obtained.

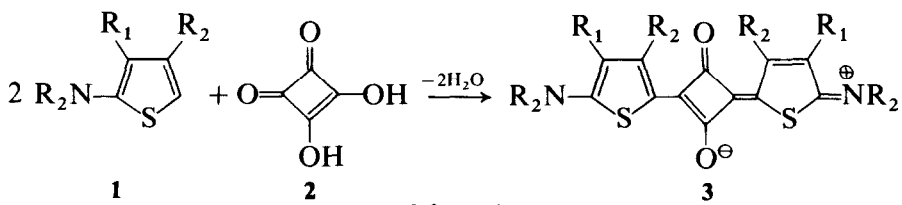
TABLE 1
1,3-Bis-(2-dialkylamino-5-thienyl) squaraines (**3**)

Number	NR_2	R_1	R_2	*Method*	*Yield (%)*	*Mp. (°C)*
3a	Morpholino	H	H	B	25–30	>360
3b	Pyrrolidino	H	H	B	30–35	>360
3c	Piperidino	H	H	B	20–30	308–310[a]
3d	Morpholino	Phenyl	Phenyl	A	35–50	305–307[a]
3e	Piperidino	Phenyl	Phenyl	A	40–45	285–288[a]
3f	Morpholino	3-Methoxyphenyl	Phenyl	A	35–50	265–267[a]
3g	Morpholino	Phenyl	4-Bromophenyl	A	30–40	305–307[a]
3h	Morpholino	Phenyl	2-Chlorophenyl	A	30–40	>360

[a] Decomposition.

In most cases the dyes crystallized during the heating of the reaction mixture and could, therefore, be readily separated from the cooled solution by filtration. Where the reaction products did not crystallize immediately, the reaction mixture was concentrated and diluted with a non-polar solvent, such as diethyl ether or *n*-hexane. The latter procedure also gave good separation of the desired dyes from the by-products simultaneously formed. Due to their poor solubility in most solvents, the dyes could only with very great difficulty or, sometimes not at all, be purified by recrystallization. In these cases, extraction of the dye pigment with an aromatic solvent, such as toluene, or methanol, was sometimes suitable for its purification.

The dye-forming condensation step depends, to some extent, on the structure of the *N*,*N*-substituted 2-aminothiophene used. Sterically bulky 2-aminothiophenes (**1**), such as the 3,4-diphenyl-substituted derivatives, required a longer reaction time (6–8 h) than the non-phenyl-substituted analogues, which required a maximum of 3 h for nearly complete condensation. The yields of the appropriate condensation products were, in general, moderate and the analytical and spectroscopic data of the products was compatible with structures typified by formula **3**. Chromatographic analyses of the reaction mixture revealed, in all cases, the formation of several by-products, the structure of which has not yet been elucidated. In accord with previous findings,[8,17] it is assumed that some of these correspond to an isomeric 1,2-squaranine structure, and to a 1:1 condensation product, in addition to oxydation products of the starting aminothiophenes.



1 **2** **3**

Scheme 1

Properties of 1,3-bis-(2-dialkylamino-5-thienyl)-substituted squaraines (3)

The 2-aminothiophenic-substituted squaraines (**3**) are, in general, deeply coloured and high-melting microcrystalline solids with a low solubility in most organic solvents. Their solubility depends significantly on the substitution pattern in the thiophenic fragments. Squaraines which are non-substituted by aryl groups in the 3- and 4-position of the thiophene moiety, e.g. **3a**–**3c**, were moderately soluble in aromatic hydrocarbons and chlorinated hydrocarbons, such as chloroform or methylene chloride, alcohols and lower alkyl ketones, whereas squaraines (**3**) with aryl groups in

the thiophene moieties were scarcely soluble in most organic solvents, except in chlorinated hydrocarbons in which they had considerable solubility.

Analogous to other similar squaraines containing carbocyclic side-groups, the thiophene-substituted compounds (**3**) exhibited in their IR spectra bands at about 1600 cm^{-1} and at about 3050, 1400 and 880 cm^{-1} (see Table 2). The first band can be attributed to the pseudoaromatic squarat ring, the others to the substituted thiophene rings. The absence of bands at about 1700 cm^{-1} can be explained by the highly polar character of the central four-membered oxygen-substituted ring.

The ^{1}NMR-spectra of the squaraines are also in accordance with the proposed structure (see Table 2). For example, the signals of the protons attached at the N-bonded alkyl group in compound **3a** are equivalent, and exhibit nearly the same chemical shift as the C-bonded protons at the amino group in the starting 2-aminothiophenes (**1a**). The chemical shift of the phenyl-bonded protons are also nearly identical (e.g. **3d** and **1d**). Some differences can be demonstrated, however, between the chemical shifts of thiophenic-bonded protons in the squaraine derivatives and in the non-phenyl-substituted thiophenic educts. As can be seen from compound **3a** and its thiophene precursor **1a**, the proton linked at the 4-position of the thiophene moiety in the dye is strongly shifted towards a lower field than in the parent thiophene **1a** ($\delta = 1{\cdot}39$ ppm). This difference indicates a strong interaction between this proton and the neighbouring oxygen atom of the central four-ring system in the dye molecule and is relatable to an interaction which is similar to that in the carbocyclic aminophenyl-substituted squaraine analogues.[18]

Further information can be derived from the electronic spectra of the squaraines. The longest-wavelength absorption bands, which are centred for all the products prepared at about 700 nm (in solution) with an extinction coefficient larger than 10^5 l mol^{-1} cm^{-1}, are in accordance with formula **3**, in which both the 2-aminothiophene moieties are linked at the 1,3-position of the central squaric-acid fragment and not at its 1,2-position (see Table 2). The significant dependence of the longest-wavelength absorption maximum, as well as its extinction on the substitution pattern in the thiophene subunits, is relatable to a steric effect which is operative in the phenyl-substituted derivatives, and suggests a twisting of the thiophene moieties from the plane of the central carbocylic building block.

Finally, the strong panchromatic effect that can be observed in the spectra of the dyes (**3**) by going from solution to a dispersion or to the solid state (see Fig. 1) indicates the strong polar character of the aminothiophenic squaraines. This polar character appears to be of the same order of magnitude as in the carbocyclic analogues of the dyes studied, and suggests the potential use of the aminothiophenic squaraines (**3**) as photoactive

TABLE 2
Spectroscopic Data of the 1,3-Bis-(2-dialkylamino-5-thienyl) squaraines (**3**)

Number	*IR* (cm^{-1}, *in KBr*)	^{1}*H-NMR* (*ppm* (*assignment*))	*VIS-NIR* (*nm* (log ε)
3a	3 080 w, 2 950–2 850 w, 1 600 s, 1 400 s, 880 s	3·48 (m, 8H); 3·86 (m, 8H);[2] 6·39 (d, 2H; $J = 4{\cdot}6$ Hz); 8·00 (d, 2H; $J = 4{\cdot}6$ Hz)	653 (5·27)
3b	3 080 w, 2 900 w, 1 600 m, 1 450 s, 890 s	1·56 (s); 3·21 (s); 6·23 (d, 2H; $J = 4{\cdot}6$ Hz); 7·98 (d, 2H, $J = 4{\cdot}6$ Hz)	653 (5·54)
3c	3 080 w, 2 900–2 820 w, 1 400 s, 870 s	1·72 (m, 12H); 3·5 (t, 8H); 6·33 (d, 2H; $J = 4{\cdot}7$ Hz) 7·95 (d, 2H); $J = 4{\cdot}7$ Hz)	663 (5·48)
3d	3 100 w, 2 950–2 850 w, 1 600 s, 1 400 s, 900 s	3·12 (m, 8H); 3·6 (m, 8H);[b] 6·8–7·4 (m, 20H)	689 (5·34)
3e	3 100 w, 2 920–2 830 w, 1 600 s, 1 400 s, 880 m	1·5 (m, 12H); 3·13 (m, 8H); 6·9–7·4 (m, 20H)	704 (5·34)
3f	3 050 w, 2 950–2850 m, 1 600 s, 1 595 s, 1 400 s, 880 m	3·14 (m, 8H); 3·58–3·62 (m, 14H)	689 (5·28)
3g	3 050 w, 2 950–2 850 w, 1 600 m, 1 400 m, 890 m	3·15 (m, 8H); 3·56 (m, 8H); 6·75–7·4 (m, 18H)	697 (5·24)
3h	3 100 w, 2 950–2 850 w, 1 600 m, 890 m	3·12 (m, 8H); 3·60 (m, 8H); 6·9–7·4 (m, 18H)	689 (—)

[a] ^{1}H-NMR data of the educt **1a**: 3·1 (m, 4H); 3·82 (m, 4H); 6·13 (d, 1H); 6·61 (d, 1H); 6·78 (d, 1H).
[b] ^{1}H-NMR data of the educt **1d**: 2·84 (m, 4H); 3·64 (m, 4H); 6·83 (s, 1H); 7·0–7·4 (m, 10H).

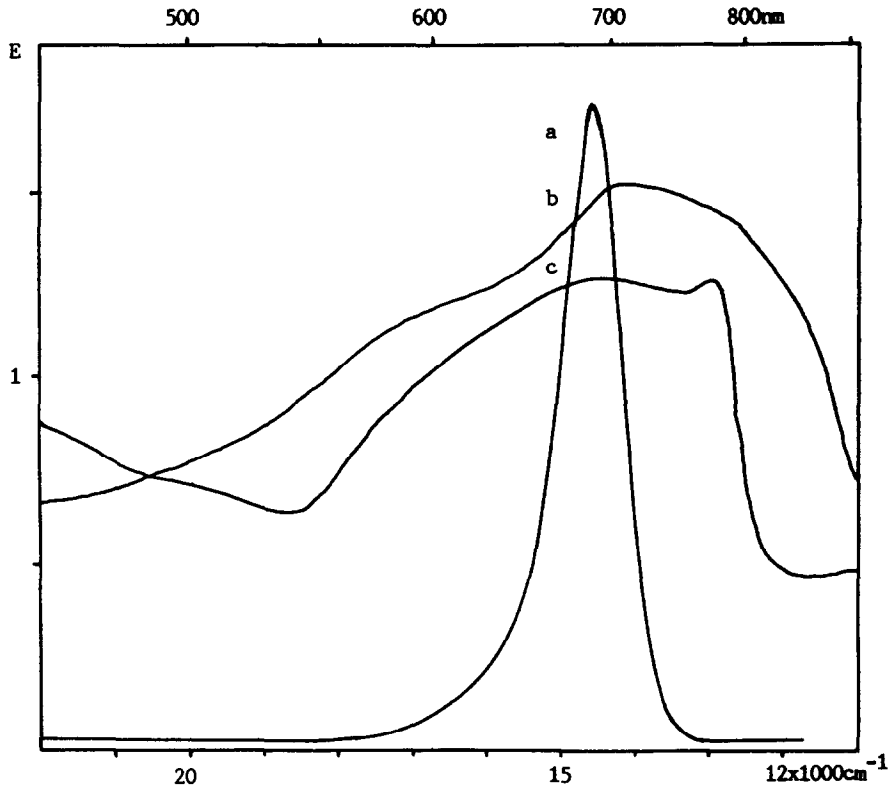


Fig. 1. (a, b) Absorption and (c) reflection spectra of the squarylium dye (**3d**), measured in (a) chloroform and in a (b, c) polyvinyl-acetate dispersion.

pigments in laser-driven data recording and storaging systems.[19] Further studies on these dyes are in progress.

EXPERIMENTAL

Melting points were determined using a Kofler heating-table microscope and are corrected. IR-spectra were recorded in potassium-bromide pellets using a Specord IR 70 spectrometer (Carl Zeiss, Jena, Germany), ^{1}H-NMR spectra using a FT-NMR spectrometer (Tesla enterprise, Brno, Czechoslovakia) and visible–near-IR spectra using a Specord M 40 spectrometer (Carl Zeiss).

Dye dispersions embedded in a polyvinyl butyral film were prepared as follows. Two grams of the appropriated squaraine dye were finely ground in a mixture comprising 2 g of polyvinyl butyral, 8 g of methylene chloride and 8 g of 1,2-dichloroethane by means of a ball-mill rotating at 1000–5000 rpm

for at least 4 h. The resulting dispersion was cast with a thickness of about 1 μm on a polyethylene-terephthalate sheet and dried at 60°C for 2 h.

N,N-Disubstituted 2-aminothiophenes were prepared according to the literature by reaction of 2-mercaptothiophene with an appropriate secondary amine[11] or by a triethylamine mediated ring-closure of *S*-aroylmethylene-arylthioacetamidinium bromides.[13]

Preparation of the 1,3-bis-(2-dialkylamino-5-thienyl) squaraines (**3**) was carried out by two methods.

Method A. 0·114 g (1 mmol) squaric acid (Merck, Darmstadt, FRG) and 2 mmol of the appropriate *N,N*-disubstituted 2-aminothiophene were dissolved in a mixture comprising 25 ml of 1-butanol and 25 ml of toluene and refluxed for 2–6 h. After cooling, the precipitate which formed during the heating was filtered and washed with diethyl ether and then several times with methanol. The product was further purified by recrystallizing from chloroform or by extraction of the by-products with 1-butanol, toluene or xylene.

Method B. 0·114 g (1 mmol) squaric acid (Merck, Darmstadt, FRG) was dissolved in a mixture comprising 20 ml of 1-butanol and 20 ml of toluene at reflux. Then 2 mmol of the appropriated *N,N*-disubstituted 2-aminothiophene was dissolved in a mixture comprising 5 ml of 1-butanol and 5 ml of toluene was then added and the mixture refluxed and monitored by visible spectroscopy until no enhancement of the absorptivity at about 700 nm could be observed. The solution was then concentrated to approximately half volume and diluted with a similar amount of diethyl ether. After standing at room temperature for several hours, the precipitate formed was filtered and washed several times with ether. The product was finally purified by column chromatography using silica (diameter 0·2–0·5 mm) using benzene–methanol (10:1) as eluent.

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