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Dyes and Pigments 44 (2000) 149–153

DYES and PIGMENTS

Preparation and characterisation of 2-amino-5-selenazolyl-substituted squaraines

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Received 30 July 1999; accepted 18 August 1999

Abstract

By refluxing squaric acid **4** with *N,N*-disubstituted 2-amino-selenazoles **8** in a mixture of toluene and 1-butanol a new type of 2-amino-5-selenazolyl-substituted squaraines **9** was obtained. These compounds are deeply coloured dyes with intense long-wavelength absorptions at about 620–700 nm in solution and at about 900 nm in the solid state.

Keywords: Squarylium dyes; Synthesis; UV/VIS spectra; IR spectra; ^{1}H NMR spectra

1. Introduction

N,N-disubstituted anilines **1** are versatile educts for preparing organic dyes. For example, they are able to react with squaric acid **4** to give deeply coloured compounds of the general structure **5** [1–5]. These compounds, called squaraines, can be used, due to their ability to form thermal and photochemical stable solids with a remarkably electric conductivity, as photoactive pigments in electrophotographic devices [6].

Recently, we have demonstrated that *N,N*-disubstituted 2-amino-thiophenes (**2**) and *N,N*-disubstituted 2-amino-thiazoles (**3**), the sulphur analogues of **1**, are able to condense with squaric acid to give the sulphur analogues **6** [7,8] and **7** [9,10] of the squaraines **5**. Analogously to the latter compounds **5** they exhibit a deep colour and a high agregation tendency. Therefore, they are good candidates as photoactive pigments for manufacturing electrophotographic devices [11].

2. Results and discussion

Very recently we have reported a simple route for preparing *N,N*-disubstituted 2-amino-selenazoles **8** and described a series of such new compounds [12]. We describe here their use as educts for the preparation of squaraines of the general structure **9**. The potential use of these compounds as electrophotographic active pigments has been previously described [11,13].

The squaraines **9** can be obtained in a simple manner by heating the starting materials **4** and **8**

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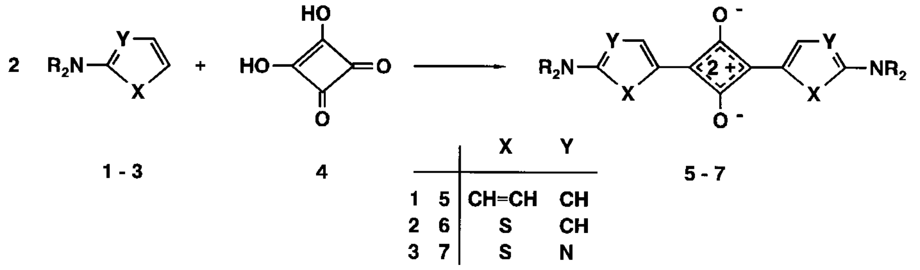
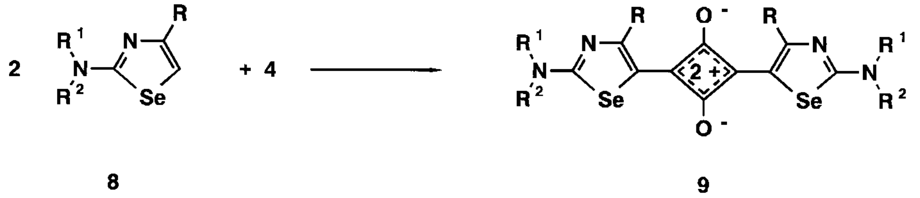
PII: S0143-7208(99)00080-7



Scheme 1.



Scheme 2.

in a 1-butanol/toluene mixture at reflux temperature (Method A), or by heating squaric acid **4** at about 80–90°C in a 1-butanol/toluene mixture until obtaining a clear solution, followed by addition of the required 2-aminoselenazole **8** into the hot reaction mixture (Method B). In Table 1 the 2-aminoselenophene-derived squaraines **9** are listed; the yield of the products are mostly moderate.

The prepared *N,N,N′,N′*-tetrasubstituted 1,3-bis-(2-aminoselanazolyl)-squaraines **9** are, in general, deeply coloured micro-crystalline solids with defined melting or decomposition points and with a low solubility in most organic solvents. Their solubility depends, however, to some extent significantly on the substitution pattern at their selenazole moieties. Squaraines **9h–9q** which are derived from 4-alkyl-substituted 2-aminoselenazoles are moderately soluble in chlorinated hydrocarbons, such as trichloromethane or dichloromethane, while squaraines **9a–9g** derived from 4-aryl-substituted 2-amino-selenazoles are almost insoluble in most of the organic solvents. The purification of such compounds can be achieved, if necessary, by Soxhlet-extraction of their impurities.

The constitution of the prepared *N,N,N′,N′*-tetrasubstituted 1,3-bis-(2-amino-selenazolyl)-squaraines **9** follows unambiguously from their elemental analysis and spectroscopic data (see Tables 1 and 2).

Thus, the selenazole-derived squaraines **9** exhibit, analogously to their sulphur analogous **6** and **7**, characteristic bands at about 1600 cm^{-1} in their IR spectra. These bands can be attributed to the pseudoaromatic squarate moiety containing very strong polar C—O moieties.

The selenazole-derived squaraines **9** exhibit, furthermore, in their ^1H NMR spectra, characteristic signals which can be attributed to their functional groups. Thus, *N*-linked alkyl moieties give rise to proton signals between 1.3 and 2 ppm and between 3.5 and 4.5 ppm, while aromatic protons give rise to signals at about 7–8 ppm.

In the UV/VIS spectra of the squaraines **9**, characteristic absorption in solution are found between 630 and 700 nm and their extinctions attain values more than 10^5 l mol^{-1} cm^{-1}. This fact demonstrated unambiguously that the 2-amino-selenazolyl moieties are linked with their 5-position at the 1,3-positions of the central squaric moiety and not, as documented in the literature for several other condensation products between squaric acid derivatives (**4**) and other electron-rich heterocyclic systems, such as pyrroles, heterocyclic methylene bases, or *N,N*-dialkylanilines, at their 1,2-positions [14,15,5].

Table 1
Characteristic data of the *N,N*-disubstituted 2-amino-5-selenazolyl-squaraines **9**

No.	R^1R^2	R	Method	Yield (%)	mp (°C) (decomp.)	Formula (mw)		C	H	N
9a	*N,N*-dimethylamino	Phenyl	A	60–65	297	$C_{26}H_{22}N_4O_2Se_2$	calcd.	53.80	3.82	9.65
						(580.42)	found	53.54	3.94	9.50
9b	*N,N*-diethylamino	Phenyl	A	65–70	250	$C_{30}H_{30}N_4O_2Se_2$	calcd.	56.61	4.75	8.80
						(636.52)	found	56.81	4.98	8.74
9c	*N,N*-dibenzylamino	Phenyl	A	55–60	280	$C_{50}H_{38}N_4O_2Se_2$	calcd.	67.87	4.33	6.33
						(884.81)	found	67.54	4.51	6.43
9d	Morpholino	Phenyl	A	55–60	283	$C_{30}H_{26}N_4O_4Se_2$	calcd.	54.23	3.94	8.43
						(664.49)	found	54.39	4.11	8.34
9e	Pyrrolidino	Phenyl	A	60–65	283	$C_{30}H_{26}N_4O_2Se_2$	calcd.	56.97	4.14	8.86
						(632.49)	found	56.76	4.30	8.77
9f	Piperidino	Phenyl	A	60–65	269	$C_{32}H_{30}N_4O_2Se_2$	calcd.	58.19	4.58	8.48
						(660.55)	found	58.58	4.78	8.36
9g	*N*-methyl-*N*-phenyl	Phenyl	A	15–20	252	$C_{36}H_{26}N_4O_2Se_2$	calcd.	61.37	3.72	7.95
						(704.56)	found	61.09	3.72	7.64
9h	*N,N*-dimethylamino	*tert*-butyl	B	35–40	314	$C_{22}H_{30}N_4O_2Se_2$	calcd.	48.90	5.60	10.37
						(540.43)	found	48.93	5.56	10.62
9i	*N,N*-dimethylamino	*tert*-butyl	B	40–45	309	$C_{26}H_{38}N_4O_2Se_2$	calcd.	52.35	6.42	9.39
						(596.54)	found	51.99	6.72	9.30
9j	*N,N*-dibenzylamino	*tert*-butyl	B	35–40	244	$C_{46}H_{46}N_4O_2Se_2$	calcd.	65.40	5.49	6.63
						(844.83)	found	65.54	5.54	6.52
9k	Morpholino	*tert*-butyl	B	25–30	326	$C_{26}H_{34}N_4O_4Se_2$	calcd.	50.01	5.49	8.97
						(624.51)	found	50.48	5.51	8.70
9l	Pyrrolidino	*tert*-butyl	B	15–20	330	$C_{26}H_{34}N_4O_2Se_2$	calcd.	52.71	5.78	9.46
						(592.51)	found	52.82	5.73	9.94
9m	Piperidino	*tert*-butyl	B	20–25	310	$C_{28}H_{38}N_4O_2Se_2$	calcd.	54.19	6.17	9.03
						(620.56)	found	54.38	6.16	8.89
9n	*N*-methyl-*N*-phenyl	*tert*-butyl	B	25–30	325	$C_{32}H_{34}N_4O_2Se_2$	calcd.	57.83	5.16	8.43
						(664.58)	found	57.92	4.92	8.31
9o	*N,N*-dibenzylamino	Methyl	B	40–45	240	$C_{40}H_{34}N_4O_2Se_2$	calcd.	63.16	4.51	7.37
						(760.67)	found	63.31	4.60	7.36
9p	Morpholino	Methyl	B	35–40	293	$C_{20}H_{22}N_4O_4Se_2$	calcd.	44.46	4.10	10.37
						(540.35)	found	44.51	4.05	10.33
9q	*N*-methyl-*N*-phenyl	Methyl	B	15–20	283	$C_{26}H_{22}N_4O_2Se_2$	calcd.	53.80	3.82	9.65
						(580.42)	found	53.79	3.78	9.99

The position of the intense long-wavelength absorption bands of the squaraines **9** are influenced by substituents in the 4-position of the heterocyclic moieties (see Fig. 1). Thus, the absorption maxima of 4-alkyl substituted squaraines **9** are found at about 30–50 nm shorter wavelength than those of 4-aryl substituted derivatives. In the same sequence, the extinction coefficients decrease and the bands are broaden. In contrast, the alkyl or aryl substituents at the terminal amino groups have only a small influence on the absorption bands of the squaraines **9**.

A strong spectral effect was observed, however, by measuring the solid state absorption spectra of the squaraines **9** (see Fig. 2). Thus, by measuring a film prepared by dispersion of the corresponding squaraine dye **9** in a polymer, such as polyvinyl butyral, a strong broadening of the absorption band, as well as a strong bathochromic shift of $\lambda_{\max}$ was observed. This fact indicates a strong dipolar intermolecular interaction of the single squaraine molecules in their solid states giving rise to dye pigments which should be useful as spectral sensitisers in laser-driven recording and storage materials. Some studies in this direction are in progress and have been published, in some aspects, in Ref. [11].

Table 2
Spectral data of the 2-amino-5-selenazolyl-squaraines **9** prepared

No.	^{1}H NMR, δ-values (in CDCl$_3$)	ν_{IR} (C=O) (cm^{-1}) (in KBr)	λ_{max} (nm) (in CHCl$_3$)	log ϵ
9a	3.32 (s, 12H, NCH$_3$); 7.45–7.48 (m, 10H, CH$_{Ar}$); 7.78–7.82 (m, 4H, CH$_{Ar}$)	1610	686	5.21
9b	1.30 (t, 12H, CH$_3$); 3.63 (broad, 8H, N-CH$_2$); 745–7.81 (m, 10H, CH$_{Ar}$)	1614	694	5.18
9c	4.83 (broad, 8H, CH$_2$); 7.27–7.83 (m, 20H, CH$_{Ar}$); 7.44–7.49 (m, 6H, CH$_{Ar}$); 7.84–7.87 (m, 4H, CH$_{Ar}$)	1616	698	5.21
9d	3.81 (m, 8H, NCH$_2$); 3.84 (m, 8H, OCH$_2$); 7.44–7.51 (m, 6H, CH$_{Ar}$); 7.79–7.82 (m, 4H, CH$_{Ar}$)	1613	691	5.17
9e	2.15 (m, 8H, CH$_2$); 3.48 (s, 4H, NCH$_2$); 4.00 (s, 4H, NCH$_2$, 7.45–7.53 (m, 6H, CH); 7.79–7.83 (m, 4H, CH$_{Ar}$)	1610	689	5.16
9f	1.74 (m, 12H, CH$_2$); 3.73 (m, 8H, NCH$_2$); 7.43–7.48 (m, 6H, CH); 7.78–7.82 (m, 4H, CH$_{Ar}$)	1615	696	5.18
9g	3.69 (s, 6H, CH$_3$); 7.36–7.78 (m, 20H, CH$_{Ar}$)	1619	699	5.12
9h	1.59 (s, 18H, CH$_3$); 3.29 (s, 12H, NCH$_3$)	1596	658	5.40
9i	1.29 (t, 12H, CH$_3$); 1.55 (s, 18H, CH$_3$); 3.63 (broad, 8H, CH$_2$)	1599	665	5.44
9j	1.58 (s, 18H, CH$_3$); 4.48–4.53 (m, 4H, NCH$_2$); 4.97–5.03 (m, 4H, NCH$_2$); 7.24–7.34 (m, 20H, CH$_{Ar}$)	1604	669	5.48
9k	1.50 (s, 18H, CH$_3$); 3.76 (m, 16H, CH$_2$) (in DMSO-d_6)	1601	664	5.43
9l	1.52 (s, 18H, CH$_3$); 1.56 (m, 8H, CH$_2$); 2.08 (m, 8H, N CH$_2$)	1595	663	5.44
9m	1.57 (s, 18 H, CH$_3$); 1.73 (broad, 12H, CH$_2$); 3.71 (broad, 8H, NCH$_2$)	1598	669	5.44
9n	1.57 (s, 18 H, CH$_3$); 3.64 (s, 6 H, N CH$_3$); 7.36–7.50 (m, 20 H, CH$_{Ar}$)	1605	671	5.33
9o	3.00 (s, 6 H, CH$_3$); 4.85 (m, 8 H, CH$_2$); 7.24–7.39 (m, 20 H, CH$_{Ar}$)	1612	642	5.42
9p	2.92 (s, 6 H, CH$_3$); 3.72 (m, 8 H, NCH$_2$); 3.81 (m, 8H, OCH$_2$)	1617	636	5.44
9q	2.92 (s, 6H, CH$_3$); 3.66 (s, 6H, CH$_3$); 7.36–7.49 (m, 10H, CH$_{Ar}$)	1611	643	5.29

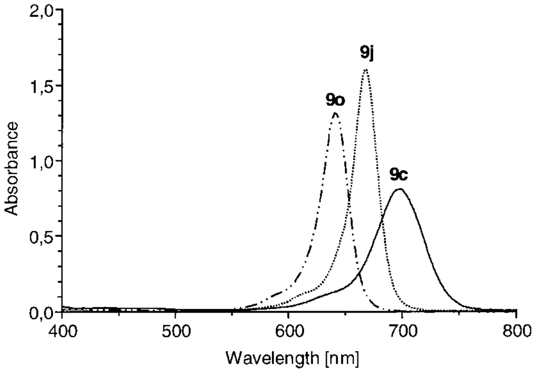


Fig. 1. Absorption spectra of some 2-amino-5-selanazolyl-substituted squaraines, measured in trichloromethane; concentration 10^{-5} M, path length: 0.5 cm.

3. Experimental

The melting or decomposition points of the dyes were recorded by using a differential scanning calorimeter (Mettler, Toledo) using a heating rate of 5°C/min. The IR spectra were recorded in KBr pellets using an FTIR spectrometer FTS-25 (BIO-RAD); the ^{1}H NMR spectra were recorded using a 300 MHz Varian Gemini 2000 Spectrometer; and UV/VIS/NIR spectra were recorded by means of a Zeiss M40 spectrometer.

The preparation of the *N,N*-disubstituted 2-aminoselenazole precursors **8** has been recorded recently elsewhere [12].

3.1. Preparation of N,N,N′,N′*-tetrasubstituted 1,3-bis-(2-amino-selenazolyl)-squaraines* **9** *(*general procedure*)*

3.1.1. Method A

Squaric acid **4** (114 mg, 1 mmol) and a *N,N*-disubstituted 2-aminoselenazole **8** (2 mmol) were refluxed in a mixture of 1-butanol (25 ml) and toluene (25 ml) for 1–2 h. After cooling the precipitate formed during the reaction was filtered off and washed several times with hot 1-butanol or toluene.

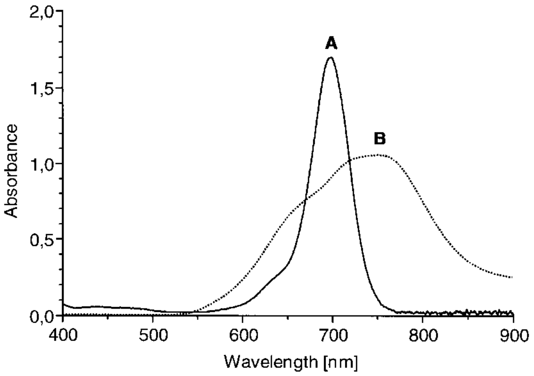


Fig. 2. Absorption spectrum of compound **9c**; A: in trichloromethane, B: as solid in a polyvinylbutyral matrix on a polyester sheet.

3.1.2. Method B

After dissolving squaric acid **4** (114 mg, 1 mmol) at 80–90°C in a mixture of 1-butanol (20 ml) and toluene (20 ml), an appropriate *N,N*-disubstituted 2-aminoselenazole (2 mmol) dissolved in a mixture of 1-butanol (5 ml) and toluene (5 ml) was added in three portions. The mixture was refluxed until no enhancement of its absorptity at about 650 nm could be recorded, and the liquor was then cooled to room temperature. The dyes formed were filtered, washed several times with diethyl ether, and dried. For the dyes which did not crystallise, their solutions were concentrated to a half of their origin volume under reduced pressure and then diluted with an equal amount of diethyl ether. After standing at room temperature for several hours, the precipitate formed was filtered, washed with diethyl ether, and dried. The products were purified by recrystallisation from trichloromethane.

3.2. Preparation of dye dispersions

An appropriate squaraine dye **9** (0.6 g) was finely grounded in a mixture of polyvinyl butyral (0,6 g) and THF (25 ml) by means of a ball-mill rotator at 1000–5000 rpm for at least 4 h. The resulting dye dispersion was diluted with THF (35 ml) and subsequently casted with a thickness of about 1 μm on a polyethylene terephthalate sheet and dried at 60°C for 2 h.

Acknowledgements

The authors thank Miss. C. Mueller and Mrs. A. Konetzke, Syntec GmbH, Wolfen, and Dr. G. Mistol, FEW Forschungs- und Entwicklungsgesellschaft Wolfen mbH, for recording the IR and UV/VIS/NIR spectra. They also thank Mrs. C. Koenig, FH Merseburg, for recording the NMR spectra and Dr. G. Diener, Syntec GmbH, Wolfen, for preparing the dye dispersions.

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