ELSEVIER

Dyes and Pigments 49 (2001) 161–179

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Synthesis and characterization of a new class of unsymmetrical squaraine dyes

Dietmar Keil [a], Horst Hartmann [b,*]

[a] *Syntec GmbH, Chemiepark, Arial A, Werkstattstrasse 10, D-06766 Bitterfeld-Wolfen, Germany*
[b] *Fachbereich Chemie der Fachhochschule Merseburg, Geusaer Str., D-06217 Merseburg, Germany*

Received 15 October 2000; received in revised form 16 January 2001; accepted 15 March 2001

Abstract

By starting from several types of nucleophilic compounds **XH**, such as electron-rich ethylenic, aromatic, or heteroaromatic compounds, and either sqaric acid dichloride $\mathbf{QCl_2}$ or dialkyl squarates $\mathbf{Q(OR)_2}$ as activated squaric acid derivatives, some new semisquaric acid derivatives **QXOH** have been prepared. These compounds condense with a further nucleophilic compound **YH** to yield unsymmetrically substituted squaraines **XQY** whose analytical and spectroscopic data are recorded. The squaraines **XQY** are deeply coloured, strongly solvatochromic compounds whose longest-wavelength absorption maxima are hypsochromic shifted in comparison to the ones of the corresponding symmetrically substituted squaraines **XQX** and **YQY**. The shift can be correlated with the donor strength of the nucleophilic compounds **XH** or **YH** used as educts and, hence, with their reactivity in the condensation reaction with squaric acid and its derivatives.

Keywords: Dyes; Heterocycles; Semisquaric acid derivatives; Unsymmetrical squaraines; UV–vis; NIR spectroscopy

1. Introduction

Electron-rich benzene or alkene derivatives as well as electron-rich heteroaromatic compounds of the general formula **XH** (or **YH**), such as the dialkylanilines **AH** and **BH**, the phenole derivatives **CH**, the heterocyclic methylene bases **DH**, or the pyrrole derivatives **EH** and **FH**, resp. are able to condense with squaric acid $\mathbf{Q(OH)_2}$ due to their strong nucleophilic character [1]. The reactions are usually performed in protic solvents such as acetic acid or *n*-alkanols or in mixtures of these with aromatic hydrocarbons like toluene. As reactive intermediates diacetoxy or dialkyl squarates of the general formula $\mathbf{Q(OR)_2}$ are assumed [2] (Scheme 1).

Depending on the structure of the educts used and the condition applied, different types of condensation products are formed. Thus, as bis-condensation products of squaric acid with a nucleophilic compound **XH** the compounds **XQX** and $\mathbf{QX_2}$ can be formed. Whereas the first formula denotes a product with a 1,3-linking of its nucleophilic group at the squaric moiety the second formula denotes a product with a 1,2-linking of the same group at the squaric moiety. As known, the most interesting types of such condensation products are the 1,3-substituted squaraines of the general structure

* Corresponding author. Tel.: +49-3461-462192; fax: +49-3461-462192.
E-mail address: horst.hartmann@cui.fh-merseburg.de (H. Hartmann).

0143-7208/01/$ - see front matter
PII: S0143-7208(01)00016-X

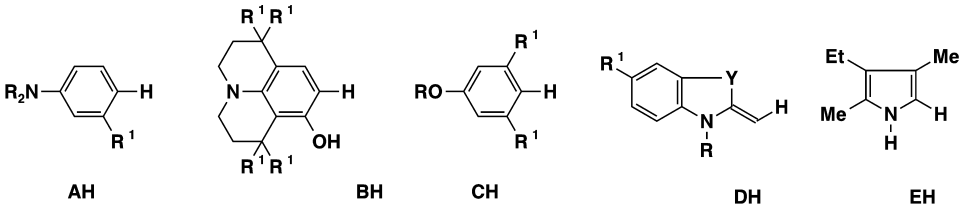
XQX. They exhibit, in contrast to their 1,2-isomers $\mathbf{QX_2}$ a deep and intense colour as well as a low solubility in organic solvents. Therefore, such squaraines **XQX** can be used as pigment dyes, e.g. in electrophotograpic materials [3] (Scheme 2).

Recently unsymmetrically substituted squaraines of the general structure **XQY** as 1:1:1 condensation products of squaric acid with equivalent amounts of **XH** and **YH** condensed at the 1,3-position of $\mathbf{Q(OR)_2}$ have also received a special interest. For example, unsymmetrically substituted squaraines **AQC** derived from different aryl-substituted *N,N*-dialkylanilines **AH** and the semisquaric acid $\mathbf{QC^1OH}$ exhibit intense absorption bands at about 550–600 nm in solution and at about 400–800 nm with an increased absorptivity at about 400–600 nm in dispersed or sublimated form [4]. Owing to their intense absorptions in the visible region such compounds have been claimed to apply as spectral sensitizers for electrophotographic materials, especially in copiers and multifunctional copier-printers [3,5]. Unsymmetrically substituted squarines derived from two different substituted *N,N*-dialkylanilines **AH** and **A′H** have been claimed, due to their intense absorptions at about 600–800 nm in dispersed or sublimated form, to apply as spectral sensitizers for laser diode driven photoactive materials, especially for electrophotographic materials in laser printers [4d]. Very recently, it has been demonstrated that some types of unsymmetrical squaraines **XQY**, e.g. squaraines of the general formula $\mathbf{C^1QD^1}$, exhibit large second order hyperpolarizabilities which allow their use for manufacturing materials with high non-linear optical activities [6]. Furthermore, unsymmetrically substituted squaraines $\mathbf{AQC^1}$ have been used as fluorescence indicators for measurement the solvent polarity [7]. Unsymmetrically substituted squaraines **DQD′** derived from different heterocyclic methylene bases **DH** and **D′H** can be used, in so far as they are specifically functionalised at one of their heterocyclic moieties, as labels for indicating special biological substrates, or, as self-assembled sensors for the detection of metal ions by surface plasmon resonances [8].

Although for the synthesis of unsymmetrically substituted squaraines **XQY** the simultaneous condensation of squaric acid $\mathbf{Q(OH)_2}$ with two different nucleophiles **XH** and **YH** seems to be the simplest way, it does not usually work. This is due to the fact that either one of the symmetrically substituted squaraine is exclusively formed or mixtures of all the possible symmetrically and unsymmetrically substituted products **XQX**, **XQY** and **YQY**, respectively, were obtained their separation into their individual components requires a high expense on time and materials. Moreover, the reaction of a nucleophilic compound **YH** with a semisquaric acid **QXOH** also frequently fails because the required semisquaric acids **QXOH** are not easily available from their educts $\mathbf{Q(OH)_2}$ and **XH** by a 1:1 condensation step. For example, by condensation of squaric acid $\mathbf{Q(OH)_2}$ with the pyrrole derivative **EH** only a low amount of the corresponding semisquaric acid **QEOH** was obtained while a larger amount of the corresponding squaraine **EQE** was formed. Indeed, the separation of the semisquaric acid **QEOH** from the squaraine derivative **EQE** simultaneously formed was difficult and has been performed only by means of special procedures [9].

The facts referred to agree with our efforts to prepare unsymmetrically substituted squaraines by starting from $\mathbf{Q(OH)_2}$ and mixtures of two reactive amino-substituted heterocyclic compounds **KH**–**MH**, which recently have been successfully used for the synthesis of corresponding squaraines **KQK**–**MQM** [10–12]. Although the symmetrically substituted squaraines **KQK**–**MQM** have been obtained in detectable extents, the desired semisquaric acids **QKOH**–**QMOH** could not be obtained thereby, even if the components mentioned are used in a stoichiometric ratio.

Due to the failure to prepare semisquaric acids **QXOH** by means of a simple condensation of the educts $\mathbf{Q(OH)_2}$ and **XH**, an intensive search for a better synthetic availability of these compounds has been undertaken. One of the synthetic routes which was found and mainly applied for the synthesis of aryl-substituted semisquaric acids **QCOH** or **QAOH** consists in the cycloaddition reaction of reactive aryl ketene derivatives or alkenes with suitable olefins [4a,4d,13]. (However, under such conditions, but without use of any alkene, a dimerisation reaction of the reactive ketene intermediate occurs giving rise, as demonstrated in the experimental part, to



A	R_2N	R^1
1	Me_2N	H
2	Me_2N	F
3	Me_2N	OH
4	Et_2N	OH

B	R^1
1	H
2	Me

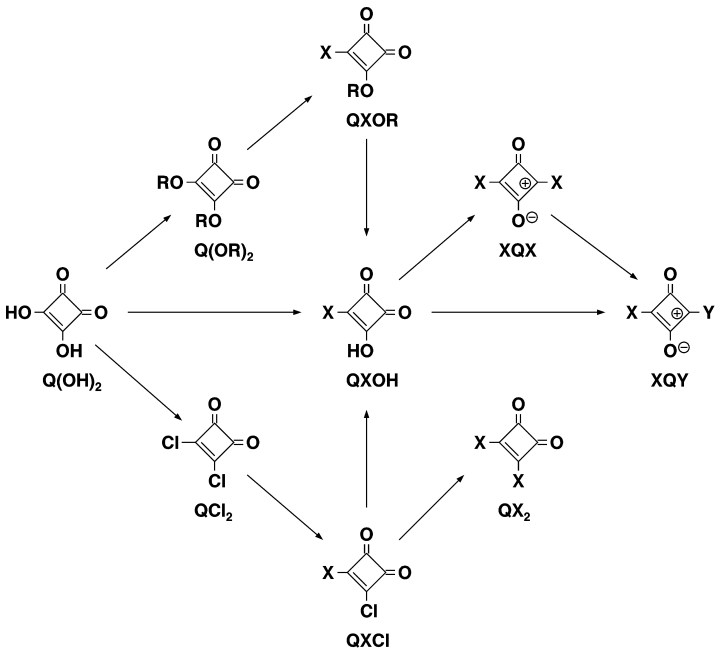
C	RO	R^1
1	MeO	H
2	HO	H
3	HO	HO

D	Y	R	R^1
1	CMe_2	Me	H
2	CMe_2	Me	Cl
3	S	Et	H

K	R_2N	R^1
1	Me_2N	H
2	Pyrr	H
3	Pip	H
4	Pip	Ph

L	R_2N	R^1
1	Pip	Me
2	Et_2N	Me
3	Bz_2N	Me
4	Me_2N	Ph

Scheme 1.



Scheme 2.

the formation of symmetrically substituted squaraines, such as the compound $\mathbf{C^1QC^1}$) [14]. Further methods consist of the reaction of arylacetylenes with tetrahalogenoethylenes [15], the reaction of the parent semisquaric acid **QHOH** (Moniliformin) [13a,16] with aryldiazonium salts, [17] or the reaction of metal organyls with fluoro-substituted cyclobutene derivatives [1b,18].

The most useful method for preparing semisquaric acids **QXOH** which has been reported in the literature, however, consists in the reaction of an activated squaric acid derivative with an nucleophilic component **XH**. As activated squaric acid derivatives, the dialkyl squarates $\mathbf{Q(OEt)_2}$ and $\mathbf{Q(OBu)_2}$ or the squaric acid dichloride $\mathbf{QCl_2}$ have been used. Thus, by starting from $\mathbf{Q(OEt)_2}$ [20] or $\mathbf{Q(OBu)_2}$ [2a] and the nucleophiles $\mathbf{A^1H}$, **DH,** or **EH** the corresponding semisquarates $\mathbf{QA^1OEt}$, [21] $\mathbf{QD^2OEt}$, $\mathbf{QD^3OBu}$, [8a,19] and **QEOEt**, [9] respectively, have been obtained in satisfactory yields. By starting with $\mathbf{QCl_2}$ [22] and the educt $\mathbf{A^1H}$, the semisquaric chlorides $\mathbf{QA^1Cl}$ [1c,4d,21] have been prepared. The products so obtained can primarily be transformed into the corresponding semisquaric acids **QXOH** by heating them in aqueous acetic acid.

2. Results and discussion

In continuing our efforts to prepare unsymmetrical squaraines derived from e.g. the amino-substituted heterocycles **KH**–**MH** [10–12], it was found that the condensation of activated squaric acid derivatives $\mathbf{Q(OR)_2}$ with these nucleophiles is also suitable for the synthesis of semisquaric acids **QKOH** derived from the 2-aminothiophenes **KH** (see Scheme 1). Thus, by condensing of dibutyl squarate $\mathbf{Q(OBu)_2}$ with stoichiometric amounts of 2-*N,N*-dimethylaminothiophene $\mathbf{K^1H}$, the corresponding *n*-butyl semisquarate $\mathbf{QK^1OBu}$ has been obtained in satisfactory yields. Its transformation into the desired semisquaric acid $\mathbf{QK^1OH}$ has been affected by means of its heating in a mixture of aqueous acetic acid and hydrochloric acid, as mentioned above.

Furthermore, the same semisquaric acid $\mathbf{QK^1OH}$ has been obtained by starting from squaric acid dichloride $\mathbf{QCl_2}$ also. Thus, by heating of $\mathbf{QCl_2}$ with 2-*N,N*-dimethylaminothiophene $\mathbf{K^1H}$ in a equimolar ratio without using any catalyst (which is claimed e.g. for the synthesis of $\mathbf{QA^1Cl}$ from $\mathbf{QCl_2}$ and $\mathbf{A^1H}$) [21] the corresponding semisquaric chloride $\mathbf{QK^1Cl}$ has been obtained. By its heating in aqueous acetic acid the corresponding semisquaric acid $\mathbf{QK^1OH}$ has been obtained in satisfactory yield.

Analogously, by condensing squaric acid dichloride $\mathbf{QCl_2}$ with the 2-aminothiazole derivative $\mathbf{L^4H}$ in a 1:1 ratio, the corresponding semisquaric chloride $\mathbf{QL^4Cl}$ has been obtained in satisfactory yield. It can be transformed by heating in aqueous acetic acid into the corresponding semisquaric acid $\mathbf{QL^4OH}$.

However, by changing the stoichiometric ratio of the components different results have been obtained. Thus, by heating 2-dimethylaminothiophene $\mathbf{K^1H}$ with squaric acid dichloride $\mathbf{QCl_2}$ in a 2:1 ratio, the symmetrically substituted condensation product $\mathbf{Q(K^1)_2}$ has been obtained. The same compound has also been obtained by heating $\mathbf{QK^1Cl}$ with a second equivalent of $\mathbf{K^1H}$. Other than its isomeric squaraine derivative $\mathbf{K^1QK^1}$, which is available by condensation of squaric acid $\mathbf{Q(OH)_2}$ with 2-dimethylaminothiophene $\mathbf{K^1H}$, the compound $\mathbf{Q(K^1)_2}$ exhibits a long-wavelength absorption maximum at 523 nm and absorbs, in accordance with the absorption properties of other bis-condensation products of the general formula $\mathbf{QX_2}$ in which their carbocyclic or heterocyclic moieties **X** are linked in 1,2-position at the squaric moiety, [2a,9,15] at considerably shorter wavelengths than the corresponding squaraine derivative $\mathbf{K^1QK^1}$.

In Table 1 some of the characteristic spectral data of the new semisquaric acids **QXOH** and semisquaric acid derivatives **QXOBu** and **QXCl** prepared are summarised. As can be seen, all the compounds exhibit in the IR region two intense bands at about 1700–1800 cm^{-1}, which can be attributed to both of their CO groups. Remarkably, the wavelength difference between both these bands varies significantly with their substitution pattern and ranges from about 30 cm^{-1} to about 110 cm^{-1}.

The semisquaric acids **QXOH** and semisquaric acid derivatives **QXOBu** and **QXCl** exhibit in their ^{1}H-NMR spectra characteristic signals which can

Table 1
Spectral properties of semisquaric acids **QXOH** and their derivatives **QXCl** and **QXOR**

QXCl/QXOR	λ_{max} (nm) (in methanol)	ν (cm^{-1}) (in KBr)	$\Delta\lambda$ (cm^{-1})	^{1}H-NMR, δ-values (ppm) (assignment) (in DMSO-d_6)
QA^{2}OH	273	1768, 1710	58	2.99 (s, 6H, NCH_3), 6.55 (dd, 1H, CH), 6.92 (dd, 1H, CH), 7.95 (dd, 1H, CH)
QC^{1}Cl	333[a]	1806, 1786, 1765	20, 41	3.92 (s, 3H, OCH_3), 7.18 (d, 2H, CH), 8.22 (d, 2H, CH) (in acetonitrile-d_3)
QC^{1}OH	333	1788, 1718	70	3.82 (s, 3H, OCH_3), 7.09 (d, 2H, CH), 7.95 (d, 2H, CH)[17]
QC^{2}Cl	333[a]	1788, 1764, 1750	24, 33	6.86 (d, 2H, CH), 7.85 (d, 2H, CH), 11.15 (s, 1H, OH)
QC^{2}OH	335	1792, 1713	79	6.90 (d, 2H, CH), 7.87 (d, 2H, CH), 10.23 (broad, 2H, OH)
QD^{1}OBu	422	1773, 1712	61	0.99 (t, 3H, CH_3), 1.52 (m, 2H, CH_2), 1.61 (s, 6H, CH_3), 1.87 (m, 2H, CH_2), 3.44 (s, 3H, NCH_3)
				4.85 (t, 2H, OCH_2), 5.40 (s, 1H, CH), 7.07–7.38 (m, 4H, CH) (in acetone-d_6)
QD^{1}OH	422	1777, 1709	86	1.56 (s, 6H, CH_3), 3.34 (s, 3H, NCH_3), 5.45 (s, 1H, CH), 6.98- 7.39 (m, 4H, CH)
QEOBu	383	1788, 1712	76	0.92 (t, 3H, CH_3), 0.97 (t, 3H, CH_3), 1.42 (m, 2H, CH_2), 1.79 (m, 2H, CH_2), 2.23 (s, 3H, CH_3),
				2.28 (s, 3H, CH_3), 2.33 (q, 2H, CH_2), 4.78 (t, 2H, OCH_2), 10.72 (s, 1H, NH)
QEOH	378	1790, 1682	108	0.98 (t, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.34 (q, 2H, CH2), 10.55 (s, 1H, NH)
QFOBu	348	1777, 1718	59	0.98 (t, 3H, CH_3), 1.51 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 2.14 (d, 3H, CH_3), 2.65 (s, 3H, CH_3),
				3.49 (s, 3H, NCH_3), 4.85 (t, 2H, OCH_2), 6.32 (d, 1H, CH) (in acetone-d_6)
QFOH	347	1787, 1704, 1695	83, 92	2.17 (d, 3H, CH_3), 2.61 (s, 3H, CH_3), 3.41 (s, 3H, NCH_3), 6.31 (d, 1H, CH)
QK^{1}Cl	437[a]	1785, 1767, 1750	18, 35	3.22 (s, 6H, NCH_3), 6.56 (d, 1H, CH), 7.94 (d, 1H, CH)
QK^{1}OBu	434	1777, 1716	61	0.98 (t, 3H, CH_3), 1.51 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 3.15 (s, 6H, NCH_3), 4.83 (t, 2H,
				OCH_2), 6.23 (d, 1H, CH), 7.65 (d, 1H, CH) (in acetone-d_6)
QK^{1}OEt	433	1778, 1715	63	1.44 (t, 3H, CH_3), 3.10 (s, 6H, NCH_3), 4.80 (q, 2H, CH_2), 6.29 (d, 1H, CH), 7.61 (d, 1H, CH)
QK^{1}OH	425	1781, 1690	91	3.05 (s, 6H, NCH_3), 6.19 (d, 1H, CH), 7.53 (d, 1H, CH)
QL^{4}Cl	423[a]	1782, 1761, 1745	21, 37	3.29(s, 6H, NCH_3), 7.53–7.60 (m, 5H, CH) (in acetone-d_6)
QL^{4}OH	396	1766, 1715	51	3.17 (s, 6H, NCH_3), 7.33–7.55 (m, 5H, CH)

[a] Measured in acetonitrile.

be attributed to the substituents at their heterocyclic moieties and, as far as the *n*-butyl semisquarates **QXOBu** are considered, to their butoxy moieties. In contrast, the signals for the protons at the OH moiety in the semisquaric acids **QXOH** can, in most cases, not be detected unambiguously due to presence of traces of water in the solvents used.

The availability of some of the new semisquaric acids **QXOH** and semisquaric acid derivatives **QXOBu** and **QXCl** allows us to prepare a series of unsymmetrically substituted squaraines **XQY** hitherto unknown and to study their physical and chemical properties. The synthesis of such compounds normally succeeds by heating a semisquaric acid **QXOH** with a suitable nucleophile **YH** by means of one of the following procedures A–C. The required semisquaric acids **QXOH** are available by the hydrolysis of the corresponding semisquaric acid derivatives **QXOBu** or **QXCl**, as mentioned above.

According to method A both the components **QXOH** and **YH** are mixed in a stoichiometric ratio and heated together in a 1-butanol/toluene mixture until the condensation (while being performed it is controlled by thin-layer chromatography) is complete. According to method B, the required nucleophilic compound **YH** is dissolved or suspended in a toluene/1-butanol mixture and added dropwise or in small portions, respectively, to the hot solution of the corresponding semisquaric acid **QXOH** in the same solvent. Finally, according to method C the semisquaric acid **QXOH** is dissolved or suspended in a toluene/1-butanol mixture and added dropwise or in small portions, respectively, to the boiling solution of the corresponding nucleophilic compound **YH** in the same solvent mixture.

Whereas method A is better suited for preparing sparingly soluble dyes, e.g. unsymmetrical squaraines **XQY** derived from the pyrrole **FH** and from the *N,N*-dialkylanilines **AH** or the julolidene derivative **BH**, method B is better suited for preparing unsymmetrical substituted squaraines **XQY** derived from the highly reactive heterocycles **EH** and **KH** as well as from the heterocyclic methylene bases **DH**. Method C is preferred by starting with the less reactive nucleophiles, such as with 2-*N,N*-dimethylamino-4-phenylthiazole $\mathbf{L^4H}$ and 2-piperidino-3,4-diphenylthiophene $\mathbf{K^4H}$. In general, the dye forming process required reaction times between 0.5 and 2 h. The reaction extent can be monitored, in all cases, by means of UV–vis spectroscopy or thin-layer chromatography. An unnecessarily long-time heating of the appropriate components or heating with an excess of the nucleophilic compound has to be avoided because exchange-reactions at the carbocyclic or heterocyclic side-groups [9] or forming of an 1:3 addition product [2b] (or both of them) [2c] giving rise to the formation of complex mixtures of products or ring-splitting reactions at the central squaric acid moiety [2a] preventing the formation of the desired unsymmetrically substituted squaraines **XQY** in high yields can occur under such circumstances.

In the course of our efforts to prepare unsymmetrically substituted squaraines **XQY** a further method D for their synthesis haven been found. It avoids the use of semisquaric acid derivatives but starts from symmetrically substituted squaraines **XQX** which were allowed to react with an appropriate nucleophilic compound **YH** to replace one of its groups **X** as **XH**. This method is applicable if the starting symmetrically substituted squaraine **XQX** is sufficently soluble in a polar sovent, such as 1-butanol, and if the nucleophile **YH** used exhibit a better nucleophilicity than the nucleophile **XH** replaced. Thus, the unsymmetrically substituted squaraine $\mathbf{C^3QK^1}$ was prepared by allowing to react the squaraine $\mathbf{C^3QC^3}$ with an equivalent amount of 2-dimethylaminothiophene $\mathbf{K^1H}$ in 1-butanol.

The unsymmetrical squaraines **XQY** prepared usually crystallise from the reaction mixture after cooling at room temperature. In this case, the products can be isolated by suction from their reaction mixture. For products which do not crystallise at cooling their reaction mixture is concentrated in vacuum and diluted, subsequently, by adding of a non-polar solvent, such as diethyl ether or *n*-hexane. As far as necessary, the products obtained can be purified by recrystallisation from hot chloroform or acetonitrile or by column chromatography on silica.

In Table 2 the new unsymmetrical squaraines **XQY** obtained by means of one the four methods

Table 2
Characteristic data of the symmetrically and unsymmetrically substituted squaraines **XQX** and **XQY**, respectively, prepared

X	Y	Yield (%) (method)	m.p. (°C) (decomp.)	ν_{CO} (cm^{-1}) (in KBr)	δ-values (ppm) (assignment)[a]	Solvent
A²	**K¹**	30–35 (B)	285	1618	3.09 (s, 6H, NCH_3), 3.34 (s, 6H, NCH_3), 6.39 (dd, 1H, CH_{ph}), 6.49 (d, 1H, CH_{th}), 6.51 (dd, 1H, CH_{ph}), 8.30 (d, 1H, CH_{th}), 8.39 (dd, 1H, CH_{ph})	$CDCl_3$
A²	**K²**	50–55 (B)	275	1618	2.11 (m, 4H, CH_2), 3.03 (s, 6H, NCH_3), 3.77 (m, 4H, NCH_2), 6.53 (dd, 1H, CH_{ph}), 6.62 (dd, 1H, CH_{ph}), 6.96 (d, 1H, CH_{th}), 8.09 (d, 1H, CH_{th}), 8.11 (dd, 1H, CH_{ph})	DMSO-Dd_6
A²	**K³**	30–35 (B)	248	1618	1.69 (m, 6H, CH_2), 3.02 (s, 6H, NCH_3), 3.77 (m, 4H, NCH_2), 6.51 (dd, 1H, CH_{ph}), 6.60 (dd, 1H, CH_{ph}), 7.18 (d, 1H, CH_{th}), 8.08–8.13 (m, 1H, CH_{ph}), 8.11 (d,1H, CH_{th})	DMSO-d_6
D¹	**K³**	15–20 (B)	251	1606	1.75 (s, 6H. CCH_3), 1.77 (m, 6H, CH_2), 3.58 (m, 4H, NCH_2), 3.69 (s, 3H, NCH_3), 5.95 (s, 1H, CH), 6.57 (d, 1H, CH_{th}), 7.21–7.49 (m, 4H, CH_{benzo}), 7.91 (d, 1H, CH_{th})	Acetone-d_6
D¹	**L¹**	25–30 (B)	235	1608	1.73 (m, 6H, CH_2), 1.77 (s, 6H, CCH_3), 2.85 (s, 3H, CH_3), 3.68 (m, 4H, NCH_2), 3.80 (s, 3H, NCH_3), 6.09 (s, 1H, CH), 7.3–7.58 (m, 4H, CH_{benzo})	Acetone-d_6
D¹	**L²**	25–30 (B)	251	1609	1.29 (t, 6H, CH_3), 1.77 (s, 6H, CCH_3), 2.87 (s, 3H, CH_3), 3.67 (q, 4H, NCH_2) 3.79 (s, 3H, NCH_3), 6.08 (s, 1H, CH), 7.30–7.55 (m, 4H, CH_{benzo})	Acetone-d_6
D¹	**L³**	30–35 (B)	214	1611	1.76 (s, 6H, CCH_3), 2.99 (s, 3H, CH_3), 3.68 (s, 3H, NCH_3), 4.74 (s, 4H, NCH_2), 6.04 (s,1H, CH), 7.09–7.40 (m, 14H, $CH_{ph} + CH_{benzo}$)	$CDCl_3$
D¹	**L⁴**	25–30 (A, B)	251	1612	1.77 (s, 6H, CCH_3), 3.29 (s, 6H, NCH_3), 3.66 (s, 3H, NCH_3), 6.02 (s, 1H, CH), 7.09–7.27 (m, 2H, CH_{benzo}), 7.34–7.46 (m, 5H, CH_{ph}), 7.76–7.79 (m, 2H, CH_{benzo})	$CDCl_3$
D¹	**M**	45–50 (B)	251	1610	1.34 (t, 6H, CH_3), 1.76 (s, 6H, CCH_3), 3.63 (s, 3H, NCH_3), 3.63–3,67 (m, 4H, NCH_2) 5.97 (s, 1H, CH), 7.06–7.24 (m, 2H, CH-benzo), 7.33–7.46 (m, 5H, CHph), 7.78–7.81 (m, 2H, CH_{benzo})	$CDCl_3$
E	**A³**	40–45 (A, B)	242	1627	1.02 (t, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.39 (q, 2H, CH_2), 3.09 (s, 6H, NCH_3), 6.09 (d, 1H, CH_{ph}), 6.49 (dd, 1H, CH_{ph}), 7.84 (d, 1H, CH_{ph}), 11,50 (s, 1H NH), 12.22 (s, 1H, OH)	DMSO-d_6
E	**A⁴**	40–45 (A, B)	231	1625	1.02 (t, 3H, CH_3), 1.15 (t, 6H, CH_3), 2.36 (s, 3H, CH_3), 2.40 (q, 2H, CH_2), 3.47 (q, 4H, NCH_2), 6.09 (dd, 1H, CH_{ph}), 7.84 (d, 1H, CH_{ph}), 11.50 (s, 1H, NH), 12.24 (s, 1H, OH)	DMSO-d_6

(continued on next page)

Table 2 (*continued*)

X	Y	Yield (%) (method)	m.p. [°C] (decomp.)	ν_{CO} (cm^{-1}) (in KBr)	δ-values (ppm) (assignment)[a]	Solvent
E	**B[1]**	55–60 (A, B)	222	1628	1.01 (t, 3H, CH_3), 1.85 (m, 4H, CH_2), 2.32 (s, 3H, CH_3), 2.37 (q, 2H, CH_2), 2.57 (m, 4H, CH_2), 3.35 (t, 2H NCH_2), 3.37 (t, 2H, NCH_2), 7.48 (s, 1H, CH_{ph}), 11.10 (s, 1H, NH), 12.47 (s, 1H, OH)	DMSO-d_6
E	**B[2]**	55–60 (A, B)	241	1621	1.02 (t, 3H, CH_3), 1.20 (s, 6H, CH_3), 1.39 (s, 6H, CH_3), 1.69 (m, 4H, CH_2), 2.33 (s, 3H, CH_3), 2.38 (q, 2H, CH_2), 3.35 (m, 2H, NCH_2), 3.47 (m, 2H, NCH_2), 7.83 (s, 1H, CH_{ph}), 11.25 (s, 1H, NH)	DMSO-d_6
					1.08 (t, 3H, CH_3), 1.29 (s, 6H, CH_3), 1.46 (s, 6H, CH_3), 1.70–1.77 (m, 4H, CH_2), 2.31 (s, 3H, CH_3), 2.42 (q, 2H, CH_2), 2.54 (broad, 3H, CH_3), 3.30–3.34 (m, 2H, NCH_2), 3.41–3.45 (m, 2H, NCH_2), 7.91 (s, 1H, CH_{ph})[A], 8.00 (s, 1H, CH_{ph})[B], 12.12 (s, 1H, OH)[A], 12.46 (s, 1H, OH)[B]	$CDCl_3$[b]
F	**A[3]**	40–45 (A)	252	1625	2.20 (d, 3H, CH_3), 2.81 (s, 3H, CH_3), 3.15 (s, 6H, NCH_3), 3.47 (s, 3H, NCH_3), 6.12 (d, 1H, CH_{ph}), 6.53 (d, 1H, CH), 6.57 (dd, 1H, CH_{ph}), 7.88 (d, 1H, CH_{ph})	DMSO-d_6
F	**A[4]**	15–20 (A)	212	1625	1.16 (t, 6H, CH_3), 2.19 (d, 3H, CH_3), 2.79 (s, 3H, CH_3), 3.47 (s, 3H, NCH_3), 3.52 (q, 4H, NCH_2), 6.11 (d, 1H, CH_{ph}), 6.52 (d, 1H, CH), 6.56 (dd, 1H, CH_{ph}), 7.87 (d, 1H, CH_{ph})	DMSO-d_6
F	**B[1]**	30–35 (A)	216	1629	1.85 (m, 4H, CH_2), 2.18 (d, 3H, CH_3), 2.58 (m, 4H, CH_2), 2.75 (s, 3H, CH_3), 3.40 (t, 2H, NCH_2), 3.42 (t, 2H, NCH_2), 3.44 (s, 3H, NCH_3), 6.45 (d, 1H, CH), 7.51 (s, 1H, CH_{ph})	DMSO-d_6
C[1]	**K[1]**	25–30 (B)	238	1620	3.38 (s, 6H, NCH_3), 3.87 (s, 3H, OCH_3), 6.59 (d, 1H, CH_{th}), 6.96 (d, 2H, CH_{ph}), 8.25 (d, 2H, CH_{ph}), 8.35 (d, 1H, CH_{th})	$CDCl_3$
C[1]	**K[2]**	40–45 (B)	249	1619	2.18 (m, 4H, CH_2), 3.64 (m, 4H, NCH_2), 3.86 (s, 3H, OCH_3), 6.52 (d, 1H, CH_{th}), 6.95 (d, 1H, CH_{ph}), 8.20 (d, 1H, CH_{ph}), 8.28 (d, 1H, CH_{th})	$CDCl_3$
C[2]	**K[4]**	15–20 (A, C)	275	1615	1.59 (m, 6H, CH_2), 3.49 (m, 4H, NCH_2), 6.79 (d, 2H, CH_{ph}), 7.04–7.28 (m, 10H, CH_{ph}), 7.79 (d, 2H, CH_{ph}), 10.09 (s, 1H, OH)	DMSO-d_6
K[1]	**A[3]**	50–55 (B)	285	1624	3.06 (s, 6H, NCH_3), 3.35 (s, 6H, NCH_3), 6.09 (d, 1H, CH_{ph}), 6,44 (dd, 1H, CH_{ph}), 6.89 (d, 1H, CH_{th}), 7.74 (d, 1H, CH_{ph}), 7.97 (d, 1H, CH_{th}), 11.79 (s, 1H, OH)	DMSO-d_6
K[1]	**A[4]**	50–55 (B)	242	1623	1.12 (t, 6H, CH_3), 3.32 (s, 6H, NCH_3), 3.42 (q, 4H, NCH_2), 6.05 (d, 1H, CH_{ph}), 6.39 (dd, 1H, CH_{ph}), 6.84 (d, 1H, CH_{th}), 7.72 (d, 1H, CH_{ph}), 7.92 (d, 1H, CH_{th}), 11.79 (s, 1H, OH)	DMSO-d_6

(continued on next page)

Table 2 (*continued*)

X	Y	Yield (%) (method)	m.p. [°C] (decomp.)	ν_{CO} (cm^{-1}) (in KBr)	δ-values (ppm) (assignment)[a]	Solvent
K[1]	**B[1]**	55–60 (B)	230	1625	1.86 (m, 4H, CH_2), 2.55–2.63 (m, 4H, CH_2), 3.28 (s, 6H, NCH_3), 3.33 (t, 2H, NCH_2), 3.35 (t, 2H, NCH_2), 6.69 (d, 1H, CH_{th}), 7.39 (s, 1H, CH_{ph}), 7.84 (d 1H, CH_{th}), 12.08 (s, 1H, OH)	DMSO-d_6
K[1]	**D[1]**	30–35 (B)	259	1605	1.75 (s, 6H, CCH_3), 3.19 (s, 6H, NCH_3), 3.59 (s, 3H, NCH_3), 5.91 (s, 1H, CH), 6.23 (d, 1H, CH_{th}), 6.99- 7.36 (m, 4H, CH_{benzo}), 7.98 (d, 1H, CH_{th})	$CDCl_3$
K[1]	**E**	20–30 (B)	240	1621	1.02 (t, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.37 (q, 2H, CH_2), 6.64 (d, 1H, CH_{th}), 7.89 (d, 1H, CH_{th}), 10.96 (s, 1H, NH)	DMSO-d_6
K[1]	**F**	25–30 (B)	267	1608	2.21 (d, 3H, CH_3), 2.89 (s, 3H, CH_3), 3.26 (s, 6H, NCH_3), 3.43 (s, 3H, NCH_3), 6.36 (d, 1H, CH_{th}), 6.75 (d, 1H, CH), 8.14 (d, 1H, CH_{th})	$CDCl_3$
K[1]	**K[4]**	60–65 (A, C)	259	1618	1.55 (m, 6H,CH_2), 3.19 (m, 10H, NCH_3, NCH_2), 7.05–7.25 (m, 10H, CH_{ph}), 7.97 (d, 1H, CH_{th})	$CDCl_3$
K[1]	**L[4]**	25–30 (A, C)	264	1614	3.19 (s, 6H, NCH_3), 3.35 (s, 6H, NCH_3), 6.98 (d, 1H, CH_{th}), 7.35–7.65 (m, 5H, CH_{ph}), 7.97 (d 1H, CH_{th})	DMSO-d_6
K[1]	**C[3]**	55–60 (B, D)	327	1632	3.41 (s, 6H, NCH_3), 5.73 (s, 2H, CH_{ph}), 7.10 (d, 1H, CH_{th}), 8.02 (d, 1H, CH_{th}), 10.19 (s, 1H, OH), 11,50 (s, 2H, OH)	DMSO-d_6
B[2]	**B[2]**	60–65 (A)b)	337	1602	1.28 (s, 12H, CH_3), 1.46 (s, 12H, CH_3), 3.30 (broad, 4H, NCH_2), 3.40 (broad, 4H, NCH_2), 7.83 (s, 1H, CH_{ph}[A]), 7.93 (s, 1H, CH_{ph}[B]), 11.34 (s, 2H, OH[A]), 12.00 (s, 1H, OH[B])	$CDCl_3$
K[1]	**K[1]**	30–35 (B)	279	1605	3.22 (s, 12H, NCH_3), 6.55 (d, 2H, CH_{th}), 7.75 (d, 2H, CH_{th}),	DMSO-d_6
					3.21 (s, 12H, NCH_3), 6.23 (d, 2H, CH_{th}), 7.97 (d, 2H, CH_{th}),	$CDCl_3$
K[2]	**K[2]**	30–35 (B)	308	1607	see Ref. [10a]	
K[3]	**K[3]**	40–45 (B)	256	1610	see Ref. [10a]	
K[4]	**K[4]**	50–55 (A)	281	1621	see Ref. [10a]	
M	**M**	40–45 (B)	250	1614	1.31 (t, 12H, CH_3), 3.63 (q, 8H, NCH_2), 7.24–7.81 (m, 10H, CH_{ph})	DMSO-d_6
					see Ref. [12b]	$CDCl_3$

[a] ph = phenyl; th = thienyl.
[b] Compound exists in this solvent possibly in two isomeric forms A and B, see Ref. [7b].

A–D are listed. Their constitution follow from their analytical and spectroscopic data. Whereas the latter are summarised in Table 2 the elemental analytic data are summarised in Table 3.

Similar to their corresponding symmetrical squaraines **XQX** the new unsymmetrical squaraines **XQY** exhibit in their IR. spectra characteristic absorption bands at about 1600, 3000–3100,

Table 3
Elemental analytic data of the squaraines **XQY** prepared

X	Y	Formula (M_w)		C	H	N	S
A²	**K¹**	$C_{18}H_{17}FN_2O_2S$	Calcd.	62.77	4.98	8.13	9.31
		(344.4)	Found	62.66	5.16	8.19	9.41
A²	**K²**	$C_{20}H_{19}FN_2O_2S$	Calcd.	64.85	5.17	7.56	8.65
		(370.4)	Found	64.58	5.38	7.47	8.79
A²	**K³**	$C_{21}H_{21}FN_2O_2S$	Calcd.	65.61	5.51	7.29	8.34
		(384.5)	Found	66.01	5.77	7.18	8.40
D¹	**K³**	$C_{25}H_{26}N_2O_2S$	Calcd.	71.74	6.26	6.69	7.66
		(418.6)	Found	71.58	6.35	6.70	7.65
D¹	**L¹**	$C_{25}H_{27}N_3O_2S$	Calcd.	69.26	6.28	9.69	7.39
		(433.6)	Found	69.39	6.87	9.54	7.20
D¹	**L²**	$C_{24}H_{27}N_3O_2S$	Calcd.	68.38	6.46	9.97	7.61
		(421.6)	Found	68.30	6.79	9.63	7.30
D¹	**L³**	$C_{34}H_{31}N_3O_2S$	Calcd.	74.84	5.73	7.70	5.88
		(545.7)	Found	74.45	5.92	7.63	5.69
D¹	**L4**	$C_{27}H_{25}N_3O_2S$	Calcd.	71.18	5.53	9.22	7.04
		(455.6)	Found	71.22	6.14	9.08	6.69
D¹	**M**	$C_{29}H_{29}N_3O_2Se$	Calcd.	65.66	5.51	7.92	–
		(530.5)	Found	64.92	6.12	7.90	–
E	**A³**	$C_{20}H_{22}N_2O_3$	Calcd.	70.99	6.55	8.28	–
		(338.4)	Found	71.02	7.14	8.14	
E	**A⁴**	$C_{22}H_{26}N_2O_3$	Calcd.	72.11	7.15	7.64	–
		(366.5)	Found	72.02	7.08	7.57	
E	**B¹**	$C_{24}H_{26}N_2O_3$	Calcd.	73.82	6.71	7.17	–
		(390.5)	Found	73.90	6.91	7.23	–
E	**B²**	$C_{28}H_{34}N_2O_3$	Calcd.	75.31	7.67	6.27	–
		(446.6)	Found	74.53	7.69	6.15	–
F	**A³**	$C_{19}H_{20}N_2O_3$	Calcd.	70.35	6.21	8.64	–
		(324.4)	Found	70.31	6.31	8.34	
F	**A⁴**	$C_{21}H_{24}N_2O_3$	Calcd.	71.57	6.86	7.95	–
		(352.4)	Found	71.36	6.82	7.92	
F	**B1**	$C_{23}H_{24}N_2O_3$	Calcd.	73.38	6.43	7.44	–
		(376.5)	Found	73.37	6.54	7.25	
C¹	**K¹**	$C_{17}H_{15}NO_3S$	Calcd.	65.16	4.82	4.47	10.23
		(313.37)	Found	64.87	5.17	4.46	9.97
C¹	**K²**	$C_{19}H_{17}NO_3S$	Calcd.	67.24	5.05	4.13	9.45
		(339.4)	Found	67.34	5.45	4.19	9.33
C²	**K⁴**	$C_{31}H_{25}NO_3S$	Calcd.	75.74	5.13	2.85	6.52
		(491.6)	Found	75.95	5.26	2.90	6.41
K¹	**A³**	$C_{18}H_{18}N_2O_3S$	Calcd.	63.14	5.30	8.18	9.36
		(342.4)	Found	62.65	5.54	8.07	9.51

(continued on next page)

Table 3 (*continued*)

X	Y	Formula (M_w)		C	H	N	S
K¹	**A⁴**	$C_{20}H_{22}N_2O_3S$	Calcd.	64.84	5.99	7.56	8.65
		(370.5)	Found	65.08	6.09	7.59	9.09
K¹	**B¹**	$C_{22}H_{22}N_2O_3S$	Calcd.	66.98	5.62	7.10	8.13
		(394.5)	Found	67.23	5.89	7.03	8.55
K¹	**B²**	$C_{26}H_{30}N_2O_3S$	Calcd.	69.30	6.71	6.22	7.12
		(450.6)	Found	68.49	6.72	5.93	7.06
K¹	**D¹**	$C_{22}H_{22}N_2O_2S$	Calcd.	69.81	5.86	7.40	8.47
		(378.5)	Found	68.01	6.04	7.17	8.18
K¹	**E**	$C_{18}H_{20}N_2O_2S$	Calcd.	65.83	6.14	8.53	9.76
		(328.4)	Found	65.74	6.13	8.56	9.81
K¹	**F**	$C_{17}H_{18}N_2O_2S$	Calcd.	64.94	5.77	8.91	10.20
		(314.4)	Found	64.40	6.22	8.62	10.21
K¹	**K⁴**	$C_{31}H_{28}N_2O_2S_2$	Calcd.	70.96	5.38	5.34	12.22
		(524.7)	Found	71.17	5.85	5.39	12.10
K¹	**L⁴**	$C_{21}H_{19}N_3O_2S_2$	Calcd.	61.59	4.68	10.26	15.66
		(409.5)	Found	61.67	4.57	10.24	15.86
K¹	**C³**	$C_{16}H_{13}NO_5S$	Calcd.	58.00	3.95	4.23	9.68
		(331.3)	Found	57.94	3.80	4.31	9.90
K¹	**K¹**	$C_{16}H_{16}N_2O_2S$	Calcd.	57.81	4.85	8.43	19.29
		(332.5)	Found	57.79	4.84	8.33	19.24
K²	**K²**	$C_{20}H_{20}N_2O_2S_2$	Calcd.	62.47	5.24	7.29	16.68
		(384.5)	Found	62.53	5.26	7.14	16.29
K³	**K³**	$C_{22}H_{24}N_2O_2S_2$	Calcd.	64.05	5.86	6.79	15.54
		(412.6)	Found	64.20	5.90	6.62	15.22
K⁴	**K⁴**	$C_{46}H_{40}N_2O_2S_2$	Calcd.	77.06	5.62	3.91	8.95
		(717.0)	Found	76.80	5.61	3.82	8.92
M	**M**	$C_{30}H_{30}N_4O_2Se_2$	Calcd.	56.61	4.75	8.80	–
		(636.5)	Found	56.81	4.98	8.84	–
B²	**B²**	$C_{36}H_{44}N_2O_4$	Calcd.	76.02	7.80	4.93	–
		(568.8)	Found	75.60	7.67	4.90	–

2800–3000 and 1500 cm^{-1}. Whereas the first band can be attributed to the pseudoaromatic squarate moiety, the other ones can be attributed to their characteristic groups in their adjacent moieties. The absence of any bands at about 1700 cm^{-1} can be explained with the highly polar character of the central four-membered ring which gives rise to very polar carbonyl groups therein. Moreover, the absence of any IR bands in this region which are found, e.g. for compound **Q(K¹)₂** at 1745 and 1713 cm^{-1} can be used as an argument for a 1,3-linking of the carbocyclic or heterocyclic groups at the central four-membered squarate ring.

The new unsymmetrically substituted squaraines **XQY** prepared are deeply coloured micro-crystalline solids with a remarkable high thermal stability and a considerable solubility in polar organic solvents. In solution they exhibit in their UV/Vis spectra intense bands having maxima at about 560–660 nm and extinction coefficients at about 10^5 l mol^{-1} cm^{-1} (see Table 4).

For illustration, in Fig. 1 the typical absorption spectrum of an unsymmetrical squaraine **A²QK¹** is depicted and contrasted to the absorption spectra of both its symmetrical squaraines **A²QA²** and **K¹QK¹**. As can be seen, the absorption maxima of

Table 4
Spectral data of the squaraines **XQY** prepared

X	Y	λ_{max} (nm)	log ε	λ_{max} (nm)	$\Delta\lambda$	Ref.
A²	**K¹**	622	5.27	642	−20	–
A²	**K²**	621	5.26	646	−25	–
A²	**K³**	625	5.25	647	−22	–
D¹	**K³**	649	5.40	649	0	–
D¹	**L¹**	630	5.33	–[a]	–[a]	–
D¹	**L²**	629	5.37	631	−2	–
D¹	**L³**	629	5.31	634	−5	–
D¹	**L⁴**	644	5.19	65	−11	–
D¹	**M**	657	5.22	664	−7	–
E	**A³**	600	5.43	601	−1	–
E	**A⁴**	604	5.44	604	0	–
E	**B¹**	619	5.44	617	+2	–
E	**B²**	619	5.43	617	+2	–
F	**A³**	580	5.29	583	−3	–
F	**A⁴**	581	5.31	586	−5	–
F	**B¹**	591	5.29	598	−7	–
C¹	**K¹**	564	5.14	597	−33	–
C¹	**K²**	563	5.13	601	−38	–
C²	**K⁴**	590	5.09	–[b]	–[b]	–
K¹	**A³**	643	5.45	646	−3	–
K¹	**A⁴**	648	5.51	649	−1	–
K¹	**B¹**	662	5.48	661	+1	–
K¹	**D¹**	645	5.48	644	+1	–
K¹	**E**	612	5.45	610	+2	–
K¹	**F**	587	5.22	591	−4	–
K¹	**K⁴**	677	5.33	679	−2	–
K¹	**L⁴**	655	5.12	665	−10	–
K¹	**C³**	609	–[c]	613	−4	–
		599[d]	5.11[d]			–
A¹	**A¹**	627	5.49			[3,29]
A²	**A²**	630	5.09			[3,29]
A³	**A³**	637	5.52			[3,29]
A⁴	**A⁴**	643	5.55			[3,29]
B¹	**B¹**	668	5.54			[3,30]
B²	**B²**	670	5.56			–
C¹	**C¹**	540	5.15			[31]
C²	**C²**	–[b]	–[b]			–
C³	**C³**	571	5.21			[2b]
D¹	**D¹**	634	5.47			[2b,32]
E	**E**	565	5.34			[2b]
F	**F**	528	5.00			[2c]
K¹	**K¹**	654	5.46			–
K²	**K²**	662	5.54			[10]
K³	**K³**	663	5.46			[10]
K⁴	**K⁴**	703	5.27			[10]
L¹	**L¹**	–[a]	–[a]			–
L²	**L²**	628	5.35			[11a]
L³	**L³**	633	5.41			[11a]
L⁴	**L⁴**	675	5.16			[11a]
M	**M**	694	5.18			[12]

[a] Data are not available, because the compound **L¹QL¹** is stable only for a short time in the reaction mixture.
[b] Data are not available, because the compound **C²QC²** can not be prepared by common methods [2b].
[c] Due to the low solubility of compound **K¹QC³** in trichloromethane the data are not recordable.
[d] Measured in 2-butanone.

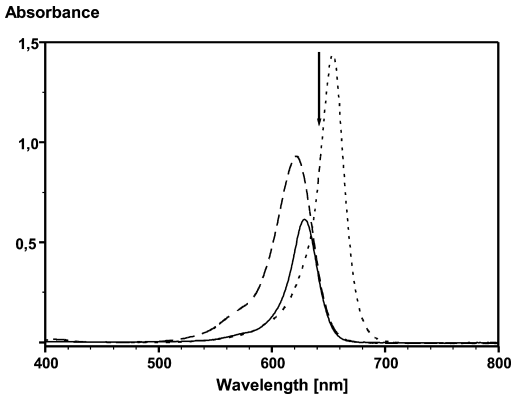


Fig. 1. Visible absorption spectrum of the unsymmetrically substituted squaraine dye **A²QK¹** (- - - -) in respect to the spectra of the symmetrically subsituted analogues **A²QA²** (—) and **K¹QK¹** (· · · · ·); spectra measured in trichloromethane, concentration 1×10^{-5} M l^{-1}; the arrow indicates the arithmetic mean value (λ'_{max}) according to Eq. (1).

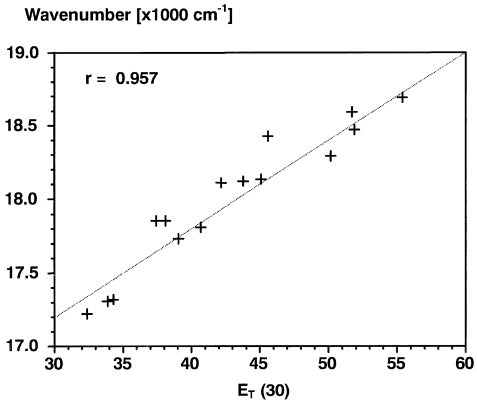


Fig. 2. Correlation of the reciprocal absorption maxima, measured in 1000 cm^{-1}, of compound **C¹QK¹** against the solvent polarity parameter $E_T(30)$.

the unsymmetrical squaraine **XQY** is significantly blue-shifted with respect to the absorption maxima of their symmetrical squaraines **XQX** and **YQY**.

By comparing the λ_{max} value of the absorption maximum of a unsymmetrically substituted squaraine dye **XQY**, designed as λ_{max}(XQY), with the ones of their symmetrically substituted parent dyes **XQX** and **YQY**, designed as λ_{max} (XQX) and λ_{max}(YQY), respectively, one can see that λ_{max}(XQY) is, in general, not the same as the arithmetic mean value λ_{max} of both the symmetrical

Table 5
Solvent polarity parameters $E_T(30)$ and UV–vis-absorption data of compound **C[1]QK[1]**

Solvent	$E_T(30)$ (kcal mol^{-1})	λ_{max} (nm)	$1/\lambda_{max}$ (10^{-5} m^{-1})
Tetrachloromethane	32.4	580.6	17.223
Toluene	33.9	577.9	17.304
Benzene	34.3	577.3	17.322
Tetrahydrofuran (THF)	37.4	560.2	17.850
Ethyl acetate	38.1	560.2	17.850
Trichloromethane	39.1	564.0	17.730
Dichloromethane	40.7	561.5	17.809
Acetone	42.2	552.2	18.109
N,N-dimethylformamide (DMF)	43.8	551.9	18.119
Dimethylsulfoxide (DMSO)	45.1	551.5	18.132
Acetonitrile	45.6	542.6	18.429
1-Butanol	50.2	546.7	18.291
Acetic acid	51.7	537.9	18.590
Ethanol	51.9	541.4	18.470
Methanol	55.4	535.0	18.691

dyes **XQX** and **YQY** calculated by means of Eq. (1). For the most compounds, the λ_{max}(XQY) value of an unsymmetrical dye is hypsochromic shifted in respect to the arithmetic mean value λ_{max} of both the symmetrical dyes. This phenomenon seems to be a general one in the series of squaraines studied and corresponds with analogous phenomenons found in other series of unsymmetrical squaraine dyes [6d,8b] or, e.g.

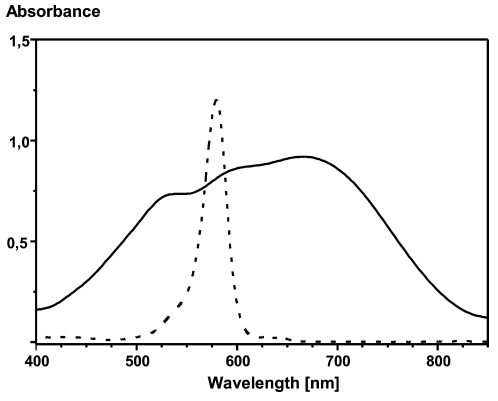


Fig. 3. Visible and NIR absorption spectra of the dye **FQA[3]** in solution (trichloromethane) and in dispersion on a polyester sheet.

polymethine dyes [23,24]. Moreover, the position of the longest-wavelength absorption bands of the unsymmetrical substituted squaraines **XQY**, λ_{max}(XQY), and the deviation ($\Delta\lambda$) of the arithmetic mean values of the symmetrically substituted squaraines **XQX** and **XQY**, λ'_{max}, calculated according to Eq. (2), is strongly influenced by the groups linked at the 1,3-positions of the central squaraine moiety.

$$\lambda'_{max} = {}^{1/2}\,[\lambda_{max}(XQX) + \lambda_{max}(YQY)] \quad (1)$$

$$\Delta\lambda = \lambda'_{max} - \lambda_{max}(XQY) \quad (2)$$

To see, if the deviation found can be correlated with a characteristic property of the compounds studied we have measured the condensation tendency of a compounds **XH** towards squaric acid **Q(OH)$_2$** in comparison to the one of a second compound **YH** and this relative tendency compared with the corresponding $\Delta\lambda$ value. The condensation tendency was estimated by heating an equimolar mixture of two different compounds **XH** and **YH** with squaric acid in a 1-butanol/benzene mixture at boiling temperature under a nitrogen atmosphere and quantified by the measurement of the extinctions of the reaction mixture after several time intervals at wavelengths which are characteristic for the longest-wavelength maxima of the possible squaraines **XQY**, **XQX** and **YQY**. The measurements have been supported by means of thin-layer chromatography in such a way that the time was registered in which one of the possible condensation products could be detected as a well-defined spot on the chromatogram. Thus, the following reactivity sequence has been estimated:

EH > D[1]H > K[1]H > FH >> C[3]H > A[3]H > L[4]H > A[2]H > C[1]H

As can seen from the values of Table 4, this condensation tendency correlates qualitatively with the $\Delta\lambda$ values estimated, e.g. of the unsymmetrical squaraines **XQK[1]** derived from the compounds **XH** and the compound **K[1]H**. Thus, for the squaraines **EQK[1]** and **D[1]QK[1]** slight positive $\Delta\lambda$ values were found in contrast to the squaraines **A[3]QK[1]**, **C[3]QK[1]**, and **FQK[1]** or to the squaraines

C[1]QK[1] and **A[2]QK[1]** for which slightly or strongly negative $\Delta\lambda$ values, respectively, were estimated in contrast to values in the literature for squaraines of structures **C[1]QA[1]** [6d] and **DQD′** [8b].

The sequence documents, e.g. that the heterocyclic pyrroles **EH** and **FH** as well as the 2-dialkylamino-substituted thiophenes **KH** are more reactive than their carbocyclic analogues **AH**, and that these carbocyclic compounds have a reactivity similar to the one of the 2-dialkylamino-substituted thiazole **LH**.

As a further interesting fact, the dependence of the absorption maximum of the unsymmetrically substituted squaraines **XQY** from the polarity of the solvent used has to be mentioned. As seen from Fig. 2, in which the reciprocal wavelength $1/\lambda$ (measured in 10^{-5} m) of the longest-wavelength maximum of the compound **C[1]QK[1]** (see Table 5) is opposed to the solvent polarity parameter $E_T(30)$ estimated by Reichardt [25,26], there is a rather good correlation (correlation coefficient $r = 0.957$) between both sets of data. Hence, the unsymmetrically substituted squaraines **XQY** prepared should be used as indicators for measuring the solvent polarity. Corresponding studies are in progress and will be published later. Moreover, due to the strong solvatochromism found, the unsymmetrically substituted squaraines **XQY** here described are good candidates for manufacturing materials with non-linear optical properties [27]. As is known, the non-linear optical properties of an appropriate compound depend, *inter alia*, on the changes of the dipole moments by going from the ground to its excited state as well as from the oscillator strength of its longest-wavelength absorption band [28]. Indeed, both these values are significantly large for the unsymmetrically substituted squaraines **XQY** described here.

Finally, the influence of the aggregation states on the spectral properties of the unsymmetrically substituted squaraines **XQY** prepared should also to be mentioned. Fig. 3 depicts the absorption spectra of the unsymmetrically substituted squaraine **FQA[3]** in chloroform solution as well as in a dispersed form. There is a strong shift both in the position of the absorption band and in the shape of this band by going from the solution to the solid state. Hence, the unsymmetrically substituted squaraine **XQY**, especially the dyes **FQA** and **CQK**, are good candidates for using as photosensitive and electrically active pigments in electrophotographic devices.

3. Experimental

3.1. General

Melting points were determined by means of a differential scanning calorimeter (Mettler, Toledo) using a heating rate of 5°C/min. IR spectra were recorded in potassium bromide pellets with a FTIR spectrometer PU 9624 (Philips, Eindhoven) or with a FTIR spectrometer FTS 25 (BIO-RAD Laboratories GmbH, Krefeld), whereas visible and near infrared spectra were recorded with a UV spectrometer UV-2501 PC (Shimadzu, Tokyo) or with a spectrometer M 40 (Carl Zeiss, Jena). NMR spectra were recorded with a Varian Gemini 300 spectrometer (Varian, Zurich) operating at 300 MHz. Elemental analysis data were obtained with a LECO CHNS 932 analyser.

3.2. Preparation of 1-substituted 2-butoxycyclobuten-3,4-diones *QXOBu* — general procedure

Dibutyl squarate (**Q(OBu)$_2$**, [2a], 33.9 g, 0.15 mol) and the appropriate nucleophilic component **XH** (0.15 mol) were heated in acetic acid or 1-butanol (150 ml) for 1 h. After standing for 12 h the product formed was isolated by filtration, washed with ether, and dried at 70°C for 8 h. For further purification the product was recrystallised from acetic acid.

The following products were obtained: 1-[2-(1,3,3 - trimethylindolin - 2 - ylidene) - methyl] - 2 - butoxycylobuten-3,4-dione (**QD[1]OBu**) from 2-methylene-1,3,3-trimethylindoline in a yield of 50%; m.p. 126°C. $C_{20}H_{23}NO_3$ (325.41): calcd. C 73.82, H 7.12, N 4.30; found: C 74.13, H 7.19, N 4.29. 1-(3,5-Dimethyl-4-ethylpyrryl)-2-butoxycyclobuten-3,4-dione (**QEOBu**) from 2,4-dimethyl-3-ethylpyrrole in a yield of 52%; m.p. 159°C. $C_{16}H_{21}NO_3$ (275.35): calcd. C 69.79, H 7.69, N 5.09; found C 69.81, H 7.67, N 5.08. 1-(1,2,5-Trimethyl-3 - pyrryl) - 2 - butoxycyclobuten - 3,4-dione (**QFOBu**) from 1,2,5-trimethylpyrrole in a yield of

20%; m.p. 134°C. $C_{15}H_{19}NO_3$ (261.32): calcd. C 68.94, H 7.33, N 5.36; found C 69.04, H 7.40, N 5.91. 1-(2-*N,N*-dimethylamino-5-thienyl)-2-butoxy-cyclobuten-3,4-dione (**QK^{1}OBu**) from 2-*N,N*-dimethylaminothiophene [10c] in a yield of 29%; m.p. 120°C. $C_{14}H_{17}NO_3S$ (279.35): calcd. C 60.19, H 6.13, N 5.01, S 11.48; found C 60.10, H 6.24 N, 5.21, S 11.01.

*3.3. Preparation of 1-substituted 2-chloro-cylobutene-3,4-diones (**QXCl**) — general procedure*

3.3.1. Method A

1,2-Dichlorocyclobuten-3,4-dione (**QCl$_2$** [22], 15.1 g, 0.1 mol) and the appropriate nucleophilic component (**XH**, 0.1 mol) were dissolved in dried benzene (250 ml) and refluxed for 6 h. After cooling, the reaction mixture was poured in ice water (500 ml) and the two layers formed were separated. The organic layer was washed with water (250 ml), dried, and evaporate in vacuum. The residue obtained was used without further manipulation for the next procedures or, as far as it is necessary, could be recrystallised from benzene or toluene and precipitated by adding of some hexane to the cold solution.

3.3.2. Method B

This method is the same as method A, but dried methylene chloride was used as the solvent and anhydrous $AlCl_3$ (13.3 g, 0.1 mol) was added to the reaction mixture before heating. The following 2-chlorocyclobuten-3,4-diones were obtained: 2-chloro-1-(4-methoxyphenyl)-cyclobuten-3,4-dione (**QC^{1}Cl**) from anisole according to the method B in a yield of 61%; m.p. 120°C. $C_{11}H_7ClO_3$ (222.63): calcd. C 59.35, H 3.17, Cl 15.95; found C 59.63, H 3.26, Cl 15.67. 2-Chloro-1-(4-hydroxy-phenyl)-cyclobuten-3,4-dione (**QC^{2}Cl**) from anisole according to the method B by using 10 (!) equivalents of $AlCl_3$ in a yield of 49%; m.p. 208°C. $C_{10}H_5ClO_3$ (208.60): calcd. C 57.58, H 2.42, Cl 17.00; found C 56.75, H 2.55, Cl 16.38. 2-Chloro-1-(2-*N,N*-dimethylamino-5-thienyl)-cyclo-buten-3,4-dione (**QK^{1}Cl**) from 2-*N,N*-dimethyl-aminothiophene accordingly to the method A in a yield of 71%; m.p. 198°C (dec.). $C_{10}H_8ClNO_2S$ (241.69): calcd. C 49.70, H 3.34, N 5.80, S 13.26; found C 49.48, H 3.56, N 5.80, S 13.06. 2-Chloro-1-(2-*N,N*-dimethylamino-4-phenyl-5-thiazolyl)-cyclobuten-3,4-dione (**QL^{4}Cl**) from 2-*N,N*-dimethylamino-4-phenylthiazole [11a] according to method A in a yield of 57%; m.p. 205°C (dec.). $C_{15}H_{11}ClN_2O_2S$ (318.78): calcd. C 56.52, H 3.48, N 8.79, S 10.06; found C 56.94, H 3.81, N 8.81, S 10.39.

*3.4. Preparation of semisquaric acids **QXOH** — general procedure*

A 1-substituted 2-butoxy-cylobuten-3,4-dione or a 2-chlorocyclobuten-3,4-dione (**QXOBu** or **QXCl**, respectively, 0.02 mol) was dissolved in a mixture of acetic acid (50 ml), water (50 ml), and 2 N HCl (4 ml) and refluxed for 2 h. After cooling at room temperature, the product crystallised was isolated by filtration, washed with ether, and dried.

The following semisquaric acids (**QXOH**) were obtained: 2-hydroxy-1-(4-methoxyphenyl)-cyclo-buten-3,4-dione (**QC^{1}OH**) from 2-chloro-1-(4-methoxyphenyl)-cyclobuten-3,4-dione (**QC^{1}Cl**) in a yield of 64%; m.p. 232°C (dec.), lit. m.p. 221–223°C [4a]. $C_{11}H_8O_4$ (204.18): calcd. C 64.71, H 3.9; found C 64.22, H 3.95. 2-Hydroxy-1-(4-hydroxyphenyl)-cyclobuten-3,4-dione (**QC^{2}OH**) from 2-chloro-1-(4-hydroxyphenyl)-cyclobuten-3,4-dione (**QC^{2}Cl**) in a yield of 26%; m.p. 273°C (dec.). $C_{10}H_6O_4$ (190.16): calcd. C 63.16, H 3.18; found C 62.86, H 3.31. 2-Hydroxy-1-[2-(1,3,3-trimethylindolin-2-ylidene)-methyl]-cylobuten-3,4-dione (**QD^{1}OH**) from 2-butoxy-1-[2-(1,3,3-trimethylindolin-2-ylidene)-methyl]-cylobuten-3,4-dione (**QD^{1}OBu**) in a yield of 24%; m.p. 207°C (dec.). $C_{16}H_{15}NO_3$ (269.30): calcd. C 71.36, H 5.61, N 5.20; found C 71.42, H 5.63, N 5.21. 1-(3,5-Dimethyl-4-ethylpyrryl)-2-hydroxycyclobuten--3,4-dione (**QEOH**) from 1-(3,5-dimethyl-4-ethyl-pyrryl)-2-butoxycyclobuten-3,4-dione (**QEOBu**) in a yield of 71%, m.p. 265°C (dec.). $C_{12}H_{13}NO_3$ (219.24): calcd. C 65.74, H 5.98, N 6.39; found C 65.70, H 5.99, N 6.39. 2-Hydroxy-1-(1,2,4-trimethyl-3-pyrryl)-cyclobuten-3,4-dione (**QFOH**) from 2-butoxy-(1,2,4-trimethyl-3-pyrryl)-cyclobuten-3,4-dione (**QFOBu**) in a yield of 46%; m.p. 243°C (dec.). $C_{11}H_{11}NO_3$ (205.21): calcd. C 64.38, H 5.40, N 6.83; found C 64.62, H 5.39, N 6.86. 1-

(2-*N,N*-dimethylamino-5-thienyl)-2-hydroxycyclobuten-3,4-dione (**QK^{1}OH**) from 2-butoxy-1-(2-*N,N*-dimethylamino-5-thienyl)-cyclobuten-3,4-dione (**QK^{1}OBu**) in a yield of 70% or from 2-chloro-1-(2-*N,N*-dimethylaminothienyl)-cyclobuten-3,4-dione (**QK^{1}Cl**) in a yield of 52%; m.p. 243°C (dec.). $C_{10}H_9NO_3S$ (223.25): calcd. C 53.80, H 4.06, N 6.27, S 14.36; found C 54.27, H 4.47, N 6.26, S 14.31. 1-(2-*N,N*-Dimethylamino-4-phenylthiazolyl)-2-hydroxycyclobuten-3,4-dione (**QL^{4}OH**) from 2-chloro-1-(2-*N,N*-dimethylamino-4-phenylthiazolyl)-cyclobuten-3,4-dione (**QL^{4}Cl**) in a yield of 23%; m.p. 284°C (dec.). $C_{15}H_{12}N_2O_3S$ (300.33): calcd. C 59.99, H 4.03, N 9.33, S 10.67; found C 59.08, H 4.30, N 9.25, S 10.60.

In contrast to what was previously described in the literature, the following semisquaric acids **QA^{2}OH** and **QC^{2}OH** were prepared.

*3.5. 1-(4-N,N-dimethylamino-2-fluorophenyl)-2-hydroxycyclobuten-3,4-dione (**QA^{2}OH**)*

N,N-dimethylamino-3-fluoroaniline (375.8 g, 2.7 mol) and squaric acid (153,9 g, 1.35 mol) were heated in a 1:1 toluene/1-butanol mixture (8.0 l) for 8 h at a Dean–Stark trap. After cooling, the symmetrically substituted squaraine **A^{2}QA^2** formed was isolated by filtration. The filtrate was heated at 99°C in vacuum at 15 torr and, after no more distillate was formed, at 200°C in vacuum at 3 torr. After 12 h the viscous residue was cooled and mixed with acetic acid (250 ml), water (250 ml), and conc. aqueous hydrochloric acid (10 ml). Then the mixture is repeatedly refluxed for 1 h and subsequently filtrated. After cooling at room temperature the product formed crystallises. It was isolated by filtration, washed with diethyl ether, and dried for 8 h at 80°C. The semisquaric acid **QA^{2}OH** formed was isolated in a yield of 11 g (3.5%); m.p. 260°C (dec.). $C_{12}H_{10}FNO_3$ (235.21): calcd. C 61.28, H 4.29, N 5.95; found C 60.59, H 4.26, N 5.72.

*3.6. 2-Hydroxy-1-(4-hydroxyphenyl)-cyclobuten-3,4-dione (**QC^{2}OH**)*

A mixture of 2-hydroxy-1-(4-methoxyphenyl)-cyclobuten-3,4-dione (**QC^{1}OH**, 2 g, 9.79 mmol), acetic acid (5 ml), and 35% aqueous hydrobromic acid (5 ml) was refluxed for 2 h. After filtration the mixture was cooled and the product crystallised was isolated by filtration. The formed semisquaric acid **QC^{2}OH** was isolated in a yield of 0.5 g (27%); m.p. 273°C (dec.). This product is identical with the one obtained as previous described.

The semisquaric acid derivative 1-(2-*N,N*-dimethylamino-5-thienyl)-2-ethoxycyclobuten-3,4-dione (**QK^{1}OEt**) has been prepared from 2-chloro-1-(2-*N,N*-dimethylaminothienyl)-cyclobuten-3,4-dione (**QK^{1}Cl**) as follow: a mixture of 2-chloro-1-(2-*N,N*-dimethylaminothienyl)-cyclobuten-3,4-dione (3.63 g, 15 mmol) and ethanol (400 ml) was refluxed for 20 h. After filtration the solution was cooled at room temperature and the product crystallised was isolated by filtration. For purification the product was extracted with *cyclo*-hexane (60 ml) by means of a Soxhlet-extractor. The ethyl semisquarate **QK^{1}OEt** is obtained in a yield of 2.5 g (66%); m.p. 167°C. $C_{12}H_{13}NO_3S$ (251.31): calcd. C 57.35, H 5.21, N 5.57, S 12.76; found C 57.72, H 5.31, N 5.44, S 12.77.

*3.7. Preparation of unsymmetrically substituted squaraines **XQY** — general procedure*

3.7.1. Method A

A mixture of the appropriate nucleophilic compound **YH** (0.01 mol) and the semisquaric acid **QXOH** (0.01 mol), dissolved in toluene (25 ml) and *n*-butanol (25 ml) was heated by using a Dean–Stark trap for 0.5–2 h. After cooling the product formed was isolated by filtration, washed with ether, and dried at 80°C.

3.7.2. Method B

To a solution or a suspension of a semisquaric acid (**QXOH**, 0.01 mol) in a mixture of toluene (25 ml) and *n*-butanol (25 ml) heated at about 80–85°C the appropriate nucleophilic compound (**YH**, 0.01 mol), solved in a mixture of toluene (25 ml) and *n*-butanol (25 ml), was added dropwise under argon and refluxed by using a Dean–Stark trap. After cooling at room temperature the product formed crystallises from the reaction mixture. It was isolated by filtration, washed with ether, and dried at 80°C.

3.7.3. Method C

To a solution or suspension of the appropriate nucleophilic compound (**YH**, 0.01 mol) in a mixture of toluene (25 ml) and 1-butanol (25 ml) the appropriate semisquaric acid (**QXOH**, 0.01 mol), dissolved or suspended in mixture of toluene (25 ml) and *n*-butanol (25 ml), was added dropwise or in small portions, respectively, under argon and refluxed by using a Dean–Stark trap. After cooling at room temperature the product formed crystallises from the reaction mixture. It was isolated by filtration, washed with ether, and dried at 80°C.

3.7.4. Method D

To a mixture of the appropriate symmetrically substituted squaraine **XQX** (0.001 mol) in 1-butanol (20 ml) the nucleophilic compound **YH** (0.001 mol) required, dissolved in 1-butanol (10 ml), was added at once. Then, the resulting mixture was heated for 1 h. After cooling, the product formed was isolated by filtration, washed with dietehyl ether, and dried at 80°C. The unsymmetrically substituted squaraines **XQY**, prepared by means of one of the previous methods, are collected in Table 2.

*3.8. Preparation of 2,4-bis-(4-methoxyphenyl)-cyclobutenium-1,3-diolate (**C^{1}QC^1**)*

3.8.1. 2,4-Bis-(4-methoxyphenyl)-3-(4-methoxyphenylacetoxy)-cyclobutenone

To a mixture of 4-methoxyphenacetylchloride (19 g, 0.103 mol) in anhydrous diethyl ether (170 ml) triethylamine (9.4 g, 0.093 mol), dissolved in anhydrous diethyl ether (170 ml) was added dropwise under stirring for 2 h. After further stirring for 45 min at room temperature the mixture was filtered, and the filtrate is concentrated in a vacuum. The residue crystallised is isolated by filtration and dried. This was obtained in a yield 3.5 g (23%); m.p. 110–112°C (114–114.5°C) [14].

3.8.2. 2,4-Bis-(4-methoxyphenyl)-3-hydroxy-cyclobutenone

A mixture of 2,4-bis-(4-methoxyphenyl)-3-(4-methoxyphenylacetoxy)-cyclobutenone (0.89 g, 2 mmol), ethanol (20 ml), water (20 ml), sodium hydroxide (1 g) was heated under stirring at 40°C for 0.5 h. After acidification of the reaction mixture with conc. hydrochloric acid, the product formed crystallises. It was isolated by filtration and purified by recrystallisation from acetone. The product was obtained in a yield 0.3 g, (51%); m.p. 150–155°C; (152–154°C) [14].

*3.8.3. 2,4-Bis-(4-methoxyphenyl)-cyclobutendylium-1,3-diolate (**C^{1}QC^1**)*

To a solution of 2,4-bis-(4-methoxyphenyl)-3-hydroxycyclobutenone (0.5 g, 1.68 mmol) in dichloromethane (100 ml) a mixture of bromine (0.32 g, 2 mmol) and dichloromethane (20 ml) was added under stirring. The product formed crystallises during the bromine addition. It was isolated by filtration, washed with diethyl ether, and dried at 60°C. The product was obtained in a yield of 0.1 g (20%); m.p. 230°C (dec.); (212–214°C) [31].

*3.9. Preparation of 1,2-bis-(2-N,N-dimethylamino-5-thienyl)-cyclobuten-3,4-dione **Q(K^1)$_2$***

To a solution of 2-chloro-1-(2-*N,N*-dimethylamino-5-thieny)-cyclobuten-3,4-dione (**QK^{1}Cl**, 605 mg, 2.5 mmol) in chlorobenzene (100 ml), a mixture of 2-*N,N*-dimethylaminothiophene (636 mg, 5 mmol) and chlorobenzene (50 ml) was added dropwise. After refluxing for 7 h the resulting mixture was filtrated and the solution was cooled in a refrigerator. The product crystallised after standing over night was isolated by filtration, washed with diethyl ether, and recrystallised from $CHCl_3$. It was obtained in a yield of 0.2 g (24%); m.p. 244°C. λ_{max}, in nm, (log ε), in chloroform: 369 (4.49), 426 (4.15), 523 (4.74). IR (KBr): 1745, 1713 cm^{-1}; ^{1}H-NMR ([d_6]DMSO): $\delta = 3.14$ (s, 12H, NCH_3), 6.35 (d, 1H, CH), 7.96 (d, 1H, CH). $C_{16}H_{16}N_2O_2S_2$ (332.45); calcd.: C 57.81 H 4.85 N 8.43 S 19.29; found C 57.72 H 4.85 N 8.58 S18.63.

*3.10. Condensation of equimolar mixtures of squaric acid **Q(OH)$_2$** with two different nucleophilic components **XH** and **YH** and analysis of the product formed*

In a mixture of 1-butanol (150 ml) and benzene (100 ml) squaric acid (1.14 g, 0.01 mol) was

added and the resulting mixture was heated at 80°C. At this temperature an equimolar mixture (0.01 mol) of two different nucleophilic compounds **XH** and **YH**, dissolved in benzene (50 ml), was added at once under stirring. In intervals of 1, 2, 5, 10, 30 and 60 min small portions (0.2 ml) of the solution were separated and analysed by means of UV–vis spectroscopy and thin-layer chromatography using silica 60 (Merck, Germany) and a mixture of toluene (10 ml), methanol (1 ml), and *cyclo*-hexane (1 ml) as eluent. The squaraines formed were detected visually. The carbocyclic or heterocyclic compounds used as educts were detected by means of an UV-lamp on the chromatographic substrate. For a quantitative estimation of the products formed the reaction probes were analysed by UV–vis spectroscopy by measuring their extinctions at wavelengths which are characteristic for the longest-wavelength maxima of the possible squaraines **XQY**, **XQX**, and **YQY**.

3.11. Preparation of a dye dispersion

A mixture consisting of the corresponding squaraine dye **XQY** (0.6 g), polyvinylbutyral (0.6 g), and THF (25 ml) was turbined in a ball-mill at 3000 rpm for 4 h. Then, the mixture was poured on a polyester sheet to a thickness of about 1–2 μm and dried for 12 h at 60°C. Finally, the spectral properties of the layers obtained were analysed spectroscopically.

Acknowledgements

The authors thank Mrs. Anett Konetzke and Mr. Gerhard Diener, Syntec GmbH, Wolfen, as well as Mrs. Anke Schroeder, FH Merseburg, for recording the IR and UV–vis spectra and for preparing the dye dispersions, respectively. They also thank Mrs. Christel Koenig, FH Merseburg, for recording the ^{1}H-NMR spectra.

References

[1] (a) Mahs G, Hegenberg P, Angew Chem 1966;78:927; Angew Chem Int Ed Engl 1966;5:888. (b) Schmidt AH, Ried W. Synthesis 1978:1. (c) Knorr H. Ried W. Synthesis 1978:649. (d) Schmidt AH, Ried W. Synthesis 1978:869. (e) Schmidt AH. Synthesis 1980:961. (f) Seitz G, Imming P. Chem Rev 1992;92:1227. (g) Frauenrath H. Oxocarbone, In: Kropf H, Schaumann E, editors. Houben-Weyl, Methoden der Organischen Chemie, vol. E 15/2. Stuttgart: Georg Thieme, 1993. p. 1468–1597.

[2] (a) Law KY, Bailey FC. Can J Chem 1986;64:2267. (b) Treibs A, Jacob K. Liebigs Ann Chem 1966;699:153. (c) Treibs A, Jacob K, Tribollet R. Liebigs Ann Chem 1970;741:101.

[3] (a) Law KY. Chem Rev 1993;93:449. (b) Law KY. J Imaging Sci Technol 1992;36:567. (c) Law KY. Organic photoconductive materials for xerographic photoreceptors, In: Nalwa HS, editor. Handbook of organic conductive molecules and polymers, vol. 1, charge-transfer salts, fullerenes, and photoconductores. New York: John Wiley & Sons, 1997. p. 487–551.

[4] (a) Law KY, Bailey FC. J Org Chem 1992;57:3278. (b) Law KY, Bailey FC. J Chem Soc, Chem Commun 1990:863. (c) Law KY. Chem Mater 1992;4:605. (d) Law KY, Bailey FC. Can J Chem 1993;71:494.

[5] Law KY. J Imaging Sci Technol 1992;36:567.

[6] (a) Chen CT, Marder SR, Cheng LT. J Chem Soc, Chem Commun 1994:259. (b) Chen CT, Marder SR, L. T. Cheng LT. J Am Chem Soc 1994;116:3117. (c) Dirk CW, Herndon WC, Cervantes-Lee F, Selnau H, Martinez S, Kalamegham P, et al. J Am Chem Soc 1995;117:2214. (d) Meyers, F, Chen, Ct, Marder, SR, Brédar, JL. Chem Eur J 1997;3:530.

[7] (a) Law KY. Chem Phys Lett 1992;200:121. (b) Law KY. J Phys Chem 1995;99:9818.

[8] (a) Terpetschnig E, Lakowicz JR. Dyes and Pigments 1993;21:227. (b) Terpetschnig E, Szmacinski H, Lakowicz JR. Analyt Chim Acta 1993;282:633. (c) Kim SH, Han SK, Kim JH, Lee MB, Koh KN, Kang SW. Dyes and Pigments 2000;44:55.

[9] Treibs A, Jacob K. Liebigs Ann Chem 1968;712:123.

[10] (a) Keil D, Hartmann H, Moschny T. Dyes and Pigments 1991;17:19. (b) Hartmann H, Keil D, Moschny T. DD 294 962; Chem Abstr 1992;116:108306. (c) Scheithauer S, Hartmann H, Mayer R. Z Chem 1968;8:181.

[11] (a) Keil D, Hartmann H. Liebigs Ann Chem 1995:979. (b) Hartmann H, Keil D, Ackermann R. DE 4 122 563; Chem Abstr 1994;120:137108.

[12] (a) Hartmann H, Moschny T, Keil D. DE 4 215 826; Chem Abstr 1994;120:273061. (b) Keil D, Hartmann H. Dyes and Pigments 2000;44:149. (c) Keil D, Hartmann H. Phosphorus, Sulfur and Silicon 1999;152:169.

[13] (a) Bellus D, Fischer H, Greunter H, Martin P. Helv Chim Acta 1978;61:1785. (b) Scheeren JW, Staps RJFM, Nivard RJT. Rec Trav Chem 1973;92:11. (c) Scheeren JW, Stevens W. Rec Trav Chem 1969;88:897. (d) Bellus D. J Am Chem Soc 1978;100:8026.

[14] Farnum DS, Johnson JR, Hess RE, Marshall TB, Webster B. J Am Chem Soc 1965;87:5191.

[15] Ried W, Schmidt AH, Kunz W. Chem Ber 1971;104:2622.

[16] (a) Schmidt AH, Maibaum H. Synthesis 1986:134. (b) Bellus D, Fischer HP. In: Geisbühler H, editor. Advances in pesticide science. Oxford: Pergamon Press, 1979. p. 373. (c) Scharf HD, Frauenrath H. In: West R, editor. Oxocarbons. New York: Academic Press, 1980. p. 101. (d) Bellus D. In: West R, editor. Oxocarbons. New York: Academic Press, 1980. p. 169.
[17] Schmidt AH, Schmitt G, Diedrich H. Synthesis 1990:579.
[18] (a) Broser W, Seekamp M. Tetrahedron Lett 1966;51: 6337. (b) Seekamp M. PhD thesis, FU, Berlin, 1969.
[19] Kampfer H, Verbille KE. US 3 617 270; Chem Abstr 1972;77:158756.
[20] Cohen S, Cohen SG. J Am Chem Soc 1966;88:1533.
[21] Kazmaier PM, Burt RA, Baranyi G. US 4 624 904; Chem Abstr 1987;106:205165.
[22] De Selms RC, Fox CJ, Riordan RC. Tetrahedron Lett 1970;781.
[23] (a) Brooker LGS, Keyes GH, Williams WW. J Am Chem Soc 1942;64:199. (b) Brooker LGS, Sklar AL, Cressman HWJ, Keyes GH, Smith LA, Sprague RH et al. J Am Chem Soc 1945;67:1875. (c) Brooker LGS. Rev Mod Phys 1942;14: 275.
[24] Fabian J, Hartmann H. Light absorption of organic colorants. Berlin, Heidelberg, New York: Springer, 1980.
[25] Reichardt C. Solvents and solvents effects in organic chemistry. Weinheim: VCH Publishers, 1988.
[26] Suppan P, Ghoneim N. Solvatochromism. Cambridge: The Royal Society of Chemistry, 1997.
[27] (a) Williams DJ. Angew Chem 1984;96:637; Angew Chem Int Ed Engl 1984;23:690. (b) Marder SR, Perry JW. Adv Mater 1993;5:804. (c) Bredas JL, Adant C, Tackx P, Persoons A. Chem Rev 1994;94:243. (d) Wolff JJ, Wortmann R. Adv Phys Org Chem 1999;32: 212. (e) Bosshard C, Sutter K, Pretre P, Hulliger J, Flörsheimer M, Kaatz P et al. Organic nonlinear optical materials. Basel: Gordon & Breach, 1995.
[28] (a) Zyss J, Ledoux I. Chem Rev 1994;94:77. (b) Marder SR, Perry JW. Adv Mater 1993;5:804. (c) Marder SR, Gorman CB, Meyers F, Perry JW, Burhill G, Brédas L et al. Science 1994;265:632.
[29] Law KY. J Phys Chem 1987;91:5184.
[30] Law KY. US 4471 041; Chem Abstr 1985;102:14790.
[31] Farnum DG, Webster B, Wolf AD. Tetrahedron Lett 1968;48:5003.
[32] Yasui S, Matsuoka M, Kitao T. Dyes and Pigments 1988;10;:13.