

# Synthesis and Spectral and Structural Elucidation of Some Pyridinium Betaines of Squaric Acid: Potential Materials for Nonlinear Optical Applications

By Tsonko M. Kolev,\* Denitsa Y. Yancheva, and Stefan I. Stoyanov

A series of substituted pyridinium betaines of squaric acid have been prepared by quaternization reaction of 3- and 4-substituted pyridines with squaric acid. The products were characterized by means of elemental analysis, melting points, and their UV-vis and IR spectra. The UV-vis spectra of all investigated compounds in five different solvents were studied in detail. The UV-vis spectral elucidation has given evidence of the clearly distinct negative solvatochromism of the pyridinium betaines of squaric acid, characteristic for compounds with a dipolar electronic ground state structure. The two absorption bands observed in the visible region show a charge-transfer character, which determines their strong dependence on the polarity of the medium and the nature of the substituent. The investigation of the spectral behavior of pyridinium betaines of squaric acid has revealed their potential nonlinear optical and electro-optical properties. Furthermore, these compounds exhibit remarkable thermal stability, required for such applications. The eventual technical application of these colored single crystals is discussed.

## 1. Introduction

The nonlinear optical properties of organic molecules and crystals are of great interest in physics, chemistry, and applied technologies, with a view to expanding the application of organic materials in nonlinear optics (NLO). The photonics and the technologies of optoelectronics based on NLO effects have gradually replaced classical electronics in communication technologies. One of the most important applications of NLO materials is their use for fast data transfer, combined with a very high signal-to-noise ratio, even over long distances. In recent years, different applications of NLO and photorefractive (PR) materials have been developed, for example, optical frequency conversion, electro-optical modulation, dynamic holography, optical writing, and optical guiding of laser beams. It is known that certain classes of organic compounds show very high NLO and electro-optical (EO) effects. The electron nonlinearity is based on molecular units containing a strongly delocalized  $\pi$ -electron system, with donor and acceptor groups at opposite ends of the molecules.

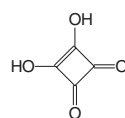
Due to its very high degree of coherence, high power per unit, and information transfer speed, laser radiation can be

used for high-speed, large-volume-transfer, high-density information writing and storage. For complete realization of the different optical functions of the laser beam, however, materials with NLO properties of second, third, and higher order are needed.

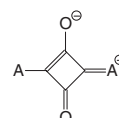
Some main classes of organic compounds with different dimensions<sup>[1–3]</sup> are known in the literature: one-dimensional (dipoles), like 4-nitroaniline and its derivatives; two-dimensional (quadrupoles), such as 4,6-dinitroresorcinol and its derivatives; and three-dimensional (octupoles), such as the guanidinium cation and its derivatives.<sup>[2,3]</sup> Organic materials can also be divided into ionic, non-ionic, and internally charged systems (betaines).

This work gives a description of the synthesis and UV-vis and IR spectral characterization of a series of 3- and 4-substituted pyridinium betaines of squaric acid. The investigated compounds have sufficient activity, good thermal stability, are relatively easy to synthesize, crystallize easily, and have appropriate flexibility for molecular design and morphology.

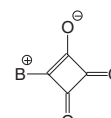
Squaric acid (**I**) gives rise to two structurally different classes of derivatives, which can be described by the general molecular structures I,II.



Squaric acid (I)



1,3-*N*-squarenes (I)



Betaines (II)

In contrast to the well-known class of *N*-squarenes (I) ( $A = NR_2$ ),<sup>[4,5]</sup> the betaines (II), like pyridinium squarate ( $B = Py$ ) for example, are poorly studied and spectral data for these compounds are missing from the literature. Betaines are obtained from a so-called “three-component” reaction, as described in the literature.<sup>[6–8]</sup>

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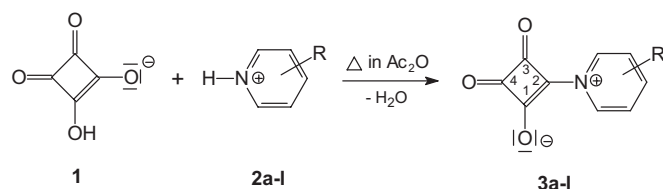
[\*\*] We thank the Ministry of Education and Science, National Council for Scientific Research (grant X-1213), German Academic Exchange Service (DAAD)–Stability Pact for South-Eastern Europe and INFU–University of Dortmund. T. K. thanks the Alexander von Humboldt Foundation, Bonn, Germany.

2-(4-Benzoylpyridinium-1-yl)-3,4-dioxocyclobut-1-en-1-olate is the first compound from this class whose molecular structure has been determined by X-ray analysis. The compound has a melting point of 301–302 °C and crystallizes easily: it crystallizes in the orthorhombic crystal group with the noncentrosymmetric space group  $Pna2_1$ .<sup>[9]</sup> All these characteristics make it a serious candidate for application in second-order NLO or any even-order NLO. It has been reported that aza-analogs of benzophenone have potential NLO activity, due to their  $\Lambda$ -type conformation, and that they crystallize preferably in noncentrosymmetric space groups.<sup>[10]</sup> Bearing in mind the high laser-damage thresholds of substituted benzophenones<sup>[11]</sup> of around 30 GW cm<sup>-2</sup>, which is the highest value measured so far, not only just for organic materials but for all other compounds as well, a sufficiently high value for the benzoylpyridinium betaine can be expected.

## 2. Results and Discussion

### 2.1. IR Spectra

A strong characteristic absorbance in the region of  $\tilde{\nu} = 1800$ – $1600$  cm<sup>-1</sup> is observed in the IR spectra of the pyridinium betaines of squaric acid **3a–l** (see Scheme 1, Table 1). The stretching vibration of the C=O group in the 4-position is characterized by a strong absorption band in the range  $\tilde{\nu} = 1797$ – $1775$  cm<sup>-1</sup> ( $\Delta\tilde{\nu} = 22$  cm<sup>-1</sup>). In most cases the intensity of this band shows a weak dependence on the nature and the position



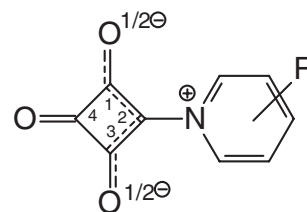
**Scheme 1.** Reaction scheme for the synthesis of pyridinium betaines of squaric acid **3a–l**.

**Table 1.** Respective R groups of the pyridinium betaines **3a–l**.

3	R	3	R
a	H	g	3-C <sub>6</sub> H <sub>5</sub> CO
b	4-Me	h	4-CH=N- NMe <sub>2</sub>
c	4-NMe <sub>2</sub>	i	3-CH=N- NMe <sub>2</sub>
d	4-CN	j	4-CH=N-
e	3-CN	k	4-CH=N-
f	4-C <sub>6</sub> H <sub>5</sub> CO	l	3-N=CH-

of the substituent R, meaning that this vibration is characteristic of the compound.

The symmetric vibration of the 1,3-carbonyl groups belonging to the fragment O–(C-1)–(C-2)–(C-3)–O of the molecular structure:



is located in the range  $\tilde{\nu} = 1769$ – $1742$  cm<sup>-1</sup> ( $\Delta\tilde{\nu} = 27$  cm<sup>-1</sup>). The bands of this vibration show only a weak dependence on the nature and the position of the substituent R, unlike the bands of the asymmetric vibration of the same fragment, which are intense and appear in the range  $\tilde{\nu} = 1748$ – $1726$  cm<sup>-1</sup> ( $\Delta\tilde{\nu} = 22$  cm<sup>-1</sup>).

The band at  $\tilde{\nu} = 1696$  cm<sup>-1</sup> in the IR spectrum of the unsubstituted compound **3a** belongs to the stretching vibration 8a of the pyridinium ring, according to the Wilson nomenclature.<sup>[12,13]</sup> Quantum-chemical calculations for this molecule confirm this interpretation. The high intensity of the band is due to the partial positive charge at the N-atom in the pyridinium ring.

The very intense band at  $\tilde{\nu} = 1615$  cm<sup>-1</sup>, predicted by ab initio (RHF) 6-31G\* and DFT (B3LYP) 6-31G\* calculations, is attributed to the 8b stretching vibration of the pyridinium ring, which is influenced by the positive charge on the N-atom.<sup>[14]</sup>

The frequency and the intensity data of the bands for the vibration of the carbonyl groups in the cyclobutenedione ring of all compounds **3a–l** are given in the experimental section.

### 2.2. UV-Vis Spectra

There is no IR or UV-vis data in the literature for this class of compounds, even though their good physical characteristics make them promising materials for NLO and EO applications.

An important requirement for applications in NLO is the efficiency of the material, a requirement directly concerning  $\lambda_{\text{max}}$ . Furthermore, the electronic-structure characterization of the compounds with internal charge separation, especially the pyridinium betaines **3a–l**, is impossible without knowing their UV-vis absorption behavior.

The pyridinium betaines **3a–l** can be divided into two groups:

- Group I: donor-acceptor-substituted pyridinium betaines, directly substituted at the aromatic ring of the pyridinium fragment.
- Group II: pyridinium betaines with substituents bound to the pyridinium ring through the –C=N– group (varying nature and length of the conjugated system).

In order to clarify the influence of the medium polarity on the absorbance and to estimate the solvatochromic properties of the compounds, the UV-vis spectra of pyridinium betaines

of squaric acid were measured in five solvents of different polarity. These compounds are poorly soluble and thus qualitative spectra were made only in acetonitrile and in 1-methylpyrrolidin-2-one (NMP); the accessed concentrations are of the order of  $2 \times 10^{-4} \text{ mol L}^{-1}$ .

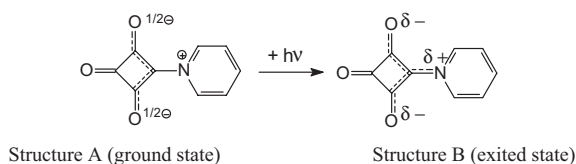
### 2.2.1. UV-Vis Spectra of the Betaines 3a–g of Group I

The spectral characteristics of pyridinium betaines 3a–g measured in 1-methylpyrrolidin-2-one solvent are given in Table 2, the UV-vis spectra of some selected betaines of Group I in NMP are shown in Figure 1, and the UV-vis spectral data of some basic pyridinium betaines of squaric acid in all solvents employed are compared in Table 3.

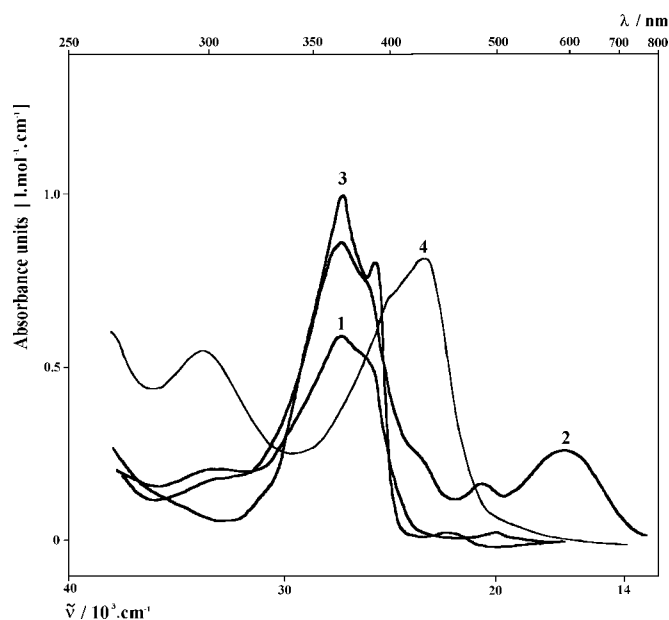
**Table 2.** Spectral characteristics of pyridinium betaines 3a–g measured in 1-methylpyrrolidin-2-one at room temperature.

Compound	Dye concentration [mol L <sup>-1</sup> ]	Spectral characteristics	
		$\lambda_{\text{max}}$ [nm]	$\epsilon$ [L mol <sup>-1</sup> cm <sup>-1</sup> ]
<b>3a</b>	$5.14 \times 10^{-4}$	302.6	3890
		367.0	11 290
		382.0 s	10 500
		496.0	430
		305.3 s	2130
<b>3b</b>	$4.23 \times 10^{-4}$	368.0	10 165
		485.5	2010
		591.7	3070
		281.0 s	4240
<b>3c</b>	$3.30 \times 10^{-4}$	370.0	30 610
		389.1	24 850
		451.5	680
		294.5	7060
<b>3d</b>	$3.40 \times 10^{-4}$	425.0	14 120
		599.0 s	360
		276.6 s	8440
		384.6	16 560
<b>3e</b>	$3.20 \times 10^{-4}$	488 s	1560
		296.7	14 470
		400.1	13 160
		532.0 s	330
<b>3f</b>	$3.04 \times 10^{-4}$	294.0 s	18 330
		391.4	33 470
		500.0 s	1000
<b>3g</b>	$2.51 \times 10^{-4}$		

2-(Pyridinium-1-yl)-3,4-dioxocyclobut-1-en-1-olate (**3a**): The resonance structures A and B (electronic ground and excited states, respectively) of **3a** are given below.



This suggestion was confirmed by the X-ray data of 2-(4-benzoylpyridinium-1-yl)-3,4-dioxocyclobut-1-en-1-olate,<sup>[9]</sup> whose molecular structure shows that the lengths of both C–O bonds



**Figure 1.** UV-vis spectra of the pyridinium betaines of squaric acid 3a–d (Group I) in NMP: 1) **3a** ( $5.14 \times 10^{-4} \text{ M}$ ); 2) **3b** ( $4.23 \times 10^{-4} \text{ M}$ ); 3) **3c** ( $3.30 \times 10^{-4} \text{ M}$ ); 4) **3d** ( $3.40 \times 10^{-4} \text{ M}$ ).

adjacent to the carbon atom bound to the pyridinium ring are equal and have an order intermediate between a single and a double bond. The IR data suggest that the vibrations of these two carbonyl groups are conjugated—symmetric and asymmetric vibrations of the fragment O–(C-1)–(C-2)–(C-3)–O appear in the spectrum.

The value of  $\Delta \tilde{\nu}_{\text{C=O}}$  ( $\tilde{\nu}_{\text{C=O}}^{\text{as}} = \tilde{\nu}_{\text{C=O}}^{\text{s}}$ ) is around  $130 \text{ cm}^{-1}$ , which is in agreement with our previous IR spectroscopy elucidation of anions of  $\beta$ -dicarbonyl compounds with structures analogous to the above mentioned fragment.<sup>[15]</sup>

The pyridinium betaine of squaric acid (PBSQ) clearly shows a negative solvatochromism, which is revealed by the hypsochromic shift of the long-wavelength CT (charge-transfer) absorption band with increasing polarity of the solvent. Moreover, the position, shape, and intensity of the bands change (Table 3). Thus, for example, the most intense band in the visible region has a vibrational structure that is evident in a nonpolar medium (like 1,2-dichloroethane; 1,2-DCE) but disappears when the medium polarity increases.

In principle, the existence of a negative solvatochromism is a sign of a dipolar ground-state structure, where the dipolarity decreases on excitation. The more polar solvent stabilizes the ground-state structure to a higher extent and this leads to an increase of the electron transition energy. In the UV region the negative solvatochromism is not so evident.

2-(4-Methylpyridinium-1-yl)-3,4-dioxocyclobut-1-en-1-olate (**3b**): The spectrum of **3b** was also measured in five standard solvents in the UV and visible regions. The concentration in the measured samples is qualitative, except for in those spectra taken in acetonitrile and NMP. Compound **3b** is the nearest analog of the unsubstituted compound (**3a**). Its negative solvatochromism is quite evident, and the most intense band in the visible region also possesses a vibrational structure in a nonpo-

**Table 3.** Solvatochromic properties of the charge-transfer absorption bands ( $\lambda_1$  and  $\lambda_2$  in nm) of some basic pyridinium betaines of squaric acid, compared with the normalized Reichardt's parameter  $E_T^N$  [16] for five selected solvents of different polarity.

Compound	Solvent ( $E_T^N$ )	1,2-DCE [a] (0.327)	NMP [b] (0.355)	CH <sub>3</sub> CN (0.460)	C <sub>2</sub> H <sub>5</sub> OH (0.654)	H <sub>2</sub> O (1.00)	$\Delta\lambda$ [c] [nm]
<b>3a</b>	$\lambda_1$	515	496	496	476	443	$\Delta\lambda_1 = 72$
	$\lambda_2$	373	367	362	353	339	$\Delta\lambda_2 = 34$
<b>3b</b>	$\lambda_1$	476	483	482	462	454	$\Delta\lambda_1 = 29$
	$\lambda_2$	388	367	375	351	339	$\Delta\lambda_2 = 49$
<b>3c</b>	$\lambda_1$	446	452	440	422	400	$\Delta\lambda_1 = 52$
	$\lambda_2$	369	370	364	357	352	$\Delta\lambda_2 = 18$
<b>3d</b>	$\lambda_1$	600	599	580	540	493	$\Delta\lambda_1 = 107$
	$\lambda_2$	441	425	422	396	380	$\Delta\lambda_2 = 61$
<b>3e</b>	$\lambda_1$	565	523	488	455	435	$\Delta\lambda_1 = 130$
	$\lambda_2$	417	391	385	375	361	$\Delta\lambda_2 = 56$

[a] 1,2-DCE = 1,2-dichloroethane. [b] NMP = 1-methylpyrrolidin-2-one. [c]  $\Delta\lambda_1$  and  $\Delta\lambda_2$  are solvatochromic shifts of the first two absorption bands in nm.

lar medium (Table 3). The introduction of a CH<sub>3</sub> group (weak donor substituent) most probably decreases the dipolar character of the ground state of **3b** and, as a result, the negative solvatochromism in the visible region is more weakly expressed than in the unsubstituted compound.

**2-[4-(Dimethylamino)pyridinium-1-yl]-3,4-dioxocyclobut-1-en-1-olate (3c):** The N(CH<sub>3</sub>)<sub>2</sub> group in the 4-position is the strongest neutral donor substituent, so a strong influence on the position and the intensity of the absorption bands could be expected. Indeed, a negative solvatochromism is observed similar to the UV-vis spectra of the above structures, although it is less distinct in the visible region (Table 3) for similar reasons to those discussed for **3b** above. However, the vibrational structure of the most intense band appears not only in 1,2-DCE, but also in the other solvents. This absorption band shows a weak dependence on the nature of the substituent (CH<sub>3</sub>- or N(CH<sub>3</sub>)<sub>2</sub>-), in contrast with the longest wavelength absorption band, which has a relatively weak intensity and shifts towards blue when the donor strength of the substituent (H < CH<sub>3</sub> < N(CH<sub>3</sub>)<sub>2</sub>) increases. For example, in CH<sub>3</sub>CN,  $\lambda_{\max}$  (H) = 496 nm,  $\lambda_{\max}$  (CH<sub>3</sub>) = 482 nm, and  $\lambda_{\max}$  (N(CH<sub>3</sub>)<sub>2</sub>) = 440 nm.

Obviously, both bands are connected with charge transfer within the dipolar structure; however, the introduction of a donor substituent in the pyridinium ring leads to a decrease of the positive charge on the N-atom and thus the charge transfer becomes less weakly expressed. The crystal structure of this compound was determined previously (space group *P2<sub>1</sub>/m*).<sup>[17]</sup>

**2-(4-Cyanopyridinium-1-yl)-3,4-dioxocyclobut-1-en-1-olate (3d):** The values of  $\lambda_1$  and  $\lambda_2$  for **3d** are shown in Table 3.  $\lambda_1$  is 107 nm, which is higher than the value for the unsubstituted betaine (PBSQ;  $\Delta\lambda_1 = 72$  nm). The second CT band ( $\lambda_2$ ) of **3d** varies from  $\lambda_{\max} = 441$  to 380 nm ( $\Delta\lambda_2 = 61$  nm), which is also significantly higher than  $\Delta\lambda_2$  of PBSQ. Hence, the CN group in the 4-position enhances the dipolar structure in comparison to the unsubstituted compound.

**2-(3-Cyanopyridinium-1-yl)-3,4-dioxocyclobut-1-en-1-olate (3e):** The values of  $\Delta\lambda_1$  and  $\Delta\lambda_2$  of **3e** are higher than the cor-

responding values for unsubstituted **3a**. A possible explanation of this phenomenon is the augmentation of the dipolar structure as a result of the inductive effect of the 3-CN group.

**2-(4-Benzoylpyridinium-1-yl)-3,4-dioxocyclobut-1-en-1-olate (3f):** The benzoyl group is a substituent with strongly expressed acceptor properties. Donor substituents destabilize the dipolar structure by decreasing the positive charge on the N-atom in the pyridinium ring, therefore an acceptor group should stabilize it. Indeed, the presence of an acceptor leads to a shift of around 40 nm towards red of both long-wavelength bands ( $\lambda_{\max} = 400$  and

532 nm; PBSQ:  $\lambda_{\max} = 367$  and 496 nm). This is evidence for the charge-transfer character of these bands. In this case the negative solvatochromism is also distinct from the more intense absorption around  $\lambda_{\max} \approx 400$  nm. Unfortunately, the limited solubility of this betaine and the low absorption peak intensity of the longest-wavelength absorption make its precise investigation difficult.

**2-(3-Benzoylpyridinium-1-yl)-3,4-dioxocyclobut-1-en-1-olate (3g):** In this case the acceptor group is in the 3-position. However, the changes in the UV-vis spectra are analogous to those of the 4-isomer. The absorption maxima keep their shapes and relative positions. Both CT bands in the visible region are at  $\lambda_{\max} = 357$  and 507 nm in acetonitrile. The first, most intense band ( $\lambda_2$ ) has a clear vibrational structure in 1,2-DCE, which can be observed also in the dipolar structures **3a–c**. The negative solvatochromism of this compound is also well expressed in the visible region.

When the characteristics of the betaines of Group I are compared, the following main features can be pointed out:

- All betaines exhibit a negative solvatochromism, but in the UV spectra of the compounds with donor substituents this is not so strongly expressed (Table 3). The reason for this is that the donor group decreases the dipolar nature of the electronic ground state structure.
- Acceptor substituents in the pyridinium ring stabilize the dipolar structure: an acceptor group in the 3-position has a weaker stabilizing effect than the same group in the 4-position, which is in accordance with general views about substituent effects (Table 3).
- The most intense CT band ( $\lambda_2$ ) shows a weak dependence on the nature of the substituent. The other CT band (low intensity, longest-wavelength absorption band  $\lambda_1$ ) shifts towards blue when the donor strength of the substituent increases.
- Acceptor substituents lead to a red-shift of both CT bands and when the acceptor is in the 4-position the effect is stronger.

## 2.2.2. UV-Vis Spectra of Betaines **3h–l** of Group II

The quantitative spectral characteristics of pyridinium betaines **3h–l** of Group II in 1-methylpyrrolidin-2-one are given in Table 4. The solvatochromic properties of the charge-transfer bands  $\lambda_1$  and  $\lambda_2$  of selected pyridinium betaines of squaric acid (Group II) are given in Table 5.

**Table 4.** Spectral characteristics of pyridinium betaines of Group II in 1-methylpyrrolidin-2-one.

Compound	Dye concentration [mol L <sup>-1</sup> ]	Spectral characteristics	
		$\lambda_{\max}$ [nm]	$\epsilon$ [L mol <sup>-1</sup> cm <sup>-1</sup> ]
<b>3h</b>	$2.65 \times 10^{-4}$	302.0	4530
		467.3	23 960
<b>3i</b>	$3.58 \times 10^{-4}$	310.0 s	6700
		338.2	9780
		369.6	11 170
		461.0 s	1120
<b>3j</b>	$3.69 \times 10^{-4}$	280.2	3660
		380.0 s	12 060
		480.0	4610
<b>3k</b>	$3.21 \times 10^{-4}$	277.8	7790
		406.5	6230
		580.3	20 090
<b>3l</b>	$3.47 \times 10^{-4}$	303.9	6810
		369.6	13 040
		386.8	12 170
		516.0 s	290

**2{[4-(E)-(Dimethylhydrazono)methyl]pyridinium-1-yl}-3,4-dioxocyclobut-1-en-1-olate (**3h**):** In this case the negative solvatochromism is rather weakly expressed. The intense CT-transition, which has a  $\lambda_2$  at 367 nm in the unsubstituted compound (Table 2), is strongly shifted by 100 nm towards red (467 nm; Table 4). On the other hand, the low intensity, longest-wavelength CT transition cannot be observed, most probably due to overlapping.

**2{3-[(E)-(Dimethylhydrazono)methyl]pyridinium-1-yl}-3,4-dioxocyclobut-1-en-1-olate (**3i**):** This structure also exhibits a negative solvatochromism, although it is more weakly expressed as a result of the presence of a donor substituent ( $-\text{N}(\text{CH}_3)_2$ ) bound to the pyridinium ring through the 3-azo-

methine group, which destabilizes the ground-state structure. It is interesting that here the long-wavelength CT band  $\lambda_1$  is shifted hypsochromically ( $\Delta\lambda_1 = 35$  nm) relative to the corresponding value for PBSQ.

**2-(4-[(E)-[(2,4-Dimethoxyphenyl)imino]methyl]pyridinium-1-yl)-3,4-dioxocyclobut-1-en-1-olate (**3j**):** The observed negative solvatochromism is clearly expressed for both CT bands (Table 5). The presence of an azomethine bridge ( $-\text{CH}=\text{N}-$ ) binding the pyridinium ring to the substituted phenyl ring, leads to a bathochromic shift of both longest-wavelength absorption bands. The extension of the chain causes a small bathochromic effect of about 10–15 nm for the most intense  $\lambda_2$  absorption band, which indicates a relatively moderate  $\pi$ -electron conjugation along the entire molecule.

**2-{[4-(E)-[4-(Dimethylamino)phenyl]imino]methyl]pyridinium-1-yl}-3,4-dioxocyclobut-1-en-1-olate (**3k**):** **3k** is an extremely polar compound. Its melting point is over 320 °C and the compound shows a strong crystallographic chromism. It is soluble only in NMP and 1,2-DCE in concentrations sufficient to obtain qualitative spectra (Fig. 2).

A strong absorbance at  $\lambda_{\max} = 407$  nm and a very strong absorbance at  $\lambda_{\max} = 580$  nm can be observed in the spectrum in NMP. The appearance of these two strong CT bands can be related to the presence of a molecular symmetry plane as a unique molecular symmetry element. The fact that the molecule has a symmetry plane in the solid state is beyond doubt, since the X-ray structures of similar donor–acceptor-substituted compounds with strong charge transfer demonstrate perfect coplanarity.<sup>[18–20]</sup> However, the structure in solution could be different as rotation around the simple bonds could generate different conformers.

It should be noted that the intensity ratio of the discussed bands could be significantly changed by addition of a nonpolar solvent, like 1,2-DCE, to an NMP solution of the compound. This change concerns two absorption bands with very interesting properties, whose detailed elucidation remains to be performed.

The good solubility of this compound only in NMP is strong evidence for its dipolar structure, as the solvent is also dipolar.

**2-{[3-[(E)-[4-(Dimethylamino)phenyl]imino]methyl]pyridinium-1-yl}-3,4-dioxocyclobut-1-en-1-olate (**3l**):** In **3l** the azomethine bridge binds the pyridinium ring to a substituted phenyl ring containing the strongest neutral donor group ( $\text{N}(\text{CH}_3)_2$ ) in the 3-position. In the visible region the two CT bands are slightly bathochromically shifted in comparison to the initial unsubstituted structure. A possible non-coplanarity of the azomethine fragment could be expected.

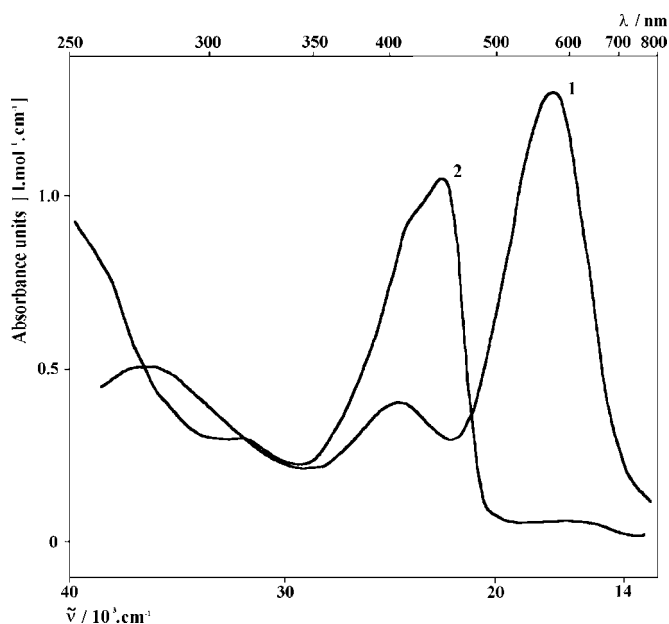
In comparison with **3k**, both CT bands are hypsochromically shifted by about  $\Delta\lambda = 60$  and 40 nm for  $\lambda_1$  and  $\lambda_2$  respectively (Table 4). Obviously in this case the different binding of the azomethine fragment ( $-\text{N}=\text{CH}-$  instead of  $-\text{CH}=\text{N}-$ ) leads to less effi-

**Table 5.** Solvatochromic properties of charge-transfer bands ( $\lambda_1$  and  $\lambda_2$ ) of selected pyridinium betaines of squaric acid (**3h**, **3j**, **3k**), compared with the normalized Reichardt's parameter  $E_T^N$  for five selected solvents of different polarity.

Compound	Solvent ( $E_T^N$ )	1,2-DCE[a] (0.327)	NMP[b] (0.355)	CH <sub>3</sub> CN (0.460)	C <sub>2</sub> H <sub>5</sub> OH (0.654)	H <sub>2</sub> O (1.00)	$\Delta\lambda$ [c] [nm]
<b>3h</b>	$\lambda_1$	—	—	—	—	—	
	$\lambda_2$	476	467	462	460	466	$\Delta\lambda_2 = 10$
<b>3j</b>	$\lambda_1$	493	480	475	472	447	$\Delta\lambda_1 = 46$
	$\lambda_2$	401	380	375	368	350	$\Delta\lambda_2 = 51$
<b>3k</b>	$\lambda_1$	582	580	579	—	—	$\Delta\lambda_1 = 3$
	$\lambda_2$	445	407	397	—	—	$\Delta\lambda_2 = 48$

[a] 1,2-DCE = 1,2-dichloroethane. [b] NMP = 1-methylpyrrolidin-2-one. [c]  $\Delta\lambda_1$  and  $\Delta\lambda_2$  are solvatochromic shifts of the first two absorption bands in nm.





**Figure 2.** UV-vis spectra of **3k**: 1) in NMP ( $3.21 \times 10^{-4}$  M); 2) in 1,2-DCE ( $2.86 \times 10^{-4}$  M).

cient conjugation and a diminished coplanarity between both fragments. Similarly to all the other compounds discussed in this work, **3i** also shows negative solvatochromism, but it is more weakly expressed than in **3j**. The reason for this is most probably the suggested noncoplanarity, leading to a relative decrease of the influence of the strong donor dimethylamino group.

Compound **3i** is soluble only in NMP and a quantitative spectrum could be measured only in this solvent (Table 4).

Comparing the characteristics of the betaines of Group II, the following fundamental aspects can be observed:

- The pyridinium betaines of this group can be divided into two subgroups: structures containing substituents directly bound to the azomethine bridge, and structures containing a substituted phenyl ring bound to the azomethine bridge.
- All betaines exhibit negative solvatochromism. In the compounds containing a donor substituent directly bound to the azomethine bridge it is more weakly expressed. The reason for this is the decrease of the dipolar character of the ground-state structure.
- A donor substituent bonded directly to the azomethine bridge in the 3-position destabilizes the betaine structure, while the same fragment in the 4-position stabilizes it.
- When the  $N(CH_3)_2$  group is directly bonded to the azomethine bridge in the 4-position (**3h**), the intense CT transition is shifted bathochromically ( $\Delta\lambda \approx 100$  nm) in comparison to the initial unsubstituted structure **3a**. When the  $N(CH_3)_2$  group is directly bonded to the azomethine bridge, but in the 3-position, the long-wavelength CT band is shifted slightly hypsochromically in comparison with the initial structure **3a**.

### 3. Conclusions

The UV-vis spectral elucidation of the pyridinium betaines of squaric acid **3a–i** gives evidence of their clearly distinct negative solvatochromism, which is characteristic of compounds with a dipolar ground-state structure. Donor substitution in the pyridinium group or through the azomethine group leads to a decrease of the negative solvatochromism as a result of electron-density transfer towards the positively charged pyridinium ring. The two absorption bands observed in the visible region have CT character, which explains their strong dependence on the polarity of the medium and the nature of the substituent. This investigation of the spectral behavior of the pyridinium betaines of squaric acid with potential NLO and EO properties could help in their complete characterization with regard to future design, synthesis, and application.

The spectral and structural elucidation of the present series of pyridinium betaines of squaric acid shows that the compounds possess a combination of properties that suggest their potential second-order and third-order NLO applications. The transparency/efficiency trade-off for some of them is optimal for these purposes. All investigated compounds, without exceptions, are crystals with high melting (decomposition) points (over  $300^\circ\text{C}$  in some cases). This good thermal stability is highly favorable for their eventual technical application.

### 4. Experimental

Heating of the pyridinium squarates, formed as intermediates upon addition of 3- or 4-substituted pyridines to squaric acid, in acetic anhydride, affords the desired pyridinium betaines of squaric acid in good yields as crystalline compounds (Scheme 1). Squaric acid **1** (1.0 g, 8.7 mmol) was dissolved in acetic anhydride (30 mL) and heated under reflux in a round-bottomed flask, equipped with a magnetic stirrer, for 10 min. A solution of the substituted pyridine **2a–i** in acetic anhydride (8.7 mmol) was added and the reaction mixture was heated under reflux for 30 min. After cooling to room temperature, the precipitate formed was filtered off and air-dried. The products were recrystallized from ethanol or acetonitrile (or dimethylsulfoxide (DMSO) in some cases).

**3a:**  $C_9H_5NO_3$ . Small, yellow plates of mp  $278\text{--}279^\circ\text{C}$  ( $H_2O$ ); yield 80 %; IR (KBr): 1792, 1762, 1743, 1697,  $1615\text{ cm}^{-1}$ ; calc. C 61.73 %, H 2.86 %, N 8.00 %; found C 62.09 %, H 3.01 %, N 8.10 %.

**3b:**  $C_{10}H_7NO_3$ . Orange plates of mp  $215\text{--}216^\circ\text{C}$  (EtOH); yield 82 %; IR (KBr): 1787,  $\sim 1760$ , 1732, 1623,  $1617\text{ cm}^{-1}$ ; calc. C 63.51 %, H 3.70 %, N 7.40 %; found C 63.54 %, H 3.65 %, N 7.42 %.

**3c:**  $C_{11}H_{10}N_2O_3$ . Yellow needles of mp  $392\text{--}395^\circ\text{C}$  (EtOH); yield 90 %; IR (KBr): 1798, 1762, 1727, 1645,  $1622\text{ cm}^{-1}$ ; calc. C 60.57 %, H 4.58 %, N 12.84 %; found C 60.59 %, H 4.74 %, N 12.65 %.

**3d:**  $C_{10}H_4N_2O_3$ . Brown needles of mp  $250\text{--}252^\circ\text{C}$  (EtOH); yield 90 %; IR (KBr): 1789, 1757, 1736, 1698,  $1626\text{ cm}^{-1}$ ; calc. C 60.02 %, H 2.00 %, N 13.99 %; found C 59.55 %, H 2.64 %, N 13.97 %.

**3e:**  $C_{10}H_4N_2O_3$ . Brown needles of mp  $220\text{--}222^\circ\text{C}$  (EtOH); yield 84 %; IR (KBr): 1786, 1746,  $1633\text{ cm}^{-1}$ ; calc. C 60.02 %, H 2.00 %, N 13.99 %; found C 59.59 %, H 2.44 %, N 13.58 %.

**3f:**  $C_{16}H_9NO_4$ . Orange needles of mp  $301\text{--}302^\circ\text{C}$  ( $CH_3CN$ ); yield 90 %; IR (KBr): 1789, 1757, 1736, 1698,  $1626\text{ cm}^{-1}$ ; calc. C 68.81 %, H 3.23 %, N 5.02 %; found C 68.52 %, H 3.40 %, N 5.27 %.

**3g:**  $C_{16}H_9NO_4$ . Brown blocks of mp  $244\text{--}245^\circ\text{C}$  ( $CH_3CN$ ); yield 82 %; IR (KBr): 1782, 1775, 1747, 1672,  $1623\text{ cm}^{-1}$ ; calc. C 68.81 %, H 3.23 %, N 5.02 %; found C 68.23 %, H 3.33 %, N 5.28 %.

**3h:**  $C_{12}H_{11}N_3O_3$ . Orange plates of mp 277–281 °C ( $CH_3CN$ ); yield 76 %; IR (KBr): 1784, ~1760, 1724, 1641, 1616  $cm^{-1}$ ; calc. C 58.77 %, H 4.49 %, N 17.14 %; found C 58.46 %, H 4.60 %, N 17.17 %.

**3i:**  $C_{12}H_{11}N_3O_3$ . Orange blocks of mp 290–291 °C ( $CH_3CN$ ); yield 85 %; IR (KBr): 1787, ~1760, 1737, 1608  $cm^{-1}$ ; calc. C 58.77 %, H 4.49 %, N 17.14 %; found C 58.74 %, H 4.64 %, N 17.40 %.

**3j:**  $C_{18}H_{14}N_2O_5$ . Small, red blocks of mp > 300 °C (DMSO); yield 85 %; IR (KBr): 1789, 1774, 1760, 1734, 1686, 1627  $cm^{-1}$ ; calc. C 63.90 %, H 4.14 %, N 8.28 %; found C 63.40 %, H 4.25 %, N 8.19 %.

**3k:**  $C_{18}H_{15}N_3O_3$ . Amorphous metallic green product of mp > 310 °C (insoluble); yield 61 %; IR (KBr): 1777, 1731, 1708, 1692, 1622, 1618  $cm^{-1}$ ; calc. C 63.70 %, H 4.42 %, N 12.39 %; found C 63.74 %, H 4.50 %, N 12.37 %.

**3l:**  $C_{18}H_{15}N_3O_3$ . Small metallic gray crystals of mp > 310 °C (insoluble); yield 52 %; IR (KBr): 1793, 1743, 1702, 1638  $cm^{-1}$ ; calc. C 63.70 %, H 4.42 %, N 12.39 %; found C 63.66 %, H 4.48 %, N 12.34 %.

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