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Synthesis of 4-[N-methyl-4-pyridinio]-phenolate (POMP) and negative solvatochromism of this model molecule in view of nonlinear optical applications

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Abstract—4-[*N*-Methyl-4-pyridinio]-phenolate or [4-(phenyloxido)-*N*-methylpyridinium, POMP] has been synthesized via Suzuki cross-coupling reaction. POMP undergoes a strong negative solvatochromism (blue shift) as the solvent polarity increases and behaves qualitatively as the famous empirical polarity parameter $E_{T}(30)$. However, it should be noted that the previously published theoretical investigations of POMP revealed unexpected difficulties in the interpretation of its structure. Interestingly, it is confirmed here in the sense that the experimental transition energy in nonpolar solvents seems by far less important than predicted by different computational methods. Therefore, POMP is highly prospective for (i) the comprehension of betaines solvatochromism, (ii) the development of new molecules with large first and second hyperpolarizabilities useful for doping polymers, the aim being to elaborate efficient processable materials for quadratic optics.

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1. Introduction

Materials with high nonlinear optical (NLO) activities are increasingly used as electro-optic switching elements for telecommunication and optical information processing. There is, thus, a tremendous need of organic molecules exhibiting large first and second hyperpolarizabilities. This is generally achieved by extended π -conjugated systems, which are mostly very solvent sensitive, undergoing bathochromic shift as the polarity increases. As a consequence, depending on the medium in which they should be embedded, the chromophore transparency in the visible region—an essential property for many photonic applications—may be eroded. Fortunately, there are also molecules which undergo negative solvatochromism, essentially merocyanines or zwitterionic compounds. We report here for the first time

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the synthesis of 4-[*N*-methyl-4-pyridinio]-phenolate or [4-(phenyloxido)-*N*-methylpyridinium, POMP], see Chart 1. This betaine is constituted by two oppositely charged heteroatomic rings linked directly. It is a model compound of a series of new zwitterionic molecules,¹ which are potentially very promising to dope photopolymerizable systems for the elaboration of organic optical devices offering good quadratic NLO properties.^{2,3} To the best of our knowledge, only two derivatives of POMP have been experimentally investigated until now, compound **2**, in view of NLO applications³ and compound **3** as a putative polarity indicator.⁴

2. Synthesis

POMP was synthesized by Suzuki cross-coupling reaction between the protected bromophenol 7 and the pyridineboronic ester 9 in THF with $Pd(PPh_3)_4$ as catalyst and CsCO₃ as base. The O-protection of 4-bromophenol 6 in methylal with P_2O_5 in CH₂Cl₂ led to 7 in good yield.⁵ The borinic ester 9 was obtained by metal-halide





Chart 1.



3. Solvatochromism

Figure 1 gives the absorption spectrum of POMP in two polarity representative solvents: water and acetonitrile. The absorption bands of betaines are generally broad.⁹ As a consequence, an overlap with the actinic light can constitute a serious drawback when the molecules are introduced in a photopolymerizable matrix. Fortunately, it can be seen that POMP has a moderately large and structureless band. On the other hand, as usual for zwitterionic structures, the solubility of POMP becomes weak for low polar solvents. However, this can be circumvented by appropriate substitutions.¹ Note that it is crucial to control the basicity of solvents. In neat solvents, especially hydroxylic ones, another band located at ca. 350 nm is observed, which can be safely attributed to the protonated form of POMP 12. Table 1 gathers the transition energies of the neutral form in the solvents spanning the available polarity range. POMP clearly





Figure 1. Transition energies of POMP versus the empirical parameter of polarity $E_{\rm T}(30)$. Insert: POMP absorption spectra in moderate (acetonitrile) and high polarity (water) solvents.

Table 1. Comparison of transition energies in kcal/mol of POMP (solvents for which solubility is good) with the data $E_T(30)^9$

	POMP		$E_{\rm T}(30)^{9}$	2^{3b} λ , nm
	kcal/mol	λ, nm		
Water	72.6	394	63.1	
Methanol	68.4	418	55.4	482
Propan-1-ol	64.9	441	50.7	
Propan-2-ol	63.7	457	48.4	
Butan-2-ol	62.2	460	47.1	
CH ₃ CN	60.6	472	45.6	503
DMSO	60.5	473	45.1	
Acetone	59.7	479	42.2	512

undergoes a strong blue shift as the polarity increases (negative solvatochromism). Moreover, the transition energy of POMP is linearly correlated with those of compound $E_{\rm T}(30)$, the well-known empirical parameter of polarity.⁹ $E_{\rm T}(30)$ is also a betaine, related to POMP but with a different location of N⁺ atom and with five phenyl substituents (Chart 1). As the slope in Figure 1 is significantly lower than unity (0.66), it can be deduced that POMP cannot compete with $E_{\rm T}(30)$ as a polarity indicator despite its strong solvatochromism.

By the way, it can be seen from Table 1 that POMP absorbs at higher energies than the POMP derivative 2, in agreement with the well-known *t*-butyl substituent effect on UV–visible absorption spectrum. More importantly, the difference in energy is very large for methanol which indicates a stronger solvatochromism for POMP compared to 2. This is due to the fact that in the case of 2, the two *t*-butyl substituents preclude any hydrogen bonding from the methanol with the oxygen atom, the basic center of betaines. Note that this effect is still much debated in the interpretation of the betaines solvatochromism.⁹

POMP being a "model" molecule, has already been theoretically investigated. Ratner and co-workers¹⁰ using the AM1 model Hamiltonian investigated the key role played by the torsional angle θ in the values of the transition dipole moment and the hyperpolarizability. More relevant to the present experimental investigation is the single configuration interaction (SCI) study on conjugated betainic chromophores based on DFT optimized geometries recently published by Fabian and co-workers.¹¹ The ground and excited state dipole moments of POMP were calculated to be $\mu_g = 15.2 \text{ D}$ and $\mu_e = 14.2 \text{ D}$, respectively. Upon excitation, the dipole moment decreases therefore, only slightly: 1D. This is qualitatively in agreement with the experimental negative solvatochromism reported presently, but can hardly explain quantitatively the strong shift observed.

Moreover, the ab initio SCI calculations correctly predict an intense electronic transition mainly of the $\pi \to \pi^*$ character for the nine betaines computed. But, in the case of the seven compounds for which experimental data are available, the SCI absorption wave numbers as well as oscillator strengths are greatly overestimated. Interestingly, most of the experimentally known absorption wave numbers are well reproduced by the energy difference of the frontier KS orbitals (DFT HOMO-LUMO energy gap). We report here their data relevant to POMP, which includes also semi-empirical methods (see Table 3 of the original paper¹¹ for details on the methods used): $SCI/6-31+G^{**}$ (324 nm); PM3/CI (435 nm); ZINDO/5 (345 nm); CNDOL/22 (366 nm); DFT (433 nm). In a first approach, the comparison with the value found in acetone $(\lambda = 479 \text{ nm})$ qualitatively confirms their conclusions. Even more remembering, that the reported computed values correspond to the gas phase (i.e., the solvent is not included in the methods used), it is instructive to 'evaluate' the corresponding experimental value of POMP. From Figure 1, it can be estimated that in a nonpolar solvent like tetramethylsilane $(E_T(30) \sim$ 30.7 kcal/mol⁻¹) POMP would absorb at 550 nm and in the gas phase $(E_T(30) \sim 27.1 \text{ kcal/mol}^{-1})$ at 580 nm. Both values are now in large disagreement with the nearest value computed within the DFT frame (433 nm).

As indicated in Chart 1, the molecular structure of POMP can be described as a combination of two limit structures/zwitterionic and quinoid. These two limit forms differ principally by their electronic distribution (the total charge of the heterocyclic ring moiety indicates the charge transferred from the donor and acceptor fragment of the molecule) and their bond lengths (especially the $C_{1'}=0$ or $C_{1'}=0^{-1}$ and $C_{4}=C_{4'}$ or $C_4 = C_{4'}$ single or double bonds). Interestingly, in his detailed theoretical investigation of the POMP structure, Fabian¹¹ was puzzled by the data obtained. Briefly said, the different pieces of information about the POMP structure were inconsistent. On one hand, a relatively long interfragmental bond C_4 - $C_{4'}$ and C-C bonds showing the expected quinoid bond alternation were found, the aromaticity criteria confirming this classification. On the other hand, these bond distances differed

Table	2.	Co	mparison	ı of	^{13}C	NMR	chemical	shifts	of	4-phenyl
pyridii	niur	n 4	, sodium	phen	olate	5, quir	none and H	POMP	in C	D ₃ OD

	4	POMP	5	0=0
C1	49	46.3		
$C_2 - C_6$	146.7	144.2		
C_3-C_5	125.8	120.7		
C_4	157.1	156.4		
$C_{4'}$	135.0	117.3	115.2	
C3-C5'	129.1	131.1	129.9	
$C_{2'} - C_{6'}$	130.9	121.7	119.7	137.6
$C_{1^{\prime}}$	133.3	177.1	167.4	188.8

not greatly from typical zwitterionic structure **1**. Even more intriguing was the large dipole moment found (see supra) and its small decrease in the excited state which implies a negative solvatochromism, as experimentally found in the present work. However, positive solvatochromism is rather expected from quinoid formula. Anyhow, inspection of the literature shows that the search for correct description of the betaine structure (zwitterionic/quinoid) is a tricky task (e.g., the recent publication of Morley and the references therein¹²).

Clearly, POMP appears as a challenge for theoretical chemistry, which underlines the interest of its present synthesis. Finally, it is useful to recall that ¹³C NMR spectroscopy is a suitable tool for the confirmation of partial positive or negative charges on certain carbon atoms. However, in the case of POMP, low solubility severely restricted the number of solvents for which reliable data are available. However, ¹³C NMR data argue in favour of a zwitterionic structure for POMP (Table 2). Actually, the data of the pyridine moiety of POMP are close to those of 4-phenyl pyridinium 4 and those of the phenyl moiety close to phenolate ion 5.

4. Conclusion

The optimization of materials for nonlinear optical devices requires on one side a thorough understanding of NLO processes involved as a function of electronic and geometrical molecular structures. On the other side, a concomitant tailoring of the doped polymers is necessary in order to be in accordance with industrial expectations. Works are in progress in these two directions with the aim to find the adequate compound among the series of POMP derivatives. By the way, we hope to shed light on the old but still unsolved debate concerning the betaine structures and their solvent dependencies.

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References and notes

- 1. Diemer, V.; Chaumeil, H.; Defoin, A.; Carré, C.; Fort, A., in preparation.
- Soppera, O.; Diemer V.; Bombenger, J.-P.; Feuillade, M.; Croutxe-Baghorn, C.; Chaumeil, H.; Defoin, A.; Mery, S.; Mager, L.; Fort, A.; Carré, C. *Proc. Macro 2004 (World Polymer Congress)-IUPAC*, Paris, 2004 (CD).
- (a) Fort, A.; Boeglin, A.; Mager, L.; Amiot, C.; Combellas, C.; Thiebault, A.; Rodriguez, V. Synth. Met. 2001, 124, 209; (b) Boeglin, A.; Fort, A.; Mager, L.; Combellas, C.; Thiebault, A.; Rodriguez, V. Chem. Phys. 2002, 282, 353; (c) Boeglin, A.; Rodriguez, V.; Combellas, C.; Diemer, V.; Chaumeil, H.; Defoin, A.; Fort, A. Proc. SPIE, Linear and Nonlinear Optics of Organic Materials 2004, 5517, 88.
- 4. Reichardt, C.; Milart, P.; Schafer, G. Liebigs Ann. Chem. 1990, 441.
- 5. Fuji, K.; Nakano, S.; Fujita, E. Synthesis 1975, 276.
- 6. Coudret, C. Synth. Commun. 1996, 26, 3543.
- 7. Combellas, C.; Subra, S.; Thiebault, A. *Tetrahedron Lett.* **1992**, *33*, 4923.
- 8. Spectroscopic data of POMP: mp(dec) = $120 \,^{\circ}$ C. ¹H NMR (400 MHz, CD₃OD, δ , ppm): 4.13 (s, 3H, N⁺– CH₃), 6.67 (d, H_{2'}, H_{6'}, 8.8 Hz), 7.76 (d, H_{3'}, H_{5'}, 8.8 Hz), 7.99 (d, H₃, H₅, 7.0 Hz), 8.34 (d, H₂, H₆, 7.0 Hz). ¹³C NMR (100.6 MHz, CD₃CN, δ , ppm): 122.0 (C_{2'}, C_{6'}), 131 (C₃, C_{3'}, C₅, C_{5'}), 142.93 (C₂, C₆). Anal. Calcd for C₁₂H₁₁NO, 2H₂O (221.25): C, 65.14; H, 6.83, N, 6.33. Found: C, 65.5; H, 6.7; N, 6.6.
- 9. Reichardt, C. Solvents and Solvents Effects in Organic Chemistry; Wiley, VCH: Weinheim, 2003.
- Albert, I. D. L.; Mark, T. J.; Ratner, M. A. J. Am. Chem. Soc. 1998, 120, 11174.
- 11. Fabian, J.; Rosquete, G. A.; Montero-Cabrera, L. A. J. *Mol. Struct. (Theochem)* **1999**, *469*, 163.
- Morley, J. O.; Parfield, J. J. Chem. Soc., Perkin Trans. 2 2002, 1698.