Second-Order Hyperpolarizability of Pyridinium Cations

Anwar, Xuan-Ming Duan, Kyoji Komatsu, Shuji Okada, Hiro Matsuda,† Hidetoshi Oikawa, and Hachiro Nakanishi*
Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aobaku, Sendai 980-77
†National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305

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The second-order hyperpolarizability (β) of pyridinium cations with cutoff (λ_{co}) shorter than 400 nm were studied by semiempirical calculation and the hyper-Rayleigh scattering (HRS) technique. The β value of 4-dimethylaminopyridinium (λ_{co}= 390 nm) was evaluated to be about 1.5 times larger than that of *p*-nitroaniline (λ_{co}= 473 nm) in methanolic solution using 1064 nm light as a fundamental beam.

A number of extensive calculation and experimental research has been devoted to find organic materials having large nonlinear optical (NLO) properties.[1,2] One of the topic in this field is to establish the materials for second harmonic generation (SHG) and optical parametric oscillation (OPO) of laser diodes, which are requested to have large second-order NLO susceptibility and absorption cutoff wavelength (λ_{co}) shorter than 400 nm. Though several electrically-neutral organic π-conjugated compounds have been proposed for such requirements, their performance is not enough for applications so far.

In our previous studies, we have found that stilbazolium derivatives have extremely large β.[3,4] Noncentrosymmetric alignment of stilbazolium in crystal was achieved by changing counter anion[5-7] and the maximum SHG coefficient d_{11} of 500 pm/V at 1064 nm for the compounds without absorption at 532 nm was obtained for the hydroxy derivative with *p*-toluenesulfonate (*p*TS).[8] However, the stilbazolium derivatives in the previous studies show λ_{co} near or longer than 400 nm. For the ionic species with λ_{co} shorter than 400 nm, *p*TS anion was found to have two-thirds of β of *p*-nitroaniline (*p*NA).[9]

In this study, we investigated cationic species without absorption in visible region. The π-conjugated cationic system we selected was substituted 1-methylpyridinium derivatives, which is considered as shrunk π-conjugation of stilbazolium to shorten λ_{co}.

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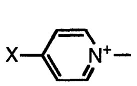

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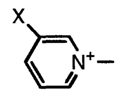

Figure 1. Chemical structures of substituted 1-methylpyridinium.

The β investigated by semiempirical calculation and hyper-Rayleigh scattering (HRS) of the substituted pyridinium derivatives are reported.

The absorption spectra were measured in about 4×10^{-5} M methanolic solution, while the cutoff wavelength was determined from the 99% transmittance of about 1×10^{-2} M methanolic solution. The calculation of fully optimized geometric structures in vacuum and their β was performed on program system MOPAC with MNDO Hamiltonian and PM3 parametrization. The calculation method was described previously.[10] Hereafter, the calculated β is abbreviated to be β_{calc}. The β of the compounds were also evaluated experimentally using the HRS technique in methanolic solution. Experimental setup for the HRS measurement and determination procedure of were previously reported in detail.[3,11,12] The determined β values by this technique were corrected for those at zero frequency using the two-level model.[13] These static β are symbolized by β_{expt}.

The chemical structure of the compounds in this study and their symbolic abbreviations are shown in Figure 1. These substituted 1-methyl-pyridinium cations were obtained as iodide by quaternalization of corresponding pyridine derivatives with

Table 1. Hammett σ constants for each substituent, absorption maximum and cutoff, and β of pyridinium cations in methanol together with those of *p*NA

Compound	σ^a	$\lambda_{max}{}^b$	$\lambda_{co}{}^b$	$\varepsilon_{max}{}^c$	$\beta_{calc}{}^d$	$\beta_{expt}{}^d$
1a	0	260	330	1.2	0.02	9
1b	-0.17	256	310	1.0	2.2	12
1c	-0.15	255	310	0.6	2.1	12
1d	-0.66	270	315	2.7	4.1	8
1e	-0.83	286	390	3.2	7.1	36
1f	0.36	267	370	0.8	2.0	7
1g	0.45	275	390	1.0	1.6	9
1h	0.66	273	370	1.0	2.5	7
2f	0.28	267	330	0.9	1.8	11
2g	0.37	264	320	0.7	1.4	9
2i	0.37	275	375	0.5	7.8	10
*p*NA[10]		371	473	1.5	6.6	15

[a]The Hammett constant σ_p and σ_m are selected for the compounds **1** and **2**, respectively, [b]in nm, [c]in $\times10^4$ mol/l.cm, [d]in $\times10^{-30}$ esu.

iodomethane in ethylacetate or in methanol. The crude products were recrystallized from methanolic solution. Results of elemental analysis for those crystals satisfied their compositions.

The β_{calc} of the cations are always larger than those of corresponding neutral pyridines, though almost no difference in absorption spectra between the corresponding cation and neutral species. For example, the β_{calc} of 4-methylpyridine, i.e. neutral species of **1b**, having λ_{max} of 254 nm is about one-seventh of that after quaternalization with only a 2-nm redshift. It can be understood that quaternalization of pyridine does not affect the extention of π-conjugation on the aromatic ring, but changes π-electron distribution due to the charge.

Table 1 represents the values of absorption maxima (λ_{max}), λ_{co}, β_{calc} and β_{expt} together with the Hammett σ constant[14] for each substituent, in which all the pyridinium have λ_{co} within UV region. For all compounds, β_{calc} are much smaller than β_{expt}. This is mainly due to solvent effects and intermolecular interactions which were not taken into account in calculation. The β vary depending on electron withdrawing or donating ability of the substituents which is represented with σ. Linear relationship between β and σ for 1,4-disubstituted benzenes has already been reported.[15] In the case of pyridinium cations, both β_{calc} and β_{expt} increase with decreasing σ especially for negative σ, though large difference were not observed for positive σ, as shown in Figure 2a-b. This correlation indicates that pyridinium cation part takes the role of an electron acceptor, therefore a strong donor substituent gives large β.

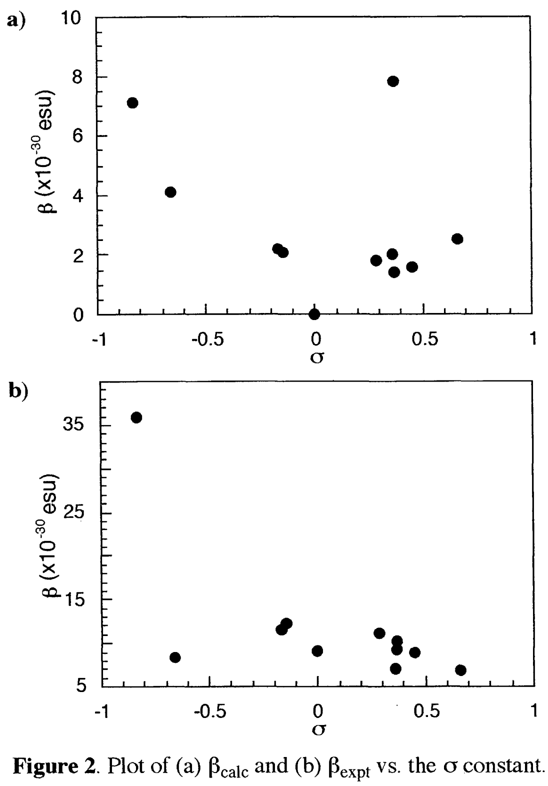

Figure 2. Plot of (a) β_{calc} and (b) β_{expt} vs. the σ constant.

Dimethylamino-substituted pyridinium **1e** with strongest donor exhibits the largest β among the compounds. The experimental β at 1064 nm of **1e** was evaluated to be 56×10^{-30} esu and is about 1.5 times larger than that of *p*NA. Since the resonance effect of HRS for **1e** is not so dominant compared with that of *p*NA at 1064 nm, the static β of **1e** becomes 2.4 times as much as that of *p*NA as shown in Table 1. One of the reasons for enhanced β of **1e** may be large ε_{max} which is the proof of the large oscillator strength from the ground state to the exited state.

In summary, we found that **1e** is a good candidate of SHG materials for laser diodes because of large β combined with short cutoff of about 390 nm. Research on complexation of **1e** with proper counter anion for noncentrosymmetric crystals is in progress.

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