-Conjugated Organic Compounds for Second-Order Nonlinear Optical Materials

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Chapter 1　General Introduction

Organic second-order nonlinear optical materials have been extensively studied by theoretical and experimental methods, since they have been expected to be used as frequency doubler, electro-optic modulator and photorefractive media. The focus of recent research has been on conjugated donor-acceptor-substituted organics, because the delocalized π-electrons of these molecules give rise to large electronic hyperpolarizabilities. The large delocalization of the π-electrons of organic conjugated molecules induces cooperative effects and produces very large nonlinear responses. However, nonsubstituted conjugated molecules as so as benzene are often centrosymmetric and the contribution of the delocalized electrons to β vanishes. The quadratic polarizability of the conjugated molecules thus arises from the distortion of the π-electron distribution caused by one or more substituents. The magnitude

and sign of the effects depend on both the nature and the number of substituents as well as the length of the conjugated system. The role of mesomeric interaction resulting in intramolecular charge transfer between conjugated donor and accepter substituents are thought to be important in organic conjugated molecules. However, the trade-off relationship between β values and absorption wavelengths of organic π-conjugated molecules have been shown clearly by many previous studies. This relationship limits the application of organic materials and they could not be used as frequency doubler or EO modulation for laser diode. Because the organic materials with larger $\chi^{(2)}$ and short absorption cutoff wavelength ($\lambda_{cutoff} <$ 400nm), which is needed for application of diode laser, could not be obtained, in order to break the trade-off relationship, I focused on organic ions species and their related compounds.

Although large macroscopic second-order optical nonlinearity of many organic ionic crystals have been reported, their microscopic second-order optical nonlinearity, β, have not yet been experimentally figured out, because the well-known EFISH method is not applicable to ionic species. Thus, for more improvement of optical nonlinearities, it is important to study the second-order hyperpolarizabilities (β) of organic π-conjugated ions, and to find the origin of β of organic π-conjugated ionic molecules and clarify the possibility of ionic species of organics for nonlinear optical materials.

The purposes of this work are listed follows:

1. Evaluating the second-order hyperpolarizabilities of organic π-conjugated ionic molecules.
2. Enhancing our understanding on the mechanism of the organic π-conjugated ionic molecules with large β values.
3. Designing the organic π-conjugated ionic molecules with large β values.
4. Investigating the influence of surroundings to molecular β value of organic π-conjugated ionic molecules.
5. Figuring out the guideline to break the trade-off relationship between the β values and absorption wavelengths of organic π-conjugated molecules.

Chapter 2 Evaluation Method of Molecular Optical Nonlinearity

The evaluation methods used in this work is introduced. Because the hyper Rayleigh scattering (HRS) method used in this study is the newest and only technique to evaluate β values of ionic species, the theory, experimental set-up and evaluation procedure are described in detail, and its advantages and limitations are pointed out. As theoretical evaluation method of β value, the time dependence Hartree-Fock (TDHF) method has been used. Here, the theory and calculation method have also been mentioned.

Chapter 3 Stilbazolium Cations

The second-order hyperpolarizabilities (β) values of stilbazolium cations (4-(2-(4-substituted phenyl)vinyl)pyridinium) were evaluated experimentally by the HRS method and theoretically by the MNDO-PM3/TDHF method. This is the first time of systematic evaluation on β values of ionic molecules.

The β values of stilbazolium cations are several times larger than those of nitrostilbenes, when compared with non-ionic molecules having similar absorption maximum. Among them, halogenated stilbazoliums showed larger β values than the unsubstituted stilbazolium with similar cutoff wavelength and absorption maximum. Chlorinated derivative was an exception with comparatively large β value in spite of its short absorption maximum wavelength. The calculated and experimental β values of stilbazolium cations show a similar dependence on the substituents, i.e. the β values generally increase with increasing electron-donating ability of the substituent at phenyl group.

The origin for enhanced β of stilbazolium derivatives was estimated to be the large difference in dipole moment between ground and excited states. This result can be explained in terms of the very strong electron-withdrawing ability of the cationic pyridinium ring.

The calculation procedure used in this study seems to be useful for the investigation of the β values of ionic organic species and for understanding origin of their large β values. The macroscopic second-order nonlinear optical coefficient d of (dimethylamino)stilbazolium p-toluenesulfonates has been calculated by oriented-gas model using the β values of (dimethylamino)stilbazolium cation obtained by experiment and calculation. The results show good agreement between the calculated and reported d constants. It was found that the experimental and calculated methods used in this study are reliable for obtained β values.

Chapter 4　Extended Conjugated Cations

The electronic structures and second-order hyperpolarizabilities (β) of extended conjugated cationic molecules with various donors, conjugated bridges, and cationic acceptors, have been investigated by the MNDO-PM3／TDHF method, and compared with nitrostilbenes.

The stilbazolium polyene analogues were found to have large β values. The β values of these polyenic cations show larger enhancement than non-ionic nitrostilbene polyene analogues. However, the increase is saturated when the number of double bonds becomes larger than 8. This result could be explained by limiting distance of the communication of electrons between donor and acceptor groups. Because the ionic compounds have large β values, the polyenic stilbazolium cations are expected to be used as electro-optic materials for application.

The stilbazolium-based cations with fused ring for extending π-conjugation system, 4-(2-(4-substituted phenyl)vinyl)quinolinium, 4-(2-(6-substituted-2-naphthyl)vinyl)pyridinium, 6-(2-(4-substituted phenyl)vinyl) isoquinolinium, etc., were investigated. The electronic structures in HOMO and LUMO of these fused ring cations were found to be efficient from that non-ionic (dimethylamino)nitrostilbene (DANS). These cationic molecules have larger $\Delta \mu$ than DANS, and the inverted μ_g and μ_e could be obtained and be tuned by changing donors, conjugated bridges, and cationic acceptors. In order to increase β values, π-conjugation extension of acceptor parts is more effective than that of conjugated bridges. The collaboration among enhancing μ_{eg}^2, $\Delta \mu$, and E_{eg}^2 have to be noted for obtained large β values. These conjugated cations have potential β values for obtained the best molecules and application as materials

for second-order nonlinear optics.

Chapter 5 Influence of Surrounding on Second-Order Hyperpolarizability for Cations

The environmental effects on electronic structures and nonlinear optical properties for stilbazolium cations have been demonstrated in two cases: One was the solvent effect and the other one was the effect from counter anion.

On the solvent effect, the calculated results obtained by the MNDO-PM3／COSMO method suggest that the solvent effect for stilbazolium cations is stronger than for non-ionic nitrostilbene derivatives, and the more stable structure in ground state of stilbazolium cation may be obtained in polar solvents than in vacuum. The β values of stilbazolium cations decrease with increasing dielectric constants of solvents. It is a different changing tendency with nitrostilbene derivatives.

On the other hand, the effect from counter anion was also discussed for (dimethylamino) stilbazolium cation (DAS$^+$) on its geometries, electronic structures and nonlinear optical properties. It was clearly demonstrated that changes in nonlinear optical properties of DA S$^+$-based zwitterion depending on the position of anion center. For both β and γ, the better selection is the type put anion center on the line obtained by extrapolation of the bond between the amino-substituted carbon of benzene ring and nitrogen atom in amino group, and the most effective points for β and γ are these distance between nitrogen atom at amino group and anion center of 11.0 Å and 4.8 Å, respectively. Though in practice, we have to take into account local field factors, this kind of theoretical consideration will constitute good guidelines for designing of zwitterion systems.

Chapter 6 Benzenesulfonate and Benzoate Anions

The electric properties and second-order hyperpolarizabilities (β) of both benzenesulfonate and benzoate anions along with their electronically neutral directives, methyl esters, for comparison, have been investigated by experimental measurement and by molecular orbital calculation.

Benzenesulfonate anions were found to have comparatively large β values of $10 \sim 20 \times 10^{-30}$ esu by measurement of the hyper Rayleigh scattering method irrespective of short cutoff wavelength within UV region. The calculated results on electronic structures of benzenesulfonate anions show that the sulfonate group plays a role of donor. Contrary to this, sulfonate methyl group of benzenesulfonate methyl esters plays a role of acceptor. The μ values of the benzenesulfonate anions decrease and β values increase with increasing electron withdrawing ability of substituents. Since the benzenesulfonate anions were found to have comparatively large β value and short cutoff wavelength, they are concluded to be worth investigating as potential chromophores for second-order nonlinear optical materials.

On the other hand, benzoate anions were also found to have comparatively large β values and short cutoff wavelengths. Like the case of benzenesulfonate anions and benzenesulfonate methyl esters, anionic carboxylate group behaves as a donor in benzoate anions, and methoxycarbonyl group shows weak electron accepting property. Substituent effect at *para-*

position of these derivatives were discussed in the context of relationship between Hammett constant and calculated values such as $\Delta \varepsilon$, μ and β. Methyl benzoates with a weak acceptor at *para*-position were found to be promising for obtaining organic second-order nonlinear optical materials of diode lasers.

Chapter 7 Chained Chromophores

A novel approach to break the trade-off relationship between second-order nonlinear optical property and absorption wavelength of organic molecules and materials is established. The chained chromophores, i.e. 4-methoxybenzoate ester oligomers, are designed as nonlinear optical active molecules which are expected to be used as chromophores for poled polymers. When the nonlinear optical moieties are combined linearly in head-to-tail manner, the μ and β will be linearly enhanced with increasing the number of moieties, n. Thus, the $\mu\beta$ of chained chromophores, which is a important factor describing efficiency of molecular alignment in poling process, will become into $n^2\mu\beta$. The calculated and experimental results supported the concept that the chained chromophoric system is actually useful to enhance poling efficiency of poled polymers.

Chapter 8 Conclusion

The results and discussions described from Chapter 3 to Chapter 7 are summarized.

論文審査の結果の要旨

　光波マニピュレーション用素子材料として期待されている有機二次非線形光学材料の高性能なものを得るためには，まず，大きな二次分子超分極率 β を持つ分子を設計，合成すること，そしてその分子を対称心のない結晶にすること，さらにその分子が相互作用する光に対して吸収のないことが必要である。しかしながら，これまで報告された有機分子は，特性と吸収の間にトレードオフ関係が存在するという問題点があった。

　そこで本研究では，今まで検討されていなかったイオン性の有機 π 共役化合物など新しい分子種を取り上げ，実験・計算の両面で β を検討し，トレードオフ打破の可能性を明らかにすることを目的とした。

　その結果，(1)本研究で用いた β の計算法及び測定法，いずれも，信頼性が高いことを明らかにし，イオン性化合物に対する分子設計法を初めて確立した。(2)これらの手法を用いて，同じ波長を持つ非イオン性分子種との比較を行った結果，イオン性分子種の方が数倍大きな β 値を持つことが分かった。(3)このようにイオン性化合物が従来のトレードオフ関係を打破できる原因を計算化学的に解析した結果，イオン性化合物では，基底状態と励起状態の双極子モーメントの差，$\Delta \mu$ が大きいためであることを明らかにした。(4)本研究で確立した計算方法を用いて，合成可能で且つ高性能な新しいイオン性分子種を多々設計，提案した。さらに，(5)イオン性分子種の β に及ぼす溶媒効果及びカウンターイオンの効果についても検討した。(6)高分子分散用の色素として，従来のトレードオフ関係を打破できる新しい分子種（チェインドクロモファー）を考案し，その性能を実証した。

　以上，著者が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示しており，よって段宣明提出の論文は博士（理学）の学位論文として合格と認める。