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# Second Order Hyperpolarizabilities of Barbituric Acid Derivatives

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Barbituric acid derivatives with electron donors at 5-position were synthesized and their second order nonlinear optical properties were investigated by electric field induced second harmonic generation (EFISH) method. It was found that barbituric acid units were strong acceptors and contributed to the large second order hyperpolarizabilities.

There is growing interest in the design of organic molecules with large hyperpolarizabilities for the future application of optical signal processing and optical computing. Many organic compounds have been synthesized and investigated in order to obtain useful nonlinear optical materials.1) Particularly molecules with intramolecular charge transfer (CT) interactions i.e., strong donor-acceptor pairs have been revealed to have large hyperpolarizabilities. An acceptor (or donor) strength should be estimated by Hammett's $\sigma$ values and actually the relationship between second order hyperpolarizabilities and $\sigma$ values was demonstrated by Katz, et al.2) However, it is known that only several $\sigma$ values of conventional substituents such as nitro, cyano, amino and hydroxy groups among the many substituents have been determined and it is difficult to determine $\sigma$ values of more complicated ones.

In the previous paper,3) we have pointed out the relationship between acceptor strength and pKa values of active methylene compounds such as nitromethane, malononitrile and cyclopentadiene, which are starting materials in the Knoevenagel reaction. Low pKa values of active methylene compounds lead to stabilization of carbanion in CT state and effective CT interactions to non-

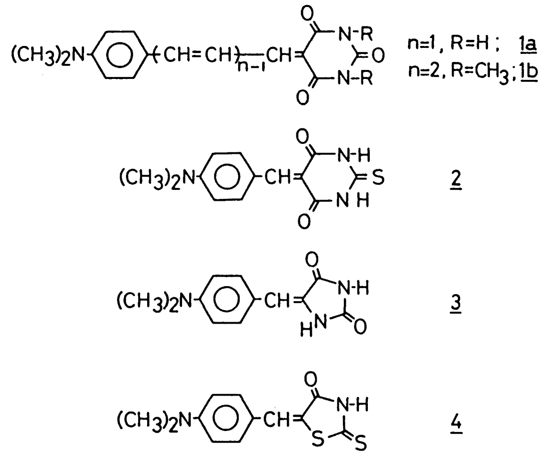

Fig. 1. Chemical structures of barbituric acid derivatives investigated in the present work.

linear optics. Therefore pKa values should be the good measure of donor-acceptor interaction as well as $\sigma$ values. From this point of view, barbituric acid is strong acid of pKa=4.01[4] and was expected to be a strong acceptor. On the other hand, Ochiai, et al. paid attention to the similar chemical structure of barbituric acid to that of urea, which is one of the most famous materials for second harmonic generation, and have observed the macroscopic second order susceptibilities of barbituric acid derivatives in crystalline powders.[5] The microscopic hyperpolarizabilities of the molecule for a series of barbituric acid derivatives, however, have never been measured.

In the present paper, we report measurements of the second order hyperpolarizabilities of barbituric acid, hydantoin and rhodanine derivatives.

The chemical structures of barbituric acid derivatives are shown in Fig. 1. Barbituric acid derivatives (1a, 1b, 2) and hydantoin derivative (3) were prepared according to the usual method.[6] Rhodanine derivative (4) purchased from Tokyo Kasei Co. Ltd. was used without further purification.

The absorption maxima of this series of molecules in dimethylsulfoxide (DMSO) solutions are listed in Table 1. 2-Thiobarbituric acid derivative 2 was bathochromic by 30 nm than barbituric acid derivative 1a. This phenomena is attributed to the effect of chalcogen at 2-position, which should be connected to the $\pi$-electron system through the partial double bond property of amide bond (3,4- or 1,6-positions). Rhodanine derivative 4 was also bathochromic by 90 nm than hydantoin derivative 3 and this is due to the same effect of chalcogen as mentioned above.

The electric field induced second harmonic generation (EFISH) method was used to determine the second order hyperpolarizabilities of molecules. The

Table 1. Second order hyperpolarizabilities and absorption maxima of molecules[a)]

| Molecule | λ max/nm | Re( $\mu_o\beta$ ) | Im( $\mu_o\beta$ ) |
|---|---|---|---|
| 1a | 470 | 630 | 0 |
| 1b | 540 | 1330 | 5200 |
| 2 | 500 | 1150 | 600 |
| 3 | 390 | 120 | 0 |
| 4 | 480 | 1050 | 310 |

a)Hyperpolarizabilities are given in units in $10^{-48}$ esu.

All samples were dissolved in dimethylsulfoxide.

Re and Im stand for real and imaginary part, respectively.

experimental method was similar to that of Garito, et al.[7)] The measurements were performed using a fundamental input beam (1.06 μm) from a Nd:YAG laser (Quanta-Ray, DCR-3D, 8 ns, 100 kW). The samples were dissolved in DMSO solutions in the concentration range from $10^{-6}$ to $10^{-2}$ mol/l. Both real and imaginary parts of $\mu_o\beta$ were obtained from the concentration dependence of second harmonic (SH) intensity, where $\mu_o$ is the dipole moment and $\beta$ is the second order hyperpolarizability. Here it should be noted that when the values of $\mu_o\beta$ were estimated, re-absorption of SH by solute molecules was taken into account and strongly related to the values of imaginary part of $\mu_o\beta$ .

The results of EFISH measurements are summarized in Table 1. The compound 1b has large imaginary part of $\mu_o\beta$ and this is attributed to the two photon absorption effect,[8)] since λ max of 1b (540 nm) is very close to second harmonics (532 nm). The real part of the product, Re( $\mu_o\beta$ ), was found to be 630 x $10^{48}$ esu in the barbituric acid derivative 1a. This value is larger than that of 2-methyl-4-nitroaniline (Re( $\mu_o\beta$ )=180 x $10^{-48}$ esu in DMSO solution), which is the typical material for second harmonic generation. The compound 1b has one more double bond compared to the chemical structure of 1a, and the value of Re( $\mu_o\beta$ ) was found to be 1330 x $10^{-48}$ esu. This value was two times larger than that of 1a. It is well known that the molecules with long conjugated chain have the large values of $\beta$ and the two photon absorption effect enhances not only Im( $\mu_o\beta$ ) but also Re( $\mu_o\beta$ ). Therefore it is difficult to justify which effects should mainly contribute to the large value of Re( $\mu_o\beta$ ) of 1b. The Re( $\mu_o\beta$ ) of 2-thiobarbituric acid derivative 2 was two times larger than that of 1a. This result is consistent with that of bathochromic shift in visible absorption of 2-thiobarbituric acid derivative. It was concluded that the $\pi$-electron system is partially extended on the chalcogen at 5-position in barbituric acid derivatives. The Re( $\mu_o\beta$ ) of hydantoin derivative 3 was found to be 5 times smaller than that of 1a. It seems that both two carbonyl groups at 4- and 6-positions in barbituric acid contribute hyperpolarizability. The Re( $\mu_o\beta$ ) of rhodanine derivative 4 was found to be 9 times larger than that of 3. This enhancement of Re( $\mu_o\beta$ ) is also attributed to the effect of chalcogens.

Studies on the optical nonlinearities of barbituric acid derivatives are further in progress.

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