Molecular hyperpolarizabilities of barbituric acid and cyclobutene-1,2-dione derivatives. Electronic and steric effects

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A series of merocyanine dyes containing various donors and barbituric acid and cyclobutene-1,2-dione moieties as the acceptors have been synthesized and their first-order hyperpolarizabilities β were determined. The β values of barbituric acid derivatives increase as the strength of the donor is increased from 4-dimethylaminophenyl to trimethylindolinyl to benzothiazolinyl, apparently due to the gradual decrease in the bond length alternation (BLA) from a large positive value to an optimum one by a stronger donor. In contrast, the β values for the cyclobutene-1,2-dione derivatives decrease with the same variation of the donors even though the cyclobutene-1,2-dione is a poorer acceptor than the barbituric acid moiety. The results have been attributed to the electron-donating ability of the donors and the increased distortion of the chromophores from planarity.

There are considerable research efforts in the field of nonlinear optics to find high performance materials for second harmonic generation or electrooptic applications.[1-11] A large number of organic compounds have been examined experimentally and by theoretical calculations to establish the structure–property relationships of the nonlinear optical molecules. Results of these studies reveal that π donor–acceptor compounds with small charge transfer (CT) energy and large differences between the ground- and excited-state dipole moments as well as large oscillator strength can exhibit large molecular second-order optical nonlinearities.[1b,7-10] According to the two level model, the β value can be expressed as eqn. (1), where ω_{eg} and ω are the

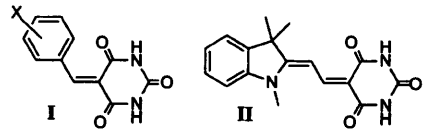
$$\beta \cong \frac{3\,e^2}{2\,\hbar m}\,\frac{\omega_{eg} f \Delta\mu}{(\omega_{eg}^2 - \omega^2)(\omega_{eg}^2 - 4\omega^2)} \qquad (1)$$

frequencies of the optical transition and fundamental light, f is the oscillator strength, and $\Delta\mu$ is the difference between the ground- and excited-state dipole moment.[1b]

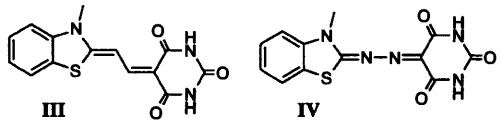
One of the strongest candidate groups for the generation of NLO organic solids is that consisting of the barbituric acid derivatives **I–IV**. It is well established that the barbituric acid moiety is a moderate electron-acceptor. In addition, its derivatives have large extinction coefficients and sharp cut-off in the UV–VIS spectra, both of which are required for a good chromophore.[5] Recently, we reported the results of hyper-Rayleigh scattering measurements for several barbituric acid derivatives.[12] Although they showed only small β values, the value could be improved if a better donor is used.

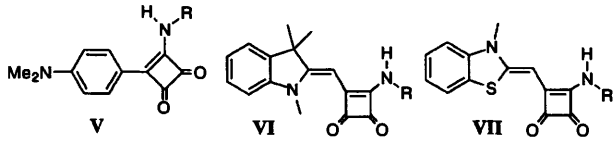
Other possible candidates for a good NLO chromophore are the squaric acid derivatives **V–VII**. Compound **Va** shows electronic absorption at relatively short wavelength with λ_{max} = 397 nm (ε = 39 000), $\lambda_{cut\ off}$ = 460 nm, but it has large molecular nonlinearity (β = 116 × 10^{-30} esu).[13] Since it is well established that the molecular hyperpolarizability is strongly influenced by relative donor–acceptor abilities,[1-9] the β value of this compound may be greatly enhanced if an appropriate donor is employed. However, the effect of varying the donor strength upon the molecular hyperpolarizability of these compounds has not been investigated.

In this work, we have synthesized compounds **I–VII** with varying donor strengths and studied the effects of their



X = *p*-Me_2N (**a**), 3,4-$(MeO)_2$ (**b**), 4-OH-3,5-$(Bu^t)_2$ (**c**)





R = (R)-CH_2CHCH_3 (**a**), (R)-$CHCH_3$ (**b**), (R)-$CHCH_2CH_3$ (**c**), (R)-$CHCH_3$ (**d**)

structures on the β values. The results of these studies are reported here.

Experimental

Materials

Substituted benzylidenebarbituric acids Ia–c. A mixture of the appropriate substituted benzaldehyde (10 mmol) and barbituric acid (10 mmol) was heated in the presence of Et_3N (12 mmol) in water–ethanol until a clear solution was obtained. The solution was heated for 2 h at that temperature. After cooling, ethanol was added to precipitate the product. The product was pulverized, filtered, washed several times with water and acetone, and then air dried. The products were usually pure enough for use. The yields, melting point, IR, NMR and analytical data of **Ia–c** are as follows. (J values in Hz).

5-(4′-N,N-Dimethylaminobenzylidene)hexahydropyrimidine-2,4,6-trione **(Ia).**—Yield (2.1 g, 81%), mp 262–263 °C (lit.,[14] mp 264 °C decomp.).

5-(3',4'-*Dimethoxybenzylidene)hexahydropyrimidine*-2,4,6-*trione* (**Ib**).—Yield (2.2 g, 80%), mp 308–312 °C (lit.,[15] mp > 290 °C).

5-(3',5'-*Di-tert-butyl-4'-hydroxybenzylidene)hexahydropyrimidine*-2,4,6-*trione* (**Ic**).—Yield (2.8 g, 81%), mp 244–246 °C, (ν_{max}/cm^{-1}) 1741 (CO), 3222 (NH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.41 (s, 18 H), 8.23 (s, 1 H), 11.15 (s, 2 H) (Found: C, 66.13; H, 7.20; N, 8.18. Calc. for $C_{19}H_{24}O_4N_2$: C, 66.26; H, 7.02; N, 8.13%).

5-[2-(1',3',3'-*Trimethylindolin*-2-*ylidene)ethylidene*]*hexahydropyrimidine*-2,4,6-*trione* (**II**).—Fischer aldehyde (5.1 g, 27 mmol) prepared by the literature procedure[16] was reacted with barbituric acid (3.4 g, 27 mmol) by the same procedure as described above. The product was purified by column chromatography using ethyl acetate as an eluent. Yield (2.2 g, 71%), mp 350 °C (decomp.), ν_{max}/cm^{-1} 1713 (CO), 3176 (NH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.64 (s, 6 H), 3.53 (s, 3 H), 7.21–7.59 (m, 5 H), 8.44 (d, 1 H), 10.53 (s, 1 H), 10.67 (s, 1 H) (Found: C, 68.58; H, 5.89; N, 9.45. Calc. for $C_{17}H_{17}O_3N_3$: C, 68.44; H, 6.08; N, 9.39%).

5-[2-(3'-*Methylbenzothiazolylidene)ethylidene*]*hexahydropyrimidine*-2,4,6-*trione* (**III**).—The solution containing 2,3-dimethylbenzothiazolium iodide (2.9 g, 10 mmol), 5-anilinomethylenebarbituric acid[16] (2.3 g, 10 mmol), and Et_3N (1.2 g, 12 mmol) in pyridine (10 ml) was refluxed for 24 h. Excess water was added to the reaction mixture to precipitate the product. The product was recrystallized from DMF. Yield (0.3 g, 10%), mp 337 °C, ν_{max}/cm^{-1} 1717 (CO), 3191 (NH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 3.80 (s, 3 H), 7.40–8.09 (m, 6 H), 10.41 (s, 1 H), 11.49 (s, 1 H) (Found: C, 55.74; H, 3.85; N, 14.16; S, 10.44. Calc. for $C_{14}H_{11}O_3N_3S$: C, 55.80; H, 3.68; N, 13.94; S, 10.64%).

5-[(3'-*Methyl*-2'-*benzothiazolylidene)hydrazono*]*hexahydropyrimidine*-2,4,6-trione (**IV**).—To a solution of 3-methyl-2-benzothiazolone hydrazone[17] (0.30 g, 1.7 mmol) and alloxane (0.29 g, 2.0 mmol) in 50 ml ethanol was added a few drops of piperidine. The solution was refluxed for 6 h, cooled to room temperature, and filtered. The yellow solid was recrystallized from DMF. Yield (0.07 g, 14%), mp 309 °C, ν_{max}/cm^{-1} 1699 (CO), 3400 (NH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 3.92 (s, 3 H), 7.36–7.93 (m, 4 H), 11.07 (s, 2 H) (Found: C, 47.82; H, 3.26; N, 22.79; S, 10.32. Calc. for $C_{12}H_9O_3N_5S$: C, 47.52; H, 2.99; N, 23.09; S, 10.57%).

1-[(1',3',3'-*Trimethylindolin*-2-*ylidene)methyl*]-2-*alkylaminocyclobutene*-3,4-*dione* (**VIa–d**).—1-(1',3',3'-Trimethylidolin-2-ylidenemethylene)-2-ethoxycyclobutene-3,4-dione[18] (0.98 g, 3.3 mmol) and appropriate amine (3.3 mmol) were dissolved in ethanol (40 ml). The solutions were stirred for 16 h at room temperature and the products were worked up as described above. The yields, melting point, IR, NMR and combustion analysis data of **VIa–d** are as follows.

1-[(1',3',3'-*Trimethylindolin*-2-*ylidene)methyl*]-2-(*R*)-(2''-*hydroxypropylamino)cyclobutene*-3,4-*dione* (**VIa**).—Yield (1.0 g, 93%), mp 210–212 °C, ν_{max}/cm^{-1} 1680, 1765 (CO), 3255 (NH), 3382 (OH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.10 (d, 3 H), 1.55 (s, 1 H), 3.60 (m, 2 H), 3.80 (m, 2 H), 4.90 (d, 1 H), 5.60 (s, 1 H), 6.90 (t, 1 H), 7.00 (d, 1 H), 7.25 (t, 1 H), 7.35 (d, 1 H), 8.65 (t, 1 H) (Found: C, 70.12; H, 6.85; N, 8.42. Calc. for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.80; N, 8.58%).

1-[(1',3',3'-*Trimethylindolin*-2-*ylidene)methyl*]-2-(*S*)-(1''-*hydroxypropan*-2''-*ylamino)cyclobutene*-3,4-*dione* (**VIb**).—Yield (0.73 g, 68%), mp 255–257 °C, ν_{max}/cm^{-1} 1680, 1760 (CO), 3194 (NH), 3414 (OH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.20 (d, 3 H), 1.62 (s, 6 H), 3.33 (s, 3 H), 3.45 (t, 2 H), 4.25 (m, 1 H), 5.02 (t, 1 H), 5.61 (s, 1 H), 7.10 (t, 1 H), 7.35 (q, 2 H), 7.65 (d, 1 H), 8.45 (d, 1 H) (Found: C, 69.93; H, 6.64; N, 8.52. Calc. for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.80; N, 8.58%).

1-[(1',3',3'-*Trimethylindolin*-2-*ylidene)methyl*]-2-(*R*)-(1''-*hydroxybutan*-2''-*ylamino)cyclobutene*-3,4-*dione* (**VIc**).—Yield (1.0 g, 89%), mp 205–207 °C, ν_{max}/cm^{-1} 1679, 1763 (CO), 3250 (NH), 3367 (OH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.45 (m, 1 H), 1.60 (d, 6 H), 1.65 (m, 1 H), 3.35 (s, 3 H), 3.45 (m, 2 H), 4.05 (m, 1 H), 4.95 (t, 1 H), 5.60 (s, 1 H), 6.95 (t, 1 H), 7.00 (d, 1 H), 7.25 (t, 1 H), 7.35 (d, 1 H), 8.30 (d, 1 H) (Found: C, 70.61; H, 7.01; N, 7.94. Calc. for $C_{20}H_{24}N_2O_3$: C, 70.58; H, 7.11; N, 8.23%).

1-[(1',3',3'-*Trimethylindolin*-2-*ylidene)methyl*]-2-(*S*)-(1''-*phenylethylamino)cyclobutene*-3,4-*dione* (**VId**).—Yield (0.8 g, 65%), mp 180–181 °C, ν_{max}/cm^{-1} 1670, 1763 (CO), 3214 (NH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.50 (d, 6 H), 1.60 (d, 3 H), 3.40 (s, 3 H), 5.45 (q, 1 H), 5.60 (s, 1 H), 7.00 (t, 1 H), 7.05 (d, 1 H), 7.25 (t, 1 H), 7.30 (t, 1 H), 7.35 (d, 1 H), 7.45 (m, 4 H), 8.85 (d, 1 H) (Found: C, 77.40; H, 6.50; N, 7.52. Calc. for $C_{24}H_{24}N_2O_2$: C, 77.40; H, 6.49; N, 7.52%).

1-[(2'-*Methylbenzothiazol*-2-*ylidene)methyl*]-2-*ethoxycyclobutene*-3,4-*dione*.—A mixture of *N*-methyl-2-methylbenzothiazolium iodide (1.9 g, 6.4 mmol), 3,4-diethoxycyclobutene-1,2-dione (1.1 g, 6.4 mmol), and triethylamine (0.65 g, 6.4 mmol) in ethanol (40 ml) was stirred for 12 h at room temperature. The product was worked up as described above. Yield (1.1 g, 60%), mp 217–219 °C, ν_{max}/cm^{-1} 1693, 1765 (CO), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.50 (t, 3 H), 3.55 (s, 3 H), 4.80 (q, 2 H), 5.40 (s, 1 H), 7.05 (t, 1 H), 7.15 (t, 1 H), 7.30 (t, 1 H), 7.45 (d, 1 H) (Found: C, 61.14; H, 4.51; N, 4.84; S, 11.36. Calc. for $C_{14}H_{13}NO_3S$: C, 61.07; H, 4.76; N, 5.09; S, 11.65%).

1-[(2'-*Methylbenzothiazol*-2-*ylidene)methyl*]-2-*alkylaminocyclobutene*-3,4-*dione* (**VIIa–d**).—1-(2'-Methylbenzothiazol-2-ylidenemethyl)-2-ethoxycyclobutene-3,4-dione (1.5 g, 5.0 mmol) and appropriate amine (5.0 mmol) were dissolved in ethanol (40 ml). The solutions were stirred for 16 h at room temperature and the products were worked up as described above. The yields, melting point, IR, NMR and combustion analysis data of **VIIa–d** are as follows.

1-[(2'-*Methylbenzothiazol*-2-*ylidene)methyl*]-2-(*R*)-(2''-*hydroxypropylamino)cyclobutene*-3,4-*dione* (**VIIa**).—Yield (1.3 g, 82%), mp 215–217 °C, ν_{max}/cm^{-1} 1659, 1763 (CO), 3224 (NH), 3425 (OH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.10 (d, 3 H), 3.45 (m, 1 H), 3.50 (s, 3 H), 3.60 (m, 1 H), 3.80 (m, 1 H), 4.90 (d, 1 H), 5.85 (s, 1 H), 7.05 (t, 1 H), 7.30 (m, 2 H), 7.65 (d, 1 H), 8.30 (t, 1 H) (Found: C, 60.59; H, 5.11; N, 8.90; S, 10.23. Calc. for $C_{16}H_{16}N_2O_3S$: C, 60.75; H, 5.10; N, 8.85; S, 10.13%).

1-[(2'-*Methylbenzothiazol*-2-*ylidene)methyl*]-2-(*S*)-(1''-*hydroxypropan*-2''-*ylamino)cyclobutene*-3,4-*dione* (**VIIb**).—Yield (1.0 g, 63%), mp 200–202 °C, ν_{max}/cm^{-1} 1687, 1760 (CO), 3225 (NH), 3382 (OH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.20 (d, 3 H), 3.40 (t, 2 H), 3.50 (s, 3 H), 4.25 (m, 1 H), 5.00 (t, 1 H), 5.80 (s, 1 H), 7.05 (t, 1 H), 7.30 (m, 2 H), 7.70 (d, 1 H), 8.20 (d, 1 H). Elemental analysis (Found: C, 60.84; H, 5.35; N, 8.84; S, 9.86. Calc. for $C_{16}H_{16}N_2O_3S$: C, 60.75; H, 5.10; N, 8.85; S, 10.13%).

1-[(2'-*Methylbenzothiazol*-2-*ylidene)methyl*]-2-(*R*)-(1''-*hydroxybutan*-2''-*ylamino)cyclobutene*-3,4-*dione* (**VIIc**).—Yield (1.3 g, 79%), mp 225–227 °C, ν_{max}/cm^{-1} 1656, 1759 (CO), 3384 (NH, OH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 0.90 (t, 3 H), 1.45 (m, 1 H), 1.65 (m, 1 H), 3.45 (t, 2 H), 3.50 (s, 3 H), 3.95 (m, 1 H), 4.90 (t, 1 H), 5.85 (s, 1 H), 7.05 (t, 1 H), 7.30 (m, 2 H), 7.70 (d, 1 H), 8.10 (d, 1 H) (Found: C, 61.91; H, 5.50; N, 8.54; S, 9.45. Calc. for $C_{17}H_{18}N_2O_3S$: C, 61.80; H, 5.49; N, 8.48; S, 9.70%).

1-[(2'-*Methylbenzothiazol*-2-*ylidene)methyl*]-2-(*S*)-(1''-*phenylethylamino)cyclobutene*-3,4-*dione* (**VIId**).—Yield (1.2 g, 66%), mp 200–202 °C, ν_{max}/cm^{-1} 1671, 1761 (CO), 3219 (NH), δ_H[300 MHz, $(CD_3)_2SO$, $SiMe_4$] 1.60 (d, 3 H), 3.50 (s, 3 H), 5.40 (m, 1 H), 5.80 (s, 1 H), 7.15 (t, 1 H), 7.35 (m, 3 H), 7.45 (m, 4 H), 7.65 (d, 1 H), 8.65 (d, 1 H) (Found: C, 69.69; H, 5.10; N, 7.45; S, 8.58. Calc. for $C_{21}H_{18}N_2O_2S$: C, 69.61; H, 5.01; N, 7.73; S, 8.85%).

Spectroscopic properties

The λ_{max} values and extinction coefficients for **I–IV** have been measured with Varian 3E UV–VIS spectrophotometer.

Table 1 Optical properties and dihedral angles between the donor and acceptor for barbituric acid derivatives[a]

Compound	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	$\beta/10^{-30}$ esu[b]	$\beta(0)/10^{-30}$ esu[c]	θ[d]/°
Ia	464	2.24	20.6	3.99	116.6
Ib	392	2.80	35.0	13.8	−96.4
Ic	478	4.73	15.3	2.35	−70.4
II	466	8.50	331	62.3	1.35
III	478	10.5	389	59.8	0.199
IV	418	2.80	*e*	*e*	0.177

[a] Solvent was Me_2SO. [b] Measured by hyper-Rayleigh scattering using 1064 nm light as the fundamental wavelength. [c] Calculated using the two-level model.[24] [d] Dihedral angle between the donor and acceptor calculated using the PM3 semiempirical calculation method. [e] Small scattering was detected.

Table 2 Optical properties and calculated dihedral angles between the donor and acceptor for cyclobutene-1,2-dione derivatives[a]

Compound	λ_{max}/nm	$\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1}	$\beta/10^{-30}$ esu[b]	$\beta(0)/10^{-30}$ esu[c]	θ[d]/°
Va[e]	397	3.90	116[f]	—	4.62
VIa	430	5.60	39.2	11.4	43.2
VIb	430	6.49	82.8	24.4	44.1
VIc	430	4.95	49.8	14.7	20.3
VId	432	5.92	94.0	26.7	51.1
VIIa	452	4.99	15.5	3.5	59.9
VIIb	452	5.85	128.8	29.3	50.7
VIIc	452	5.64	35.4	8.0	32.6
VIId	452	6.13	55.7	12.6	48.0

[a] Solvent was DMF. [b–d] See corresponding footnotes in Table 1. [e] Solvent was methanol.[10] [f] Determined by the solvatochromic method.[10]

Measurement of the β values

The β values of compounds **I**–**IV** have been determined by hyper-Rayleigh scattering using 1064 nm light as the fundamental wave as reported previously.[12]

Calculation of the structures

The structures of the compounds **I**–**IV** were estimated with the PM3 semiempirical calculation method.[19]

Results and discussion

Barbituric acid derivatives **I**–**IV** have been synthesized by the reactions of appropriate aldehydes with barbituric acid in moderate to high yields.[14,15] Cyclobutene-1,2-dione derivatives **VI**–**VII** have been synthesized by reacting 2-methylene-1′,3′,3′-trimethylindoline and 3,4-diethoxycyclobutene-1,2-dione in ethanol to afford 1-(1′,3′,3′-trimethylindolin-2-ylidenemethylene)-2-ethoxycyclobutene-3,4-dione, followed by the substitution of the ethoxy group by an appropriate amine in ethanol. The β values have been determined by hyper-Rayleigh scattering using 1064 nm light as the fundamental wavelength as reported previously.[12]

The linear and nonlinear optical properties of the barbituric acid derivatives **I**–**IV** are summarized in Table 1. In general, both the λ_{max} and β values increase as the strength of the donor is increased. Considering that these compounds have a limited conjugation length, the β values of 331–389 × 10^{-30} esu observed for **II** and **III** are remarkable. It has been well established that the β value increases until it reaches a maximum and then decreases as the bond length alternation (BLA) decreases from a large positive value towards a negative one.[5,7–10] In view of the fact that the BLA is expected to decrease as the strength of the donor increases in the order 4-dimethylaminophenyl < trimethylindolinyl < 3-methylbenzothiazolidinyl, the present result can readily be attributed to the gradual decrease in the BLA from a large positive value toward the optimum with the same variation of the donor. In addition, a PM3 semiempirical calculation[19] has revealed that **II**–**IV** are almost planar but **Ia**–**c** are significantly distorted from planarity apparently because of the steric interactions between the donor and acceptor groups. This would interrupt the conjugation between the two groups to increase the BLA for the latter. Therefore, the large β values observed for **II** and **III** can most reasonably be attributed to both the increased donor abilities and the greater planarity.

In contrast to the large β value observed for **III**, the azo compound **IV** showed negligible β value, even though it has the same donor–acceptor pair and exhibits a large ε value (Table 1). This result underlines the importance of the conjugation bridge in determining the β values.[20] It is interesting to note that the 3,4-dimethoxyphenyl derivative **Ib** exhibit a considerably larger β value than the 4-dimethylaminophenyl derivative **Ia**, despite the fact that the 3,4-dimethoxy group is usually regarded as less electron-donating than the 4-dimethylamino group. A similar result was observed in the β-nitrostyrene derivatives.[21] Although the exact reason for this dichotomy is not clear at present, the 3,4-dimethoxy substituent appears to have a unique ability in enhancing the molecular hyperpolarizability.

The importance of the steric effect in determining the molecular hyperpolarizability is also demonstrated in the β values of cyclobutene-1,2-dione derivatives **V**–**VII** (Table 2). Although the data for **Va** were determined in a different solvent, the physical properties are sufficiently different that a useful comparison can be made. The λ_{max} and ε values are much larger for **VI** and **VII** than those for **Va**, reflecting stronger electron-donating abilities of the donors in the former. Surprisingly, however, the β values for **V**–**VII** are smaller than that for **Va**. Since the cyclobutenedione group is expected to be a weaker acceptor than the barbituric acid moiety,† the BLA should decrease with a stronger donor to increase the β values (*vide supra*). However, the result is in conflict with this prediction. On the other hand, the present result can readily be attributed to the structures of **V**–**VII**. A PM3 calculation has revealed that the structure of **Va** is planar but **VI** and **VII** are twisted from planarity by the dihedral angles of 20–60° (Table 2). As previously mentioned, this would interrupt the conjugation to increase the BLA, which would in turn decrease the β value. Therefore, the smaller β values observed for **VI** and **VII** can most reasonably be attributed to the distorted structure caused by the steric interaction between the donor and acceptor. The decrease in the β value with increased distortion from planarity has also been observed in the β-nitrostyrene derivatives.[21]

It is interesting to note that the β values are also influenced by the nature of the *N*-alkyl substituent. Thus the β values for **VI** and **VII** decrease with the *N*-alkyl group variations in the order –CH(Ph)Me > $-CH(CH_2OH)Me$ > $-CH(CH_2OH)Et$ > $-CH_2CH(OH)Me$, and $-CH(CH_2OH)Me$ > –CH(Ph)Me > $-CH(CH_2OH)Et$ > $-CH_2CH(OH)Me$, respectively. The most distinct difference arises between $-CH(CH_2OH)Me$ and $-CH(CH_2OH)Et$. Since the substitution of the Me in the former by the Et is expected to influence neither the excitation energy nor the dipole moment, the β value should remain almost constant with this variation of the alkyl substituent. Although **VIb** exhibit larger ε value than **VIc**, which could in turn increase the oscillator strength f [eqn. (1)] to increase the β value, no

† The pK_a values of barbituric acid and squaric acid are 4.03 and 1, respectively.[22,23] Although the pK_a value of the methyl C–H bond in 3-methylcyclobutenedione is not available in the literature, it can be estimated to be approximately 16 based upon the ΔpK_a value of 15 for acetic acid and acetone. Therefore, the cyclobutenedione should be a much weaker electron acceptor than the barbituric acid moiety.

clear trend is observed for **VIIb** and **VIIc**. At present, the origin of the unusual substituent effect is not clear.

The present results clearly demonstrate that the molecular hyperpolarizability of the merocyanine dyes is strongly influenced not only by the electronic effect but by the steric effect.

Acknowledgements

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