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Steric Effect on the Molecular Hyperpolarizabilities of β -Nitrostyrene Derivatives

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The steric effect on the first order hyperpolarizability of the β -nitrostyrene derivatives has been investigated by comparing the β values and the dihedral angles between the aryl and nitroalkenyl groups. In general the β value increased with the electron-donating ability of the substituent. The larger β value for 3,4-dimethoxy- β -nitrostyrene than that for *p*-methoxy- β -nitrostyrene has been attributed to the lower charge transfer energy for the former. The most striking substituent effect was observed in the β -methyl- β -nitrostyrene derivatives. Thus the β values for 3,4-dimethoxy- and *p*-methoxy derivatives of the latter decreased to near zero, probably because of the large distortion from planarity caused by the steric repulsion between the β -methyl and the aryl groups. The larger β value for *p*-dimethylamino- β -methyl- β -nitrostyrene has been interpreted with an increased electron-donating ability of the substituent and increased co-planarity.

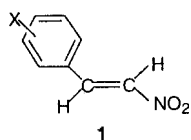
Introduction

There are considerable research efforts in the field of

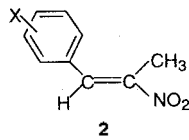
nonlinear optics to find high performance materials for second harmonic generations or electro-optic applications.¹ A large number of organic compounds have been examined

by experiments and theoretical calculations to establish the structure-property relationships of the nonlinear optical molecules.^{1,2} Results of these studies reveal that the molecular hyperpolarizability of the NLO chromophores vary strongly, depending upon the donor-acceptor abilities as well as the nature of the conjugated double bonds. In contrast, much less is known about the steric effect of the substituent.²

The steric effect of substituents has been utilized to introduce molecular chirality to the NLO chromophore to enhance the $\chi^{(2)}$ value by inducing noncentrosymmetrical arrangement in the solid state.³ If a substituent can distort the molecular plane by introducing the steric effect it may also influence the extent of π -orbital conjugation, which would in turn change the value of the first-order hyperpolarizability β . In order to provide an insight into the steric effect on the molecular hyperpolarizability we have synthesized β -nitrostyrene derivatives **1**, **2**, and compared the β values with their structures.



1
X = *p*-MeO (a), 3,4-(MeO)₂ (b),
p-Me₂N (c)



2
X = *p*-MeO (a), 3-MeO-4-OH (b),
p-Me₂N (c)

Experimental

Materials. β -Nitrostyrene derivatives have been synthesized by reacting appropriate arylaldehydes with nitromethane or nitroethane as described in the literature.⁴⁻⁶ A mixture of arylaldehyde (0.01 mol), nitromethane or nitroethane (0.02 mol), fused sodium acetate (0.02 mol) and glacial acetic acid (10 mL) were refluxed for several hours.⁴ The progress of the reaction were followed by TLC. After cooling, the mixture was extracted with ether and recrystallized from 1:4 benzene-hexane. Compounds **2b** was prepared by the same procedure after protecting the hydroxy group with acetic anhydride. Compounds **1b** was synthesized by reacting a mixture of arylaldehyde, nitromethane, and OH⁻ in 2:1 methanol-water.⁵ The melting points and spectroscopic data of these compounds were found to be consistent with the literature data,⁴⁻⁶ thus indicating successful synthesis of desired compounds.

Measurements of the β values. The β values have been determined by hyper-Rayleigh scattering using 1064 nm light as the fundamental wave as reported previously.⁷

Semiempirical Calculations. The geometries of the compounds were calculated using the PM3 procedure implemented in the MOPAC program by minimizing the energy without any restricted geometric parameters.

Results and Discussion

The X-ray crystallographic data and the results of semiempirical calculations reveal that the nitroalkenyl moieties are planar for all compounds. However, the dihedral angles between the aryl and nitroalkenyl groups vary strongly depend-

Table 1. Linear and Nonlinear Optical Properties Determined in Methanol and the Dihedral Angles

Compound	λ_{max} , nm	$10^{-4} \epsilon$	$10^{30} \beta^a$, esu	Dihedral Angle ^{b,c}
1a	348	1.96	13.3 (17)	1 (1)
1b	360	1.56	89	2 (2)
1c	434	3.17	150 (50)	0 ^d (1)
2a	330	1.64	0 ^e	27.1 (50)
2b	362	1.35	0 ^e	23.7 (37)
2c	420	2.13	79.2	4.8 (50)

^aThe numbers in the parenthesis are the literature values determined in CHCl₃.¹⁰ ^bDihedral angle between the aryl and nitroalkenyl moieties.^{9,12} ^cThe numbers in the parenthesis are calculated by using PM3. ^dEstimated from the calculated value. ^eSmall scattering was detected.

ding upon the substituents.^{8,9} Therefore, the linear and nonlinear optical properties of the β -nitrostyrene derivatives are compared with the dihedral angle with respect to the aryl group in Table 1.

The β value of 13.3×10^{-30} esu for **1a** agrees well with the literature value of 17×10^{-30} esu determined in CHCl₃.¹⁰ In general, the β value increases as the electron donating ability of the substituent increases. Considering that these compounds have a limited conjugation length, the β values of $80\text{--}150 \times 10^{-30}$ esu observed for **1b**, **1c**, and **2c** are remarkable. The largest β value for **1c** can be attributed to the electron donating ability of the substituent. Since these chromophores are expected to have a much greater bond length alternation (BLA) than the optimum value, the β value should increase with the electron-donating ability of the substituent.² In addition, the β value for **1c** in MeOH is approximately 3-fold larger than that determined in CHCl₃. The much greater solvent effect observed for **1c** can also be ascribed to the substituent effect. Since the Me₂N group is expected to stabilize the charge-separated resonance structure more than other substituents, the polarity of **1c** should be larger than those for **1a** and **1b**. This would predict that the β value of **1c** should be more sensitive to the solvent effect, as observed.^{2d} Similarly, the nearly 7-fold increase in the β value with the change in the aryl substituent from 3-methoxy (**1a**) to 3,4-dimethoxy (**1b**) can also be explained with the substituent effect. Since *m*-methoxy group is usually regarded as an electron-withdrawing group as indicated by the Hammett substituent constant of 0.12, the λ_{max} value should have decreased rather than increased, if the electronic effect were the dominant factor.^{1,2,11} On the other hand, the λ_{max} value for **1b** is larger than that for **1a**, indicating that the charge transfer energy is decreased by the same substituent. Therefore, the large increase in the β value for **1b** apparently results from the greater contribution of the latter.

The most striking substituent effect was observed in the β -methyl- β -nitrostyrene derivatives. Thus the β values for **2a** and **2b** decreased to nearly zero by the β -methyl group. Since the latter is not expected to influence the extent of π -electron delocalization significantly and the electronic effects of 3,4-dimethoxyphenyl and 3-hydroxy-4-methoxyphenyl groups are expected to be similar, the result can only be

explained with the steric effect. The dihedral angles for **1a** and **1b** determined by both X-ray diffraction and PM3 calculation are close to zero degree. Although that for **1c** is not available in the literature, it can readily be estimated to be near zero from the calculated value since the agreements between the experimental and calculated values for **1a** and **1b** are nearly perfect. In contrast, the dihedral angles are much larger for **2**, apparently because of the steric repulsion between the β -methyl and the aryl groups (*vide infra*). Therefore, the near zero β values for **2a** and **2b** can most reasonably be attributed to a greater distortion from planarity. Similar interpretation was put forwarded to explain the smaller β values observed for the merocyanine dyes.¹²

It is interesting to note that the calculated dihedral angles for **2** are much larger than those determined by X-ray diffraction. This result indicates that there is a substantial steric interaction between the aryl and β -methyl group, and the minimum energy is achieved when the molecules are distorted with such angles at the cost of the conjugation energy. The smaller dihedral angle in the solid state underlines the importance of the planarity for the molecules to pack into a crystal lattice.¹³ In addition, since the planar structure should be more polar due to the enhanced transmission of the electron density from the donor to the acceptor and the intermolecular force should increase as the polarity of the molecules increase, the molecules would have a greater tendency to attain planar structure in the solid state than in the gas phase. The largest discrepancy between the experimental and calculated values observed for **2c** can also be explained similarly because the latter effect should become more important for compounds with a stronger electron donating group. Although it is difficult to predict the conformations of **2** in methanol, it should more closely resemble those in the solid state because the polar structures would be better solvated. Therefore, the much larger β value for **2c** can most reasonably be interpreted with an increased electron-donating ability of the substituent and increased co-planarity.

In conclusion, these results clearly demonstrate that the molecular hyperpolarizabilities of the β -nitrostyrene derivatives are strongly influenced not only by the electronic effect but by the steric effect of the substituents.

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