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RELATIONSHIP AMONG MOLECULAR STRCTURES, MOLECULAR HYPERPOLARIZABILITIES AND CRYSTAL STRUCTURES OF PHENYLCYCLOBUTENEDIONES

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Abstract The relationship among molecular structures, hyperpolarizabilities and crystal structures of cyclobutenediones were discussed to predict optical non-linearity in the crystals according to the two level model.

INTRODUCTION

Having a high potential application in the future technology of opto-electronics, nonlinear optical devices such as green and blue laser and high speed optical switching, are desired. Recently, much attention are focused on organic materials, in particular, the one that shows larger nonlinearity compared to inorganic materials.

Nonlinear optical coefficients in the crystal are predicted by calculating the magnitude of hyperpolarizabilitiy β and molecular arrangement in a macroscopic level.

This paper discusses β in cyclobutenediones crystals in relation to the molecular structures. Specifially, it discusses the rotation effect of substituent to predict optical non-linearity in the crystals.

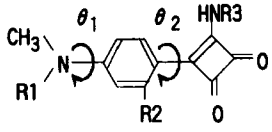
MOLECULAR STRUCTURE

The chemical structure of two phenyl-cyclobutnediones (P-CDs), DAD[1,2] and DEAC are listed in Table 1. Chirality was introduced for DAD and DEAC to create noncentrosymmetrical structure in crystallization; moreover, a bulky substituent (an ethyl group in this case) is introduced for DEAC in the ortho-position of the benzene ring to study its effect. The chemical structure suggests that the CD ring twists out of the benzene ring.

Figure 1 shows the absorption spectrum of DAD and DEAC in Dioxane and Methanol (MeOH). There were 2 absorption peaks (λ_1:380-400nm, λ_2:270-280nm) in DAD solution; however, 3 peaks (plus λ_3:340-350nm) were observed in DEAC. As the polarity of the solvent decreases smaller, a blue shift in λ_1 of DAD was observed; this suggests the polarity effect of the solvent. However, the variation of absorption coefficient of DEAC indicates geometric transformation.

A good correlation of experimental and theoretical absorption spectrum was observed. λ_1 was assigned to intramolecular charge-transfer (CT) transition from the dimethylamino group to the CD ring. λ_2 and λ_3 were assigned to the transition in the CD ring from the methyl group to the CO group and the transition from the dimethylamino group to the benzene ring.

TABLE 1 Chemical structure of P-CDs. θ_1 and θ_2 show torsional angle.



	R1	R2	R3
DAD	CH_3	H	CH_2*CHOHCH_3
DEAC	CH_3	C_2H_5	*CH(C_2H_5)CH_3OH

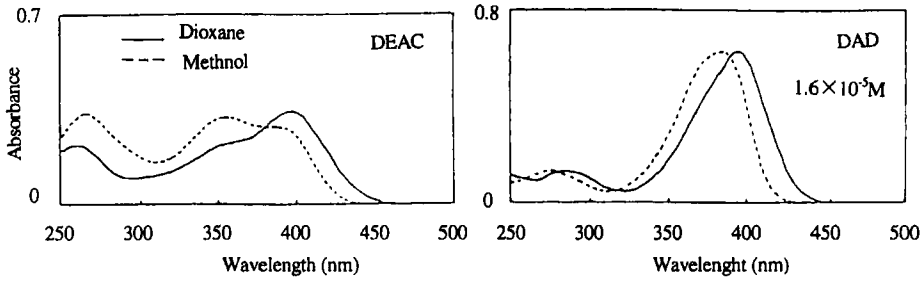


FIGURE 1 Absorption spectrum of DAD and DEAC.

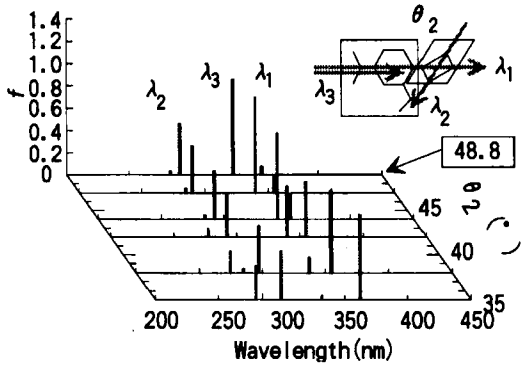


FIGURE 2 The relation between θ_2 and the absorption spectrum of DEAC.

Figure 2 shows the absorption spectrum of DEAC as the torsional angle θ_2 changes from 35° to 49° . In addition to the relatively large red shift of CT state, a decrease in oscillator strength f was observed. The theoretical absorption spectrum at 38° and 44° were similar in form to the experimental absorption in methanol and Dioxane solution. In the optimized geometry obtained by quantum-chemical calculation, the torsional angle θ_2 was estimated to be 48.8° [The calculation was done under the condition ϵ =1(vacuum)]. The theoretical results suggests that θ_2 of DEAC molecule in the solution decreases as the polarity of the solvent increases.

MOLECULAR STRUCTURE AND β VALUES

β was measured using the solvatochromic (SC) method[3] based on the two level model.

TABLE 2 $\lambda_1, f, \Delta\mu, er$ and β^{SC} of CDs.

Material	Solvent	λ_1(nm)	f	$\Delta\mu$ (D)	er	β^{SC} (10^{-30}esu)
DAD	Dioxane	388	0.6591	21.2	17.5	140
	MeOH	398	0.6603	21.5	17.8	145
DEAC	Dioxane	392	0.4658	18.3	14.9	83
	MeOH	398	0.5854	21.5	17.1	124

TABLE 3 Torsional rotation θ_1, θ_2 and β of DAD calculated by CNDO/S method.

θ_1(θ_2=0°)	0	15	30	45	60	75	90
β ($\times 10^{-30}$esu)	115	124	116	109	100	85	90.2
θ_2(θ_1=0°)	0	15	30	45	60	75	90
β ($\times 10^{-30}$esu)	115	119	106	79.1	68.5	68.6	71.7

Table 2 shows λ_1, f, er and β^{SC} of P-CDs, where e and r indicate electron charge and conjugated length, respectively. β^{SC} of DAD hardly showed the influence of solvent. β^{SC} was compensated against the polarity of the solvent[3], nevertheless, β^{SC} of DEAC decreased as the polarity of the solvent became smaller. Being proportional to r^n and dependent on the polarity of the solvent, a decrease in β^{SC} implies a change in r.

The nonlinear optical effect originates from polarization of the delocalized π-electrons. Hence, the β values are expected to be affected by the π-π overlaps between the donor/acceptor group and the conjugated π-system (substrate, e.g. benzene). Considering the two level model, the variation in r of DEAC appears to a consequence to the change of the π-π overlaps.

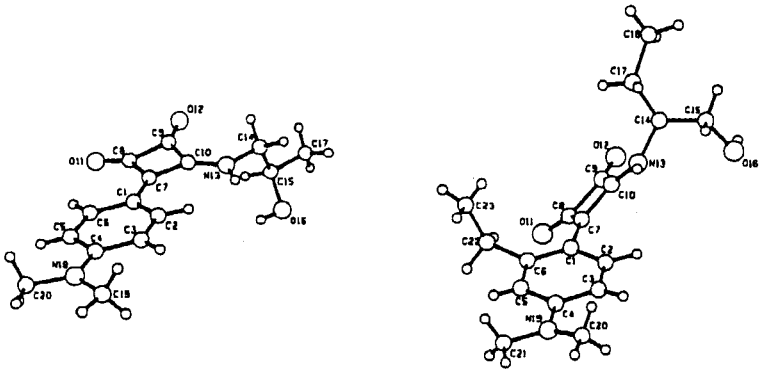
These effects were examined using DAD, as shown in Table 3. In this study, the torsional angles of the rigid groups, θ_1 and θ_2, are allowed to vary and the β-values were calculated by CNDO/S method. The torsional rotation caused variations in the β-values. These changes could be directly related to the π-π overlaps of the CD group and the dimethylamino group with the phenyl substrate. Specifically, π-π overlaps interaction of the CD group with the phenyl substrate was strong.

MOLECULAR STRUCTURE AND PREDICTED β IN THE CRYSTAL

To study the relationship between molecular structure in the crystals and β, we measured molecular structure in the crystal and calculated β in Cartesian coordinate.

Absolute molecular configurations were determined by X-ray structure analysis. Single crystals were obtained by dissolving DAD and MACD in MeOH solutions.

Figure 3 shows θ_1, θ_2 and β of the molecular structure in the crystal, with optimized geometry. C and O represent crystal and optimized structure, respectively. θ_1 of DAD and DEAC in the crystal, agreed with that of the optimized geometry. In the crystal, the CD rings of DAD were co-planar with the benzene ring, but the CD ring of DEAC twisted out of the benzene with the torsion angle θ_2 of 38.8°. θ_2 in the crystal was smaller than that in the optimized structure and β^C was larger than β^O. Considering θ_2 in the crystal, the optimized structure and the calculated absorption spectrum mentioned above, β^C in the crystal was closer to β^{SC} measured in the MeOH solvent than to the one measured in the



Material	(A) DAD	(C) DEAC
(θ 1, θ 2, β)^C	(3.9°, 3°, 142)	(0.8°, 38.8°, 127)
(θ 1, θ 2, β)^O	(1°, 7.3°, 115)	(1.8°, 48.8°, 78)

FIGURE 3 Molecular structure in the crystal, dihedral angle (θ_1, θ_2) and β. C and O represent the crystal structure and the optimized structure obtained by calculation, respectively.

Dioxane solvent. This suggests that the molecule-molecule interaction in the crystal has an influence on π - π overlaps interaction of the CD group with the phenyl substrate which results in variation of the β itself.

CONCLUSIONS

We have investigated β in the cyclobutenediones crystal in relation to the molecular structure. Specifically, the rotation effect of substituent was studied by measurement and calculation. From the results, DAD showed planar structure, but the CD ring of DEAC with steric hindrance twisted out of the benzene ring, in the solution and the crystal. Reflecting the result, β of DAD showed larger values than that of DEAC. This result is related to the intramolecular π - π overlap controlled by the torsional rotation of θ_2.

The torsional angle of DEAC suggests that it is controlled by the polarity of the solvent; moreover, it is observed that the torsional angle in the crystal is closer to the one measured in the MeOH solvent than to the one measured in the dioxane solvent. This fact indicates that the circumstance in the crystal is similar to that in the polar solvent.

Therefore, we conclude that the polar solvent is suitable for the measurement of molecular hyperpolarizabilities to predict optical non-linearity in the crystals.

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