

## Theoretical Study on the Unusual Effect of Phenyl Substituent on Second-order Hyperpolarizability

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The second-order hyperpolarizability ( $\beta_x$ ) of 2-[cyano(methoxycarbonyl)methylene]-4-phenyl-1,3-dithiole (1) is found theoretically to decrease sharply when the phenyl group is orientated at an angle of around 30° to the plane of the dithiole ring.

Second-harmonic generation (SHG) of an organic molecule is governed by both the molecular structure and the crystalline arrangement.<sup>1</sup> First, the molecule must have a large second-order hyperpolarizability ( $\beta$ ), which is dominated by the electronic properties of the whole molecule. Secondly, the crystal must have an acentric arrangement, which may be accomplished by electronic or steric properties. To obtain large  $\beta$  and large SHG values, substituents are sometimes introduced into a structural skeleton that change the properties of the molecule both electronically and sterically. The change in electronic properties is closely correlated with  $\beta$  as well as the packing of the molecules, while the change in the steric properties primarily affects the crystalline arrangement. Generally alkyl type substituents give steric effects rather than electronic effects, whereas aryl substituents and others such as amino, nitro, and cyano are expected to lead to both effects, and thus are more attractive to study. In this work, we report the unusual mesomeric effect of the phenyl group on  $\beta$  in one of the stereoisomers (1) of 2-[cyano(methoxycarbonyl)methylene]-4-phenyl-1,3-dithiole.<sup>2</sup>

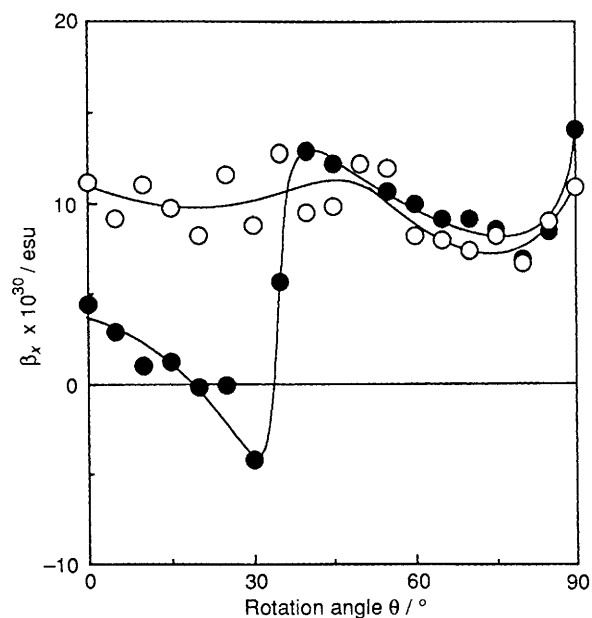
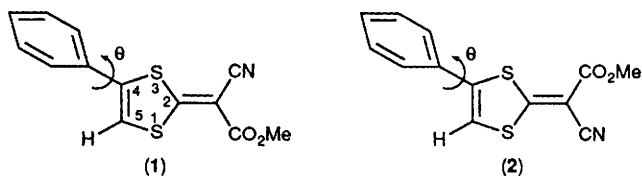
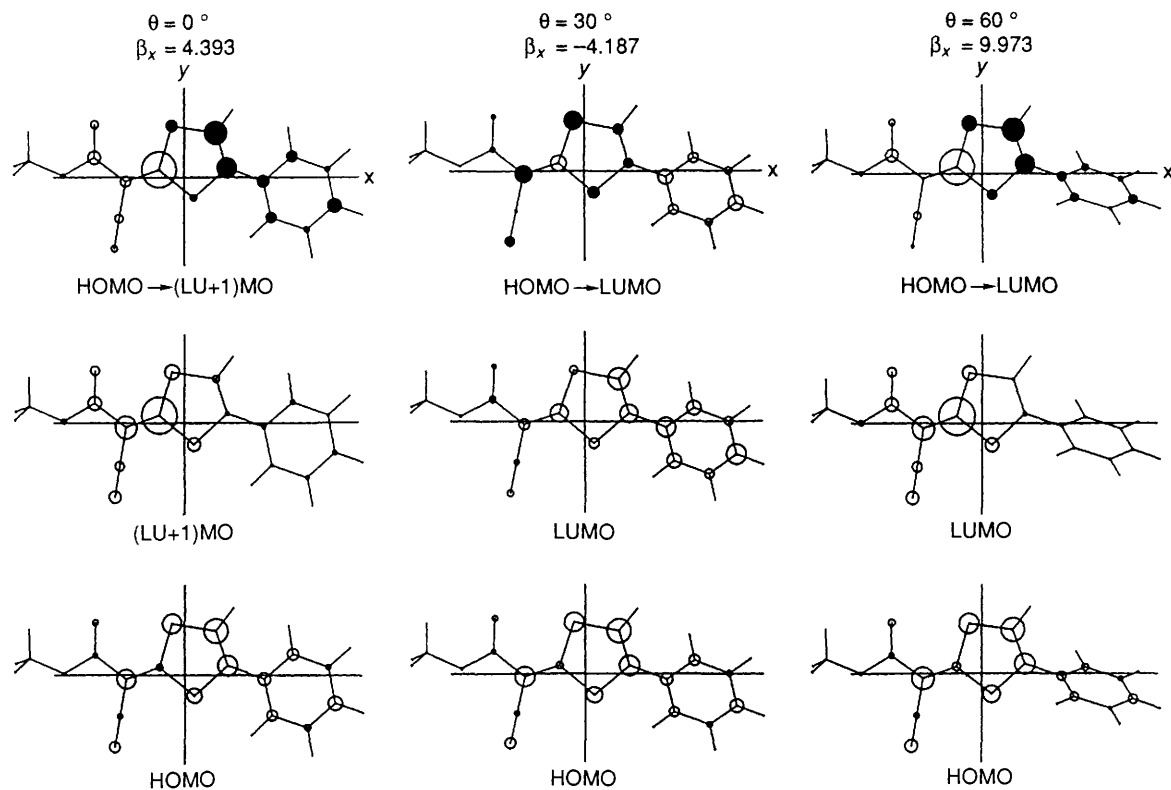
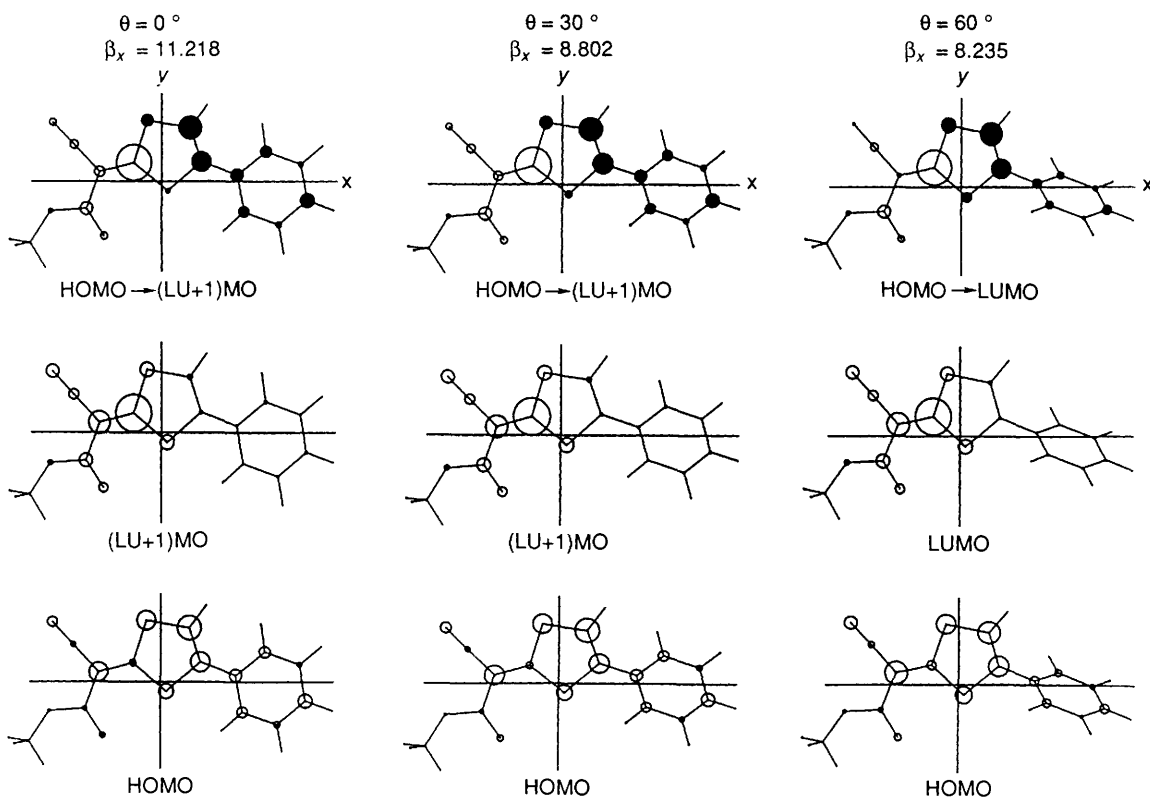


Figure 1. Relation between second-order hyperpolarizability ( $\beta_x$ ) and rotation angle ( $\theta$ ) of the phenyl group: ●, (1); ○, (2).

## (a) Isomer (1)



## (b) Isomer (2)



**Figure 2.** Electron density for (a) isomer (1); (b) isomer (2). Top figure represents the change in electron density; positive and negative values are indicated by white and black areas.

The  $\beta$  value was calculated by using a semi-empirical SCF-CI basis set (CNDO/S MO method<sup>3</sup>) and the second-order perturbation theory equation for  $\beta$  with a method using the sum over all singly excited states (SOS)<sup>4</sup> at an applied frequency of 1.064  $\mu\text{m}$ . Before the CNDO/S calculation, the molecular structures of (1) and (2) were optimized by the MNDO MO method<sup>5</sup> using the Fletcher-Powell algorithm. In the CNDO/S calculation, two-centre coulomb integrals were calculated by the Mataga formula and d-orbitals were used. The configuration interaction (CI) calculations included 60 singly excited configurations, which was sufficient for our purpose.

Figure 1 shows the relations between the rotational angle ( $\theta$ ) of the phenyl ring and the calculated  $\beta_x$  value<sup>†</sup> of (1) and (2). It should be noted that  $\beta_x$  of (2) is almost independent of  $\theta$  while  $\beta_x$  of (1) depends significantly upon  $\theta$ . The characteristic result concerning (1) is that  $\beta_x$  has trough (negative) at *ca.* 30° and a maximum at *ca.* 40°. Interestingly, other calculated physical properties such as dipole moment and total energy showed only monotonic changes for both (1) and (2).

To account for the behaviour of  $\beta_x$  of (1), we analysed the electronic configurations which largely contribute to  $\beta_x$ . Figure 2(a) and (b) shows the changes in the electron populations of the molecular orbitals of (1) and (2), respectively, corresponding to the most strongly contributing electron configuration at longer wavelength. When  $\theta$  is less than *ca.* 30°, the HOMO  $\rightarrow$  (LU + 1)MO transition dominates the electronic transition for both (1) and (2), while above *ca.* 30° the HOMO  $\rightarrow$  LUMO transition becomes dominant. Below *ca.* 30°, the direction of the dipole moment change from HOMO to (LU + 1)MO is positive in both isomers. At 30°, however, it becomes negative only in the case of (1), and returns to a positive value at more than 30°. In the isomer (2),

no such behaviour was observed. All these findings relating to the dipole moment are readily compatible with the dependency of  $\beta_x$  on  $\theta$  shown in Figure 1.

In most of the HOMO  $\rightarrow$  (LU + 1)MO transitions of (1), electron transfer occurs primarily from the 4- and 5-positions to the 2-position and consequently the dipole moment gives a positive change. At  $\theta = \text{ca. } 30^\circ$ , however, the electron transfer indicated above occurs to a much lower extent and the electron migration into the phenyl ring carbons becomes prominent, which is responsible for the reversion of the dipole moment change. This suggests that in the isomer (1) the phenyl substituent behaves as an electron-accepting group when  $\theta$  is *ca.* 30°. In other orientations, however, the phenyl group appears to have electron-donating ability. Although the origin of the unusual effect is ambiguous at present, it may be due to the special interaction of the orbitals between the phenyl group and the sulphur atom at the 3-position.

In this work, we have theoretically found an abnormal decrease of the  $\beta_x$  value for (1) in a certain conformation. This suggests that aromatic groups may be able to generate a special mesomeric effect on  $\beta$  values, and that they may be used to control  $\beta$  in non-linear optical materials.

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<sup>†</sup> In this work, a vectorial value  $\beta_x$  is used instead of the third-rank tensor, calculated by the following equation:

$$\beta_x = \beta_{xxx} + (1/3) \sum_{j \neq x} (\beta_{xjj} + 2 \beta_{jjx})$$