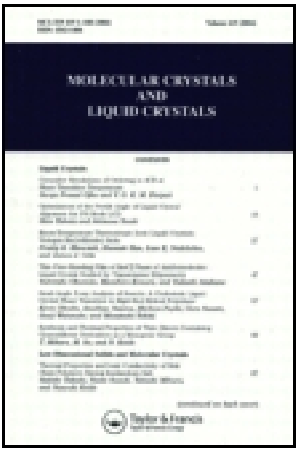

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# Novel Molecular Design for Enhanced Second-Order Nonlinear Optical Response with Wide Transparency: Cyanovinyl Aromatics

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# NOVEL MOLECULAR DESIGN FOR ENHANCED SECOND-ORDER NONLINEAR OPTICAL RESPONSE WITH WIDE TRANSPARENCY: CYANOVINYL AROMATICS

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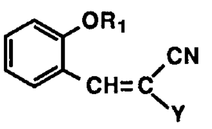
Abstract Several cyanovinyl aromatics and related compounds were newly designed and synthesized for the enhancement of second-order nonlinear optical susceptibility (β) without narrowing the optical transparency. The values of net dipole moment and second-order nonlinear optical susceptibility were tuned by control of vector direction of dipole moment and β in tetra-substituted benzene compounds.

## INTRODUCTION

A lot of efforts have been done to search for new organic materials that possess large second-order optical nonlinearities and also have suitable physical properties for practical applications such as crystal growth, wide optical transparency and wide acceptance for phase-matching. From the view point of chemistry, systematic ideas of molecular design have succeeded to some degree in the enhancement of molecular second-order optical susceptibility (β). From the view point of physics, the molecular orientation in the crystalline state significantly influences on macroscopic second-order nonlinear optical responses. Several approaches have been taken to control the polar orientation of molecules in crystalline state such as introducing steric hindrance,[1] hydrogen bonding,[2] chiral center[3], combination of these factors,[4] and reducing the electrostatic dipole-dipole interaction.[5]

The molecular origin of β in organic molecules has been mainly studied by the structure-property relationships. These researches suggest that organic molecules which consist of a π-electron conjugated system terminated with a donor(D) and acceptor(A) pair have a large value of β. According to a two-level model, β is proportional to the charge-transfer (CT) between the first molecular excited state and the ground state ($\Delta\mu$),[6] oscillator strength, and so on.[7] However, the absorption maximum, (optical absorption edge) and the magnitude of β cannot be independently optimized in wellstudies class of CT compounds, *e.g.*, benzene and stilbene derivatives substituted with D and/or A groups in *para*-position. Efficient CT or increase of β value seem to induce the narrowing of optical band gap.

One of the practical applications of second-order nonlinear optical material is frequency conversion to obtain a wide spectrum from the laser source. Material should meet several requirements for these applications such as wide transparency, large second-order nonlinear optical susceptibility and so on. Recently a novel amino acid crystal, L-pyrrolidone-2-carboxylic acid, has been found to be phase matchable for second harmonic generation (SHG) down to UV region (266 nm).[8] Although the crystal has wide optical transparency, this molecule does not havea large β value due to the limited polarizable structure. We found cyanovinyl aromatics (shown in Figure 1) which possess an alkyloxy group as an electron donor and cyanovinyl group as an electron acceptor in *ortho*-position exhibit efficient second-order nonlinear optical responses in the crystals and wide optical transparency.[9] We have reported phase-matched second harmonic generation (SHG) at a wavelength of 812 nm as a fundamental light in **DIVA** (dicyanovinylanisole, **DA 1**) crystal.[10] In this paper we propose new approach of molecular design to enhance the molecular second-order nonlinear optical susceptibility without narrowing optical transparency.



**DA 1** : $R_1=CH_3$, Y=CN (DIVA)
**DA 2** : $R_1=CH_2CH_2OCH_2CH_3$, Y=CN
**DA 3** : $R_1=CH_3$, $Y=COOCH_3$

FIGURE 1 Structural of cyanovinyl aromatics.

## EXPERIMENTAL

### Synthesis and Characterization

Cyanovinylaromatics were obtained by the Knoevenagel condensation reaction of the corresponding aldehydes with active methylene compounds such as malononitrile and methyl cyanoacetate in the presence of piperidine. Obtained compounds were fully characterized by NMR, IR, UV and elemental analysis. Dipole moment of the molecule was determined from the concentration dependence of dielectric constants in 1,4-dioxane solution.

## RESULTS AND DISCUSSION

### Molecular Design

DIVA (**DA 1**) has polar substituents on one side of a benzene ring, and the molecular dipole moment roughly points from dicyanovinyl to the methoxyl group.[9] The molecular orbital calculation of **DIVA** molecule suggests the effective CT occurs only through the C=C bond of the benzene ring substituted with methoxy and dicyanovinyl groups. This means that the other C=C bonds of benzene ring do not contribute to the effective CT for second-order nonlinear optical response. The tetra-substituted benzene compounds which have two pairs of D and A groups possess two CT axes in one molecule. Symmetrically substituted benzene compounds such as **(DA)$^2$** in Figure 2 have the enhanced molecular dipole moment because two vectors of dipole moment are parallel each other. Moreover the enhancement of β in the additive way can also be expected. On the other hand, another type of tetra-substituted benzene compounds such as **DAAD** in Figure 2 has anti-parallel direction of dipole moments and β. In this **DAAD** molecules the reduced dipole moment and β values can be expected due to the cancellation of each vector of dipole moment and β. In this molecular design of **(DA)$^2$** such as control of the vector direction in the dipole moment and β, we can enhance the β values without narrowing optical transparency in comparison with usual way of enhancement of β, that is, extended conjugation or introduction of strong D and A groups.

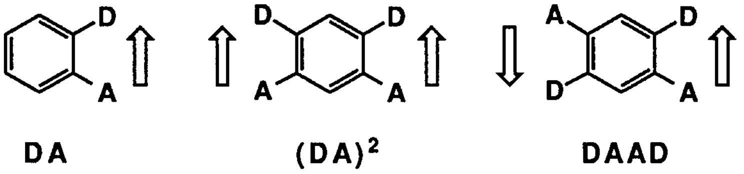
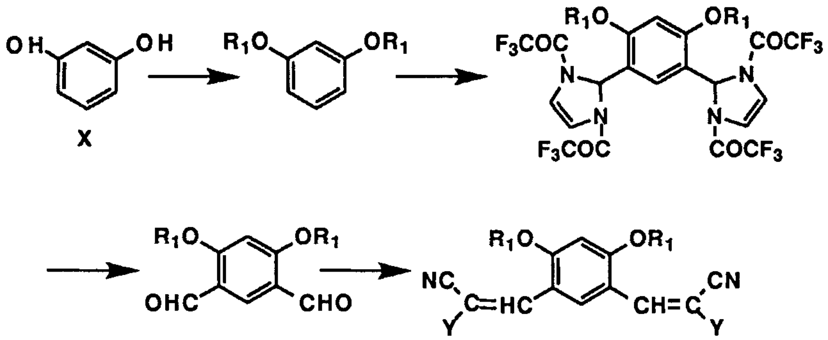


FIGURE 2 Schematic dipole moment vector for intracharge transfer compounds.

Schemes I and II indicate the synthesis route of **(DA)$^2$** and **DAAD** molecules from *m*-alkyl benzene and *p*-alkyloxybenzene as a starting material. Intermediate dimethoxy dialdehydes show poor solubility in normal organic solvents. In order to increase the solubility and the steric hindrance in a crystalline state, ethoxyethyl group was introduced to the OH group of *m*-hydroxy- and *p*-hydroxybenzene, respectively, although this is less electron donative group. The detail synthesis and characterization results will be published elsewhere.

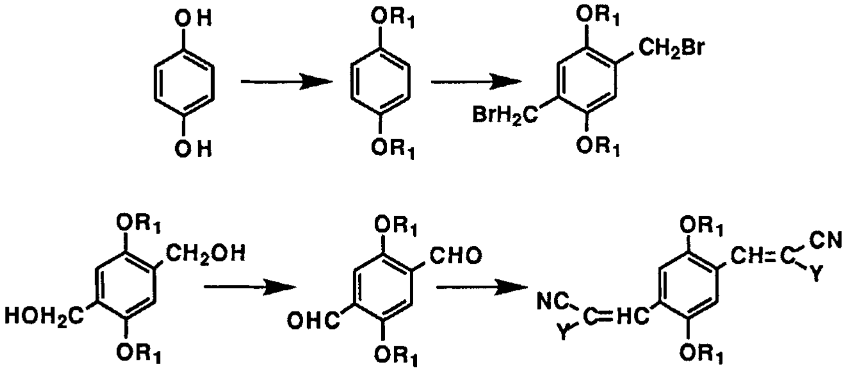


(DA)$^2$ **1** $R_1 = CH_3$, $Y = CN$

(DA)$^2$ **2** $R_1 = CH_2CH_2OCH_2CH_3$, $Y = CN$

(DA)$^2$ **3** $R_1 = CH_3$, $Y = COOCH_3$

SCHEME I Synthesis of 1, 3, 4, 6-tetrasubstituted benzene compounds ((DA)$^2$ ).



DAAD **1** $R_1 = CH_3$, $Y = CN$

DAAD **2** $R_1 = CH_2CH_2OCH_2CH_3$, $Y = CN$

DAAD **3** $R_1 = CH_3$, $Y = COOCH_3$

SCHEME II Synthesis of 1, 2, 4, 5-tetra-substituted benzene compounds (DAAD).

## Optical Properties

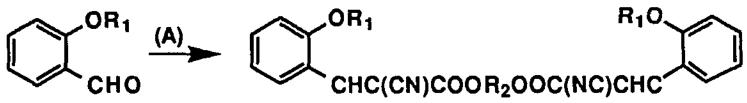
The UV data for **(DA)**$^2$ compounds show bathochromic-shifted $\lambda_{max}$ and larger molecular absorbity ($\varepsilon$) value than corresponding **DA** compounds in Table I. This indicates **(DA)**$^2$ type molecules show the higher delocalized structure than **DA** molecules. On the other hand, **DAAD** shows bathochromic-shifted $\lambda_{max}$ and smaller $\varepsilon$ value. These enhancement of $\varepsilon$ in **(DA)**$^2$ and reduction of $\varepsilon$ in **DAAD** indicate the proof of molecular design shown in Figure 2. The substitution of a cyano group with a methoxycarbonyl group in **DA 1** or **(DA)**$^2$ **1** produced a hyposochromic shifted $\lambda_{max}$ of 8-9 nm (**DA 3** or **(DA)**$^2$ **3**) and a little bathochromic-shifted $\lambda_{max}$ (**DAAD 1** or **DAAD 3**). These compounds showed the same tendency for the SHG efficiency, and hence their packing structure in crystals might be independent of the molecular structure.

TABLE I Optical properties of cyanovinyl aromatics.

| compound (yield %) | $\lambda_{max}$ (nm) (in $CH_2Cl_2$) | $\varepsilon$ |
|---|---|---|
| **DA 1** | 367.5, 304.0 | 19500, 21800 |
| **DA 2** (10) | 367.0, 304.5 | 12300, 14500 |
| **DA 3** (20) | 358.0, 299.0 | 12900, 14200 |
| **(DA)**$^2$ **1** (5) | 392.5, 355.5, 311.0 | 23300, 33000, 28200 |
| **(DA)**$^2$ **2** (1) | 391.5, 356.0, 312.5 | 18800, 28000, 23500 |
| **(DA)**$^2$ **3** (5) | 384.0, 350.0, 308.5 | 21500, 29100, 25100 |
| **DAAD 1** (< 1) | 370.5, 278.5 | 6800, 6700 |
| **DAAD 2** (< 1) | 462.0, 344.5 | 12900, 23000 |
| **DAAD 3** (2) | 372.0, 281.5 | 8000, 14400 |
| **DA dimer 1** (15) | 360.5, 300.5 | 20200, 22100 |
| **DA dimer 2** (40) | 358.5, 299.0 | 24100, 26400 |
| **DA dimer 3** (30) | 356.0, 299.0 | 25800, 28300 |
| **DA dimer 4** (30) | 358.5, 300.0 | 26000, 29100 |

## DA Dimers

Among organic second-order nonlinear optical materials, poled polymers are one of the suitable systems for device applications. In this section we propose dimeric nonlinear optical chromophore to improve physical properties of chromophore in polymer matrix such as thermal stability and low diffusion constants. These dimers or oligomers can be expected to exhibit different properties from point like monomer molecules based on the chemical structure.[11] Dimers of 1, 2-substituted benzene compounds were synthesized from *o*-methoxybenzaldehyde and bis(cyanoacetate)s as shown in Scheme III. From the UV data, it is suggested that **DA dimer 1-4** have also larger intramolecular charge-transfer than **DA 1** or **DA 3**, although they are not highly delocalized. In the electric-field induced alignment these compounds are expected to fold into a U-shape with donor and acceptor groups fixed at alternating apexes for increasing the molecular dipole moment.



**A = $CNCH_2COOR_2OOCCH_2CN$**

**$R_1 = CH_3$,**

**DA dimer 1** $R_2 = (CH_2)_2$

**DA dimer 2** $R_2 = (CH_2)_6$

**DA dimer 3** $R_2 = (CH_2)_{10}$

**DA dimer 4** $R_2 = p\text{-}CH_2C_6H_4CH_2$

SCHEME III Synthesis of 1, 2-disubstituted benzene compounds (**DA dimer**).

## Powder Second Harmonic Generation Activity

Although the powder SHG efficiency depends on both β values and molecular packing in a crystal, the powder test method is a convenient screening method for many organic compounds. Therefore the SHG properties were checked according to the conventional powder technique using a Q-switched pulsed Nd:YAG laser (1064 nm).[12] The results are shown in Table II. Only three compounds **DA 1**, **DA 3** and **(DA)$^2$ 2** have SHG activity. In the case of DIVA, noncentrosymmetric packing was generated due to the highly anisotropic molecular structure in which polar substituents were introduced in one side of benzene ring.

TABLE II Dipolemoment and powder SHG activity of cyanovinyl aromatics.

| compound | dipole moment (D) | SHG activity |
|---|---|---|
| DA 1 | 6.8 | O |
| DA 2 | 6.5 | x |
| DA 3 | | O |
| (DA)$^2$ 1 | 7.8 | x |
| (DA)$^2$ 2 | 11.8 | O |
| (DA)$^2$ 3 | | x |
| DAAD 1 | 6.1 | x |
| DAAD 2 | 2.3 | fluorescence |
| DAAD 3 | | x |
| DA dimer 1 | | x |
| DA dimer 2 | | x |
| DA dimer 3 | | x |
| DA dimer 4 | | x |

The molecular design for enhancement of $\beta$ such as (DA)$^2$ compounds does not always meet this requirement for efficient noncentrosymmetric packing of molecules. Presumably this approach is effective for development of second-order nonlinear optical molecules for poled polymer applications.

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