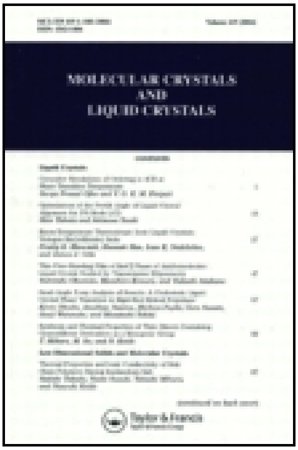

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Molecular Modeling of a Polar Rod-Like Aromatic Polyester Forming Nematic Liquid Crystal. Part 1. *Ab Initio* Study of Origin of Strong SHG-Activity

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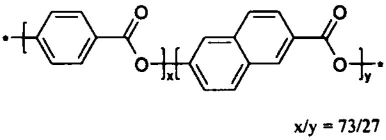
The aromatic copolyester of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphtoic acid (HNA) shows strong SHG-activity in the nematic phase as well as the crystalline phase in spite of no absorption in the visible region. *Ab initio* quantum chemistry calculations of the copolyester have been carried out in order to clarify the origin of this strong SHG-activity. The second-order hyperpolarizability of the HBA dimer is comparable to that of *p*-nitroaniline and it increases with the degree of polymerization. The large hyperpolarizability of the aromatic polyester is ascribed to the large electronic transition moment.

Keywords: polar rod-like aromatic polyester; nematic liquid crystal; *ab initio* molecular orbital calculation; second-order hyperpolarizability; two-level model

Introduction

The nonlinear optical (NLO) properties have been expected to play an important role in the technology of photonics in which photons instead of electrons in the field of electronics are used. The NLO properties of organic compounds have been investigated both theoretically and experimentally, because of this potential application. Most second-order NLO organic molecules have both electron-donating groups (EDG) and electron-withdrawing groups (EWG) bridged through an intervening π-conjugation backbone. Although it is established that extending the π-conjugation system between EDG and EWG increases the hyperpolarizabilities (β), the extension of the π-conjugation system simultaneously causes a red-shift by intramolecular charge transfer. Thus the high transparency in the visible region is lost. This is the so-called trade-off problem.

Stuetz [1] and Asada [2] reported an aromatic polyester in the crystalline phase which shows an extraordinarily large second-order harmonic generation (SHG) without visible absorption. The SHG-active polymer was an aromatic random copolyester comprising *p*-hydroxy benzoic acid (HBA) and 6-hydroxy-2-naphtoic acid (HNA) in a molar ratio of 73 / 27 which is known as 'Bektra', a super-engineering polyester (see Scheme 1). The highly efficient SHG active liquid crystal polymer is very attractive for preparing stable SHG polymeric fibers.



Scheme 1.

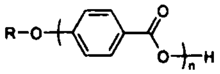
We found a polar ordering of the aromatic polyester comprised of HBA and HNA in the nematic liquid crystal phase.[3] The SHG- activity appears when the degree of polymerization is high enough. The aromatic copolyester of HBA and HNA has no absorption in the visible region in spite of exhibiting a large β value, *i.e.*, this aromatic copolymer overcomes the trade-off problem.

As SHG-active organic compounds with high transparency, Λ-type compounds [4] have been proposed. Λ-type compounds have weak-electron conjugation, where the π-orbital overlap between each neighboring group is small. These molecules may have large β values at the molecular level. However, if they have centrosymmetry structures at the macroscopic level, such as in crystals, the macroscopic susceptibility, $\chi^{(2)}$, is zero. Therefore, it is important for SHG-active materials to assemble these molecules in a noncentrosymmetric phase. This is, in general, still technically difficult to assemble SHG-active molecules in a noncentrosymmetric phase. In this sense, the liquid crystal polymer, Bektra, is attractive.

In this work, we attempted to clarify theoretically the origin of the strong SHG-active aromatic polyester without visible absorption. As a model of the aromatic polyester, an HBA oligomer was investigated. The molecular dynamics simulation for the polar ordering of the aromatic polyester will be discussed in Part 2.[5]

Computational detail

HBA and its oligomers, and acetylated HBA (denoted as ac-HBA) and its oligomers were selected as model molecules for the HBA polymer (see Scheme 2).



HBA oligomer : R = H, n = 1-4
ac-HBA oligomer : R = CH_3CO, n = 1-3

Scheme 2

All molecular orbital calculations have been performed with Gaussian 94[6] programs. The geometries of all the molecules were optimized at the Hartree-Fock level by using the 6-31G* basis set (denoted as HF/6-31G*).[7]

The tensor components of the β values were calculated using the coupled-perturbed Hartree-Fock (CPHF) formalism based on *ab initio* SCF wavefunctions.[8,9] Then, the β values were estimated from the components projected on the net dipole moment, μ, as follows [10]:

$$\beta = \frac{3}{5}\sum_i \beta_i \mu_i / \|\mu\| \; ; \; i = x, y, z \qquad (1)$$

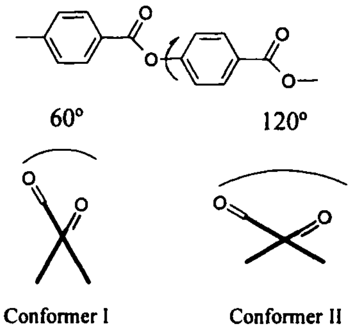
Assuming Kleinman relations,[11] it follows :

$$\beta_i = \sum_j \beta_{ijj} ; \; i = x, y, z \qquad (2)$$

The excitation energy and electronic transitions of the compounds were calculated by the configuration interaction singles (CIS).[12]

Result and Discussion

It is known that neighboring monomer units of the HBA polymer have two possible low energy conformations.[13] The carbonyl group and the attached benzene are coplanar. One low energy conformation has an angle of 60° between the adjacent C=O planes of the polyester and another has an angle of about 120° (denoted as conformer I and II, respectively, and see Scheme 3).



Scheme 3. Schematic representations of two low energy conformers of aromatic polyester.

The dihedral angle between two benzene planes of the HF/6-31G* optimized HBA dimer I is –66.0°, and the angle of the dimer II is –119.6°. The angles between the neighboring benzene planes of trimer I are –65.3° and 68.2°, and the angles of trimer II are –120.9° and 119.8°. For the HBA tetramer I the dihedral angles are –64.9°, 67.3° and –68.1°, while for tetramer II the angles are –121.5°, 119.9° and –119.0°.

The dihedral angles between neighboring benzene plane of ac-HBA series are similar to that of HBA series. For each compound, total energy differences between conformer I and conformer II are less than 0.1 kcal/mol.

The calculated μ and β values are listed in Table 1. The μ and β values for HBA and ac-HBA monotonically increase with increasing number of repeating units up to the tetramer and trimer. Though the β value of the HBA monomer I (1.672×10^{-30} esu) is less than that of *p*-NA (3.217×10^{-30} esu), the dimer, trimer and tetramer of HBA showed larger β values. The acetylation of the terminal –OH group of HBA lowers β; the β value of monomer I (0.885×10^{-30} esu) is less than that of *p*-NA and that of the dimer is nearly equal to that of *p*-NA (dimer I is 2.808×10^{-30} esu and dimer II is 3.356×10^{-30} esu). However, the trimer showed a larger β value (trimer I is 5.034×10^{-30} esu and the trimer II is 5.760×10^{-30} esu). These linear relations between the β values and the degree of polymerization agree with the result of semi-empirical molecular orbital calculations for the polyesters in spite of having different terminal groups.[3,14]

Here, we try to clarify the origin of strong SHG-activity of aromatic polyester by using the two-level model. The two-level model has been used extensively to describe β and to identify promising NLO chromophores.[15,16] In this model, a single electronic transition is assumed to make the dominant contribution to β. Therefore the model is useful for providing a simple picture to us. Within the framework of the two-level model, the static β value ($\beta_{t\text{-}l}$) is expressed as:

$$\beta_{t\text{-}l} = \frac{3}{2}\frac{(\mu_e - \mu_g)\mu_{eg}^{\ 2}}{E_{eg}^{\ 2}}$$

where μ_g is the dipole moment of the ground state, μ_e is the dipole moment of excited state, μ_{eg} is the transition moment between the ground state and excited state, and E_{eg} is the energy gap between the ground state and the excited state.

The μ_e, μ_g, μ_{eg} and E_{eg} parameters were estimated by the configuration interaction singles (CIS) using the 6-31G* basis set. Shown in Table 2 are the estimated results for the μ_e, μ_g, μ_{eg}. E_{eg} and $\beta_{t\text{-}l}$ parameters for the first excited state of each compound. These E_{eg} values show only a small decrease with increasing the number of repeating units, that is, the red-shift involved with polymerization is small. On the other hand, the transition moment μ_{eg} increases with increasing a degree of polymerization. In general, the extension of the conjugation system causes the decrease in the HOMO-LUMO gap as well as the increase in the transition moment μ_{eg}. However in Bektra, the HOMO-LUMO gap is scarcely decreased and the increase of the transition moment results from the extension of a through-bond interaction and delocalization as increasing with the degree of polymerization. Therefore, we have concluded that the large value of β is mainly ascribed to the transition moment μ_{eg}.

Table 2. Calculated values of μ_e-μ_g, μ_{eg}, E_{eg} and $\beta_{t\text{-}l}$ at CIS/6-31G* for HBA oligomers

	μ_e-μ_g / 10^{-30} Cm	μ_{eg} / 10^{-30} Cm	E_{eg} / 10^{-19} J	$\beta_{t\text{-}l}$ / 10^{-30} esu
HBA	2.185	9.430	9.897	0.053
dimer I	5.287	15.410	9.762	0.355
dimer II	4.973	15.447	9.754	0.336
trimer I	5.394	19.890	9.708	0.610
trimer II	5.380	20.324	9.690	0.638
tetramer I	5.277	23.579	9.679	0.844
tetramer II	5.193	24.113	9.656	0.873

Conclusion

The aromatic copolyester of 4-hydroxy benzoic acid (HBA) and 6-

hydroxy-2-naphtoic acid (HNA) shows strong SHG-activity although it has no absorption in the visible region. Our molecular orbital calculations show that the origin of the large hyperpolarizabilities of the aromatic polyester is mainly ascribed to the transition moment between the ground state and excited state. From the study, we propose that the aromatic polyester provides a new class of strong SHG-active materials without absorption in the visible region.

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