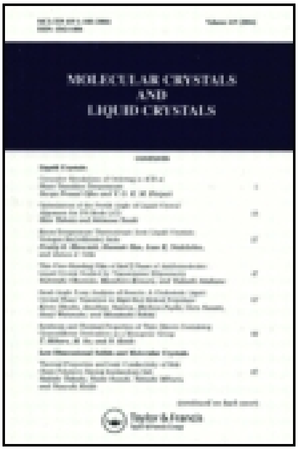

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Molecular Orbital Calculations of Nonlinear Optical Parameters for Test Molecules of a Highly Amphoteric and Polar Molecule (HAPM)

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Molecular Orbital Calculations of Nonlinear Optical Parameters for Test Molecules of a Highly Amphoteric and Polar Molecule (HAPM)

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Semiempirical molecular orbital calculations of 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-ethylenedithio-1,3-dithiole and its analogues, as test molecules towards a highly amphoteric and polar molecule (HAPM) designed on the basis of combination of electron-donating and accepting molecular segments with a pseudo-delocalized electron system were carried out to estimate several molecular parameters, in particular, those regarding the second-order optical nonlinearity, in order to examine a difference between the proposed molecular design and the conventional one for the 'push-pull' type of molecules. Large values of the first molecular hyperpolarizability are obtained for the present molecules, however, it is turned out that the trade-off relation between hyperpolarizability and transparency of a material is also concerned with these materials. This indicates that the proposed molecular design toward HAPM is unique and can be useful to bring about novel materials with remarkable properties.

Keywords: amphoteric molecule, intramolecular charge transfer, electronic delocalization, hyperpolarizability, second harmonic generation

1. INTRODUCTION

Aiming at a highly amphoteric and polar molecule (HAPM) which could enable us to assemble novel organic solid-state structures, a molecular design by combining electron-donating and accepting molecular segments with a pseudo-delo-

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calized electron system has recently been proposed.[1],[2] Such a molecule is different in principle from the conventional 'push-pull' type of molecules which have widely been studied in search of efficient organic nonlinear optical materials,[3]-[5] in particular, the second harmonic generators. This is because our design lays stress on a moderately high degree of electron delocalization on the binding unit between two segments in different electronic nature, which corresponds to a moderately high degree of intramolecular charge transfer between them. Further, the resulting approximate maintenance of their nature for the respective segments open to distinctive manners of intermolecular charge transfer interactions can be expected to lead to characteristic forms of molecular aggregation, in accordance with a balance between intramolecular and intermolecular charge transfer interactions, tempting notable electronic properties in the solid state.

On the other hand, both electronic and steric factors are important for the design of HAPM. The former consists chiefly of a moderately high degree of intramolecular charge transfer between donor and acceptor segments though a proper binding unit, and, moreover, the latter contains planarity and right length of a molecule appropriate for molecular stacking and multicentered interactions in the aggregated forms, respectively.

With bearing in mind these factors which are necessary to realize various molecular packing manners in the solid state, four molecules shown in Figure 1, each comprised by a (substituted) 1,3-dithiolene group as a donor segment, a dicyanomethylene group as an acceptor segment and a quinoid structure (of different number of repeating units) as a linker, were employed in our recent study on HAPM.[2] Among them 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-ethylenedithio-1,3-dithiole **2** has closely been studied as a test molecule for HAPM, while 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-1,3-dithiole **1**, synthesized previously by Gompper et al.[6] with taking notice of intramolecular charge transfer in an isolated molecule in terms of physical organic chemistry, can be regarded as a prototype one.

This kind of molecules appear to be indistinguishable from the conventional push-pull type of molecules, since the difference in bonding nature of the binding units may be estimated little on account of apparently common conjugation structures drawn for the respective molecules. It could therefore be worth while examining also molecular parameters relating to nonlinear optical properties for several test molecules of HAPM, when we accept that they can be grouped into the push-pull type of molecules at any rate and try to capture their characteristics to the full.

In the present work we have evaluated such molecular parameters for the four molecules above on the basis of semiempirical molecular orbital (MO) calcula-

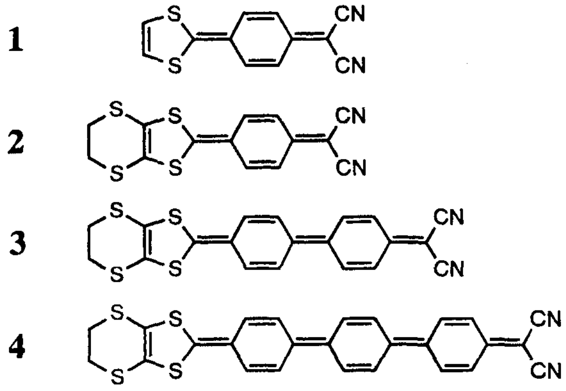


FIGURE 1 Structures of test molecules towards HAPM: 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-1,3-dithiole, **1**; 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-ethylenedithio-1,3-dithiole, **2**; extended analogues of **2** with diphenoquinoid and triphenoquinoid linkers, **3** and **4**, respectively

tions. The obtained results will be discussed in comparison with the corresponding parameters of a few push-pull type of molecules and zwitterionic compounds such as pyridinium 1,3-dioxo-2-indanylide.

2. MO CALCULATIONS

In order to calculate molecular geometries and molecular parameters for the four compounds shown in Figure 1 semiempirical MO methods,[7],[8] that is, the AM1 and ZINDO/S approaches on the HyperChem program in the version of R4.5 were employed. The AM1 method was applied for the molecular geometry optimization. On the other hand, molecular parameters were calculated using the ZINDO/S method which is parametrized particularly to reproduce optical transitions but is known as the method being not necessarily useful for molecular geometry optimization.[7]

3. RESULTS AND DISCUSSION

3.1. Molecular Geometry and Charge Distribution

The geometry optimization calculations of **2** to **4** yielded two stable structures with different conformations of the ethylenedithio group as predicted. The molecular structure with its staggered conformation (*e.g.*, the molecular total energy $E_T = -13231.5$ kJ mol^{-1} in the case of **2**) is more stable than that with its eclipsed one (*e.g.*, $E_T = -13220.6$ kJ mol^{-1} in the same case). The former molecular conformation has therefore been applied for further calculations of the three molecules. These molecules are completely flat with neglecting ethylenedithio groups at their ends as is their simplest analogue **1**, so that the symmetry axis coinciding with the long one can be defined as the x axis for those four molecules.

It has been turned out that geometrical structures around hexagonal carbon rings in optimized geometries for the four molecules are characterized by an obvious quinonoid structure. For example, the lengths for two pairs of C-C single bonds inside the ring (1.445 and 1.450 Å) and those for three kinds of C=C double bonds (1.352, 1.371 and 1.372 Å) in the case of **2** are typical for the bonds in a quinoid structure[2]: *e.g.*, 1.446 Å for each C-C bond inside the ring and 1.352 and 1.374 Å for C=C bonds inside and outside the ring, respectively, in the case of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).[9] Such a molecular structure characterized by the efficiently planar π-electron system comprising a dithiole ring, a quinonoid structure and a dicyanomethylene group could be supported by a molecular structure of 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-bis(methylthio)-1,3-dithiole, which is a ring-opened analogue of **2**, preliminarily determined from its crystal structure analysis.[10]

Such characteristics in the molecular structure result in a fairly high degree of intramolecular charge transfer as revealed by the notably asymmetric atomic charge distribution calculated using the AM1 method: in the case of **2**, for example, +0.17 *e* and +0.10 *e* charges are distributed mainly over the ethylenedithiolene and quinonoid fragments of the molecule, respectively, and −0.27 *e* charges on the small acceptor fragment of dicyanomethylene,[2] where *e* is the elementary charge. These results indicate that the donor and acceptor segments in a molecule are linked with each other with their original electronic characteristics preserved mostly as aimed in the molecular design.

3.2. Nonlinear Optical Parameters

The test molecules of HAPM above have not been designed toward nonlinear optical materials, however, it will be useful to examine also their nonlinear optical parameters because of their push-pull nature which seems to be in line with a principle to develop organic nonlinear-optical materials. Thus, several physical quantities concerning nonlinear optics, in particular second harmonic generation (SHG), have been calculated for each compound.

It is widely known that the first hyperpolarizability β of a molecule is a key parameter to SHG characteristics of its aggregate at the molecular level. In the case of a push-pull type of molecule the intramolecular charge transfer contributes predominantly to the β value. On the basis of the two-level model in which only one excited state of the largest contribution to the optical process is taken into account, β is expressed by the following equation:[11]

$$\beta = -(6\pi^2/h^2)(\mu_e - \mu_g)M^2{\omega_{eg}}^2/({\omega_{eg}}^2 - \omega^2)({\omega_{eg}}^2 - 4\omega^2), \tag{1}$$

where h, μ_e, μ_g, M, ω_{eg} and ω are the Planck constant, dipole moment in the excited state, dipole moment in the ground state, transition dipole moment, circular frequency for the lowest excitation and circular frequency of light, respectively. First, the four molecular parameters in the right side of equation (1) were calculated using the ZINDO/S method and are listed together with the value of $\Delta\mu = \mu_e - \mu_g$ and oscillator strength f in Table I, where μ_g values obtained by the AM1 method are also shown for comparison.

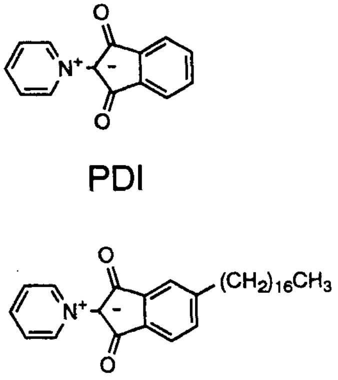
TABLE I Dipole moments in the ground and the first excited states, their difference, circular frequency and wavelength for the lowest excitation, oscillator strength and transition dipole moment, calculated for each compound from **1** to **4**

Compound	μ_g / D	μ_e / D	$\Delta\mu / D$	$\omega_{eg} / 10^{15}\, s^{-1}$	λ_{eg} / nm	f	M / D
1	13.65 *9.25*	16.76	3.11	4.78	394	1.63	11.7
2	14.57 *11.44*	20.35	5.78	4.63	406	1.64	11.9
3	20.42 *15.40*	20.90	0.48	3.60	523	2.86	17.8
4	28.03 *20.64*	21.77	-6.26	2.88	653	4.21	24.2

μ_g and $\mu_e$are obtained to be the same values as their components along the molecular x axis (1 D ≅ 3.33564 × 10^{-30} C m). *Italic* values for μ_g, calculated using the AM1 method, are shown for comparison. $\Delta\mu = \mu_e - \mu_g$.

3.2.1. Molecular electric dipole moments

The calculated results by the ZINDO/S method have demonstrated that both μ_g and μ_e coincide with their components along the x axis as the molecular long axis. The μ_g value of each molecule is considered to be large, and, on the other hand, the behavior of the μ_e value seems to be rather unique. In the case of **1** and **2** μ_e increases considerably from μ_g via the electronic excitation, which indicates that the intramolecular charge-transfer (CT) interaction from the donor segment to the acceptor one in these molecules is enhanced by the excitation. However, the μ value of **3** is apparently common for the ground and excited states; further, the longest analogue **4** shows a μ value in the first excited state much smaller than that in the ground state. These results can be understood by considering that not only intramolecular CT interaction but also local excitation contribute to the electronic transition in the above molecules. This indicates that a pseudo-delocalized electron system is realized by quinoid structures between electron-donating and accepting molecular segments as expected in the molecular design.



PDI

C17PDI

FIGURE 2 Molecular structures of pyridinium 1,3-dioxo-2-indanylide (PDI) and pyridinium 1,3-dioxo-5-heptadecyl-2-indanylide (C17PDI)

It is widely accepted that a large $\Delta\mu$ value in contrast to a small μ_g value is expected for a molecule of high SHG activity; small μ_g is considered to be advantageous to the formation of non-centrosymmetric crystals. For example, in the case of *p*-nitroaniline (*p*-NA), which is known as one of the typical push-pull type molecules showing SHG activity at least at the early stage of the research field, its μ_g and $\Delta\mu$ values are 6.8 D[12] (1 D $\cong$ 3.33564 $\times$ 10^{-30} C m) and 12.3 D,[11] respectively; μ_e= 19.1 D is derived in consistency with them. The μ_g value is smaller than halves of those for **1** and **2**, which seems to be a reason why orientational molecular ordering due to dipole-dipole interactions is practically suppressed in the process of crystallization of *p*-NA. On the other hand, the μ_e value is similar to those for the two compounds, and $\Delta\mu$ becomes much larger than those of them as a result.

Further, the dipole moments in Table I are compared with those of pyridinium 1,3-dioxo-2-indanylide (PDI);[13] this is a zwitterionic compound and its derivative compound, pyridinium 1,3-dioxo-5-heptadecyl-2-indanylide (C17PDI), shows SHG activity in its Z-type Langmuir-Blodgett film.[14] (The molecular structures of PDI and C17PDI are shown in Figure 2.) The μ_g and μ_e values are experimentally determined to be 4.5 D and –5.1 D, respectively,[13] then $\Delta\mu$ comes to –9.6 D. A small μ_g and a large $\Delta\mu$ (in absolute value) can be claimed to be common with the respective values of *p*-NA in comparison with those of **1** and **2**, though the sign of $\Delta\mu$ is different from *p*-NA to PDI. These results suggest that the present compounds may have difficulties in forming non-centrosymmetric crystals because of large μ_g values. Besides, a preliminary calculation indicates that the μ_g value increases from 4.5 D to 17.8 D when a *p*-phenylene group is inserted between pyridinium and 1,3-dioxo-2-indanylide of a PDI molecule.[15]

3.2.2. Molecular parameters connected with electronic excitation

The right side of equation (1) includes two molecular parameters directly connected with electronic excitation, that is, ω_{eg} and M. The former can be converted from λ_{eg} by the relation: $\omega_{eg}\lambda_{eg} = 2\pi c_0$, where c_0 is the speed of light in vacuum.

First, the ω_{eg} values in Table I are compared with those of *p*-NA and PDI, that is, 5.80×10^{15} s^{-1} ($\lambda_{eg} = 325$ nm[12]) and 4.40×10^{15} s^{-1} ($\lambda_{eg} = 428$ nm[13]), respectively. It is notable that *p*-NA shows *a* ω_{eg} value much larger than those of the other compounds, which are settled down in the visible light region, with a notable bathochromic shift from **2** to **4**. Further, it has been claimed that the maximum absorption wavelength of **2** in a liquid solution ($\lambda_{max} \approx 670$ nm) is observed to be rather longer than the calculated value, with such a difference unexplained exactly.[2] As it is confirmed that the solubility of **2** in most organic solvents is rather low, its ring-opened analogue, 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-bis(methylthio)-1,3-dithiole, has preliminarily been synthesized and examined for spectral shifts of its electronic spectra in several liquid solvents with different relative permittivity ε_r ranging from 2.10 (for 1,4-dioxane) to 46.7 (for dimethyl sulfoxide) at room temperature.[10] For these solvents the spectral shift of 12 nm at most was observed at around 650 nm in wavelength, which fairly corresponds to the above behaviors in dipole moments listed in Table I. With taking account of those behaviors, each compound in Table I appears, therefore, to bear a well-known trade-off relation between nonlinear optical characteristics and transparency of a material,[6] as a counter to the recognized amphotericity.[2]

The oscillator strength f and the transition dipole moment M, the correlation of which are expressed by the equation of $f = (4\pi m_e/3he^2)\omega_{eg}M^2$, are large enough to be noted for the compounds listed in Table I, where m_e and e are the rest mass of electron and the elementary charge, respectively. The M value calculated for

PDI, −13.4 D,[13] which gives $f = 1.97$ on the basis of the above equation, appears to be almost similar in magnitude to their values except for that of the longest analogue **4**; the derived f value is much larger than the experimental value of 0.29.[13] This kind of difference between calculated and experimental f values is also pointed out in the case of **2**: the former is 1.64 and the latter is 0.75 which is still large.[2] Such a large f value is considered to reflect characteristic electron delocalization involving the intramolecular charge transfer in those molecules.

3.2.3. Polarizabilities and the first hyperpolarizabilities

To check the optical nonlinearity of the test molecules toward HAPM more directly, with bearing in mind that there is a common nature in molecular designs for organic nonlinear-optical materials of the 'push-pull' type and HAPM, values of molecular polarizability α and the first hyperpolarizability β were also calculated, as shown in Table II.

TABLE II Molecular polarizabilities along the x, y, z axes of the molecule, mean polarizabilities, the three largest first molecular hyperpolarizability components and the first molecular hyperpolatizabilities projected onto the molecular x axis, calculated using the AM1 method for the compounds **1** to **4**

Compound	α_{xx}	α_{yy}	α_{zz}	$<\alpha>$	β_{xxx}	β_{xyy}	β_{xzz}	β_x
1	164.4	48.0	8.0	73.6	−71.9	−5.7	0.4	−46.3
2	213.9	63.2	14.1	97.2	−112.2	−12.2	0.8	−74.1
3	474.8	76.1	16.9	189.5	−482.3	−23.5	1.3	−302.7
4	961.0	90.0	19.2	357.3	−1583.7	−44.6	2.1	−975.7

α_{xx}, α_{yy}, α_{zz} and $<\alpha>$ are in 10^{-24} esu (1 esu $\cong 1.11265 \times 10^{-16}$ J^{-1} C^2 m^2) and β_{xxx}, β_{xyy}, $\beta_{xzz}$and β_x are in 10^{-30} esu (1 esu $\cong 3.71140 \times 10^{-21}$ J^{-2} C^3 m^3).

The largest component of the molecular polarizability of each molecule is obtained along the x axis as the molecular long axis, on the other hand, the smallest one perpendicular to the molecular plane. The obtained values are rather large in comparison with the corresponding values for, *e.g.*, anthracene[16] as a typical π-conjugated molecule, that is, $\alpha_{xx} = 40.0 \times 10^{-24}$esu (1 esu $\cong 1.11265 \times 10^{-16}$ J^{-1} C^2 m^2 for molecular polarizability), $\alpha_{yy} = 23.4 \times 10^{-24}$ esu, $\alpha_{zz} = 14.5 \times 10^{-24}$ esu and $<\alpha> = 26.0 \times 10^{-24}$ esu, where $<\alpha> = (1/3)\,(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$. It is also notable that $<\alpha>$ of p-NA is 14.3×10^{-24} esu,[17] which is obtained by *ab initio* calculation, and is much smaller than those of the four compounds in Table II.

The first molecular hyperpolarizability projected onto the molecular i axis, β_i with $i = x$, y and z, can be calculated by the following formula: $\beta_i = (3/5)$

($\beta_{ixx} + \beta_{iyy} + \beta_{izz}$), where x and y denote the long and short molecular axes, respectively, and z axis perpendicular to the molecular plane. The obtained β_y and $\beta_z$values are practically equal to zero, which means that the β_i value stands practically along the molecular long axis, that is, $\beta_i = \beta_x$. Such a directivity is in good agreement with that in the electric dipole moment, as described above. These characteristics could be common in quasi-one dimensional molecules of 'push-pull' nature to be feasible to the application in nonlinear optics.[18]

To recognize sizableness of the first molecular hyperpolarizabilities for **2** and its extended analogues, the (static) values of $\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$ calculated for other dipolar compounds showing notable optical nonlinearities are compared as follows: $\beta = 12.0 \times 10^{-30}$ esu (1 esu $\cong 3.71140 \times 10^{-21}$ J^{-2} C^3 m^3 for the first hyperpolarizability) for *p*-NA and 43.4×10^{-30} esu for 4-(dimethylamino)-4'-nitrostilbene (DANS).[19] On the other hand, the calculated and experimental β values of PDI are reported to be 138.8×10^{-30} esu and 138×10^{-30} esu, respectively.[14] In addition, the following empirical formula which corresponds to equation (1) with $\omega = 0$ substituted is often used to evaluate the β value within the framework of the two-level model:[11],[18]

$$\beta = -(6\pi^2/h^2)(\mu_e - \mu_g)M^2/\omega_{eg}{}^2. \qquad (2)$$

This independent evaluation with applying the molecular parameters shown in Table I gives $\beta = -25.1 \times 10^{-30}$ esu, -51.5×10^{-30} esu and 596×10^{-30} esu for **1, 2** and **4**, respectively, which are of the same order as the corresponding β_x values in Table II; **3** gives $\beta = -15.8 \times 10^{-30}$ esu, which is much smaller than the corresponding β_x value in the absolute value.

With bearing in mind that the first molecular hyperpolarizabilities listed in Table II are remarkably large for **2** and its extended analogues **3** and **4**, it seems that these compounds have a possibility for the second harmonic generators when they could form non-centrosymmetric crystals. However, when their electronic absorption data shown above are remembered, the trade-off relation between hyperpolarizability and transparency of a material[6] weighs on our mind and the reduction of their usefulness in the field of optical nonlinearity could be estimated as a counter to the recognized amphotericity.[2]

4. CONCLUDING REMARKS

In the present work molecular orbital calculations regarding nonlinear optical parameters for test molecules of a highly amphoteric and polar molecule (HAPM), designed with laying stress upon combining the π-electron donating and accepting segments by the bonding system with a moderately high degree of electron delocalization,[1],[2] has been carried out using the semiempirical methods.

The obtained results of molecular dipole moments in the ground and excited states and molecular parameters in relation with the electronic excitation show that 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-ethylenedithio-1,3-dithiole **2** as a key material of the present molecules has notable molecular characteristics as expected by the molecular design. The comparison of those characteristics among its simple or longer analogues is also worth while to proceed the molecular design in line with the present concept.

The first molecular hyperpolarizabilities as most direct parameters regarding the second-order optical nonlinearity have also been calculated for the four compounds, to suggest that these compounds have potentiality for such a property in molecular nature. On the other hand, their molecular excitation energies evaluated not necessarily in agreement with experimental results appear to be involved in the trade-off relation between hyperpolarizability and transparency of a material. It is therefore implied that **2** and its analogues could be less useful as the second harmonic generators than the conventional 'push-pull' type of nonlinear optical materials such as *p*-nitroaniline (*p*-NA) or pyridinium 1,3-dioxo-2-indanylide (PDI), at least exactly as they are.

Thus, the present results on molecular parameters of those test molecules for HAPM indicate that the proposed molecular design can be distinguished from the conventional push-pull type of molecular design, while several common aspects between them are noticed. Accordingly, the design toward HAPM is expected to bring about novel materials with remarkable properties other than optical nonlinearity, whereas a modified design from the proposed one is considered to be useful for developing organic nonlinear optical materials.

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Condolence

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References

[1] N. Sato and I. Kawamoto, in: *Research report on novel electronic states in molecular conductors*, S. Kagoshima (ed.) (Report of scientific research on priority area No. 253 aided by the Ministry of Education, Science, Sports and Culture of Japan, 1995), pp. 239–242.

[2] N. Sato, I. Kawamoto, T. Sakuma, E. A. Silinsh and A. J. Jurgis, *Mol. Cryst. Liq. Cryst.*, **333**, 243 (1999).

[3] D. S. Chemla and J. Zyss (eds.), *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic Press, Orlando, 1987).

[4] J. Zyss (ed.), *Molecular Nonlinear Optics: Materials, Physics, Devices* (Academic Press, Boston, 1993).

[5] C. Mosshard, K. Sutter, Ph. Prêtre, J. Hulliger, M. Flörsheimer, P. Kaatz and P. Günter, in: *Advances in Nonlinear Optics, Vol. 1*, A.F. Garito and F. Kajzar (eds.), (Gordon and Breach, Basel, 1995).

[6] R. Gompper, H.-U. Wagner and E. Kutter, *Chem. Ber.*, **101**, 4123 (1968).

[7] *HyperChem Computational Chemistry: Part 1, Practical Guide; Part 2, Theory and Methods*, Hyper Cube, HC 40–00–03–00 (1994).

[8] *HyperChem for Windows: Reference Manual*, Hyper Cube, HC 40–00–02–01 (1994).

[9] R. E. Long, R. A. Sparks and K. Trueblood, *Acta Cryst.*, **18**, 932 (1965).

[10] T. Sakuma, N. Sato, A. Izuoka and T. Sugawara, unpublished result.

[11] J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, **66**, 2664 (1977).

[12] J. F. Nicoud and R. J. Twieg, in: *Nonlinear Optical Properties of Organic Molecules and Crystals*, (eds.) D. S. Chemla and J. Zyss, (Academic Press, Orlando, 1987), p. 254.

[13] M. A. Rutkis, L. E. Gerca, E. A. Silinsh, O. Y. Neilands, M. P. Roze, E. L. Berzinsh, A. B. Klimkans and S. Larsson, *Adv. Mater. Opt. Electron.*, **2**, 319 (1993).

[14] M. A. Rutkis, E. Wistus, S. E. Lindquist, E. Mukhtar, G. Liberts, V. A. Zauls, A. B. Klimkans and E. A. Silinsh, *Adv. Mater. Opt. Electron.*, **3**, 39 (1996).

[15] E. A. Silinsh and A. J. Jurgis, unpublished results.

[16] E. A. Silinsh, *Organic Molecular Crystals: Their Electronic States*, (Springer-Verlag, Berlin, 1980), p. 84.

[17] C. Daniel and M. Dupuis, *Chem. Phys. Lett.*, **171**, 209 (1990).

[18] E. A. Silinsh, *Proc. SPIE* **2968**, 2 (1997).

[19] J. Abe and Y. Shirai, *J. Am. Chem. Soc.* **118**, 4705 (1996).