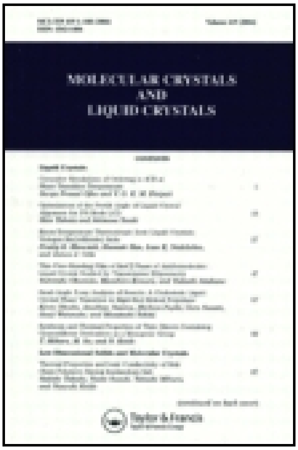

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Theoretical Calculation of Nonlinear Optical Susceptibilities

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Theoretical Calculation of Nonlinear Optical Susceptibilities

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A theoretical calculation method of nonlinear optical susceptibilities of organic materials is reported. The method consists of semi-empirical (CNDO/S3-CI) and *ab initio* molecular orbital calculations to evaluate molecular hyperpolarizabilities and a crystal energy calculation to evaluate the crystallization property.

In the hyperpolarizabilities calculation, the semi-empirical molecular orbital (MO) calculation is applied to the study of second harmonic generation (SHG) materials, and a suitable chemical structure is described. The *ab initio* MO calculation for hyperpolarizabilities is performed and basis set dependence of the hyperpolarizability values calculated by a time independent perturbation method and a coupled-perturbed Hartree-Fock method is investigated.

A space group limiting calculation for crystal energy of second order nonlinear materials by the accelerating convergence method is described. The calculated structures agree well with the experimental data.

Keywords: nonlinear optical susceptibility, molecular orbital, time independent perturbation method, coupled-perturbed Hartree-Fock method, crystal energy calculation

INTRODUCTION

Recently, theoretical and experimental attention has been focused on nonlinear optical phenomena, with the introduction of high power lasers. In particular, organic systems have been recognized as good candidates for nonlinear optical materials due to their large optical nonlinearities and ultra-fast response time.[1,2] Although much work on organic materials has been done, no compounds with satisfactory characteristics for device applications have been discovered. Conventionally, in material development, materials are engineered experimentally and qualitatively, in a "trial and error" method. However, quantitative information and analysis are needed for design and development of sophisticated nonlinear materials.

To obtain quantitative information about nonlinearity, a theoretical investigation is required. However presently, there is no suitable method which predicts the nonlinear optical properties of materials. For molecular nonlinearity, a description in the framework of a molecular orbital method (MO) has been attempted.[3–20]

However, on the practical side, an approach which treats the macroscopic (crystal), as well as the microscopic, nonlinearity is desirable.

A theoretical method to predict macroscopic nonlinear susceptibility was therefore investigated. The method consists of calculations of molecular hyperpolarizabilities and crystal energies.

CALCULATION METHOD OF NONLINEAR OPTICAL SUSCEPTIBILITIES

This section describes the theoretical calculation method of crystal macroscopic nonlinear optical susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$ which govern the second and third nonlinear optical phenomena, respectively. With the oriented gas model,[21] where the interaction between each molecule is neglected, $\chi^{(2)}$ and $\chi^{(3)}$ are expressed as a sum of N molecular contributions. From the model, if the molecular hyperpolarizability tensors and the molecular crystal structure are calculated, $\chi^{(2)}$ and $\chi^{(3)}$ can be obtained theoretically. This was attempted using two calculation methods: a molecular orbital (MO) calculation for the molecular hyperpolarizabilities and a crystal energy calculation for the crystallization properties.

There are several approaches to the calculation of molecular hyperpolarizabilities of nonlinear optical materials. In the first, the hyperpolarizability is obtained from the differential of the ground state energy with respect to the electric field. The ground state energy is derived by the self consistent procedure in the existence of an external electric field and therefore, implicitly, it includes information about the field. The differential of the energy value can be performed numerically (coupled Hartree-Fock, CHF)[22] or analytically (coupled-perturbed Hartree-Fock, CPHF).[23] The former, which is sometimes called the finite field method, is a more practical and popular approach,[8] however, the latter gives a more accurate description.[20] In both cases, the applied field is usually considered to be static.

As a second approach, the standard time independent perturbation theory is used. The hyperpolarizability is obtained by the electric dipole perturbation in terms of the expansion of the one-electron molecular orbitals, which is equivalent to an expansion on many electron states.[17] The one-electron molecular orbital is derived by a single self consistent field (SCF) calculation without any external field. This approach easily calculates the hyperpolarizability.

The standard time dependent perturbation theory is used as a third approach. In this case, the perturbed states are expanded by the molecular eigenstates which are constructed by considering the electron correlation, for example, with the configuration interaction method.[9] This method provides the frequency dependence of the hyperpolarizabilities, which are of practical interest. The calculation formulas of the hyperpolarizability for these approaches are shown in Figure 1.

For each approach, there are a number of studies on nonlinear optical materials by using semi-empirical MO[3-16,18,19] and *ab initio* MO methods.[17,20] In general, the latter are a much larger scale calculation than the former. Since the molecules of interest are often large systems, more attention has naturally been focused on semi-empirical methods as shown in Table I.

(1) Coupled Hartree-Fock Method (Finite-Field Method)

$$\beta_{ijk} = \frac{1}{2}\frac{\partial^3}{\partial F_i \partial F_j \partial F_k}\langle\psi(F)|H(F)|\psi(F)\rangle\Big|_{F=0}^{a}$$

$$H = H_0 + \sum_{i=1}^{n} \mathbf{r}_i \cdot \mathbf{F} \text{ (coupled Hartree-Fock)}$$

F : applied electric field

ψ : molecular eigenstate function

H_0 : unperturbed Hamiltonian

r : electron coordinate

[a] The third derivatives are numerically evaluated using the following formula:

$$\beta_{ijk} = \{E(F) + E(-F) - 2E(0)\}/2F_iF_jF_k,$$

where $E(F) = \langle\psi(F)|H(F)|\psi(F)\rangle$.

Coupled-perturbed Hartree-Fock Method

$$\beta_{ijk} = -2 \sum_{st} D_{st}^{jk} h_{st}^{i}$$

$$D_{st}^{jk} = \frac{\partial^2}{\partial F_j \partial F_k} \sum_{a} C_{sa}^{*} C_{ta}$$

$$h_{st}^{i} = \frac{\partial}{\partial F_i}\langle s|h|t\rangle$$

C_{sa} :LCAO coefficient

h : one-electron Hamiltonian

$|s>$, $|t>$: molecular orbital

(2) Time-independent Perturbation Method (Rayleigh-Schrödinger)

$$\begin{aligned}\beta_{ijk} &= \frac{1}{2}\frac{\partial^3}{\partial F_i \partial F_j \partial F_k} E^{(3)} \\ &= P\left[\sum_{atu} \frac{\langle t|\mu_i|a\rangle\langle a|\mu_j|u\rangle\langle u|\mu_k|t\rangle}{6(\varepsilon_t - \varepsilon_a)(\varepsilon_u - \varepsilon_a)} \right. \\ &\quad \left. - \sum_{abt} \frac{\langle t|\mu_i|a\rangle\langle a|\mu_j|b\rangle\langle b|\mu_k|t\rangle}{6(\varepsilon_t - \varepsilon_a)(\varepsilon_t - \varepsilon_b)}\right]\end{aligned}$$

$$H_1 = \sum_{i=1}^{n} \mathbf{r}_i \cdot \mathbf{F}$$

$|a\rangle, |b\rangle$: occupied molecular orbital

$|t\rangle, |u\rangle$: unoccupied molecular orbital

$E^{(3)}$: third order correction for ground state energy

P : permutation operator for i,j,k

μ_i : dipole matrix

$\varepsilon_a, \varepsilon_b, \varepsilon_t, \varepsilon_u$: molecular orbital energy

FIGURE 1 Calculation methods of molecular hyperpolarizability.

(3) Time-dependent Perturbation Method

$$\beta_{ijk}(-2\omega{:}\omega,\omega) = \mathrm{P}\sum_{AB}\left[\left\{\frac{\langle G|\mu_k|A\rangle\langle A|\mu_i|B\rangle\langle B|\mu_j|G\rangle}{4\,(E_A-E_G-\hbar\omega)(E_B-E_G+\hbar\omega)} + \frac{\langle G|\mu_i|A\rangle\langle A|\mu_j|B\rangle\langle B|\mu_k|G\rangle}{4\,(E_A-E_G+2\hbar\omega)\,(E_B-E_G+\hbar\omega)} + \frac{\langle G|\mu_j|A\rangle\langle A|\mu_k|B\rangle\langle B|\mu_i|G\rangle}{4\,(E_A-E_G-\hbar\omega)\,(E_B-E_G-2\hbar\omega)}\right\} + \{\omega \rightarrow -\omega\}^{b}\right]$$

$|G\rangle$: ground state
$|A\rangle$, $|B\rangle$: excited state
E_G : ground state energy
E_A, E_B : excited state energy
ω : frequency of an incident beam
${}^{b}\{\omega \rightarrow -\omega\}$ means an abbreviated expression that differs by a sign of ω.

FIGURE 1 (*continued*)

A similar method to Garito et al.[9] was chosen to calculate the hyperpolarizability; they used the time dependent perturbation approach[24] with the CNDO/S3 method[25,26] including a limited singly excited configuration interaction (CI), in order to search for suitable materials for the SHG device of a diode laser.

The hyperpolarizabilities were also calculated using both time independent perturbation theory and the CPHF method with *ab initio* MO method. The purpose was to investigate molecular hyperpolarizabilities deeply by a more rigorous method.

For the calculation of the crystal properties, we chose a crystal energy minimization procedure using empirical atom-atom pairwise potentials with the accelerating convergence method of Ewald[27] for Coulomb energy.

MOLECULAR HYPERPOLARIZABILITY CALCULATION BY SEMI-EMPIRICAL METHOD

In work previously reported,[28] a semi-empirical MO calculation by the CNDO/S3-CI method[25,26] with time dependent perturbation, was applied to a search for suitable materials for the SHG device. There are two important characteristics required for such a molecule: a large first hyperpolarizability β and a cut-off wavelength shorter than 400 nm. Based on the calculated results, several compounds which satisfy these requirements were found.[28] For this kind of MO calculation, some points should be mentioned. First, optimization of molecular structures by the MO method such as the MNDO method[29] or molecular mechanics method[30] is important, in particular, in the case of molecules which have steric hindrance, to evaluate the hyperpolarizabilities reliably. In the second, the number which

TABLE I

Summary of the calculations of molecular hyperpolarizabilities

No.	Authors	Molecules	Method[a] (approximation of HF matrix)	Reference
1	Flytzanis et al. ('76, '77, '78)	polymers	time dep. PT (Hückel)	3, 4, 5
2	Hameka et al. ('78, '80)	conjugated hydrocarbons	time indep. PT (Hückel, PPP)	6, 7
3	Zyss ('79)	benzene derivatives	CHF (INDO)	8
4	Garito et al. ('79, '88)	benzene derivatives, polyene	time dep. PT (CNDO/S)	9, 10
5	Waite and Papadopoulos ('82, '85)	conjugated hydrocarbons	coupled SCF PT (CNDO/2)	11,12
6	Docherty et al. ('85)	conjugated compounds	time dep. PT (CNDO/S)	13
7	Svendsen et al. ('85)	water, urea	variational method (CNDO/2)	14
8	Li et al. ('86)	conjugated compounds	time dep. PT (PPP)	15
9	De Melo et al. ('87)	polyene	coupled SCF PT (PPP)	16
10	André et al. ('87)	polyene	time indep. PT, CHF (ab initio)	17
11	Kirtman ('87)	polyene	CHF (INDO)	18
12	Pierce ('88)	polyene	time dep. PT (INDO)	19
13	Clementi et al. ('88)	polyene	CPHF (ab initio)	20

[a] PT: perturbation theory; CHF: coupled Hartree-Fock method
SCF: self consistent field; CPHF: coupled-perturbed Hartree-Fock method.

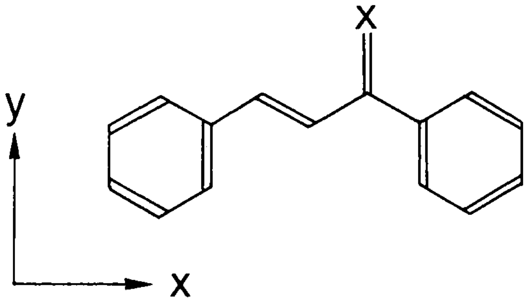

FIGURE 2 Molecular structure of a:X = O and b:X = CH_2.

expresses the upper limit included in the intermediate summation should be carefully determined since parameters of this method were derived to reproduce several lower excited states.[26] The number of configurations was restricted in the present calculations so that the energy difference between an occupied molecular orbital and a vacant one, which can replace each other by a single electron excitation, is within a certain region which is relevant to the first parametrized region.

Using a microscopic description, we investigated why these compounds should have the desired properties. For this purpose we chose chalcone (X = O, in Figure 2) as a typical example and compared it with a similar compound (X = CH_2). The electronic states were calculated by the CNDO/S3-CI method, in order to investigate the role of the carbonyl group. The results are shown in Table II.

From a comparison of a with b, it was found that their electronic states were incompletely conjugated all over the molecule and thus should have nearly the same and relatively higher lowest excited energies $\hbar\omega$. Nevertheless, β values were quite different from each other; the β value of a (chalcone) was higher than that of b as shown in Table II. The large β value of chalcone could be explained by the large value of $\Delta\mu$ which is the difference in the dipole moments between the ground state and the lowest excited state. The corresponding MO diagrams, shown in Figures 3 and 4, which are the most significant contributions for the lowest excitation, illustrate how the large $\Delta\mu$ value arose in chalcone. There was a redistribution of the electron density from the left phenyl site to the right phenyl site occurring in the lowest unoccupied molecular orbital and this resulted in the large dipole moment change between the ground and the excited states in compound a.

TABLE II

Physical values calculated by CNDO/S3-Cl method

Compounds*	$\hbar\omega$/eV	$\Delta\mu_X$/D	$\Delta\mu_Y$/D	$\beta^{**}_{XXX}/10^{-30}$ esu	$\beta^{**}_{YYY}/10^{-30}$ esu	$\beta^{**}_{XXY}/10^{-30}$ esu
a	4.32	−4.47	−2.40	−14.0	−2.20	−7.42
b	4.38	−2.61	−1.84	−0.94	−3.79	−4.07

*a and b are compounds shown in Figure 1 with X = O and X = CH_2, respectively.
**Calculated at 1.06 μm.

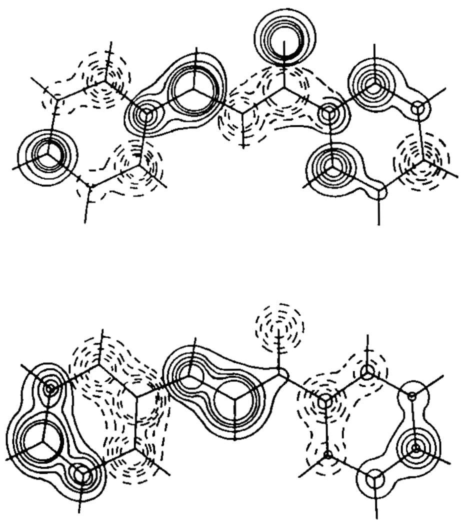

FIGURE 3 Contour diagram of the highest occupied (bottom) and lowest unoccupied (top) molecular orbitals of compound a (X = O, in Fig. 2) drawn for z = 0.3Å. Positive and negative values are indicated by solid and dashed lines, respectively. Outer contour lines have a magnitude of 0.1, with successive lines increasing (decreasing for negative contours) by 0.1 increments toward atomic sites.

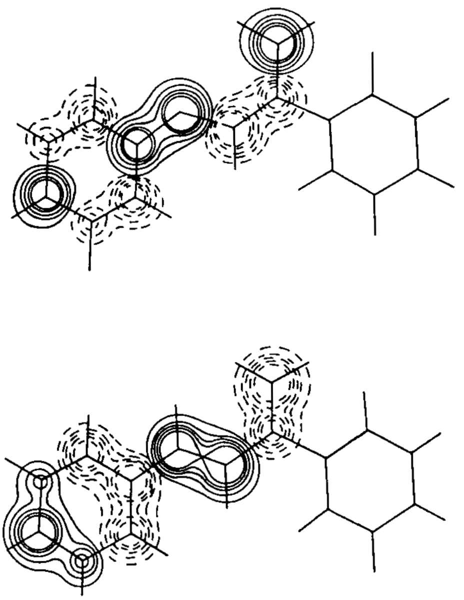

FIGURE 4. Contour diagram of the highest occupied (bottom) and lowest unoccupied (top) molecular orbitals of compound b (X = CH_2, in Fig. 2) drawn for z = 0.3Å. Positive and negative values are indicated by solid and dashed lines, respectively. Outer contour lines have a magnitude of 0.1, with successive lines increasing (decreasing for negative contours) by 0.1 increments toward atomic sites.

On the other hand, such a redistribution of electronic states did not occur in the case of compound b.

The above investigation may suggest the effectiveness of the carbonyl group between two conjugated moieties for our purpose. In fact, several compounds with chemical structures similar to those discussed above have been found as suitable materials for SHG applications.[27]

MOLECULAR HYPERPOLARIZABILITY CALCULATION BY *AB INITIO* METHOD

In order to continue the theoretical study of hyperpolarizabilities and to investigate the mechanism and origin of nonlinearity by a more rigorous approach, the hyperpolarizabilities were calculated by an *ab initio* method.

In the first step, the basis set dependence of hyperpolarizabilities and the difference between the hyperpolarizability values calculated by the time independent perturbation theory and the CPHF method shown in Figure 1, were investigated. The calculation were done by using the GAUSSIAN 80 program[31] for the time independent perturbation theory and the HONDO version 7 program[32] for the CPHF method; in neither case was an electron correlation considered, i.e. Hartree-Fock level calculations were done, in the manner of Clementi et al.[20] and André et al.[17] On the basis set dependence, Clementi et al.[20] showed the importance of the diffuse functions to calculate correctly the second hyperpolarizabilities of polyene oligomers. André et al.[17] compared the linear polarizability values of polyene oligomers calculated by the former method with the latter one and indicated that the latter was more accurate.

The calculated results of the first hyperpolarizabilities, β of urea and *p*-nitroaniline (*p*-NA), as examples, are shown in Table III, in which the influence of the basis sets are also shown. The calculation using the CPHF with extended bases gave values in agreement with the experimental ones. Table III shows that the

TABLE III

β values in units of 10^{-30} esu calculated by ab initio method

	Basis Set	STO-3G	3-21G	4-31G	6-31G	6-31G*	LP-31G (ECP)[a]	Experimental[33]
Urea	CPHF[b]	0.177	0.501	0.555	0.559	0.485	0.522	0.45
	time indep. PT[c]	0.163	0.451	0.460	0.530	0.473	0.495	(at 1.06 μm)
p-NA	CPHF[b]	4.210	8.038	9.994	10.194		9.202	9.6
	time indep. PT[c]	2.503	3.641	4.013	4.200		3.930	(at 1.907 μm)

[a] ECP: effective core potential method.[34]
[b] CPHF: coupled-perturbed Hartree-Fock method.
[c] Time indep. PT: time independent perturbation theory.

calculated values were improved by extending bases and the CPHF values of *p*-NA were closer to the experimental ones[33] than those obtained by the perturbation method. This situation was similar to the case of the linear polarizabilities of polyene oligomers,[17] while urea had nearly the same values at each basis in both methods. This was considered to reflect the fact that the CPHF method included the average electron-electron interaction self-consistently under the electric field perturbation, as indicated by André et al. for linear polarizabilities[17] and the large π conjugate system, such as *p*-NA, was significantly influenced by the interaction.

The results of an effective core potential (ECP) method[34] indicated that the core electron could be satisfactorily replaced by the effective core potential, this also meant that the calculations according to a valence-electron MO method, such as the semi-empirical MO method, could be used validly. Details of this calculation and the more accurate calculation are to be discussed elsewhere.

CALCULATION OF CRYSTALLIZATION PROPERTIES

In this section, calculation of crystallographic properties of the molecular crystals, which are needed for estimation of the macroscopic (crystal) nonlinear optical property is described. Crystal structure is very important for the even-order nonlinearity, for example SHG, which is caused by its nonlinear odd rank susceptibility tensor, since the crystal optical nonlinearities are exactly zero if the crystal structures are centrosymmetric.

For this purpose, the intermolecular interaction energy was studied, because molecules generally crystallize in a structure in which the energy is a minimum; the energy represents the sum of all intermolecular interactions in the crystal.

In a previous paper,[28] as a first step, the intermolecular interaction energy between two molecules was calculated by using the empirical potential functions and the relationship between the calculated results and the existence of an inversion center in the crystals was investigated.

The extension of the method to a crystal energy calculation including a large number of molecules was considered. To evaluate the energy minimum calculation a specific approach was used in which a space group was assumed. This procedure drastically reduced the degrees of freedom to be considered in the calculation. Under this condition, the crystal energy was optimized on various degrees of freedom generated by combining six parameters of the crystal (lattice constants) to six parameters of the molecule (translation and rotation). The same calculations were repeated in order for the other space groups. Finally the required crystal structure was obtained by selecting the one which had the minimum energy from the minimum energy structure of each space group. The advantage of this method is shown by the fact that several particular space groups appear dominantly in the molecular crystals.[35]

We chose a calculation method from the empirical crystal energy calculation methods using atom-atom pairwise potentials. In our method intermolecular interaction energy is expressed as

$$V_T = U_v + U_E \tag{1}$$

$$U_v = \frac{1}{2}\sum_i \sum_j (-A_{ij}/r_{ij}^6 + B_{ij}/r_{ij}^{12}) \tag{2}$$

$$U_E = \frac{1}{2}\sum_i \sum_j Q_i Q_j/\epsilon r_{ij} \tag{3}$$

where U_V is the van der Waals potential including the repulsion by the electron orbital overlap, which is known as the Lennard-Jones potential function, U_E is the electrostatic Coulomb potential, r_{ij} is the interatomic distance, A_{ij} and B_{ij} are Lennard-Jones parameters, Q_i is the partial charge of the i th atom, which is obtained by a semi-empirical molecular orbital calculation (CNDO or MNDO), ϵ is the dielectric constant. The summations with respect to i and j are taken for atoms included in the unit cell and in the crystal, respectively. In principle, the latter should be taken from atoms at infinite distance. In practice, the range of the summation is limited to a certain finite distance, at which the crystal energy is considered to be convergent.

A difficult problem arises from the convergence of the calculated crystal energy due to the contribution of the electrostatic potential energy which is not convergent in the long distance region, due to the long range interaction property.

The calculated convergence property of each potential is shown in Figure 5 where r is the cut-off length which limits the region to be considered. As shown in Figure

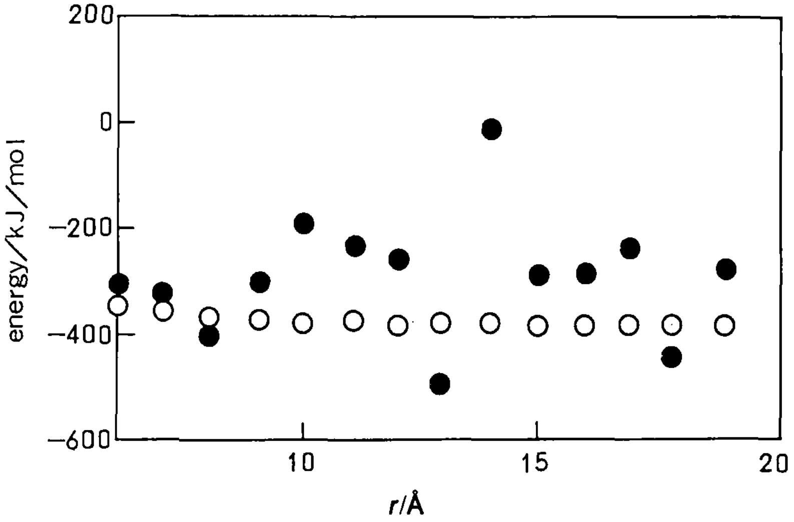

FIGURE 5 Crystal energies versus cut-off distance r for an MNA molecule (●: electrostatic Coulomb energy; ○: van der Waals energy).

5, the van der Waals energy at $r = 10$ Å was nearly the same value (96%) as that of the convergent value, however, the electrostatic energy did not converge at all even at 19 Å, which was considered to be the upper limit for a realistic cpu time.

The convergence problem was studied and it was demonstrated that, in principle, convergence was always achieved for the crystal without a total electric charge.[36] An adaptation of the accelerated convergence method developed by Ewald[27,36] was made, in which the electrostatic energy is expressed as

$$U_{\mathrm{E}} = \frac{1}{2}\sum_{i}\sum_{j} Q_{\mathrm{i}}Q_{\mathrm{j}}r_{\mathrm{ij}}{}^{-1}\,\phi\,(r_{\mathrm{ij}}) + \frac{1}{2}\sum_{i}\sum_{j} Q_{\mathrm{i}}Q_{\mathrm{j}}r_{\mathrm{ij}}{}^{-1}\,[1 - \phi\,(r_{\mathrm{ij}})] \tag{4}$$

$$\phi\,(r_{\mathrm{ij}}) = \frac{\Gamma(1/2,\ \mathrm{K}^2\pi r^2{}_{\mathrm{ij}})}{\Gamma(1/2)} = \int_{\pi \mathrm{K}^2 \mathrm{r}^2 \mathrm{ij}}^{\infty} \exp(-t^2)dt = \mathrm{ERFC}(a) \tag{5}$$

$$a^2 = \pi \mathrm{K}^2 r^2{}_{\mathrm{ij}} \tag{6}$$

where ϕ is the convergence function, Γ is the gamma function, K is the parameter, and ERFC is an error function. Inserting Equations (5) and (6) into Equation (4) and performing a Fourier transformation for the second summation gives

$$\begin{aligned} U_{\mathrm{E}} = {} & \frac{1}{2}\sum_{ij} Q_{\mathrm{i}}Q_{\mathrm{j}}r_{\mathrm{ij}}{}^{-1}\,\mathrm{ERFC}(a) + \frac{1}{2\,\pi\,V}\sum_{\mathbf{h}\lambda \neq 0} |\,\mathrm{F}(\mathbf{h}_\lambda)\,|^2\mathbf{h}_\lambda^{-2}\exp(-b^2) \\ & - \mathrm{K}\sum_{\mathrm{CELL}} Q_{\mathrm{i}}^2 \end{aligned} \tag{7}$$

$$F\,(\mathbf{h}_\lambda) = \sum_{\mathrm{CELL}} \mathrm{Q}_{\mathrm{j}}\exp(-2\,\pi i\mathbf{h}_\lambda \cdot \mathbf{r}_{\mathrm{ij}}) \tag{8}$$

$$b^2 = \pi \mathbf{h}_\lambda^2/\mathrm{K}^2 \tag{9}$$

where V is the volume of the unit cell, and $\mathbf{h}_\lambda$ is the reciprocal-space vector. In this particular method, the summation is done for both real and reciprocal spaces.

Figure 6 illustrates the convergence behavior of the crystal energy of MNA by this method using the convergence constant K = 0.3, which most effectively accelerated the convergence of the Coulomb energy of our target materials. In this case, it was found that the convergence of the electrostatic energy was achieved at around 7.4 Å and 0.9 Å^{-1}, in the real and reciprocal spaces, respectively.

Table IV shows the minimum energy structure calculated by optimizing the orientation of the molecules and the lattice constants and fixing the position of the center of gravity of the first molecule using the space groups experimentally obtained.[37–39] Good agreement was achieved between the experimental[37–39] and

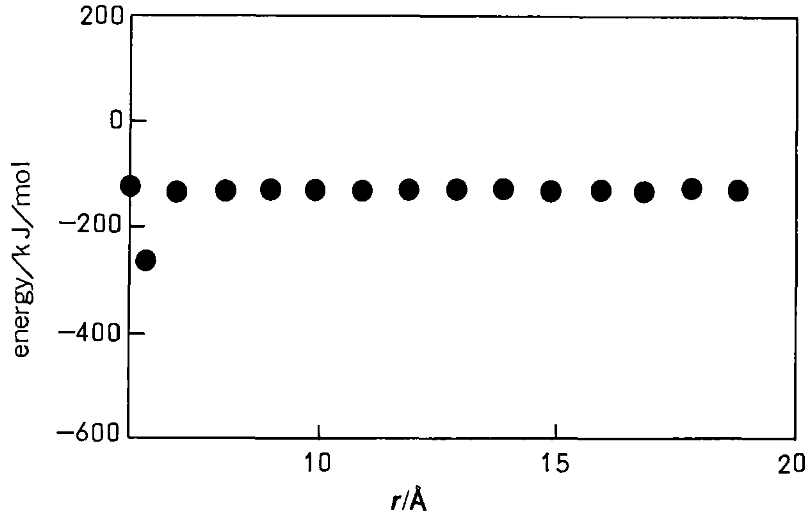

FIGURE 6 Convergence property of the electrostatic Coulomb energy at K = 0.3 for an MNA molecule.

calculated structures. It should be noted that the empirical parameters,[40] which were not developed for the purpose of the crystal optimization calculation of our target materials, reproduced observed crystal structures very well. There was still some slight difference, which might be improved by raising the accuracy of the calculation of partial charges, for example, by the *ab initio* method. This is now in progress in the author's laboratory.

The components of the crystal energy are shown in Table V. In Table V, the ratio of the electrostatic energy to the total crystal energy is also shown. It should be noted that the ratios were larger than 10% for these compounds. The electro-

TABLE IV

Cell dimensions of observed and minimum energy crystal structures

		Cell Dimensions				Crystal Energies
Molecules		a /Å	b /Å	c /Å	β /deg.	/kJ mol^{-1}
MNA	Exp.[37]	8.2525	11.62	7.585	94.08	−431.32[a]
	Calc.	8.2	11.6	7.6	94.1	−444.42
p-NA	Exp.[38]	12.336	6.07	8.592	91.45	−445.99[a]
	Calc.	12.5	6.1	8.8	91.5	−451.22
xanthone	Exp.[39]	13.63	14.11	4.86	90.0	−428.45[a]
	Calc.	13.8	14.3	4.9	90.0	−435.74
2-7-dinitroxanthone	Exp.[b]	6.136	36.892	5.089	90.0	−682.03[a]
	Calc.	6.5	36.1	5.3	90.0	−703.38

[a] calculated using observed crystal structures.
[b] the details of these crystallographic data will be described elsewhere.

TABLE V

Crystal energies of the nonlinear optical materials in units of kJ/mol

Compounds	V_T	U_V	U_E	U_E/V_T
MNA (CNDO)	−431.32	−361.27	−70.05	0.162
MNA (MNDO)	−443.62	−361.27	−82.38	0.186
p-NA (CNDO)	−384.04	−313.53	−70.51	0.184
p-NA (MNDO)	−445.99	−313.53	−132.46	0.297
xanthone	−428.45	−393.62	−34.83	0.081
2-7-dinitroxanthone	−682.03	−588.54	−93.49	0.137

V_T: total energy; U_V: van der Waals energy; U_E: electrostatic energy.

static contribution for the total crystal energy of ordinary organic crystals has been conventionally described as almost negligible,[41] however, this is not always valid, especially for nonlinear optically interesting compounds which often have large dipole moments. These findings are from the first stage of our calculations on crystal energy. Further investigation and application to nonlinear optical susceptibilities are in progress.

CONCLUSION

The final goal is to establish a calculation method of crystal nonlinear susceptibilities of organic materials. Crystal optical nonlinearity, in particular of even-order, are affected drastically by the way molecules aggregate in the crystal. Therefore, a calculation which predicts molecular orientations in the crystal or crystal structure from the chemical structures of the molecules was necessary. Thus the theoretical calculation consisted of two parts; calculation of molecular hyperpolarizabilities; and calculation of crystallization properties. These two were performed by molecular orbital methods and crystal energy calculations, using atom-atom pairwise potentials, respectively. In this paper, current progress is described.

The semi-empirical calculation for the molecular hyperpolarizabilities was applied to a search for SHG materials. The reason for coexistence of a large nonlinearity and a short cut-off wavelength was investigated and oxygen, included in a carbonyl group, was found to make an important contribution.

In many hyperpolarizability calculations, semi-empirical MO methods are suitable from the viewpoint of accuracy and cpu time. However, there are some cases in which the parameters for calculation are missing and in which more rigorous hyperpolarizability calculations and other physical quantities are required. In these cases *ab initio* MO calculations are necessary since these require no parameters and can calculate a lot of physical quantities with equal accuracy. The hyperpolarizability calculation by *ab initio* methods was investigated to assess reliability and limitations.

As the first step, basis set dependences of the first hyperpolarizability values calculated by a time independent perturbation and a coupled-perturbed Hartree-

Fock (CPHF) methods were investigated. To reproduce the correct values of hyperpolarizability, at least split-valence type bases were necessary. The values calculated by the latter method were more accurate than those of the former. These results seemed to be reasonable in consideration with each approximate level.

In order to predict crystal structure, crystal energy calculations, using empirical atom-atom pairwise potentials, were performed. The crystal energy, since the Coulombic part is a long range interaction, was obtained from calculations using the accelerating convergence method. Under the restriction of a real space group, calculated energy minimum structures of some typical organic nonlinear materials agreed well with experimental ones.

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