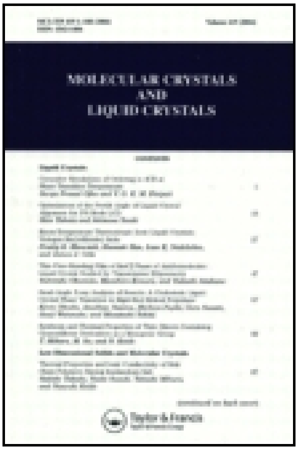

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Molecular Design for New Second-Order Nonlinear Optical Materials

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Molecular Design for New Second-Order Nonlinear Optical Materials

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A molecular design method of second-order nonlinear optical materials for SHG device applications of diode lasers is proposed. The method consists of a semi-empirical MO calculation (CNDO/S3-CI) to evaluate molecular nonlinear optical properties of a molecule and an intermolecular interaction energy calculation to evaluate its crystallization property, in particular whether it crystallizes in a centrosymmetric structure or not. Using this method we design novel second-order nonlinear optical materials for our target applications: xanthone and benzophenone derivatives which have relatively large optical nonlinearity and short absorption cut-off wavelength.

INTRODUCTION

Organic nonlinear optical materials offer large nonlinear optical properties and high speed response compared with inorganic materials.[1,2] Until now, while much work on organic nonlinear optical materials has been done, no material which has sufficient characteristics for device applications has been discovered.[1] For example, merocyanine has a very large second-order hyperpolarizability, but an absorption cut-off in excess of 600 nm.[3] On the other hand urea has a transparency down to 200 nm, but a relatively low second-order hyperpolarizability.[4]

Of the many potential applications of organic nonlinear materials to optics technology, we restricted the purpose of our research to develop suitable materials for SHG (second harmonic generation) devices of a diode laser. Nonlinear optical materials for this application should have at least two important characteristics: a large second-order nonlinear susceptibility as a crystal and a cut-off length shorter than 400 nm. The latter is required not to absorb the second harmonic of the fundamental light from a semiconductor laser of which the wavelength is around 800 nm.

One of the simplest ways in which an organic molecule can be engineered to have a large optical nonlinearity is by possessing a conjugated system of bonds which give rise to a strong π-electron delocalization. Moreover, the addition of donor and acceptor groups at the opposite ends of the conjugated system further enhances its optical nonlinearity. This enhancement is explained as due to the strong intramolecular charge transfer between such groups operating across the entire extended system.[5-8] Accordingly the longer the conjugation length of the molecule is and the stronger the donor and acceptor groups are, the larger the hyperpolarizability of the molecule is. Unfortunately, such a molecule with the chemical structure described above, however, has a relatively long absorption cut-off edge usually longer than 500 nm. Then the two important requirements of organic nonlinear materials for SHG devices are at cross purposes. To overcome this and to design suitable chemical structures for SHG materials, quantitative analyses and a novel way to design these materials are required. For this purpose we quantitatively calculated the hyperpolarizability and the lowest excited energy of the molecule by a semi-empirical MO method (CNDO/S3-CI). These were then used as guidelines to select suitable chemical structures.

Our next concern was that the molecule is able to crystallize in a structure lacking a center of inversion, since even though it has the two desired characteristics mentioned above, all components of second-order hyperpolarizability tensor vanish for a centrosymmetric crystal. Therefore in the second state we must select the chemical structure which is expected to crystallize in a noncentrosymmetric structure. For this purpose we also took a quantitative method, that is, intermolecular interaction energy calculations which are described in detail in the next section.

We used the two calculation methods to select and to design the suitable chemical structure for our target materials. We then synthesized molecules with the designed chemical structures, some of which had relatively large second-order optical nonlinearity and very short cut-off wavelength.

THE MOLECULAR DESIGN METHOD

We selected suitable chemical structures by two steps. First the chemical structures which were calculated to have large hyperpolarizabilities and a large lowest excited energies were selected from heterocyclic compounds containing nitrogen and/or oxygen by using a quantum chemical MO method. We chose these compounds because we did not think the simple π-electron conjugation system, for example benzene and polyphenyl derivatives, could possess the two characteristics at the same time, as mentioned in the previous section. In the next step the molecules, which had a tendency to crystallize in a noncentrosymmetric structure, were selected by intermolecular interaction energy calculations, from the molecules which had been selected by the MO method. Our calculation process for designing chemical structures is summarized in Figure 1.

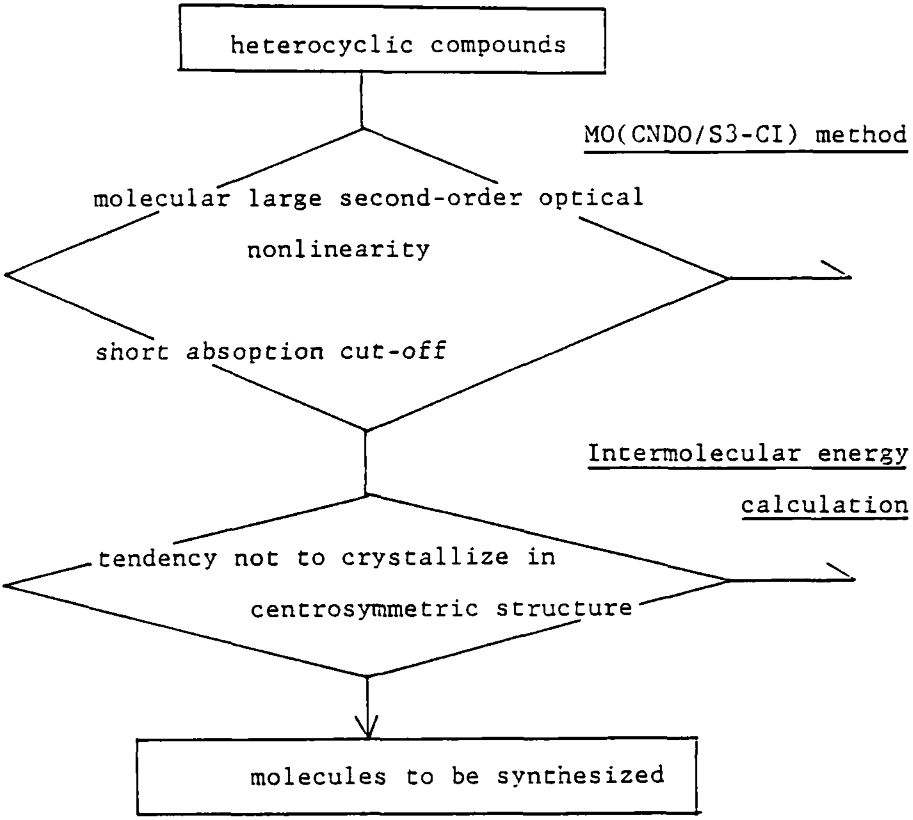


FIGURE 1 Molecular design procedure.

Calculations of nonlinear optical properties of a molecule

The second-order hyperpolarizability β_{ijk} for SHG far from the resonant region is given by the time dependent perturbation theory with the perturbing Hamiltonian $H' = -e\mathrm{E}.\mathrm{r}\sin\omega t$ as follows[9]:

$$\beta_{ijk} + \beta_{ikj} = -\frac{e^3}{4\hbar^2}\Bigg[\sum_{\substack{n \neq n' \\ n \neq g \\ n' \neq g}} (r^j_{gn'} r^i_{nn'} r^k_{gn} + r^k_{gn'} r^i_{n'n} r^j_{gn})$$

$$\times \left(\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)}\right)$$

$$+ (r^i_{gn'} r^j_{n'n} r^k_{gn} + r^i_{gn'} r^k_{n'n} r^j_{gn})$$

$$\times \left(\frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)}\right)$$

$$+ \left(r^j_{gn'} r^k_{n'n} r^i_{gn} + r^k_{gn'} r^j_{n'n} r^i_{gn}\right)$$

$$\times \left(\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + 2\omega)} \right)$$

$$+ 4\Sigma[r^j_{gn} r^k_{nn} \Delta r^i_n (\omega^2_{ng} - 4\omega^2)$$

$$+ r^i_{gn}(r^k_{gn}\Delta r^j_n + r^j_{gn}\Delta r^k_n)(\omega^2_{ng} + 2\omega^2)] \frac{1}{(\omega^2_{ng} - \omega^2)(\omega^2_{ng} - 4\omega^2)}$$

Here $r_{gn} = \langle g|r^i|n\rangle$, $r_{nn'} = \langle n|r^i|n'\rangle$ are matrix elements of the transition moments along the ith axis between the molecular ground state $|g\rangle$ and an excited state $|n\rangle$ and between two excited states, $|n\rangle$ and $|n'\rangle$, respectively. $\Delta r_n = r_{nn} - r_{gg}$ is the difference of the dipole moments between an excited state $|n\rangle$ and the ground state $|g\rangle$. $\hbar\omega_{ng}$ is the difference in the energy between an excited state $|n\rangle$ and the ground state $|g\rangle$ and ω is the frequency of the incident light.

We used a semi-empirical MO Method, that is CNDO/S3 including singly-excited configuration interaction (CNDO/S3-CI), to calculate quantum mechanical values in Eq. (1) similar to Lalama and Garito[10] who were able to calculate accurate values of β and their dispersion for some benzene derivatives.[11] A precise description of electron–electron interactions of molecules is needed to evaluate a meaningful value of β. We thus adopted this MO method since it is known to reproduce an accurate electronic structure, in particular the excited states due to configuration interaction (CI), of widely varying conjugated molecules including hetero atoms. Another reason was that the method can calculate a relatively large molecule within a realistic cpu time because it neglects less important integrals and empirically approximates the important integrals of Hartree-Fock matrix to adjustable parameters. This feature was very important as we intended to search for suitable molecules for SHG device applications from a vast number of molecules.

The required input parameters, valence-state ionization energies, resonance integrals, Coulomb repulsion integrals, and Slater orbital exponents, were taken from those obtained by Lipari and Duke.[12] No reparametrization was performed because the calculated values of β agreed reasonably with the experimental ones shown in Table I.

TABLE I

β and the lowest excited energy

Molecule	Calculated $\hbar\omega_{\min}$/eV	Observed[a] $\hbar\omega_{\min}$/eV	Calculated[b] $\beta_{xxx}/10^{-30}$ esu
Benzophenone	3.87	3.55	0.29
4-Methoxy-4′-nitro-benzophenone	4.00	4.24	−1.45
Xanthone	4.13	3.65	−3.30
2-Nitroxanthone	4.52	3.72	−2.72
3-Nitroxanthone	3.96	3.55	−3.30

[a] From spectra in ethanol.
[b] Calculated at 1.06 μm.

For the CI calculation in our semi-empirical MO method, we noticed that the number of excited states included in the CI calculation had the great influence on the calculated value of β. In the case of the ab initio method the calculation with the largest possible number of excited states i.e. a full CI calculation, gives the most accurate excited electronic structure of a molecule. In the case of a semi-empirical method, however, it is not clear whether it is valid or not to carry out the CI calculation, including a large number of higher excited states, because the parameters used are determined in the lower excited states region. In practice, the calculation with too large a number of excited states included in the CI calculation gives somewhat inaccurate lower excited states for a molecule when compared with experimental ones. Further discussion of this problem is not included here.

It is necessary to explain our method for determining the number of configurations included in the CI calculation of a molecule. The configurations included are restricted so that the energy difference between an occupied and a vacant molecular orbital, which are replaced each other when the electron configuration is constructed, is lower than a specific value which is determined to correspond to the first parameterized energy region.

A fixed molecular geometry is required, and moreover, higher accuracy of the geometry is needed for this calculation since the value of β depends considerably on the bond lengths and the bond angles of which atoms are conjugated. Thus as the input molecular geometry, that obtained from the published x-ray crystallographic studies or from the calculated optimized structure by a semi-empirical MO method (MNDO), was used.

Calculated results on the lowest excited states and the hyperpolarizabilities β of several molecules are listed in Table I. Good agreement between calculated and experimental values is obtained, which suggests that our method of calculation of β could be used for molecular design of our target, second-order nonlinear optical materials.

Investigation of intermolecular interaction by empirical energy calculation method

In the previous section, we discussed the nonlinear property of one molecule using the MO calculation method. Next we must consider a macroscopic (crystal) nonlinear optical property.

For second-order nonlinear optical materials, the crystal structure is very important because second-order nonlinear susceptibility is a third rank tensor. It is well known that all components of third rank tensors vanish for a centrosymmetric crystal.[13] To design a suitable crystal structure for second-order nonlinear optical materials, the relationship between the chemical structure of a molecule and its crystal structure, in particular whether it is centrosymmetric or not, should be clarified. So far only qualitative discussions on this point have been done as summarized here. Crystallization of a molecule into a noncentrosymmetric structure can be achieved by attaching to it suitable substituents which cause a steric hindrance, or form hydrogen-bonds, or have asymmetric carbons.[1,14,15] Reasons as to why these procedures are effective are, however, very qualitative. Except for the last kind of molecules, which are enantiomers, it is uncertain whether a noncentrosymmetric structure will always be obtained. Accordingly it is necessary to examine whether the crystal structure of the molecules which are designed as materials for SHG applications is centrosymmetric or not after actually synthesizing them, although syntheses of new molecules spend both time and money.

To obtain some quantitative information about the crystallization property of the molecule before synthesis, we calculated intermolecular interaction energies of the molecules which determine their crystal structure.

Molecules generally crystallize in a structure in which the energy is minimum; this energy represents the sum of all intermolecular interactions in the crystal. Therefore, knowing the intermolecular interaction energy provides information about their crystal structure. A number of crystal energy calculation methods have been investigated by many researchers so far.[16,17] We chose a calculation method for the intermolecular interaction energy from empirical crystal energy calculation methods using atom–atom pair-wise potentials.[16,17,18] In our method intermolecular interaction energy is expressed as follows:

$$V = \Sigma U_{Vij} + U_{Eij} \tag{2}$$

$$U_{Vij} = -A_{ij}/r_{ij}^{6} + B_{ij}/r_{ij}^{12} \tag{3}$$

$$U_{Eij} = Q_i Q_j/\epsilon r_{ij} \tag{4}$$

Here V is the total intermolecular interaction energy, U_V is a Van der Waals interaction including a repulsion term which occurs owing to overlapping electron shells, and U_E is electrostatic interaction energy. U_V is well known to be called a Lennard-Jones potential function. A_{ij} and B_{ij} are potential parameters varying for types of atoms, such as C(sp^2), C(sp^3) etc. r_{ij} is the distance between two interacting atoms, Q_i and Q_j are partial charges of atoms in molecules which can be evaluated by MO calculation of the molecules, and ϵ is the dielectric constant.

In our calculation the Lennard-Jones potential parameters obtained by Hopfinger[18] were used. These parameters are given in Table II. The parameters obtained by other researchers[19,20] were also used in our calculations but the results were similar to those evaluated by using Hopfinger's parameters. Thus only the results using Hopfinger's parameters are given hereafter. Partial charges of atoms of a molecule were calculated by the MNDO method.[21] The input molecular structure was optimized also by the MNDO method. Using Eqs. (2)–(3), intermolecular interaction energies of two molecules of various intermolecular configurations were calculated and the configuration with the minimum interaction energy was searched for. We thought that the molecule would have the tendency to crystallize in a centrosymmetric structure if the minimum energy intermolecular configuration of the two molecules had a center of inversion.

To examine the reliability of this approach, the intermolecular interaction energies of typical organic nonlinear materials, that is *p*-nitroaniline (*p*-NA) and *m*-nitroaniline (*m*-NA), were calculated. The reason why we took these molecules as typical was as follows: *m*-NA is SHG active, but *p*-NA is not in their crystalline

TABLE II

A_{ij} and B_{ij} for the Lennard-Jones potential function[a]

	H		$C(sp^2)$		$C(sp^3)$	
Atom	A_{ij}	B_{ij}	A_{ij}	B_{ij}	A_{ij}	B_{ij}
H	46.7	0.446	165.8	1.924	127.4	3.743
$C(sp^2)$	165.8	1.924	600.2	19.62	465.3	19.70
$C(sp^3)$	127.4	3.743	465.4	19.70	372.5	28.58
$N(sp^2)$	129.4	2.710	571.4	14.50	366.4	21.63
O(sp)	128.5	1.391	452.4	9.753	346.1	8.650
$O(sp^2)$	123.9	2.503	461.9	11.48	367.2	20.52

	$N(sp^2)$		O(sp)		$O(sp^2)$	
Atom	A_{ij}	B_{ij}	A_{ij}	B_{ij}	A_{ij}	B_{ij}
H	124.9	2.710	128.5	1.391	123.9	2.503
$C(sp^2)$	571.4	14.50	452.5	9.753	461.9	11.48
$C(sp^3)$	366.4	21.63	346.1	8.650	367.2	20.52
$N(sp^2)$	362.9	16.09	344.3	6.085	365.0	15.28
O(sp)	344.3	6.085	344.8	7.448	348.7	7.538
$O(sp^2)$	365.0	15.28	348.7	7.538	367.2	14.49

[a] The A_{ij} are given in units of kcal A^6/mole and the B_{ij} 10^{-4} kcal A^{12}/mole.

state, although both molecules have large hyperpolarizabilities. This difference was attributed to the difference in their crystal structures. The crystal structure of *p*-NA is centrosymmetric (space group, $P2_1/n$), as determined by x-ray crystallographic analysis[22] and thus SHG inactive. On the other hand that of *m*-NA is noncentrosymmetric ($Pbc2_1$).[23] Contour maps of intermolecular interaction energies of *p*-NA(a) and *m*-NA(b) calculated by the above method are shown in Figure 2. The horizontal axis represents the distance between molecular planes of the two molecules and the vertical one is the rotation angle of one molecule to another around the axis normal to the molecular plane illustrated in the upper left of Figure 2. These contour maps represent a two-dimensional section of multi-dimensional interaction energy space. The reason why we chose this section is that it could clearly represent whether the intermolecular configuration with an inversion center was at the energy minimum or not. As the result of this calculation, in the case of *p*-NA, the energy minimum intermolecular configuration has an inversion center marked by the dark arrow, while the energy minimum configuration is not centrosymmetric in the case of *m*-NA, as shown in Figure 2. The calculation also indicates that 2-methyl-4-nitroaniline (MNA) is SHG active, according to the obtained noncentrosymmetric energy minimum configuration. These results indicate that our computational method for evaluating intermolecular interaction energies of molecules is effective at least as far as inferring whether a molecule crystallizes in a centrosymmetric structure or not. Application of this method to design molecules for SHG materials will be discussed in the following section.

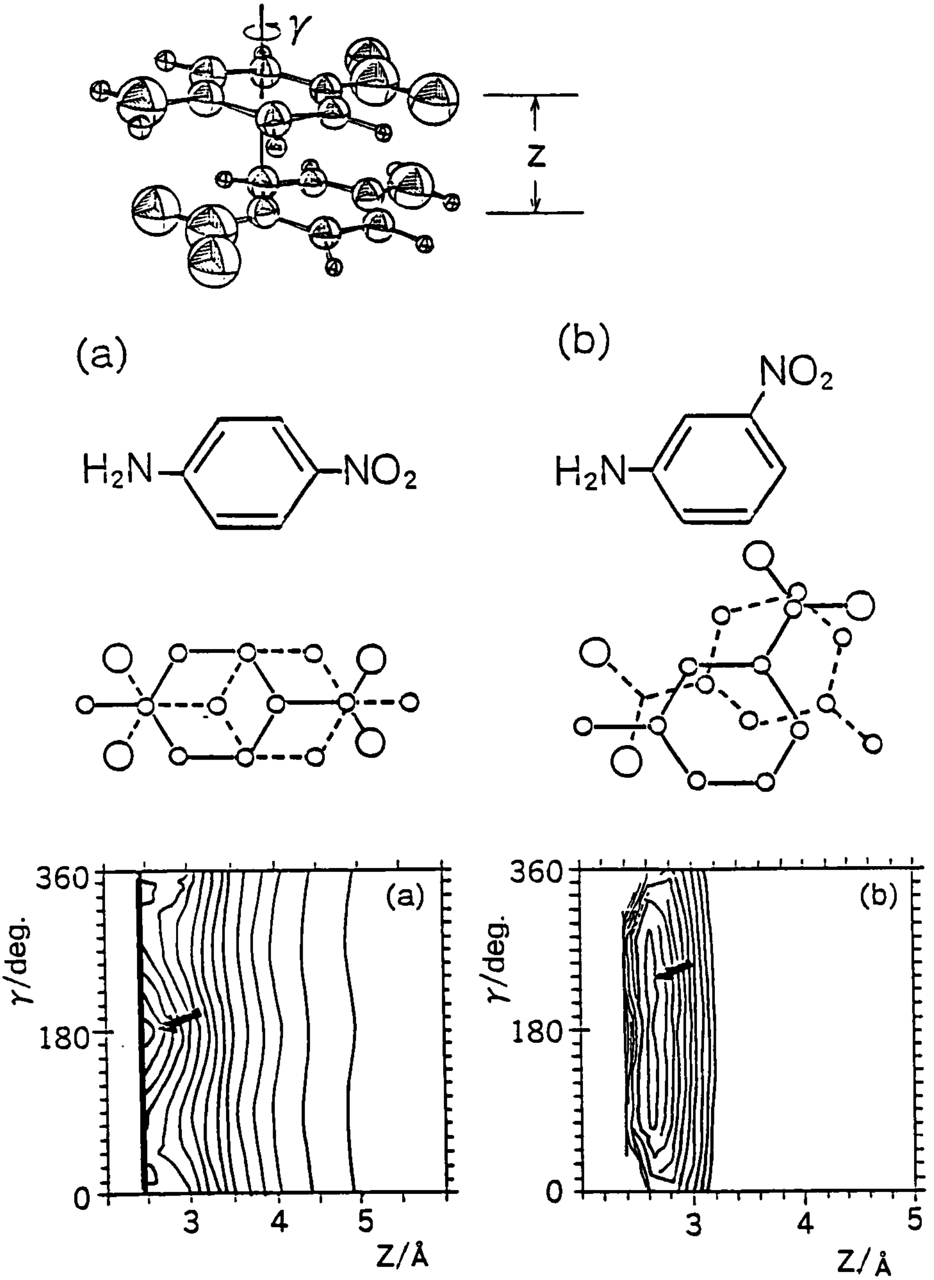


FIGURE 2 Contour maps of intermolecular interaction energies of two molecules: (a) *p*-NA. (b) *m*-NA.

MOLECULAR DESIGN FOR NEW SECOND-ORDER NONLINEAR OPTICAL MATERIALS

Our goal in designing a molecule was to get one which has a large hyperpolarizability and short cut-off wavelength. The latter property is especially necessary for SHG materials for diode lasers. A simple way to get a molecule with a large second-order optical nonlinearity is to design one which has a long π-electron conjugation system, but this is thought to cause a long cut-off length of the molecule. The relationship between hyperpolarizability and the lowest excited energy of molecules which represents the cut-off length, calculated by the CNDO/S3-CI method described in the previous section, is shown in Figure 3, when conjugation lengths of the molecules were increased. The molecules studied were polynuclear aromatic ring compounds, polyphenyl and stylbene derivatives. The figure shows that values of β increase and the lowest excited energies decrease as the π-electron conjugation system is lengthened, which clarifies the difficulty of satisfying the above two requirements in the simple π-electron conjugation systems.

Therefore we decided to look at another type of molecule, heterocyclic compounds in which π-electron conjugation systems are rather complicated. The calculated values of β and the lowest excited energies of several excellent molecules selected from a large number of calculated molecules are shown in Figure 4. Except for chalcones these are our newly proposed second-order nonlinear optical materials. These have two superior properties: large optical nonlinearity and short cut-off wavelength. Moreover, the addition of donor and/or acceptor groups to these molecules does not cause the lengthening of the cut-off wavelength, although the calculated results are not shown here. These favorable characteristics seem to be due to inclusion of oxygene around which the molecular orbital density concentrates in the lowest excited state, and to the π-electron delocalization divided more or less by a oxygene or a carbonyl group. Detailed analysis of these phenomena, by the MO method, is continuing in our laboratory.

Next we turned to the crystallization property of the molecule. In particular, we wanted to see whether they crystallized in centrosymmetric structures or not, by using the intermolecular energy calculation method described in the previous section. The results for several molecules, including typical organic nonlinear materials, are listed in Table III. In the table, *y* and *n* mean that the molecule is predicted to crystallize in a centrosymmetric structure and a noncentrosymmetric one, respectively. Good agreement between calculated and experimental results, expressed as SHG activity of crystal powders of the molecules, is achieved. Here SHG inactive means the crystal structure is centrosymmetric, since the calculated β values for all molecules listed in Table III are large enough to detect second harmonic light from the powder if the structure is not centrosymmetric. It should be pointed out that this good agreement is achieved only for our selected molecules, which are planar and have a relatively large electrostatic interaction. Our intermolecular energy calculation is still in a rough state and intermolecular energy calculations should be done more precisely especially for non-planar molecules. We are trying to do this kind of energy calculation in our laboratory, although it is very difficult due to the large number of degrees of freedom of the calculation.

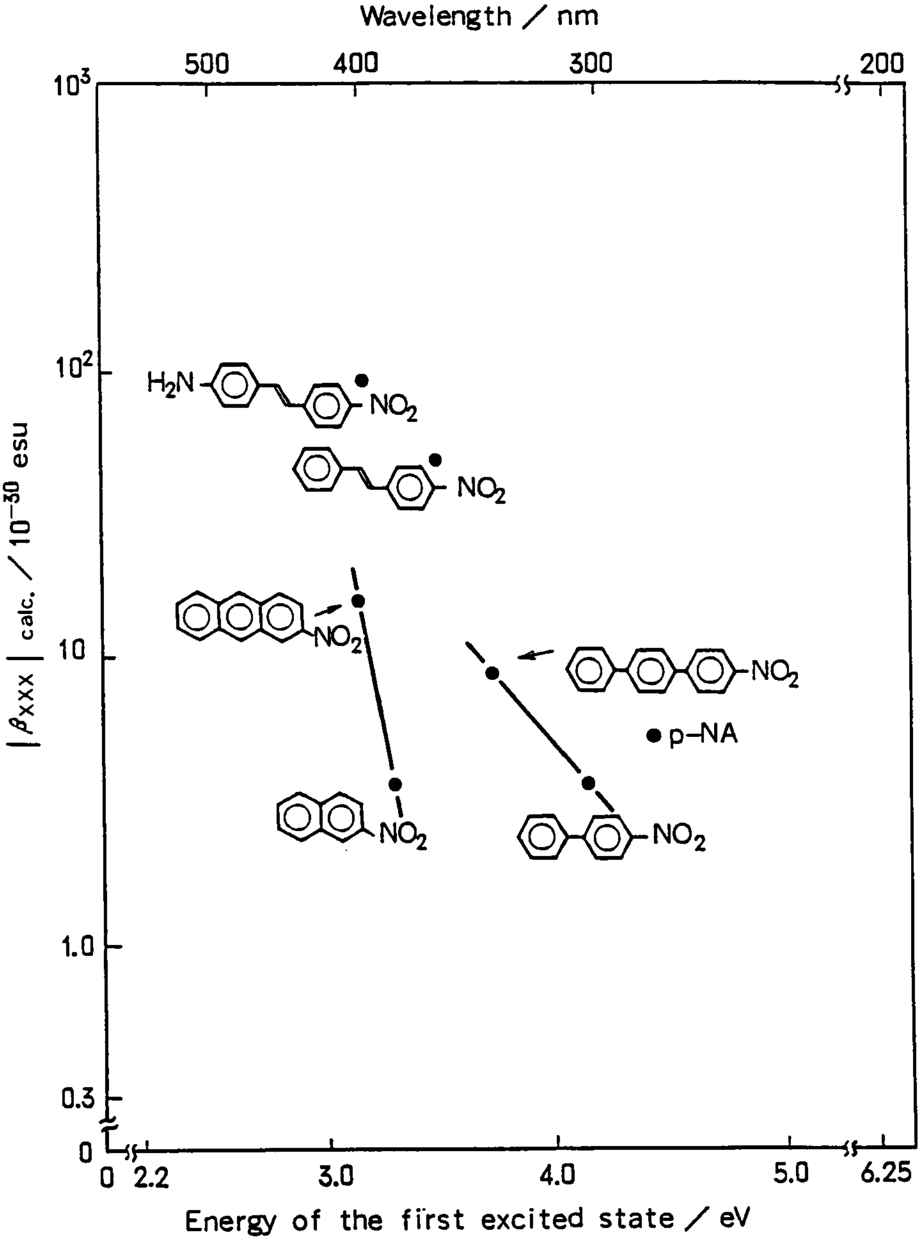


FIGURE 3 Calculated values of $|\beta_{xxx}|$. Molecular coordinates are chosen so that x-axes are in the direction of the large molecular length.

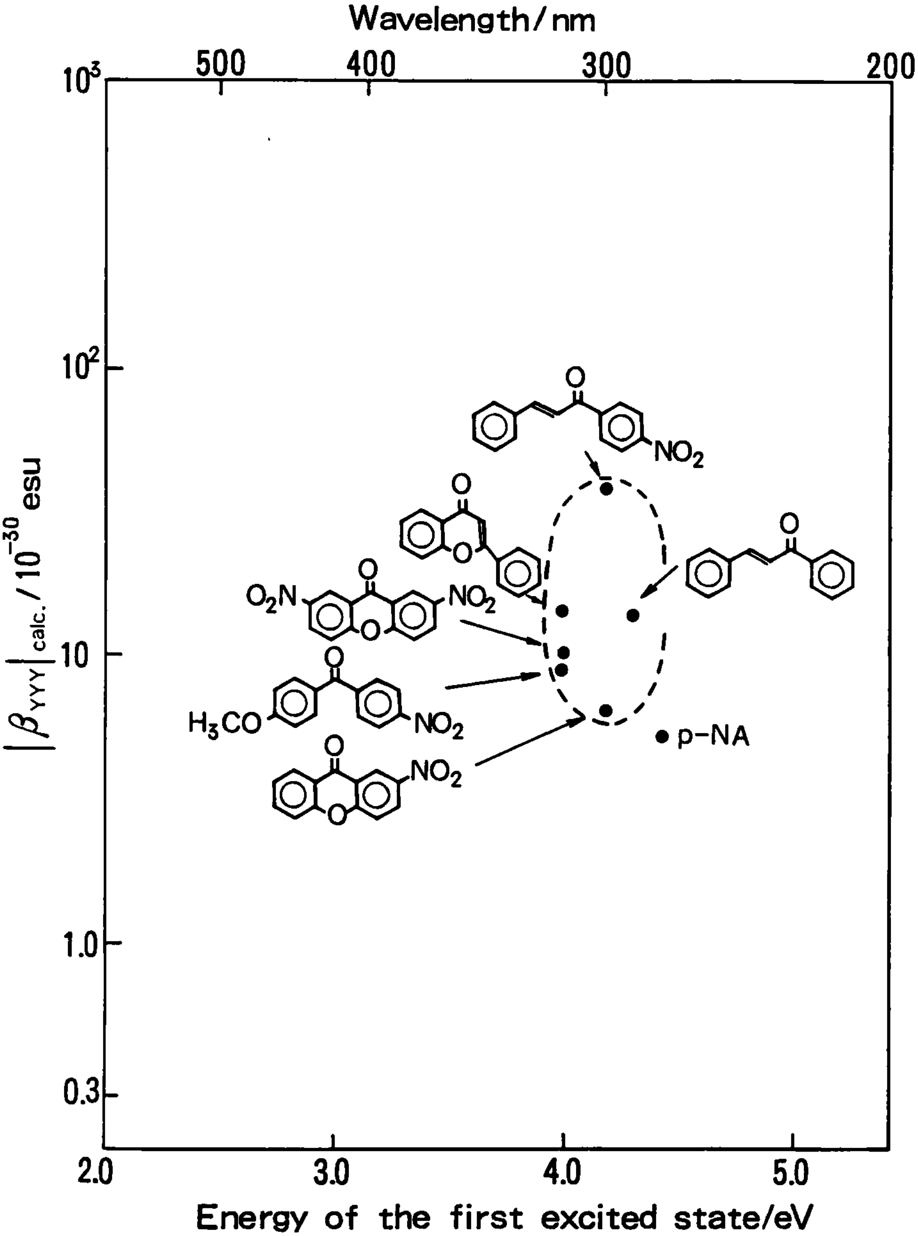
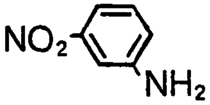
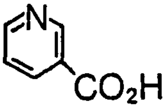
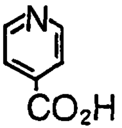
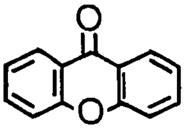
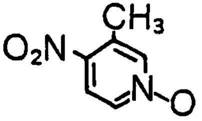
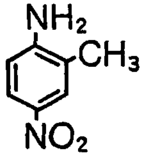


FIGURE 4 Calculated values of $|\beta_{yyy}|$. y axes are the same as the direction of the molecular dipole moments.

TABLE III

SHG activity and results of intermolecular energy calculation

Compounds	Structure	χ_{eff} *)	I
p-nitroaniline		0	y
m-nitroaniline		8	n
nicotinic acid		0	y
isonicotinic acid		0	y
xanthone		1.1	n
POM		13	n
MNA		22	n

[a]Relative powder efficiency to urea.

TABLE IV

The powder efficiency and cut-off wavelength

Molecule	χ_{eff}	cut-off wavelength/nm
2-nitroxanthone	4.5	390
2,7-dinitro-xanthone	4.4	380
4-methoxy-4′-nitrobenzophenone	5.3	380

Using the above interaction energy calculation method, we selected chemical structures with tendency to crystallize in a noncentrosymmetric structure from selected ones by the MO method, and then synthesized them.

Finally the relative powder efficiencies and absorption cut-offs of new second-order nonlinear optical materials, designed by our calculation method were evaluated as shown in Table IV. The absorption spectra of these molecules are shown

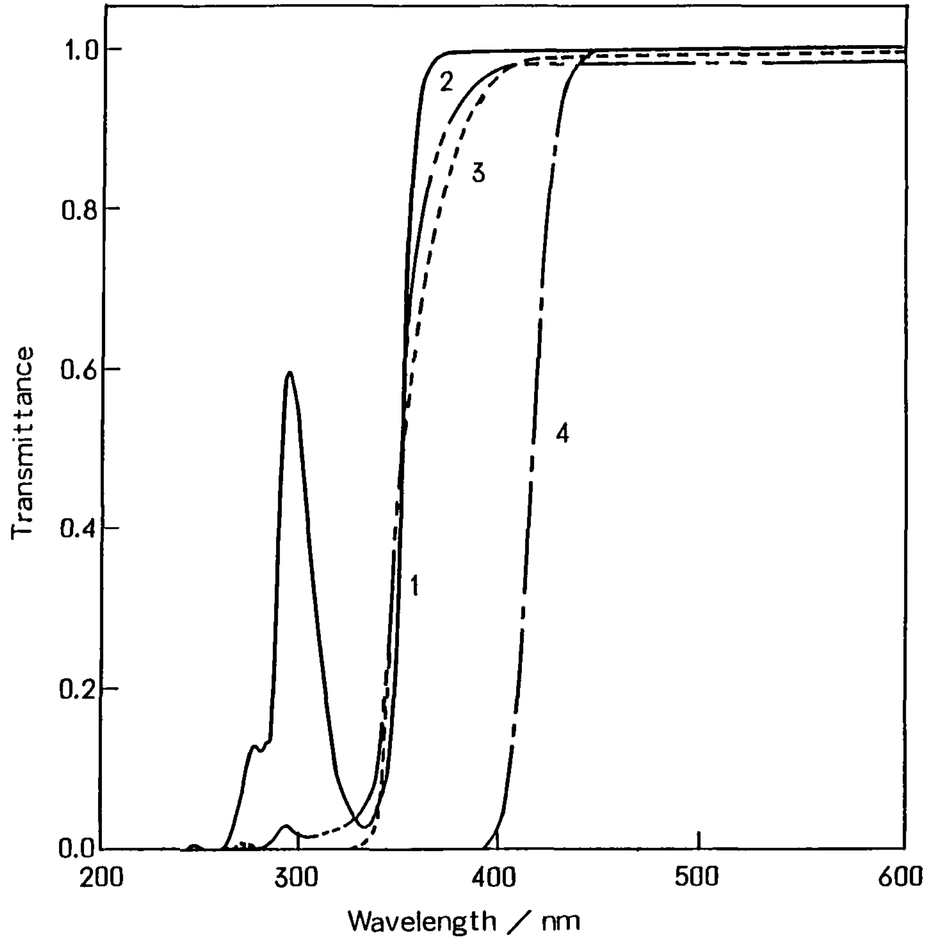


FIGURE 5 Absorption spectra: (1) xanthone in ethanol, (2) 2-nitroxanthone, (3) 2,7-dinitroxanthone in acetonitrile and (4) 3-methyl-4-nitroaniline in acetone.

in Figure 5. They clearly exhibit excellent absorption cut-off properties. Detailed nonlinear optical properties such as phase matching and the value of each components of the nonlinear susceptibility tensor and other physical properties will be presented elsewhere.

CONCLUSION

Calculation methods which evaluated molecular nonlinear optical properties and crystallization properties from chemical structure were proposed and applied to design second-order nonlinear optical materials of SHG devices for a diode laser. Several new second-order nonlinear optical materials, xanthone derivatives and benzophenone derivatives which have relatively large second-order optical nonlinearity comparable to *m*-nitroaniline and cut-off wavelength short enough to be applied to SHG devices of diode laser, were examined.

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