Organic Second-Order Nonlinear Optical Materials with Transparency in the Blue Wavelength Region: Ethylene Derivatives Possessing Electron-Donor and Acceptor Groups

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A series of ethylene and methanimine derivatives possessing both electron-donor and -acceptor groups were synthesized in order to obtain frequency doublers of infrared semiconductor lasers. Their second-harmonic-generation (SHG) was investigated by means of a powder method and an electric-field-induced second-harmonic method. Three ethylene derivatives were found to be SHG active without any absorption in the blue wavelength region. X-Ray crystallographic analyses were made for two of them. It was found that strong donor and acceptor substituents tend to twist the central C=C double bond, thereby resulting in smaller β-values than those expected for non-twisted molecular structures. Based on the molecular and crystal structures, some strategies are presented regarding the synthesis of SHG materials of these push-pull ethylenes and methanimines.

Organic intramolecular π-conjugated charge-transfer (CT) molecules have been known to give second-order nonlinear optical materials with large second-order hyperpolarizabilities (β).[1] One of the most attractive applications of these materials is a frequency doubler for infrared semiconductor lasers, since lasers are inexpensive and are being commercialized as a component of compact disk memory. If the second-harmonic (SH) wave of semiconductor lasers is used for such fabrications as optical memories, the memory density could be quadrupled. In order to obtain the SH wave of semiconductor lasers, the nonlinear optical materials should be transparent in the blue wavelength region.[2,3] Since the absorption edges of conjugated organic molecules tend to shift to the longer wavelength region along with extention of π-electron conjugation, intramolecular CT molecules with a small conjugation length should be used for the frequency doubler of semiconductor lasers. Typical small π-electron conjugated molecules are ethylene and methanimine. Therefore, a series of ethylenes or methanimines, the hydrogens of which are substituted with both electron-donor and -acceptor groups, are attractive for the above-mentioned purpose. We synthesized several such molecules, and then measured the SHG by a powder method.[4] The β-values of the SHG active molecules were measured using an electric-field-induced second-harmonic (EFISH) method. X-ray crystallographic analyses were carried out for SHG active materials. Based on the molecular and crystal structures, some strategies were developed for the synthesis of SHG materials of push-pull ethylenes and methanimines. The materials used in this study were classified into four types, and are denoted as **I**, **II**, **III**, and **IV** (shown below, Chart 1). Each material is classified by the substituent groups, R and R′, as listed in Table 1. These materials contain amino, methylthio, or alkoxyl group as a donor group, and cyano or alkoxycarbonyl group as an acceptor group.

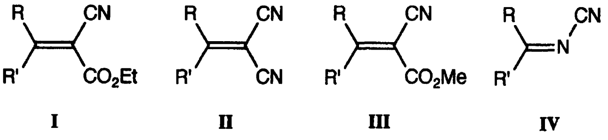


Chart 1.

Experimental

Synthesis of Materials. All of the push-pull ethylene and methanimine derivatives were synthesized from the corresponding alkali metal salts ($(NaS)_2C=CXY$ (X=CN, Y=CO_2Et, CO_2Me) or $(KS)_2C=NCN$) as starting materials by previously reported methods.[5] The reaction products were identified by ^1H NMR (JEOL JNM-GX-270), IR (JASCO IRA-1), and mass (Shimadzu QP-1000) spectroscopies.

Measurements of SHG. The intensity of the optical SH wave was estimated in comparison with that of urea, by means of the usual powder technique, using an Nd:YAG laser (wavelength 1.064 μm; repetition rate, 10 Hz) as a fundamental wave. The optical second-order hyperpolarizabilities (β) were determined by means of an EFISH method in dioxane[6] with nitrobenzene used as a reference.

X-Ray Crystal-Structure Analysis. The crystal data, details of data collection and structure refinement are listed in Table 2. Intensity data of **I**-1 were collected using a Rigaku AFC-5R diffractometer with a graphite monochromator. No absorption corrections were applied. The structure was solved by the direct method using the program MITHRIL.[7] Hydrogen atoms were located from the calculation. Full-matrix least-squares[8] were used for refinements of the structure with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were included in the calculations of the structure factors with isotropic temperature factors equal to those of the bonded carbon atoms, but were not refined. $w(|F_c|-k^{-1}|F_o|)^2$ was minimized, where $w=1/(\sigma^2(F_o))$. For **I**-4, intensity data were collected using a Rigaku AFC-4 diffractometer with a graphite monochromator. An absorption correction was applied numerically.

Table 1. SHG Efficiencies, Melting Points, and Solvents of Recrystallization of Push-Pull Ethylenes and Methanimines

Entry	R	R′	SHG[a)]	Mp/°C	Recryst. Solv
I-1	MeS	MeS[b)]	5.5	57—59	Ethanol
2	MeS	NH_2[c)]	—[e)]	186—187	Methanol
3	MeNH	MeNH[c)]	—	125—126.5	Methanol
4	MeS	Me_2N	0.8	92—93	Ether–hexane
5	EtNH	EtNH[c)]	—	116	Methanol
6	MeS	p-$MeOC_6H_4NH$[c)]	—	82.5—83.5	CH_2Cl_2–hexane
7	NH_2	NH_2	—	175—177	CH_2Cl_2–ethanol
8	NH_2	C_6H_5NH[d)]	—	170—172	Ethanol
9	$-SCH_2S-$		—	117—119	CH_2Cl_2–hexane
10	$-S(CH_2)_2S-$		—	111—113	Ethanol
11	$-S(CH_2)_3S-$		—	88—89	Ethanol
12	$-NH(CH_2)_2NH-$		—	184—186	Chloroform
II-1	MeS	NH_2	—	229—230	Methanol
2	MeS	Me_2N	0.5	72—73	CH_2Cl_2–hexane
3	$-SCH_2CH(OH)S-$		—	179—182	Ethanol
4	$-S(CH_2)_2O-$		—	94—96	CH_2Cl_2–hexane
5	$-S(CH_2)_2NH-$		—	176—178	Ethyl acetate
6	$-O(CH_2)_2NH-$		—	163—165	CH_2Cl_2–hexane
7	$-NH(CH_2)_2N(Me)-$		—	179—181	2-Propanol
III-1	$-S(CH_2)_2S-$		—	113—115	Methanol
2	$-S(CH_2)_3S-$		—	140—142	Methanol
IV-1	MeS	MeS	—	53—55	CH_2Cl_2–hexane
2	$-S(CH_2)_2S-$		—	73.5—74	CH_2Cl_2–hexane

a) Second-harmonic intensity relative to that of urea obtained by a powder method, by using Nd : YAG laser as a fundamental wave. b) An *E*-isomer determined by X-ray crystal structure analysis. c) An *E*- or *Z*-isomer (not determined). d) A mixture of *E*- and *Z*-isomers. e) Not detectable.

The structure was solved by the direct method using the program SHELX86,[9)] and was refined using block-diagonal least squares[10)] with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen atoms. $w(|F_c|-k^{-1}|F_o|)^2$ was minimized, where $w=1/(\sigma^2(F_o)+0.00151|F_o|^2)$. Atomic scattering factors were used from International Tables for X-Ray Crystallography.[11)] The final atomic parameters of **I**-1 and **I**-4 are listed in Tables 3 and 4, respectively.[12)] The computations of **I**-4 were performed on an IBM3090-180S Computer of the Information Processing Center of the University of Electro-Communications.

Calculation of Dipole Moments. The molecular dipole moments (μ) were calculated using the MINDO level in MOPAC ver. 6.0,[13)] based on the molecular structure found from X-ray crystallography. The positions of the hydrogens were determined by geometrical optimization of the molecular-orbital calculation.

Results and Discussion

Second-Harmonic Generation. All of the samples synthesized were colorless, and satisfied the required condition of transparency in the blue wavelength region. The SHG of the samples was investigated by the powder method, by using a Q-switched Nd-YAG laser as a fundamental wave. Table 1 summarizes the materials investigated, relative SHG intensities, melting points, and solvents of recrystallization. Unfortunately, most of the materials were SHG inactive, and only three materials (**I**-1, **I**-4, and **II**-2) were SHG active with SHG intensities of 5.5-, 0.8-, and 0.5-times as large as that of urea, respectively. The low probability of finding SHG active materials, which we usually experience in intramolecular CT molecules, may arise from the fact that a donor group of a molecule tends to interact with an acceptor group of the adjacent molecule in the solid; this effect gives rise to a centrosymmetric crystal structure in most cases. The β-values (β_{obsd}) were measured for SHG active materials using the EFISH method in dioxane, and are listed in Table 5. During an analysis of the EFISH data, the ground-state dipole moments of the molecules were obtained. This table also summarizes the absorption-peak positions, absorption-cutoff wavelengths, as well as the observed and calculated ground-state dipole moments (μ_{obsd} and μ_{calcd}, respectively). Further, it shows the corresponding data for ethyl-2-cyano-2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-acetate (**1**)[2,3)] and 2-methyl-4-nitroaniline (**2**)[1,14)] for the sake of a comparison, because these two materials are typical second-order nonlinear optical materials.

In a previous paper, we reported material **1** as being an efficient SHG active material which is transparent in the blue wavelength region (Chart 2).[2)] The SHG active materials (**I**-1, **I**-4, and **II**-2) found in this study have absorption-cutoff and absorption-peak wavelengths shorter than those of **1** and **2** (see Table 5). This is caused by the fact that the conjugation lengths of the former materials are shorter than those of the latter. In general, the β-value tends to become larger as the absorption cutoff wavelength becomes longer.

Table 2. Crystal Data, and Details of Data Collection and Structure Refinement

	I-1	**I**-4
Color	Colorless	Colorless
Crystal shape	Plates	Plates
Molecular formula	$C_8H_{11}NO_2S_2$	$C_9H_{14}N_2O_2S$
Formula weight	217.31	214.29
Crystal size/mm	0.8×0.6×0.2	0.53×0.24×0.14
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a/Å	8.754(2)	18.443(3)
b/Å	14.399(2)	8.794(2)
c/Å	4.156(5)	6.731(1)
β/deg	90.47(4)	90.0
V/Å^3	523.7(7)	1091.6(3)
Z	2	4
D_c/Mg m^{-3}	1.378	1.304
Radiation	Mo $K\alpha$	Mo $K\alpha$
λ/Å	0.71069	0.71069
μ/mm^{-1}	0.457	0.262
Scan range 2θ/°	2—55	2—55
Scan mode	2θ–ω	2θ–ω
Monitored reflections (every 50 reflections)	$0\bar{4}0$, $2\bar{2}0$, 200	600, 020, 002
Variation of intensities/%	6.6	5.8
No. of reflections		
Measured	1334	3084
Observed ($\lvert F_o\rvert > 3\sigma(F_o)$)	1221	1881
R	0.033	0.062
wR	0.041	0.073

Table 3. Fractional Coordinates and Equivalent Isotropic Temperature Factors of Non-Hydrogen Atoms in **I**-1

B_{eq} is defined using anisotropic temperature factors, β_{ij}, as,

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij}\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j.$$

Atom	x	y	z	B_{eq}/Å^2
S(1)	0.03819(8)	0.4618	1.0273(2)	4.65(3)
S(2)	0.15526(8)	0.28758(7)	0.7385(2)	4.65(3)
O(1)	−0.0844(3)	0.1729(2)	0.6083(8)	6.4(1)
O(2)	−0.3259(2)	0.2017(2)	0.7427(6)	5.4(1)
N(1)	−0.3600(3)	0.3891(3)	1.2013(7)	5.7(1)
C(1)	0.0001(3)	0.3501(2)	0.8797(6)	3.4(1)
C(2)	−0.1426(3)	0.3119(2)	0.8823(6)	3.6(1)
C(3)	−0.1775(3)	0.2220(2)	0.7293(7)	4.1(1)
C(4)	−0.3705(4)	0.1146(3)	0.589(1)	6.2(2)
C(5)	−0.5284(5)	0.1209(4)	0.491(1)	7.3(2)
C(6)	−0.2636(3)	0.3561(2)	1.0562(7)	3.9(1)
C(7)	0.3146(4)	0.3657(3)	0.768(1)	6.3(2)
C(8)	−0.1132(4)	0.5333(2)	0.8736(8)	4.7(1)

In consideration of this point, the observed β-value of **I**-1 (29×10^{-40} m^4 V^{-1}) is relatively large, in spite of the short cutoff wavelength (370 nm). This value is comparable to, or may be even larger than, that of **1**, which is one of the best frequency doublers for the infrared semiconductor lasers. On the other hand, the observed β-values of **I**-4 and **II**-2 are small (2.5×10^{-40} and 3.8×10^{-40} m^4 V^{-1}, respectively). The large β-value of **2** (176×10^{-40} m^4 V^{-1}) is a matter of course, since its cutoff wavelength is located near to the SH wavelength (530 nm) of the YAG laser, and it has strong donor and acceptor groups (amino and nitro groups, respectively). However, this material can not be used for the frequency doubler of semiconductor lasers because of the presence of a large absorption in the blue wavelength region. The observed dipole moments shown in

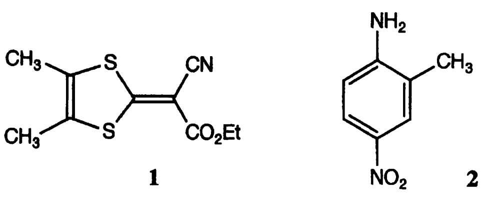
Table 4. Fractional Coordinates and Equivalent Isotropic Temperature Factors of Non-Hydrogen Atoms in **I**-4
See Table 3 for the definition of B_{eq}.

Atom	x	y	z	$B_{\mathrm{eq}}/\text{Å}^2$
S(1)	0.2575(1)	0.2621(1)	0.0526(2)	3.65(2)
O(1)	0.3806(2)	0.1192(4)	0.5957(4)	4.15(8)
O(2)	0.4319(2)	0.3521(3)	0.6156(4)	3.49(7)
N(1)	0.3498(2)	0.0519(4)	0.1653(5)	3.08(8)
N(2)	0.3831(2)	0.5739(4)	0.2330(6)	4.13(10)
C(1)	0.2165(2)	0.4054(5)	0.2045(7)	3.82(11)
C(2)	0.3303(2)	0.1971(4)	0.1968(6)	2.72(8)
C(3)	0.3675(2)	0.2929(4)	0.3283(6)	2.81(8)
C(4)	0.3757(2)	0.4497(5)	0.2770(6)	3.00(9)
C(5)	0.3929(2)	0.2430(5)	0.5226(6)	3.11(8)
C(6)	0.4586(3)	0.3147(6)	0.8129(7)	4.33(12)
C(7)	0.5331(3)	0.2539(6)	0.8026(8)	5.04(13)
C(8)	0.3043(3)	−0.0566(5)	0.0613(8)	4.02(11)
C(9)	0.4213(3)	−0.0032(5)	0.2176(8)	4.23(12)

Table 5. The Wavelengths of Absorption Maximum and Absorption Cutoff, Observed Molar Optical Second-Order Hyperpolarizabilities, and Observed and Calculated Ground State Dipole Moments of the SHG Active Materials

Entry	λ_{max}	$\lambda_{\mathrm{cutoff}}$	β_{obsd}	μ_{obsd}	μ_{calcd}
	nm	nm	10^{-40} m^4 V^{-1}	10^{-30} C m	10^{-30} C m
I-1	330	370	29	11	8.8
I-4	320	355	2.5	21	12.2
II-2	305	340	3.8	14	18.9
1	369	415	19	15	16.8
2	375	470	(176)$^{\mathrm{d)}}$	23$^{14)}$	22.4

a) Measured in a methanol solution (5×10^{-5} mol dm^{-3}). b) Determined by the EFISH method in a dioxane solution with an irradiation of an Nd-YAG laser (1064 nm). The SHG of dioxane was subtracted from the observed SHG of the solution. c) Calculated for the molecules with geometrical optimization of hydrogen atoms. d) Uncorrected value due to the SHG of dioxane.



1 **2**

Chart 2.

Table 5 can be reproduced fairly well by calculations using MOPAC ver. 6.0,[13] except for that of **I**-4. In the case of **I**-4, the twisting angle at the central C=C double bond (37.2(2)°) is exceptionally large (vide infra). We suppose that part of the origin of the large twisting angle arises from the intermolecular force, and that the twisting angle in dioxane solution might be smaller than 37.2(2)°. Since the calculated dipole moment was obtained on the basis of the molecular structure, which was determined by an X-ray crystallographic analysis, the observed dipole moment might be much larger than the calculated value.

Molecular and Crystal Structures of SHG-Active Materials. The molecular structures of SHG-active materials (**I**-1 and **I**-4) are shown in Fig. 1.[15] An X-ray crystallographic analysis of **II**-2 was previously reported;[16] its molecular structure is also shown in Fig. 1.[15] The arrows in this figure show the vectors of the dipole moment in the ground state (μ_{calcd}), which were calculated using MOPAC ver. 6.0.[13] Figure 2 shows stereoscopic views of the molecular dipole

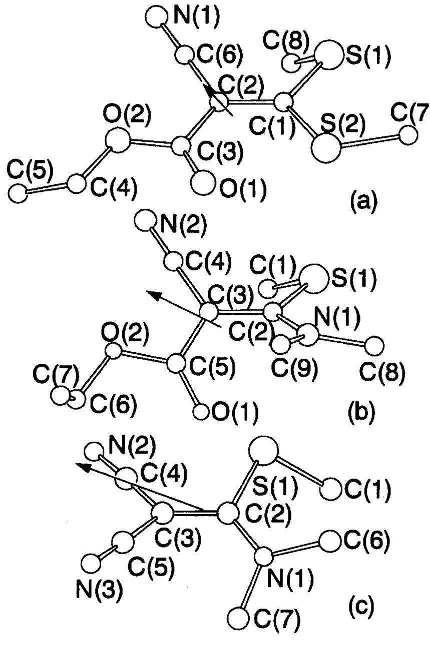


Fig. 1. Molecular structures and dipole-moment vectors of **I**-1, **I**-4, and **II**-2. Hydrogen atoms were omitted. The arrows represent the dipole moments, and their origins are located at the molecular centers of mass. The lengths of the arrows are drawn in proportion to the calculated values of the dipole moments. (a) **I**-1, (b) **I**-4, (c) **II**-2.

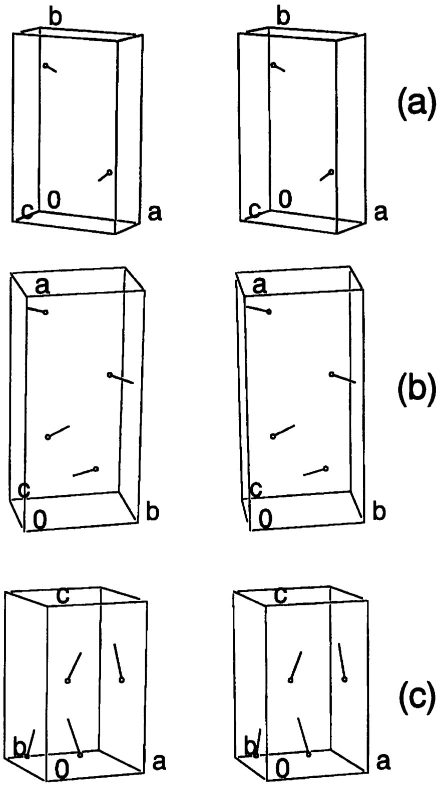


Fig. 2. Stereoscopic views of the arrangement of the molecular dipole moments in unit cells of **I**-1, **I**-4, and **II**-2. The circles represent the center of mass of each molecule. The lengths of the arrows are drawn in porportion to the calculated values of the dipole moments. (a) **I**-1, (b) **I**-4, (c) **II**-2.

moments in the unit cells of **I**-1, **I**-4, and **II**-2. This figure shows that most of the ground-state dipole moments of the **I**-1 molecules cancel each other in the crystal, and that only their *b*-components survive as a whole. Molecule **I**-1 is nonplanar, and the central C=C double bond is twisted by 10.7(2)°. The bond distance of the central C=C double bond (1.365(4) Å) is longer than that of ethylene (1.337 Å). Figure 2 shows that the ground-state dipole moments are completely cancelled in the **I**-4 crystal. Yet, it has a noncentrosymmetric space group ($P2_12_12_1$), thereby giving rise to SHG. This molecule is nonplanar, and the central C=C double bond is twisted by 37.2(2)°. The bond distance of the central C=C double bond (1.354(5) Å) is longer than that of ethylene. Figure 2 shows that the *c*-components of the ground state dipole moment survive in the **II**-2 crystal as a whole. This molecule is nonplanar, and the central C=C double bond is twisted by 21.7(5)°.[16] The bond distance of the central C=C double bond (1.397(8) Å)[16] is longer than that of ethylene. The fact that the bond distances of the central C=C double bonds of these molecules are longer than that of ethylene can be undestood in terms of the contribution of the following resonance structure of intramolecular charge-transfer (Chart 3), therby affording some single bond character to the C=C bonds.

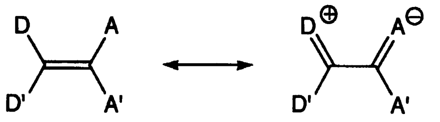


Chart 3.

Here, D and D′ denote the electron donor groups, and A and A′ the electron acceptor groups (Chart 3). The twisting of the central C=C double bond is caused by its single bond character (described along with the abovementioned resonance structures), thereby allowing its internal rotation. No simple correlation was found between the bond distances and the twisting angles at the central C=C double bonds among **I**-1, **I**-4, and **II**-2. If only the donor and acceptor abilities of the substituent groups are taken into account, the bond distances of the C=C double bonds may increase along with increasing the twisting angles. However, the intermolecular force also affects the molecular geometry, and no sinple correlation was found. The twisting of the central C=C double bond may be a drawback for the production of these push-pull ethylene derivatives from the viewpoint of SHG materials with large β-values, since any intramolecular charge-transfer upon irradiation of laser light is interrupted to some extent, due to insufficient π-electron conjugation.

Summary. Various push-pull ethylene and methanimine derivatives have been synthesized for the development of SHG materials of infrared semiconductor lasers. All of these materials were transparent in the blue wavelength region. Only three materials were found to be SHG active with SH intensities 0.6—5.5 times as large as that of urea. Push-pull ethylenes possessing strong donor and acceptor groups tend to arrange in a centrosymmetric space group in a solid, because of the strong intermolecular charge-transfer interaction. Furthermore, such molecules tend to give a twisted structure at the central C=C double bond, due to a resonance contribution of the intramolecular charge-transfer structure. This bond-twisting is undesirable for producing molecules with large β-values. Therefore, push-pull ethylene derivatives with relatively weak donor and acceptor substituent groups may be promising candidates for SHG materials used for infrared semiconductor lasers.

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