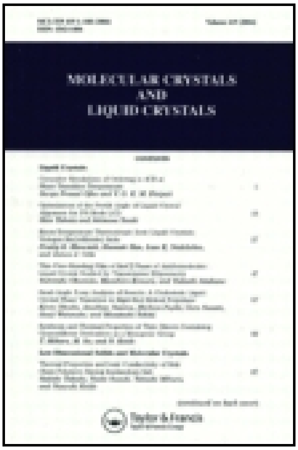

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Cyanovinylheteroaromatics for Organic Nonlinear Optics

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Effects of various substituents including chromophores on the second harmonic generation (SHG) of cyanovinylheteroaromatics were examined. The molecular polarizability was calculated by the PPP MO method to correlate SHG responsiveness with chemical structures. 3-[(2-cyano-2-ethoxycarbonyl)ethenyl]indole 8b exhibited good SHG efficiency (PE = 25 U). The X-ray analysis of 8b showed that the crystals belong to novel and the most favorable P1 space group.

Keywords: cyanovinylheteroaromatics, molecular design, nonlinear optics, PPP MO, X-ray crystal analysis

1. Introduction

Study of the nonlinear properties of organic compounds is of scientific and technological interest for the development of optoelectronic devices in high technology.[1,2] The second harmonic generation (SHG, frequency doubling) is the most important and attractive nonlinear optical property in the fields of optical device technology.[3] Inorganic materials have been studied for a decade, but recent results suggest that organic compounds with π-electron conjugated systems exhibit good nonlinear properties. Organic molecules have the advantages of good SHG responsiveness, better resistance to light, and multiplicity for molecular modifications. Experimental research into new organic materials possessing properties desirable for nonlinear optical devices has led almost exclusively to molecules with strong intramolecular charge-transfer functionality.[4] However, macroscopic properties of an organic crystal must also be considered for the successful engineering with high SHG efficiency.[5,6] The molecular polarizability (β) of compounds can be calculated by the PPP MO method and their SHG efficiencies are evaluated by means of the powder test method using a YAG laser as a light source. The powder test method is a convenient screening method for many organic compounds. However, powder efficiency (PE) is the product of bulk second order nonlinear coefficient and coherence length, which strongly depends on measuring conditions, that is, angular distribution, powder layer thickness, average particle size and laser beam diameter. Consequently the value of PE cannot be directly compared with the calculated β values.

The structural analyses of some SHG active crystals are carried out by the X-ray analysis method. The relationship between SHG efficiency of organic compounds and their crystal structures is rationalized and applied practically to search the SHG active molecules.

In this paper a series of cyanovinylheteroaromatics was synthesized and their SHG efficiencies correlated with the chemical structures on the basis of the calculated β values and the X-ray analysis data. Cyanovinyl groups are well known to be strong acceptors and heteroaromatics play a role as a donor: These compounds thus have a favorable chromophoric system with noncentrosymmetry and strong intramolecular charge-transfer character.

2. Results and Discussion

2.1. Molecular design by the PPP MO method

Molecular design of a SHG active compound can be conducted by the PPP MO method.[7,8] The molecular polarizability β_{CT} of intramolecular charge-transfer chromophores is defined by Oudar's equation.[9]

Macroscopic SHG efficiency should be expected for compounds with larger β values. Compounds having a large $(\mu_e - \mu_g)$ value and/or large oscillator strength (f) are expected to give a large β value in molecular design. It is also desirable to minimize the ΔE value. In using the diode laser as a light source (wavelength 780–830 nm), there is a restriction to the minimization of ΔE because absorbance by the materials at 400 nm is forbidden. The λ_{max}, μ_g, μ_e and f values can be calculated quantitatively by the PPP MO method and then appropriate chromophores can be designed to give effective SHG materials. The PPP MO calculation is a convenient and useful method to estimate the β value of compounds.[8] A good correlation between the PPP MO calculated values and the observed β values by means of the DC-SHG method has been obtained for many chromophores.[10]

2.2. Nonlinear property of cyanostyryls and related compounds

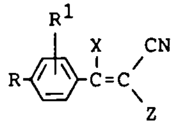
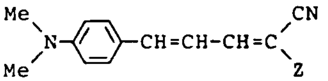
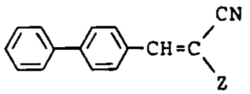
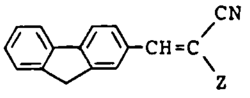
Cyanostyryls were obtained by a condensation reaction of aldehydes with active methylene compounds in the presence of piperidine.

Cyanostyryls 1 contain a chromophore with intramolecular charge-transfer character. These compounds have the good crystallinity required to produce efficient SHG materials for optical devices.

The results of SHG efficiency and some other properties of cyanostyryls and related compounds are summarized in Table 1.

TABLE 1

SHG efficiency and properties of cyanostyryls and related compounds

	No.	R	R^1	X	Z	mp. (°C)	λ_{max}[a]	β[b]	SHG[c]	PE[d]
	**1a**	$N(Me)_2$	H	H	CN	178-179	428	88	o	—[e]
	1b	$N(Me)_2$	H	H	CO_2Me	140-141	421	38	x	
	1c	$N(Me)_2$	H	H	CO_2Et	119-121	420	38	o	—[e]
	1d	$N(Me)_2$	H	H	$CONH_2$	190-191	410	32	x	
	1e	$N(Me)_2$	2-Me	H	CN	203-204	439	—	x	
	1f	$N(Me)_2$	3-Me	H	CN	125-126	415	—	x	
	1g	$N(Me)_2$	H	CN	CN	169-170	512	326	x	
	1h	$N(Et)_2$	H	H	CN	130-132	434	88	x	
	1i	$N(Et)_2$	H	H	CO_2Me	77-79	427	38	o	9
	1j	$N(Et)_2$	H	H	CO_2Et	80-81	426	38	o	16
	1k	$N(Et)_2$	H	H	$CONH_2$	130-131	417	32	o	—[e]
	**2a**				CN	146-148	480	409	x	
	2b				CO_2Et	179-181	464	235	x	
	**3a**				CN	138-140	347	—	o	1.4
	3b				CO_2Me	164-166	338	—	x	
	3c				CO_2Et	127-128	339	—	x	
	3d				$CO_2Pr(n)$	96-97	340	—	x	
	3e				$CONH_2$	170-171	333	—	x	
	**4a**				CN	203-204	372	52[f]	o	—[e]
	4b				CO_2Me	221-222	362	29[f]	x	
	4c				CO_2Et	161-162	362	29[f]	o	—[e]
	4d				$CO_2Pr(n)$	154-156	362	29[f]	x	
	4e				$CONH_2$	196-197	355	6[f]	x	

a) Measured in ethanol (nm).
b) Calculated by the PPP MO method at 1064 nm of YAG laser, ($\times 10^{-30}$ esu).
c) Powder test method by YAG laser (1064 nm), o; active, x; not detectable.
d) Powder efficiency against urea.
e) Not determined because of the weak SHG efficiency.
f) Calculated as a coplanar structure.

When dimethylamino groups are present as donors, 1a and 1c showed SHG efficiency, whereas 1b and 1d did not. The substitution of a cyano group for an alkoxycarbonyl group in 1a decreased the calculated β value from 88 to 38, and the λ_{max} produced a hypsochromic shift of 7–8 nm. Introduction of a methyl group to a benzene ring of 1a caused a big difference in mp and λ_{max}, and 1e and 1f did not show SHG efficiency. Their packing modes in crystals might be changed into undesirable orientation for SHG efficiency. On the other hand, diethylamino derivatives 1i and 1j showed an SHG efficiency 9 and 16 times as strong as that of urea, respectively. Compound 1k also showed SHG efficiency. Compound 1h did not show the efficiency compared with 1a. Compounds 1g and 2 have large β values, but they did not show the efficiency. Marked differences in the macroscopic properties (PE) were observed between diethylamino compounds (1h – 1k) and dimethylamino compounds (1a – 1d). It is generally observed that an ethyl group is preferable to a methyl group for giving SHG efficiency, e.g. 1b compared with 1c, 1i with 1j, 4b with 4c, 8a with 8b in the alkoxycarbonyl moiety, and also 1b with 1i and 1c with 1j in the alkylamino moiety. The relation between microscopic and macroscopic second order nonlinearities of crystals has been reported by Zyss and Oudar.[11]

The λ_{max} of biphenyls 3 produced a hypsochromic shift of 80 nm compared with 1a. In a series of cyanovinylbiphenyls 3, only 3a showed SHG efficiency, while 4a and 4c showed it in a fluorene series. The λ_{max} of 3 produces a much more hypsochromic shift than that of the corresponding 4.

2.3. Nonlinear properties of cyanovinylheteroaromatics

Cyanovinylheteroaromatics obtained from the reaction of heterocyclic aldehydes with active methylene compounds were evaluated for SHG materials. Heteroaromatics with 6π (pyrroles, thiophenes and furans), 10π (indoles) and 14π (carbazoles) systems were evaluated to correlate their SHG efficiency with molecular structure. The donor properties of the heteroaromatics are not so strong because of their aromaticity, but the heterocycles can act as effective charge localized π-conjugated noncentrosymmetric systems compared with their carbon analogues. Replacement of the dialkylaminophenyl group in 1 with heterocycles produces a large hypsochromic shift in λ_{max}, which favors a shorter cutoff wavelength.

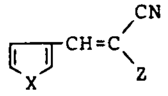
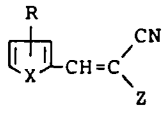
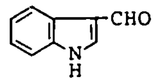
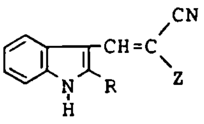
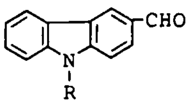
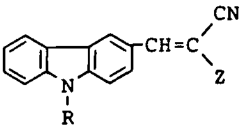
The SHG efficiency and some properties of cyanovinylheteroaromatics are summarized in Table 2. Investigation of the effects of acceptors at the 2- or 3-position of thiophenes revealed that 2-substituted compounds (5a–b) have a larger calculated β value than 3-substituted analogues (6a–b), and absorb at longer wavelengths than 6. All of the five-membered aromatics did not show SHG efficiency.

3-Formylindole 7, having a very small β value, showed SHG efficiency. The introduction of a cyanovinyl group increased the calculated β value. Compounds 8b and 8c, having alkoxycarbonyl groups as Z, showed SHG efficiency, whereas 8a and 8d did not. Compound 8b showed a good efficiency (PE = 25 U) comparable to that of MNA. Compound 8f, the 2-methyl derivative of 8b, produced a bathochromic shift of 4 nm in λ_{max} and did not show SHG efficiency. It is proposed that the 2-methyl group plays a role in breaking down the effective P1 packing of 8b in crystals.

In a series of 3-formylcarbazoles, 9a showed SHG efficiency (PE = 5.5 U). The N-alkyl substituents have a large effect on SHG efficiency of 9. When 3-cyanovinylcarbazole 10 is superimposed with cyanostyryls 1, the structural analogy reveals that annelation of a phenyl moiety to 1 gives 10. Compounds 10, having a larger

TABLE 2

SHG efficiency and properties of cyanovinylheteroaromatics

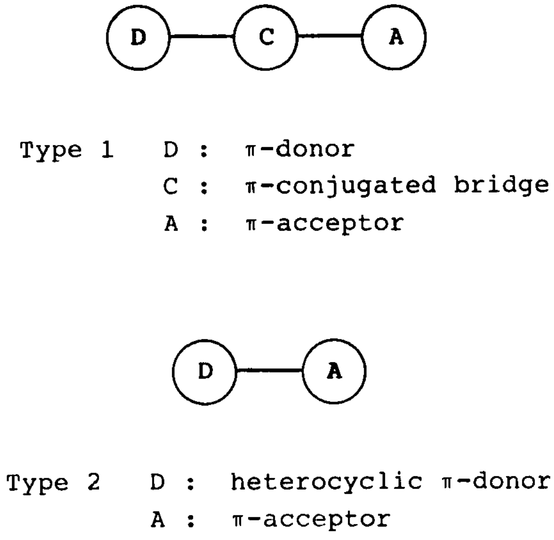
	No.	X	R	Z	mp. (°C)	λ_{max} a)	β b)	SHG c)	PE d)
	5a	S		CN	86-87	322	4	x	
	5b	S		CO_2Et	68-69	316	5	x	
	6a	S		CN	94-95	347	26	x	
	6b	S		CO_2Et	92-93	343	21	x	
	6c	O		CO_2Et	82-83	340	—	x	
	6d	NH		CO_2Et	136-138	363	—	x	
	6e	S	3-Me	CO_2Et	107-108	350	—	x	
	6f	O	5-Me	CO_2Et	71-72	356	—	x	
	6g	N-Me		CO_2Et	112-114	375	—	x	
	7				195-198	296	1.6	o	1.5
	8a		H	CO_2Me	187-188	382	13	x	
	8b		H	CO_2Et	161-163	383	13	o	25
	8c		H	$CO_2Pr(n)$	164-165	383	13	o	— e)
	8d		H	$CO_2Bu(n)$	153-154	384	13	x	
	8e		H	$CONH_2$	236-238	376	—	x	
	8f		Me	CO_2Et	245-246	387	—	x	
	9a		Me		79-82	329	13	o	5.5
	9b		Et		90-92	330	13	x	
	9c		n-Pr		88-90	330	13	o	— e)
	9d		i-Pr		110-111	332	13	x	
	9e		p-MeOPh		122-123	328	17	x	
	10a		Me	CN	197-199	407	82	o	— e)
	10b		Me	CO_2Et	196-197	398	50	o	— e)
	10c		Et	CO_2Et	139-140	398	50	o	0.5
	10d		p-MeOPh	CN	203-204	407	123	x	
	10e		p-MeOPh	CO_2Et	176-177	398	74	o	— e)

a)–e) The same as Table 1.

14π-system compared with an 8π-system of 1, absorb at much shorter wavelengths of 27–28 nm compared with 1. All of dyes 10, except for 10d, showed SHG efficiency. The difference between alkyl groups and aryl groups in R did not change the λ_{max} of compounds, thus R can be modified to achieve effective molecular packing in crystals.

2.4. Absorption spectra and cutoff wavelength

The relationship between the chemical structure and SHG efficiency of cyanovinylheteroaromatics to give effective SHG materials was examined. Great SHG efficiency has been observed from chromophores with intramolecular charge-transfer characteristics. There are two types of compounds whose molecular design will result in effective SHG materials (Scheme 1).



Type 1 D : π-donor
C : π-conjugated bridge
A : π-acceptor

Type 2 D : heterocyclic π-donor
A : π-acceptor

Scheme 1

Type 1: This type consists of three functional parts: donor (D), conjugated bridge (C) and acceptor (A) as in cyanostyryls.

Type 2: This type consists of two functional parts: donor (D) and acceptor (A) as in cyanovinylheteroaromatics.

Absorption spectra of cyanovinylaromatics are shown in Figure 1. A bathochromic shift in λ_{max} was observed in the order 1 > 10 > 8 > 6. Type 2 chromophores produce a hypsochromic shift in λ_{max} compared with type 1. This effect plays an important role in the design of SHG active materials with shorter cutoff wavelengths, especially when a diode laser is used as a light source. In the series of type 2 chromophores, cyanovinyl indoles and carbazoles have good SHG efficiency.

2.5. X-Ray analysis of the SHG active compounds

Crystal technology is another major factor in the production of better SHG efficiency for organic nonlinear materials. The molecules should not have a symmetric center, and the crystals should not have a centrosymmetric point for SHG efficiency. A macroscopic dipole moment of the crystals must remain along some directions for SHG efficiency. X-Ray diffraction analysis is necessary to correlate SHG ef-

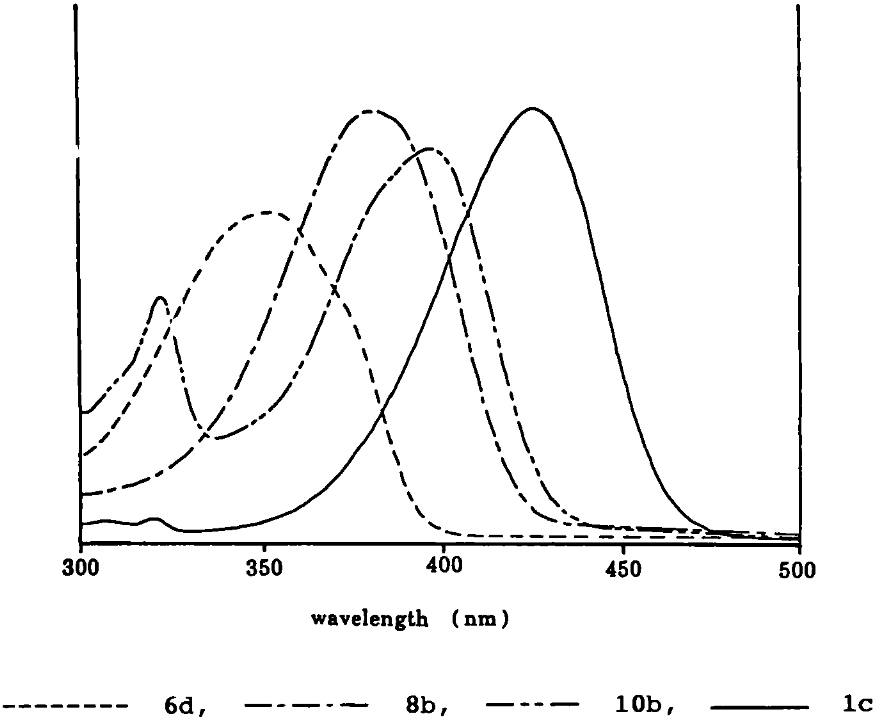


FIGURE 1 Absorption spectra of cyanovinylaromatics.

ficiency with the chemical structure. The following factors are empirically known to give an effective packing of molecules for SHG active crystals:

1. intermolecular hydrogen bonding;
2. control of the dipole moment;
3. introcution of a substituent to disrupt molecular symmetry;
4. introduction of a chiral center.

X-Ray crystal analyses of 1a, 1g and 8b have been carried out. The needle crystals of 1a obtained from a methanol solution belong to the noncentrosymmetric, monoclinic space group of $P2_1$.

The space group of 1g is somewhat ambiguous: the analysis shows that the real space group is $P2_1$ and the cell contains four molecules, but the molecules almost lie on a plane perpendicular to the *b*-axis. Thus the centrosymmetric pseudo-space-group of $P2_1/m$ is assumed, and therefore 1g shows no SHG efficiency. Some results of 1a have been reported previously.[8]

The needle crystals of 8b obtained from an ethanol solution belong to the triclinic, noncentrosymmetric space group of P1, with one molecule in a unit cell. The most effective molecular packing to give SHG efficiency would be crystals with space group P1, because the molecular dipole moments do not cancel each other out. Thus the present crystal structure of 8b, shown in Figures 2–4, is typical for the arrangement of SHG active molecules in the solid state.

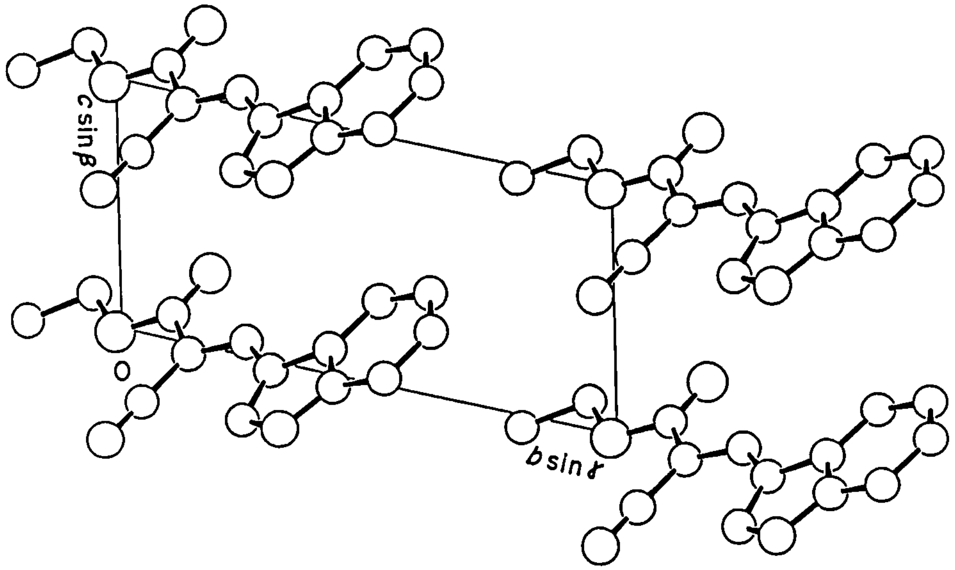


FIGURE 2 Crystal structure of 8b viewed along the *a* axis.

In the crystal structure all the planar molecules nearly lie on the ($\bar{1}$ 2 $\bar{1}$) plane. The molecules are packed in such a way that the acceptor moiety of a molecule is surrounded by the donor moieties of the adjacent molecules and vice versa. The hydrogen bonding is present between the N-H group and the carbonyl oxygen atom, the N . . . O distance being 2.779 Å. This hydrogen bonding is considered to play a great role for the effective P1 packing of 8b.

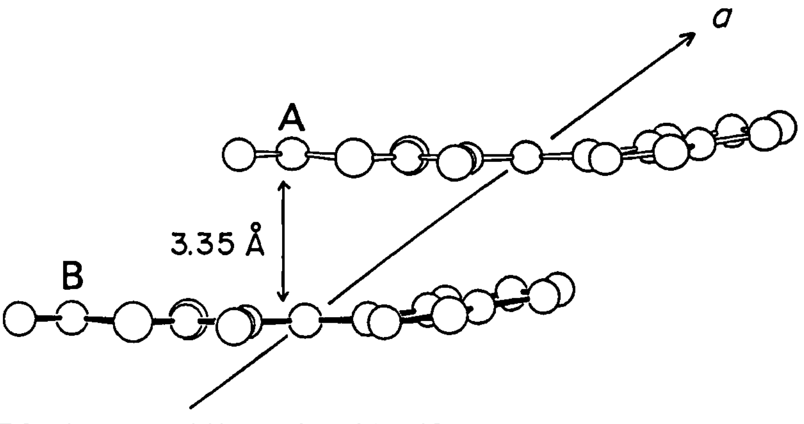


FIGURE 3 The nearest neighbor overlaps of A and B molecules of 8b in crystals viewed parallel to molecular planes.

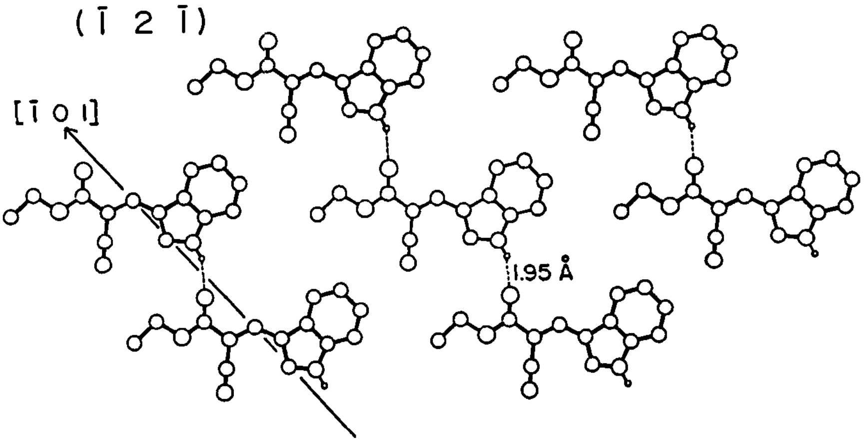


FIGURE 4 Partial crystal structure of 8b viewed perpendicular to $(\bar{1}\,2\,\bar{1})$ plane showing intermolecular hydrogen bonding.

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