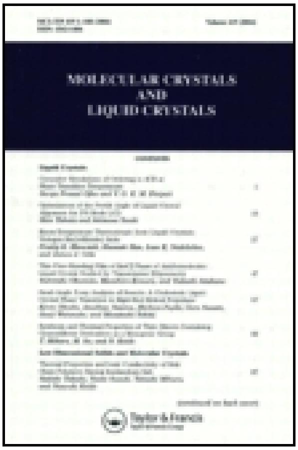

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Prominent Second-Order Nonlinear Optical Properties of Novel Ketone Derivatives

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PROMINENT SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF NOVEL KETONE DERIVATIVES

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Abstract We have studied the substituent effect of bis(benzylidene)-cycloalkanones (BBCAs) on the second-order nonlinear properties. As the result of strong donor introduction, the effective second-harmonic generation (SHG) coefficient of 2,6-bis(4'-dimethylaminobenzylidene)cyclohexanone (DMABCH) was found to be 5.3 times as large as that of *m*-nitroaniline at 1.06 μm. The cutoff wavelength is determined to be 530 nm. The space group symmetry of DMABCH is observed to be *mm*2, as is the case for BBCAs without strong donor. As for chiral effect, the SHG coefficients of chiral BBCAs are as large as that of *m*-nitroaniline.

INTRODUCTION

Organic materials with large second-order optical nonlinearity have attracted much interests in view of their potential applicability to nonlinear optics and optoelectronics.[1,2] In order to develop an efficient second-order nonlinear-optical organic crystal, it is necessary for a comprising molecule to possess a large second-order hyperpolarizability. Moreover, the molecules must be crystallized in a non-centrosymmetric form so as not to cancel out their induced polarizations.[3]

It is well known that a molecule with a strong intramolecular charge-transfer system exhibits a large hyperpolarizability.[2] Therefore, almost all second-order nonlinear optical organic crystals studied up until now are ones equipped with strong donor and acceptor, as is typically the case for *p*-nitroaniline derivatives. However, such molecules have a tendency to crystallize in a centrosymmetric or pseudo-centrosymmetric form due to the intermolecular dipole-dipole interaction.[3] Therefore, many attempts have been made to obtain a non-centrosymmetric crystal structure with a large molecular hyper-polarizability in order to realize efficient second harmonic generation (SHG). For example, the use of chirality for nonlinear optical organic crystals was recognized at the very early stage of investigation.[2]

For developing a nonlinear optical crystal, a somewhat different principle of crystal engineering may also be considered. Molecules also have a tendency to crystallize with maximum density and minimum free volume.[4] Based on this principle, we have attempted to find out a molecule which crystallizes in a non-centrosymmetric form. Namely, we have designed somewhat bend molecules, i.e., a series of bis(benzylidene)-cycloalkanones (BBCAs ; Fig. 1). As a result, we have found a few prominent SHG crystals from BBCAs.[5] It is noted that these molecules are not equipped with either strong donors or chiral center.

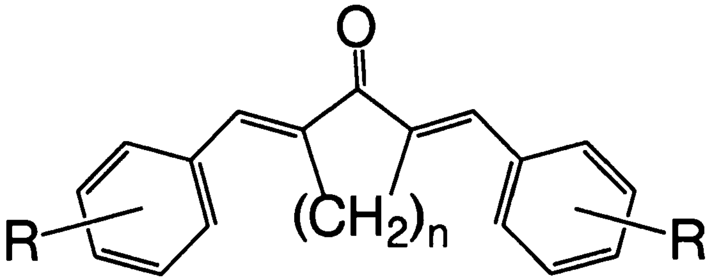

FIGURE 1 Chemical formula of 2,5-bis(benzylidene)cyclopentanone (n = 2), 2,6-bis(benzylidene)cyclohexanones (n = 3) and 2,7-bis(benzylidene)cycloheptanones (n = 4).

In this paper we have made further modifications for BBCAs. First, we have introduced dimethylamino substituents as a strong donor. As a result, we have found that 2,6-bis(4'-dimethylaminobenzylidene)-cyclohexanone (DMABCH) exhibits a very large effective SHG coefficient, i.e., 2 times as large as that of 2,5-bis(4'-methylbenzylidene)cyclopentanone (MBCP),[6] which exhibits the largest SHG coefficient among the BBCAs without a strong donor. Second, we have also synthesized a group of chiral BBCAs, i.e., 2,5-bis(benzylidene)-*R*-3-methylcyclopentanones and 2,6-bis(benzylidene)-*R*-3-methylcyclohexanones. We will report that the SHG coefficients for chiral derivatives are as large as that of achiral ones.

EXPERIMENTAL

A series of BBCAs were synthesized in a similar way described in our previous paper.[5] The SHG intensity of powder crystalline sample thus synthesized was measured at 1.06 μm wavelength. The SHG coefficient was estimated by using the second-harmonic wave generated with the evanescent wave (SHEW) method.[7] The Kurtz method[8] was also utilized as an auxiliary method. A beam from a repetitively Q-switched Nd-YAG laser was used for excitation. The SHEW measurement was made in a similar way to the reported one,[7] by using the same experimental setup. Powder crystals with the initial particle sizes ranging from 50 to 150 μm were mounted in a sample holder. The magnitude of d_{eff} was determined by comparing the observed intensity of the SHEW signal with that for a reference sample of 3-nitroaniline (*m*-NA);[9] in the SHEW method, d_{eff} can be deduced as an average of all SHG tensor elements over the entire directions. The values by the method developed by Kurtz and Perry[8] were also estimated with the use of a standard material of urea powder. The particle size dependence of the signal intensity was measured over a range from 20 to 150 μm in average diameter. No apparent dependence of the signal intensity on particle size beyond 100 μm was observed for all samples. The SHG intensity measured for sufficiently large particle size, i.e., 150 μm in diameter, relative to that of urea at the same average size, was adopted as a SHG coefficient d_{pm}, which is the effective coefficient in the phase-matching case.

RESULTS and DISCUSSION

As a group of BBCAs with strong donors, we have studied three dimethylamino derivatives of BBCA; i.e., 2,5-bis(4'-dimethylaminobenzylidene)-

cyclopentanone (DMABCP), 2,6-bis(4'-dimethylaminobenzylidene)cyclohexanone (DMABCH) and 2,7-bis(4'-dimethylaminobenzylidene)cycloheptanone (DMABCHep).

For the chiral BBCAs, we have studied 2,5-bis(benzylidene)-*R*-3-methylcyclopentanone (BBMCP), 4'-methyl analogue of BBMCP (MBMCP), 4'-methoxy analogue of BBMCP (MOBMCP), 2,6-bis-(benzylidene)-*R*-3-methylcyclohexanone (BB3MCH), 4'-methyl analogue of BB3MCH (MB3MCH) and 4'-methoxy analogue of BB3MCH (MOB3MCH).

1. BBCAs with dimethylamino substituents

Those SHG coefficients of the dimethylamino derivatives estimated by means of the SHEW and Kurtz methods are listed in Table I together with their cutoff wavelengths. The absolute coefficients in the SHEW measurement are also presented, which were evaluated with d_{33} = 21 pm/V, the d_{max} of *m*-NA.[9] The absolute values in the Kurtz measurement were evaluated under the assumption that both the angle tolerance and walk-off angle between all BBCAs and urea are the same. For comparison, the values for MBCP are also listed.

TABLE I Comparison of *d* coefficients determined in the SHEW and Kurtz measurements (See text) and cutoff wavelengths for the dimethylamino derivatives of BBCAs. The cutoff wavelengths are slightly longer than that in crystalline state.

Compound	SHEW d_{eff} relative to *m*-NA	SHEW d_{eff} absolute pm/V	Kurtz *d* relative to urea	Kurtz *d* absolute pm/V	cutoff wave-length nm
DMABCP	0	0	0	0	550
DMABCH	5.3	111	50	14	530
DMABCHep	0	0	0	0	480
MBCP	2.7	57	30	11	440

As shown in Table I, only DMABCH which is a cyclohexanone derivative exhibits SHG activity. This result is consistent with the previous one that a noncentrosymmetric form may be attained more easily in the cyclohexanone skeleton than in cyclopentanone and cycloheptanone skeleton.[5]

The value of DMABCH, 111 pm/V estimated by the SHEW method is very large. The value is 2 times as large as that of MBCP. However, the coefficients by the Kurtz method for both DMABCH and MBCP are much smaller than those by the SHEW method. This is reasonable because a d_{pm} coefficient, which is not directly related to that of d_{max}, dominates the signal intensity in the Kurtz measurement, whereas the magnitude of d_{eff} is in most cases dominated by the largest one, d_{max} among the SHG tensor element, irrespective of the phase-matching characteristics[7]. The situation is such that for the phase-matching angle of those crystals at 1.06 μm the largest tensor element does not effectively contribute to d_{pm}.

The cutoff wavelengths of the dimethylamino derivatives are considerably long as compared with those of BBCAs without strong donor like MBCP. It indicates that the intramolecular charge-transfer effect should become large by introduction of the dimethylamino substituent, causing the hyperpolarizability to be enhanced. As mentioned above, molecules with large hyperpolarizability inclines to crystallizing in a centrosymmetric form. However, DMABCH exhibits such a large d_{eff} coefficient. This fact indicates that the basic skeleton of BBCH has the advantage of being crystallized in a noncentrosymmetric form which can utilize large molecular hyperpolarizability effectively.

We have made an X-ray analysis for DMABCH. The preliminary results are summarized in Table II. The space group symmetry of DMABCH is determined to be orthorhombic $Pca2_1$. According to our preliminary crystal analysis, the molecular alignment of DMABCH resembles that of BBCAs without strong donors.10 Therefore, it may be natural to consider that by utilizing the basic skeleton of BBCH, we may find out an efficient nonlinear optical organic crystal which is composed of molecules with very large hyperpolarizability. In this connection, we have synthesized 2,6-bis(4'-dimethylaminocinnamylidene)cyclohexanone (DMACCH). Its cutoff wavelength was estimated to be 650 nm, indicating that it should exhibit very large hyperpolarizability. According to our preliminary SHG test, DMABCH also exhibits large SHG coefficient. The results will be presented in a forthcoming paper.

TABLE II Structural data for DMABCH crystal.

Formula	$C_{24}H_{28}ON_2$
Density	1.220 g / cm^3
Melting Point	> 250 °C (decomp.)
Crystal System	orthorhombic
Symmetry	*mm*2
Z Number	4
Space Group	$Pca2_1$
Unit Cell	
a	9.319(6) Å
b	21.841(11) Å
c	9.643(2) Å
V	1962.6(17) Å^3

2. SHG characteristic of chiral BBCAs

The results for chiral BBCAs are listed in Table III, as is the case for the dimethylamino derivatives. For comparison, the values of achiral analogues, i.e., 2,5-bis(4'-methoxybenzylidene)cyclopentanone (MOBCP) and 2,6-bis(4'-methylbenzylidene)-4-methylcyclohexanone (MBMCH)[6] are also tabulated.

All chiral BBCAs exhibit SHG activity, reflecting the introduction of chirality. The cutoff wavelengths were almost the same as those of the achiral ones with the same substituent. The coefficients observed for the chiral BBCAs by the SHEW method are as large as those of achiral ones.

According to our preliminary examination, a coefficient of a chiral BBCA by Kurtz method is smaller than that of SHG active achiral ones. Therefore, only two analogues were examined by SHEW method. However, the d_{eff} coefficient for MB3MCH is found to be one of the largest values among BBCHs without strong donors.[6] Therefore, a possibility is left that some other chiral BBCAs unexamined, especially with strong donor might show prominent characteristics.

TABLE III Comparison of *d* coefficients determined in the SHEW and Kurtz measurements (See text) and cutoff wavelengths for chiral derivatives of BBCAs.

Compound	SHEW d_{eff} relative to *m*-NA	SHEW d_{eff} absolute pm/V	Kurtz *d* relative to urea	Kurtz *d* absolute pm/V	cutoff wave-length nm
BBMCP	-	-	2.9	3	410
MBMCP	0.8	17	0.8	2	410
MOBMCP	-	-	1.2	2	440
BB3MCH	-	-	5.9	5	400
MB3MCH	0.7	15	8.0	6	400
MOB3MCH	-	-	1.4	2	420
MOBCP	0.7	15	19	9	440
MBMCH	0.7	15	24	10	410

- unmeasured

CONCLUSION

The substituent effects of BBCAs have been examined. We have found that DMABCH, equipped with dimethylamino substituents as strong donors, exhibits very large SHG coefficient, i.e., 5.3 times as large as that of *m*-nitroaniline at 1.06 μm. The DMABCH molecules are crystallized in orthorhombic *mm*2 point group symmetry, as is the case for analogues without strong donors. From this fact, we can conclude that by utilizing the bis(benzylidene)cyclohexanone skeleton, it might be possible to find out even more efficient nonlinear optical organic crystal which is composed of molecules with very large hyperpolarizability.

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