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New Second-Order Nonlinear Optical Materials with a Cutoff Wavelength of 350 nm. 3-Benzylidene-D-camphor Derivatives

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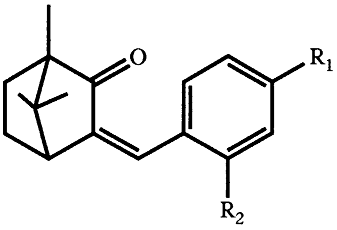
A series of 3-benzylidene-D-camphor derivatives has been synthesized in order to examine the second-harmonic generation (SHG) efficiency along with the transparent wavelength region. Through reflection powder measurement, 3-cinnamylidene-D-camphor having a cutoff wavelength of 350 nm, shows the efficiency 10 times as large as that of urea.

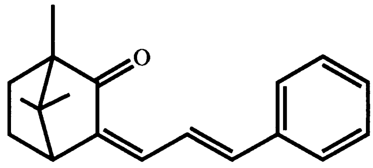
The organic crystals with a large SHG (second-harmonic generation) coefficient developed up until now, are mostly equipped with strong donor and/or acceptor groups such as -NH_2 and -NO_2 at the terminals of a π-conjugated system.1) As a result of the intramolecular charge-transfer interaction induced thereby in a molecule, those have a long cutoff wavelength of typically 450-500 nm.2)

In this Letter, we have examined 3-benzylidene-D-camphor derivatives in order to develop new SHG materials with a short cutoff wavelength. One possible way of attaining this characteristics may be to utilize a large oscillator strength of a molecule with a short wavelength absorption edge to enhance the magnitude of hyperpolarizability ß. For this purpose, a group of benzene derivatives conjugated with a carbonyl group, which is recognized to work as a weak acceptor,3) may be good candidates. This has already been justified to some extent from the fact that vanillin exhibits a rather short cutoff wavelength of 370 nm although it has a large SHG efficiency.3,4) However, aldehydes are too labile. As for ketones, we have already studied bis(benzylidene)cycloalkanones (BBCAs).5) The result is, however, rather negative for the present purpose since their cutoff wavelengths turn out to range from 400-450 nm. Considering that this characteristic is presumably caused by two aromatic rings involved, we have adopted the present materials with a keto-group conjugated with single benzene ring.



1

a:R_1=R_2=H
b:R_1=CH_3, R_2=H
c:R_1=CH_3O, R_2=H
d:R_1=F, R_2=H
e:R_1=Cl, R_2=H
f:R_1=Br, R_2=H
g:R_1=H, R_2=Cl
h:R_1=CF_3, R_2=H
i :R_1=$N(CH_3)_2$, R_2=H
j :R_1=CH_3S, R_2=H



2

The desired compounds (**1**,**2**) were not obtained by a method of conventional Crossed-Aldol condensation between D-camphor and benzaldehyde derivatives in methanol under the presence of a catalytic amount of sodium hydroxide. Therefore, all compounds were obtained by following procedure. First, 3 g (0.020 mol) of D-camphor was dissolved in 300 ml of toluene. Then, 2.5 g (0.022 mol) of potassium-*tert*-butoxide was added. The mixture was refluxed with stirring until the solution became yellowish-brown (for a few hours). Then, 0.020 mol of benzaldehyde derivative was added dropwisely and boiled with stirring until the solvent was decoloured (for half a day). After boiling with active carbon, the filtrate was evaporated to yield a crude product. The products were purified by repeated recrystallizations from methanol solution. The results of elemental analysis are in good agreement with the composition of the desired compounds. For example, Found : C, 74.27 ; H, 6.95 ; Cl, 12.90%. Calcd for $C_{17}H_{19}OCl$ (**1e**) : C, 74.32 ; H, 6.92 ; Cl, 12.93%.

The SHG efficiency was estimated by powder technique$^{6)}$ with the use of an repetitively pulsed Nd-YAG laser at 1.06 µm. The dependence of SHG efficiency on particle size over a range from 50 to 150 µm in an average size was examined. No appreciable dependence was observed in any of the present compounds, suggesting that the phase matching should be possible.$^{6)}$ A calorimetric measurement was made by using an differential scanning calorimeter. The cutoff wavelength was determined from absorption spectrum for solution as a value extrapolated from the steepest tangent in the absorbance curve. The details of these measurements are described in our previous paper.$^{5)}$ All those results are summarized in Table 1.

Table 1 shows that all compounds examined exhibit SHG activity, reflecting optical-activity. The powder SHG efficiency of **2** is found to be 10 times as large as that of urea, while that of benzylidene derivative (**1a**) 2.0 times. The magnitude of β for **2** estimated by using PPC-MO calculation method$^{7)}$ is $30\text{x}10^{-30}$ esu, whereas **1a** is $10\text{x}10^{-30}$ esu. This result seems to be in reasonable agreement with the ratio of the observed powder SHG efficiency which is proportional to the square of β,$^{6)}$ although it is pointed out that the latter usually becomes smaller than the ratio of the square of β.$^{8)}$ For **1a**-**1j**, large SHG efficiencies that we have expected have not been observed. Since the keto-group of camphor moiety behaves as an acceptor group, β should be enhanced by introduction of a donor group at the position of R_1 or R_2. However, the SHG efficiencies of **1a**-**1j** are inclined to decrease thereby. From this fact, it is speculated that **1a**-**1j** have a tendency to crystallize so as to cancel out the amount of polarization of each molecule.

Table 1. Summary of the data measured in this study

Compounds	SHG(x urea)	Cutoff wavelength(in cyclohexanone)/nm	Melting point/°C
1a	2.0	320	96
1b	0.50	330	99
1c	0.13	340	126
1d	3.0	320	94
1e	2.1	320	106
1f	1.9	320	131
1g	0.62	320	81
1h	1.3	310	99
1i	<0.1	380	144
1j	0.10	350	88
2	10	350	88

Next, the cutoff wavelengths of **1a**-**1j** except dimethylamino derivative (**1i**) are shorter than 350 nm. The cutoff wavelength of **2** is by 30 nm longer than that of **1a**, which is caused by elongation of the conjugated system due to addition of a unit of C-C double bond. Nevertheless, it is still short enough.

The melting points of **1a**-**1j** and **2** are also summarized in Table 1. For practical application, the crystals must be thermally stable at room temperature. These values are high enough. Owing to the dense camphor moiety, **1a**-**1j** and **2** have a high melting point without increasing the bulk of unconjugated alkyl moiety that is independent of intramolecular charge-transfer interaction. In this connection, from an DSC measurement, no solid-to-solid phase transition is recognized above room temperature for all compounds.

Now, let us discuss in a bit more detail the present motivation already described on the basis of the observed result. The effectiveness of utilizing a large oscillator for the present purpose may be justified by assuming the Oudar's equation.9) As for the difference between the respective dipole moment of the ground and excited states therein, the magnitude in the conjugated ketones in question may be comparable to that in the *p*-nitroaniline, judging from the case of chalcone.10) A group of carbonyl compounds conjugated with aromatic ring has generally a larger oscillator strength with a short absorption edge, compared to nitro-compounds. For example, the maximal value of the molar extinction coefficient for aqueous solution of acetophenone is 9800 at 245 nm, whereas 7800 at 269 nm for that of nitrobenzene with a similar molecular size to the former.11) As another example, the oscillator strength of chalcone which has a large SHG coefficient, is known to be large even without any donor, i.e., 0.51, which is worth comparing to the value of 0.36 for *p*-

nitroaniline.[10)] These might be enough for us to expect that molecules equipped with a conjugated carbonyl moiety as an acceptor should have a large-enough magnitude of ß without strong donor. The present result for **2** supports validity of the above conjecture. As for other compounds, the result indicates that controlling the intermolecular interaction for a crystal is another key to attaining the purpose, which is self-evident.

In conclusion, 3-cinnamylidene-D-camphor is found to be 10 times more efficient in SHG than urea through the reflection measurement in powder form. Furthermore, the transparency for visible light is satisfactory enough to apply for the second harmonic generation of a GaAs diode laser (750-830 nm). From the viewpoint of human toxicity, it is noted that the ketones conjugated with π-electron system are harmless materials[12)] unlike nitroaniline derivatives.[13)] Though a further reliable estimation of the nonlinear- and linear-optical constant is needed for a single crystal, this work has demonstrated that 3-cinnamylidene-D-camphor should be a promising nonlinear optical material, in particular, in the short-wavelength region.

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