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Study on second harmonic generation of 9-benzylidene-substituted-10-methyl-9,10-dihydroacridines

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Abstract

Eight 9-benzylidene-substituted-10-methyl-9,10-dihydroacridine derivatives were synthesized from acridine as starting material and were characterized by ¹H-NMR, ¹³C-NMR, Ms and elemental analysis. The second harmonic generation (SHG) values of these compounds were determined in powder using Nd:YAG as a laser source, as compared with urea powder, and the values of second-order polarizabilities (β_{xxx}), the values of the composite magnitude ($\beta_{CT\mu g}$) of molecular hypersusceptibilities and their moment of these compounds were obtained by the solvatochromic method under ground state for everyone. The results showed that SHG value of 10 is higher than that of urea; the $\beta_{CT\mu g}$ of 5 (107.8 × 10⁻³⁰ esu) is lower than that of 4-nitro-*N*,*N*-dimethylaniline (30×10^{-30} esu); the $\beta_{CT\mu g}$ of 7 (350.8×10^{-30} esu) and 10 (244.6×10^{-30} esu) are higher than that of 4-nitro-*N*,*N*-dimethylaniline; the $\beta_{CT\mu g}$ of 8 (3553×10^{-30} esu), 11 (1187×10^{-30} esu) and 12 (1163×10^{-30} esu) are much more higher than that of 4-nitro-*N*,*N*-dimethylaniline. The results demonstrated that this series of compounds possesses good second-order nonlinear optical (NLO) property. The regular relationship could not be obtained between electronegativity of substituents (*R*) attached to benzylidene ring and SHG values or $\beta_{CT\mu g}$ values although the *R*s are different in electronegativity and should make an effect on the extent of intramolecular electron-transfer and would consequently influence SHG or $\beta_{CT\mu g}$. The electron-withdrawing ability of *R* from benzylidene ring played an important role on λ_{max} of these compounds. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 9-Benzylidene-10-methyl-9,10-dihydroacridines; Second harmonic generation; Second-order polarizability

1. Introduction

With the development of laser technology, to prepare and study second-order nonlinear optical (NLO) materials has been the subject of recent attention [1,2], this is because that organic materials possess high NLO coefficient, short time for responding to light, little dielectric constant and easy to be designed and processed. For an application purpose, it is better to have NLO organic materials as crystals, however, in the most cases it is not possible to obtain crystal [3]. Therefore, it is necessary to develop some new methods to evaluate those NLO organic materials, which are not crystals. Presently, many new methods have been developed for this purpose, such as electronic field

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induced method [4,5], solvatochromic method [6], and Kurtz powder method [7]. A second harmonic generation (SHG) measurement system for organic compound powders were built based on the Kurtz method in our laboratory, and recently we reported the SHG values of 10-hydrocarbylacridone derivatives measured by this system [8,9]. In this paper we report SHG values determined by this setup, the second-order polarizabilities (β_{xxx}), the values of the composite magnitude (β_{CTug}) of molecular hypersusceptibilities and their moment of these compounds obtained by the solvatochromic method, and syntheses of another kind of organic material. 9-benzylidene-10-methyl-9,10-dihydroacridine derivatives. Their structures and steps to synthesize them are outlined in Fig. 1.

2. Results and discussion

Based on equation Eq. (1) [6,10] β_{xxx} may be obtained,

$$\beta_{\rm xxx} = \frac{1.5 \ h^{-2} \mu_{\rm eg}^2 (\mu_{\rm e} - \mu_{\rm g}) \omega_{\rm eg}^2}{(\omega_{\rm eg}^2 - \omega^2) (\omega_{\rm eg}^2 - 4\omega^2)} \tag{1}$$

where ω_{eg} , μ_{eg} , μ_{e} , μ_{g} and ω are the transition frequency of sample molecule from ground state to first excited state, the transition dipole moment between ground state and excited state, the permanent dipole moment of sample molecule in ground state, the permanent dipole moment of sample molecule in excited state and the laser frequency, respectively. Here the ω_{eg} could be obtained simply from the band maximum of the ultra violet (UV)– visible absorption spectrum of the sample molecule. μ_{eg} is related to the intensity of the transition and could be found out by Eqs. (2) and (3) [11] from the area under the absorption band:

$$area = \frac{2\pi\omega_{eg}N_0n\mu_{eg}^2M}{3(2.303)\varepsilon_0ch}$$
(2)
$$\mu_{eg}^2 = \frac{6.909Hr_{1/2}\varepsilon_0ch}{2\pi\omega_{eg}N_0nM}$$
$$\mu_{eg}^2 = \frac{32.11662 \times 10^{-61}Hr_{1/2}}{nM\omega_{eg}} (C^2 m^{-1} mol)$$
$$\mu_{eg}^2 = \frac{3.211662 \times 10^{-58}Hr_{1/2}M}{n\omega_{eg}} (C^2 m^2)$$
(3)

where M, N_0 , n, ε_0 , c and h in Eq. (2) are concentration of sample, Avogadro's number, solvent refractive index, speed of light in a vacuum and the plank constant, respectively. H, $r_{1/2}$ and m in Eq. (3) are height of peak, half-width at the middle of peak, and molecular weight. The values of μ_{eg} are calculated with Eq. (3) through the values of ω_{eg} .

According to Eq. (1), in order to get β_{xxx} , it is necessary to found out the values of $\mu_e - \mu_g$ and presented in Tables 1–5. In our work, only values



Fig. 1.

Table 1													
The data	of	$\lambda_{\mathrm{a}},$	λ _e ,	Н,	$r_{1/2},$	μ_{eg}	and	stokes	shift	in	carbon	tetrachl	oride ^a

Samples	5	7	8	10	11	12
$\lambda_{\rm a}$ (nm)	392.7	392.9	455.0	393.5	394.3	393.3
$\lambda_{\rm e}$ (nm)	401	402.5	410	404	405	403
Н	0.037	0.034	0.008	0.024	0.041	0.016
$r_{1/2} (\mathrm{cm}^{-1})$	1825	1889	2500	872.9	412.0	569.2
Stokes shift	527	608	2412	630	640	612
μ_{eg} (10 ⁻³⁰ cm)	12.526	12.204	14.430	7.418	6.670	4.855
$\beta_{\rm xxx} \ (10^{-30} \ {\rm m}^5 \ {\rm c}^{-1})$	20.824	6.749	60.844	1.672	2.73	3.160

^a The dielectric constant of carbon tetrachloride is 2.238 (CRC Handbook of Chemistry and Physics Data, 58th; the data in the following tables were all obtained from this book).

of $\mu_e - \mu_g$ are obtained with Bilot-Kawski Eq. (4) [12] and are listed in Table 5.

$$V_{a} - V_{f} = A + B(BK)$$

$$B = \frac{2(\mu_{e} - \mu_{e})^{2}}{hc\alpha^{3}}$$

$$BK = \left[\frac{(D-1)}{(2D+1)} - \frac{(n^{2}-1)}{(2n^{2}+1)}\right] \div \left[\frac{1 - (n^{2}-1)}{2n^{2}+1}\right]^{2}$$

$$\div \left[\frac{1 - (D-1)}{(2D+1)}\right]$$
(4)

where A and B are constants, V_a and V_f are wave numbers of UV-visible absorption and fluorescence emission of sample molecule, α is the radius of a spherical cavity in the solvent occupied by the sample molecule and it is assumed that α was 0.7 times of the molecular length. D is dielectric constants of solvent.

From Eqs. (1) and (5) could be derived:

 $\beta_{\rm xxx}$

$$= \frac{1.5(6.6262 \times 10^{-34})^{-2} \text{ J}^{-2} \text{ S}^{-2} \mu_{eg}^{2}(\mu_{e} - \mu_{g})\lambda_{e}^{2}}{c(1 - \omega^{2}/\omega_{e}^{2})(1 - 4\omega^{2}/\omega_{e}^{2})}$$

$$\beta_{xxx}$$

$$= \frac{3.8012(9^{-1} \times 10^{-9} \text{ C}^{2} \text{ m}^{-1})^{-2}\mu_{eg}^{2}(\mu_{e} - \mu_{g})\lambda_{e}^{2}}{(1 - \lambda_{e}^{2}/\lambda_{a}^{2} \times 1 - 4\lambda_{e}^{2}/\lambda_{a}^{2})}$$
(5)

where $\lambda_{\rm e}$ and $\lambda_{\rm a}$ are wavelength of fluorescence emission and maximum absorption wavelength of sample molecule, the values of $\beta_{\rm xxx}$ could be calculated from the values of $\mu_{\rm eg}$, $\mu_{\rm e} - \mu_{\rm g}$ and $\lambda_{\rm e}$ with the Eq. (5).

According to the Eq. (6) [6,13], $\beta_{CT\mu g}$ could be calculated (Table 5):

$$\beta_{\rm CT\mu g} = \frac{4.612 \times 10^{29} f(\lambda_{\rm a}) \varepsilon \Delta v_{1/2} \Delta v_{\rm max} \alpha^3}{\Delta f(D)}$$
$$f(\lambda_{\rm a}) = \frac{\lambda_{\rm a}^3 \lambda_0^4}{(\lambda_0^2 - 4\lambda_{\rm a}^2)(\lambda_0^2 - \lambda_{\rm a}^2)}$$
$$f(D) = \frac{2(D-1)}{(2D+1)} \tag{6}$$

where λ_a , ε , $\Delta v_{1/2}$, Δv_{max} , λ_0 are absorption wavelength of sample molecule in excited state, and here, is assumed as the wavelength of absorption of sample molecule in dipolar solvent, maximum absorption coefficient in dipolar solvent, the difference of the width of peaks at the middle, shift of maximum absorption, wavelength of base frequency, respectively, α is the same thing as in Eq. (3).

Dipole moments and bond length were taken from CRC Handbook of Chemistry and Physics Data, 60th, F214.

The λ_{max} of 9-(substituent-benzylidene)-10methyl-9,10-dihydroacridine in solution originates from the n- π^* electron transition. When an electron-withdrawing group R is attached to benzylidene ring, the electron-withdrawing conjugating action of R and the stronger electron-donating conjugating action of $>N-CH_3$ exist at the same time and the two actions are in the same direction, that is, a certain extent of intramolecular chargetransfer would take place in the molecule. As the intramolecular charge-transfer action makes the energy level of ' π^* ' orbit lower, little energy is needed for electron transition from 'n' orbit to ' π^* ' orbit, the λ_{max} of 9-(substitutent-benzylidene)-10methyl-9,10-dihydro-acridine shifts to longer wavelength. Therefore, λ_{max} of this series of compounds increases with the increases of the electron-withdrawing capacity of *R*. For example, compound 8, the strong electron-withdrawing action of NO₂ gives rise to a greater extent of intramolecular charge-transfer, which obviously decreases the ' π '' orbit energy, so λ_{max} of 8 is the biggest one among these compounds.

For the same electron-withdrawing *R*, *R* has a stronger electron-withdrawing conjugating action at the *p*-position than that at the *o*-or *m*-position of benzylidene ring, consequently, λ_{max} of 11 is longer than that of 10.

On the contrary, when an electron-donating *R* is attached to benzylidene ring, the electron-donating conjugating action of *R* and >N–CH₃ exist at the same time, but in the contrary direction. The coordinating action mentioned above could not occur in this kind of molecules. For this reason, the energy level of ' π *' orbit of a compound with an electron-donating *R* in the benzylidene ring is higher than that of a compound without an electron-donating *R* and much more energy was needed for electron transition from 'n' orbit to ' π *' orbit, as compared with the compound without an electron-donating *R*. Thus, the values of λ_{max} of these compounds in chloroform decrease with the increase of the electron-donating capacity of *R*.

	<i>p</i> -	<i>m</i> -	<i>p</i> -	<i>m</i> -	Н
	$NO_2 >$	$NO_2 >$	Cl>	Cl>	
λ_{\max}	463.9	400.5	400.1	399.5	394.9
(nm)					

The $\beta_{CT\mu g}$ of 5 (107.8 × 10⁻³⁰ esu) was lower than that of 4-nitro-*N*,*N*-dimethylaniline (30 × 10⁻³⁰

Table 2 The data of λ_a , λ_e , *H*, $r_{1/2}$, μ_{eg} and stokes shift in chloroform^a

esu) [14]; the $\beta_{CT\mu g}$ of 7 (350.8 × 10⁻³⁰ esu) and 10 (244.6 × 10⁻³⁰ esu) were higher than that of 4-nitro-*N*,*N*-dimethylaniline; the $\beta_{CT\mu g}$ of 8 (3553 × 10⁻³⁰ esu), 11 (1187 × 10⁻³⁰ esu) and 12 (1163 × 10⁻³⁰ esu) were much more higher than that of 4-nitro-*N*,*N*-dimethylaniline. The reason for $\beta_{CT\mu g}$ value of 8 is higher than that of 4-nitro-*N*,*N*-dimethylaniline is suggested herein that compound 8 has longer conjugating chain than 4-nitro-*N*,*N*-dimethylaniline does, the greater extent of intramolecular charge-transfer would take place in the molecule of 8 than that in the molecule of 4-nitro-*N*,*N*-dimethylaniline.

The results demonstrated that the β_{xxx} and the $\beta_{\rm CT\mu g}$ of 8 are the highest in the six compounds in this five solvents, u_{eg} of 5 is the highest in the six compounds in carbon tetrachloride, chloroform, 1,2-dichloroethane and ethanol. This is because that NO₂ possesses strong electron-withdrawing action. When NO₂ was attached to the 'p' position of benzyldiene ring, unshared electron-pair on nitrogen atom could transfer to NO₂ along the conjugation system in the most beneficial method, which meant that the extent of intramolecular charge-transfer is the largest one in the six states. When NO_2 was attached to the other position of the benzyldiene ring, the intramolecular chargetransfer of 7 could not take place in the most beneficial method as compared with 5. So u_{eg} , β_{xxx} and $\beta_{\rm CT\mu g}$ of 8 are lower than that of 5.

The SHG of 9 is the highest in the six compounds. The $\beta_{CT\mu g}$ values of these samples were obtained in solution in our work, these values actually reflect the second NLO property. The SHG values of these samples were measured in powder. The pattern of crystal of these com-

Samples	5	7	8	10	11	12
λ_a (nm)	393.7	400.5	463.9	399.5	400.1	396.9
$\lambda_{\rm e}$ (nm)	405	413	415	410	411	409
Н	0.058	0.044	0.056	0.024	0.042	0.048
$r_{1/2} (\mathrm{cm}^{-1})$	1881	2391	2495	1382.6	550	1851
Stokes shift	648	638	2482	641	663	715
μ_{eg} (10 ⁻³⁰ cm)	16.02	13.141	21.261	9.353	7.778	15.305
$\beta_{\rm xxx} \ (10^{-30} \ {\rm m^5 \ c^{-1}})$	33.531	7.337	155.23	2.859	3.984	32.80

^a The dielectric constant of chloroform is 4.086.

Samples	5	7	8	10	11	12
$\lambda_{\rm a} \ ({\rm nm})$	400.9	402.3	464.3	399.5	399.3	396.1
$\lambda_{\rm e}$ (nm)	413	413	416	410	411	409
Н	0.037	0.034	0.039	0.025	0.049	0.033
$r_{1/2} (\mathrm{cm}^{-1})$	2004	2496	3026	1763	753	2053
Stokes shift	731	644	2559	641	684	796
$\mu_{eg} (10^{-30} \text{ cm})$	12.203	14.976	19.557	10.902	9.972	13.355
$\beta_{\rm xxx} \ (10^{-30} \ {\rm m^5 \ c^{-1}})$	21.748	9.744	132.35	3.884	6.484	24.732

Table 3 The data of λ_a , λ_e , H, $r_{1/2}$, μ_{eg} and stokes shift in 1,2-dichloroethane^a

^a The dielectric constant of 1,2-dichloroethane is 9.08.

pounds, a form in which molecules piled up, certainly causes an effect on the polarization of molecules, the effect on the polarization of molecules varies as the pattern of crystal of these compounds, and the different form of crystal also gives rise to different extent of intramolecule charge-transfer. When an organic compound possesses a higher $\beta_{\rm CT\mu g}$ value in solution, it does not mean that this kind of organic compound is of a higher SHG value in solid state. So the SHG of 8 is not the highest in the six compounds, although $u_{\rm eg}$, $\beta_{\rm xxx}$ and $\beta_{\rm CT\mu g}$ of it are the highest in the six samples.

3. Experimental

3.1. Synthesis of 10-methyl-9-(substituted-benzyldene)-9,10-dihydroacridine

The ¹H-NMR and ¹³C-NMR spectra (300 MHz) were recorded in CdCl₃. Solvents and starting materials were purchased from commercial sources where available. The salt of *N*-methylacridinium methylsulfate 2 was prepared as reported [15]; 3 was synthesized as literature [16]; yield 61.0%, m.p. 86-88 °C (uncorrected, literature 89-91 °C [16]).

3.2. 9-Benzyldene-10-methyl-9,10-dihydroacridine (5)

The solution of 2.34 g (7.0 mmol) of 3 in dry THF was stirred to cool to -78 °C under nitrogen atmosphere. To this solution was added the suspension of 0.45 g (7.0 mmol) of butyllithium in

5 ml of hexane, then the mixture became yellow. After the mixture was stirred for 10 min, the solution of 0.74 g (7.0 mmol) of benzaldehyde in 3 ml of THF was added to this mixture by dropwise. The mixture was stirred continuously for other 10 min, then removed the cooling bath, the mixture was stirred under room temperature for another 5 h. Evaporated the solvent under reduced pressure, 250 ml of water was added into the container. The water layer was extracted with 150 ml of methylene chloride for three times, the combined extracts were dried over anhydrous magnesium sulfate. Evaporated the methylene chloride under reduced pressure to give yellowish solid product, which was recrystallized in the mixture of methanol and benzene to give 1.00 g (50.4%) of vellowish product; m.p. 139-141 °C $(142-144 \ ^{\circ}C \ [17])$. ¹H-NMR (CdCl₃), δ 3.48 (s, 3H), 6.70 (s, 1H), 6.80-7.70 (m, 11H), 7.80 (d, J = 7.2 Hz, 2H); Ms for C₂₁H₁₇N(M)⁺ (Fab), 283; UV (CHCl₃, λ_{max} (nm), ε), 393.7 (13440), 300.3 (16010), 242.1 (35880).

3.3. 9-(o-Nitrobenzyldene)-10-methyl-9,10dihydroacridine (6)

Compound 6 was obtained from 2.34 g (7.0 mmol) of 3 and 1.06 g (7.0 mmol) of *o*-nitrobenzaldehyde as 5 was prepared, expert for the solution became dark red when the solution of 2-nitrobenzaldehyde in THF was added. The solid product was recrystallized from the mixture of methanol and benzene to give 0.8 g (34.8%) of dark red crystal; m.p. 180–182 °C. ¹H-NMR (CdCl₃), δ 3.56 (s, 3H), 6.60 (s, 1H), 7.04–7.23 (m, 11H), 8.01 (d, J = 6.9 Hz, 1H), 8.20 (t, J = 2.1 Hz, 1H); Ms for C₂₁H₁₆N₂O₂(M)⁺ (Fab), 328; anal. calcd. for C₂₁H₁₆N₂O₂, C, 76.81; H, 4.91; N, 8.53. Found C, 77.11; H, 5.10; N, 8.55. UV (CHCl₃, λ_{max} (nm), ε), 399.3 (6294), 242.3 (41900).

3.4. 9-(m-Nitrobenzyldene)-10-methyl-9,10dihydroacridine (7)

Compound 7 was made as 5 synthesized from 2.34 g (7.0 mmol) of 2 and 1.06 g (7.0 mmol) of 3-nitrobenzaldehyde, expert for the solution became red when the solution of 3-nitrobenzaldehyde in THF was added. The solid product was recrystallized from the mixture of methanol and benzene to give 1.70 g (74.0%) of dark red crystal, m.p. 179–180 °C (182–185 °C [16]). ¹H-NMR (CdCl₃), δ 3.56 (s, 3H), 6.64 (s, 1H), 6.68–7.90 (m, 11H), 8.20 (s, 1H). Ms for C₂₁H₁₇N₂O₂ (M + H)⁺ (Fab), 329; UV (CHCl₃, λ_{max} (nm), ε), 401.5 (15850), 285.3 (22420), 241.7 (45520).

3.5. 9-(p-Nitrobenzyldene)-10-methyl-9,10-dihydroacridine (8)

Compound 8 was obtained as 5 from 2.00 g (6.0 mmol) of 3, 4 ml (6.4 mmol) of suspension of butyllithium in THF and 0.91 g (6.0 mmol) of *p*-nitrobenzaldehyde, expert for the solution became dark when the solution of *p*-nitrobenzaldehyde in THF was added. The solid product was recrystallized to give 0.70 g (50.0%) of dark brown crystal, m.p. 166–168 °C (169–171 °C [18]). ¹H-NMR (CdCl₃), δ (ppm), 3.60 (s, 3H), 6.62 (s, 1H), 6.74–7.72 (m, 10H), 7.95 (d, J = 6.3

Table 4 The data of λ_a , λ_e , *H*, $r_{1/2}$, μ_{eg} and stokes shift in DMSO^a

Hz, 1H), 8.20 (d, J = 6.6 Hz, 1H); Ms for $C_{21}H_{16}N_2O_2$ (M)⁺ (Fab), 328; UV (CHCl₃, λ_{max} (nm), ε), 468.7 (16510), 305.1 (12750), 241.7 (35430).

3.6. 9-(o,p-Dinitrobenzyldene)-10-methyl-9,10-dihydroacridine (9)

Compound 9 was prepared as 5 from 2.34 g (7.0 mmol) of 3 and 1.37 g (7.0 mmol) of 2,4-dinitrobenzaldehyde, expert for the solution became brown when the solution of 2,4-dinitrobenzaldehyde in THF was added. The solid product was recrystallized to give 0.91 g (35.0%) of brown crystal, m.p. 194–196 °C. ¹H-NMR (CdCl₃), δ 3.82(s, 3H), 7.22–7.71 (m, 10H), 8.55 (dd, J = 1.6, 1.6 Hz, 2H); ¹³C-NMR (CdCl₃), δ 33.98, 115.14, 121.60, 122.86, 128.74, 134.16, 142.91, 178.47; Ms for C₂₁H₁₅N₃O₄ (M)⁺ (Fab), 373; anal. calcd. for C₂₁H₁₅N₃O₄, C, 67.56; H, 4.05; N, 11.25. Found, C, 67.83; H, 4.09; N, 11.12; UV (CHCl₃, λ_{max} (nm), ε), 399.9 (27840), 381.3 (20870), 276.1 (37730), 257.7 (107400).

3.7. 9-(m-Chlorobenzyldene)-10-methyl-9,10-dihydroacridine (10)

Compound 10 was synthesized as 5 from 0.98 g (7.0 mmol) of *m*-chlorobenzaldehyde, the product was recrystallized to give 1.20 g (54.0%) of yellow pure product, m.p. 115–117 °C; ¹H-NMR (CdCl₃), δ 3.53 (s, 3H), 6.61 (s, 1H), 6.80 (t, J = 7.4 Hz, 1H), 7.04 (m, 6H), 7.15–7.20 (m, 4H), 7.72 (d, J = 7.6 Hz, 1H); ¹³C-NMR (CdCl₃), δ (ppm), 34.02, 112.91, 113.80, 120.47, 121.05, 121.75, 123.93, 126.66, 127.10, 128.67, 128.89,

Samples	5	7	8	10	11	12
λ_{a} (nm)	399.3	404.1	470.3	407.5	403.3	401.1
$\lambda_{\rm e}$ (nm)	416	415	418	419	415	415
H	0.046	0.028	0.025	0.045	0.048	0.039
$r_{1/2} (\mathrm{cm}^{-1})$	2020	2348	2380	1939	985	1372
Stokes shift	889	650	2660	674	699	835
μ_{eq} (10 ⁻³⁰ cm)	14.732	13.468	13.823	15.320	11.219	11.811
$\beta_{\rm xxx} (10^{-30} {\rm m}^5 {\rm c}^{-1})$	31.205	8.059	74.445	8.478	8.624	20.570

^a The dielectric constant of DMSO is 46.86.

Table 5														
The data	of λ_a ,	$\lambda_{\rm e},$	Н, 1	r _{1/2} ,	μ_{eg} ,	$\mu_{\rm e}\!-\!\mu_{\rm eg}$, stokes	shift,	$\beta_{\rm xxx}$	in	ethanol,	and	$\beta_{\rm CT\mu g},$	SHG ^a

Samples	5	7	8	10	11	12
λ_{a} (nm)	394.7	397.9	456.1	399.9	402.1	391.1
$\lambda_{\rm e}$ (nm)	416	414	415	423	423	416
Н	0.038	0.028	0.045	0.041	0.041	0.039
$r_{1/2} (\mathrm{cm}^{-1})$	1806	3293	2383	1696	867	1973
$\varepsilon \times 10^{-4} \text{ (mol}^{-1} \text{ l}^{-1} \text{ cm}^{-1}\text{)}$	10 222	8792	14 130	12 444	12 444	11 061
Stokes shift	1297	977	2171	1365	1229	1531
$\mu_{e} - \mu_{g}$	11.576	3.370	10.597	2.625	5.250	11.610
μ_{eg} (10 ⁻³⁰ cm)	13.114	13.758	19.625	14.109	10.117	14.571
$\beta_{\rm xxx} (10^{-30} {\rm m}^5 {\rm c}^{-1})$	23.379	7.788	108.07	6.540	6.911	27.728
$\beta_{\rm CTug} \times 10^{-30}$ (esu)	107.8	350.8	3553	244.6	1187	1163
SHG (sample/urea)	0.000	0.124	0.061	1.457	0.084	0.000

^a The dielectric constant of ethanol is 24.30.

129.18, 129.28, 129.78, 134.25; Ms for $C_{21}H_{16}NCl$ (M)⁺ (Fab), 317; anal. calcd. for $C_{21}H_{16}NCl$, C, 79.36; H, 5.07; N, 4.41. Found, C, 79.08; H, 5.00; N, 4.44; UV (CHCl₃, λ_{max} (nm), ε), 399.5 (15240), 301.9 (15690), 263.5 (19660), 241.3 (42400).

3.8. 9-(p-Chlorobenzyldene)-10-methyl-9,10-dihydroacridine (11)

This compound was obtained from 2.34 g (7.0 mmol) of 3 and 0.98 g (7.0 mmol) of *p*-chlorobenzaldehyde as 6, expert for the solution became orange when the solution of *p*-chlorobenzaldehyde in THF was added. It was recrystallized from the mixture of methanol and benzene to give 1.60 g (72.0%) of orange crystal, m.p. 127– 129 °C (130–132 °C [18]). ¹H-NMR (CdCl₃), δ 3.52 (s, 3H), 6.60 (s, 1H), 6.70–7.41 (m, 9H), 7.80 (d, *J* = 6.9 Hz, 2H); Ms for C₂₁H₁₆NCl (M)⁺ (Fab), 317; UV (CHCl₃, λ_{max} (nm), ε), 399.9 (15780), 303.7 (14870), 277.3 (11520), 241.1 (41150).

3.9. 9-(p-Methoxybenzyldene)-10-methyl-9,10-dihydroacridine (12)

Compound 12 was obtained from 2.34 g (7.0 mmol) of 3 and 0.95 g (7.0 mmol) of *p*-methoxybenzaldehyde as 6, the solid product was recrystallized from the mixture of methanol and benzene to give 1.10 g (51.40%) of yellow crystal product; m.p. 150–152 °C (155–156 °C [16]). ¹H- NMR (CdCl₃), δ 3.50 (s, 3H), 3.81 (s, 3H), 6.64 (s, 1H), 6.78–6.81 (m, 3H), 6.98–7.06 (m, 3H), 7.26–7.29 (m, 4H), 7.37 (m, 1H), 7.69 (d, *J* = 6.3 Hz, 1H); ¹³C-NMR (CdCl₃), δ 33.92, 55.60, 112.68, 113.57, 114.01, 120.33, 121.63, 122.89, 123.79, 128.13, 128.65, 129.05, 130.10, 158.54; Ms for C₂₂H₁₉NO (M)⁺ (Fab), 313; UV (CHCl₃, λ_{max} (nm), ε), 394.9 (15250), 303.3 (15910), 263.5 (21830), 241.7 (42530).

4. The determination of SHG values

Using Nd:YAG (1.06 μ m) as a laser source, the conditions for measuring SHG values of 9-(substituted-benzylidene)-10-methyl-9,10-dihydroacridines were examined. The pulse energy of incidence to the powder sample surface was about $6.5 \times$ 10^{-3} J. The light area of incidence to the sample surface was 0.02 mm². The thickness of the sample was about 0.1 mm, and the sample was placed in between two pieces of glass. Fluorescence background was glass piece, and thickness of the glass piece was all the same. Urea was used as contrast sample (urea, analytical reagent, was ground). SHG value for 9-(substituted-benzylidene)-10methyl-9,10-di-hydroacridines measured by this way is a quantity of times of the SHG value of urea. The SHG values of 9-(substituted-benzylidene)-10-methyl-9,10-dihydroacridines were listed in Table 5, Fig. 2.



Fig. 2. Setup of powder second harmonic generation measurement. (1) Nd:YAG laser; (2) EM; (3) quartz crystal; (4) sample; (5) PMT; (6 and 6') filters; (7) computer.

4.1. Sample preparation

The concentrations of 9-(substituted-benzylidene)-10-methyl-9,10-dihydroacridines were 1 µg ml⁻¹, the *n* values of the solution of samples were supposed to equal to the *n* values of solvent, due to the solutions too dilute. The λ_a and λ_e of samples were recorded by Shimadzu UV-240 spectrophotometer and Hitachi-850 fluorometer. The results were listed in Tables 1–5. Five solvents, carbon tetrachloride, chloroform, 1,2-dichloroethane, ethanol and di-methyl sulfoxide (DMSO), was used in order to obtain $\mu_e - \mu_g$.

CGS unit system was adopted, the calculated results were listed in Tables 1-5.

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