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First hyperpolarizability of new sulfonamide amphiphiles by calculation, and hyper-Rayleigh scattering

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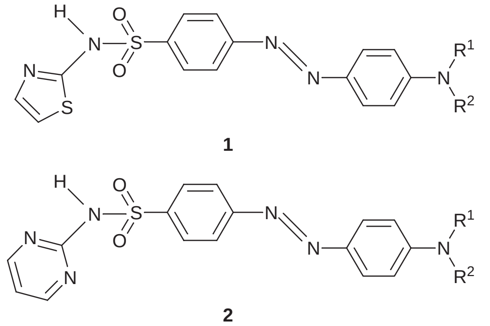
The first hyperpolarizability β of the 4-(4′-*N*-methyl-*N*-alkylaminophenylazo)-*N*-(thiazol-2-yl)benzenesulfonamides (**1**) and 4-(4′-*N*-methyl-*N*-alkylaminophenylazo)-*N*-(pyrimidin-2-yl)benzenesulfonamides (**2**) was evaluated by *ab initio* (GAUSSIAN and GAMESS), and semiempirical (INDO1/S) calculations for isolated molecule and in DMF solution (SCRF option). The values of β (static) of the amphiphiles having a dodecyl chain were of the same range and were: 215.6 and 212.4 (GAMESS), and 203.1 and 189.4 (GAUSSIAN), all in 10^{-40} m^4 V^{-1}, for **1** and **2**, respectively. The SCRF option used in calculations resulted in increase of β by *ca.* 55–65%. Direct determination of β by hyper-Rayleigh scattering measurement in DMF solution gave the values equal to: 763 and 775 (at $\lambda = 1319$ nm), and 1625 and 1722 (at $\lambda = 1064$ nm), for **1** and **2**, respectively (units as above). On a relative scale, referred to *p*-nitroaniline (PNA) as an external standard, the first hyperpolarizability values of the amphiphiles were in the range of 6.3–9.7 times that of PNA, depending on the method of evaluation. Based on the results of the quantum chemical calculations, the role of the molecular structure fragments on β was discussed.

Introduction

There has been growing interest in using organic materials for nonlinear optical (NLO) devices, functioning as second-harmonic generators, frequency convertors, electro-optical modulators *etc.*, because of the large second-order electric susceptibilities of organic materials. Since the second-order electric susceptibility is related to the first hyperpolarizability, β, the search for organic chromophores (NLO-phores) with large β is fully justified. The latest decade has brought a number of monographs,[1–6] review articles,[8–11] and numerous papers in various specialized periodicals. The organic compounds showing high hyperpolarizability are those containing an electron-donating group (D) and an electron withdrawing group (A) interacting through a system of conjugated double bonds. These compounds exhibit an intramolecular charge transfer transition upon excitation with light and the electron density shifts from the donor group to the acceptor group manifested by a large change in dipole moment. A high value of the first hyperpolarizability of the isolated molecule is not sufficient because the orientation of the molecules in a macroscopic sample of matter determines the second order susceptibility. Making crystalline samples would be a possible method of obtaining NLO materials but most organics crystallize in a centrosymmetric form and these are not useful for second order NLO effects. In this context, the Langmuir–Blodgett (LB) technique has been recommended as a possible method to force molecular orientation on an aqueous subphase, followed by one-direction deposition of the monolayer onto a solid support.[3,6,12–16] In such a way, the dipoles point out approximately in the same direction.

The NLO-phores processable *via* the LB technique should generally have a specific structure with a hydrophilic element anchoring the molecule to a water/air interface, and with a long hydrophobic chain responsible for creation of the organized structure by van der Waals interaction in a compressed monolayer. The papers published up to date[12–24] describe in detail the requirements which the amphiphile should fulfil to be able to generate a NLO response in LB mono- and multi-layers. The authors of this work have contributed to this subject by synthesizing a series of heteroaromatic compounds containing NLO fragments in the form of azo derivatives of sulfonamides, phenylhydrazones, betaines *etc.*[25–27]

In the case of sulfonamides, the electron withdrawing group is the sulfonyl group. The ability of this group to play the above-mentioned role has been reported by other authors,[28–34] but generally the nitro group was preferred, as this could be situated at the end of the molecule without distortion of its elongated shape. In this work we deal with two homologous series of amphiphiles: azo derivatives of sulfathiazole (structure **1**) and sulfadiazine (structure **2**), both shown in Fig. 1. Both groups have similar structures to those described by us in ref. 27 except that instead of an alkanoyl hydrophobic chain, the compounds in question have a methyl alkylamine group playing the role of a hydrophobe. The tertiary amine group is expected to be an effective electron donor. We aimed to evaluate at *ab initio* and semiempirical levels of quantum chemical calculations, the first hyperpolarizability of the 4-(4′-*N*-methyl-*N*-alkylaminophenylazo)-*N*-(thiazol-2-yl)benzenesulfonamides **1** and 4-(4′-*N*-methyl-*N*-alkylaminophenylazo)-*N*-(pyrimidin-2-yl)benzenesulfonamides **2**, and to compare the calculations with measurements of the first hyperpolarizability by the hyper-Rayleigh scattering method. The authors of this work described previously the NLO properties of analogous compounds,[27] having a long alkanamide chain as the hydrophobe. It was found that the carbonyl group of the



$R^1 = CH_3$; $R^2 = n\text{-}C_{12}H_{25}$

Fig. 1 Chemical formulae of the sulfonamides.

alkanamide weakened the donor ability of nitrogen atom, so a natural consequence was to replace the –NH–C(O)– group in the amphiphiles by a tertiary methyl alkylamine group. In this way, we expected to improve the second-order hyperpolarizability of the amphiphiles.

From our measurements with a Wilhelmy balance it can be shown that both groups of amphilphiles in question are able to form monolayer films on an aqueous subphase, as is shown in Fig. 2. This means that it is possible to build organized NLO structures by transfer of the monolayer onto a solid support. This will be the subject of a separate publication.

Materials and methods

The synthesis of the amphiphiles of structural types **1** and **2** was carried out similarly to that described in ref. 25. The exact procedures and the physicochemical and spectral properties of the compounds will be published elsewhere. For purposes of this study the derivatives containing: $R^1=CH_3$, and $R^2=n$-$C_{12}H_{25}$, n-$C_{14}H_{29}$ and n-$C_{16}H_{33}$ were taken into account. Their surface pressure–area isotherms are shown in Fig. 2. All the amphiphiles were orange crystalline solids having melting points above 423 K. Computational methods were also applied to dimethylamino derivatives; $R^1=R^2=CH_3$ to find an effect of the alkyl chain length on value of the first hyperpolarizability.

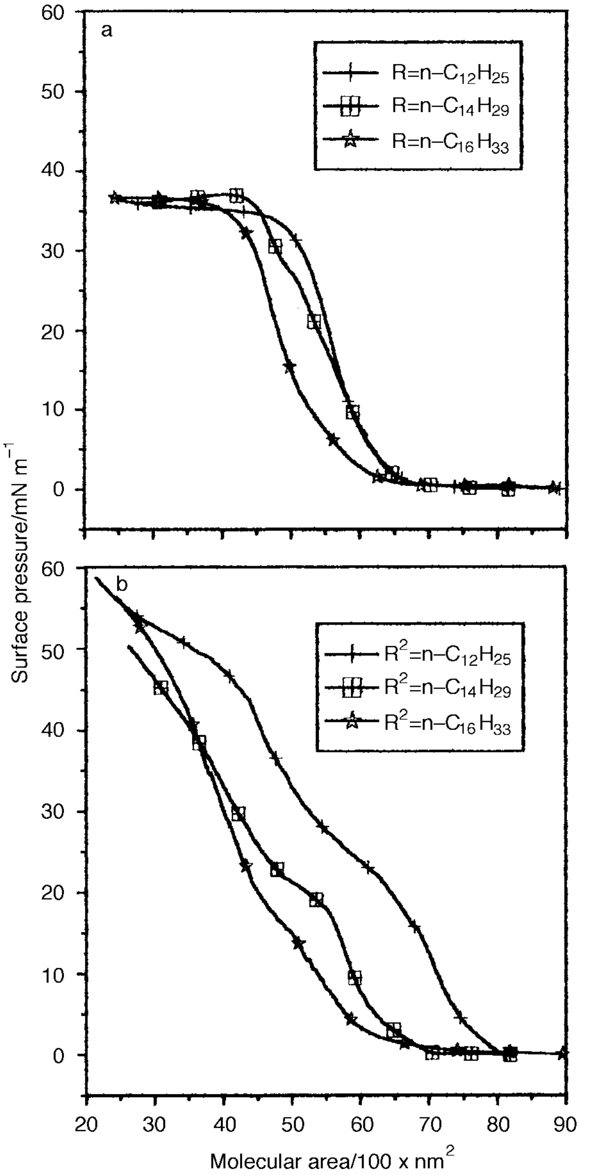


Fig. 2 Surface pressure isotherms of the amphiphiles: a) structure **1**, b) structure **2**, as in Fig. 1.

The UV–VIS spectra of the solutions in organic solvents were recorded in quartz 10 mm cuvettes, using a Hewlett Packard Modell 8452A apparatus. The solutions of concentration 10^{-5} to 10^{-4} mol dm^{-3} were prepared using spectrophotometric grade solvents.

Surface pressure–molecular area isotherms were recorded at an ambient temperature of 294 K with a computer-controlled device of our construction. The PTFE tray had effective dimensions 10.1 × 36.8 cm and was equipped with two moving hydrophilic barriers. The measuring device was a NIMA SP4 sensor with a paper plate. The tray and sensor were interfaced to a personal computer to control the measurements and data acquisition. Doubly-distilled water, passed through a mixed ion-exchanger and adsorbent bed, and finally filtered using a 0.2 μm Pall filter, was used as a subphase. Typically, 3 mmol solutions of amphiphiles in $CHCl_3$ were used to spread an organic phase on the water surface. The barrier movement at a speed of 5 mm min^{-1} was started after a 30 min waiting period for solvent evaporation.

Quantum chemical calcultions were carried out at Wrocław Supercomputer Center with an IBM R6000 RISC machine using GAUSSIAN 94,[35] GAMESS[36] and INDO1/S program[37,38] being a part of the MSI ZINDO package. The calculations comprised geometry optimization with GAUSSIAN 94 at the restricted Hartree–Fock (RHF) *ab initio* level with a split-valence 3-21G basis set, calculation of NLO response (using the structures optimized at this level of theory) with GAMESS TDHF (time dependent Hartree–Fock, RHF), GAUSSIAN CPHF (coupled perturbed Hartree-Fock) and INDO1/S sum-over-states (SOS) procedures.

Experimental determination of the first hyperpolarizability, β, was carried out by the hyper-Rayleigh scattering (HRS) technique. The scheme of the equipment and the details of the methodology have been described previously.[39,40] The measurements were carried out using the amphiphiles in diluted DMF solutions and as the first hyperpolarizability is little dependent on the length of the hydrophobe, only n-dodecyl derivatives of the series **1** and **2** were used.

Results and discussion

The nonlinear optical response of an isolated molecule in an electric field E_i (ω) can be presented as a Taylor series expansion of the total dipole moment, μ_i, induced by the field [eqn. (1)]

$$\mu_i=\mu_i^{\mathrm{p}}+\sum_j \alpha_{ij}E_j+\frac{1}{2}\sum_{j,k}\beta_{ijk}E_jE_k+\ldots \tag{1}$$

where α is linear polarizability, μ_i^{p} is the permanent dipole moment, and β_{ijk} are the first hyperpolarizability tensor components. The NLO response of the material in the molecular state can be determined by computation and by measuring it experimentally. As the values obtained by different methods may be different, it seems necessary to give an exact definition. In this paper we will consider only the frequency doubling process, *i.e.* $\beta=\beta\ (-2\omega,\omega,\omega)$, and define in a molecule fixed coordinates [eqn. (2) and (3)]

$$\beta_i=\beta_{iii}+\frac{1}{3}\sum_{j\neq k}(\beta_{ikk}+\beta_{kik}+\beta_{kki}) \tag{2}$$

$$\beta=(\beta_x^{2}+\beta_y^{2}+\beta_z^{2})^{1/2} \tag{3}$$

where i, $k=\in$ (x, y, z).

For calculation of the first hyperpolarizability by quantum chemical methods the GAUSSIAN and GAMESS programs were chosen at RHF (restricted Hartree–Fock) *ab initio* level of theory with a split-valence 3-21G basis set. This relatively simple basis set appeared to be a good compromise between accuracy and calculation duration. The geometry of the molecules was fully optimized at the 3-21G level and checked for a stationary point by running a frequency calculation. The absence of an imaginary frequency in the output file proved for the stationary point. The hyperpolarizability calculations were carried out with GAMESS TDHF (time dependent Hartree–Fock) and GAUSSIAN CPHF (coupled perturbed Hartree–Fock) procedures. The former produced 18 tensor components, the latter 10. With help of eqn. (2) and (3), the proper β values were obtained. *p*-Nitroaniline (PNA) served as an external standard in each case. Molecules **1** and **2** having an elongated shape in the direction of the charge-transfer coordinate, *i.e.* alongside the *x* axis, the β_x values calculated by eqn. (2) bears as much as *ca.* 95% of total β_v value obtained by eqn. (3). The values of β obtained at 3-21G *ab initio* level of theory are shown in Table 1.

For an isolated molecule, the values of β° (static) are slightly higher for derivatives of **1**, and reach 200.2×10^{-40} and 215.6×10^{-40} m^4 V^{-1}, for a dimethyl and methyldodecyl derivative, respectively. The increase of alkyl chain length (in R^2) from methyl to dodecyl, is manifested by *ca.* 7.5% increase of β^o. A similar tendency is observed in the **2** series, and the corresponding values are: 191.1×10^{-40} and 212.4×10^{-40} m^4 V^{-1}. Comparing β° values with that of *p*-nitroaniline gives the relative scale of first hyperpolarizability in multiples of β° of PNA, which is between 6.31 and 7.11. In reference to another NLO standard which is DANS [4-(dimethylamino)-4′-nitrostilbene], the β° values of the amphiphiles in question are of the same range.

The β° values obtained by GAUSSIAN are in good agreement with those obtained by GAMESS for dimethyl derivatives, while they are higher by *ca.* 10% for methyldodecyl derivatives. When the external field is set (corresponding to $\lambda = 1064$ nm) the values of β increase by *ca.* 50% for the amphiphiles in question and by *ca.* 41.7% for PNA. This explains the increase of values related to PNA. To find the effect of the solvent on the first hyperpolarizability, the SCRF option was applied in calculation programs. This requires additional data entry such as relative permittivity and cavity radius. The latter value was obtained from GAUSSIAN volume calculation. The effect of a polar solvent on β is significant. In our case, the DMF used as solvent, gave an increase of β° by *ca.* 55% (dimethyl derivatives), and *ca.* 65% (methyldodecyl derivatives), for an isolated molecule. Simulating the external field (at 1064 nm) enhanced this effect even more.

An enormous increase of β° was obtained by GAUSSIAN SCRF calculation, and in this context the values of the first hyperpolarizability from GAUSSIAN differed considerably from those produced by GAMESS. The possible source of discrepancy probably lies in the way the programs treat the excluded cavity for the amphiphile in solution. This is assumed by the programs to be a sphere while the shape of the amphiphiles is elongated. It should be mentioned that the GAUSSIAN calculation of hyperpolarizability in the solution is very sensitive to variation in cavity radius.

Among semiempirical methods used to calculate the first hyperpolarizability, the INDO1/S may be the best one.[37,38] This program, which reproduces the spectroscopic response of the molecule in an isolated state and in solution has been widely used for evaluation of the NLO properties by sum-over-state (SOS) method.[6,9,41–47] In this work we used in the INDO1/S program the amphiphile structures (atomic coordinates) optimized by GAUSSIAN 3-21G runs, the same as mentioned above. We assumed singlet state configuration interaction, and the space for calculation was HOMO − 50 to LUMO + 50 that produced 2500 configurations. Twenty electronic states were generated and the state S$_1$ (the first excited state with oscillator strength $f>0$) was a dominant state responsible for the Π–Π* charge transfer process. The parameters of the state S$_1$ and S$_o$ were used to determine the charge transfer first hyperpolarizability, β_{CT}, in a two-level model according to eqn. (4)

$$\beta^\circ_{\mathrm{CT}} = \frac{3(\mu_{\mathrm{e}} - \mu_{\mathrm{g}})\mu_{\mathrm{t}}^2}{2\varepsilon_{\mathrm{o}}\, h^2 c^2 v_{\mathrm{t}}^2} \tag{4}$$

where μ_e, μ_g are dipole moments in the excited and ground state, respectively, μ_t is the transition moment between the excited and ground state, ε_o is vacuum permitivity, h is Planck's constant and v_t is the transition frequency from ground state to first excited state. The frequency response of β for the frequency doubling process can be obtained from eqn. (5)

$$\beta(-2\omega,\omega,\omega) = \frac{{\omega_{\mathrm{t}}}^4}{({\omega_{\mathrm{t}}}^2 - 4\omega^2)({\omega_{\mathrm{t}}}^2 - \omega^2)}\,\beta^\circ_{\mathrm{CT}} \tag{5}$$

where ω is the applied field frequency. Compounds **1** and **2** showed a strong nonlinearity along a charge transfer axis and the component β_{xxx} of the hyperpolarizability tensor could be assumed to be a good approximate for β. The amphiphiles **1** and **2** have the charge transfer path from the –NR^{1}R^2 amine group up to a sulfonyl group *via* Π conjugation through phenyl rings and an azo group. The cosine of the angle between direction of the ground state dipole moment and that of the S$_1$ excited state dipole moment was 0.95–0.97. The results of the INDO1/S calculations of the first hyperpolarizability (Table 2) are in fair agreement with GAMESS and GAUSSIAN *ab initio* option for isolated molecules. For molecules in solution (SCRF), INDO1/S gives a more moderate increase of β with solvent polarity as compared with GAMESS. It is probably so because INDO uses three parameters to emulate the solvent milieu (a cavity radius, relative permittivity and refractive index). The results for PNA are

Table 1 Dipole moments and first hyperpolarizability calculated by GAMESS and GAUSSIAN with 3-21G basis set (RHF)

			GAMESS				GAUSSIAN
Structure	R^2	SCRF (Solvent)	$\mu_g/10^{-30}$ C m	$\beta^\circ/10^{-40}$ m^4 V	$\beta^{1064}/10^{-40}$ m^4 V	$\beta^\circ/\beta^\circ_{\mathrm{PNA}}$	$\beta^\circ/10^{-40}$ m^4 C
1	*n*-CH$_3$	None	37.01	200.2	313.6	6.61	203.1
	n-CH$_3$	DMF	48.78	310.3	535.6	7.42	905.0
	n-C$_{12}$H$_{25}$	None	38.89	215.6	339.5	7.11	241.1
	n-C$_{12}$H$_{25}$	DMF	49.32	360.7	631.0	8.63	1247.0
2	*n*-CH$_3$	None	30.34	191.1	296.8	6.31	189.4
	n-CH$_3$	DMF	41.18	307.9	502.8	7.37	1054.0
	n-C$_{12}$H$_{25}$	None	32.12	212.4	333.7	7.00	232.1
	n-C$_{12}$H$_{25}$	DMF	47.26	349.0	608.4	8.35	1082.0
p-Nitroaniline (PNA)		None	25.81	30.3	38.8	1.0	30.1
		DMF	31.07	41.8	55.0	1.0	64.4
	DANS[a]	None	32.20	180.3			212.2

[a] DANS = 4-(dimethylamino)-4′-nitrostilbene.

Table 2 Dipole moments and first hyperpolarizability calculated by INDO1/S (two-level model), structure optimization by Gaussian 3-21G

Structure	R^2	Solvent	$\mu_g/10^{-30}$ C m	$\mu_e/10^{-30}$ C m	$\mu_t/10^{-30}$ C m	$v/10^6$ m^{-1}	$\beta^\circ/10^{-40}$ m^4 V
1	n-$C_{12}H_{25}$	None	41.77	71.84	30.52	2.4623	200.4
		Chloroform	45.07	78.14	30.78	2.3056	251.5
		Chlorobenzene	45.28	78.59	30.80	2.2890	257.3
		1,2-Dichloroethane	45.85	79.50	30.78	2.2853	260.4
		Acetone	46.24	80.18	30.81	2.2893	262.2
		DMF	46.41	80.87	30.76	2.28.53	266.4
2	n-$C_{12}H_{25}$	None	36.24	63.94	30.44	2.4798	178.1
		Chloroform	39.19	69.86	30.65	2.3292	226.6
		Chlorobenzene	39.42	70.28	30.67	2.3128	231.5
		1,2-Dichloroethane	39.91	71.19	30.72	2.311	235.9
		Acetone	40.26	71.85	30.75	2.3157	237.6
		DMF	40.42	72.14	30.75	2.3002	241.9
p-nitroaniline (PNA)		None	28.55	63.76	20.78	3.1952	63.6
		DMF	31.78	67.90	21.34	2.6670	98.2
DANS[a]		None	30.06	82.04	31.07	2.5757	323.2

[a]DANS = 4-(dimethylamino)-4′-nitrostilbene.

included for comparison, but here the β° of the PNA is rather high because the excited state dipole moment obtained here, 63.76×10^{-30} C m, exceeded by *ca.* 16×10^{-30} C m the value obtained experimentally.[48]

The values of β calculated for the amphiphiles in solutions with INDO1/S are *ca.* 20% higher than those obtained for isolated molecules and they were little dependent on solvent polarity. The calculated frequency of the transitions was nearly independent of the solvent type for the S_o–S_1 transition. The frequency of this transition was within 2.285–2.392×10^6 m^{-1}. This value was simply verified by UV–VIS spectra of the amphiphiles in solutions. Fig. 3 shows the experimental spectrum of the amphiphile (**2**, R^2 = dodecyl) in 1,2-dichloroethane and frequency bars calculated by INDO1/S. For all the solutions, the character of the Π–Π* transition band, *i.e.* that assumed at a higher wavelength, was similar and the maximum of the absorption was also nearly independent of the solvent polarity (Table 3). This means that the amphiphiles in question show no solvatochromic shift, and this is probably a feature of the sulfonyl derivatives as similar observations were reported by other authors.[28,29,27]

From the UV–VIS spectra we calculated the transition moments of the amphiphiles in solutions from the relationship given in eqn. (6)

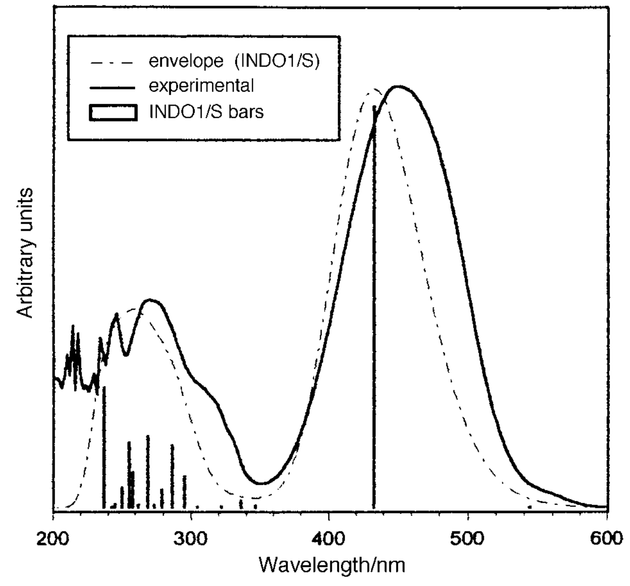


Fig. 3 UV–VIS spectrum (solid line) of the sulfadiazine derivative (**2**, R^2 = dodecyl) in 1,2-dichloroethane solution. Bars indicate frequencies and oscillator strength form INDO1/S calculation, dotted line is the calculated Gaussian envelope.

$$\mu_t{}^2=\frac{3hc\varepsilon_o n}{2\Pi^2 N_a\varphi(n)^2\omega_t}\int\kappa\,\mathrm{d}\omega \tag{6}$$

where N_a is Avogadro's number, ω_t is transition frequency, the integral means the integral absorbance over the entire absorption band (SI units) ascribed to the Π–Π* transition, and κ is the molar extinction coefficient. The parameter $\varphi(n)$ represents the local field factor taken from Lorentz approximation, given by eqn. (7).

$$\varphi(n)=\frac{n^2+2}{3} \tag{7}$$

The parameter, a, in Table 3 is the cavity radius calculated for the amphiphile in the solution. It differs from that used in the quantum chemical calculations due to the contribution of the solvent molecule.[27] The transition moments obtained by eqn. (4) and shown in Table 3 are *ca.* 75% of the μ_t values calculated by INDO1/S.

To complete the studies on the first hyperpolarizability of the amphiphiles **1** and **2** the experimental measurements of β were carried out by the technique of hyper-Rayleigh scattering (HRS) in DMF solution. The amphiphiles (only dodecyl derivatives) did not exhibit two-photon fluorescence, contrary to the alkanoyl derivatives[27] described previously, so the values shown in Table 4 are real β values. The measurements were made at the energy level of the field corresponding to $\lambda = 1319$ and 1064 nm. The HRS values of β are rather high and exceed those obtained by GAMESS calculation for a wavelength of 1064 nm. But as is seen in Fig. 3 (the UV–VIS spectrum), in the region of frequency doubling there is a tail in the absorption band. In such a case, a resonance may eventually affect the value of β.[49,50] For the incident wavelength of 1319 nm the frequency doubling region is beyond the absorption band and here no side-effects of the resonance type should take place.

The β values of the amphiphiles determined by HRS in DMF solutions are high and are: 763×10^{-40} and 775×10^{-40} m^4 V^{-1} at 1319 nm, and 1625 and $1772\ 10^{-40}$ m^4 V^{-1} at 1064 nm, for amphiphiles **1** and **2**, respectively. That means that the difference in molecular structures of the amphiphiles has practically no effect on the β value. The experimental values are much higher as compared with those obtained by GAMESS but a discrepancy between the first hyperpolarizability values obtained by various methods was reported in the literature.[9] The values of β of PNA determined in DMF under similar experimental conditions are also higher than those obtained by GAMESS. Using PNA as a standard to which the β values of the amphiphiles may be related, one obtains more realistic figures. At the wavelength of 1319 nm

Table 3 Spectral characteristics of the amphiphiles

Structure	Solvent	UV–VIS $\nu_s/10^6\ m^{-1}$	$\kappa_{max}/m^2\ mol^{-1}$	Cavity radius $a/10^{-10}$ m	$\mu_t/10^{-30}$ C m
1	Chloroform	2.242	3113	7.202	23.64
	Chlorobenzene	2.242	3132	7.333	22.54
	1,2-Dichloroethane	2.212	3251	7.195	24.35
	Acetone	2.252	3372	7.158	24.45
	DMF	2.203	3104	7.182	24.08
2	Chloroform	2.303	3205	7.201	23.98
	Chlorobenzene	2.212	3134	7.332	22.71
	1,2-Dichloroethane	2.183	3272	7.194	24.28
	Acetone	2.227	3122	7.157	24.55
	DMF	2.183	3246	7.181	24.58
PNA	Acetonitrile	2.747	1203	4.83	19.38

Table 4 HRS first hyperpolarizability of the amphiphiles in DMF solution ($R^2=n$-dodecyl)

Structure	$\beta^{1319}/10^{-40}\ m^4\ V^{-1}$	$\beta^{1064}/10^{-40}\ m^4\ V^{-1}$	β^{1319}/β_{PNA}	β^{1064}/β_{PNA}	$\beta^{\circ}/10^{-40}\ m^4\ V^{-1\ a}$
1	763	1625	6.20	9.18	443
2	775	1722	6.30	9.72	462
p-Nitroaniline	123	177	1.00	1.00	76

Calculated based on the two-level model [eqn. (5)] from data at 1319 nm.

the β of the amphiphiles was: 6.2–6.3, and at 1064 nm, 9.18–9.72 times that of PNA, related to the same wavelength. These relative values are comparable with those obtained by GAMESS; the latter are higher by *ca.* 25%.

The calculation methods of quantum chemistry yield a variety of data that can be helpful in discussing the effect of the amphiphile structure on the first hyperpolarizability. The authors made calculations within a group of the compounds based on azo derivatives of sulfonamides, sketched schematically in Fig. 4. The variation of the substituents R^1, R^2 and the type of heterocyclic ring helped us to relate the β values with the structure elements of the sulfonamides. Table 5 contains the lengths of the most important bonds, referred to Fig. 4. It should be mentioned that the plane of the heterocyclic ring is perpendicular to that of the phenyl ring.[27] A key role in generating the second order polarizability seems to be played by the N atom at the phenyl ring (labeled no. 1) and bond 2–1. The length of this bond reaches the highest value when R^2 is an alkanoyl radical [–C(O)R] and $R^1=H$. The presence of the carbonyl group seems to pull the N atom from the phenyl ring. The same tendency is observed in the case of the bonds: 8–5 and 10–9. It means that the presence of the carbonyl group weakens the conjugation alongside the system of conjugated double bonds, as compared with other compounds. A structural difference between thiazolyl (**1**) and pyrimidinyl (**2**) amphiphiles can be seen on an example of the bond between the sulfonyl group and the nitrogen atom (bond 17–16) which for pyrimidinyl derivatives is shorter by 0.012 Å, and the bond Het–17 is slightly longer.

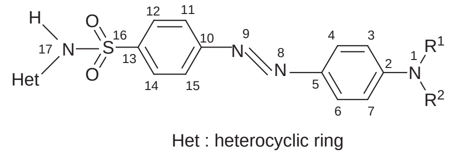


Fig. 4 Structure of the sulfonamides related to the data of Table 5 and 6.

As has been mentioned the key role in the calculation of β_{CT} by INDO1/S was ascribed to the transition between the first excited state and the ground state of the molecule. This transition may be assumed to be a HOMO–LUMO charge transfer (the prevailing contribution to this transition). Table 6 shows the difference in the Mulliken electronic charge of the selected structural units of the amphiphiles between the first excited state and the ground state. The amount of the electronic charge donated by the $-N(R^1R^2)$ group is dependent on its substituents R^1 and R^2. If it is a substituted amine group it donates more charge as compared with an unsubstituted $-NH_2$

Table 5 Bond lengths of the structures shown in Fig. 4. Geometry optimization by Gaussian 3-21G

Bond	Bond length/Å $R^1=CH_3$ $R^2=C1_2H_{25}$ Het = pyrimidinyl	$R^1=CH_3$ $R^2=C_{12}H_{25}$ Het = thiazolyl	$R^1=H$ $R^2=C(O)C_9H_{19}$ Het = thiazolyl	$R^1=R^2=H$ Het = thiazolyl
2–1	1.3733	1.3725	1.3999	1.3645
3–2	1.4051	1.4055	1.3960	1.3981
4–3	1.3747	1.3741	1.3756	1.3745
5–4	1.3833	1.3838	1.3869	1.3854
8–5	1.4086	1.4075	1.4163	1.4083
9–8	1.2440	1.2444	1.2413	1.2440
10–9	1.4259	1.4255	1.4274	1.4257
11–10	1.3892	1.3894	1.3844	1.3893
12–11	1.3775	1.3774	1.3809	1.3775
13–12	1.3763	1.3766	1.3729	1.3766
16–13	1.7980	1.7975	1.7987	1.7977
17–16	1.7076	1.7205	1.7199	1.7204
Het–17	1.3706	1.3638	1.3644	1.3640

Table 6 Difference in electronic charge (Mulliken) of the structure elements in the ground (S_o) and first excited state (S_1)calculated by INDO1/S. Molecular structure as shown in Fig. 4

Structure element (atom numbers)	Electronic charge $R^1=CH_3$ $R^2=C_{12}H_{25}$ Het = thiazolyl	 $R^1=R^2=H$ Het = thiazolyl	 $R^1=CH_3$ $R^2=C(O)C_9H_{19}$ Het = thiazolyl	 $R^1=CH_3$ $R^2=C_{12}H_{25}$ Het = pyrimidinyl	 $R^1=CH_3$[a] $R^2=C_{12}H_{25}$ Het = pyrimidinyl
–N(R^1 R^2)	+0.1324	+0.1115	+0.0824	+0.1298	+0.1409
phenyl (1-6)	+0.3732	+0.3779	+0.3430	+0.3700	+0.3852
–N=N–	−0.4452	−0.4153	−0.3712	−0.4496	−0.4401
phenyl (9-14)	−0.0679	−0.0756	−0.0553	−0.0594	−0.0954
$>SO_2$	+0.0012	+0.0025	+0.0031	+0.0013	+0.0008
>N– (19)	+0.0001	−0.0001	−0.0001	+0.0001	+0.0001
Het	−0.0001	−0.0008	−0.0006	−0.0002	−0.0002
Other (C,H)	+0.0064	−0.0003	0.0	+0.0080	+0.0006
β° (INDO1/S)/10^{-40} m^4 V	200.4	153.5	114.5	178.1	235.9

[a]In dichloroethane solution.

group. The carbonyl group weakens the donating ability of the nitrogen atom due to its competing ability to withdraw electronic charge. The net donor group is also the neighbouring phenyl ring, while the charge acceptors are the azo group and the second phenyl ring. Surprisingly, the sulfonyl group which might be expected to be an electron acceptor, acts as a weak electron donor, at least at the HOMO–LUMO transformation. The heterocyclic ring plays the role of a weak charge acceptor. Table 6 also contains the β values obtained by INDO1/S which originate from the above charge transfers.

Conclusions

The amphiphiles **1** and **2** containing long hydrophobic chains form monolayer films on an aqueous subphase, and therefore they can be used for preparation of ordered structures by transfer of the monolayer onto a solid support. The presence of the D–A system typical for NLO-phores, brings an opportunity to use their ordered structures in NLO applications. The ability of the amphiphiles to show NLO properties expressed in terms of the second harmonic generation is relatively good in the molecular state. This was proved by quantum chemical calculations using *ab initio* and semiempirical methods, as well by measuring the second harmonic generation by the HRS technique.

The analysis of the data obtained from INDO1/S calculations for azo derivatives of similar structures made it possible to relate the first hyperpolarizability values with the structure of the sulfonamides in question. It was found that a key role in the determination of the first hyperpolarizability was played by the nitrogen atom at the electron donating phenyl ring. The incorporation of the substituted amine group increased considerably the ability to generate the second harmonic while the presence of an alkanoyl group (see ref. 27) enhanced the ability for monolayer formation at the cost of a lower value of the first hyperpolarizability.

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