

# First Hyperpolarizability of the Heterocyclic Sulfonamides for Langmuir–Blodgett Films by Calculation, Solvatochromism, and Hyper-Rayleigh Scattering

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The first hyperpolarizability  $\beta$  of *n*-alkanamides of 4-amino-*N*-(thiazol-2-yl)benzenesulfonamide (A) and 4-amino-*N*-(pyrimidin-2-yl)benzenesulfonamide (B) was evaluated by *ab initio* (Gaussian, GAMESS) and semiempirical (INDO1/S) calculations. The results obtained at the *ab initio* level showed that the values of  $\beta$  of the chromophores were 3.5–4 times that of *p*-nitroaniline. The calculations by INDO1/S gave preference to A and in absolute scale the  $\beta$  values were  $104.6$  and  $90.9 \times 10^{-40}$  m<sup>4</sup>/V for A and B, respectively, and they were slightly lower than those from *ab initio*. Fluorescence solvatochromism and hyper-Rayleigh scattering (HRS) was applied to determine experimentally the first hyperpolarizability of two amphiphiles containing *n*-hexadecanoyl (A) and *n*-decanoyl (B) radical. The values of  $\beta$  obtained by the fluorescence solvatochromism were in the same range for A and B, and were  $(94\text{--}100) \times 10^{-40}$  m<sup>4</sup>/V while the HRS procedure gave preference to B yielding 252.1 and 197.8 (at 1064 nm), and 113.1 and 88.8 (static) for B and A, respectively (all in  $\times 10^{-40}$  m<sup>4</sup>/V). The role of the heterocyclic ring of the chromophore molecule in the electron donating–accepting process was shortly discussed.

## Introduction

Organized organic molecular structures have been intensively investigated with the hope of utilizing functional properties of organic compounds, such as conductivity and semiconductivity, sensing ability, radiation sensitivity, or optical or optoelectronic properties. Special attention has been paid to molecular films which offer arrangement on the molecular scale level. This becomes interesting from the point of view of technology, as the tendency to construct miniature electronic or optoelectronic devices now approaches gradually dimensions comparable with the molecular scale.<sup>1–7</sup> As examples, resists and photoresists for VLSI, organic photoconductors for printing and copying, liquid crystals for displays, or color films for photography contain elements smaller in dimension than 1  $\mu\text{m}$ . It is no surprise that in this context, the technique of Langmuir–Blodgett (LB) films becomes a promising one, as it actually enables manipulation of material at the dimension of single molecular layers. The LB technique is based on the formation of a monomolecular film on aqueous subphase followed by transfer of the organized monolayer (the organization forced by lateral compression) onto a solid support. The transfer can be made in three different ways: by alternating dipping and removal or only by one-way (in or out) movement of the solid support. The latter method enabling an additional arrangement of the sequential monolayers of the type head to tail is of particular interest if materials having nonlinear optical properties are used for LB film formation. As is known, the condition to show first hyperpolarizability is an acentrosymmetric electronic structure of the molecule. In the macroscopic scale this means that the molecules must be oriented with their dipoles pointing out approximately in the same direction. Such an arrangement of the dipoles can be easily obtained with the LB technique by one-direction deposition of the monolayer film. However,

modeling molecules for LB applications which at the same time would have nonlinear optical (NLO) properties, one has to compromise two features of the molecules: the ability for monolayer formation and the presence of a chromophore group.<sup>7–11</sup> The first hyperpolarizability,  $\beta$ , depends on the strength of donor and acceptor substituents and on the extension of the  $\Pi$ -electron system. Well suited for these purposes are the molecules containing two aromatic or heteroaromatic rings connected via a system of double bonds. The papers of Laschewsky,<sup>12,13</sup> Ledoux,<sup>14</sup> Ashwell,<sup>7,15–20</sup> and others<sup>21–26</sup> described in detail the requirements which should fulfill the amphiphile to generate NLO response in LB mono- or multilayers. Working on synthesis of new amphiphiles for LB applications, the authors<sup>27,28</sup> obtained two homologous series shown in Figure 1, namely alkanamides of azoderivatives of sulfathiazole (structure A) and sulfadiazine (structure B). The amphiphiles containing the alkanoyl aliphatic group with straight alkyl chain R which had 9–17 C were found to be excellent in forming monolayer films (examples shown in Figure 2). Their structure with the azo bridge between phenyl rings and the donor–acceptor system within the molecule is typical for NLO-phores. The ability of the sulfonyl group to act as an electron acceptor was reported.<sup>29–34</sup> Contrary to the nitro group, the sulfonyl group cannot be a terminal group, because the valence of S atom is 6. Usually, it was placed in the neighborhood of a hydrocarbon<sup>29,33,34</sup> or fluorocarbon<sup>30–32,35</sup> chain, also as side-chain components in NLO polymeric materials. Among the references cited, the paper of Le Breton et al.<sup>30</sup> dealt with amphiphiles forming LB films where a donor and an acceptor were tertiary amine nitrogen and sulfonyl group, respectively.

In this contribution, we aimed to evaluate at the *ab initio* and semiempirical level the first hyperpolarizability of the chromophore amphiphiles shown in Figure 1 to find relationships between ability to generate the second harmonic and their molecular structure, and particularly to determine the role of the structure components: amide  $\text{—NHCO—}$  group as an electron donor and sulfonyl group as an electron acceptor, and eventually the role of the heterocyclic ring. These calculations

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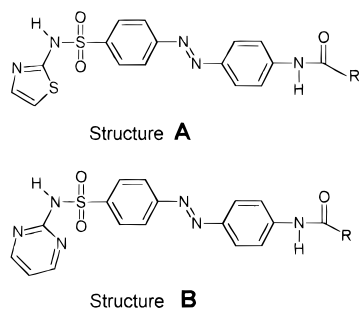


Figure 1. Chemical formulas of the alkanamides.

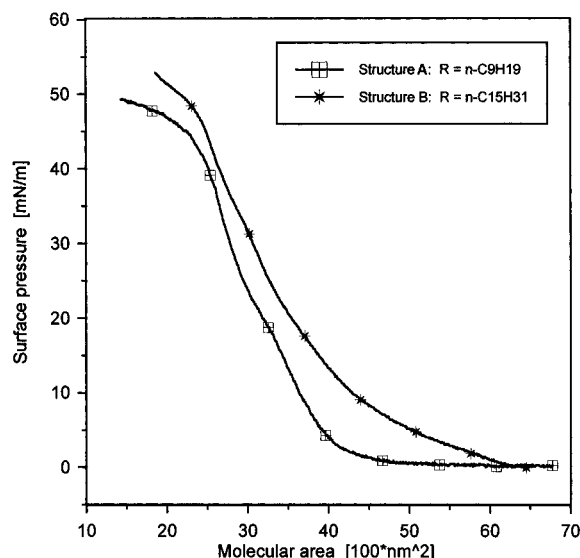


Figure 2. Surface pressure isotherms of the long chain alkanamide amphiphiles: A, R =  $n\text{-C}_{15}\text{H}_{31}$ ; B, R =  $n\text{-C}_9\text{H}_{19}$ .

were accompanied by absorption and fluorescence spectroscopy to determine in this way the experimental values of the first hyperpolarizability and were completed by hyper-Rayleigh scattering determination of this parameter. It is worth mentioning that the amphiphiles in question have not been described so far in the available literature.

## Materials and Methods

The synthesis and properties of the amphiphiles of A and B type structure were described in ref 27. For purposes of this work, only one representative of each type was selected for experimental measurements, namely,  $n$ -hexadecylamide of 4-amino- $N$ -(thiazol-2-yl)benzenesulfonamide (structure A, R =  $n\text{-C}_{15}\text{H}_{31}$ ) and  $n$ -decylamide of 4-amino- $N$ -(pyrimidin-2-yl)benzenesulfonamide (structure B, R =  $n\text{-C}_9\text{H}_{19}$ ), and their surface pressure isotherms are shown in Figure 2. Both amphiphiles were yellow solids having very high melting points (above 620 K). Computational methods were also applied to the amphiphiles having shorter alkyl chains.

The UV-vis spectra of the solutions in organic solvents were recorded using Hewlett Packard Model 8452A in quartz 10 mm cuvettes. The solutions of concentration  $10^{-5}$ – $10^{-4}$  mol/dm<sup>3</sup> were prepared using spectrophotometric grade solvents. The fluorescence spectra of the same solutions were recorded using Perkin Elmer spectrofluorimeter Model MPF-44.

Quantum chemical calculations were carried out at Wrocław Supercomputer Center with an IBM R6000 RISC machine using GAUSSIAN 94,<sup>38</sup> GAMESS,<sup>39</sup> and INDO1/S program<sup>40,41</sup> (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), and INDO1/S SOS procedures.

Experimental determination of the first hyperpolarizability,  $\beta$ , was carried out by the hyper-Rayleigh scattering (HRS) technique and the scheme of the equipment and the details of the methodology were described previously.<sup>42</sup>

## Results and Discussion

The nonlinear optical response of the materials in molecular state can be evaluated by computational methods as well as by experiment and because of the variety of approaches, the problem sometimes arises how the hyperpolarizability data obtained by different methods can be compared.<sup>43</sup> The NLO response of an isolated molecule in an electric field  $E_i(\omega)$  can be presented as a Taylor series expansion of the total dipole moment,  $\mu_i$ , induced by the field

$$\mu_i = \mu_0 + \alpha_{ij}E_j + \frac{1}{2}\beta_{ijk}E_iE_j + \dots \quad (1)$$

where  $\alpha$  is linear polarizability,  $\mu_0$  is permanent dipole moment, and  $\beta_{ijk}$  are the first hyperpolarizability tensor components. 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

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

where  $i = x, y, \text{ or } z$ .

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

Prior to calculations of the NLO by quantum chemical methods the geometry of the molecules was fully optimized at the restricted Hartree-Fock (RHF) ab initio level with a split valence 3-21G basis set. The choice of the 3-21g basis set was a compromise between computational costs and quality of results as application of more extended basis set with polarization and diffuse functions increased drastically computation time particularly for the large molecules we had to do with, and the values of hyperpolarizability, obtained in some instances with extended basis sets, were nearly the same as those obtained with 3-21g. The optimized geometry was additionally checked by running the frequency calculations. No imaginary frequency present indicated that the calculations reached the stationary point. The structure of the chromophores at the stationary point is best presented in Figure 6, with phenyl rings and azo group situated nearly in the same plane with sulfonyl oxygens in parallel but slightly above this plane. The dihedral angle between heterocyclic ring and the closest phenyl ring was ca. 90°. To find the effect of the alkyl chain on first hyperpolarizability, we also took into account the homologs of the structure A and B having shorter alkyl chains.

All calculations of the hyperpolarizability were carried out using optimized molecular coordinates. For the calculation of the first hyperpolarizability the GAMESS TDHF (time-dependent Hartree-Fock) procedure was used which yielded 18 tensor  $\beta$  components both static and  $\beta$  at 1064 nm. With help of eqs 2 and 3 the proper  $\beta$  values were obtained. The same procedure was used for  $p$ -nitroaniline which served as an external standard throughout this work. The shape of molecules A and B is elongated in the direction of the charge transfer, so that the vector properties predominate alongside charge-transfer coordinate, in our case alongside the  $x$  axis. The  $\beta_x$  value obtained

TABLE 1: Dipole Moments and First Hyperpolarizability Calculated by GAMESS<sup>39</sup> with 3-21g Basis Set (RHF)

| structure                    | R   | SCRF (solvent) | $\mu_g^a$ | $\beta^0^b$ | $\beta^{1064}^b$ | $\beta^0/\beta_{\text{PNA}}^0$ | $\beta^{1064}/\beta_{\text{PNA}}^{1064}$ |
|------------------------------|---|----------------|-----------|-------------|------------------|--------------------------------|--|
| A                            | <i>n</i> -C <sub>2</sub> H <sub>5</sub>   | none           | 34.52     | 107.4       | 159.6            | 3.54                           | 4.11                                     |
|                              | <i>n</i> -C <sub>5</sub> H <sub>11</sub>  | none           | 36.48     | 110.8       | 166.3            | 3.65                           | 4.29                                     |
|                              | <i>n</i> -C <sub>9</sub> H <sub>19</sub>  | none           | 36.89     | 114.1       | 178.6            | 3.76                           | 4.60                                     |
|                              | <i>n</i> -C <sub>15</sub> H <sub>31</sub> | none           | 36.80     | 112.3       | 175.7            | 3.71                           | 4.52                                     |
|                              | <i>n</i> -C <sub>2</sub> H <sub>5</sub>   | acetonitrile   | 50.09     | 235.8       | 403.4            | 7.78                           | 10.40                                    |
| B                            | <i>n</i> -C <sub>5</sub> H <sub>11</sub>  | acetonitrile   | 51.29     | 220.7       | 375.6            | 7.28                           | 9.68                                     |
|                              | <i>n</i> -C <sub>2</sub> H <sub>5</sub>   | none           | 28.61     | 102.5       | 151.3            | 3.38                           | 3.90                                     |
|                              | <i>n</i> -C <sub>9</sub> H <sub>19</sub>  | none           | 28.21     | 107.9       | 160.3            | 3.56                           | 4.13                                     |
|                              | <i>n</i> -C <sub>2</sub> H <sub>5</sub>   | acetonitrile   | 34.35     | 135.7       | 205.0            | 4.48                           | 5.28                                     |
|                              | <i>n</i> -C <sub>9</sub> H <sub>19</sub>  | acetonitrile   | 35.57     | 154.4       | 233.1            | 5.10                           | 5.99                                     |
| <i>p</i> -nitroaniline (PNA) |   | none           | 25.81     | 30.3        | 38.8             | 1.00                           | 1.00                                     |

<sup>a</sup> Dipole moments in [Cm]/10<sup>-30</sup>. <sup>b</sup> Values of  $\beta$  in [m<sup>4</sup>/V]/10<sup>-40</sup>; the last two columns contain first hyperpolarizability data related to *p*-nitroaniline.

by eq 2 bears as much as ca. 98% of total  $\beta_v$  value obtained by eq 3. The results of TDHF calculations, shown in Table 1, indicate that at the 3-21G level of theory the compounds of type A have higher dipole moments as compared with those of type B. The values of the first hyperpolarizability (static, isolated molecule) show moderate NLO ability of both structures reaching (102–114)  $\times 10^{-40}$  m<sup>4</sup>/V (24.3–27.2 esu), with tendency to increase these values by ca. 50% when an external field corresponding to  $\lambda = 1064$  nm was set. The variation of alkyl chain length seems to have little effect on  $\beta$ . A slight increase of  $\beta$  is observed with increasing length of the alkyl chain. However, the first hyperpolarizability of the compounds with related structure having no azo group appeared to be sensitive to the size of the substituent at the carbonyl group.<sup>28</sup>

The GAMESS TDHF calculation of  $\beta$  was verified by similar calculation of NLO response of *p*-nitroaniline (PNA). The  $\beta$  values obtained for this compound were 30.3 (static) and 38.8  $\times 10^{-40}$  m<sup>4</sup>/V (at 1064 nm) and if these values could be treated as external standard, then the hyperpolarizability of the amphiphiles A and B may be expressed in relative units as being 3.5–4 times that of PNA. It is to be mentioned that Abe obtained for PNA 37.7  $\times 10^{-40}$  m<sup>4</sup>/V with CPHF (coupled perturbed Hartree–Fock) option at the 6-31g basis set.<sup>46</sup>

Application of self-consistent reaction field (SCRF) in NLO calculation by GAMESS gave an indication on solvent effect of dipole moment and hyperpolarizability. The values in Table 1 refer to TDHF data obtained with additional input data concerning spherical cavity radius of the solute (obtained from Gaussian) and dielectric constant of the solvent. The calculation done for acetonitrile showed that short-chain derivatives of A were very sensitive to the solvent polarity as they had higher dipole moments in isolated state as compared with B. The increase of dipole moment caused by the presence of solvent was higher for A as compared with structure B. The same was valid for hyperpolarizability.

An alternative method of hyperpolarizability calculation applied for the amphiphiles in question was that implemented by INDO1/S.<sup>41,42</sup> This program predestined to reproduce spectroscopic response of the molecule in isolated state as well as in solutions has been widely applied for evaluation of the NLO properties of organic molecules by sum-over-state (SOS) method.<sup>10,11,43,44–49</sup> In this work we used in INDO1/S programs the amphiphile structures optimized by Gaussian 3-21g runs, the same structures which were used in GAMESS TDHF calculations. Choosing the singlet state configuration interaction, we selected the space from HOMO–30 to LUMO+30 which produced 961 configurations. Twenty electronic states were generated and the state S1 (the first singlet state with oscillator strength  $f > 0$ ) was found to be a dominant state responsible for the  $\Pi$ – $\Pi^*$  charge transfer process. The calculated parameters of the state S<sub>0</sub> and the state S<sub>1</sub> was used

to determine charge transfer hyperpolarizability,  $\beta_{\text{CT}}$ , in a two-level model according to eq 4

$$\beta_{\text{CT}}^0 = \frac{3(\mu_e - \mu_g)\mu_t^2}{2\epsilon_0 h^2 c^2 \nu_t^2} \quad (4)$$

where  $\mu_e$  and  $\mu_g$  are dipole moments in the excited and ground state, respectively,  $\mu_t$  is the transition moment between the excited and ground state,  $\epsilon_0$  is vacuum permittivity,  $h$  is Planck constant, and  $\nu_t$  is the transition frequency from ground state to first excited state. The frequency response of  $\beta$  for the frequency-doubling process can be obtained by

$$\beta(-2\omega, \omega, \omega) = \frac{\omega_t^4}{(\omega_t^2 - 4\omega^2)(\omega_t^2 - \omega^2)} \beta_{\text{CT}}^0 \quad (5)$$

where  $\omega$  is applied field frequency. The two-level model holds quite well for many organic compounds where the energy to reach the first excited state lies close to photon energy. In our case there is a strong nonlinearity along charge transfer axis and the component  $\beta_{\text{xxx}}$  of the hyperpolarizability tensor along this axis is so predominant (as shown by GAMESS TDHF calculations) that it can be assumed a good approximate for  $\beta_v$ . The two-level model bears some simplification due to the assumption mentioned above, i.e., charge transfer along the dipole moment and no reorientation of the solvent dipoles upon excitation if the chromophore in a solvent is considered.

The amphiphiles A and B have a charge transfer path from –NHCO– (donor) to sulfonyl group (acceptor) via  $\Pi$  conjugation through phenyl rings and azo group. The direction of the S<sub>1</sub> excited state dipole moment was found to be close to that of the ground state dipole moment and cosine of the angle between them was ca. 0.97. The results of the semiempirical INDO1/S calculations of the first hyperpolarizability with STO-6G basis set (Table 2) indicate fairly good agreement with those obtained by GAMESS ab initio option. Lower  $\beta$  values were obtained for the amphiphile B but the difference is not high, not exceeding principally 10%. The same calculation carried out for *p*-nitroaniline gave  $\beta^0$  value equal to 63.66  $\times 10^{-40}$  m<sup>4</sup>/V, i.e., twice as much as that from GAMESS TDHF. The explanation of this fact may be found in the too high value of the excited state dipole moment, here 63.76  $\times 10^{-30}$  C m, while the value determined experimentally is ca. 47.4  $\times 10^{-30}$  C m.<sup>53</sup> In the case of DANS (4-(dimethylamino)-4'-nitrostilbene) used as another external standard, the discrepancy between calculated and experimental  $\mu_e$  value was below 1 D (3.335  $\times 10^{-30}$  C m).

With the INDO1/S program it was possible to simulate the solvent effect on molecular properties with the SCRF option which included also the refractive index of the solvent. In this

**TABLE 2: Dipole Moments and First Hyperpolarizability Calculated by INDO1/S (Two-Level Model), Structure Optimization by Gaussian 3-21g**

| structure                    | R   | solvent            | $\mu_g^a$ | $\mu_e^a$ | $\mu_t^a$ | $\nu \text{ m}^{-1}/10^6$ | $\beta^0 a$ | $\beta^{1064} a$ |
|------------------------------|---|--------------------|-----------|-----------|-----------|---------------------------|-------------|------------------|
| A                            | <i>n</i> -C <sub>15</sub> H <sub>31</sub> | none               | 42.43     | 64.51     | 30.53     | 2.9002                    | 104.6       | 201.5            |
|                              |   | chlorobenzene      | 44.55     | 69.57     | 30.41     | 2.8019                    | 126.2       | 258.5            |
|                              |   | 1,2-dichloroethane | 44.85     | 70.27     | 30.44     | 2.8005                    | 128.3       | 263.1            |
|                              |   | acetone            | 45.07     | 70.77     | 30.44     | 2.8027                    | 129.5       | 265.1            |
|                              |   | acetonitrile       | 45.06     | 70.90     | 30.42     | 2.7932                    | 130.9       | 269.8            |
|                              |   | DMF                | 45.16     | 70.99     | 30.42     | 2.7939                    | 130.9       | 269.8            |
| B                            | <i>n</i> -C <sub>9</sub> H <sub>31</sub>  | none               | 36.97     | 56.46     | 30.75     | 2.9160                    | 90.9        | 173.5            |
|                              |   | chlorobenzene      | 39.17     | 61.96     | 30.35     | 2.8061                    | 114.0       | 232.9            |
|                              |   | 1,2-dichloroethane | 39.49     | 62.77     | 30.34     | 2.8044                    | 116.5       | 238.3            |
|                              |   | acetone            | 39.72     | 63.33     | 30.33     | 2.8071                    | 117.8       | 240.5            |
|                              |   | acetonitrile       | 39.82     | 63.40     | 30.32     | 2.7950                    | 119.5       | 245.7            |
|                              |   | DMF                | 39.82     | 63.57     | 30.32     | 2.7968                    | 119.7       | 246.1            |
| <i>p</i> -nitroaniline (PNA) | none                                      | 28.55              | 63.76     | 20.78     | 3.1952    | 63.6                      | 106.5       |                  |
|                              | acetonitrile                              | 32.18              | 68.93     | 21.84     | 2.7543    | 98.2                      | 208.0       |                  |
| DANS <sup>b</sup>            |   | none               | 30.06     | 82.04     | 31.07     | 2.5757                    | 323.2       | 797.6            |

<sup>a</sup> Units as in Table 1. <sup>b</sup> DANS, 4-(dimethylamino)-4'-nitrostilbene**TABLE 3: First Hyperpolarizability of the Chromophores with Different Aliphatic Chain Length (Calculations Made with INDO1/S (Two-Level Model), Structure Optimization with Gaussian 3-21g)**

| structure | R   | $\mu_g^a$ | oscillator strength | $\beta^0 b$ |
|-----------|---|-----------|---------------------|-------------|
| A         | <i>n</i> -C <sub>2</sub> H <sub>5</sub>   | 42.15     | 1.1903              | 104.5       |
|           | <i>n</i> -C <sub>5</sub> H <sub>11</sub>  | 43.27     | 1.1760              | 104.5       |
|           | <i>n</i> -C <sub>9</sub> H <sub>19</sub>  | 43.40     | 1.1774              | 104.9       |
|           | <i>n</i> -C <sub>15</sub> H <sub>31</sub> | 43.35     | 1.1728              | 104.6       |
|           |   |           |                     |             |
| B         | <i>n</i> -C <sub>2</sub> H <sub>5</sub>   | 37.61     | 1.1878              | 90.6        |
|           | <i>n</i> -C <sub>9</sub> H <sub>19</sub>  | 36.97     | 1.1441              | 90.9        |

<sup>a</sup> Units as in Table 1.

way the influence of the solvent on dipole moments and first hyperpolarizability could be presented in a more balanced form. The values of  $\beta$  calculated for the amphiphiles in solvent continuum were 25–30% higher than those obtained for isolated molecules and there was little effect of the solvent polarity on the  $\beta$  values. The calculated transition frequency was also nearly independent of the solvent kind. The frequency of the transition  $S_0 \rightarrow S_1$  was nearly constant at  $(2.7932\text{--}2.807) \times 10^6 \text{ m}^{-1}$  and this fact was confirmed by UV–vis spectroscopy for both amphiphiles; this aspect will be dealt with in the next paragraphs. Little (or no) solvatochromic shift is probably a feature of the sulfonyl-containing chromophores and has been reported by other authors.<sup>29–31</sup> To check additionally the effect of the hydrophobic chain on the first hyperpolarizability, the calculations with INDO1/S were carried out for chromophores listed in Table 1. The results of these calculations (Table 3) showed independence of the two-level  $\beta_{CT}^0$  on the amphiphile chain length; the proper values were close to  $\pm 104.5 \times 10^{-40}$  and  $90.6 \times 10^{-40} \text{ m}^4/\text{V}$  for structures A and B, respectively.

The choice of the two-level model for calculation of first hyperpolarizability resulted from the fact that it can be simply approached by determination of the UV–vis absorption spectra in different solvents. The solvatochromic shift observed in solutions of D– $\Pi$ –A charge transfer molecules of the solvents having different refractive index,  $n$ , and dielectric constant,  $\epsilon$ , can be expressed by<sup>49,53–57</sup>

$$\nu_a^s - \nu_a^0 = \frac{1}{4\pi\epsilon_0 a^3 hc} [2(\mu_e - \mu_g)\mu_g(F(\epsilon) - F(n)) + (\mu_e^2 - \mu_g^2)F(n)] \quad (6)$$

where

$$F(\epsilon) = \frac{\epsilon - 1}{\epsilon + 2}, \quad F(n) = \frac{n^2 - 1}{n^2 + 2} \quad (7)$$

$\nu_a^s$  and  $\nu_a^0$  are wavenumbers corresponding to CT absorption of a solute molecule in a solvent and of the isolated molecule. The parameter  $a$  is a cavity radius occupied by the solute molecule in the solvent continuum. The cavity radius, assumed spherical, was approximated by

$$a = R_A + 0.5R_S \quad (8)$$

where  $R_A$  and  $R_S$  are the radii of the amphiphile (solute) and solvent molecule, respectively, estimated from densities ( $\rho$ ) and molar masses ( $M$ ) according to

$$R_i^3 = \frac{3M_i}{4\pi\rho_i N_A} \quad (i = A, S) \quad (9)$$

The value of  $a$  differs from the value of  $a_0$  used in GAMESS and INDO1/S calculations by the contribution of the solvent. Knowing the solvatochromic shift in the function of solvent properties ( $\epsilon$  and  $n$ ), and ground state dipole moment,  $\mu_g$ , makes it possible to determine excited state dipole moment,  $\mu_e$ . At the same time, the UV–vis spectrum is also helpful in the determination of the transition dipole moment,  $\mu_t$ , related to oscillator strength which can be calculated from integral absorbance given by

$$\mu_t^2 = \frac{3hc\epsilon_0 n}{2\pi^2 N_A \phi(n)^2 \omega_t} \int \kappa d\omega \quad (10)$$

The parameter  $\phi(n)$  stands for the local field factor taken from Lorentz approximation,<sup>10</sup> given by eq 11. The parameter  $\kappa$  in

$$\phi(n) = (n^2 + 2)/3 \quad (11)$$

eq 10 is the molar extinction coefficient, and the integral is over the entire absorption band (SI units) ascribed to the  $\Pi$ – $\Pi^*$  transition.

The UV–vis spectra recorded for the amphiphile A and B in solvents of different refractive index and dielectric constant revealed that there is no solvatochromic shift and both amphiphiles can be characterized by the CT absorption in the region of 368–378 nm, as expressed by wavelength at the absorption maximum. This is in good agreement with INDO1/S calculations. The UV–vis spectra gave us possibility to determine transition moments with using eq 10. The data in Table 4 are slightly lower than those calculated by INDO1/S but taking into

**TABLE 4: Spectral Characteristics and Values of First Hyperpolarizability<sup>a</sup>**

| structure | solvent            | UV-vis                      |  | $a/(m/10^{-10})$ | $\mu_e^b$ | $\mu_t^b$ | $\beta^0$ | $\beta^{1064}$ |
|-----------|--------------------|-----------------------------|--|------------------|-----------|-----------|-----------|----------------|
|           |                    | $\nu_a/10^6 \text{ m}^{-1}$ | $\chi_{\text{max}}/(m^2 \text{ mol}^{-1})$ |                  |           |           |           |                |
| A         | chlorobenzene      | 2.717                       | 1186                                       | 7.45             | 80.97     | 21.89     | 100.5     | 218.9          |
|           | 1,2-dichloroethane | 2.747                       | 1694                                       | 7.31             | 71.53     | 27.60     | 114.8     | 244.4          |
|           | acetone            | 2.717                       | 1745                                       | 7.28             | 71.33     | 29.92     | 136.4     | 297.1          |
|           | DMF                | 2.688                       | 1361                                       | 7.30             | 72.53     | 27.26     | 118.1     | 263.2          |
|           | acetonitrile       | 2.732                       | 1694                                       | 7.11             | 66.60     | 26.09     | 84.1      | 181.1          |
|           | DMSO               | 2.653                       | 1831                                       | 7.26             | 74.57     | 28.17     | 141.7     | 325.5          |
| B         | chlorobenzene      | 2.717                       | 1951                                       | 7.02             | 76.20     | 28.01     | 167.0     | 363.7          |
|           | 1,2-dichloroethane | 2.717                       | 2294                                       | 6.89             | 69.93     | 30.20     | 160.6     | 349.8          |
|           | acetone            | 2.688                       | 1961                                       | 6.85             | 69.20     | 28.58     | 143.0     | 318.8          |
|           | DMF                | 2.732                       | 1868                                       | 6.67             | 67.63     | 29.59     | 144.6     | 322.3          |
|           | acetonitrile       | 2.688                       | 2208                                       | 6.88             | 61.89     | 31.25     | 124.0     | 267.0          |
|           | DMSO               | 2.646                       | 2008                                       | 6.83             | 69.83     | 28.99     | 143.8     | 332.3          |
| PNA       | acetonitrile       | 2.747                       | 1203                                       | 4.83             | 49.39     | 19.38     | 36.7      | 78.1           |

<sup>a</sup> Ground state dipole moments and transition frequency of isolated molecule taken from INDO1/S calculation (Table 2), excited state dipole moments by eq 6. <sup>b</sup> Units as in Table 1.

account the accuracy of the determination method based on peak area integration, the difference within ca. 1 D ( $3.335 \times 10^{-30}$  C m) between calculated and determined  $\mu_t$  may be assumed as a tolerable agreement of the calculated and determined data. The exception is the amphiphile A in chlorobenzene solution where we probably had to work with the solutions close to the solubility region. Comparison of the determined  $\mu_t$  values of amphiphile A and B indicates the structure B as having slightly higher transition moment.

For calculation of  $\beta_{\text{CT}}^0$  by eq 4 from experimental data it is necessary to know  $\mu_e$  and  $\mu_t$  or at least their difference. We found problems in determining ground state dipole moments of the amphiphiles with the capacitance bridge because of their poor solubility in unpolar solvents. We made use of eq 6 to calculate the difference between excited state and ground state dipole moments. As input data the ground state dipole moments and CT frequency of the isolated molecule from INDO1/S calculations (Table 2) were used. This compromise issue yielded the values of charge transfer  $\beta$  shown in Table 4. The same procedure was also applied for PNA which again was treated as an external standard. The value of  $\beta_{\text{CT}}^0$  of this compound was  $36.7 \times 10^{-4} \text{ m}^4/\text{V}$  and was within the limits of the literature data.<sup>11,42,53</sup> Relating the  $\beta$  values of the amphiphiles toward PNA one realizes that the compounds in question show 3–4 times higher values than this standard. The dependence of the  $\beta$  on the solvent is evident and indicates probably specific interactions between solutes and the solvents and maximum values of  $\beta$  were obtained for the solutes in 1,2-dichloroethane and acetone.

The amphiphiles in question were found to exhibit fluorescence in solutions of organic solvents. This brought an opportunity to utilize the Stokes shift  $\nu_a - \nu_f$  to determine the difference  $\mu_e - \mu_g$  by fluorescence solvatochromism. There are many equations relating Stokes shift with solvent properties:<sup>49,58–64</sup> we used two options which can be presented by the following equations.

$$\nu_a - \nu_f = \frac{2(\mu_e - \mu_g)^2}{a^3 hc} (F(\epsilon) - F(n))F^B(n) + \text{const} \quad (12)$$

$$F^B(n) = \frac{2n^2 + 1}{n^2 + 2} \quad (13)$$

Equation 12 in its present form is known as the Bakhshiev formula<sup>64</sup> whereas the equation without the  $F^B(n)$  term is called the MacRae equation.<sup>65</sup> Both equations are valid under several simplifying assumptions. If there are no specific interactions

**TABLE 5: Fluorescence Solvatochromism and Two-Level Hyperpolarizability,  $\beta_{\text{CT}}^0$ , of the Amphiphiles**

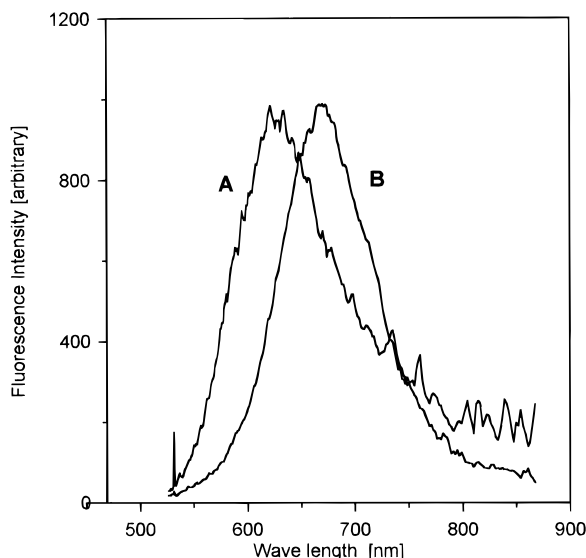
| solvent               | structure A                 |                             | structure B                 |                             |
|-----------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                       | $\nu_a/10^6 \text{ m}^{-1}$ | $\nu_f/10^6 \text{ m}^{-1}$ | $\nu_a/10^6 \text{ m}^{-1}$ | $\nu_f/10^6 \text{ m}^{-1}$ |
| chlorobenzene         | 2.7174                      | 2.299                       | 2.7170                      | 2.725                       |
| 1,2-dichloroethane    | 2.7472                      | 2.041                       | 2.7170                      | 2.364                       |
| acetone               |                             |                             | 2.6880                      | 2.212                       |
| acetonitrile          |                             |                             | 2.7320                      | 2.020                       |
| $\mu_e - \mu_g^a$     | 22.61                       |                             | 20.04                       |                             |
| $\mu_e - \mu_g^b$     | 23.68                       |                             | 19.28                       |                             |
| $\mu_t$ (averaged)    | 26.81                       |                             | 27.97                       |                             |
| $\beta_{\text{CT}}^0$ | 94.0                        |                             | 100.4                       |                             |
| $\beta_{\text{CT}}^0$ | 98.3                        |                             | 96.6                        |                             |

<sup>a</sup> From MacRae slope.<sup>59</sup> <sup>b</sup> From Bakhshiev slope.<sup>64</sup>

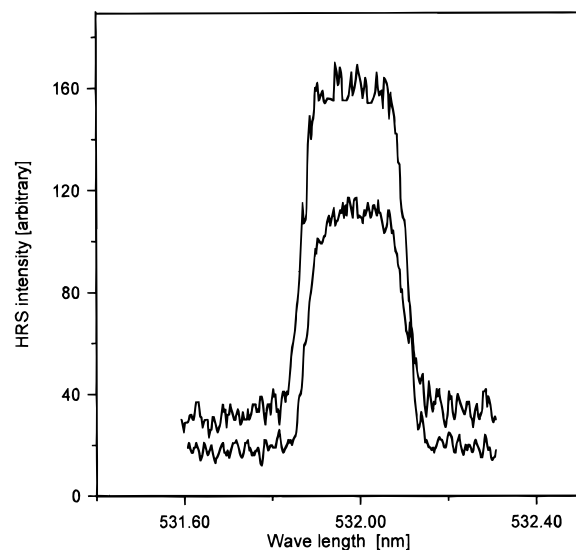
between a solute and a solvent the difference  $\mu_e - \mu_g$  can be obtained from the slope  $\nu_a - \nu_f$  vs  $(F(\epsilon) - F(n))F^B(n)$  or vs  $F(\epsilon) - F(n)$ . For the amphiphile B both relationships were linear for four solvents used and the coefficient of determination was ca. 0.95. The dipole moments difference calculated from the slopes was  $20.04 \times 10^{-30}$  (MacRae) and  $19.28 \times 10^{-30}$  (Bakhshiev) C m.

For the amphiphile A only two solvents of least polarity could be taken into account and the difference between excited and ground state dipole was  $22.6 \times 10^{-30}$  (MacRae) and  $23.68 \times 10^{-30}$  (Bakhshiev) C m. The values obtained by this method are smaller than those resulting from data of Tables 2 and 4 but their feature is that they have been obtained experimentally and that they refer to a hypothetical unpolar solvent. To use them in eq 4 we averaged the transition dipole moments contained in Table 4 and calculated  $\beta_{\text{CT}}^0$  from all experimental data. The values obtained (Table 5) were 94.0 and 98.3 for amphiphile A, and 96.5 and 100.4 (all  $\times 10^{-40} \text{ m}^4/\text{V}$ ) depending on the set of  $\Delta\mu$  data. If one takes into account the assumptions which are attributed to the solvatochromic and fluorescence solvatochromic method, the agreement between  $\beta$  values calculated by GAMESS ab initio and INDO1/S semiempirical methods and those obtained from experimental data by indirect procedure is unexpectedly good.

It is a good practice that the indirect computational methods of determination of a property be verified with direct experimental measurement of this property. In our case, it was the determination of the first hyperpolarizability by hyper-Rayleigh scattering (HRS) applicable to the solutions of chromophores. The determinations were carried out with laser incident radiation at 1319 and 1064 nm in DMF solutions at concentrations 0.0155 (A) and 0.0119 (B) mol/dm<sup>3</sup>. As the amphiphiles in question exhibited fluorescence, it was necessary to avoid interference



**Figure 3.** Two-photon induced fluorescence spectra with irradiation at 1064 nm, corrected for the relative response to the spectrometer and for absorption by the solution (in DMF). Normalized to 1000 counts at maximum. A, R =  $n\text{-C}_{15}\text{H}_{31}$ ; B, R =  $n\text{-C}_9\text{H}_{19}$ .



**Figure 4.** Hyper-Rayleigh scattering intensity signal at irradiation at 1064 nm. Spectral slit width ca.  $4.5\text{ cm}^{-1}$  near 532 nm. Concentration of the amphiphile solutions (in DMF): A (lower),  $0.0155\text{ mol/dm}^3$ ; B (upper)  $0.0119\text{ mol/dm}^3$ .

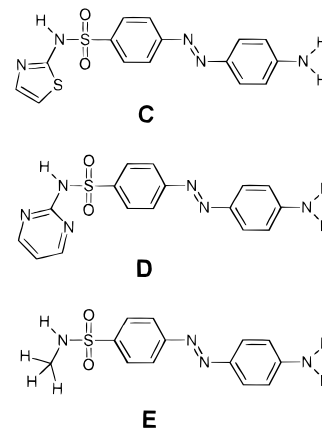
of any fluorescence signal with that of second harmonic generation. Figure 3 shows a large two-photon fluorescence of the amphiphiles generated with irradiation at 1064 nm. The fluorescence spectrum of the amphiphile A was shifted toward shorter wavelengths and, therefore, the two-photon fluorescence signal at  $2\omega$ , i.e., at 532 nm, was more pronounced. For irradiation at 1319 nm, the two-photon signals were nearly negligible.

The data of HRS frequency doubling at irradiation of 1064 nm is shown in Figure 4. The signal level of SHG at 532 nm is higher for the structure B as compared with that of A, indicating explicitly the better ability of B for SHG in DMF solution. The values of  $\beta$  were calculated from HRS intensity signals assuming the  $C_{2v}$  symmetry of the molecules which might involve a relative inaccuracy in the range of 5–10%. The values of  $\beta$  at 1319 nm were 152.9 and 189.8, and at 1064 nm they were  $197.8 \times 10^{-40}$  and  $252.1 \times 10^{-40}\text{ m}^4/\text{V}$  for the amphiphiles A and B, respectively. When these values are related to those of PNA, one gets 2.25–2.30 (structure A) and

**TABLE 6: HRS First Hyperpolarizability of the Amphiphiles (R = Pentadecyl (A), Nonyl (B))**

| structure                           | $\beta^{1319\text{ a}}$ | $\beta^{1064\text{ a}}$ | $\beta^0\text{ a,b}$ |
|-------------------------------------|-------------------------|-------------------------|----------------------|
| A                                   | 152.9                   | 197.8                   | 88.8                 |
| B                                   | 189.8                   | 252.1                   | 113.1                |
| <i>p</i> -nitroaniline <sup>c</sup> | 66.9                    | 87.6                    | 41.2                 |

<sup>a</sup> Units as in Table 1. <sup>b</sup> Calculated based on the two-level model from data at 1064 nm. <sup>c</sup> In dioxane, ref 42.



**Figure 5.** Chemical formulas of the compounds related in structure to A and B.

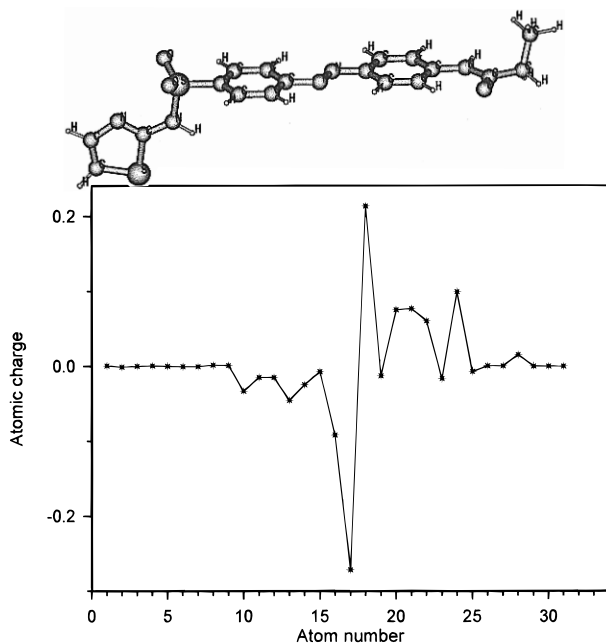
2.84–2.98 (structure B) expressed in multiples of  $\beta$  of PNA (Table 6). Recalculation of HRS results to zero frequency with the two-level model made it possible to compare this direct measurement method with indirect ones which were described previously. The  $\beta$  values of A calculated by INDO1/S for DMF solutions are in reverse order to those from HRS and, in the absolute scale, they look overestimated. For the amphiphile B the agreement between both methods is very good. The results obtained by solvatochromic and fluorescence solvatochromic method (Table 5) are also in agreement with HRS results, and the discrepancies in static  $\beta$  are less than 15%.

The quantum chemical calculations help to understand the relation between chemical structure and properties. In this context, three more chemical compounds were taken into account to answer the following questions: how much competitive is the carbonyl group situated at the electron donor atom of the structure A and B toward sulfonyl group, and what is the role of the heterocyclic ring. Three additional species (presented in Figure 5) were taken into account and calculations to get their optimized structures were carried out, as previously, by Gaussian 94 and 3-21g basis set. In fact, the compounds C and D were substrates for the synthesis of structures A and B, respectively, and were described in ref 27. The amphiphiles A and B were designed for Langmuir–Blodgett film technique and had to have a group anchoring the molecule to the aqueous subphase and a long-chain hydrophobe to form stable monolayer by van der Waals attraction. The structures A–E have similar path of D– $\Pi$ –A charge transfer from N (right) to  $\text{SO}_2$ . The heterocyclic ring is twisted by ca.  $90^\circ$  toward phenyl rings plane and separated by two single bonds from the sulfonyl group. The comparison of the static  $\beta$  (calculated by GAMESS TDHF), of the structure E with that of C and D clearly shows that the chromophores with heterocyclic ring have the higher values of  $\beta$  by ca. 20% (Table 7). The bond length between the heterocyclic ring and neighboring nitrogen atom is 1.36–1.37 Å and is typical for  $\text{sp}^2\text{-N}$  bond, while the analogous bond length between nitrogen atom and the methyl group C atom of the structure E is 1.477 Å indicating a  $\text{sp}^3\text{-N}$  bond type in this molecule fragment. It means that in the ground state, the

**TABLE 7: Bond Lengths, Dipole Moments, and First Hyperpolarizabilities of the Compounds Relative in Structure to A and B (Figure 5) Calculated with the 3-21g Basis Set. Structure Optimization with Gaussian 94, Hyperpolarizability with GAMESS TDHF Option**

| compd | bond length, nm*10             |        |                      |        | $\mu_g^a$ | $\beta^{0a}$ |
|-------|--------------------------------|--------|----------------------|--------|-----------|--------------|
|       | phenyl<br>C-S(O <sub>2</sub> ) | S-N(H) | N-C<br>(heterocycle) | N-H    |           |              |
| A     | 1.7985                         | 1.7207 | 1.3643               | 0.9993 | 36.80     | 112.3        |
| B     | 1.7999                         | 1.7069 | 1.3713               | 1.0003 | 28.21     | 107.9        |
| C     | 1.7977                         | 1.7204 | 1.3640               | 0.9994 | 35.38     | 153.5        |
| D     | 1.7982                         | 1.7075 | 1.3708               | 1.0003 | 28.88     | 146.4        |
| E     | 1.7949                         | 1.7047 | 1.4769 <sup>b</sup>  | 1.0055 | 31.08     | 123.2        |

<sup>a</sup> Units as in Table 1. <sup>b</sup> N-CH<sub>3</sub> bond.



**Figure 6.** Difference in charge (Mulliken) of the heavy atoms in the ground ( $S_0$ ) and first excited state ( $S_1$ ) calculated by INDO1/S.A. Atom numbers are as follows: 1–5, thiazole ring; 6–9, N-SO<sub>2</sub>; 10–15, C atoms of the left phenyl ring; 16, 17, azo group; 18–23, C atoms of the right phenyl ring; 24, N (alkanamide).

heterocyclic ring shows a kind of conjugation with the rest of the molecule and it plays a role of an additional electron donor as its results from the balance of the electronic charge of the ring in the ground state.

Figure 6 shows the atomic charge shift in the amphiphile A during the charge transfer process between ground state  $S_0$  and the excited state  $S_1$  determined by INDO1/S which could be assumed as HOMO–LUMO charge transfer (prevailing contribution of this transfer). The figure presents the difference of charge of the heavy atoms (Mulliken charges) of the optimized molecule as the charges on the hydrogen atoms are the same in the  $S_0$  and  $S_1$  state. The heterocyclic ring and –N(H)–S(O<sub>2</sub>)– fragment unexpectedly take nearly no part in this charge transfer maintaining its electronic charge practically unchanged. The same behavior of the sulfonyl group has also been observed in the case of compound E and this probably explains why sulfonyl compounds are weaker NLO-phores than the corresponding nitro compounds. Nitrogen atoms of the azo group play the role of the main charge-accepting atoms, while the electron donors are alkanamide N atom and carbon atoms closest to the phenyl ring. The charge difference of the alkanamide N atom in the ground and the first excited state is +0.082, while the same difference for the compound C is +0.11, but here we have an amine group in the analogous place. This means that the amine group is

able to donate more charge into the  $\Pi$  system and it is manifested by higher value of the first hyperpolarizability of the compound C ( $153.5 \times 10^{-40}$  m<sup>4</sup>/V) as compared with that of A ( $112.3 \times 10^{-40}$  m<sup>4</sup>/V). Similar tendency has also been observed in the case of the pair of the compounds B and D (Table 7).

## Conclusions

The sulfonyl-containing alkanamide amphiphiles A and B are modest NLO-phores; their first-hyperpolarizability values are 3.5–4 times that of *p*-nitroaniline. The evaluation of their NLO properties based on the ab initio GAMES TDHF procedure and INDO1/S semiempirical method was confronted with the experimental determination of the first hyperpolarizability  $\beta$  by fluorescence solvatochromism and hyper-Rayleigh scattering. It was established that within tolerable discrepancies, a fair agreement was observed between computational and experimental methods. The molecules of the compounds in question have heterocyclic thiazole or pyrimidine rings. It may be assumed that a kind of conjugation exists between the ring and the rest of the molecule resulting in the net electron donor action from the side of the ring and this positively affects the first hyperpolarizability.

Unfortunately, neither heterocyclic ring nor sulfonamide fragment (–NH–SO<sub>2</sub>–) takes part in the internal charge transfer process between ground state and first excited state and this is probably a reason why the sulfonyl-containing compounds show lower first hyperpolarizability as compared with analogous nitro compounds.

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## References and Notes

- (1) Roberts, G. G., Ed. *Langmuir-Blodgett Films*; Plenum: New York, 1990.
- (2) Swallen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J. *Langmuir* **1987**, *3*, 932.
- (3) Marks, T. J.; Ratner, M. A. *Angew. Chem.* **1995**, *34*, 155.
- (4) Petty, M. C. *Thin Solid Films* **1992**, *210/211*, 417.
- (5) Roberts, G. G. *Molecular Electronics Using Langmuir-Blodgett Films*; Adv. Chem. Ser. Bowden, M., Turner, R. S., Eds.; American Chemical Society: Washington, DC, 1988; Vol. 218, p 229.
- (6) Gabrielli, G.; Rustichelli, F. *Proc. VIII Int. Conf.: Organized Mol. Films, Thin Solid Films* **1996**, 284–285.
- (7) Ashwell, G. J.; Dawney, E. J. C.; Kuczynski, A. P.; Martin, P. J. *Proc. SPIE, Phys. Concepts Mater. Novel Optoelectron. Device Appl.* **1990**, 1361.
- (8) Messier, J.; Kajzar, P.; Prasad, P. N.; Ulrich, D. *Organic Molecules for Nonlinear Optics*; Kluwer: Dordrecht, 1989.
- (9) Lindsay, G. A.; Singer, K. D., Eds. *Polymers for Second-Order Nonlinear Optics*, ACS Symp. Ser. No. 601; American Chemical Society: Washington, DC, 1995.
- (10) Bosshard, C.; Sutter, K.; Prêtre, P.; Hulliger, J.; Flörsheimer, M.; Kaatz, P. *Organic Nonlinear Optical Materials*; Gordon & Breach: Basel, Switzerland, 1995.
- (11) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.
- (12) Laschewsky, A.; Paulus, W.; Ringsdorf, H.; Lupo, D.; Ottenbreit, P.; Prass, W.; Bubeck, C.; Neher, D.; Wegner, G. *Macromol. Chem., Macromol. Symp. Ser.* **1991**, *46*, 205.
- (13) Bubeck, C.; Laschewsky, A.; Lupo, D.; Neher, D.; Ottenbreit, P.; Paulus, W.; Prass, W.; Ringsdorf, H.; Wegner, G. *Adv. Mater.* **1991**, *3*, 55.
- (14) Ledoux, I.; Josse, D.; Fremaux, P.; Piel, J.-P.; Post, G.; Zyss, J.; McLean, T.; Hann, R. A.; Gordon, F. P.; Allen, S. *Thin Solid Films* **1988**, *160*, 217.
- (15) Ashwell, G. J.; Hargreaves, R. C.; Baldwin, C. E.; Bahra, G. S.; Brown, C. R. *Nature* **1992**, *357*, 393.
- (16) Ashwell, G. J.; Jefferies, G.; Dawney, E. J. C.; Kuczynski, A. P.; Lynch, D. E.; Gongda, Y.; Bucknall, D. G. *J. Mater. Chem.* **1995**, *5*(7), 975.

- (17) Ashwell, G. J.; Jackson, P. D.; Jefferies, G.; Gentle, J. R.; Kennard, G. H. L. *J. Mater. Chem.* **1996**, 6(2), 137.
- (18) Ashwell, G. J.; Jefferies, G.; George, C. D.; Ranjan, R.; Charters, R. B.; Tatam, R. P. *J. Mater. Chem.* **1996**, 6(2), 131.
- (19) Ashwell, G. J.; Walker, T. W.; Gentle, J. R.; Foran, G. J.; Bahra, G. S.; Brown, C. R. *J. Mater. Chem.* **1996**, 6(6), 969.
- (20) Xia, W. S.; Huang, C. H.; Cheng, T. R.; Gan, L. B.; Zhao, X. S.; Yu, A. C. *J. Mater. Chem.* **1996**, 6(9), 1493.
- (21) Hann, R. A.; Bloor, D. *Org. Mater. Nonlinear Opt. II. Proc. 2nd Symp. R. Soc. Chem. Cambridge*, **1991**.
- (22) Wijekon, W. M. K. P.; Asgarian, B.; Prasad, P. N.; Geisler, T.; Rosenhilde, R. *Thin Solid Films* **1992**, 208, 137.
- (23) Liu, X.; Liu, L.; Lu, X.; Zheng, J.; Wang, W. *Thin Solid Films* **1992**, 217, 174.
- (24) Miyamoto, Y.; Kaifu, K.; Koyano, T.; Saito, M.; Kato, M. *Thin Solid Films* **1992**, 210/211, 178.
- (25) Stone, P. J. W.; Miller, L. S.; Walton, D. J.; Sethi, R. S. *Organic Materials for Nonlinear Optics*; Ashwell, G. J., Bloor, D., Eds.; Royal Soc. Chem.: London, 1993; Vol. 3, p 88.
- (26) Percec, S. H. Ou.; Mann, J. A.; Lando, J. B. *Langmuir* **1994**, 10, 905.
- (27) Kucharski, S.; Janik, R. *Bull. Polish Acad. Sci. (Chem.)*, in press.
- (28) Kucharski, S.; Janik, R.; Bieñkowski, M.; Sworakowski, J. *VIIIth Int. Conf. Organized Molecular Films, Asilomar*, August, 1997.
- (29) Ulman, A.; Willand, C. S.; Köhler, W.; Robello, D. R.; Williams, D. J.; Handley, L. J. *Am. Chem. Soc.* **1990**, 112, 7083.
- (30) Le Breton, H.; Letard, J.-F.; Lapouyade, R.; Le Calvez, A.; Maleck Rassoul, R.; Freysz, E.; Ducasse, A.; Belin, C.; Morand, J.-P. *Chem. Phys. Lett.* **1995**, 242, 604.
- (31) van Hutten, P. F.; Hadzioannou, G.; Bursi, R.; Feil, D. *J. Phys. Chem.* **1996**, 100, 85.
- (32) Motschman, H. R.; Penner, T. L.; Armstrong, N. J.; Ezengilimba, M. C. *J. Phys. Chem.* **1993**, 97, 3933.
- (33) Kim, H. K.; Lee, H. J.; Lrr, M. H.; Han, S. K.; Kim, H. Y.; Kang, K. H.; Min, Y. H.; Won, Y. H. Thermally Stable NLO Moyety-Doped Polyimides for Photonic Devices, in ref 9, p 111.
- (34) Shi, Y.; Ranon, P. M.; Steier, W. H.; Xu, C.; Wu, B.; Dalton, L. R. *Appl. Phys. Lett.* **1993**, 63, 2168.
- (35) Nemoto, N.; Miyata, F.; Nagase, Y.; Abe, J.; Hasegawa, M.; Shirai, Y. *J. Mater. Chem.* **1996**, 6, 711.
- (36) Barzoukas, M.; Josse, D.; Zyss, J.; Gorden, P.; Morley, J. O. *J. Chem. Phys.* **1989**, 139, 359.
- (37) Cheng, L.-T. Empirical Systematics of Molecular Quadratic Optical Polarizability, in ref 8, p 121.
- (38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian*, 94, Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1994.
- (39) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, 14, 1347.
- (40) Thomson, M. A.; Zerner, M. C. *J. Am. Chem. Soc.* **1990**, 112, 7828; **1991**, 113, 8210.
- (41) Thomson, M. A.; Zerner, M. C.; Fajer, J. *J. Phys. Chem.* **1991**, 95, 5693.
- (42) Kaatz, P.; Shelton, D. P. *J. Chem. Phys.* **1996**, 105, 3918.
- (43) Willets, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, 97, 7590.
- (44) Albert, I. D. L.; Morley, J. O.; Pugh, D. *J. Phys. Chem.* **1995**, 99, 8024.
- (45) Albert, I. D. L.; Morley, J. O.; Pugh, D. *J. Phys. Chem.* **1997**, 101, 1763.
- (46) Abe, J.; Shirai, Y. *J. Am. Chem. Soc.* **1966**, 118, 4705.
- (47) Abe, J.; Nemoto, N.; Nagase, Y. *J. Phys. Chem. B* **1997**, 101, 1910.
- (48) Abe, J.; Nemoto, N.; Nagase, Y.; Shirai, Y. *Chem. Phys. Lett.* **1996**, 261, 18.
- (49) van Walree, C. A.; Franssen, O.; Maarsman, A. W.; Flipse, M. C.; Jenneskens, W. *J. Chem. Soc., Perkin Trans. 2* **1997**, 799.
- (50) van Walree, C. A.; Maarsman, A. W.; Marsman, A. W.; Flipse, M. C.; Jenneskens, L. W.; Smeets, W. J. J.; Spek, A. L. *J. Chem. Soc., Perkin Trans. 2* **1997**, 809.
- (51) Blanchard-Desce, M.; Wortman, R.; Lebus, S.; Lehn, J.-M.; Krämer, P. *Chem. Phys. Lett.* **1995**, 243, 526.
- (52) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, 66, 2664.
- (53) Oudar, J. L. *J. Chem. Phys.* **1977**, 67, 446.
- (54) Paley, M. S.; Harris, J. M.; Looser, H.; Baumert, J. C.; Bjorklund, G. C.; Jundt, D.; Twieg, R. J. *J. Org. Chem.* **1989**, 54, 3774.
- (55) Miniewicz, A.; Palewska, K.; Lipiński, J.; Kowal, R.; Swedek, B. *Mol. Cryst. Liq.* **1994**, 253, 41.
- (56) Sworakowski, J.; Lipiński, J.; Ziółek, L.; Palewska, K.; Nešpůrek, S. *J. Phys. Chem.* **1996**, 100, 12288.
- (57) Ziółek, L.; Sworakowski, J.; Palewska, K.; Lipiński, J. Nešpůrek, S. *Mol. Cryst. Liq. Cryst.* **1996**, 283, 125.
- (58) Yu, J.; Zerner, M. C. *J. Chem. Phys.* **1994**, 100, 7487.
- (59) Limm, E. C., Ed. *Excited States*, Academic Press: New York, 1974.
- (60) Kowski, A. *Acta Phys. Polonica* **1966**, 39, 507.
- (61) Mantulin, W. W.; Song, P.-S. *J. Am. Chem. Soc.* **1973**, 95, 5122.
- (62) Rosenberg, H. M.; Eimutis, E. *Spectrochimica Acta* **1966**, 22, 1751.
- (63) Párkányi, C.; Oruganti, S. R.; Abdelhamid, A. O.; Szentpály, L. *J. Mol. Struct. (THEOCHEM)* **1986**, 135, 105.
- (64) Aaron, J. J.; Maafi, M.; Párkányi, C.; Boniface, C. *Spectrochim. Acta* **1995**, 51A, 603.
- (65) Bakhshiev, N. G. *Opt. Spektrosk.* **1961**, 10, 717.
- (66) McRae, E. G. *J. Phys. Chem.* **1957**, 61, 562.