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Silicon-Bridged donor-acceptor compounds

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Chapter 5

Determination of the first hyperpolarizability, β, of DσA-compounds and fragments thereof by hyper-Rayleigh scattering

5.1 Introduction

Over the last decades, the interest in organic materials that show large second order molecular polarizability has grown tremendously [1], due to their promising potential applications in optical signal processing. The molecular structure of the NLO-active compounds that are synthesized and investigated so far usually consists of a π-conjugated bridge connecting two aromatic moieties substituted with either a donor or acceptor group, inducing an asymmetrical charge distribution. Variation in donor-acceptor strength , length and type of the π-conjugated system (e.g. stilbenes, tolans, diazo-compounds, polyenes, acetylenes and even σ-conjugated systems) has led to numerous investigations on structure-hyperpolarizability relationships, both experimental and theoretical [2-7]. The main objective in these studies is the understanding of the parameters that govern the optical nonlinearities and to achieve a favourable nonlinearity-transparency trade-off. Many of these compounds, possessing a high β value, are absorbing in the visible and near-UV spectrum, due to the presence of an intramolecular charge-transfer (ICT) (π–π*)-transition. For many applications (e.g. frequency doubling of the fundamental wavelength of a 820 nm laser) complete transparency in the visible and near-UV spectrum is required. For this reason we have synthesized (σ-π)-conjugated organic NLO-molecules with a σ-conjugated silicon backbone. This σ-conjugation leads to a better transparency, but, as a consequence, to lower optical nonlinearities compared to π-conjugated systems. Compounds of this structure have been described first by Mignani et al. [8a-d]. They have investigated the nonlinear optical properties of compounds with a dicyanovinyl-acceptor. The first hyperpolarizability, β, was measured by the Electric Field Induced Second Harmonic Generation technique [9], which was, until recently, the only technique for measuring the first hyperpolarizability, β, in solution. Recently, a new technique, namely hyper-Rayleigh scattering (HRS), i.e. incoherent scattering of second-harmonic light, was introduced by Clays and Persoons as a new method to determine the first hyperpolarizabilty in solution [10a, b]. This can be done in a direct and accurate manner, since the HRS signal is directly proportional to β^2 and the solvent acts as an internal reference. In this respect, HRS has some advantages over the more commonly used EFISHG technique. The latter involves alignment of molecules in a solvent through their dipole moment, μ, by applying a static electric field. The quantity measured is $\gamma + \mu\beta/kT$ after suitable local-field correction at zero frequency. Values of γ (the second hyperpolarizability) and μ are needed to calculate β from the measurement. Due to the alignment, only the projection component of the molecular hyperpolarizability tensor along the dipole moment can be measured. Because HRS does not require alignment, hyperpolarizabilities of molecules with zero dipole moment (e.g. with an octupolar charge distribution) [11, 12] or ionic molecular species can be obtained [13, 14]. Comparison of HRS and EFISHG data allows the determination of the angle between the molecular dipole moment, μ, and the vectorial component of the β tensor. This might be especially useful for donor-acceptor compounds of which the major component of β does not necessarily lie along the dipole axis, i.e. for compounds not having a planar structure. In this chapter, the HRS-method will be applied for determining the hyperpolarizabilities, β, of a series of silicon-bridged DσA-compounds, focussing mainly on the dicyanovinyl and perfluorobutylsulfonyl-acceptor compounds. The results are explained in comparison with EFISHG measurements (for the dicyanovinyl-acceptor compounds) and ZINDO calculations (on the perfluorobutylsulfonyl-acceptor compounds and fragments thereof).

5.2 Experimental

Hyper-Rayleigh scattering

Although second-harmonic generation in isotropic liquids is forbidden for reasons of symmetry, second-order light scattering in isotropic samples has been observed [15, 16]. The second-order light scattering process mainly originates from fluctuations in molecular orientation, which induces asymmetry in an isotropic solution; this is different from linear light scattering, where the scattering is mainly due to density and concentration fluctuations.

The intensity of the second- harmonic light, $I(2\omega)$, is proportional to the number of scattering centers (N), the square of the first hyperpolarizability, (β^2), and the square of the intensity of the harmonic light ($I^2_0(\omega)$):

$$I(2\omega) = GB^2 I_0^2(\omega) = G\sum_s N_s \beta_s^2 I_0^2(\omega) \qquad (5.1)$$

The factor G depends on the scattering geometry (scattering angle and solid angle of photon collection) and includes the appropriate averages of the direction cosines, the instrumental factors and local field corrections at optical frequencies. N_s is the number density of a species with a first hyperpolarizability of β_s. For a two component solute-solvent system, equation (5.2) is valid:

$$B^2 = N_{solvent}\beta^2_{solvent} + N_{solute}\beta^2_{solute} \tag{5.2}$$

The number density of solvent molecules will be constant for the low concentrations that are used in the measurements. Measurements of $I\ (2\omega)$ as a function of incident fundamental light intensity $I_0(\omega)$ at various number densities of the solute then yield a linear dependence of GB^2 on N_{solute} at a fixed light intensity. β_{solute} can be calculated from the intercept, $GN_{solvent}\ \beta^2_{solvent}$, and the slope, $G\beta^2_{solute}$,, when $\beta_{solvent}$ is known, or vice versa. When an accurate value of $\beta_{solvent}$ is known, one can calibrate the experimental setup using this value:

$$\left\langle \beta^2_{solute} \right\rangle \Big/ \left\langle \beta^2_{solvent} \right\rangle = slope \Big/ intercept * N_{solute} \tag{5.3}$$

This method makes use of the solvent as internal reference and completely eliminates the need for local field correction factors, since the local field will be the same for both solute and solvent. Examples of the quadratic dependency of $I(2\omega)$ on $I_0(\omega)$ and the linear relation between number density and second-harmonic intensity are shown in Figure 5.1 for different concentrations of *p*-nitroaniline in chloroform. An important characteristic of the HRS technique is that only relative values of β can be obtained.

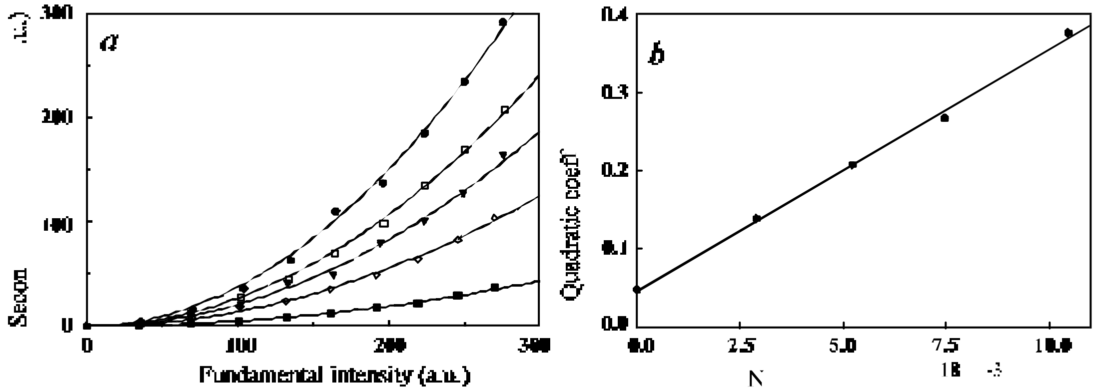


Figure 5.1. a) *Quadratic dependence of the second-harmonic scattered light versus the fundamental intensity at different concentrations of p-nitroaniline in chloroform;* b) *quadratic coefficient (I(2ω)/I^2_0(ω)) as a function of the concentration of pNA in chloroform.*

HRS-measurements

The HRS-setup, which has been used for the measurement of the second harmonic generation, has been built up in our laboratory after a model described by Clays and Persoons [10b]. We have used an injection-seeded (INJ: Spectra Physics, Model 6350) Q-switched Nd-YAG laser (Spectra-Physics, GCR-130-50 Hz) which is able to deliver up to 100 mJ per 8 ns at 1064 nm (with a repetition rate of 50 Hz instead of 10 Hz for faster measurements). As a cell we used a 5 cm path length UV cuvette (Hellma, 110 QS, 50 mm) with polished windows. Solutions were made by starting with 5 ml of the highest concentration and diluting to lower concentrations by adding the proper amount of filtered solvent up to a total volume of 15 ml. The solutions were passed through a 0.2 or 0.45 μm filter before entering the cell. The solvent (chloroform) was spectral grade (Merck, Uvasol) and was purged with argon before use. The signal of each concentration was referenced to that of a standard *para*-nitroaniline (*p*NA) solution. The HRS signal was measured as a function of concentration at a fixed fundamental intensity, except for the reference *p*NA solution, for which a quadratic dependency of the HRS signal as a function of fundamental intensity was established.

Calculations of the first hyperpolarizability, β, by means of ZINDO

The molecular electronic states were calculated within the semi-empirical INDO/S framework (ZINDO) [17-18]. The ZINDO calculation was applied to the geometry obtained from AM1 (MOPAC program) [19]. C_s symmetry was imposed, i.e. a mirror plane perpendicular to the (parallel) plane(s) of the phenyl ring(s) was assumed. This symmetry implies that any Si atom(s) will be in this mirror plane, as will be the lone pair on the nitrogen atom of the donor and the S-C_4 tail of the acceptor, if present. For compounds with the methoxy and methylthio donor, the symmetry is lower, since these donors lie in the same plane as the phenyl ring which they are bonded to with the methyl groups pointing sideways. For disilanes, a *trans*-type conformation of the central C_{ar}-Si-Si-C_{ar} bonds in the symmetry plane was used, in line with our x-ray study [20], although the latter shows that the molecules deviate somewhat from the ideal C_s symmetry. The perfluoroalkyl tail of the -$SO_2C_4F_9$ acceptor was also taken to be fully *trans* and to point away from the Si-Si bridge on the other side of the ring. The Si-Si bond length of disilanes was fixed at 2.34 Å, the result of several experimental studies including our own [20-22]. When unconstrained, AM1 consistently yielded too large values (ca. 2.53 Å) for the Si-Si bond of permethylated disilanes.

In order to remain consistent with the parametrization, only one-electron excitations were considered [23]. The range of orbitals from which singly excited configurations were generated extended from HOMO-13 to LUMO+13. This produced 196 configurations, close to the maximum of 210 in the standard version of ZINDO. 50 electronic states were generated through configuration interaction (CI). These were used in the calculation of β through the Sum-Over-States (SOS) formalism [24]. As a function of the number of states in the SOS, the value of β usually levelled off around 40 states. The SOS calculation was carried out for ω = 0 and for ω = 1.165 eV; the latter energy corresponds to the wavelength of 1064 nm used in the HRS experiment.

Frequency-dispersion correction

For compounds that are absorbing at a wavelength of 532 nm, the β values are enhanced by resonance effects and need therefore to be corrected, giving static (ω=0) β_0 values. The dispersion correction is performed by employing the two-level model [9a, 25]:

$$\beta \approx \frac{3e^2\hbar^2}{2m} f\Delta\mu_{ge} F(\omega) \qquad (5.4)$$

with the dispersion factor, $F(\omega)$, given by

$$F(\omega) = \frac{\omega_{ge}}{(\omega_{ge}^2 - \omega^2)(\omega_{ge}^2 - 4\omega^2)} \qquad (5.5)$$

for ω=0 5.4 becomes

$$\beta_0 \approx \frac{3e^2\hbar^2}{2m\omega_{ge}^3} f\Delta\mu_{ge} \tag{5.6}$$

Combination of 5.4 and 5.6 leads to

$$\beta = \beta_0 \frac{(\omega_{ge}^4)}{(\omega_{ge}^2 - \omega^2)(\omega_{ge}^2 - 4\omega^2)} \tag{5.7}$$

In the above equations, ω_{ge} is the lowest-energy transition, being related to λ_{max}^{-1}, ω is the fundamental frequency (1064 nm), *e* and *m* are the electronic charge and mass, respectively, *h* is Planck's constant, *f* the oscillator strength and $\Delta\mu_{ge}$ the difference between ground- and excited-state dipole moment, accompanying ω_{ge}.

5.3 Results and discussion

5.3.1 Reference method

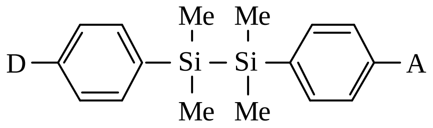
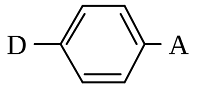
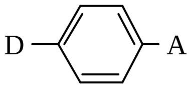
The HRS method can only determine a ratio between the solvent hyperpolarizability and that of the solute molecules. In order to use the HRS technique, it is therefore necessary to have a reference material with a known hyperpolarizability. We have used the value of chloroform, determined by the EFISHG method ($CHCl_3$: $\beta = -0{,}49\ (\pm 0.05) * 10^{-30}$ esu) [26] to calculate the first hyperpolarizability of *p*-nitroaniline (*p*NA). With the internal reference method (IRM), in which the slope and intercept of the number density-quadratic coefficient (ND-QC) plot are used to determine β, we have found several values for *p*NA from independent measurements: 23, 33.2 and 40.1 (10^{-30} esu). The differences are due to changes in the instrumental factors, since the measurements have been performed under different HRS-setup conditions. For this reason the β values obtained by different sets of measurements, are all referenced to a *p*NA value of $23 * 10^{-30}$ esu by multiplying with the appropriate factors. Previously reported β values of *p*NA determined with HRS are found in the same range: 23, 32 and 38 (10^{-30} esu) [10a, 27, 28]. Published values obtained by EFISHG vary from $8.6 * 10^{-30}$ (frequency-independent, $CHCl_3$) [29], $16.9 * 10^{-30}$ (1064 nm, *p*-dioxane) [30] and $34.5 * 10^{-30}$ esu (1064 nm, MeOH) [25]. Therefore, when comparisons are made with β values determined by EFISHG, the fundamental frequency and solvent used should be given. The solvent is an important parameter, since it has been shown that the first hyperpolarizability of *p*NA is solvent-dependent, due to a change in the wavelength of the absorption maximum with the polarity of the solvent [29]. The *p*NA value of $23 * 10^{-30}$ esu that we use as a reference gives a static (ω=0) value, β_0, of $11.8 * 10^{-30}$ esu (corrected for absorption at 348 nm in chloroform).

5.3.2 Donor and acceptor substituent effects on the hyperpolarizability, β

In Table 5.1 the β values of the various DσA-compounds and fragments thereof are presented. These values are obtained by comparison of the slopes of the number density-quadratic coefficient (ND-QC) plot of the DσA-compound and that of *p*NA. In Figures 5.2 and 5.3 the β values are presented as (ND-QC) plots for the dicyanovinyl- and the perfluorobutylsulfonyl-acceptor series respectively. The correlation coefficients of the (ND-QC) plots all lie in the range of 0.97 to 0.999, a result which is much better than that found for older sets of measurements that were referenced to *p*NA after several complete concentration series had been measured (r = 0.7-0.99). In spite of the different reference techniques, a fairly good reproducibility of the ratio $\beta_{(compound)}/\beta_{(pNA)}$ is observed, especially for the dicyanovinyl-acceptor compounds (uncertainty about 10%); molecules with lower β values are somewhat less reproducible. Within one measurement series, however, the error in β is small and varies from 5-10%; the observed trends are from β values obtained by measurements with the same HRS-setup conditions and cannot be compared directly with those from a different HRS-setup. The β values presented in this chapter should therefore not be regarded as absolute values.

The highest β values are found for molecules having the dicyanovinyl-acceptor, which is one of the strongest acceptors known [31]. The Me_2N-donor-

Table 5.1. *Experimental β values (10^{-30} esu) of DσA-compounds and fragments thereof measured by HRS at 1064 nm*[a].

							
A\D	Me_2N	MeS	MeO	F	H	Me_5Si_2	Me_3Si
$CH=C(CN)_2$	190	68	62	63		58	18
$SO_2C_4F_9$	24	12	11		8	7	3
SO_2Ph	21						
CF_3	14	10					
H	10						
$SO_2C_4F_9$	20				4		
Me_5Si_2	11						
Me_3Si	6						

a) β_{HRS} values are based upon a reference value of *p*NA: 23 ∗ 10^{-30} esu; the relative error in β is 5-10%.

and $CH=C(CN)_2$-acceptor-substituted compound has the largest nonlinear optical response of all DσA-compounds presented. This value is smaller than that of the analogous stilbene: β_0 is 81 ∗ 10^{-30} esu for the disilane vs. 133 ∗ 10^{-30} esu for the stilbene (DMSO; $\beta_0 = 9 * 10^{-30}$ esu for *p*NA [32]), but is larger than that of 4-N,N-dimethylamino-4'-nitrostilbene (DANS), a frequently used reference compound, having a β_0 value of 55 ∗ 10^{-30} esu ($CHCl_3$, λ_{max} = 427 nm; β_0 of *p*NA = 7.6 ∗ 10^{-30} esu (acetone) [3a]). The values for the perfluorobutylsulfonyl-acceptor compounds are much lower, but the order in which they depend on the donor substituent is the same for either acceptor and agrees with the usual trends found for disubstituted benzenes and stilbenes [2, 3]. The large β values observed for the dicyanovinyl-acceptor compounds are due to the extension of the π-system by the dicyanovinyl group, which enlarges the conjugation path beyond the diphenyldisilane structure. This results in a far more red-shifted absorbance than observed for the perfluorobutylsulfonyl-acceptor compounds. The latter acceptor is a strong inductive electron attractor (no enlargement of the conjugated π-system) and has an acceptor strength exceeding that of the nitro group, while offering a better transparency [4]. The highly polar character of the perfluorobutylsulfonyl group results in large dipole moments of NLO compounds having this acceptor, which is of great importance for electric field orientation in e.g. a polymer matrix. In the next paragraphs we will discuss the results on the dicyanovinyl- and sulfonyl-acceptor series in more detail.

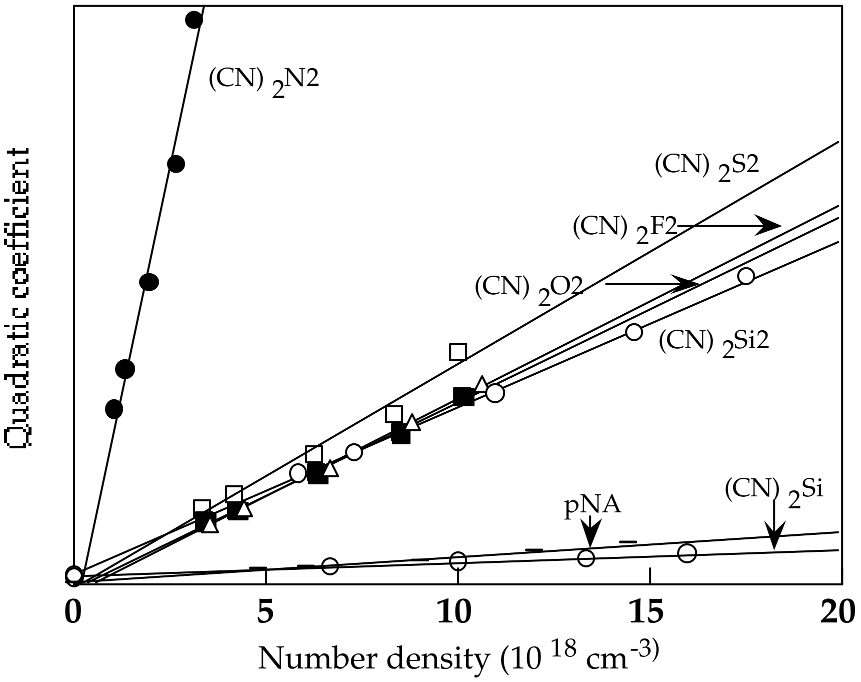


Figure 5.2. *Number Density-Quadratic Coefficient (ND-QC) plots for dicyanovinyl-acceptor compounds*

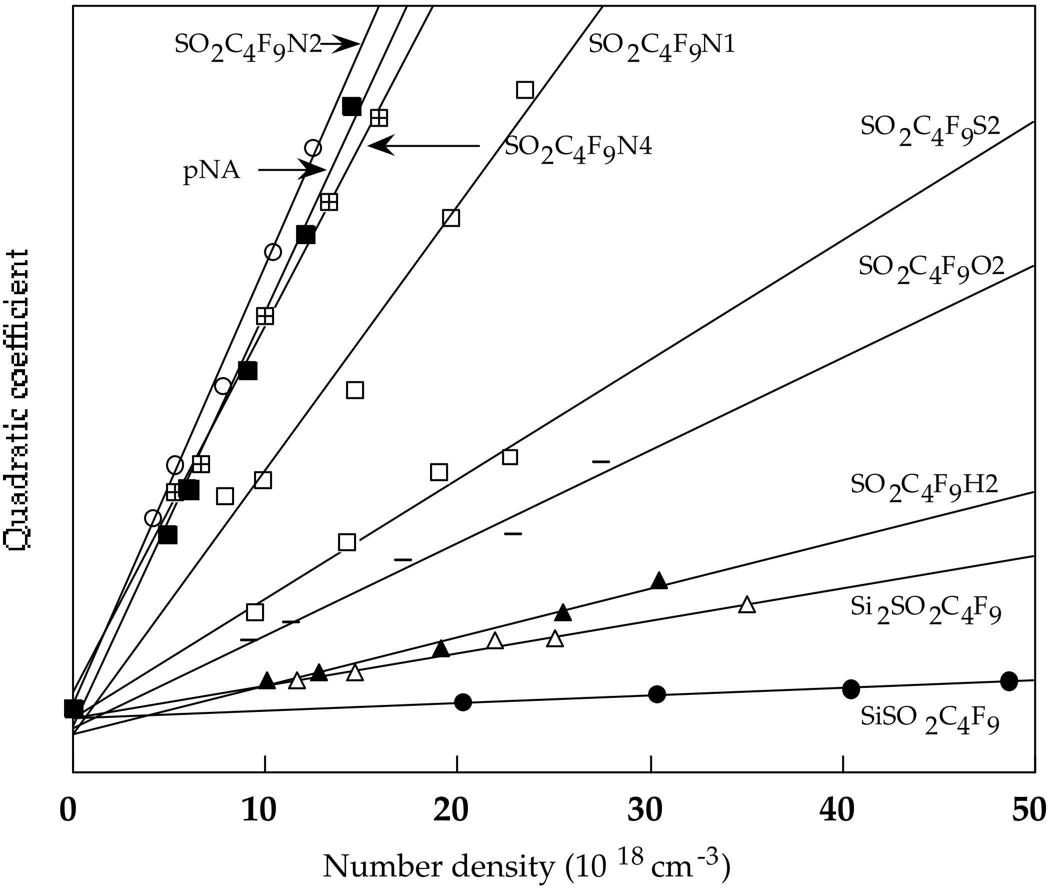


Figure 5.3. *Number Density-Quadratic Coefficient (ND-QC) plots for sulfonyl-acceptor compounds*

The CF_3-acceptor, which is mainly inductive in character but less strong than the perfluorobutylsulfonyl-acceptor (σ_p = 0.55 and 1.1 resp., Ch. 3), gives rise to lower β values.

The relative effectiveness found for the various donors is F ≈ MeO < MeS < Me_2N. A reverse order for the MeO and MeS donors has been reported by Cheng et al. for *p*-nitrostilbenes [3a], while Barzoukas presented the same order as in our work [2]. However, the differences are small and lie probably within the experimental error range. The donor strength of the fluorine substituent is found to be almost equal to that of the methoxy group. This suggests that the mesomeric (resonance) effect of the fluorine substituent contributes more to β than the inductive effect does, since the latter is large for F and would make it an electron acceptor (see Chapter 3 for substituent constants).

5.3.3 Dicyanovinyl-acceptor compounds

In Table 5.2 the β and β_0 values of the dicyanovinyl-acceptor compounds are presented, together with the wavelength (λ_{max}) that has been used for the dispersion correction and the β_0 values obtained by EFISHG [8c,e].

Table 5.2. *β values (10^{-30} esu)[a] and lowest-energy transitions, λ_{max}[b], of dicyanovinyl - acceptor compounds[c].*

compound	β (1064 nm)	β_0	λ_{max} (nm)	β_0 EFISHG [d]
$(CN)_2N2$	190	(106) 81	(329) 380	16
$(CN)_2S2$	68	36	339	-
$(CN)_2O2$	62	33	337	22
$(CN)_2F2$	63	34	335	9
$Si_2(CN)_2$	58	32	333	9
$Si(CN)_2$	18	10	318	9

a) The relative error in the β_{HRS} values is 5-10%. b) λ_{max} denotes the absorption maximum of the prominent lowest-energy transition determined in cyclohexane. c) Notation of compounds as in Chapter 2. d) measured by Mignani et al. [8c,e] in acetone.

In the two-level model, one dominant excited state, usually the intramolecular charge-transfer (ICT) lowest-energy state, is assumed to contribute mostly to β. In UV-Vis spectra of DπA-molecules this transition can be observed easily, since it usually exhibits a large oscillator strength. For the silanyl-based DσA-compounds this is less obvious. It is therefore difficult to find the absorption frequency to be used in the dispersion correction. For all dicyanovinyl-acceptor compounds, except the Me_2N-donor one, the high-intensity, lowest-energy transition at 320-340 nm is used for the dispersion correction. For $(CN)_2N2$ the low lying CT-transition, observed at 380 nm with a low intensity and lying as a shoulder on a high intensity transition at 329 nm, is used for the correction. The large β_0 found for this compound cannot, however, be the result of this CT absorption only. If the two-level model were adequate, a cubic dependence of β on λ_{max} should be observed: $\beta \approx (\lambda_{max})^3 f \Delta\mu$. The ratio of $(\lambda_{max})^3$ -values for $(CN)_2N2$ over $(CN)_2S2$ is about 1.5, while the ratio of β_0-values is 2.2. The oscillator strength, f, at λ_{max} of $(CN)_2N2$ (380 nm) is a factor 6.5 smaller than that at λ_{max} of $(CN)_2S2$ (339 nm). The large difference in β can then only be achieved if Δμ for $(CN)_2N2$ is about one order of magnitude larger than Δμ for $(CN)_2S2$, which seems very unlikely. Clearly, contributions to β from higher excited states must be considered, which will be shown later in this chapter to be of great importance.

The relation between λ_{max} and β of the dicyanovinyl-acceptor compounds is presented in Figure 5.4. A sharp increase in β and λ_{max} is observed when the Me_3Si-donor is replaced by Me_5Si_2. However, when a D-phenyl group is substituted at the disilanyl unit, in which D = MeS, MeO or F, we see only a small increase in β and λ_{max}. This indicates that the local transitions in these D-phenyl groups make a minor contribution to β for the dicyanovinyl-acceptor compounds and that the D-phenyldisilanyl moiety as a whole has the same donor efficiency as the pentamethyldisilanyl unit. Even a large red shift of the local donor-phenyl absorption (about 30 nm from MeO to MeS) does not substantially alter β. This makes the disilanyl unit a donor on dicyanovinylbenzene instead of a σ-conjugating bridge between two phenyl rings. The predominant transition determining β is therefore from the disilanyl unit to the dicyanovinyl-acceptor.

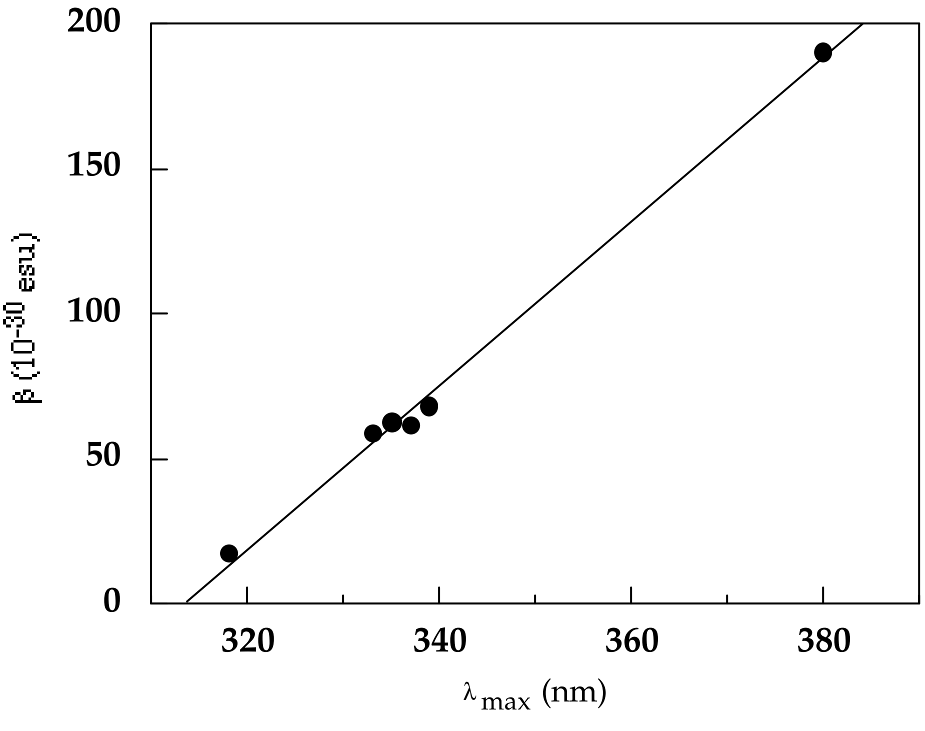


Figure 5.4. β *vs.* λ_{max} *of dicyanovinyl-acceptor compounds.*

Our findings for the dicyanovinyl-acceptor compounds do not correspond to the results obtained by Mignani et al. (Table 5.2). These authors have presented much lower β values and found the methoxy donor to be stronger than the dimethylamino one. This result has been attributed by them to a saturation of the electronic transmittance ability of the disilanyl bridge for the latter compound. We do not have any evidence for this phenomenon; in fact, we report a low lying ICT for the Me_2N-substituted compound, which is not observed for the MeO analogue, and a significantly larger β for the former compared to the latter.

Another striking difference between our findings and theirs is that we have found a larger β value for $Si_2(CN)_2$ than for $Si(CN)_2$, while they report similar hyperpolarizabilities. They propose that the ICT is restricted to the Si-Ph-CH=$C(CN)_2$ part of the molecule and that weakly donating groups such as Me_3Si or D-$PhSiMe_2$ (D is a weak donor) do not alter the ICT significantly and also that the silanyl bridge cannot be considered as a polarizable electron connection between two phenyl rings. Our results are much more consistent with the fact that the Me_5Si_2 group is a stronger (resonance) donor than the Me_3Si group, due to a larger hyperconjugation ((σ-π)-conjugation) from the (Si-Si) σ-bond of the former with the aromatic π-electrons compared to that from the (Si-C) σ-bond of the latter [33].

The fact that the hyperpolarizability of $Si_2(CN)_2$ (β_0 = 32 $*$ 10^{-30} esu) is of the same order as that of $Me_2NPhCH{=}(CN)_2$ (β_0 = 24.5 $*$ 10^{-30} esu referenced to *p*NA: β_0 = 7.6 $*$ 10^{-30} esu in acetone [3a]) indicates that the disilanyl-group has a donor strength similar to that of the dimethylamino-group (in combination with this acceptor) and confirms the strong resonance interaction of the disilanyl-donor with the aromatic π-system.

A major difference between our measurements and those by Mignani et al. is that we have used HRS, while they have used EFISHG. The EFISHG-determined β is a vectorial projection of the hyperpolarizability tensor along the molecular dipole direction denoted as β_μ. Possibly, the dipole moments of $Si(CN)_2$ and $Si_2(CN)_2$ lie in the direction of the -Ph-CH=$C(CN)_2$ dipolar axis, due to a large dipole moment contribution from the Ph-CH=$C(CN)_2$ part (4.8 D) [3a] Substitution of the Me_3Si-donor by a Me_5Si_2-donor alters the direction and magnitude of the charge transfer responsible for β, but does not significantly alter the projection of the hyperpolarizability on the direction of the dipole moment and will therefore give about similar β_μ values [8c, e].

It is clear that care must be exercised when comparing β values obtained by techniques that measure different quantities.

5.3.4 Perfluorobutylsulfonyl-acceptor compounds and fragments

Table 5.3 lists the values of hyperpolarizabilities β (10^{-30} esu) and lowest-energy transitions, λ_{max} (used for the dispersion correction), both experimentally and computationally determined, of perfluorobutylsulfonyl-acceptor DσA-compounds and fragments of the Me_2N-donor- and $F_9C_4SO_2$-acceptor-substituted diphenyldisilane, $SO_2C_4F_9N2$. Also the calculated (ZINDO) ground-state dipole moments, μ, and the difference between ground and first excited state, $\Delta\mu_{ge}$, (accompanying the lowest-energy transition) are presented.Evidently the trends of the calculated and experimental series are similar, the only discrepancy being $Me_3SiPhNMe_2$ (SiN), for which the β value has been calculated to be as large as that of the analogous disilane, while experimentally this value is much lower. Remarkable is the fact that the decrease in β, when $PhSO_2C_4F_9$ is substituted with a Me_3Si group, has been demonstrated both experimentally and computationally.

Figure 5.5 presents the experimental β values *vs.* the computational ones for the perfluorobutylsulfonyl-substituted compounds. A good linearity is observed, but the MeS- and MeO-donor-substituted disilanes, $SO_2C_4F_9S2$ and $SO_2C_4F_9O2$ respectively, are calculated somewhat high. The absolute values, however, cannot be compared directly, since the experimental series has been somewhat arbitrarily referenced to a *p*NA value of $23 * 10^{-30}$ esu. Furthermore, the λ_{max} values for the acceptor-containing fragments are not very well reproduced by the calculations.

The largest β value of the sulfonyl-acceptor series is found for $SO_2C_4F_9N2$, which is almost equal to that of *p*NA ($24 * 10^{-30}$ *vs.* $23 * 10^{-30}$ esu respectively), while its transparency is much better (*p*NA in CH_2Cl_2: λ_{max}= 350 nm). The phenylsulfonyl-acceptor compound, SO_2PhN2, has a β value which is only a little lower than that of the perfluorobutylsulfonyl analog ($21 * 10^{-30}$ *vs.* $24 * 10^{-30}$ esu), but it has a lower dipole moment (7.2 vs. 9.7 D) and will therefore be less efficient for Electric Field Induced orientation. However, the lower costs of synthesis i.e. lower costs of sulfonyl starting materials and a higher synthetic yield for SO_2PhN2 (less dimeric byproducts; see Chapter 2), make this compound also attractive for functionalization and incorporation into polymer matrices. The experimental β_0 value of $Me_2NPhSO_2C_4F_9$ ($13 * 10^{-30}$ *vs.* $12 * 10^{-30}$ esu for *p*NA) perfectly matches that of $Et_2NPhSO_2C_4F_9$ ($7.8 * 10^{-30}$ *vs.* $7.6 * 10^{-30}$

esu for *p*NA), previously reported [4], which permits us to compare the absolute β values with those of analogous π-conjugated molecules, having a fluorinated alkylsulfonyl-acceptor, taking into account a factor 1.5 for *p*NA. The experimental β_0 values of $SO_2C_4F_9O2$ and $SO_2C_4F_9N2$ are a factor 1.5 - 2.5 smaller than those of the analogous biphenyls and stilbenes; the lowest energy transitions of the π-conjugated compounds are red shifted, however, compared to those of the disilanes (up to 70 nm for the MeO-stilbene analog) [4]. A concrete answer to the question whether the disilanyldiphenyl conjugation path

Table 5.3. *Values of hyperpolarizabilities,* β *(10^{-30} esu)*[a]*, dipole moments,* μ *(D), and lowest-energy transitions,* λ_{max} *(nm)*[b]*, of perfluorobutylsulfonyl-acceptor compounds and fragments thereof*[c]*.*

	Experimental			Calculated by ZINDO				
compound	β	β_0	λ_{max}	β	β_0	μ	$\Delta\mu_{ge}$	λ_{max}
SiN	7	5	265	11	8	2.4	5.4	260
Si_2N	11	7	270	10	7	2.6	7.7	265
HN2	10	7	272	11	7	2.0	7.5	268
$SO_2C_4F_9N2$	24	15	300	22	15	9.7	15.7	277
							25.4	233
$SO_2C_4F_9S2$	12	8	285	17	12	6.9	11.0	259
$SO_2C_4F_9O2$	11	7	277	14	10	7.8	12.6	260
$SO_2C_4F_9H2$	8	5	276	9	6	7.7	11.6	255
$Si_2SO_2C_4F_9$	7	5	267	4	2.	6.6	12.1	251
$SiSO_2C_4F_9$	3	2	235	1	1	6.6	11.9	247
$PhSO_2C_4F_9$	4	3	222	2	1	6.6	11.7	249
$NPhSO_2C_4F_9$	20	13	303	18	1	9.6	14.4	312
SO_2PhN2	21	13	300	16	11	7.2		

a) The relative error in the exp. β_{HRS} values is 5-10%; b) λ_{max} denotes the absorption maximum of the lowest energy transition (not necessarily the highest intensity transition) determined in cyclohexane; c) Notation of compounds as in Chapter 2.

gives a better nonlinearity-transparency trade-off than the stilbene one can however not be given yet.

The increase of β, when $Si_2SO_2C_4F_9$ is substituted with a (donor-substituted) phenyl ring is remarkably higher than observed for the dicyanovinyl-acceptor compounds (at least 20% for the sulfonyl *vs.* 5% for the dicyanovinyl). This means that the higher energy contributions to β, arising from transitions in the donor-phenyl ring, are significantly larger for the perfluorobutylsulfonyl-acceptor series. The contribution of the donor- and acceptor-substituted parts to the total hyperpolarizability of the DσA-molecule will be discussed in terms of the additivity model presented next.

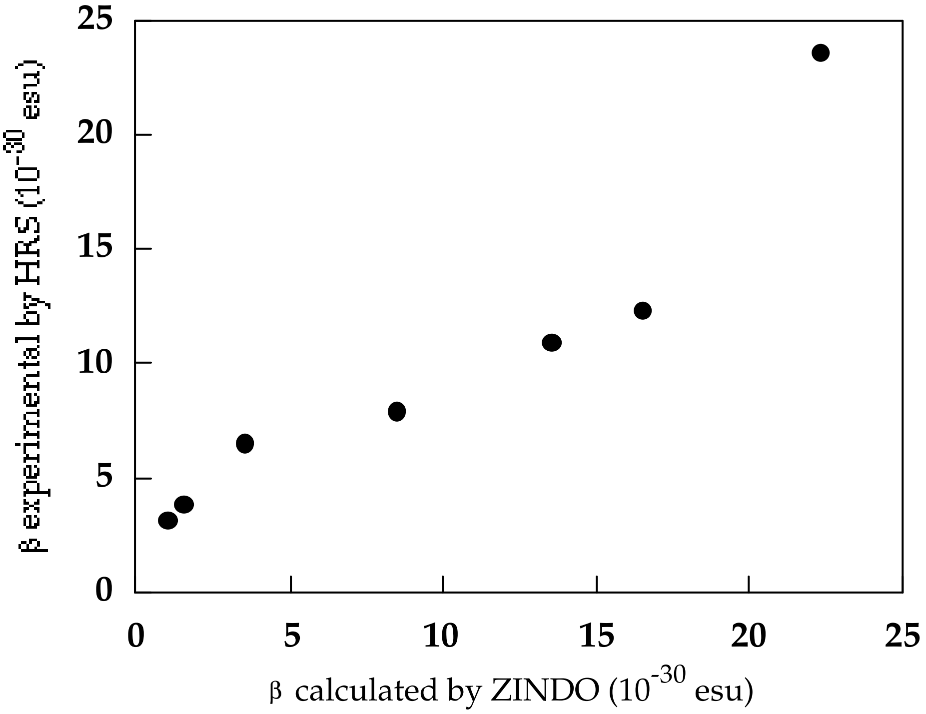


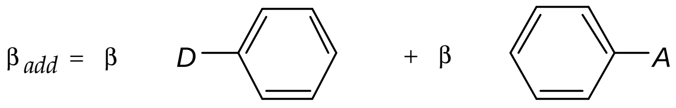
Figure 5.5. *Experimental vs. computational β values of perfluorobutylsulfonyl-acceptor (silanyl) compounds.*

In the simplest approximation , β is considered to be a sum of two contributions [30]:

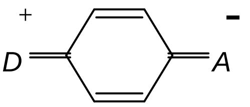
$$\beta = \beta_{add} + \beta_{ct} \tag{5.8}$$

β_{add} is due to the independent (inductive) substituent effect that induces asymmetry in the conjugated system; β_{ct} is the Intramolecular Charge Transfer

(ICT) contribution due to the resonance interaction of donor and acceptor substituents. For example in *p*-disubstituted benzenes



and β_{ct} is determined by the resonance contribution of



To achieve a high nonlinearity, β_{ct} and/or β_{add} can be increased. In π-conjugated systems, β_{ct} usually gives the largest contribution to β (e.g. β_{ct} of *p*NA is calculated to be 75% of the total β) [28]. A large value of β_{ct} can be obtained by substitution with mesomeric donor and acceptor groups or by varying the structure and increasing the length of the conjugating bridge. These approaches, however, are in conflict with the requirements of transparency. The introduction of a strong inductive electron attractor, such as the perfluorobutylsulfonyl-acceptor, will increase β_{add} while the transparency is retained.

Table 5.4 presents the experimental (dispersion-corrected) β values of some DσA-compounds together with those of the fragments that they consist of and several β_{add} values calculated by addition of the fragment nonlinearities. There are several ways of calculating β_{add} for our silanyl-bridged systems. Mignani has reported that β of $(CN)_2N2$ consists of the sum of the separate donor and acceptor monosilyl benzene nonlinearities,

$$\beta = \beta_{add} = \beta\ (Me_2NPhSiMe_3) + \beta\ (Me_3SiPhCH{=}(CN)_2)$$

where β is the projection on the permanent dipole moment, μ_{add}, defined as the vector sum of the dipole moments of each subunit [8d]. This type of addition would lead, based on our results, to a very large CT contribution to the total β value.

An alternative method is the addition of the hyperpolarizability contributions induced by the donor and acceptor substituents on the conjugated system as a whole:

$$\beta_{add} = \beta\ (DPh\text{-}SiSi\text{-}Ph) + \beta\ (Ph\text{-}SiSi\text{-}PhA)$$

Using this method of additivity, the total hyperpolarizability, β, of the perfluorobutylsulfonyl-acceptor compounds is found to be mainly determined by β_{add}. Another alternative is to calculate β_{add} by summation of the two disilanyl-substituted donor and acceptor benzenes, Si_2N and $Si_2SO_2C_4F_9$, to eliminate the extra contribution to β of the local transition in the unsubstituted phenyl ring. This method seems better, because the addition of the UV-Vis absorption spectra of Si_2N and $Si_2SO_2C_4F_9$ gives a spectrum which is almost identical to that of $SO_2C_4F_9N2$. However, the latter has a red-shifted, solvatochromic, low-intensity absorption band (obtained by substracting the spectra of the fragment molecules from that of the whole molecule) not found in the spectrum of either fragment, which has been attributed to an ICT-transition ($\lambda_{max} =$ 315 nm in cyclohexane). This red shift might be responsible for the difference between β_{add} and $\beta_{D\sigma A}$, which is β_{ct} and amounts to 20% of β, as a

Table 5.4. *Additive hyperpolarizabilities, β_{add} (10^{-30} esu), of DσA-fragments.*

Fragments of $Me_2NPh(SiMe_2)_2PhSO_2C_4F_9$			β_{add}	$\beta_{D\sigma A}$
$Me_2NPhSiMe_3$	+	$Me_3SiPhSO_2C_4F_9$	5 + 2 = 7	15
$Me_2NPhSi_2Me_5$	+	$PhSO_2C_4F_9$	7 + 3 = 10	15
$Me_2NPhSi_2Me_5$	+	$Me_5Si_2PhSO_2C_4F_9$	7 + 5 = 12	15
$Me_2NPh(SiMe_2)_2Ph$	+	$Ph(SiMe_2)_2PhSO_2C_4F_9$	7 + 5= 12	15

Fragments of $Me_2NPh(SiMe_2)SO_2C_4F_9$				
$Me_2NPhSiMe_3$	+	$Me_3SiPhSO_2C_4F_9$	5 +2= 7	12
$Me_2NPhSiMe_3$	+	$PhSO_2C_4F_9$	5 + 3 = 8	12

Fragments of $DPh(SiMe_2)_2PhCH=C(CN)_2$				
$Me_2NPhSiMe_3$	+	$Me_3SiPhCH=C(CN)_2$	5 + 10 = 15	81
$Me_2NPhSi_2Me_5$	+	$Me_5Si_2PhCH=C(CN)_2$	7+ 32 = 39	81
$MeSPhSi_2Me_5$	+	$Me_5Si_2PhCH=C(CN)_2$	x + 32	36

result of the interaction of the Me_2N-donor through the disilanyl bridge with the perfluorobutylsulfonyl-acceptor .

In $SO_2C_4F_9N2$, the donor fragment, Si_2N, contributes most to the molecule's hyperpolarizabilty (about 60% of β_{add}). The major contributions to β of other donor-sulfonyl compounds (D = MeS, MeO and H) arise from the perfluorobutylsulfonyl-acceptor part, however (Table 5.3).

Hence, although the intensities of the perfluorobutylsulfonyl-phenyl ring transitions are quite low compared to those of the donor-phenyl ring, they do make significant contributions to β of the DσA-compounds, since, in the first place, they occur at a frequency of the same order as that of the mesomeric-determined Me_2NPh-transition (due to the large inductive contribution of the sulfonyl-acceptor) and secondly, the change in dipole moment, $\Delta\mu_{ge}$, from ground to excited state, is quite large (11-12 D).

It has been shown in the previous section that $\Delta\mu$ is one of the parameters that determine β in the two-level model. This parameter might also (partly) cause the large differences in β observed for the MeS and Me_2N-donor compounds, since both position (λ_{max}) and intensity (f), the other two important parameters in the two-level model, of the MeSPh- and Me_2NPh-transitions are almost equal (experimentally), while the calculated value of $\Delta\mu_{ge}$ is much lower for the MeS-donor compound (11.0 *vs.* 15.7 D).

The additivity of the disilanyl donor and acceptor fragment spectra has also been demonstrated for the dicyanovinyl-acceptor compound, $(CN)_2N2$, which has an additional low-energy CT-absorption band. This compound is the only one in our series which has a considerable charge-transfer contribution to β (about 50%). The other half of β is attributable to β_{add}, from which the major part (80%) arises from the disilanyl acceptor fragment, $Si_2(CN)_2$. Compounds with other donors (MeS, MeO and F) do not show an ICT-absorption and the acceptor fragment contributes most to β, since the donor fragments are expected to have even lower nonlinearities than the Me_2N-donor fragment (e.g. β_0 of $MeSPhSi_2$ = 4). This result confirms our statement that the disilanyl-Ph-dicyanovinyl transition largely determines the magnitude of β, except in the case of the Me_2N-donor compound.

5.3.5 Comparison of experimental and computational results for $SO_2C_4F_9N2$

It has been shown in the previous paragraph, that β of $SO_2C_4F_9N2$ is determined for a large part (60%) by the contribution of excitations in the donor-fragment, Si_2N. Computations of β by means of ZINDO [17, 18] for this DσA-compound and its fragments show similar results [35]. A transition at 277 nm has been found to make the major contribution to β and to present only a partial charge transfer, viz. from the donor to the disilanyl bridge. Calculations have predicted an ICT (from the donor to acceptor group) at 233 nm (with a Δμ of 25.4 D) for $SO_2C_4F_9N2$. The corresponding charge distributions in the excited states have been shown in Chapter 4, Figure 4.6.

The major transitions contributing to β occur from the HOMO to several higher unoccupied molecular orbitals: excitation at 277 nm to the primary accepting (LUMO+2) Si-Si σ*-orbital and a long range charge-transfer occuring at 233 nm being primarily of HOMO-LUMO character. The LUMO comprises both p- and s (σ*)-orbitals in the acceptor tail and the π-system of the ring.

Computations using the Sum-Over-Orbitals (HYPERPOL) [36] approach confirm the above results: transitions from the HOMO account for about 70% of the total β value, mainly due to their large transition dipole moments and large permanent dipole moment differences with the LUMO (π*) and LUMO+2 (σ*). Experimentally, transitions from the donor to a local excited- and CT-state contribute to β for about 70-80% , in agreement with the calculated results.

5.3.6 Calculation of β_{ct} by the two-level model

Using the two-level model (equation 5.1), β_{ct} can be calculated when the transition dipole moment, μ_{ge}, related to the oscillator strength, *f*, the difference between ground and first excited state dipole moment, $\Delta\mu_{ge}$, the absorption angular velocity, ω_{ge}, and the excitation angular velocity, ω, are known. All these parameters can be extracted from the absorption and emission spectra, supplying a simple and fast method to obtain β_{ct}. The oscillator strength, *f*, is related to the transition dipole moment by [1a, Ch. 3]

$$f = 4.7 \times 10^{29} \nu_{max} \left|\mu_{ge}\right|^2 \qquad (5.9)$$

where ν_{max} is the energy of the absorption maximum (cm^{-1}).

The oscillator strength can be determined from the absorption spectrum by the following relation

$$f = 4.38 \times 10^{-9} \varepsilon_{max} \Delta \nu_{1/2} \tag{5.10}$$

where ε_{max} is the molar extinction coefficient and $\Delta\nu_{1/2}$ is the full band width at half height (cm^{-1}). $\Delta\mu_{ge}$ can be calculated from the difference in absorption and emission maxima, as a function of the solvent polarity, a method which has been demonstrated in Chapter 4 for the DσA-compounds CF_3N2, SO_2PhN2 and $SO_2C_4F_9N2$. For these compounds the charge-separated state can be populated by excitation in the local donor-phenyl absorption band followed by internal conversion to the CT-state or by direct excitation in the CT-band. Because a low lying CT-transition is not directly visible in the absorption spectra of the first two compounds, the calculation of β_{ct} by this method will not be possible. For $SO_2C_4F_9N2$ we have observed a low-lying, low intensity ICT-transition at 317 nm by substracting the donor and acceptor fragment spectra from that of the whole molecule. The corresponding value of $\Delta\mu_{ge}$ determined by the solvatochromic method is 40.1 D and gives a value of β_{ct} of 9 $*10^{-30}$ esu, which is about 38% of the total β value (24 $* 10^{-30}$ esu) provided that the absolute values are comparable (Table 5.5). It should be mentioned that the value of $\Delta\mu_{ge}$ is probably calculated too high, because of the large error in the cavity radius (Chapter 4, § 4.4.5). Using the value of $\Delta\mu_{ge}$ (25.4 D) calculated by ZINDO for the ICT-transition and the experimentally determined values of f and ω_{ge}, a β_{ct} value of 6 $*10^{-30}$ esu is calculated, which is about 25% of the total β value .

Table 5.5. β_{ct} *values calculated according to the two-level model with parameters obtained from the absorption and fluoresccence spectra and ZINDO calculations* ($\Delta\mu_{ge}$) *for* $SO_2C_4F_9N2$.

	ε (l mol^{-1}cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	f	$\Delta\mu_{ge}$ (D)	ω_{ge} (10^{15} s^{-1})	ω (10^{15} s^{-1})	β_{ct} (10^{-30} esu)	$\beta_{0(ct)}$ (10^{-30} esu)
exp.	3400	5330	0.078	40	5.94	1.77	9	6
ZINDO				25.4			6	4

The dispersion-corrected values (6 $*$ 10^{-30} esu (exp.) and 4 $*$ 10^{-30} esu (ZINDO)) are somewhat larger than the one obtained from the difference of $\beta_{D\sigma A}$

and β_{add}, which is $3 * 10^{-30}$ esu (Table 5.4). This is not surprising, since the intensity of the ICT-absorption band is borrowed from the local transitions of the donor and/or acceptor part of the molecule, resulting in lower intensities of the "local" transitions [37]. This means that the local excited states occuring in the DσA-compound (D*σA and DσA*) are partly mixed with the CT-state. This mixing of excited states leads to a larger value of $\Delta\mu_{ge}$ (15.7 D), calculated by ZINDO for the transition at 277 nm in $SO_2C_4F_9N2$, compared to that of the donor-fragment, Si_2N (7.7 D).

It has been shown in Chapter 4 that excitation in the local donor-phenyl absorption band leads partly to an internal conversion to the CT-state. So β_{ct} is in fact larger than the contribution of the direct ICT ($D^+\sigma A^-$) state, calculated by the two-level model. For a compound such as $SO_2C_4F_9N2$, for which the local transitions in the donor and acceptor part as well as the ICT-transition contribute to β, at least a four-level model is necessary for calculating β:

$$\beta = \frac{3e^2\hbar^2}{2m}\left[f_1\Delta\mu_1 F(\omega_1) + f_2\Delta\mu_2 F(\omega_2) + f_3\Delta\mu_3 F(\omega_3)\right] \qquad (5.11)$$

The labels 1, 2 and 3 refer to transitions from the ground to the first, second and third excited state, which are the CT-, local donor- and local acceptor-transitions, the latter two not necessarily in that order. However, most DσA-compounds have overlapping absorption bands, which makes it difficult to extract the parameters necessary for the calculation of β from the spectra.

5.3.7 Effect of silicon chain length on the hyperpolarizability, β

Table 5.6 shows the hyperpolarizability values, β, of the Me_2N-donor and $SO_2C_4F_9$-acceptor substituted silanes with increasing silicon-chain length.

Table 5.6. *β values (10^{-30} esu) and lowest-energy transitions, λ_{max}, for $Me_2NPh\text{-}(SiMe_2)_n\text{-}PhSO_2C_4F_9$ with n = 1,2,4* [a].

compound	β	β_0	λ [b]
$SO_2C_4F_9N1$	19	12.	300
$SO_2C_4F_9N2$	24	15	300
$SO_2C_4F_9N4$	22	14	300

a) see notes in Table 5.3; b) low intensity transition overlapping with the major absorption band at 270-275 nm.

There are only minor differences in β with varying silicon-chain length. This is not surprising, since the experimental absorption spectra are very similar in the region of the main absorption peak (270-275 nm) and that of the lowest-energy transition at about 300 nm, as has been shown in Chapter 4. The hexasilane, of which the β value has not been obtained due to low synthetic yields after purification, has an absorption spectrum which is almost identical to that of the tetrasilane and is therefore not expected to have a much larger β value. The β value of the tetrasilane is found to be a little lower than that of the disilane. However, β values of the tetrasilanyl-compound, obtained from previous sets of measurements, are found in a range varying from 22 to 28 $* 10^{-30}$ esu. The levelling-off of β with increasing chain length might be explained by the short range of the effect of the inductive fluorobutylsulfonyl-acceptor, which has already been demonstrated for π-conjugated systems [4]. A typical resonance-type acceptor, such as dicyanovinyl, has been shown, however, to give a large increase in β from the disilane to the hexasilane ($\beta = 22 * 10^{-30}$ *vs.* $38 * 10^{-30}$ esu)) [8b]. Furthermore, the increase of the donating and accepting ability of the silicon chain, bonded to a phenyl ring, has been shown to level off beyond two silicon atoms [35, 38], implying that the local contributions of e.g. Si_2N and Si_4N to β will be similar.

The experimentally found β value for the monosilane, $SO_2C_4F_9N1$, is remarkably higher than would be expected from the additive contributions shown in Table 5.4. Addition of the donor and acceptor fragment absorption spectra gives a spectrum which is almost identical to that of the DσA-compound (Ch. 4), although the latter is somewhat red-shifted. An increased conjugation (red-shift of λ_{max}) of the donor-fragment transition by introducing a second phenyl ring (from $Me_2NPhSiMe_3$ to $Me_2NPh(SiMe_2)PhBr$) has been demonstrated in Chapter 4. This effect will probably result in a significantly larger β value of the $Me_2NPh(SiMe_2)Ph$ fragment compared to that of $Me_2NPhSiMe_3$, resulting in a larger value of β_{add} for $SO_2C_4F_9N1$ than given in

Table 5.4. However, the difference between β_{add} and $\beta_{D\sigma A}$ must be attributed partly to an ICT-contribution, arising from the low-intensity, solvatochromic transition observed at 308 nm in cyclohexane (obtained by substracting the fragment spectra from the spectrum of the whole molecule). The quite large β value of the monosilane can be the result of a better transmitting capability of the monosilyl conjugating bridge compared to the disilanyl bridge, even though the angle between the conjugating phenyl rings is approximately 109°, due to an sp^3 hybridization of the Si atom. The disilanyl-bridged compound has a *trans*-geometry (see the crystal structure of this compound in Chapter 2), which is a favourable configuration for the (hyperconjugative) interaction of the disilanyl moiety with the aromatic rings. The geometry is therefore the most important factor regarding the β value for the disilane, while for the monosilane it is the transmitting ability of the silicon bridge.

5.3.8 Acceptor-dependency of the hyperpolarizability, β, for compounds with the structure $Me_2NPh\text{-}(SiMe_2)_2\text{-}PhA$

In Table 5.7 the β values of compounds with the structure $Me_2NPh\text{-}(SiMe_2)_2\text{-}PhA$ are presented. The values are obtained with an older reference method (see Experimental) and are not directly comparable to those in Table 5.1. Although the compounds are all transparent above 360 nm, their β values are different. In this series, the CHO-acceptor compound has the highest β value, because of its strong resonance character and the high extinction coefficient of the absorption maximum at 273 nm (ε = 36000 *vs.* 24000 for the CF_3-acceptor). This absorption band contains excitations in both donor and acceptor part of the molecule similar to the case of the perfluorobutylsulfonyl-acceptor compounds. For CF_3N2, the acceptor-phenyl ring transition occurs at much higher energy and has a lower intensity, resulting in a much lower β value compared to those of the aldehyde- and sulfonyl-acceptor compounds. Because the Me_2N-phenyl ring transitions are found at about the same frequency for all compounds, the differences in β must be caused by the various acceptor contributions (due to intensity and/or energy differences).

The dimeric compound, $(Me_2NPh\text{-}(SiMe_2)_2\text{-}Ph)_2\text{-}SO_2$, has a β value which is about 1.5 times larger than the "monomer", SO_2PhN2. The presence of a second donor-phenyl moiety, in combination with only one acceptor group, and a different geometry (Λ-shaped) than the other DσA-compounds, result in a β value which is lower than twice the value of the monomer.

Table 5.7. *β values (10^{-30} esu) [a] of compounds with the structure $Me_2NPh(SiMe_2)_2PhA$*

A	CHO	$SO_2C_4F_9$	SO_2Ph	SO_2dim^b	CF_3
β	19	15	12.	18	10
$\lambda_{max}{}^c$	300	300	300	300	273

a) reference value of 23 $*$ 10^{-30} esu for *p*NA; β values are not directly comparable to those in Table 5.1; b) SO_2dim = $(Me_2NPh\text{-}(SiMe_2)_2\text{-}Ph)_2\text{-}SO_2$.; c) λ_{max} values of 300 nm refer to low-intensity transitions partly overlapping with the major absorption band at about 270-274 nm.

5.3.9 Nonlinearity-transparency trade-off

It has been shown by various authors that there exists a nonlinearity-transparency trade-off for NLO-chromophores [2, 3, 6]. This means that an increase in β is accompanied by a red shift of the absorption maximum (CT band), the effect being dependent on the type of conjugating bridge: stilbenes, for instance, show a more favourable nonlinearity-transparency trade-off (higher nonlinearity for a given λ_{max}) than benzenes. If the two-level model were adequate, a cubic dependence of β on λ_{max} should be observed. No strict relationships have been formulated, however, since quadratic, cubic, quartic and even higher order dependencies of β on λ_{max} have been found so far [2, 3, 6].

For the silicon-bridged compounds we also have found several relationships between λ_{max} and β, for instance for the dicyanovinyl-acceptor compounds a linear relation (r = 0.98) is shown in Figure 5.3. For the perfluorobutylsulfonyl-acceptor compounds presented in Table 5.3, clearly there exists a nonlinear correlation between λ_{max} and β. For these DσA-compounds there are significant contributions of higher-energy transitions to the magnitude of β. To make a comparison, however, of the nonlinearity-transparency ratios of dicyanovinyl- and fluorobutylsulfonyl-acceptor compounds, β_0 is presented as a function of λ_{max} (Figure 5.6).

Obviously, the (disilanyl)dicyanovinyl-acceptor compounds show an increased nonlinearity compared to those of the sulfonyl-acceptor compounds, but with only a minor improvement of the trade-off between β and λ_{max} (shown by an increased slope of the ratioβ_0/λ_{max}). Important factors, however, for frequency doubling applications of an NLO material are the absorbance of the

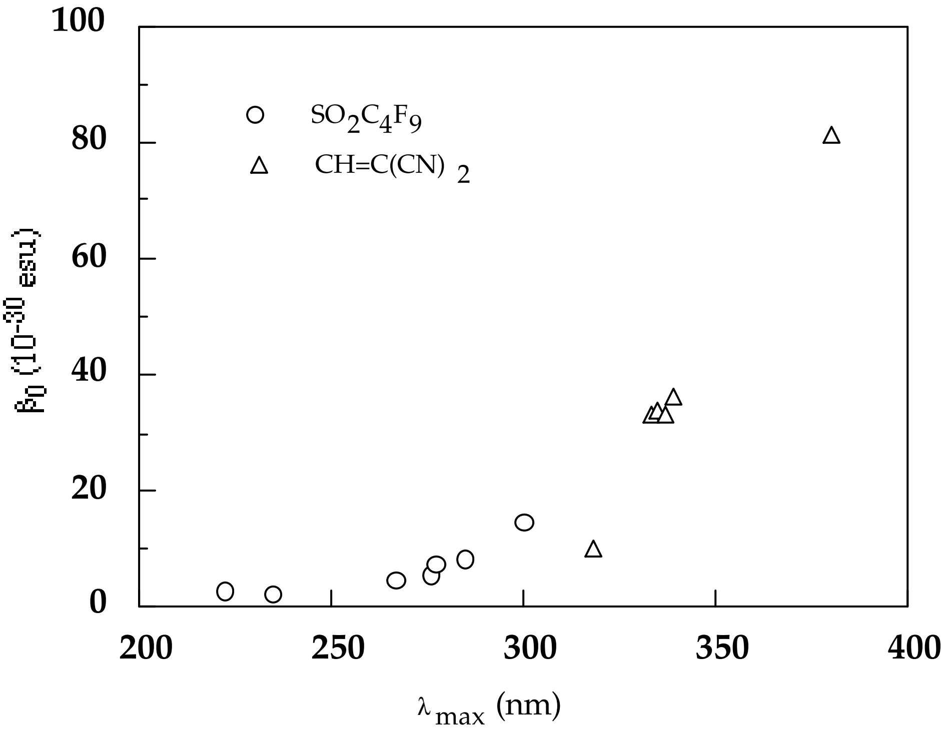


Figure 5.6. *Experimental β_0 values vs. λ_{max} of dicyanovinyl- and sulfonyl-acceptor compounds (from Tables 5.2 and 5.3).*

second-harmonic frequency at the concentration used for the application, which is much larger than the diluted concentrations used for UV-Vis spectroscopy, and the intensity and stability of the second-harmonic signal. These properties are not yet investigated for the DσA-compounds.

5.4 Conclusions

We have studied the nonlinear optical response of a large series of silanyl- bridged donor-acceptor compounds and fragments thereof by the hyper-Rayleigh scattering technique. It has been shown that with this technique the second hyperpolarizability, β , can be measured with an accuracy up to 10% for compounds with β values equal or larger than that of *para*-nitroaniline.

The highest β values are observed for compounds having the dicyanovinyl-acceptor. However, they are less transparent than compounds having the inductive perfluorobutylsulfonyl-acceptor. The effect of the latter acceptor is short-range , which means that an increase of the silicon-chain length above two silicon atoms has only a small effect on β.

The hyperpolarizability of the disilanyl-bridged DσA-compounds has been shown to consist of the additive contributions of the separate disilanyl-acceptor and disilanyl-donor fragment hyperpolarizabilities. In general the ICT-contribution to β is small, except for the dimethylamino-donor- and dicyanovinyl-acceptor-substituted diphenyldisilane, of which the β value is determined for 50% by the direct Intramolecular Charge-Transfer.

Experimental β values have been shown to be fairly well reproduced by theoretical calculations of the INDO/S-type.

The two-level model can be used to calculate the charge-transfer contribution, β_{ct}, but is inadequate for determining the total hyperpolarizibility of DσA-compounds; the donor- and acceptor-fragment contributions to β require that at least a four-level model is employed to calculate β. Because of this, the use of the dispersion correction to obtain a frequency-independent β_0 value is doubtful, since the large contributions to β of the local transitions are corrected by the same factor as that of the lowest-energy transition. Moreover, this correction neglects the intensity of the absorption band and takes only the frequency into account .

Finally, the strongly dipolar character of the perfluorosulfonyl-acceptor DσA-compounds and their transparency in the visible makes this class of compounds promising for incorporation in a polymer matrix.

5.5 References

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