Chapter 1

Introduction

1.1 Nonlinear optics

It was with the advent of the laser in 1960 and the first observation of second-harmonic generation in quartz by P. Franken in 1961, that a period began in which the field of nonlinear optics gained tremendously in interest, due to its potential application in communication and information technology [1]. Several books and reviews have appeared, dealing with the theory of nonlinear optics and the structural characteristics and applications of nonlinear optical molecules and materials [2-10].

Nonlinear optics (NLO) deals with the interaction of electromagnetic fields (light) with matter to generate new electromagnetic fields, altered with respect to phase, frequency, amplitude or other propagation characteristics from the incident field. A major advantage of the use of photonics instead of electronics is the possibility to increase the speed of information processes such as photonic switching and optical computing. One of the most intensively studied nonlinear optical phenomena is second harmonic generation (SHG) or frequency doubling. By this process, near infrared laser light (frequency $\omega$) can be converted by a nonlinear optical material to blue light ($2\omega$). The resulting wavelength is half the incident wavelength and hence it is possible to store information with a higher density. It is obvious that the required properties of the materials depend on the application that they are used for. Traditionally, the materials used to measure second order nonlinear optical behaviour were inorganic crystals, such as lithium niobate ($\text{LiNbO}_3$) and potassium dihydrogenphosphate (KDP). Organic materials, such as organic crystals and polymers, have been shown to offer better nonlinear optical and physical properties, such as ultrafast response times, lower dielectric constants, better processability characteristics and a remarkable resistance to optical damage, when compared to the inorganic materials [9]. The ease of modification of organic molecular structures makes it possible to synthesize tailor-made molecules and to fine-tune the properties to the desired application. In the case of second-order nonlinear optical processes, the macroscopic nonlinearity of the material (bulk susceptibility) is derived from the microscopic molecular nonlinearity and the geometrical arrangement of the NLO-chromophores. So, optimizing a material's nonlinearity begins at the molecular structural level,
which requires a detailed understanding of the origin of and relation between the molecular electronic structure and the induced nonlinear polarization. For this reason, much attention has been paid to the theoretical calculation of the nonlinear optical response by \textit{ab initio} and semi-empirical methods, providing the chemist with the information that indicates which synthetic strategy should be followed [10-14]. In addition, the experimental data obtained from the NLO-characterization of the chromophores can be used to verify and improve computational concepts. The theory of nonlinear optics has been described thoroughly by Chemla and Zyss [4] and by Prasad and Williams [2, 6], and will be shortly summarized.

\textit{Theory of nonlinear optics}

When electromagnetic fields impinge on matter, the charged species in the material (ions or electrons) respond to this field so as to produce an induced polarization, $p_i$. This results in new fields, created by oscillating dipoles within the material. At moderate field strength a linear relationship of the induced polarization with the applied field is observed. At sufficiently intense fields (e.g. laser light), the response becomes nonlinear with the applied field and the relationship can be expressed by a power series expansion in the electric field:

$$p = \alpha E + \beta E^2 + \gamma E^3 + \ldots$$

(1.1)

In this equation, $\alpha E$ is the linear response, where $E$ represents the electrical component of the incident laser light and $\alpha$ the linear polarizability; the second and higher terms represent the nonlinear response, with $\beta$ and $\gamma$ being the first or quadratic and second or cubic hyperpolarizability, respectively. For a macroscopic system this equation can be written as:

$$P = \chi^{(1)} \cdot E + \chi^{(2)} : EE + \chi^{(3)} : EEE + \ldots$$

(1.2)

where $\chi^{(1)}$ (a second-rank tensor) is the first-order susceptibility, $\chi^{(2)}$ (third-rank tensor) is the second-order nonlinear susceptibility, describing the action of two electric field vectors into a polarization, and $\chi^{(3)}$ (fourth-rank tensor) is the nonlinear susceptibility describing third-order processes. When equation (1.2) is written as

$$P = \chi_{\text{eff}} E$$

(1.3)
the nonlinear index of refraction becomes related to the applied electric field, \( E \), through the electric-field-dependent susceptibility, \( \chi_{\text{eff}} \), of a material:

\[
n^2 = \varepsilon = 1 + 4\pi \chi_{\text{eff}} \quad (1.4)
\]

with \( \varepsilon \) being the dielectric constant of the material at optical frequencies. The induced polarization therefore results in a modulation of the refractive index of a material. If one of the acting fields is a static dc-field \( (E_0) \) and the other an optical field, \( E(\omega) \), the polarization at the fundamental frequency \( (\omega) \) will depend on the amplitude of the applied electric field. This is known as the linear electrooptic effect (or Pockels effect), with its magnitude being proportional to \( \chi^{(2)} \). This is the nonlinear optical phenomenon responsible for optical switching [15, 16]. Other second-order nonlinear optical phenomena are sum- and difference-frequency generation (where two different fundamental wavelengths \( (\omega_1, \omega_2) \) interact with each other) and second harmonic generation (SHG) in which the two interacting fields are of the same frequency.

The manifestation of second harmonic generation can clearly be seen by substituting a sinusoidal field into the linear and first nonlinear term of the polarization expansion equation:

\[
P = \chi^{(1)} E_0 \sin(\omega t) + \chi^{(2)} E_0^2 \sin^2(\omega t) + \ldots \quad (1.5)
\]

Since \( \sin^2(\omega t) = \frac{1}{2} - \frac{1}{2} \cos(2\omega t) \), equation (1.5) becomes:

\[
P = \frac{1}{2} \chi^{(2)} E_0^2 + \chi^{(1)} E_0 \sin(\omega t) - \frac{1}{2} \chi^{(2)} E_0^2 \cos(2\omega t) + \ldots \quad (1.6)
\]

Equation (1.6) shows the presence of new frequency components in addition to that having the fundamental frequency \( \omega \): a frequency-independent one (optical rectification), and the \( 2\omega \) contribution.

**Symmetry considerations**

The response of centrosymmetric molecules to an external field is given by \( P(-E) = -P(E) \). This relation expresses the requirement that the induced polarization of centrosymmetric molecules is opposite and of equal magnitude when the field is reversed. In order for equation (1.1) to satisfy this condition, all coefficients of even power of \( E \) (\( \beta, \delta \ldots \)) have to be equal to zero. Hence, only non-centrosymmetric molecules have a non-zero \( \beta \) value, since then \( P(-E) \neq -P(E) \). This is illustrated in Figure 1.1, where the polarization in a
para-disubstituted benzene is larger in the direction from the donor (D) to the acceptor (A) than in the opposite way, since electrons are more easily moved from an electron-rich (donor) to an electron-poor (acceptor) environment.

\[ \delta^+ \quad \delta^- \]

\[ \mu \text{ ind} \]

\[ \pi \]

\[ E \]

\[ \mu \text{ perm} \]

\[ \mu \text{ perm} \]

\[ \mu \text{ ind} \]

\[ \delta^+ \quad \delta^- \]

**Figure 1.1.** Electric-field-induced polarization from donor to acceptor and vice versa in a DπA-molecule.

The requirement of non-centrosymmetry is not restricted to the molecular level, but also applies with respect to the macroscopic nonlinear susceptibility, \( \chi^{(2)} \), which means that the NLO-molecules have to be organized in a non-centrosymmetric alignment.

The first measurements of the macroscopic second-order NLO-susceptibility, \( \chi^{(2)} \), have been performed on crystals without centrosymmetry [4]. However, many organic molecules crystallize in a centrosymmetric way. Other condensed oriented phases such as Langmuir-Blodgett films and poled polymers therefore seem to be the most promising bulk systems for nonlinear optical applications.

**Structural requirements**

Organic molecules that exhibit second-order nonlinear optical properties usually consist of a frame with a delocalized \( \pi \)-system, end-capped with either a donor (D) or acceptor (A) substituent or both. This asymmetry results in a high degree of intramolecular charge-transfer (ICT) interaction from the donor to acceptor, which seems to be a prerequisite for a large second-order nonlinearity [17, 18]. Extensively studied classes of NLO-chromophores of this type are 1,4-disubstituted benzenes and stilbenes [19a-b], from which \( p \)-nitroaniline (\( p \text{NA} \))
and 4-(N,N-dimethylamino)-4'-nitrostilbene (DANS) are prototypical examples (Figure 1.2) [18, 20]:

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{Me}_2\text{N} \\
& \quad \text{NO}_2 \quad \text{NO}_2
\end{align*}
\]

\[p\text{NA} \quad \text{DANS}\]

Figure 1.2. Prototypical examples of nonlinear optical molecules.

The nonlinear part of the induced molecular polarization is the result of the polarizability of the \(\pi\)-electron system. Because of the low mass of electrons compared to that of ions in inorganic crystals, organic molecules can respond to electromagnetic fields with much higher frequencies (up to \(10^{14}\) Hz) [21]. This faster optical response is particularly interesting for applications that depend on the speed of information processing, such as optical switching.

The second-order nonlinearity can be enhanced by using stronger donor and acceptor substituents to increase the electronic asymmetry or by increasing the conjugation length between the substituents. Dulcic and Sauteret [22] were the first to study the substituent effect in \(p\)-disubstituted benzene derivatives and Oudar and LePerson reported about the effect of the conjugation length by using a stilbene instead of a benzene \(\pi\)-system [23]. Since then, many systematic studies have been performed on the structure-property relationship of NLO-chromophores [3, 8, 24-26]. Compounds with conjugating bridges such as tolans [19c, 27, 28] diazo-stilbenes [29, 30], polyenes [31-36], polyphenylenes [37] and with bridges containing heteroaromatic 5- or 6-membered rings such as thiophenes and (thi)azoles [38-42] have been investigated as well as organometallic compounds [43] and calix[4]arenes [44]. From all these investigations, some general features can be noted:

1) The nonlinear optical effect increases with chain length; e.g. \(\beta\) of polyenes increases with a quadratic to cubic dependency on the number of double bonds (\(n\)), levelling off at a value of \(n = 10\) [37, 45, 46].

2) A trade-off exists between nonlinearity and transparency: an increase in \(\beta\) is accompanied by a red shift in the absorption spectrum due to a larger conjugation length and/or stronger donor and acceptor substituents.

3) The type of \(\pi\)-conjugating system determines the trade-off value: polyenes and heteroaromatic-containing \(\pi\)-systems have larger \(\beta\) values than phenyl-
containing π-systems, such as stilbenes, for the same number of double bonds between similar donor and acceptor substituents. This is due to the lack of aromaticity for the former systems, which makes it more easy to reach an energetically favourable quinoid structure upon excitation.

4) β values of polyynes and polyphenylenes are saturated after only three subunits, due to the breaking of conjugation upon extending the chain [28, 37, 47].

5) Instead of optimizing β, it is more efficient to optimize the hyperpolarizability density ρ (ρ = β/molecular volume) which has been shown to level off at a certain maximum when lengthening the conjugation [48].

6) The hyperpolarizability of p,p-disubstituted NLO-molecules consists of additive contributions from the independent substituent effects and of a charge-transfer contribution resulting from the donor-acceptor interaction:

\[ \beta = \beta_{\text{add}} + \beta_{\text{ct}} \]  

The charge-transfer contribution, \( \beta_{\text{ct}} \), is large for DπA-compounds and is roughly related to three molecular quantities [17]:

\[ \beta_{\text{ct}} = f(\Delta \mu)\lambda_{\text{max}}^3 \]  

In this so-called two-level model the induced hyperpolarizability is assumed to be only the result of an excitation from the ground to the first excited state, which is, in the case of DπA-molecules, usually the charge-transfer excitation. β is then dependent on Δμ, the difference between the dipole moment of the ground and first excited state; the oscillator strength, f, which is related to the transition dipole moment, and the wavelength of the transition, \( \lambda_{\text{max}} \). The above-noted features are consistent with the observation of a very large nonlinearity of a julolidinyl-donor- and N,N-diethylthiobarbituric acid-acceptor-substituted polyene (Figure 1.3), for which a \( \mu\beta_0 \) value of almost 15,000 * 10^{-30} esu has been reported and a \( \lambda_{\text{max}} \) value of 680 nm. \( \mu\beta_0 \) is a quantity which can be obtained by the frequently used Electric Field Induced Second Harmonic Generation (EFISHG) method and which represents the cosine product of the molecule’s ground state dipole moment vector with the vectorial contribution of β [2, 18]. The subscript 0 denotes the frequency independency of the hyperpolarizability. The previously given \( \mu\beta_0 \) value is about 40 times larger than that of the frequently used reference molecule, DANS, which has a \( \mu\beta_0 \) value of 360 * 10^{-30} esu at 1064 nm [36].
Most DπA-compounds that show a large nonlinearity are absorbing in the visible spectrum. For an application such as frequency doubling of a red (820 nm) semiconductor laser to provide a compact blue laser source (410 nm) for high-density optical storage, complete transparency in the visible is required. One approach to achieve this property is balancing the inductive and resonance contributions of the donor and acceptor substituents. For example, compounds having a strong inductive electron attractor such as an alkylsulfonyl or perfluoroalkylsulfonyl group have shown an improved nonlinearity-transparency trade-off compared to those with the mesomeric nitro acceptor [49]. Another approach is the synthesis of molecules with a (σ-π)-conjugated frame. This thesis focuses on the synthesis and (non)linear optical characterization of NLO-molecules with the general structure given in Figure 1.4.

![Figure 1.3](image.png)

**Figure 1.3.** Structure of a julolidinyl-donor and N,N-diethylthiobarbituric acid-acceptor-substituted polyene with a very large nonlinearity.

![Figure 1.4](image.png)

**Figure 1.4.** General structure of DσA-compounds synthesized and studied in this thesis.

Compounds with this structure have first been reported by Mignani et al., who described the NLO-characterization of compounds with the dicyanovinyl-acceptor and various donor substituents [50]. In this thesis, similar compounds with various combinations of donor and acceptor substituents will be investigated and emphasis will be put on the characterization of compounds with the perfluorobutylsulfonyl acceptor.

A σ-conjugated silicon backbone is attractive because it offers a better transparency than the fully π-conjugated systems. The silicon atom is more polarizable than an sp³-hybridized carbon atom, which is demonstrated by the
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fact that polysilanes have conjugating properties similar to but weaker than those of polyalkenes [51].

In order to understand the electronic transitions responsible for the nonlinearity of the DσA-compounds, we have synthesized and characterized model compounds, viz. silyl- or disilanylbenzenes, with donor or acceptor substituents in the para position. Furthermore, the experimentally obtained results on the linear and nonlinear optical properties of these ‘fragment’ compounds are helpful in verifying theoretically calculated β values and analysing the excitations occurring in the DσA-compounds.

1.2 Conjugative properties of polysilanes and oligo(phenyl)silanes

σ-conjugation in poly- and oligosilanes

It is well known that polysilanes (SiₙR₂n₊₂) obtain conjugative properties similar to those of π-conjugated polymers, which has been attributed to delocalization of σ-electrons over the silicon backbone [51]. Due to this σ-delocalization these polymers behave as semiconductors and exhibit photoconducting properties upon doping [52, 53]. A detailed description of the bonding and delocalization in polysilanes is presented by Miller and Michl [51]. A schematic presentation of the σ-delocalization in an all-trans conformation of the silicon chain is given in Figure 1.5.

![Figure 1.5. Schematic presentation of σ-conjugation in an all-trans polysilane.](image)

The degree of delocalization is given by β₉ₑ₉/βᵥₑₑ­ with β₉ₑ₉ being the resonance interaction between two (geminal) sp³ orbitals on the same silicon atom and βᵥₑₑ the integral of two overlapping sp³ orbitals on adjacent (vicinal) silicon atoms, that point at each other and are responsible for the σ-bond formation. If this ratio vanishes (β₉ₑ₉ small or βᵥₑₑ large) the localization is strong, while for a ratio of 1, perfect delocalization occurs. The first case resembles π-conjugated systems with a large C-C bond length alternation (BLA), the latter case a system in which all the C-C bond lengths are equal (one silicon
atom corresponds to two carbon atoms in this comparison) [36]. The \( \sigma \)-conjugation is demonstrated by the strong UV-absorption of polysilanes, which has first been reported for oligosilanes by Gilman et al. [54]. They have shown that the polysilane chain itself absorbs UV-radiation with an increasing wavelength of maximum absorption and molar absorptivity with increasing chain length, comparable to \( \pi \)-conjugated systems [55]. The long-wavelength shift levels off at a chain length with \( n \) between 40 and 50 [56]. The intense transition observed in poly- and oligosilanes is of the (\( \sigma-\sigma^* \)) type (\( \sigma_{SiSi} \) to \( \sigma^*_{SiSi} \)), including empty Si 3d-orbitals in the transition or otherwise, although some authors have interpreted the long-wavelength transition as a (\( \sigma-\pi^* \))-transition (\( \sigma_{SiSi} \) to \( \pi^*_{Si-C} \)), with \( \pi \) referring to the symmetry of the substituent orbitals, in the case of peralkylpolysilanes [57, 58].

\( (\sigma-\pi) \)-conjugation in phenyl(oligo)silanes

The electronic properties of phenyl(oligo)silanes were reported by three independent groups of authors, [54, 59, 60] even before the conjugating properties of permethylated oligosilanes were reported. When one methyl group of hexamethyldisilane is replaced by a phenyl group, a dramatic increase of \( \lambda_{\max} \) is observed (> 30 nm), due to lengthening of the conjugated system. Substitution of a second phenyl ring in the vicinal position results in only a small increase of \( \lambda_{\max} \). In Table 1.1 an overview of the absorption maxima of permethylated oligosilanes and \( \alpha,\omega \)-diphenyloligosilanes is given [61].

Table 1.1. Absorption maxima (\( \lambda_{\max} \)) of permethyl- and phenylmethyl-oligosilanes.

<table>
<thead>
<tr>
<th>( n )</th>
<th>Me(SiMe(_2))(_n)Me</th>
<th>Me(_3)Si(_2)Ph</th>
<th>Ph(SiMe(_2))(_n)Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>193</td>
<td>230.5</td>
<td>236</td>
</tr>
<tr>
<td>3</td>
<td>216</td>
<td>-</td>
<td>243</td>
</tr>
<tr>
<td>4</td>
<td>235</td>
<td>-</td>
<td>250.5</td>
</tr>
<tr>
<td>5</td>
<td>250</td>
<td>-</td>
<td>257.5</td>
</tr>
<tr>
<td>6</td>
<td>260</td>
<td>-</td>
<td>265</td>
</tr>
</tbody>
</table>

The long-wavelength absorption band observed for aryldisilanes was originally assigned by Hague and Prince to a (\( \pi_{C=C} \to 3d(\pi)_{Si-Si} \)) charge-transfer transition [59]. The \( \pi \)-electron is excited to a molecular orbital derived from extended overlap of the adjacent Si-3d orbitals of the silanyl unit (Figure 1.6a).
However, Pitt et al. proposed a mechanism in which the major absorption band arises from a transition from an MO consisting of the $\sigma_{(SiSi)}$ and $\pi_{(C=C)}$ ground state orbitals to a $3d_{SiSi}$ excited state, which is stabilized by the interaction with the $\pi^*$ MO of the phenyl group and probably by a $\sigma^*_{(Si-C)}$ contribution (Figure 1.6b) [61, 62].

![Figure 1.6](image)

**Figure 1.6.** Qualitative MO models of the origin of the long-wavelength absorption band of aryl-substituted polysilanes: a) model proposed by Hague and Prince [59]; b) model proposed by Pitt et al. [61,62].

The extent of the ground state ($\sigma$-$\pi$)-interaction is determined by the energy difference of the phenyl and silanyl orbitals and can be assessed by considering the ionization potentials (IP), i.e. the energy necessary to remove an electron from the highest occupied molecular orbital (HOMO). The shift of the absorption maximum with increasing $n$ has been shown to correlate linearly with the ionization potential [62]. The IP of a hexamethyldisilane $\sigma_{SiSi}$ bonding electron is 8.69 eV while that of a benzene $\pi$ electron is 9.24 eV. This means that the energy level of the former is higher than that of the latter and that the HOMO of Me$_5$Si$_2$Ph will have more $\sigma$ than $\pi$ character (72% $\sigma$ character according to quantum-chemical calculations [63]). Since the IP’s decrease for longer oligosilanes, the ground state of the phenyloligosilanes will be predominantly of $\sigma_{SiSi}$ character and the spectral shifts will be regarded as the perturbation of the permethyloligosilane absorption by the phenyl substituent. Consequently, the perturbation of the transition by the aromatic group diminishes from its initial, large value for $n$=2 until the absorption spectrum of the phenyloligosilane is close to that of the permethyloligosilane ($n$=6) with $\lambda_{max}$ being 265 and 260 nm, respectively.

**Donor-acceptor properties of the Me$_3$Si and Me$_5$Si$_2$ group**

The effect of the Me$_3$Si substituent on the spectral transition of benzene is much smaller, than that of the oligosilanyl substituents. This is due a higher IP (10.5 eV) of tetramethylsilane, Me$_4$Si, compared to that of benzene, resulting in a
larger energy-level difference than found for the oligosilanyl-benzenes [63]. Hence, the HOMO of Me₃SiPh will consist mainly of a benzene MO, perturbed by the silyl substituent, and with a lowest-energy transition of mainly ($\pi$-$\pi^*$) character.

The influence of the Me₃Si substituent on the HOMO of benzene has been attributed to three different types of interaction, described for the first time in 1949 by Roberts and discussed further in the 50’s: a) an inductive, b) a hyperconjugative and c) a (p-d)$\pi$ backdonation effect [64-67]:

a) The Me₃Si group is a positive inductive donor compared to Me₃C since the electronegativity of Si is less than that of C (0.7 units on the Pauling scale); therefore, the IP will be lowered.
b) The Me₃Si group acts as a donor through the hyperconjugative effect, i.e. ($\sigma$-$\pi$)-conjugation. The Si-C $\sigma$-orbital overlaps with the $\pi$-orbitals of the aromatic ring with a maximum interaction when the $\sigma$-bond lies in a symmetry plane normal to the $\sigma$-plane of the benzene ring as depicted in Figure 1.7.

c) The (p-d)$\pi$-interaction acting in the opposite direction, which means transfer of $\pi$-electron density (back donation) from the aromatic ring to a low-lying primarily silicon-based unoccupied orbital ($3d\pi$ and/or $\sigma^*$ (Si-Caryl)). The three interaction types are schematically presented in Figure 1.8 for Me₃SiPh.

The first two effects (a and b) will destabilize the HOMO of a $\pi$-system, when substituted with Me₃Si, Me₅Si₂ or Me₃SiCH₂, indicating an increase of the donor strength of the substituent compared to Me₃C. The third effect, c, will increase the electron-accepting properties of the first two substituents and will
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not affect that of Me₃SiCH₂ due to the insulating methylene group. The overall result is that the Me₅Si₂ group is a stronger electron donor compared to

\[
\begin{align*}
\text{Si} & \quad \text{Me} \\
(a) & \quad (b) & \quad (c)
\end{align*}
\]

\textbf{Figure 1.8.} Possible ground-state interaction types occurring in Me₃SiPh: a and b represent electron-donating effect of silyl-substituent; c represents electron-accepting effect.

Me₃Si, while the accepting properties are almost equal. The effect of a sil(an)yl substituent on the energy level of the HOMO of a π-system is presented in Figure 1.9. Which one of the three interaction types contributes mostly to the ground state of a silyl- or disilanyl-substituted benzene, depends on the (para)-aromatic substituent(s): electron-withdrawing substituents, like p-nitro, will be in favour of the donating structures (a or b), either through a direct polar interaction between the silicon donor and para-acceptor by the inductive effect or through the intensification of the (σ-π)-conjugation of the donor with the π-electron system; electron donating substituents will enhance the accepting property (structure c) of the silyl substituent.

\textbf{Figure 1.9.} Qualitative effect of a sil(an)yl substituent on the HOMO energy level of a π-aromatic system.
1.3 Excited-state properties of aromatic disilanes

The photophysical excited-state properties of disilanyl-substituted aromatic compounds have been extensively studied [70-81]. In addition to a regular, scarcely solvent-dependent emission band arising from a transition from an aromatic (π-π*) locally excited (LE) state ($^1$L$_{b\rightarrow}$A), a broad structureless band at longer wavelength has been observed. This band is attributed to an emission from an intramolecular charge-transfer (ICT) excited state and has a large Stokes shift, which indicates a polar character of the excited state. This dual fluorescence behaviour has first been observed by Shizuka et al. for phenyl- and naphthylpentamethyl disilanes [70]. They have assigned the polar emitting state to a $^1$(2p$\pi$, 3d$\pi$*) intramolecular charge-transfer excited state produced by a transition from the 2p$\pi^*$ (aromatic ring) local excited state to a vacant 3d$\pi$ (Si-Si bond) orbital. In this case the aromatic ring and the disilanyl moiety serve as an electron donor and acceptor, respectively. To facilitate the (2p$\pi^*$→3d$\pi$) electron transfer, it is assumed that the aromatic disilane has a conformation in which the Si-Si $\sigma$-bond lies within the $\sigma$-plane of the aromatic ring. This planar conformation permits coplanar overlap of the aromatic $\pi$-orbitals and the d type $\pi$-orbitals on silicon [71-75].

However, more compatible with the Si-Si $\sigma$-bond donating character and the predominant $\sigma$-character of the HOMO is the mechanism proposed by Sakurai et al. [76-78]. This model involves a $^1$(\sigma, 2p$\pi^*$) excited state, in which the disilanyl and aromatic groups act as a donor and acceptor, respectively. Based on the effects of structure and geometry of the aromatic disilanes on the fluorescence, they proposed an Orthogonal Intramolecular Charge Transfer (OICT) mechanism, in which the Si-Si $\sigma$-bond becomes coplanar with the aromatic ring. The OICT state is formed by rotation of the Si-C(aryl) bond of the molecule in the excited state populated by an excitation from the ground state in which the Si-Si $\sigma$-bond and the aromatic $\pi$-orbitals are orientated so as to maximize the (\sigma-\pi)-interaction. The perpendicular and coplanar geometries of phenylpentamethyldisilane, PhSi$_2$Me$_5$, are shown in Figure 1.10.
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Figure 1.10. Perpendicular ground state (a) and coplanar OICT excited state (b) geometries of PhSi₂Me₅.

The $^1(\sigma, 2p\pi^*)$ OICT state is stabilized by solvation, due to its polar character, although the singlet excited state can also be stabilized by a very polar solvent without the presence of an OICT state. The OICT state resembles the (n-\pi*) TICT (Twisted Intramolecular Charge Transfer) state observed for \textit{p}-dimethylamino benzonitrile, with the nitrogen lone pair orbital and the aromatic p\pi*-orbitals being orthogonal in the excited state, and also showing dual fluorescence [82].

The occurrence of a $^1(\sigma\rightarrow2p\pi^*)$ charge transfer is supported by the absorption and emission spectra of \textit{p}-trifluoromethyl-substituted phenylpentamethyldisilane, CF₃-Ph-Si₂Me₅, which are both red-shifted relative to the parent phenylidisilane. The lowering of the HOMO and LUMO energy levels of the of trifluoromethylbenzene moiety and the increase of the (Si-Si) \sigma-contribution to the molecular HOMO facilitate the intramolecular charge-transfer transition [78]. Furthermore, Horn et al. reported electron-transfer fluorescence quenching of electron-deficient benzenes by hexamethyldisilane, supporting a \( (\sigma\rightarrow\pi^*) \) ICT mechanism [83]. The emission spectra of \textit{para}-donor- (methoxy or dimethylamino) substituted phenylidisilanes do not show any charge-transfer bands in accord with the lower IP’s of the aromatic ring compared to phenylpentamethyldisilane which discourages a \( (\sigma\rightarrow\pi^*) \) transition.

The excited-state properties of aromatic compounds substituted with longer silicon chains have been reported by Declercq et al. [79]. Charge-transfer fluorescence of a tridecamethylhexasilanyl-substituted pyrene is observed and is attributed to an emission from an $^1(\sigma, \pi^*)$ excited state obtained by a \( (\sigma\rightarrow\pi^*) \) transition, due to the lower IP of the hexasilane chain compared to that of pyrene. However, a heptamethyltrisilanyl substituent does not result in a CT emission, due to the higher IP of the trisilane compared to that of the pyrene moiety.

We have studied the excited-state properties of \textit{para}-donor- and acceptor-substituted diphenyldisilanes which show, in case of a strong acceptor,
emissions from a local as well as a charge-transfer excited state, the latter being characterized by a dipole moment much higher than that of the ground state. These results will be presented in Chapter 4.

1.4 Nonlinear optical materials

In order to exhibit second-order nonlinearity, a bulk organic material has to possess a non-centrosymmetric alignment of the (di)polar molecules which it consists of. There are several ways to achieve a parallel orientation of NLO-chromophores; those most frequently used are:

1. non-centrosymmetric crystals;
2. Langmuir-Blodgett films;
3. poled polymers.

Non-centrosymmetric crystals

Organic crystals were the first bulk organic materials to be investigated for their nonlinear optical properties [84]. About 75% of all organic molecules tend to crystallize in a centrosymmetric space group, which is a serious disadvantage of this approach. Furthermore, it is difficult to direct the crystallization of an organic compound towards a crystal of the required size, processability, environmental stability and transparency for a typical application. Strategies to favour non-centrosymmetric crystallization are incorporation of chiral substituents in the molecular structure [85], organic salts [86] or designing molecules with specific intermolecular interaction such as hydrogen bonding [87].

Langmuir-Blodgett films

Another way of organizing NLO-molecules in a parallel manner is by molecular assembly techniques such as the Langmuir-Blodgett (LB) technique [88]. The poor orientational stability of the NLO-multilayers is the major disadvantage of this method together with the difficulty to obtain thick oriented layers. Recently, blue-light (457.9 nm) guiding with low optical loss (2-6 dB cm$^{-1}$) over several centimeters has been reported in an all-polymeric Langmuir-Blodgett film, made by alternate deposition of an amphiphilic nonlinear optical polymer and poly(tert-butyl methacrylate) on Pyrex. The NLO-chromophore, is 4-[(perfluorodecyl)sulfonyl]-N-hexyl-N-methylaniline, covalently attached to the polymer backbone by the -(CH$_2$)$_6$-spacer [89]. Second-harmonic generation ($\omega =$
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0.889 \( \mu \text{m} \) in the blue domain from LB-films consisting of fluorinated sulfonylstilbenes has been reported, but the values are strongly resonance-enhanced due to absorption at the second-harmonic wavelength [90].

Poled polymers

A very promising class of bulk-nonlinear optical materials is that of the poled polymers, due to the availability of coating methods to obtain large-area, high-quality films for integrated optical applications [91]. NLO-chromophores (whether dispersed or covalently bonded) can be oriented in a glassy polymer matrix by heating the polymer just above its glass transition temperature \( (T_g) \) while applying a strong DC electric field. Due to the high dipole moments of the chromophores they will orient in the direction of the E-field in a non-centrosymmetric way in the rubbery state of the polymer. Cooling the polymer below its \( T_g \) while keeping the applied E-field on, will result in a frozen orientation of the NLO-molecules that will remain in the glassy state after the E-field has been removed. Meredith and Van Dusen were the first to report about the electric-field poling technique applied to a side-chain NLO-polymer [92]. The major strategies followed in designing NLO-polymers are aimed at achieving a high chromophore density, a high ordering parameter, a large orientational stability even at high temperatures and a good environmental stability. The simplest way to obtain a nonlinear optical polymer is to dissolve the NLO-molecules in a polymer matrix (guest-host). The main problems with these systems are the low maximum chromophore density, because of phase separation at rather low concentrations, and the low temporal stability due to the large mobility of the NLO-molecules. Increasing the size of the dopant (films of large concentrations of nitrocalix(4)arenes in a PMMA matrix and of 100% dopant were obtained [93]) increases the temporal polar order stability significantly. To obtain the desired properties, the chromophores were covalently bonded to linear polymers as a side chain or in the main chain. However, larger number densities will lower the polymer’s \( T_g \) by the plasticizing effect. To improve the temporal polar order stability, crosslinked polymers were used with the NLO-chromophores being dispersed or attached monofunctionally or bifunctionally to the polymer network as a NLO-side group or crosslinking agent, respectively. Because of the irreversibility, the crosslinking has to occur under poling conditions.

However, the primary factor that influences the relaxation rate is the \( T_g \) of the polymer system. Hence, polyimides are excellent materials to serve as a host-polymer because of their very high \( T_g \) values (> 200 °C), thermal stability (>
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300 °C) and temporal polar order stability (90° C). Usually, they are thermally cured in situ from polyamic acid precursors [94-96]. Examples of other polymer systems investigated are epoxy resins [97-99], polyurethanes- and isocyanurates [100-102], sol-gels (inorganic) and organic-inorganic hybrid polymers [103-109].

1.5 Aim and outline of this thesis

Our aim is to synthesize nonlinear optical materials that are completely transparent in the visible spectrum, since this property is a requirement for many applications involving nonlinear optical phenomena (e.g. frequency doubling of the fundamental wavelength of a 820 nm laser). Asymmetric molecules containing a fully π-conjugated frame with a donor and an acceptor group grafted on both sides of the conjugated path have been shown to exhibit a large optical nonlinearity but also to lose their transparency with increasing values of the first hyperpolarizability, \( \beta \). To resolve this problem, we have chosen the synthesis of donor-acceptor substituted compounds with a (\( \sigma-\pi \))-conjugated frame consisting of a permethylsilanylene bridge connecting two phenyl rings. Another approach (in combination with the \( \sigma \)-bridge) is the use of inductive-type acceptors, such as the perfluorobutylsulfonyl group, because of their strong electron-attracting character and the improved transparency of compounds that contain this acceptor compared to those with mesomeric-type acceptors, such as the nitro or dicyanovinyl group.

One of our aims is the understanding of the electronic transitions and the extent of (\( \sigma-\pi \))-conjugation occurring in these so called D\( \sigma \)A-compounds and to investigate the interaction between donor and acceptor substituents through the conjugated frame. To this end, we have studied the absorption and emission properties of these compounds by UV-Vis and fluorescence spectroscopy and also the relation between NMR chemical shift trends and ground state electronic properties. Furthermore, we have synthesized and characterized 'fragment' compounds consisting of a mono- or disil(an)ylbenzene moiety para-substituted with either a donor or acceptor.

Finally, we aim at incorporating D\( \sigma \)A-compounds in a polymer matrix, either dispersed or covalently linked through a functionalized donor (or acceptor) group, in order to obtain a nonlinear optical material.

Chapter 1 gives a general introduction about nonlinear optics (background, theory and materials) and about (\( \sigma-\pi \))-conjugation in and excited-state properties of phenylpermethyl-oligosilanes.
Chapter 2 describes the synthesis of a series of DσA-compounds and fragment molecules and reports about the crystallographic structures of two sulfonyl-acceptor-substituted DσA-compounds [110]; the synthesis of a diol-functionalized dialkylamino-donor and perfluorobutylsulfonyl-acceptor substituted diphenyldisilane is given in order to incorporate this NLO-chromophore in, for instance, a polyurethane matrix.

Chapter 3 reports about the relation between $^{13}\text{C}$ and $^{29}\text{Si}$ chemical shifts and the donor-acceptor substituent parameters and the relation between $^{29}\text{Si}$ chemical shifts and calculated ground-state dipole moments. In this context, the relation between $^1\text{H}$ chemical shifts and reactivity of chloro silanes towards aromatic Grignard reagents is also discussed [111].

Chapter 4 deals with the absorption and emission properties of DσA-compounds and fragments thereof, measured by UV-Vis and fluorescence spectroscopy, respectively. In contrast to the fully $\pi$-conjugated DπA-compounds, DσA-compounds show a bichromophoric behaviour, demonstrated by their UV-Vis absorption spectra that contain more than one major absorption band. Also dual fluorescence, from a local and a charge-transfer excited-state, has been observed for the DσA-compounds [111-113].

Chapter 5 gives the results of the measurements of the first hyperpolarizability, $\beta$, of our compounds by the hyper-Rayleigh scattering technique (HRS). Also a comparison of the experimentally and computationally obtained $\beta$ values is given for perfluorobutylsulfonyl-acceptor containing compounds and fragments thereof. The $\beta$ values are not much larger than the sum of the contributions of the separate chromophores [111, 113, 114].

1.6 References

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[25] Ref. 6, Ch. 7.

[26] Ref. 7, Ch. 9-12.


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[49] Ref. 7, Ch. 9 and 10.


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