Übersichtsartikel · Review Article

Organic Materials for Non-Linear Optics: The 2D Approach

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Dedicated to Prof. Dr. Horst Hartmann (Merseburg) on the Occasion of his 60th Birthday

Abstract. Conventional organic molecules for applications in second-order non-linear optics are donor–acceptor substituted π systems that show only one intense charge-transfer (CT) transition. Thus, only a single element of the second-order polarizability tensor, β, is significant in these one-dimensional systems. The advantages and optimization strategies for two new classes of molecules with multiple CT transitions and two-dimensional second-order polarizability are reviewed. These are donor–acceptor substituted π systems that lack a dipole and have a molecular symmetry of C_3 or higher, and dipolar molecules of symmetry C_{2v}. A basic introduction to the field is also given.

Many promises are associated with almost any branch of materials science, and the field of organic materials for nonlinear optics (NLO) [1] is no exception. However, the pathway from vision to reality, or, from assertion to a marketable product is hardly ever as straightforward as it may seem. Again, this is also the case for NLO of organic materials where few of the often stressed promises have been fulfilled: while in principle photonics or the hybrid technology optoelectronics allows to replace every operation that is currently effected with electron conduction in electronics, many problems are encountered in translating a molecular property into a bulk property. It comes therefore as no surprise that the initial tide of excitement has somewhat abated meanwhile. Clearly, new design strategies for organic NLO-phores and their respective bulk structures, crystals or oriented polymers, are needed. These deserve fundamental interest beyond their increased potential technological benefits: the establishment of structure–property relationships lies right at the heart of physical organic chemistry, and "crystal engineering" [2] is one of the major goals in solid-state chemistry. Only a more fundamental understanding of these issues will allow rational optimization of molecular and bulk properties. It is the purpose of this account to highlight some of the new concepts in devising NLO-phores which in the opinion of these authors can obliterate some of the obstacles on the way to implement organic materials for NLO. They also demonstrate the fundamental influence molecular symmetry has on the properties of donor–acceptor substituted π systems. Some basic introduction into the field is also given. Mathematics will be kept to a minimum, but a rational optimization of NLO properties requires an understanding of the physical principles that govern the tensorial properties of molecular polarizabilities and hyperpolarizabilities.

1 Basics of NLO

1.1 General Introduction

Nonlinear optics [1] is concerned with the interaction of one or more electromagnetic radiation fields with matter to produce a new field that differs in phase, fre-

quency, polarization or direction etc. from the initial field(s). The electromagnetic field of light can interact with matter through its electrical and magnetic component. For the ensuing discussion of NLO effects in diamagnetic organic molecules, the usually weaker interaction with the magnetic field component will be neglected, although it gives rise to a number of magneto-optical and magneto-chiral effects even in closed-shell (diamagnetic) molecules [3].

The alternating electric field E of light imparts a polarization on the charged particles in the material. The square of the electric field amplitude is proportional to the light intensity. For the frequencies of interest here, which are in the near infrared range or above, only the electrons can follow the rapid reversal of the field direction [4]. In an *optically linear* material the resulting polarization P (induced dipole per volume) is linearly proportional to the electric field strength E:

$$P = \varepsilon_0 \chi^{(1)} \cdot E \text{ (SI units)} \qquad \text{(Eq. 1)}$$

The proportionality constant is the first-order electric susceptibility, $\chi^{(1)}$, a second rank tensor and ε_0 is the vacuum permittivity (dielectric constant). For isotropic materials, the susceptibility tensor can be represented by a scalar $\chi^{(1)}$ which is related to the refractive index n of the material, a property better known in chemistry:

$$\chi^{(1)} = n^2 - 1 \qquad \text{(Eq. 2)}$$

For optical frequencies Maxwell's relation, $\varepsilon_r = n^2$, holds between the refractive index and the relative permittivity (dielectric constant) ε_r. In materials composed of molecular entities (like crystals of organic molecules) $\chi^{(1)}$ is related to the molecular (first-order) polarizability α. The macroscopic polarization results from a vectorial addition of induced molecular dipole moments p of magnitude:

$$p = \alpha \cdot E \qquad \text{(Eq. 3)}$$

E is here the local electric field acting on the molecule. It differs from the macroscopic electric field in the medium in Eq. 1, because the molecules themselves introduce additional electric fields. The differences between both fields can be taken into account by local field corrections which have recently been reviewed [5]. It is intuitively understandable that the linear relationships of Eqs. 1 and 3-reminiscent of Hooke's law–may not hold for the high electric field strengths produced by high intensity laser light. Additional terms appear because the potential well for the displacement of the electrons is obviously not a harmonic parabola as Eq. 1 implies. The polarization of *optically nonlinear* mater-

ials can be represented by a phenomenological power series expansion of the form:

$$P = \varepsilon_0(\chi^{(1)} \cdot E + \chi^{(2)} : EEE + ...) \qquad \text{(Eq. 4)}$$

where the $\chi^{(n)}$ are electric susceptibilities of n-th order. In materials composed of molecules the contributions of the induced molecular dipoles are similarly:

$$P = \alpha \cdot E + \frac{1}{2!} \beta: EE + \frac{1}{3!} \gamma : EEE + ... \qquad \text{(Eq. 5)}$$

where β and γ are second and third-order polarizabilities. Again local field corrections have to be applied. In Eq. 5 and in what follows we employ the Taylor series convention for molecular polarizabilities where the factorials n! are explicitly written in the expansion [1r]. We will use recommended S. I. units for linear and nonlinear optical polarizabilities except when the original literature values were given in esu. Conversions between S. I. and the traditional electrostatic units (esu) are: μ (molecular dipole), 10^{-30} C m = $0.2998 \cdot 10^{-18}$ esu = 0.2998 Debye; α, 10^{-40} C V^{-1} m^2 = $0.8988 \cdot 10^{-24}$ esu; β, 10^{-50} C V^{-2} m^3 = $2.694 \cdot 10^{-30}$ esu; γ, 10^{-60} C V^{-3} m^4 = $8.078 \cdot 10^{-36}$ esu.

β and $\chi^{(2)}$ are third-rank tensors with 27 elements, not all of which may be significant. In the case of one-dimensional NLO-phores (see below) one element dominates the NLO response. All coefficients of third-rank tensors vanish in centrosymmetric media; effects of the molecular polarizability of second order may therefore not be observed in them. Unfortunately, the majority of achiral organic crystals adopt centrosymmetric space groups [6]. Pure enantiomers can only crystallize in a non-centrosymmetric space group but this in itself does not guarantee optimum arrangement of the molecules to achieve optimum values of $\chi^{(2)}$. Hence, much work has been devoted to orient promising NLO-phores in polymer matrices by application of strong electric fields [7]. In the following, physical effects arising from β/ $\chi^{(2)}$ will be discussed very briefly followed by a survey of optimization strategies for second order polarizabilities.

1.2 NLO Effects

Out of the many NLO effects, only a few will be selected for a brief discussion. Some, like the Pockels and the Kerr effect, also known as the linear and nonlinear electrooptic effect, have been known for a long time. The possibility to put them into wide practical use for optical devices only arose when lasers became available. Only laser light fulfills the requirements of strong, coherent and monochromatic radiation.

Organic materials whose bulk properties arise from the addition of molecular properties that are purely elec-

tronic in origin have distinct advantages over inorganic crystals. The response of the former is very fast (femtoseconds) while, depending on the frequency, the NLO response of crystals like $LiNbO_3$ rests in part on the displacement of ions. The inherent response time of such displacements is much higher and lattice vibrations are also stimulated. Thus, highly undesirable acoustic ringing is created [8].

1.2.1 Sum and Difference Frequency Generation

Second Harmonic Generation (SHG) is the NLO effect used most for the evaluation of β tensor elements in solution. It is a second-order process where two photons of circular frequency ω are transformed into one photon of frequency 2ω. A graphical presentation is commonly used to exemplify this process and will also be used here. Consider an unsymmetrically substituted π system like p-nitroaniline. It is intuitively understandable that the polarization in the donor and acceptor directions is different. For comparison, the calculated changes in charge for the S_0–S_1 transition are shown, which has a high charge-transfer character. An oscillating charge will also emit radiation, but the emitted light will not only contain the frequency of the fundamental wave, as a Fourier analysis shows. In addition to a static component, also the second harmonic is present at double the frequency of the fundamental.
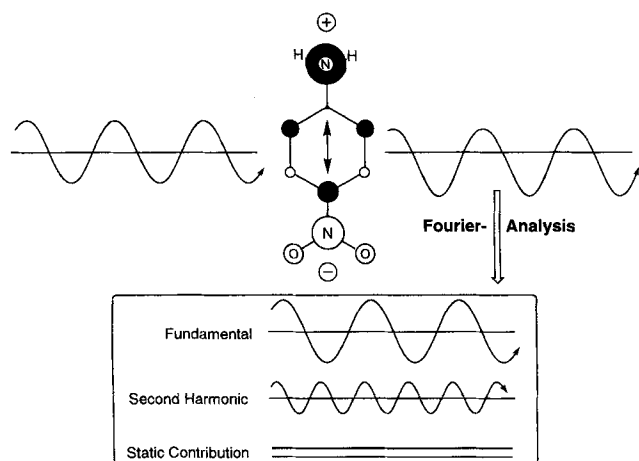

Fig. 1 Frequency doubling with p-nitroaniline. The asymmetric polarization response is exemplified by the regions of charge depletion (•) and increase (○) for the S_0–S_1 electronic transition which has a strong charge-transfer character.

In analogy sum frequency and difference frequency generation may be understood as the interaction of two fields with different ω. SHG has been advocated as a means for upconversion of laser light that is easily accessible only for comparatively long wavelengths. This requires the development of transparent materials, a condition that has not been satisfactorily fulfilled so far.

Now that blue lasers on the basis of GaN come nearer into reach, this demand has somewhat diminished.

1.2.2 The Linear Electro-optic (Pockels) Effect

The linear electrooptic effects arises from $\chi^{(2)}$. It describes a change in the refractive index of the material linearly proportional to an externally applied electric field. This effect is of technological importance in high-frequency modulation of optical signals. It can be observed in inorganic or organic crystals [1i] as well as in permanently poled polymer systems [1j]. UV–Vis absorption is not as critical as for SHG since typical optical communication wavelengths are in the near infrared at 1.3 and 1.55 μm. Still, the low-energy tails of the intense CT bands of the NLO molecules represent a primary source of absorptive losses observed [52].

1.3 Methods to Evaluate Molecular 2nd Order Polarizabilities

Two methods are available for the evaluation of NLO properties in solution, the Electric Field Induced Second Harmonic Generation (EFISHG) [9] and the Hyper Rayleigh Scattering (HRS) [10]. Both methods yield complementary information about linear combinations of β elements. Use of polarized fundamental light allows further information about molecular symmetry and tensor elements to be extracted.

1.3.1 Electric Field Induced Second Harmonic Generation (EFISHG)

In the EFISHG set-up, dipolar molecules in solution are oriented by a strong (preferably pulsed) DC field, irradiated with a strong infrared laser beam, usually a YAG laser with a fundamental of $\lambda = 1064$ nm (or higher). The intensity of the generated second harmonic at $\lambda = 532$ nm is measured against a standard like quartz. Unfortunately, there is still disagreement about the true absolute value of this material. The EFISHG technique is a coherent scattering process, so the second harmonic is collinear with the fundamental beam. It is not applicable for molecules without dipole moment and for conducting materials like salts. As the presence of an additional electric field makes this a third order process, extraction of β is not straightforward. Two molecular contributions exist: a temperature independent contribution through γ, and a temperature (orientation-) dependent one through β. The former is usually small and therefore neglected. It also requires the application of local field corrections [5] and the knowledge of the molecular ground state dipole moment, μ, which can be determined by permittivity measurements or electrooptical absorption (see below). Sometimes $\mu\beta$ values are quoted if the molecular ground state dipole is not known. EFISHG yields projections of the β tensor on the direction of the molecular dipole moment (z-axis).

For planar conjugated molecules (y, z plane), use of polarized incident light with polarization directions parallel and perpendicular to the externally applied electric field allows the determination of the following two linear combinations (Eqs. 6, 7) of tensorial elements [11]:

$$^1\beta_z = \beta_{zzz} + \beta_{zyy} \quad \text{and} \tag{Eq. 6}$$

$$^2\beta_z = \beta_{zzz} + \beta_{yzy} \tag{Eq. 7}$$

1.3.2 Hyper Rayleigh Scattering (HRS)

The HRS set-up [10] is in principle similar to the EFISHG experiment, but no electric field is applied. It relies on local deviations from centrosymmetry in the solution and is thus an incoherent process where the SH light has to be integrated over a certain solid angle. It is applicable for all compounds that are stable under the irradiation conditions of the experiment, including salts and molecules without dipole moment. Some standard has to be applied, and initially, the solvent has been used for this purpose [10b]. It is more advisable to use a standard solution of p-nitroaniline for this purpose, however. Carefully purified solvents may also be used as a reference [10d]. HRS gives a quadratic average of all components of β, $\langle\beta^2\rangle$, and thus complements the information obtained from EFISHG. Again, use of polarized light allows the determination of two different linear combinations of tensor elements. Molecular symmetry manifests itself in the two averages, $\langle\beta^2\rangle_{ZX}$ and $\langle\beta^2\rangle_{ZX}$, obtained for parallel (Z) and perpendicular (X) polarization of the scattered 2ω (SH) photons relative to the polarization (Z) of the ω (fundamental) photons and the scattering plane (XY). For example, the ratios of signals observed – called depolarization ratios – are equal to 5 for extended π systems with terminating donor and acceptor groups (1D NLO-phores, see below), but 1.5 for non-dipolar NLO-phores with C_{3h} or D_{3h} symmetry [10–12].

$$\langle\beta^2\rangle_{ZZ} = \left(24\beta_{yzy}^2 + 24\beta_{yzy}\beta_{zyy} + 6\beta_{zyy}^2\right) \tag{Eq. 8}$$

$$+24\beta_{yzy}\beta_{zzz} + 12\beta_{zyy}\beta_{zzz} + 30\beta_{zzz}^2\,)$$

$$\langle\beta^2\rangle_{ZX} = \left(16\beta_{yzy}^2 - 12\beta_{yzy}\beta_{zvy} + 18\beta_{zyy}^2\right) \tag{Eq. 9}$$

$$-12\beta_{yzy}\beta_{zzz} + 8\beta_{zyy}\beta_{zzz} + 6\beta_{zzz}^2\,)$$

1.3.3 Pitfalls of the Solution Methods

Neither method for the evaluation of NLO properties in solution is without pitfalls. The EFISHG method requires molecular parameters that are often not available or difficult to obtain, and so assumptions about

their magnitude have to be made. While the HRS technique seems to be more straightforward both in experimental set-up and evaluation of the results, the SHG efficiency with the HRS apparatus is very low (10 photons for a pump pulse of $2\cdot10^{15}$ photons have been reported for a 0.1 M solution of p-nitroaniline [10d]). Hence, the SHG signal monitored in many cases contains significant to even dominant contributions from fluorescence excited by multi-photon processes. Failure to recognize fluorescence leads to grossly overestimated values of β. Until about 1995/6, the issue of fluorescence has not been addressed for the HRS technique, and claims of unusually high NLO activities without specifically stating how fluorescence was taken into account may therefore be regarded with suspicion. Indeed, several claims of record hyperpolarizabilities [13] had to be retracted, or were at least questioned by other groups [10d–f]. Both contributions to the signal observed at 532 nm may be determined by the use of a sequence of bandpass filters with decreasing spectral width [10c, i]: while a true second harmonic signal has a very narrow spectral distribution, fluorescence light is usually quite broad. In the case of weak to moderate fluorescence contributions, extrapolation therefore becomes possible. Alternatively, a scanning monochromator [10e, i] may be used (at the cost of signal-to-noise ratio). Also, the true SHG signal has a very short rise and fall-off time, so short-pulsed lasers (picoseconds) can be used to distinguish between true SHG signals and the slowly decaying (typically nanoseconds) fluorescence [10d, f, h].

1.3.4 Electro-Optical Absorption Measurements (EOAM)

Although EOAM [14] do not yield direct information on molecular nonlinear optical polarizabilities such as β and γ, they were recently demonstrated to be a valuable tool for the experimental characterization of NLO-phores [11, 25h, 49]. In an EOAM experiment, the influence of an external electric field on the absorption of linearly polarized light along or perpendicular to the direction of the external field is probed in solution. The measured signal is a combination of two effects. The first is the electrodichroic (orientation) effect caused by the partial alignment of the dipolar molecules in the direction of the applied field. The second is the band shift (Stark) effect caused by a change of the molecular dipole moment upon excitation. Thus, the molecular dipole moment in the ground state μ and the difference $\Delta\mu$ between ground and excited state dipole moment may be determined. Polarization dependent EOAM experiments also yield information on the polarization of electronic transitions and the respective transition dipoles in the molecule-fixed frame. All these parameters are related to β (s. Eq. 10 below).

1.3.5 Kurtz Powder Test

A quick semi-quantitative check for the efficiency of NLO crystals is the Kurtz method [15] where the SHG intensity of a powdered material with defined grain size is measured against a standard, most often urea or quartz (which, incidentally, have quite moderate efficiencies). A systematic collection of organic SHG powder test data is given in [1g].

2 Optimization of Second Order Polarizabilities

2.1 σ Systems and One-dimensional π Systems

A high linear polarizability may be intuitively suspected to be an indication of high nonlinear polarizability. While this is indeed the case as the homologous series of haloforms shows, the values of β that may be achieved in σ systems substituted with heavy elements are much too low. They may be calculated simply by the addition of bond increments [16], akin to the classical computation of molar refractivities [17].

Tab. 1 NLO-Properties of Haloforms [18]

|	CHF_3	$CHCl_3$	$CHBr_3$	CHI_3
n	–	1.4486	1.6005	1.75/1.95
$<\alpha>$ [10^{-24} cm^{-3}]	2.81	8.53	11.84	18.04
β [10^{-30} esu]	–0.11	0.2	0.6	2.8
$<\gamma>$ [10^{-36} esu]	0.14	1.8	4.0	20.2

Donor–acceptor substituted π systems show much better performance due to the high anisotropic polarizability of the π electrons. Their contribution by far dominates the one arising from the σ framework which is therefore neglected in the following discussion. In the simple example of the isomeric nitroanilines [19], ortho/para-nitroaniline with 6.4 and $21.1 \cdot 10^{-30}$ esu have superior properties to their meta-congener with $4.2 \cdot 10^{-30}$ esu, a behaviour that is consistent with chemical intuition: Kekulé resonance forms can be written only for the CT in the o- and p-isomers. However, the inferior performance of m-derivatives is by no means a general observation, as we will show below. Likewise, m-isomers usually have the undesirable properties of highest λ_{max} and lowest ε of the CT transition [20], but this is also not generally the case.

Based on initial experimental evidence, it has been until recently an almost universally held view that molecules with extended linear π conjugation substituted in para-positions with a donor and an acceptor show highest β values and thus greatest promise for possible applications. This view was corroborated by the two-state model [1, 21] for the description of second-order polarizabilities: the first (virtual) HOMO–LUMO transition which has a strong charge transfer (CT) charac-

ter, by far dominates the β values observed. It is important to note that an electronic transition does not in fact occur, the electrons are just polarized. More elaborate and accurate computational methods (analytical and numerical) are available [22] and have been integrated into usual packages for quantum mechanical calculations, but the general arguments are not affected. The following equations are written for the process of second harmonic generation where two photons of circular frequency ω give one photon of 2ω. The Taylor-series convention for β is used [1r].

$$\beta(-2\omega;\omega,\omega) = \frac{6\Delta\mu \cdot (\mu^{ag})^2 \cdot \omega_{ag}^2}{\hbar^2(\omega_{ag}^2 - \omega^2)(\omega_{ag}^2 - 4\omega^2)} \tag{Eq. 10}$$

$$\beta \propto \frac{\Delta\mu \cdot (\mu^{ga})^2}{(\Delta E)^2} \tag{Eq. 11}$$
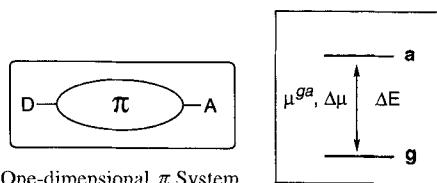
One-dimensional π System

Fig. 2 Two-state model for the decription of second-order polarizabilities (β) with a single charge transfer.

$\Delta\mu$ denotes the dipole change associated with the HOMO (g) to LUMO (a) transition, μ^{ag} the corresponding transition dipole, ω_{ag} and ω the circular frequencies of the transition and the incident light, respectively, and ΔE the energy of the HOMO–LUMO gap. Thus, the intrinsic β depends on the square of the transition dipole, the change in dipole moment, and the inverse HOMO–LUMO gap. Artificially high values will occur, however, if the frequency of the incident light or its second harmonic is close to the transition frequency ($\omega_{ag} = \omega$, or $\omega_{ag} = 2\omega$). Unfortunately, this one- and two-photon resonance enhancement is technically of limited use because the material just absorbs the fundamental or the second harmonic and the energy is dissipated. It should also be noted that the two-state model is valid only off-resonance. So, while extrapolation to the zero frequency limit ($\omega \rightarrow 0$) to give the intrinsic β_0 seems straightforward, the extrapolated values are frequently too high, as subsequent measurements at higher fundamental wavelengths have shown in a number of cases when strong resonance enhancement was present at lower fundamental wavelengths [23].

Provided the two-state model is valid, the following conclusions can be drawn for the optimization of NLO-phores:

• Since the square of the transition dipole, μ^{ag}, is a measure for the intensity of the transition, the latter should be highly (electric dipole) allowed. In other

words, the extinction coefficient of the transition should be high.

• The difference between ground state and excited state dipole moments, $\Delta\mu$, should be high. Since dipole moment equals charge times distance, the molecule should be a long conjugated π system, with strong donors and acceptors splayed apart as much as possible.

• A low HOMO–LUMO gap manifests itself in a low transition energy, that is, a bathochromic shift in the UV–Vis spectrum.

Taken together, the requirements for optimum structures devised on the basis of the two-state model partially coincide with the requirements for dyes in classical domains of application, e.g., in textile dyeing. Therefore, "good" molecular NLO-phores optimized along the guidelines of this model almost inevitably belong to known classes of dyes, especially stilbenes and merocyanines. For their optimization, it has to be noted that $\Delta\mu$, μ^{ag}, and ΔE are not independent quantities. Based on the extensive work by S. Dähne on the polymethine state [24], Marder et al. have performed model calculations that were argued to lead to chemically optimized NLO-phores. The compounds reported are merocyanines [25a]. A small selection of successful structures, mainly taken from recent publications [25] not mentioned in [1] is shown below.
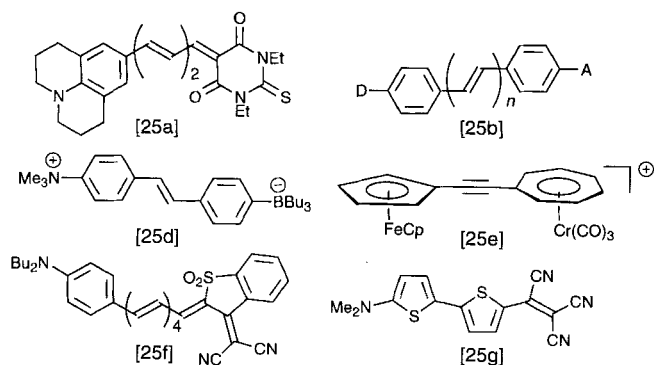
Scheme 1 One-dimensional NLO-phores with a high molecular second-order polarizability.

Unfortunately, the high absorbance and the chemical instability of long conjugated structures remains problematic for a number of applications in NLO. While high absorption in the visible range of the spectrum is tolerable for the electro-optic effect, it is not, e.g., for SHG. This dilemma is known as the "efficiency–transparency trade-off". Of course, the chemical stability may be increased somewhat by rigidifying the carbon backbone, a concept that is well-known from cyanine chemistry [26]. The synthesis becomes more difficult in most cases, however, and the compounds are more prone to (undesirable) fluorescence, and become even more colored. One possible way out is the use of two-dimensional NLO-phores.

2.2 Two-dimensional (2D) NLO-phores

2.2.1 1D and 2D Architecture

So far, frequently "β values" have been quoted although in the introduction it was stated that β is a tensor of third rank. One reason for this is purely pragmatic: until about 1993, the only technique used to evaluate NLO-properties in solution was EFISHG, which yields a projection of the β tensor on the direction of the molecular dipole moment, sometimes mistaken as "the β-value". Without the use of polarized light, only one linear combination of tensor elements is obtained (see below). More importantly, in the elongated D–A-substituted π systems discussed so far, only a single, diagonal component, β_{zzz}, is dominant anyway. Taken together with the fact that a single HOMO–LUMO transition dominates the NLO properties, this molecular architecture is therefore termed one-dimensional (1D). New strategies for the optimization of molecular polarizabilities of second order take advantage of molecules with a two-dimensional design. It is important to note that this expression is defined here solely with respect to the two-dimensional properties of the β tensor, and should not be mixed up with molecular topology itself. Two classes have been studied most extensively so far: molecules that lack a dipole moment and have a symmetry of C_3 or higher, and dipolar molecules of C_{2v} symmetry. The reason for the 2D behaviour in both cases is the occurrence of two or more low-lying CT transitions.

2.2.2 Non-dipolar 2D NLO-phores

By a group theoretical analysis [27], it has been shown that molecules without a dipole moment (C_3 and higher, but not octahedral point groups) may also show non-vanishing elements of β. Five components are significant for C_{3v} symmetry, and four (of equal absolute magnitude) for D_{3h} [1k, 12]. The modulus of β,

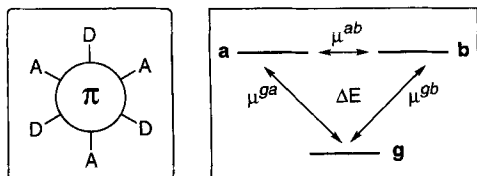$$\|\beta\| = \sqrt{\sum_{i,j,k} \beta_{ijk}^2}$$ (Eq. 12)

is therefore intrinsically higher than for comparable 1D molecules, where only one element is significant, but in practice often only one element can be used for a physical process anyway.

The term "octopolar" NLO [1k] bestowed on this class of compounds is physically correct, but somewhat misleading for chemists because the origin of NLO activity is not the permanent octopole moment of these molecules. Rather, it arises from the degenerate HOMO and/or LUMO that these compounds possess at least in a simple Hückel-type molecular orbital picture. Instead of just one virtual transition between ground and excited state, three (or possibly more) transitions between ground state and two (not necessarily degenerate) ex-

cited states become important, and the two-state model has to be extended by three-state contributions. For the case of degenerate excited states, a and b, it follows:

$$\beta(-2\omega;\omega,\omega) = \frac{12\mu^{ag}\mu^{ab}\mu^{bg}\omega_{ag}^2}{\hbar\left(\omega_{ag}^2 - \omega^2\right)\left(\omega_{ag}^2 - 4\omega^2\right)} \qquad \text{(Eq. 13)}$$

$$\beta \propto \frac{\mu^{ga}\mu^{ab}\mu^{gb}}{(\Delta E)^2} \qquad \text{(Eq. 14)}$$

Two-dimensional π systems: C_{3v}- and D_{3h}-Symmetry

Fig. 3 Three-state model for the description of second-order polarizabilities in molecules with multiple charge-transfer. For simplicity, degeneracy of excited states is assumed.

A product of three transition dipoles now appears in the numerator. While the transition between the excited states (a, b) could in principle be computed, but not easily determined experimentally, it is clear that magnification of the transition dipoles μ^{ag} and μ^{bg} requires the design of extended π systems. As a rule of thumb, all other parameters equal, the transition probability increases with the size of the π system [20].

For molecules without dipole moment the EFISHG technique can not be used, so HRS remains as the only alternative to evaluate components of β. Eight components are significant for C_{3h} symmetry, and four for D_{3h} symmetry. Unfortunately, the results obtained with HRS are prone to gross overestimation if luminescence arising from other multi-photon processes in the region of the observed second harmonic is not rigorously excluded. Large, rigid π systems, especially those containing complexed Ru^{2+} are notorious in this respect [10d, f].

Molecules without dipole moment should be intrinsically more transparent than their dipolar congeners because they show little, if at all, solvatochromism. The mutual polarization of solvent and solute is small because the solute has only higher moments of electric field distribution. It has also frequently been asserted [1k] that these molecules are more likely to crystallize in non-centrosymmetric space group, but no statistical confirmation for this claim has been given [28]. This would be of considerable importance because crystals are probably the only bulk structure with promise for applications. While dipolar 1D systems can be ordered by static electric fields in polymer matrices, this is not possible for non-dipolar molecules. The situation is ex-

acerbated by the fact that the requirements for ordering are more stringent than in the 1D case. Optical poling has been demonstrated for a non-dipolar π system [29], but no indication of long-term stability is given.

2.2.3 Examples of Non-Dipolar NLO-phores

First measurements on the (low) NLO-activity of methane [27, 30] and carbon tetrachloride [29], as well as of solid urotropine (hexamethylenetetramine) [31] were reported many years ago. The implications of these results lay dormant for two decades, when powder measurements on 1,3,5-trinitro-2,4,6-triaminobenzene (**1**) demonstrated [32] NLO efficiency (3–4 × urea). However, the published crystal structure [33] for this compound gives the space group as $P\bar{1}$, which is centrosymmetric, and therefore incompatible with the observation of strong SHG. Unfortunately, **1** is almost insoluble in all solvents. So its properties in solution could not be evaluated. Careful inspection of the microcrystalline powder revealed the presence of two polymorphic forms. The crystals of the new polymorph were so small that the structure had to be elucidated by high-resolution electron diffraction [34]. The space group is $P3_1$, and the arrangement of layers is close to optimum for NLO applications. Unfortunately, large crystals of the desired polymorph could not be grown so far, not even pure powder samples could be obtained. It should have much higher SHG efficiency (10 × urea or more) than the powder that mainly consists of the inactive polymorph [34b]. It should be noted that **1** occupies a general position in the crystal lattice, so the molecule shows no symmetry. However, small deviations from ideal symmetry do not affect the general arguments put forward above.
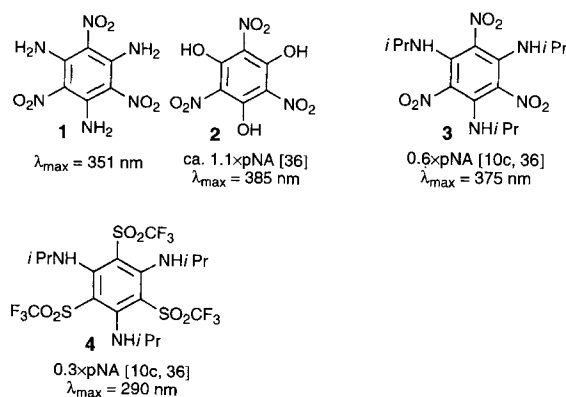
Scheme 2 NLO-active hexa-substituted benzene derivatives.

Progress in this area was greatly aided by the development of HRS into a routine method. Unfortunately, there is quite a confusion as to the β values reported because several conventions exist for the mathematical
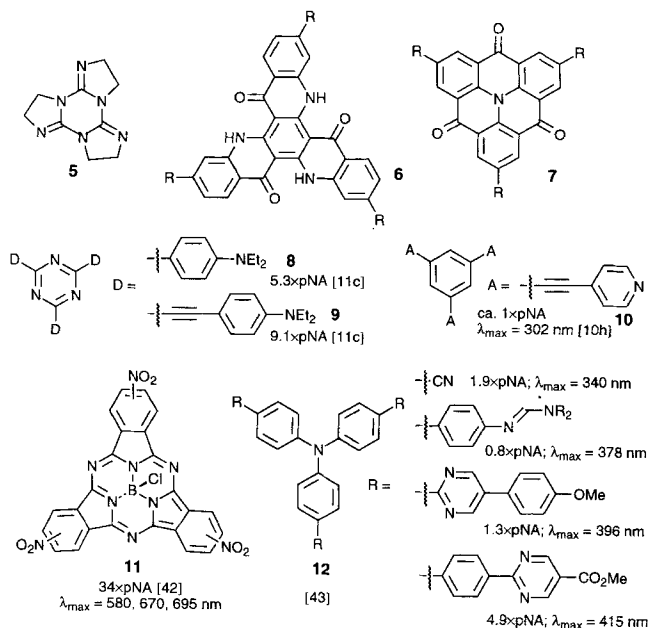
form of Eq. 5 [1r]. The results also depend on the value used for the standard which may also be under question. In the following we will restrict ourselves to values relative to p-nitroaniline (pNA), the paradigmatic 1D NLO-phore which has been widely used as a solution standard and for which high-quality EFISHG, HRS and computational data are available [35]. A true evaluation of NLO activities has also to take into account the molecular size, because it is the effectivity per volume element that counts for bulk applications. For example, it would be insincere to claim a better performance for a molecule that showed triple SHG efficiency in comparison with pNA, but had four times its molecular volume. Sometimes the molar mass M is used as an approximate measure of the molar volume. Figures of merit are then estimated by dividing the molecular NLO response by M. We have not computed such reduced values in all cases, but the informed reader will note that many systems mentioned here and in the literature do not truly surpass pNA. A quotation of the modulus of β which intrinsically favours molecules with a higher number of significant β components is also not very helpful for comparison of 2D and 1D NLO-phores because not all elements may be used simultaneously for NLO effects. The properties of small soluble molecules like guanidinium or tris-acceptor substituted benzenes were quickly evaluated [1k], but it was not until donor–acceptor substituted benzene derivatives were used that strong SHG activity could be observed. Trinitrophloroglucinol (2) [36] was convincing in this respect. Anhydrous 2 crystallizes in the non-centro-symmetric space group $P2_1$, but the arrangement of molecules is pseudocentric, and thus far from optimal [37a]. The counterintuitive results obtained with alkylamino-substituted trinitrobenzenes 3 [10c, 36] may be traced back to the conformational behaviour of these molecules. While trinitrophloroglucinol is an essentially planar molecule [37], compounds of type 3 show "benzene" rings that are widely distorted from planarity [38]. Depending on the molecular geometry, the π system adopts quinoid or cyanine-like resonance forms of approximate C_s and C_2 symmetry symmetry, respectively. Exchange of the nitro acceptor groups for sulfonyl groups in 4 does not planarize the ring but leads to more transparent systems [10c]. Unfortunately, this exchange also decreases polarizabilities of second order [10c, 39]. Simple benzene derivatives are not hyperpolarizable enough because the transition dipoles (extinction coefficients) of the CT-transitions are too low (Eqns. 13, 14). The same holds true for small neutral heterocyclic π systems like the "threefold guanidine" 5 [40], although substituted s-triazine derivatives have been shown to be somewhat superior to benzene derivatives of like substitution [41]. Large heterocycles should show improved properties because of the increased transition

dipoles. Rigid representatives like the (colorless!) sesqui-quinacridone 6 or the bridged triphenylamine 7, however, are too fluorescent [40] for meaningful HRS data to be observed. In contrast, if some rotational freedom is guaranteed, fluorescence quantum yields are lowered, and systems with high SHG efficiency result [10c]. The s-triazines 8 and 9 are good examples. 8 shows a static (extrapolated to zero frequency) β_0 of $1.4 \times$ pNA when the different molecular weights are taken into account. Alkynyl groups have also been interpolated between the two six-membered ring in order to reduce disruption of conjugation through steric interaction of the biphenyl type. Compound 9 shows a "reduced" β_0 of $2.1 \times$ pNA. Since 9 is bathochromically shifted with respect to pNA ($\lambda_{max} = 425$ nm in MeCN), a fair comparison would place the ratio close to 2. This is the highest unquestioned β/M effectivity known to us for a non-dipolar NLO-phore, especially in the light of its rather short-wavelength absorption. Several other molecules of similar design with 1,3,5-tricyano- and -trinitrobenzene have been synthesized, but their properties have not been thoroughly evaluated so far [40].
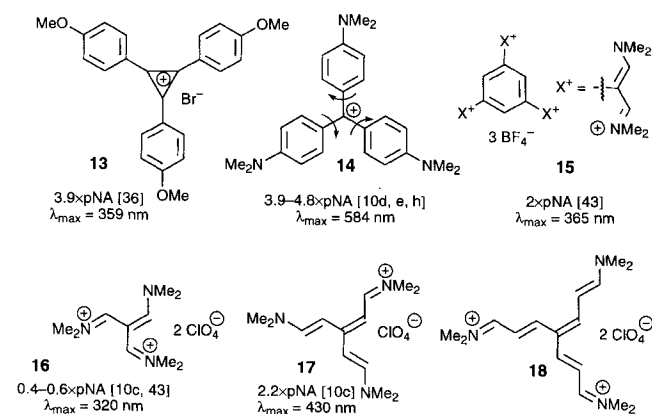
Some sub-phthalocyanines (11) have been reported to show exceptionally high β values [42]. A series of triphenylamine and trispyrimidine derivatives (12) has also been investigated [43]. Their properties seem to suffer from the decrease of conjugation known for oligophenylenes. Some organometallic complexes on the basis of s-trialkynylbenzene also show some SHG activity [45], as well as the trialkynylbenzene 10 [10h].

Charged species were among the first to be analyzed (guanidinium, trinitromethane anion, crystal violet (14), cyclopropenylium salts (13)). Ionic species have definite advantages over neutral molecules if crystals are to be used as NLO materials. This is not only due to the increased optical quality and size of the crystals, but also due to the ease with which counterions may be exchanged. Thus, while a promising NLO-phore structure is retained, crystal structures may be optimized without much synthetic effort. Cyanines are known for their high polarizabilities, but simple streptocyanines are centrosymmetric. Cross-conjugated congeners [44a–c], however, show quite promising results [10c, 44d]. The conjugation in the crossed trimethinecyanine 16 is still impeded by steric hindrance [44b] which is probably also the case for 15. While 16 probably does not exceed a β_0 of $0.4 \times$ pNA [10c, 44d], this is not the case for the higher vinylogues [44b]. Thus, 17 shows a reduced β_0 of $1.0 \times$ pNA and has UV–Vis absorption properties similar to 9 [10c]. The properties of the crossed heptamethine 18 could not be evaluated with certainty so far because of its high absorption [40].
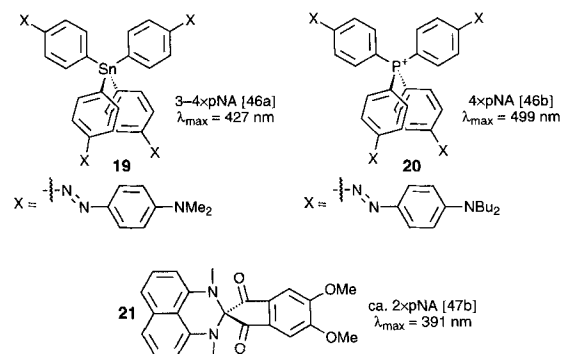
Tetrahedral structures (19, 20) have been employed occasionally [27, 31, 46]. The accessible excited state is triply degenerate, and one tensor element, β_{xyz}, is sig-

Scheme 3 NLO-phores of threefold symmetry.

5

6

7

8
5.3xpNA [11c]

9
9.1xpNA [11c]

D =

A =
ca. 1xpNA
λ_{max} = 302 nm [10h] 10

-CN 1.9xpNA; λ_{max} = 340 nm

0.8xpNA; λ_{max} = 378 nm

1.3xpNA; λ_{max} = 396 nm

4.9xpNA; λ_{max} = 415 nm

11
34xpNA [42]
λ_{max} = 580, 670, 695 nm

12
[43]

Scheme 4 Charged non-dipolar NLO-phores.

13
3.9xpNA [36]
λ_{max} = 359 nm

14
3.9–4.8xpNA [10d, e, h]
λ_{max} = 584 nm

15
2xpNA [43]
λ_{max} = 365 nm

16
0.4–0.6xpNA [10c, 43]
λ_{max} = 320 nm

17
2.2xpNA [10c]
λ_{max} = 430 nm

18

Scheme 5 Tetrahedral structures for non-dipolar NLO and spiro-conjugation.

19
3–4xpNA [46a]
λ_{max} = 427 nm

20
4xpNA [46b]
λ_{max} = 499 nm

21
ca. 2xpNA [47b]
λ_{max} = 391 nm

nificant. This makes the evaluation of properties easy, but the conjugation between the substituents on the central element is disrupted. Some enhancement by through-space coupling has been shown [46b]. Spiro-conjugation would guarantee some interaction [47], but this seems to be too weak for large NLO-activities, at least in the dipolar examples like **21** that were investigated [47b].

2.2.4 Dipolar Two-dimensional NLO-phores

Multiple charge-transfer can also occur in molecules that retain a dipole moment. They retain the advantage of non-dipolar NLO-phores, the multiple CT, but can also be ordered through electrical poling as can be done with classical 1D systems. Most investigations have focussed on donor–acceptor substituted π systems with the molecular symmetry C_{2v} [11, 48–52]. This choice is in part pragmatic: seven components are significant out of which five are independent, but since the components perpendicular to the molecular plane are negligible, only four components remain: $\beta_{yyz} = \beta_{yzy}, \beta_{zyy}$, and β_{zzz}. These can be determined by a combination of polarization-dependent EFISHG, HRS, and EOA measurements.

3,5-Dinitroaniline will be taken as an example [11]. It has long been known that a degenerate charge-transfer from the amino to the two nitro groups is possible. These couple and lead to two mutually orthogonal CT transitions. Indeed, two bands with polarization directions perpendicular, and parallel to the direction of the ground state dipole along the C_2 axis can be observed experimentally [11, 53]. The "perpendicular" band has the lower transition energy.
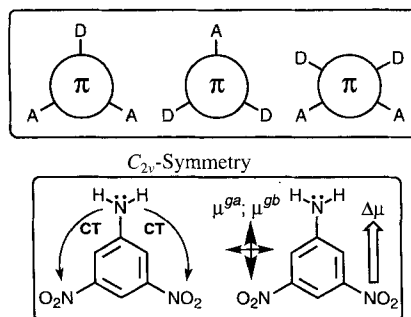
C_{2v}-Symmetry

Fig. 4 Degenerate charge-transfer in C_{2v}-symmetric π systems.

The special advantage of this situation becomes clear if frequency doubling via the "perpendicular" band is considered [11]. Suppose a perfectly ordered system, and a fundamental polarized perpendicularly with respect to the C_2 axis. The second harmonic will be polarized in the direction of the C_2 axis which is the direction of the intramolecular charge transfer. Hence, it can not be reabsorbed by the "perpendicular" transition! The transition along the C_2 axis, however, which does have

the correct polarization, is quite hypsochromically shifted [54]. Two pictures of the net change in charge for the S_0–S_1 and the S_0–S_2 transition as calculated by a simple PPP model [55] demonstrate that for both transitions the change in dipole moment is along the molecular axis. Therefore, this is also the polarization direction of the second harmonic.
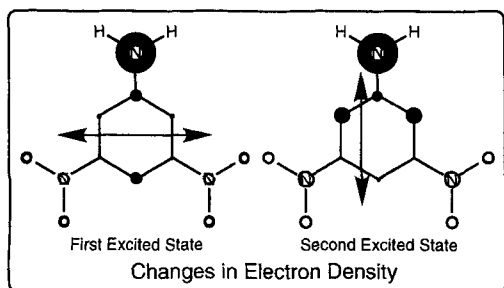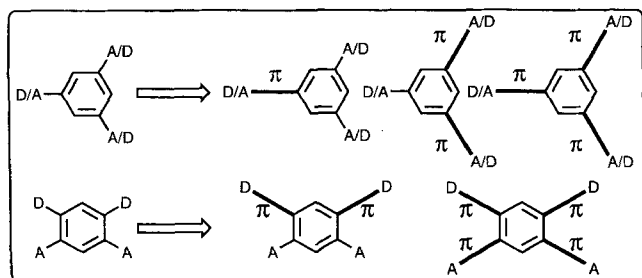

First Excited State   Second Excited State
Changes in Electron Density

Fig. 5 Transitions with parallel and perpendicular polarization in 3,5-dinitroaniline. Regions of charge depletion (•) and increase (o) for the first two electronic transition have been calculated by the PPP method [55].

As a consequence of this molecular architecture, off-diagonal elements of β become significant. Other effects will just be mentioned, although they are of physical and technological significance: the possibility of non-critical phase-matching, and the violation of Kleinman's symmetry condition [11]. Systems with two donors and one acceptor have similar properties, and the same arguments also apply in principle to tetra-substituted benzene derivatives of C_{2v} symmetry [1a, 1k, 48, 50].

From the experience with non-dipolar and 1D NLO-phores, it is to be expected that simple benzene or naphthalene derivatives are not hyperpolarizable enough. Especially the "perpendicular" transition is of quite low intensity, a fact hinted at from classical dye chemistry: meta-substituted donor–acceptor π-systems have bathochromically shifted bands of low extinction coefficients. Extension with double bonds, so successful in the 1D case, seems an obvious choice but introduces rotamers of different symmetry, so we opted once more

for the interpolation of phenyl-alkynyl bridges. The basic tri- and tetrasubstituted structures were systematically modified in 1, 2 and 3 directions.
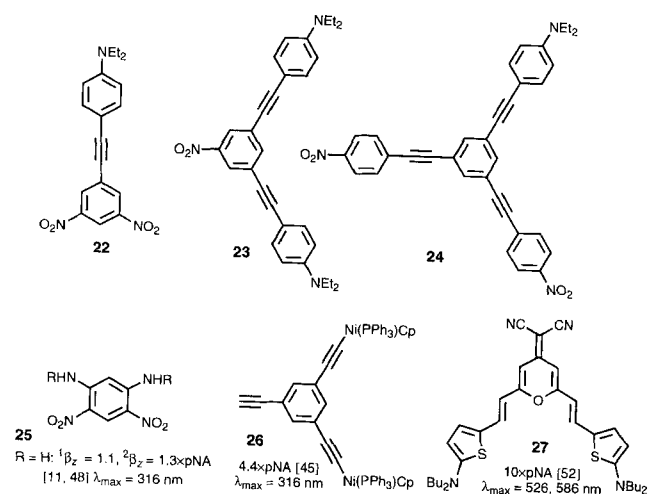
For the first time, all four independent tensor components of **22–24** were evaluated by a combination of EOAM and polarization-dependent EFISHG and HRS [49]. Elongation in one and three directions for the tri-substituted case (**22, 24**) leads to a loss of the transition with perpendicular polarization. In the latter case, however, quite transparent and active NLO-phores are obtained, just *because* the long wavelength absorption is missing. PPP calculations indicate the presence of such a band, albeit with low oscillator strength. If, however, the π system is extended in only two directions (**23**), molecules with surprisingly high off-diagonal elements are obtained that exceed the magnitude of the diagonal components.

Tab. 2 β tensor components of **22–24** [49]

	22	**23**	**24**
λ_{max}	383, 327	361	340
β_{zzz}	123 ± 22	16 ± 4	73 ± 15
β_{zyy}	6 ± 29	67 ± 4	50 ± 11
$\beta_{yzy} = \beta_{yyz}$	4 ± 15	72 ± 10	50 ± 18

The dipole moment μ lies parallel to the z axis, the y axis within the molecular plane, and the x axis perpendicular to the molecular plane. β values (at 1064 nm) are given in SI units. For comparison: β_{zzz}(pNA, 1064 nm) = (27.4±2.8) $\cdot 10^{-50}$ C m^3 V^{-2} [10c].

Several other C_{2v}-symmetric push–pull π systems, mainly tetra-substituted, have been investigated by semi-empirical and ab initio calculations [48]. In some cases (**25–27**), experimental evaluation of combinations of tensor elements are given [45, 52], but to our knowledge, no experimental determination of all tensor components has been attempted with the exception of the

Scheme 6 Extension of basic structures for dipolar 2D NLO-phores. Elongation direction(s) of the π systems is (are) shown by a bold line.

Scheme 7 2D NLO-phores for which experimental data are available.

above-mentioned study. In dihydropyranes like **27** [52] the perpendicular band is missing, and two transitions with parallel polarization contribute to the NLO activities observed.

3. Conclusion

Molecules with multiple charge transfer offer new design possibilities for the optimization of NLO-phores. In addition to improved hyperpolarizabilities and/or transparencies in some cases, new ways to circumvent the efficiency–transparency trade-off and to achieve non-critical phase-matching are provided. As an added benefit and synthetic challenge for the organic chemist, the molecular architecture of 2D NLO-phores structures deviates from that of dyes for classical applications in textile dyeing or color photography. More systematic studies will be needed to explore the full potential of this fairly new approach, and many structures are possible targets.

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