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Second order hyperpolarizability of hydroxystilbazolium salts and their betaines—relationship to chemical structure

Ulrich-W. Grummt,*[a] Frank Lehmann,[a] Sabine Rentsch,[b] Joachim Hein [b] and Mattias Helbig[b]

[a]*Institut für Physikalische Chemie, Friedrich-Schiller-Universitaet Jena, Lessingstrasse 10, D 07743 Jena, Germany*
[b]*Institut für Optik und Quantenelektronik, Friedrich-Schiller-Universitaet Jena, Max-Wien-Platz, D 07743 Jena, Germany*

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Amphiphilic hydroxystilbazolium cations and their corresponding neutral betaines exhibit large off-resonant positive and negative, respectively, second order hyperpolarizabilities which were measured by DFWM and Z-scan experiments. Quantitative structure–property relations were established from semi-empirical calculations.

1 Introduction

An increasing interest in organic materials with high optical nonlinearity has emerged in recent years due to potential applications in optoelectronics and photonics. In particular, third order optical phenomena might be exploited for high speed all-optical switching in computing and telecommunication systems.[1] The fundamental physical property of a material useful for that purpose is the third order electric susceptibility $\chi^{(3)}$. The macroscopic susceptibility $\chi^{(3)}$ can be derived theoretically from the calculated microscopic molecular second order hyperpolarizability γ if local field effects and the orientation of the molecules are accounted for. On the other hand, it is straightforward to obtain γ from experimental $\chi^{(3)}$ or the nonlinear refractive index n_2 if the experiments are carried out in the gas phase where the local field effect is negligible or in dilute solutions where the local field effect can be accounted for by the simple Lorentz approximation.[2]

For practical applications it might be advantageous to use properly oriented molecules in order to efficiently exploit the largest tensor element. Langmuir–Blodgett techniques provide an excellent possibility for that purpose.[3] All compounds in this study have been designed and synthesized to be able to form LB layers. Nevertheless, the experimental results to be presented here refer to isotropic solutions.

The molecular design of an organic material with maximized nonlinearity requires reliable theoretical prediction algorithms or knowledge of structure–property relationships. Most reliable hyperpolarizabilities of calibrational quality can be calculated by *ab initio* methods for small molecules,[4] particularly if electron correlation effects are accounted for together with further refinements. Correlation effects have been shown to influence significantly the calculated second order hyperpolarizabilities in the case of a symmetric condensed-ring conjugated system.[5]

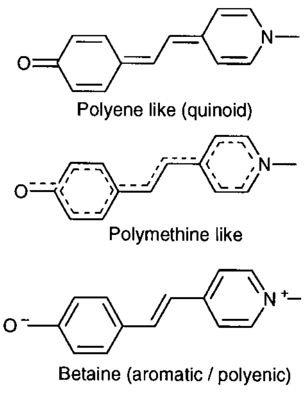
For large sets of bigger molecules like those studied in this paper sophisticated *ab initio* methods are prohibitive due to their computational cost. Therefore, semi-empirical methods are widely employed which have been proven useful particularly for trend prediction rather than for the calculation of correct hyperpolarizabilities.[6,7]

Relationships between the first order hyperpolarizability β and the chemical structure are better understood than those of γ. A simple description of β and γ in terms of state energies (E), static dipole moment changes ($\Delta\mu$) and transition dipole moments (μ) is obtained from the sum-over-states method (static limit),[8] *cf.* also the review in reference[7] [eqn. (1) and (2)].

$$\beta_{\mathrm{iii}} = \sum_{n=1} \frac{(\mu_{n0}{}^{\mathrm{i}})^2 \Delta\mu^{\mathrm{i}}}{E_{n0}{}^2} \qquad (1)$$

$$\gamma_{\mathrm{iii}} = \sum_{n=1} \frac{(\mu_{n0}{}^{\mathrm{i}})^2 (\Delta\mu^{\mathrm{i}})^2}{E_{n0}{}^3} - \sum_{n=1} \frac{(\mu_{n0}{}^{\mathrm{i}})^4}{E_{n0}{}^3} + \sum_{m,n=1} \sum_{m \neq n} \frac{(\mu_{n0}{}^{\mathrm{i}})^2 (\mu_{mn}{}^{\mathrm{i}})^2}{E_{n0}{}^2 E_{m0}} \qquad (2)$$

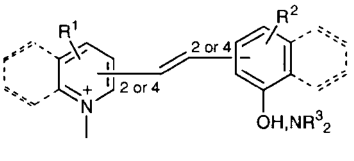
A comparison of the first term of eqn. (2) with eqn. (1) shows that large positive β can imply also large positive γ. Consequently, a very similar optimization strategy may be applied in the molecular design of compounds showing both large β and large γ as long as the first term of eqn. (2) is dominating. Hemicyanines are known to exhibit considerable charge transfer upon excitation. In particular, aminostilbazolium salts are among the most extensively investigated compounds concerning β.[9] Hydroxystilbazolium salts have not been investigated so extensively.[10,11] Because of the OH group being a weaker donor substituent in comparison to NR_2, hydroxystilbazolium salts are less interesting with respect to maximizing β. However, if the OH group is dissociated then the very strong donor substituent O^- is generated resulting in a merocyanine chromophore. Depending on the polarity of the environment and on the relative donor and acceptor strengths merocyanines might be realizations of any intermediate between a quinoid, an ideal polymethinic, and a betainic state (Scheme 1).



Scheme 1

The benzoid nature of the zwitterionic state has been confirmed experimentally for polar and non-polar solvents.[11] We use the terms polymethine and cyanine as defined by Dähne,[12,13] however, it should be pointed out that some authors use these terms with different meanings, *e.g.*[14] In an ideal polymethinic state β as well as the first positive contribution to γ should vanish. However, it can still exhibit large negative γ.[15]

It is the aim of this study to find structure–property relationships for γ within the class of hydroxystilbazolium salts. For that purpose we have synthesized a total of 21 compounds of the general formula shown in Scheme 2.



Scheme 2

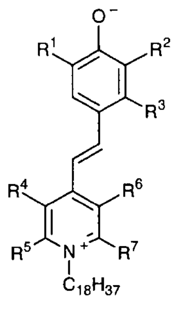
From a subset of the hydroxystilbazolium salts and their betainic counterparts we shall present experimentally determined γ values which are used for scaling the results of finite field (FF) calculations. From the latter quantitative structure–property relationships (QSPR) will be derived. We shall show that the cationic title compounds exhibit large positive γ comparable to known molecules of similar molecular weight. The corresponding neutral forms show negative γ which are among the largest ones so far published.[16]

2 Results

Structures of the compounds investigated in this study and their abbreviations are given in Schemes 3 to 6. In the following the superscripts ° and $^+$ will denote the neutral and the cationic forms of the compounds.

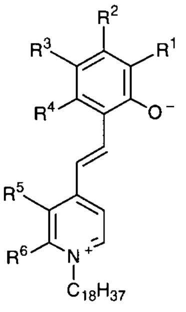
2.1. Semi-empirical quantum chemical calculations

The second hyperpolarizabilities of the cationic dyes were calculated by the finite field (FF) method after full geometry optimization of the molecules. Whereas reasonable results were obtained with the cationic dyes severe discrepancies from experimental data (see below) were obtained with the neutral merocyanines. Quinoid structures are predicted for the neutral merocyanines by all methods available in the packages used. FF calculations of γ based on those structures give erroneous results. Even the predicted sign is wrong. The merocyanines are predicted by various methods to absorb at approximately the same wavelength as their corresponding protonated counterparts or even at a lower wavelength which is also strongly at variance with experiment. Self consistent reaction field calculations with acetonitrile as a solvent as implemented in the VAMP program, for instance, did not overcome this discrepancy.



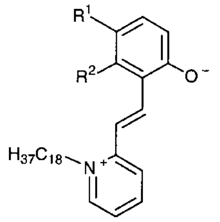
Scheme 3
4-(4-Oxystyryl)-1-octadecylpyridinium betaines

	R^1	R^2	R^3	R^4	R^5	R^6	R^7
1a	H	H	H	H	H	H	H
1b	H	H	H	C_4H_4		H	H
1c	H	C_4H_4		C_4H_4		H	H
1d	OCH_3	OCH_3	H	C_4H_4		H	H
1e	OCH_3	OCH_3	H	H	H	H	H
1f	OCH_3	H	H	C_4H_4		H	H
1g	OCH_3	H	H	H	H	H	H
1h	H	C_4H_4		H	H	H	H
1i	OCH_3	OCH_3	H	C_4H_4		C_4H_4	



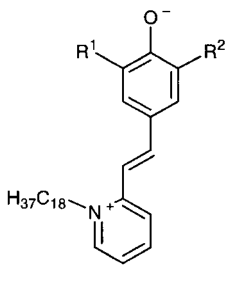
Scheme 4
4-(2-Oxystyryl)-1-octadecylpyridinium betaines

	R^1	R^2	R^3	R^4	R^5	R^6
2a	H	H	H	H	H	H
2b	H	H	H	H	C_4H_4	
2c	H	H	C_4H_4		H	H
2d	H	H	C_4H_4		C_4H_4	
2e	H	OCH_3	H	H	C_4H_4	
2f	H	OCH_3	H	H	H	H
2g	OCH_3	H	H	H	C_4H_4	
2h	OCH_3	H	H	H	H	H
2i	H	OCH_3	H	OCH_3	C_4H_4	



Scheme 5
2-(2-Oxystyryl)-1-octadecylpyridinium betaine

	R^1	R^2
3a	H	H



Scheme 6
2-(4-Oxystyryl)-1-octadecylpyridinium betaines

	R^1	R^2
4a	H	H
4b	OCH_3	OCH_3

Reasonable coincidence of the calculated γ with the experimental ones was obtained using molecular geometries optimized with the COSMO (conductor-like solvent model) algorithm which is implemented in the AMPAC package.[17] This method has been shown to deliver a molecular geometry for Brooker's merocyanine[18] which is close to the experimental one obtained by X-ray crystallography.[19] Though the solution geometry may differ from that in the crystal we expect a close resemblance because the merocyanine is hydrated in the crystal. Kurtz's method[20] for the calculation of γ fails (keywords KPOLAR and COSMO) in that again positive γ values are predicted for the betaines. Therefore, the FF method implemented in MOPAC6 was used after COSMO optimization. Also in the case of the cationic dyes the γ values from FF calculations are significantly closer to the experimental ones than those from KPOLAR. However, the solvent effect as modelled by COSMO is very small as expected. COSMO optimization was also performed with the cations merely for the sake of consistency. Changing the relative permittivity from 24.5 (ethanol) to 78.4 (water) only affects the result for the merocyanines. Since the theoretical results have to be compared to experiment ethanol was also chosen as the solvent for the COSMO calculations.

2.2 Comparison to experiment

Fig. 1 and 2 show examples of degenerate four wave mixing (DFWM) and Z-scan experiments, respectively, with compound **1d**$^+$ and its neutral counterpart **1d**$^\circ$ in ethanol solution. The Z-scan measurement is performed without the pinhole, see Fig. 5, to obtain the nonlinear absorption coefficients of the dye solutions (Fig. 2B). These Z-scans result in Lorentzian curves indicating higher absorption due to higher intensity at the focal point. With the knowledge of these curves the Z-scan with the pinhole in front of the detector could be corrected from nonlinear absorption by simple division of the data. As an example the resulting Z-scan signature for the **1d**$^\circ$ sample is shown in Fig. 2A in comparison with the Z-scan of pure ethanol. The minimum of the ethanol curve at negative z values denotes a positive sign of n_2. The smaller transmission change observed with the dye solution compared to that of the pure solvent proves that the solute **1d**$^\circ$ exhibits a negative n_2. It is assumed that the contributions to the optical nonlinearity of solute and solvent are additive.

In Table 1 the results of DFWM experiments obtained from ethanol solutions are presented together with the calculated γ values.

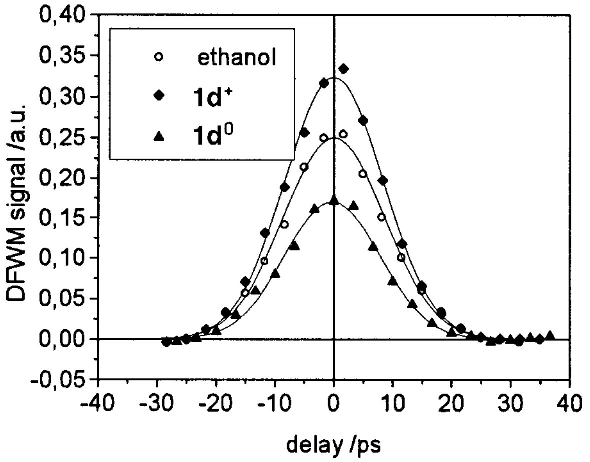


Fig. 1 Degenerate four wave mixing measurement with ethanolic solutions of **1d**$^+$ and **1d**$^\circ$. The measured DFWM signals are plotted against the delay of the backward pump pulse. The solid curves represent least squares fits to a Gaussian pulse shape.

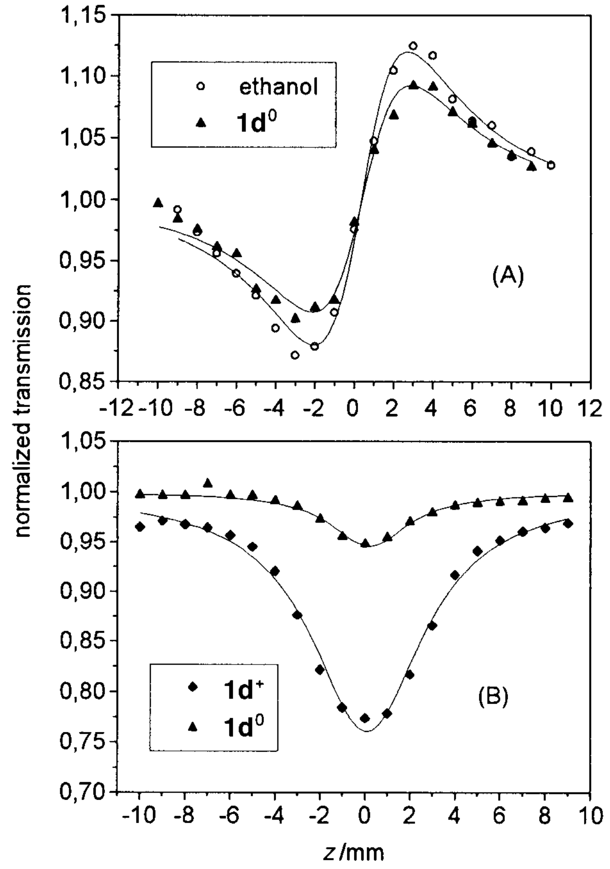


Fig. 2 Normalized nonlinear transmission of **1d**$^+$ and **1d**$^\circ$ in ethanol obtained from closed aperture (A) and open aperture (B) Z-scan experiments.

Linear correlation of the experimental to the calculated γ yields eqn. (3) and (4)

$$\gamma_{\text{calc}} = 293 \pm 37 + (0.21 \pm 0.06)\gamma_{\text{exp}}, \tag{3}$$

$$\gamma_{\text{calc}} = -46 \pm 66 + (1.1 \pm 0.2)\gamma_{\text{exp}}, \tag{4}$$

for the cationic hemicyanines and the neutral merocyanines, respectively. The correlation coefficients are $r = 0.83$ and $r = 0.95$, respectively. **1e**$^\circ$ shows significant two-photon resonance enhancement in the experiment, and was not included in the correlation. **1c**$^+$ is an outlier and was excluded from the correlation. These fairly reasonable correlations justify the use of theoretical hyperpolarizabilities instead of experimental ones in order to derive relations to the chemical structure. Aggregation at the comparatively high concentration applied for the DFWM experiments and insufficient solubility did not allow NLO investigations of the total number of compounds synthesized.

2.3 Relation between chemical structure and γ

We may encode each particular compound of the entire set by assigning $x_i = \{1 \text{ or } 0\}$ to the existence or nonexistence, respectively, of any of seven structural features i. Fitting the γ values obtained from the MOPAC calculations to eqn. (5)

$$\gamma_{calc} = a + \sum_{i=1}^{7} k_i x_i \tag{5}$$

yields the coefficients k_i and their standard deviations which are given in Table 2. The correlation coefficients are $r = 0.98$ and $r = 0.92$ for the cations and the neutral molecules, respectively.

In Fig. 3 the MOPAC γ are plotted *versus* the γ predicted from the correlation.

Table 1 Comparison of experimental (from the nonlinear refractive indices n_2) and calculated γ (MOPAC) values of selected dyes together with experimental absorption wavelengths. Geometries optimized with COSMO in ethanol

Sample	λ_{max}/nm	n_2(sample)/n_2(EtOH)	$n_2 \times 10^{-16}$/cm^2 W^{-1}	$\gamma \times 10^{-36}$/esu (exptl.)	$\gamma \times 10^{-36}$/esu (calcd.)
$1a^+$	400	+0.03	+0.23	78	328
$1a^\circ$	500	−0.16	−1.2	−407	−368
$1b^+$	450	+0.07	+0.53	180	376
$1b^\circ$	600	−0.13	−0.99	−336	−259
$1c^+$	500	+0.16	+1.2	408	602
$1c^\circ$	689	+0.05	+0.38	129	190
$1d^+$	453	+0.14	+1.1	337	372
$1d^\circ$	645	−0.22	−1.7	−577	−826
$1d^{\circ a}$	645	−0.18	−1.4	−475	−826
$1e^+$	421	+0.40	+3.0	1002	527
$1e^\circ$	564	$\approx -1^b$	$\approx -8^b$	$\approx -3300^b$	−400
$1h^+$	453	0.22	+1.67	563	384
$2c^+$	427	0.12	+0.91	307	321
$2c^\circ$	598	0.05	+0.38	128	−85
$2d^+$	484	0.41	+3.11	1127	595
$2d^\circ$	674	0.05	+0.38	128	136
$2i^+$	486	0.33	+2.50	845	367
$2i^\circ$	596	−0.09	−0.68	−230	−384

[a]Z-Scan, 1047 nm. [b]Two-photon resonance enhanced.

3 Discussion

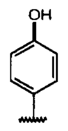
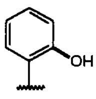
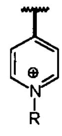
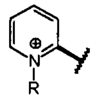
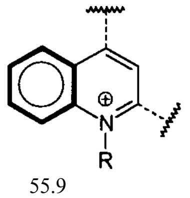
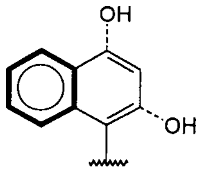
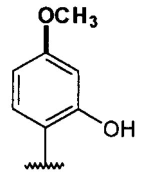
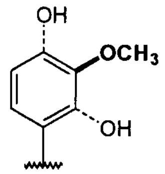
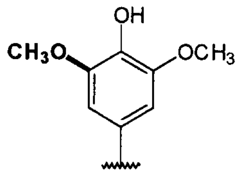
To understand the dependence of hyperpolarizabilities on chemical structure Marder *et al.* have performed pioneering work.[21] These authors discuss the nonlinear optical properties in terms of bond length and bond order alternation. This approach delivers particularly valuable insights if an unsaturated chain of a given length is considered under a variation of the donor and acceptor terminating groups or as a function of an external field. However, if a particular nonlinear optical parameter is to be maximized by a systematic variation of the structure then more structural information has to be considered than can be contained in bond length alternation (BLA) and bond order alternation (BOA) alone even within a given class of compounds.

Conformational flexibility can alter the optical and the nonlinear optical properties significantly.[22–24] This has to be taken into account when experimental results are to be compared with calculated ones. In the case of the stilbazolium salts two types of torsional motions or isomerism have to be taken into consideration: torsion of the aromatic rings around the $C_{aromatic}$–$C_{ethylenic}$ bond, and rotation of the methoxy group in the corresponding dyes. Benzocondensation causes a torsion of about 30° from coplanarity, whereas the dyes with uncondensed pyridine and benzene rings are predicted from calculations to be essentially coplanar.

The barrier for the rotation ($\approx$0.8 kJ mol^{-1}) of the methoxy groups is significantly smaller than the thermal energy ($RT \approx 2.4$ kJ mol^{-1}). However, one of the two methoxy groups in the *o*-position to OH cannot freely rotate due to hindrance by that OH group. This might be an explanation for the greater γ enhancing efficiency of the second methoxy group in comparison to the first one because the dihedral angle (COCC) has to be close to 0 or 180° in order to maximize the lone pair interaction with the aromatic π-system.

As recently pointed out by Morley[18] none of the conventional molecular orbital methods at the Hartree–Fock level are able to reproduce the correct geometry. The most promising procedure within the family of semi-empirical methods is probably the COSMO routine. There are alternative ways to

Table 2 Slopes k_i and their standard deviations σ_i of data fits to eqn. (3); upper two rows: cationic stilbazolium salts, lower two rows: neutral merocyanines

	p-OH	*p*-Acc	Acc-Bz	Don-Bz
	 *vs.* 	 *vs.* 		
k_i	168.6	135.9	55.9	139.4
σ_i	19.7	24.5	18.8	23.1
k_i	−124.2	−71.7	177.7	196.8
σ_i	38.7	48.1	36.9	45.3
	p-OCH$_3$	*m*-OCH$_3$(1)	*m*-OCH$_3$(2)	
				
k_i	139.8	41.2	113.28	
σ_i	33.4	25.4	31.6	
k_i	−25.7	17.6	−33.8	
σ_i	65.5	49.9	62.0	

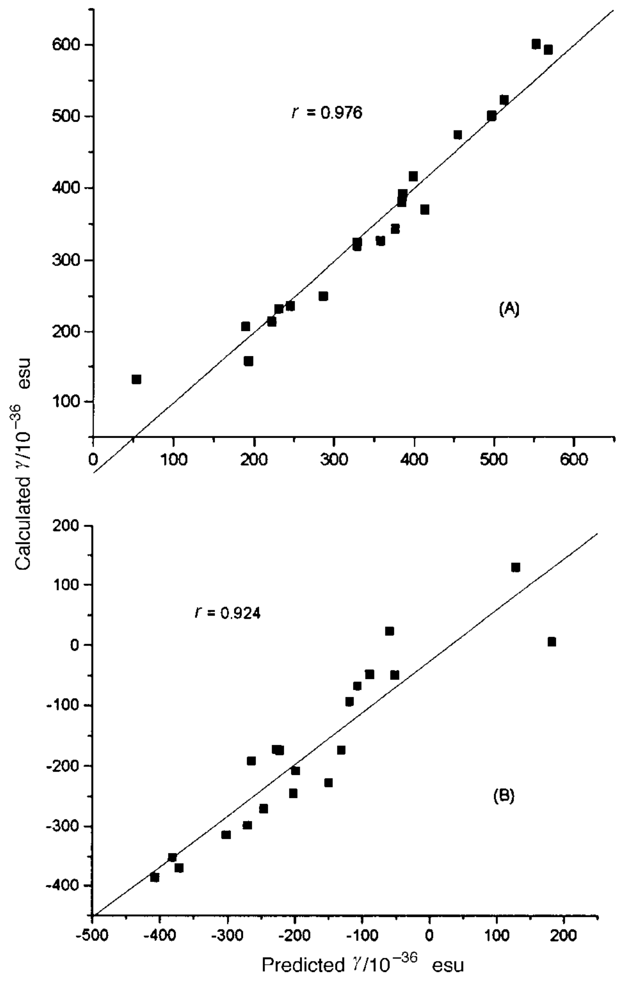


Fig. 3 Structure–property relationships for the calculated second order hyperpolarizability of the stilbazolium salts (A) and their neutral merocyanines (B).

drive the merocyanine molecules from the quinoid structure to the betainic one: optimization of the molecule in the presence of an external electric field directed parallel to the long axis,[21] or similarly, by usage of properly positioned sparkles[25] in the optimization procedure. We have performed geometry optimization with all merocyanines investigated here under a variation of the sparkle position until a structure was obtained which was closest to the ideal polymethinic state (measured by vanishing bond order alternation of the three central bonds). Significant trends of the experimental γ could be reproduced that way, however, this procedure remains highly unsatisfactory because the structures obtained that way are arbitrary. They may or may not be realized in some solvent which at least cannot be the same for all dyes. Inspection of the data given in Table 2 readily reveals the effect of the structure variation. Linking both or either of the aromatic rings of the stilbazolium salts in the *o*-position to the heterocyclic nitrogen atom or to the phenolic O atom, respectively, leads to a significantly smaller γ. Benzocondensation enhances γ, being slightly more effective at the donor moiety. Methoxy substitution in the 4-position significantly increases γ in the case of the *o*-hydroxy compounds. The effect of one *m*-methoxy group is small whereas the increasing effect of two methoxy groups is highly significant. Also with the neutral merocyanines *p*-linkages of both the donor and the acceptor moieties strongly enhance the amount of γ in comparison to the *o*-isomers. Again benzo annulation at the acceptor moiety enhances γ, that is γ becomes less negative. Two methoxy substituents in the *m*-position of the donor ring exhibit an effect on the magnitude of γ whereas a single methoxy substituent has only an insignificant influence. A similar observation was recently published by Morley[26] who found an unusual enhancement of β induced by a second alkoxy substituent and also by Hendrickx *et al.*[27] who pointed out that β depends critically on the conformation of the alkoxy groups.

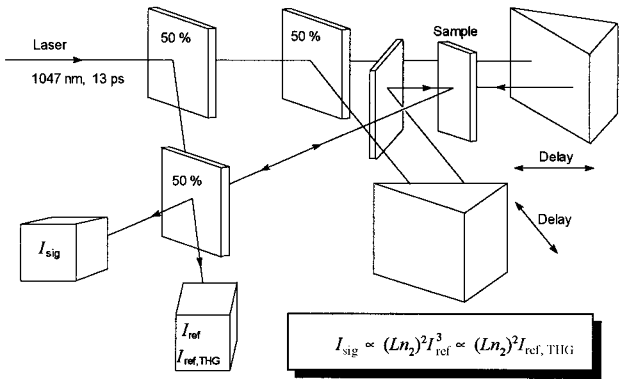


Fig. 4 Experimental setup of the DFWM experiment.

In order to assess the usefulness of the title compounds as materials for nonlinear optics, particularly as Langmuir–Blodgett multilayers, we may estimate the amount of $\chi^{(3)}$ for both the pure cationic and the neutral compounds to be in the order of magnitude of $10^{-12} < |\chi^{(3)}| < 10^{-11}$ esu. From a comparison of the averaged γ and the largest tensor element γ_{xxxx} we conclude that a five fold increase should be achievable by proper orientation of the chromophores. Finally, further structure variations are conceivable, in particular the synthesis of vinylogue compounds with hindered internal rotational degrees of freedom.

4 Experimental

4.1 Synthesis, solvents

The synthesis of the compounds has been described elsewhere.[28,29] The structures and the purity have been confirmed by ^{1}H NMR spectroscopy (Bruker DRX400). Spectroscopic grade ethanol (Merck UVASOL$^{\mathrm{TM}}$) was used for spectroscopic and NLO experiments. Concentrations close to 0.01 M were used for the DFWM measurements. It was checked prior to measurement that significant aggregation was absent by recording the absorption spectra of a capillary layer and comparing them with the spectra of a highly dilute solution ($\approx 10^{-5}$ M).

4.2 Apparatus

The measurements of the third order nonlinearities were performed using a passively mode-locked Nd : YLF-laser with a negative feedback system for pulse width and energy stabilization. The laser pulse width was 13 ps at a wavelength of 1047 nm. The measurement techniques we used were degenerate four wave mixing (DFWM) in the phase conjugation geometry (back reflection geometry) *cf.* for instance references[30] or [31] and the Z-scan method.[32,33] Fig. 4 shows the experimental setup of the DFWM experiment. The geometry of the Z-scan device can be seen in Fig. 5.

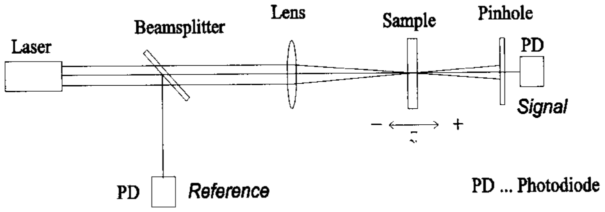


Fig. 5 Optical scheme of the Z-scan measurement.

The advantages of the DFWM measurement are a high sensitivity and the possibility of time resolved measurements. In the case of a nonlinear refraction combined with a nonlinear absorption it is difficult to extract the pure refractive effect from the absorption. To overcome the disadvantage of the DFWM technique we performed Z-scan measurements. All of the given values of n_2 are determined relative to ethanol ($n_2 = 7.6 \times 10^{-16}$ cm W^{-1}).[34] γ was calculated from n_2 according to formula (6)[35]

$$\gamma = \frac{n_2\, n_0^{2}}{f^4 N\, 3.90 \times 10^{-2}} \tag{6}$$

with the local field factor

$$f = \frac{1}{3}(n_0^{2} + 2)$$

where N is the number density and n_0 is the linear refractive index.

4.3 Calculations

The AMPAC package was used for all geometry optimizations. The AM1 hamiltonian was applied throughout together with the COSMO routine (EPS = 24.5). Electronic transitions were calculated with either the VAMP program[36] (PECI = 8) and CNDO(S) using both the Mataga–Nishimoto and the Ohno Klopman approximation or INDO1(S).[37] Second order hyperpolarizabilities were calculated with the help of the MOPAC6 package.[25] All quantum chemical calculations were performed on a DEC ALPHA 3000 workstation.

Acknowledgements

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