

One- and Two-Dimensionally Conjugated Tetraethynylethenes: Structure versus Second-Order Optical Polarizabilities

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Donor–acceptor substituted molecules, based on the two-dimensionally conjugated tetraethynylethene (TEE) framework, have been investigated for the first time for their first-order hyperpolarizabilities β by electric-field-induced second-harmonic generation (EFISH). We measured high values of up to $\beta^{\text{EFISH}} = (510 \pm 100) \times 10^{-40} \text{ m}^4/\text{V}$ at $\lambda = 1.907 \mu\text{m}$. We derived structure–property relationships by performing semiempirical calculations for all compounds. We show that such calculations give the correct trend in the hyperpolarizability β , and more importantly, give information as to the tensorial structure of β for molecules which are two-dimensionally donor–acceptor conjugated.

1. Introduction

Fully conjugated donor–acceptor substituted organic molecules are known as promising candidates for future applications in all-optical signal processing, frequency conversion, and ultrafast electrooptics. In order to optimize the nonlinear optical response of such molecules, it is important to know the influence of different donors and acceptors, the spatial molecular structure, and the type of conjugation. Derivatives of tetraethynylethene (TEE) are an interesting class of donor–acceptor substituted conjugated molecules, which allow the study of the contribution of different conjugation paths to the nonlinear optical properties. In preceding papers,^{1,2} the synthesis, structural, and optical properties of a series of donor–acceptor substituted TEEs were described. The unique TEE framework consists of a planar two-dimensional, π -conjugated core which is both rigid and sterically unencumbered. Furthermore, synthesis flexibility allows essentially every desired donor/acceptor substitution pattern to be achieved utilizing the positions R₁–R₄ (Figure 1). Structure–property relationships were derived for the second-order hyperpolarizability $\gamma^{(-3\omega;\omega,\omega,\omega)}$, based on data from third-harmonic generation (THG) measurements.³ To develop an understanding of the structure–property relationship of the TEEs, we have measured for the first time the first-order hyperpolarizability $\beta^{(-2\omega;\omega,\omega)}$ with the electric-field-induced second-harmonic generation (EFISH) method. With this technique, a combination of different tensor elements β_{ijk} is always measured. Therefore, we have also calculated the first-order hyperpolarizability tensors and the ground-state dipole moments with the software package MOPAC.⁴ Although it is not meaningful to compare in an absolute way the values from calculations to the values from measurements,⁵ we show that these calculations nevertheless give valuable insight into the contributions from the different possible conjugation paths.

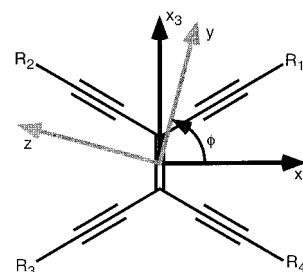


Figure 1. Molecular backbone of TEEs showing the four possible substitution positions R₁–R₄. Definition of the molecular orthogonal coordinate system y – z by the angle ϕ .

2. Electric-Field-Induced Second-Harmonic Generation

The first-order hyperpolarizability of an organic molecule is most often measured in solution by the EFISH method. A static electric field $E^{(0)}$ partially orients the molecules due to the coupling to the dipole moment. The solution becomes non-centrosymmetric, and a laser beam $E^{(\omega)}$ incident to the solution produces a second-harmonic signal. We define molecular first-order hyperpolarizability $\beta_{ijk}^{(-2\omega;\omega,\omega)}$ by

$$\mu_i^{(2\omega)} = \frac{1}{2} \epsilon_0 \beta_{ijk}^{(-2\omega;\omega,\omega)} E_j^{(\omega)} E_k^{(\omega)} \quad (1)$$

where $\mu^{(2\omega)}$ is the Fourier component at frequency 2ω of the molecular dipole moment. We choose the polarization of the incoming wave and the applied electric field in the x_3 direction. The frequency-doubled light is analyzed by a polarizer oriented along the x_3 direction. The macroscopic polarization at frequency 2ω is then given by

$$P_3^{2\omega} = \frac{1}{2} \epsilon_0 \chi_{333}^{(-2\omega;\omega,\omega)} (E^{(0)})(E_3^{(\omega)})^2 = \epsilon_0 \Gamma_L (E_3^{(\omega)})^2 E^{(0)} \quad (2)$$

$\chi_{333}^{(-2\omega;\omega,\omega)}$ is the second-order susceptibility, whereas Γ_L is a third-order susceptibility and connected to the molecular hyperpolarizabilities by

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$$\Gamma_L = Nf \left\{ \frac{3}{2} \gamma^{(-2\omega; \omega, \omega, 0)} + \frac{1}{2} \frac{\mu_g \bar{\beta}^{(-2\omega; \omega, \omega)}}{5kT} \right\} \quad (3)$$

N is the number density of molecules, μ_g the ground-state dipole moment, k the Boltzman constant, T the temperature, and γ the orientationally averaged second-order hyperpolarizability. If we choose the dipole moment along the x_3 -axis of the molecular coordinate system, the orientationally averaged first-order hyperpolarizability $\beta = \beta^{\text{EFISH}}$ is given by

$$\bar{\beta} = \frac{1}{3} \sum_{j=1}^3 (\beta_{3jj} + 2\beta_{jj3}) \quad (4)$$

TEEs are essentially planar molecules.¹ We define the molecular plane as being perpendicular to the x_1 -axis. Therefore we assume the tensor elements β_{1jk} , β_{j1k} , and β_{jk1} to be zero due to planarity. Equation 4 then simplifies to

$$\bar{\beta} = \beta_{333} + \frac{1}{3}(\beta_{322} + 2\beta_{223}) \quad (5)$$

It is thus impossible to measure single tensor elements of the first-order hyperpolarizability tensor β , and a combination of different tensor elements is measured, as given by eq 5.

For the measurements, we used a pulsed Nd:YAG laser (200 mJ, 10 Hz), which was wavelength-shifted to $\lambda = 1.907 \mu\text{m}$ using a hydrogen Raman cell. The beam was focused on a wedged cell on a translation stage containing the solution.⁶ The cell was then moved perpendicularly to the incoming beam. After the filters and analyzer, the second-harmonic intensity was detected by a photomultiplier tube. The β values were calibrated against a reference solution of 2-methyl-4-nitroaniline (MNA). The hyperpolarizability β of MNA was taken as $\beta_{\text{MNA}} = 44 \times 10^{-40} \text{ m}^4/\text{V}$,⁶ as determined by an EFISH experiment with crystalline quartz ($d_{11} = 0.277 \text{ pm/V}$ at $\lambda = 1907 \text{ nm}$) as a reference. For details on the experimental setup, see Bosshard et al.⁶ For each compound, we measured at least two different concentrations as well as the pure solvent (CHCl_3). The third-order susceptibility Γ_L is then given by⁷

$$\Gamma_L = \frac{N_A d(c) f(c)}{1 + c} \left\{ \frac{\gamma_s}{M_s} + \chi \frac{\gamma_p}{M_p} \right\} \quad (6)$$

where $\gamma_{s,p}$ is the second-order hyperpolarizability of solvent and chromophore molecules, respectively, c the concentration expressed as the total mass of chromophores divided by the total mass of the solvent, $f(c)$ contains all local field factors (Lorentz–Lorentz approximation), $d(c)$ is the density of the solution, N_A Avogadro's number, and $M_{p,s}$ the molecular masses of the chromophore and solvent molecule, respectively. We neglected the concentration dependence of the density and refractive indices, which proved to give small errors in comparison to other uncertainties for these very dilute solutions. For conjugated donor–acceptor substituted systems, the contribution in eq 3 from the second-order hyperpolarizability $\gamma^{(-2\omega; \omega, \omega, 0)}$ is much smaller than that from β , in our case less than 20% estimated from our third-harmonic generation data.³ As a consequence, $\gamma^{(-2\omega; \omega, \omega, 0)}$ was set to zero. The first-order hyperpolarizability β^{EFISH} for the chromophore (p) and the solvent molecule (s) is then given by

$$\beta_{p,s}^{\text{EFISH}} = \gamma_{p,s} \frac{10kT}{\mu_{p,s}} \quad (7)$$

where k is the Boltzman constant, T the temperature, and $\mu_{p,s}$

the dipole moment of the chromophore and solvent molecules, respectively. To obtain β^{EFISH} , one must also know the dipole moment, as seen in eq 7. It should be noted that the dipole moment is mainly determined by $\text{O}_2\text{NC}_6\text{H}_4$ -acceptor group (Table 1).

For all compounds, we used the calculated dipole moment (Table 1), which coincides well with the measured values for compounds **3** and **8**. To more accurately compare the hyperpolarizability β with measurements at other wavelengths and with the calculations, which always yield static values, we interpolated the measured value $\beta^{(-2\omega; \omega, \omega)}$ to the zero frequency value, β_0 , by using the two-level model^{8,9} (Table 1). This is only a first approximation, however, since the two-level model may be insufficient for describing two-dimensional molecules.

3. Calculation of Hyperpolarizabilities and Dipole Moments

We calculated the molecular nonlinear optical properties of the TEEs (**1–8**, Table 1), using the semiempirical finite field method¹⁰ with the MOPAC6⁴ software and the PM3 parametrization. Using MOPAC, the hyperpolarizability tensor β in the coordinate system of the main axes of the moment of inertia tensor is obtained. MOPAC uses definitions of the molecular hyperpolarizabilities that differ from those defined by eqs 1–3, and for comparison, the β_{ijk} tensor elements from MOPAC were corrected by⁵

$$\beta_0^{\text{calc}} = \frac{5}{6} \beta_{\text{vec}}^{\text{MOPAC}} \quad (8)$$

$$\beta_{ijk}^{\text{calc}} = \frac{1}{2} \beta_{ijk}^{\text{MOPAC}} \quad (9)$$

To reduce the calculation time, the nonlinear inactive moieties $\text{Si}(\text{Pr})_3$ and SiMe_3 in all compounds were replaced by a single hydrogen atom. The electronic inactivity of the trialkylsilyl groups was determined experimentally by measuring the UV spectra for molecules **2** and **5** and their desilylated analogues. The spectra showed only minimal changes in the absorption coefficients and in the wavelengths of maximum absorption, λ_{max} , which is a good indication of the validity of this approximation.

To obtain the contributions which originate from the different conjugation paths in the molecule, we calculated the angular dependence of the diagonal element β_{yyy} for compounds **5–8** (Figures 2 and 3) and of the nondiagonal element β_{zyy} for compound **8** (Figure 3). If $\mathbf{e}^y(\phi)$ and $\mathbf{e}^z(\phi)$ are unit vectors in the y and z direction, respectively (for a definition of the coordinate system, see Figure 1), then the angular dependence of the diagonal and nondiagonal element of compound n is given by eqs 10 and 11, where the tensor β_{ijk} is given in coordinate system (x_1, x_2, x_3) and summation over common indices is assumed.

$$\beta_{yyy}^{(n)}(\phi) = \beta_{ijk}^{(n)} \mathbf{e}_i^y(\phi) \mathbf{e}_j^y(\phi) \mathbf{e}_k^y(\phi) \quad (10)$$

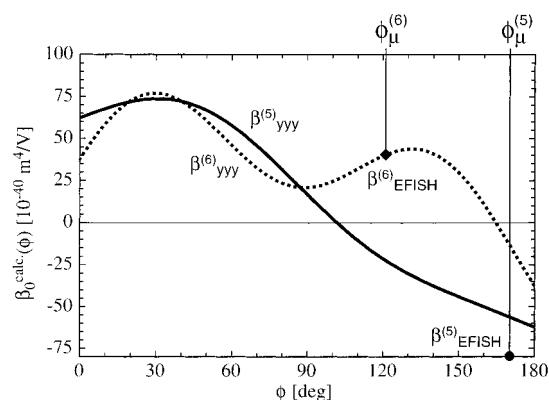
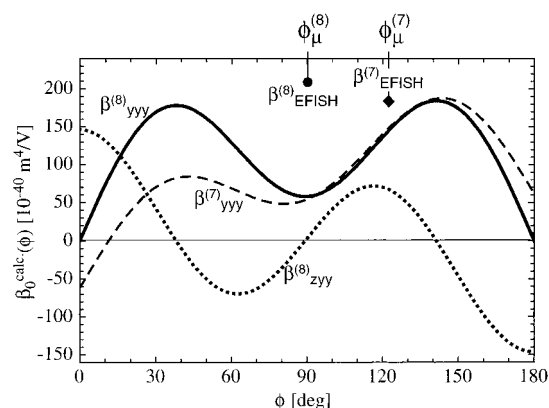
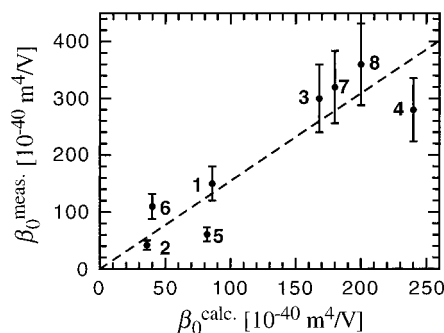
$$\beta_{zyy}^{(n)}(\phi) = \beta_{ijk}^{(n)} \mathbf{e}_i^z(\phi) \mathbf{e}_j^y(\phi) \mathbf{e}_k^y(\phi) \quad (11)$$

4. Results and Discussion

The EFISH measurements of donor–acceptor substituted TEEs showed significant values for the hyperpolarizability, as high as $\beta^{\text{EFISH}} = (510 \pm 100) \times 10^{-40} \text{ m}^4/\text{V}$ (compound **8**). The value for **8** compares well to other highly nonlinear optical organic molecules such as 4-(dimethylamino)benzaldehyde-4-nitrophenylhydrazonyl (DANPH) with $\beta^{\text{EFISH}} = 280 \times 10^{-40}$

TABLE 1: Molecular Structures, Measured Wavelengths of Maximum Absorption λ_{\max} (nm), Calculated β_0 , Measured β and β_0 (all $10^{-40} \text{ m}^4/\text{V}$), Calculated Dipole Moments μ_c , and Measured Dipole Moments μ_m (all 10^{-30} C m)

Nr.	Structure	Direction of dipole moment	λ_{\max}	Calc. β_0	Meas. β β_0	μ_c μ_m
1			433	86	190 150	6.3 —
2			382	36	51 42	16 —
3			468	168	430 300	21 22
4			481	240	400 280	26 —
5			447	82	82 61	19 —
6			471	40	150 110	17 —
7			461	180	450 320	21 —
8			486	200	510 360	24 29

**Figure 2.** Calculated angular dependence of the diagonal first-order hyperpolarizability β_{yyy} for compounds **5** and **6**. β_{EFISH} is the calculated EFISH value, indicated at the direction of the dipole moment ϕ .**Figure 3.** Calculated angular dependence of the diagonal first-order hyperpolarizability β_{yyy} for compounds **7** and **8** and of the nondiagonal component β_{zyy} for compound **8**. β_{EFISH} is the calculated EFISH value, indicated at the direction of the dipole moment ϕ .**Figure 4.** Comparison of measured and calculated first-order hyperpolarizabilities of compounds **1–8**, with an estimated overall error of 20%. The measured values were extrapolated to infinite wavelengths by the two-level model.^{8,9}

m^4/V^{11} or 4-(dimethylamino)-4'-nitrostilbene (DANS) with $\beta_{\text{EFISH}} = 430 \times 10^{-40} \text{ m}^4/\text{V}$.¹² Note that all hyperpolarizabilities were scaled for the new reference value for quartz of $d_{11} = 0.277 \text{ pm/V}$ at $\lambda = 1907 \text{ nm}$.

In Figure 4, the measured values for β_{EFISH} are compared to those calculated. The straight line is a linear fit through the origin. With an estimated uncertainty of 20%, the measured and calculated values correlate well, with the exception of compounds **4**, **5**, and **6**.

For compound **4**, the discrepancy may be explained by a twist angle in the longer backbone by solvent–chromophore interactions, which would hinder the charge transfer between donor and acceptor. For the molecules **5** and **6**, the dipole moment is

not along the charge transfer axis and a shift of the electron density along the charge-transfer axis due to solvent–chromophore interactions may therefore cause a rotation of the dipole moment direction. Such a dipolar rotation might also explain the relatively large deviation observed between measured and calculated values of β for molecules **5** and **6**.

The same effect is also possible for compound **7**, however, this molecule fits well into the relationship between measured and calculated values (Figure 4). Despite the deviations of TEEs **4**, **5**, and **6**, the calculated and measured values correlate nicely.

With the MOPAC calculations, in contrast to the EFISH measurements, values for all tensor elements β_{ijk} are obtained. Based on the observed correlation between β_0^{exp} and β_0^{calc} , the calculated tensor elements β_{ijk}^{calc} should be of realistic values.

TEE **1** with a single $\text{Me}_2\text{NC}_6\text{H}_4$ -donor substitution has a calculated value of $\beta^{(1)} = 86 \times 10^{-40} \text{ m}^4/\text{V}$, whereas compound **2** with a single nitrophenyl acceptor substitution only has $\beta^{(2)} = 36 \times 10^{-40} \text{ m}^4/\text{V}$. This is in contrast to donor/acceptor monosubstituted benzenes, where β for nitrobenzene was higher than for *N,N*-dimethylaniline.¹² For the monosubstituted stilbenes with a longer conjugation length, almost identical values were measured for β , of both the $\text{Me}_2\text{NC}_6\text{H}_4$ donor and $\text{O}_2\text{NC}_6\text{H}_4$ acceptor substituted derivatives.¹² For the more extensively conjugated compounds **1** and **2**, the $\text{Me}_2\text{NC}_6\text{H}_4$ -donor substituted **1** has a much larger value β than the $\text{O}_2\text{NC}_6\text{H}_4$ -acceptor substituted **2**. This indicates that by increasing the conjugation length, the effect of the donor group on β becomes more important with respect to the acceptor group.

TEE **3** is the combination of **1** and **2** and has a value of $\beta^{(3)} = 168 \times 10^{-40} \text{ m}^4/\text{V}$, which is higher than the sum $\beta^{(1)} + \beta^{(2)} = 122 \times 10^{-40} \text{ m}^4/\text{V}$. This well-known cooperative effect between donor and acceptor¹³ was also observed for para-disubstituted benzenes and disubstituted stilbenes¹² and others.

In the transition from compound **3** to **4**, the conjugation length is increased, which is usually accompanied with an increase in β , as has been shown for donor–acceptor substituted α -phenylpolyene oligomers and other systems.¹⁴ This initially expected trend is confirmed by the calculations, but not by the measurements. This discrepancy is attributed to the slightly twisted charge-transfer axis due to solvent–chromophore interactions as described above.

Molecule **5** shows a calculated $\beta_{yyy}^{(5)}(30^\circ)$ (direction of the donor group, Figure 2), which corresponds well to that of compounds **1**, **6**, and **7** in the same direction. This suggests that this value is mainly determined by the single $\text{Me}_2\text{NC}_6\text{H}_4$ donor group. Furthermore, β is relatively small, due to the inefficient cross conjugation between donor and acceptor groups.³ For molecule **6**, the $\text{O}_2\text{NC}_6\text{H}_4$ acceptor group and the $\text{Me}_2\text{NC}_6\text{H}_4$ donor group are located almost perpendicularly to each other. As a result, we get a value of $\beta_{yyy}^{(6)}(30^\circ) = 80 \times 10^{-40} \text{ m}^4/\text{V}$ in the direction of the donor group and $\beta_{yyy}^{(6)}(150^\circ) = 32 \times 10^{-40} \text{ m}^4/\text{V}$ in the direction of the acceptor group, which coincides very well with that of compounds **1** and **2** (Figure 2).

In addition, the measured value for **6** (cis configuration) is much lower than that measured for **3** (trans configuration). This is in contrast to the second-order hyperpolarizability γ , where comparable values for the trans- and cis-configured compounds were observed.³

However, in the third-harmonic generation (THG) measurement of γ , one obtains the rotational average of γ_{ijkl} , whereas in the EFISH measurement one gets the average in eq 4 for β , and the component along the dipole moment dominates. The

mentioned discrepancy might be a result of the different averaging in the EFISH and THG measurements.

The value of compound **7** in the direction of the push–pull charge-transfer axis of $\beta_{yyy}^{(7)}(150^\circ) = 172 \times 10^{-40} \text{ m}^4/\text{V}$ corresponds excellently with that of compound **3** and **8** in the same direction (Figure 3 and Table 1). The highest value ($\beta_{yyy}^{EFISH} = (510 \pm 100) \times 10^{-40} \text{ m}^4/\text{V}$) of this series of compounds was measured for molecule **8**. It is noted that this value mainly originates from the nondiagonal tensor element β_{zyy} , as seen by eq 5 and Figure 3. In the direction of the dipole moment, $\beta_{yyy}^{(8)}(90^\circ) = 50 \times 10^{-40} \text{ m}^4/\text{V}$ is observed, whereas for the nondiagonal element a three times larger value of $\beta_{zyy}^{(8)}(0^\circ) = 150 \times 10^{-40} \text{ m}^4/\text{V}$ is obtained. Using eq 5 and the Kleinman relation, the EFISH value is given by $\beta_{yyy}^{(8)}(90^\circ) + \beta_{zyy}^{(8)}(0^\circ) = 200 \times 10^{-40} \text{ m}^4/\text{V}$.

5. Conclusions

Large values for the first-order hyperpolarizability β of donor–acceptor substituted TEEs, comparable to other highly nonlinear optical chromophores, have been measured. These compounds provide a large measured product $\mu \cdot \beta$ of up to $15 \times 10^{-67} \text{ C m}^5/\text{V}$ for compound **8**, compared to $9 \times 10^{-67} \text{ C m}^5/\text{V}$ for DANS,¹² an important parameter for using the chromophores in a poled polymer guest–host or side-chain system.

We showed that semiempirical calculations are important in predicting trends in the nonlinearity of a series of structurally related molecules. Calculations can estimate the entire tensor structure of the first-order hyperpolarizabilities, which is especially important for two- or more-dimensional conjugation.

This knowledge leads to an understanding of the contributions from different donors and acceptors, as well as of different conjugation paths. This insight is crucial for the innovative design of improved chromophores.

In a crystal composed of a two-dimensional chromophore such as **8**, it is much more likely to find a phase matching geometry for frequency doubling than in crystals of charge-transfer molecules such as **3** with one donor–acceptor conjugation path, because it is possible to use the large nondiagonal coefficients and the refractive indices will differ only slightly for different polarizations.

The formation of suitable noncentrosymmetric crystals as well as the incorporation of highly NLO active TEE chromophores into polymers for solid-state studies is now being pursued.

References and Notes

- (1) Tykwinski, R. R.; Schreiber, M.; Gramlich, V.; Seiler, P.; Diederich, F. *Adv. Mater.* **1996**, *8*, 226.
- (2) Tykwinski, R. R.; Schreiber, M.; Carlon, R. P.; Diederich, F. *Helv. Chim. Acta* **1996**, *79*, 2249.
- (3) Bosshard, C.; Spreiter, R.; Günter, P.; Tykwinski, R. R.; Schreiber, M.; Diederich, F. *Adv. Mater.* **1996**, *8*, 231.
- (4) Kurtz, H. A.; Stewart, J. J. P.; Dieter, K. M. *J. Comput. Chem.* **1990**, *11*, 82.
- (5) Knöpfle, G. *Diss. ETH No. 11159* **1995**, 29.
- (6) Bosshard, C.; Knöpfle, G.; Prêtre, P.; Günter, P. *J. Appl. Phys.* **1992**, *71*, 1594.
- (7) Kajzar, F.; Ledoux, I.; Zyss, J. *Phys. Rev. A* **1987**, *36*, 2210.
- (8) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.
- (9) Lalama, S. J.; Garito, A. F. *Phys. Rev.* **1979**, *A 20*, 1179.
- (10) Zyss, J. *J. Chem. Phys.* **1979**, *70*, 333.
- (11) Serbutoviez, C.; Bosshard, C.; Knöpfle, G.; Wyss, P.; Prêtre, P.; Günter, P.; Schenk, K.; Solari, E.; Chapuis, G. *Chem. Mater.* **1995**, *7*, 1198.
- (12) Cheng, L. T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631.
- (13) Levine, B. F. *Chem. Phys. Lett.* **1976**, *37*, 516.
- (14) Cheng, L. T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643.