Design Strategies versus Limiting Theory for Engineering Large Second-Order Nonlinear Optical Polarizabilities in Charged Organic Molecules

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The combination of two design strategies for engineering large second-order nonlinear optical polarizabilities is critically analyzed and contrasted with a recent limiting theory for nonlinear molecular polarizabilities. Elongation of the conjugation path length and *N*-arylation in stilbazolium chromophores *both* are established engineering guidelines to enhance molecular optical nonlinearities. These two strategies have now been combined, resulting in extended *and N*-aryl substituted “stilbazolium” chromophores. The second-order nonlinear molecular polarizabilities, or first hyperpolarizabilities β, of these ionic compounds were measured by hyper-Rayleigh scattering with suppression of the multiphoton fluorescence contributions. Static first hyperpolarizabilities β_0 were estimated by using the two-level model. The resulting large β_0 values are compared with theoretical limiting values obtained from recently derived generally applicable sum-rules and with experimental values for neutral dipolar chromophores. It is concluded that the two design strategies are independently valid, and that their combination will therefore provide the maximum attainable β_0 in an ionic compound. Crystals containing optimized ionic chromophores can hence be expected to possess electrooptic coefficients far greater than those obtained so far from either ionic crystals of stilbazolium dyes or from neutral dipolar guest chromophores in polymer matrixes.

I. Introduction

The optical properties of materials are increasingly important in an era when electronics is being challenged by photonics. For communication, the electron as carrier in a metallic conductor is being replaced by the photon in an optical fiber. Multiwavelength optical communication increases the capacity of an optical network by orders of magnitude versus electronic communication. Although optical data read-out is common nowadays, the changes in reflection from an optical disk are immediately converted into electrical signals, or vice versa for writing. All-optical data manipulation based on opto-optical effects (involving changes in the optical properties of a material under the influence of light) is still far-fetched because few materials exhibit the required large third-order nonlinear optical (NLO) responses. Because data manipulation is still all-electronic at present, the interconversion between electronic and optical signals is extremely important. This interconversion can be achieved via the electrooptic (EO) effect, a second-order NLO phenomenon (arising from the molecular first hyperpolarizability β) whereby the optical properties of a material are changed under the influence of an electric field.[1] As with all even-order NLO phenomena, the EO effect can exist only in noncentrosymmetric media, but even so is often not large enough for practical applications. However, commercial EO modulators based on inorganic materials such as lithium niobate and gallium arsenide are available.

Chemistry allows the design of new materials with anticipated optical/electronic properties. In particular, synthetic organic chemistry offers a wealth of possibilities for optimizing and fine-tuning desirable properties by following molecular engineering guidelines. Organic materials have a number of advantages over inorganic materials for EO applications: (i) their dielectric constants are much smaller; (ii) their refractive indices are lower; (iii) their polarizabilities are purely electronic and, therefore, faster; and (iv) molecules are compatible with polymeric matrixes. Therefore, substantial research has gone into the second-order NLO properties of organic materials.[1] Modulation bandwidths as high as 150 GHz have been achieved in prototypical EO devices based on neutral organic chromophores dispersed in polymer matrixes.[2] An example of a recently

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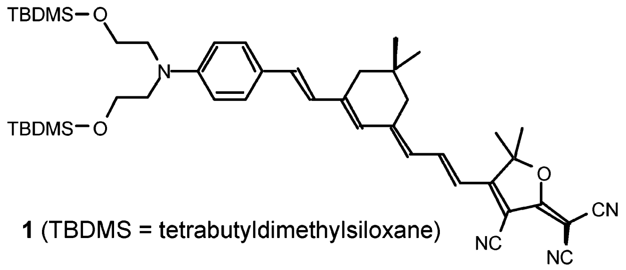
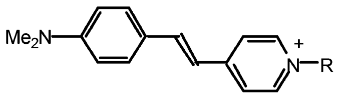
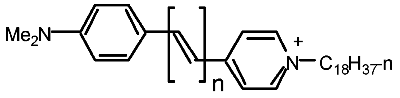
synthesized NLO chromophore is **1**, the β value of which is among the highest ever reported (about 3000×10^{-30} esu). **1** has been carefully engineered for high second-order optical nonlinearity: a long conjugated path with enforced planarity and an all-trans configuration, a highly efficient electron donor−acceptor couple following the bond-length alternation guideline, and a controlled shape to reduce the electrostatic intermolecular interactions. An EO coefficient r_{33} of over 60 pm/V, together with an impressive halfwave voltage V_π of 0.77 V at 1318 nm have recently been realized for a poled guest−host system containing **1**.[3] However, such numbers are limited by the maximum number of guest chromophores that can be hosted in the polymer matrix before negative intermolecular interactions become significant.



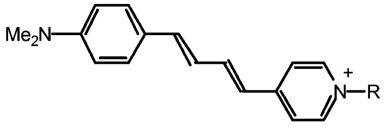
1 (TBDMS = tetrabutyldimethylsiloxane)



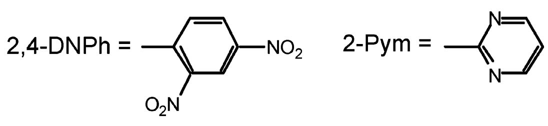
R = Me (**2**), Ph (**3**), 2,4-DNPh (**4**), 2-Pym (**5**)



n = 1 (**6**), 2 (**7**), 3 (**8**), 4 (**9**), 5 (**10**)



R = Me (**11**), Ph (**12**), 2,4-DNPh (**13**), 2-Pym (**14**)



In a polymer host matrix, the required noncentrosymmetry must be induced by orienting the dipolar guest molecules in a melt under the application of an electric field before cooling to below the glass transition temperature. This process results in a thermodynamically unstable situation that tends to relax to the isotropic, centrosymmetric, and hence inactive state. By contrast, such problems of thermal and temporal relaxation of the necessary ordering are absent in noncentrosymmetric ionic crystals. Such materials also have the advantage that they contain higher chromophore number densities than can be achieved by dispersed chromophores in a polymer matrix. In particular, crystals of *trans*-4′-(dimethylamino)-*N*-methyl-4-stilbazolium (**2**) tosylate have been found to show very pronounced NLO effects, with EO coefficients, e.g., $r_{111} = 47$ pm/V at 1535 nm[4] and second-order NLO coefficients, e.g., $d_{111} = 1010$ pm/V at 1318 nm.[5] In-line intensity modulation in a thin-film waveguide of such crystals was observed up to 18 GHz and believed to extend beyond 100 GHz.[6] It is hence clear that incorporating an ionic dye into a noncentrosymmetric crystal is a very efficient way of assembling individual chromophores in a bulk structure for EO applications. However, the chromophore **2** itself is far from optimized: the conjugated bridge is short, and the effects of modifying the electron donor and/or acceptor groups have not yet been explored.

Because practical applications of NLO materials must avoid any actual photon absorption, it is necessary to refer to static (*off-resonance*) first hyperpolarizabilities β_0. These can be estimated from experimentally determined (and therefore resonance enhanced) β values by using a two-level model for dipolar chromophores.[7] Recent synthetic efforts have succeeded in increasing the β_0 values of stilbazolium dyes along two lines: Nakanishi and co-workers have elongated the conjugation pathway, leaving the donor and acceptor groups unchanged;[8] and we have increased the acceptor strength of the pyridinium nitrogen by the attachment of *N*-aryl substituents.[9] We have now combined these two different strategies and critically assess the results herein, in the context of theoretical limiting values obtained from recently derived generally applicable sum-rules.

II. *N*-Arylation of the Pyridinium Nitrogen

Recent experimental studies on stilbazolium chromophores have shown the feasibility of enhancing β_0 by *N*-arylation of the pyridinium group. These investigations were inspired by previous work involving ruthenium(II) ammine complexes of pyridinium ligands, in which the metal centers act as electron donors and larger β_0 values arise from the stronger electron-withdrawing capabilities of *N*-aryl versus *N*-alkyl pyridinium groups.[10] The same design strategy holds for purely organic stilbazolium dyes.[9] The ions **2** and *trans*-4′-(dimethylamino)-*N*-R-4-stilbazolium [R = phenyl (Ph) **3**, 2,4-dinitrophenyl (2,4-DNPh) **4**, 2-pyrimidyl (2-Pym)

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5] were studied.[9] Their electronic absorption spectra show intense, visible intramolecular charge-transfer bands, the energy of which decreases in the order R = Me > Ph > 2,4-DNPh > 2-Pym, due to the steadily increasing electron deficiency of the pyridinium ring. The β values of the ions **2**−**5** were determined by using the hyper-Rayleigh scattering (HRS) technique.[11] To avoid overestimations of β due to multiphoton fluorescence,[12] these studies employed femtosecond HRS with fluorescence demodulation[13] at 1300 nm.[14] It was found that the *N*-aryl chromophores **3**−**5** have larger β_0 values than their *N*-methyl counterpart **2**, and the same trend was observed in the β_0 values calculated indirectly by using the two-level model and data derived from Stark (electroabsorption) spectroscopy.[9] The β_0 values of **4** are decreased by the steric effect of the *ortho*-NO_2 group which causes twisting of the 2,4-DNPh ring out of the plane of the stilbazolium unit.

III. Elongation of the Conjugation Pathway

Elongation of the conjugation pathway has long been one of the primary design rules for increasing the β_0 values of organic molecules.[15−19] This principle has been verified experimentally and is a key factor in the so-called transparency-nonlinearity tradeoff because extension of the conjugation reduces the energy level spacing between ground and excited states. However, the effects of this molecular structural change had not been systematically investigated in ionic chromophores until very recently, when higher homologues of the parent ion *trans*-4′-(dimethylamino)-*N*-(*n*-octadecyl)-4-stilbazolium (**6**) were synthesized.[8] In these longer homologues, the ethenyl linkage is replaced by a 1,3-butadienyl, 1,3,5-hexatrienyl, 1,3,5,7-octatetraenyl, or a 1,3,5,7,9-decapentaenyl unit. The corresponding compounds are labeled **7**−**10**, respectively. From this first study involving femtosecond 1300 nm HRS measurements, it was concluded that elongation is indeed a viable strategy to enhance β_0 in stilbazolium chromophores.[8] Perhaps surprisingly, the β_0 value was found to reach a maximum for the 1,3,5-hexatrienyl linkage. For the longer homologues, decreases in β_0 were ascribed to departures from the fully optimized (all-trans) configuration to single-cis configurations in the excited states. Such isomerization processes would be expected to lead to reduced β_0 responses due to attenuation of π-orbital overlap along the polyenyl chains.

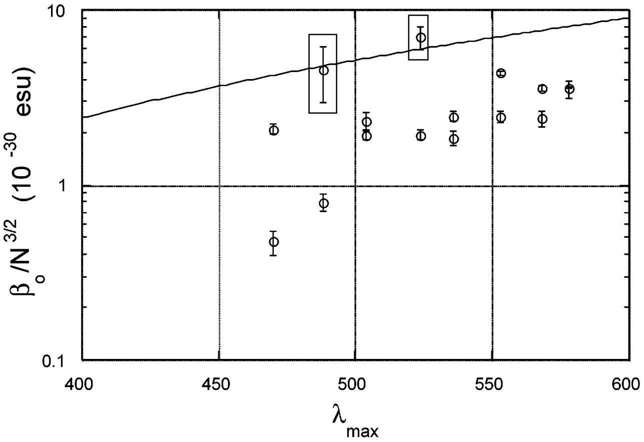

Figure 1. ENR values for the static first hyperpolarizability, $\beta_0/N^{3/2}$, as a function of wavelength of maximal absorption, λ_{max}: solid line, theoretical upper limit according to the theory by Kuzyk.[24] The two data symbols per λ_{max} are the results derived from the two β_0 values (from HRS measurements at 800 and 1300 nm). Note how the two largest values (boxed), at or even above the theoretical limit, also show the largest estimated uncertainties and correspond with the shortest fluorescence lifetime (see entries in italics in Table 1).

In one instance, electric-field-induced second harmonic generation (EFISHG) has been applied to solutions of a stilbazolium salt and its extended analogues in a solvent with a low dielectric constant.[20] This technique makes use of a coherently generated signal in the forward direction and, hence, does not need to deal with the multiphoton fluorescence. However, the resulting signal cannot be unequivocally related to a single diagonal β component, as neither the effective orientation, nor the magnitude of the dipole moment of the close-ion pair has been considered. Even so, the signal will be somehow related to the diagonal β element along the molecular charge-transfer axis. The results show the general trend of increasing molecular second-order NLO response (as determined by $\mu\beta$ values where μ = dipole moment) on elongation,[20] but they are not useful for a critical analysis and a quantitative comparison with a limiting theory.

The value that is obtained for the parent species **2** can be compared with values from the literature. Great care has to be taken, however, when comparing, because the alkyl substitution pattern,[21] the counterion,[22] the solvent,[8] the measurement technique,[12,20,23] the reference value,[14] and the measurement wavelength, all have an influence on the deduced value. Therefore, we enter in our quantitative analysis (Table 1 and Figures 1 and 2) only data that were obtained from species with the same alkyl substitution pattern (dimethylamino donor and methyl as the parent acceptor if not varied), with

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Table 1. Experimental Parameters: Wavelength of Maximal Absorption, λ_{max}; Dynamic First Hyperpolarizability at 800 nm, $\beta_{(800nm)}$; Dynamic First Hyperpolarizability at 1300 nm, $\beta_{(1300nm)}$; Fluorescence Lifetime from Demodulation and Phase at 1300 nm, $\tau_{(1300nm)}$[a]

ion	λ_{max} (nm)	$\beta_{(800nm)}$ (10^{-30} esu)	$\beta_{(1300nm)}$ (10^{-30} esu)	$\tau_{(1300nm)}$ (10^{-9} s)	$\beta_{0(800nm)}$ (10^{-30} esu)	$\beta_{0(1300nm)}$ (10^{-30} esu)	N	$\langle\beta_0\rangle$ (10^{-30} esu)	$\langle\beta_0\rangle/N^{3/2}$ (10^{-30} esu)
2	470[a]	440 ± 30	55 ± 10[b]	1 ± 1	110 ± 7	25 ± 4[b]	14	68	1.30
3	504[a]	290 ± 20	405 ± 40[b]	2 ± 6	102 ± 7	120 ± 12[b]	14	112	2.14
4	536[a]	295 ± 20	370 ± 35[b]	5.8 ± 0.3	130 ± 9	100 ± 9[b]	14	114	2.18
5	553[a]	270 ± 20	1130 ± 20[b]	3 ± 1	130 ± 9	230 ± 4[b]	14	180	3.44
11	488	166 ± 20	*770* ± 270	*0.30* ± 0.06	51 ± 6	*290* ± 100	16	51	0.80
12	524	301 ± 20	*1500* ± 220	*0.26* ± 0.09	123 ± 8	*445* ± 65	16	123	1.92
13	568	304 ± 32	1200 ± 45	1.3 ± 1.2	153 ± 16	230 ± 9	16	190	2.97
14	578	435 ± 50	1370 ± 22	NA	226 ± 26	230 ± 4	16	228	3.56

[a] Deduced parameters: static first hyperpolarizabilities β_0, derived from the experimental dynamic hyperpolarizabilities at 800 and 1300 nm. Suspiciously large values for β, β_0, and concomitant small values for τ are indicated in italics. From the molecular parameter N, the reduced number of electrons in the conjugated linkage, the electron-number-rated static first hyperpolarizability $\langle\beta_0\rangle/N^{3/2}$ is calculated from $\langle\beta_0\rangle$, the average of the $\beta_{0(800nm)}$ and $\beta_{0(1300nm)}$ values that are not in Italics. [b] Ref 9.

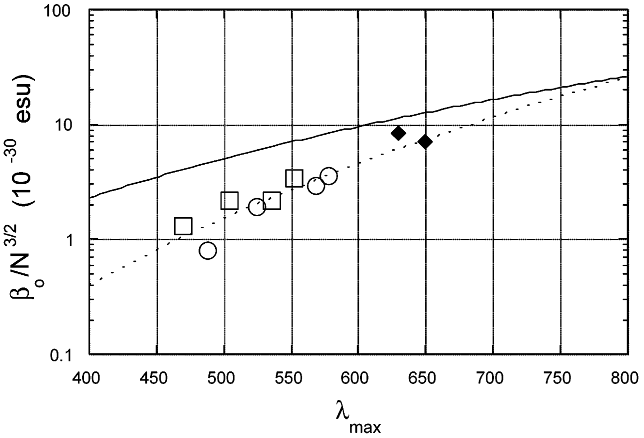

Figure 2. ENR values for the average static first hyperpolarizability, $\langle\beta_0\rangle/N^{3/2}$, as a function of wavelength of maximal absorption, λ_{max} (the electron-number-rated static first hyperpolarizability $\langle\beta_0\rangle/N^{3/2}$ is calculated from $\langle\beta_0\rangle$, the average of the $\beta_{0(800nm)}$ and $\beta_{0(1300nm)}$ values that are not in italics): solid line, theoretical upper limit according to the theory by Kuzyk;[24] squares, average result for the short series **2**−**5**; circles, average results for the longer series **11**−**14**; diamonds, best results reported so far for neutral dipolar chromophores **15** and **16**; dotted line, phenomenological power law fitting to the experimental data (data fit with λ_{max} to the power 6), indicating the limiting approach to the theoretical limit (theory fits with λ_{max} to the power 3.5)

the same hexafluorophosphate as counterion, all dissolved in acetonitrile, and derived from a frequency-resolved measurement technique that has been shown to provide reliable and accurate fluorescence-free hyperpolarizabilities.[13] This is considered to be the best methodology to deduce valuable conclusions about the effect of the elongation and *N*-arylation.

IV. Combination of *N*-Arylation and Elongation

The NLO properties of the ion *trans*-*N*-methyl-4-(4-dimethylaminophenyl-4-buta-1,3-dienyl)pyridinium (**11**) have been studied previously.[24] Inspired by the results described in parts II and III above, we have now prepared the series of extended, *N*-arylated "stilbazolium" chromophores, *trans*-*N*-R-4-(4-dimethylaminophenyl-4-buta-1,3-dienyl)pyridinium (R = Ph **12**, 2,4-DNPh **13**, or 2-Pym **14**). The details of the syntheses and other properties of these novel species will be reported elsewhere.[25]

V. Experimental Section

The experimental β values for the ions **2**−**5** and **11**−**14** have all been determined by femtosecond HRS with high-frequency demodulation of the multiphoton fluorescence, both at 800 nm[13] and at 1300 nm.[14] All of the chromophores have been shown to exhibit this additional source of incoherent photons that could lead to overestimations of β. Classical HRS with nanosecond pulses and time gating is incapable of distinguishing between the immediate scattering and the time-delayed fluorescence, since a typical fluorescence lifetime τ is on the order of only a few nanoseconds. Femtosecond pulses with very short temporal gating have been shown to provide the experimental means for discriminating between the scattering and fluorescence directly in the time domain.[26] The experimental approach used here is the Fourier transform (FT) equivalent in the time domain. A time delay between fluorescence and scattering is translated into a phase shift between the real and imaginary, or cosine and sine FT in the frequency domain; the amplitude of the total signal is the modulus of the complex FT. The phase grows from 0 to 90 degrees, while the normalized amplitude of the fluorescence contribution decays from 1 to 0 for increasing frequency. When measuring this amplitude as a function of frequency (in the frequency domain), the high amplitude at the low frequencies shows the overestimated β, and the low amplitude at the high frequencies shows β without fluorescence contributions. The high-frequency limit for β is taken as the fluorescence-free value. The data analysis affords a single diagonal hyperpolarizability tensor component, β_{zzz}, with the *z*-axis being the charge-transfer axis along the dipolar chromophore. All of the HRS measurements were carried out in acetonitrile. Reference values in this solvent are 500×10^{-30} esu for crystalviolet at 800 nm (from 340×10^{-30} esu in chloroform) and 86×10^{-30} esu for Disperse Red 1 at 1300 nm (from 54×10^{-30} esu in chloroform).[9] No concentration dependence of the hyperpolarizability was found (over the concentration range from 1×10^{-4} to 8×10^{-6} M) in agreement with a previous study of ionic species.[8] The static hyperpolarizability value, β_0, was obtained by application of the two-level model.[7] Although the applicability of this model was recently challenged,[27] it remains a viable tool for comparing the molecular nonlinearity of chromophores with a single major charge-transfer band that is resulting in a hyperpolarizability value that is resonantly enhanced.

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Although this setup is not optimized for τ measurements, an estimate for this parameter is provided from the data analysis, assuming a single-exponential fluorescence decay. When the τ value is extremely short (shorter than 1 ns), it becomes quite difficult to distinguish between the immediate scattering and the fluorescence within the bandwidth of the instrument (1 GHz). In such a case, much care needs to be taken in order to correctly interpret the data, and additional criteria may be invoked to validate the results.[8]

VI. Critical Analysis of the Combined Strategy

We now wish to analyze the HRS β_0 values for **2**−**5** and **11**−**14** against a recently developed limiting theory specifically derived for the diagonal hyperpolarizability tensor elements in the off-resonance regime.[28] First, to achieve a reliable experimental database, the initial 1300 nm HRS measurements on the series **2**−**5**[9] were complemented with measurements at 800 nm. HRS measurements at both fundamental wavelengths were also performed on **11** and the new series **12**−**14**. These measurements at two different fundamental wavelengths allow for estimates of the uncertainties on the retrieved β_0 values. Table 1 lists the wavelengths of maximal absorption $\lambda_{\max}$ and the retrieved dynamic and static hyperpolarizability data, from HRS measurements at 800 and 1300 nm. Also included are single fluorescence lifetime estimates from the frequency-dependent multiphoton fluorescence contributions to the signals.

According to the limiting theory recently developed by Kuzyk[28] the sum-rule-restricted (SR) three-level model results in a two-level-limit ($2L$) for β, depending solely on the reduced number N of electrons (with charge e and mass m) and the transition energy E_{10} between the ground and first excited state. This reduced number of electrons, i.e., only 2 electrons per double or triple bond in the conjugated π-electron system, has been shown earlier to reproduce correct linear absorption spectra and to provide the largest susceptibilities near the theoretical maximum limit.[28] The limit for β^* (the dressed first hyperpolarizability, i.e., the β value as measured in a solvent with a given refractive index n) is given by eq 1.

$$\beta_{2L}^{*SR} \leq \sqrt[4]{3}\left(\frac{n^2+2}{3}\right)^3\left(\frac{e\hbar}{\sqrt{m}}\right)^3\frac{N^{3/2}}{{E_{10}}^{7/2}} \qquad (1)$$

This theory was found to be in agreement with a large set of experimental dressed β data. For our purposes, this dressed β in the off-resonance regime, $\beta_{2L}{}^{*SR}$, is identical to the β_0 value measured in solution.[29] The same theory was recently shown to be very useful in pointing to possible systematic errors in the experiment.[29] For example, an experimental β_0 result larger than the theoretical limit strongly indicates an overestimation error due to multiphoton fluorescence.

In Figure 1 are plotted the so-called electron-number-related (ENR) first hyperpolarizability values, $\beta_0/N^{3/2}$ (symbols), as obtained directly from the β_0 data of Table 1, together with the theoretical upper limit (solid line) for this parameter. The two data points per $\lambda_{\max}$ are the two β_0 values per compound, derived from the two dynamic β values from the HRS measurements, i.e. at 800 and 1300 nm. We do not attribute much weight to the largest two values (indicated in boxes in Figure 1), for three reasons: (i) both values have large statistical uncertainties (low precision), larger than typical for the experiment (compare the error bars for the two next largest values); (ii) these are the only values at, or even over, the theoretical upper limit (a value at the upper limit indicates a molecule completely optimized for second-order NLO effects, but it is unlikely that only these two compounds (**11** and **12**) out of the series, would be completely optimized); and (iii) these two values are derived from multiphoton fluorescence contributions with the two shortest values. As seen earlier, the distinction between the immediate scattering and the shortest fluorescence decay is difficult.[8] For these three reasons, these largest two β_0 values and their corresponding β values are considered “outliers” (indicated in italics, together with the ultrasmall τ values in Table 1) and are not included in the remaining data analysis.

After this first critical comparison with the limiting theory, average static first hyperpolarizability values $\langle\beta_0\rangle$ were determined from the remaining β_0 data. This means that $\langle\beta_0\rangle$ is the average of the $\beta_{0(800\mathrm{nm})}$ and $\beta_{0(1300\mathrm{nm})}$ values that are not indicated in italics in Table 1. It can be seen that $\langle\beta_0\rangle$ increases in the pyridinium substituent order R = Me < Ph < 2,4-DNPh < 2-Pym for both the stilbazolium series **2**−**5** and for the extended series **11**−**14**. With the exception of the N-Me chromophores, $\langle\beta_0\rangle$ also increases when moving from a stilbazolium ion to its extended analogue. From the $\langle\beta_0\rangle$ values, average electron-number-related β_0 values, $\langle\beta_0\rangle/N^{3/2}$, were derived. These values are compared with the limiting theory in Figure 2. This is *not* a second iteration of the former procedure, but is aimed at evaluating the resulting trend in the obtained averages of higher accuracy in the light of the trend in the limiting curve. It can be seen that the same general trend with respect to the effect of the N-substituent is observed within both series of chromophores, i.e. $\langle\beta_0\rangle/N^{3/2}$ increases in the order R = Me < Ph < 2,4-DNPh < 2-Pym. However, the $\langle\beta_0\rangle/N^{3/2}$ values are larger for the extended chromophores compared with their stilbazolium analogues only in the cases where R = 2,4-DNPh or 2-Pym. Most importantly, no maximum is observed in Figure 2. All this taken together, the trends in the $\langle\beta_0\rangle$ and $\langle\beta_0\rangle/N^{3/2}$ values indicate that the two individual β_0-enhancing strategies operate independently, with the largest value of $\beta_0/N^{3/2}$ being obtained by combining the longest conjugated linkage with the most electron deficient pyridinium group (in **14**).

VII. Comparison with Optimized Neutral Chromophores for Guest−Host Polymeric Systems

The $\beta_0/N^{3/2}$ values obtained for **2**−**5** and **11**−**14** can be compared with those for the best dipolar, neutral NLO chromophores reported so far.[2,30] The latter chromophores, with N values of 20, have β values approaching 3000×10^{-30} esu at 1064 nm, in combination with charge-transfer absorption bands at around 650 nm.

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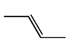
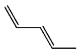
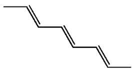
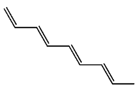
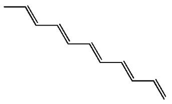
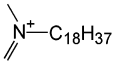
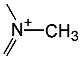
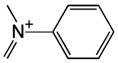
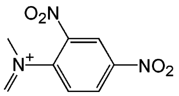
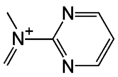
polyenyl linkage acceptor group					
	8	8	8	8	8
	9	this work			
	9	this work			
	9	this work			
	9	this work			

Figure 3. Stilbazolium and related compounds presently available, indicated by reference number to the original study, in the matrix of possible compounds along the orthogonal dimensions of independent design strategies: elongation (horizontal) and *N*-arylation (vertical).

The resulting $\beta_0/N^{3/2}$ values for **15** and **16** are included on Figure 2 as the filled diamonds. It is clear that, at this point, the second-order NLO activities of these neutral chromophores surpass those of the currently available ionic species.

VIII. Conclusions and Perspectives

Figure 2 shows that both strategies are needed to fully optimize a "stilbazolium" chromophore for second-order NLO effects. A comparison of the *phenomenological* power law fitting to the experimental data (the dotted line, data fit with $\lambda_{\max}$ to the power 6) with the one to the limiting theory (the solid line, data fit with $\lambda_{\max}$ to the power 3.5), indicates that combining *N*-arylation with further extension of the conjugation will quickly lead to ionic chromophores, fully optimized up to the theoretical upper limit. Therefore, further synthetic work is needed to provide the *N*-aryl substituted "stilbazolium" dyes with the 1,3,5-hexatrienyl, 1,3,5,7-octatetraenyl, and 1,3,5,7,9-decapentaenyl linkages. The compounds that are presently available are indicated in a two-dimensional matrix-like fashion in Figure 3. Each dimension represents one design strategy: the horizontal dimension represents elongation of the conjugation, while the vertical dimension indicates the *N*-arylation strategy. The matrix element is the reference number of the original study. Such a matrix is reminiscent of a combinatorial chemistry approach in the search for second-order NLO chromophores. However, from the experimentally demonstrated independence of both strategies, we can already predict that with a dimethylamino/pyridinium donor−acceptor combination, the largest NLO activity will be obtained for the 1,3,5,7,9-decapentaenyl *N*-2-pyrimidyl chromophore.

It should be remembered that an extended conjugation path length is only effective inasmuch as it remains in an all-trans configuration. This has been convincingly demonstrated in the first systematic study of extended "stilbazolium" chromophores, when the maximum in β_0 was obtained for the 1,3,5-hexatrienyl linkage.[8] The latter length also proved to be the best optimized in comparison with the limiting theory.[29] Strategies previously employed to fix all-trans configurations include fused-ring bridging to prevent isomerization (and to increase thermal and photochemical stability)[3,31] and inclusion in a rigid matrix.[29,32] Another consequence of locking the configuration is a decreased likelihood of nonradiative deactivation, which enhances the probability of multiphoton induced fluorescence. However, this is not necessarily a hindrance to accurate measurements of β_0 using femtosecond HRS experiments.[13,14]

Finally, the incorporation of extended "stilbazolium" ions into noncentrosymmetric bulk structures with high chromophore number densities will afford materials with high, limiting EO coefficients (derived from limiting β_0 values in structures with the highest attainable number densities). One attractive approach is crystal growth, if the crystal habit is or can be made to be noncentrosymmetric (e.g., by appropriate side-substitution, as in the noncentrosymmetric 2-methyl-4-nitroaniline crystal versus the centrosymmetric *para*-nitroaniline).[33] Intermolecular interactions have been reported to reduce the molecular nonlinearity in the solid state.[2,23]

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So, additional engineering at the crystal level might be necessary to take the best advantage in the bulk of the chromophores optimized at the molecular level. A crystal bulk system has the additional advantage of offering the ultimate in thermal and temporal stability, together with higher purity than can be achieved in amorphous materials. An alternative for noncentrosymmetric bulk engineering is Langmuir–Blodgett deposition. To this end, molecular engineering of the dyes (e.g., replacing the methyl groups at the donor side by longer alkyl chains) can impart amphiphilic properties.

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