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13. ABSTRACT (Maximum 200 words)

The search for suitable NLO materials that are stable at elevated temperatures and that can be used for blue light generation requires that novel chromophores that can be incorporated into crosslinked polymers be developed. Several new tolane as well as stilbene chromophores with functionalized electron rich donor ends and electron-poor sulfonamide, sulfonate or sulfoximide ends have been prepared. These new chromophores have been evaluated for their transparency below 400 nm, and their molecular second-order hyperpolarizability has been measured by the EFISH method that provides $\mu\beta$ values. The results of these measurements indicate that several of these new chromophores are capable of meeting the requirements for frequency doubling of a diode laser operating at 820nm. The chemistry of these new NLO chromophores allows their easy functionalization for incorporation of independently polymerizable groups at the donor and the acceptor ends of the molecules.

14. SUBJECT TERMS

NON-LINEAR OPTICS, NLO CHROMOPHORES, FREQUENCY DOUBLING, DIODE LASER, EFISH MEASUREMENTS SULFONATES, SUFONAMIDES, SULFOXIMIDE.

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New Chromophores Containing Sulfonamide, Sulfonate, or Sulfoximide Groups for Second Harmonic Generation

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Introduction

Blue light generation for use in optical storage, printing, and other integrated optical applications has become a topic of intense research. Due to the lack of efficient lasers in this spectral region, the popular method of generating blue light involves frequency doubling of near infrared (800-850 nm) diode laser light using nonlinear optical (NLO) materials. Both organic and inorganic NLO compounds have been studied to date, but neither class has yet emerged as the material of choice. Efficient blue light generation requires that materials display not only a large nonlinear response, but also optical transparency at both the laser and blue light wavelength, i.e. colorless materials. This is particularly demanding on organic materials. Many electron-donor and electron-acceptor substituted π systems, including substituted benzenes, stilbenes, azobenzenes, and diphenylacetylenes (tolanes), are known to display large NLO responses. However, while conjugated π -systems with common acceptor substituents such as NO_2 , CN or COR have large molecular hyperpolarizabilities, they suffer from low optical transparency in the region of blue light due to a low lying charge-transfer (CT) absorption.^[1,2] The sulfone group was recently introduced as another acceptor substituent.^[3,4] Donor-acceptor-substituted benzenes, styrenes, and tolanes with sulfone as the acceptor substituent show a remarkable molecular nonlinearity combined with a charge-transfer absorption band at relatively short wavelength.^[3-6] Therefore, it seemed

worthwhile to investigate the effect of the sulfonamide, sulfonate ester, and sulfoximide as acceptor groups on NLO properties. One example for sulfonamide as an acceptor for an NLO molecule is known, but no values for $\mu\beta$ have been published.^[7] In addition to the expected low wavelength CT absorption, the multifunctional nature of these acceptor groups offers an easy way to derivatize them in order to develop crosslinkable polymers as NLO materials. In this paper we report on the synthesis and results of electric-field-induced second-harmonic generation (EFISH) measurements of such substituted tolanes and stilbenes.

Results and Discussion

Synthesis

The tolanes **5-7** (Scheme 1) were synthesized from appropriately substituted aryl halides using the methods developed by *Hagihara*^[8] and *Negishi*.^[9] In the first step, the synthesis of the arylacetylenes **3**, **4a** and **4b**, was achieved by reaction of the aryl iodides **1**, **2a**, or **2b** either with trimethylsilylacetylene in the presence of catalytic amounts of $\text{PdCl}_2(\text{PPh}_3)_2$ and CuI followed by desilylation,^[8] or with ethynylzinc chloride under $\text{Pd}(\text{PPh}_3)_4$ -catalysis.^[9] The arylacetylenes **3**, **4a** and **4b** were then converted into the corresponding zinc chloride salts and coupled with aryl halides in the presence of catalytic amounts of $\text{Pd}(\text{PPh}_3)_4$ ^[9] to give the tolanes **5-7** in overall yields of 40-50%.

Stilbenes **10a-d** (Scheme 2) were prepared using the *Heck* reaction.^[10] The acceptor substituted arylbromides **8a-d** were coupled with *t*-BOC-styrene^[11] in the presence of triethylamine and catalytic amounts of palladium diacetate and tri-*o*-tolylphosphine. The product, a mixture of the stilbenes **9a-d** and the corresponding *t*-BOC-substituted stilbenes, was treated with sodium methoxide affording stilbenes **9a-d** which were then alkylated to give stilbenes **10a-d** in 30-60% overall yields.

Spectroscopic and Nonlinear Optical Properties

The UV-vis spectroscopic and nonlinear optical properties of tolans **5-7** and stilbenes **10** are summarized in Table 1. The UV-vis spectra of compounds **5-7** and **10** in CHCl_3 , each show an intense low-energy absorption band which is rather narrow (ca. 55 nm half-height width). This band is assigned to an intramolecular CT transition. The wavelengths of the CT absorption bands are comparable with those reported for a 4-alkoxy-4'-sulfonyl-substituted stilbene ($\lambda_{\text{max}} = 335$ nm in CHCl_3)^[4] or tolane ($\lambda_{\text{max}} = 310$ nm in dioxane).^[5] It should be noted that the λ_{max} of the tolans **5-7** determined in dioxane is 4-6 nm lower than λ_{max} determined in CHCl_3 . As expected,^[12] the CT-bands of the tolans are blue-shifted significantly relative to the correspondingly substituted stilbenes. A comparison within the same π -system of the three different acceptor groups used, shows that the sulfonates usually absorb at longer wavelengths than the sulfonamides. The choice of N-substitution on the sulfonamide group has a small effect on λ_{max} as revealed by a comparison of stilbenes **10b** and **c**. The absorption of sulfoximide **10d** is similar to those of sulfonamides **10b, c** and sulfonate **10a**. Exchanging the methoxy-substituent for a methylthio-substituent^[5,6,13] causes a red shift of the absorption by about 10 nm.

For electric-field poled materials, the macroscopic nonlinear optical response is directly related to the product of the molecular second-order hyperpolarizability (β), and the ground state dipole moment (μ). The values for $\mu\beta$ of the substituted tolans and stilbenes (determined by the EFISH method^[3]) are listed in Table 1. The largest values for a specific π -system, tolane or stilbene, are achieved with the sulfonate ester group. Changing from a sulfonate ester to a sulfoximide and further to a sulfonamide results in a decrease in $\mu\beta$. The values for $\mu\beta$ of the tolans are always lower^[5,12] than those of the corresponding stilbenes. Neither the exchange of a methoxy substituent for a methylthio substituent, nor the change of the N-substituent of the sulfonamide group have a profound effect on $\mu\beta$.

Although some of our data support the well known trade-off between $\mu\beta$ and λ_{\max} , they also display remarkable deviations from this correlation. Stilbenes **10a** and **c** have the same λ_{\max} , but they have very different values of $\mu\beta$. The same is true for tolans **5a** and **6b**. In addition, the CT absorption band of tolane **6a** lies at 10 nm longer wavelengths than that of the tolane **5a** but the values of $\mu\beta$ are approximately the same. For the generation of blue light, the combination of a methoxy and sulfonate ester group, as in **10a**, appears to be the best of those studied in this paper: within one π -system, this combination leads to the highest $\mu\beta$ while maintaining a low λ_{\max} . For comparison purposes 4-(6-hydroxyhexyloxy)-4'-(methylsulfonyl)stilbene was prepared by adaptation of literature procedures^[3,4] and the value of $\mu\beta$ ($\mu\beta = 97 \cdot 10^{-48}$ esu; $\lambda_{\max} = 335$ nm) determined using the same EFISH measurements. Clearly, the nonlinearity of sulfonate ester **10a** is superior to that of the 4-alkoxy-4'-sulfonylstilbene, confirming the validity of our approach to novel functional chromophores for NLO applications.

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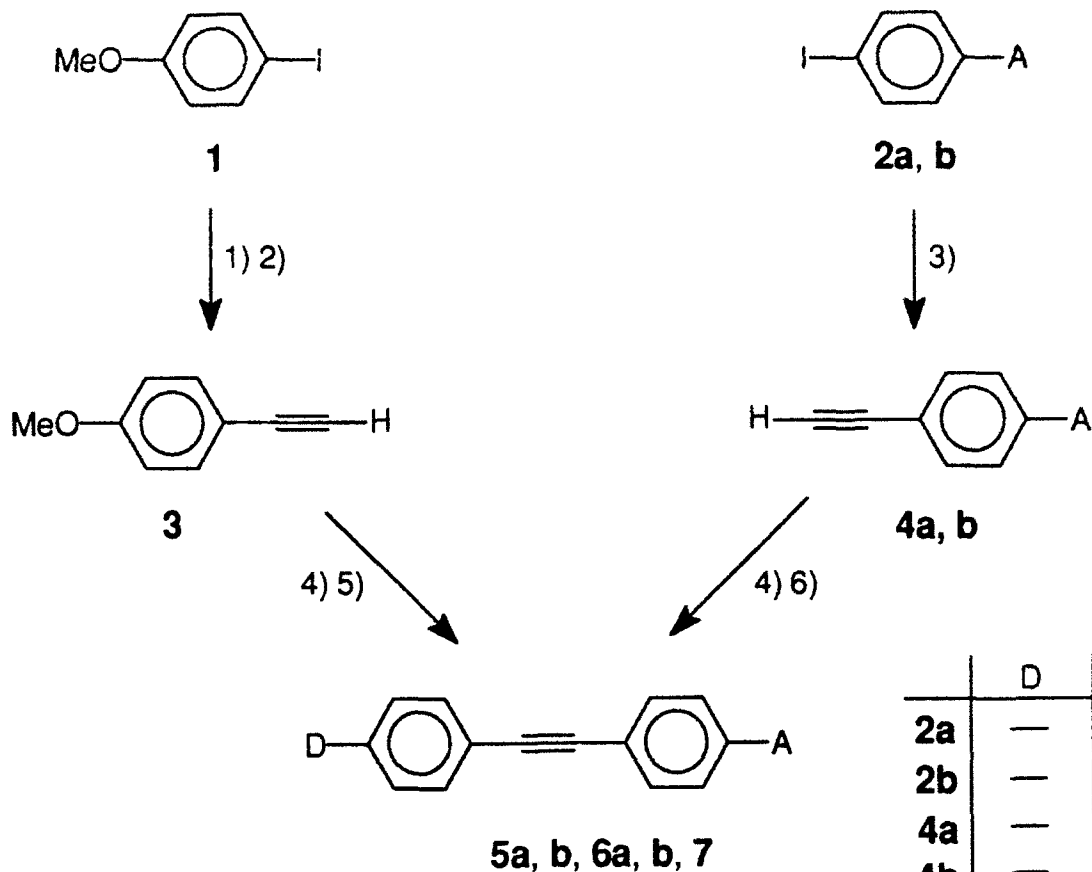
Table 1: Spectroscopic and nonlinear optical properties of the tolanses **5-7** and stilbenes **10** in CHCl_3 . $\lambda_{\text{EFISH}} = 1907 \text{ nm}$.

	Donor	Acceptor	$\lambda_{\text{max}}(\log \epsilon)$ (nm)	$\mu\beta$ (10^{-48} esu)
5a	MeO	SO_3Ph	321 (4.473)	89
5b	MeO	SO_2NBu_2	312 (4.504)	49
6a	MeS	SO_3Ph	331 (4.518)	95
6b	MeS	SO_2NBu_2	324 (4.556)	59
7	Me_2N	SO_2NBu_2	359 (4.534)	--
10a	EtO	SO_3Ph	340 (4.420)	160
10b	EtO	SO_2NBu_2	335 (4.512)	100
10c	EtO	SO_2NPh_2	340 (4.526)	95
10d	PrO	S(O)(NH)Me	338 (4.550)	130

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SCHEME 1



	D	A
2a	—	SO ₃ Ph
2b	—	SO ₂ NBu ₂
4a	—	SO ₃ Ph
4b	—	SO ₂ NBu ₂
5a	MeO	SO ₃ Ph
5b	MeO	SO ₂ NBu ₂
6a	MeS	SO ₃ Ph
6b	MeS	SO ₂ NBu ₂
7	Me ₂ N	SO ₂ NBu ₂

1) HCCSiMe₃ / Pd(PPh₃)₂Cl₂ / CuI / Et₂NH / rt;

2) NaOH / MeOH / rt;

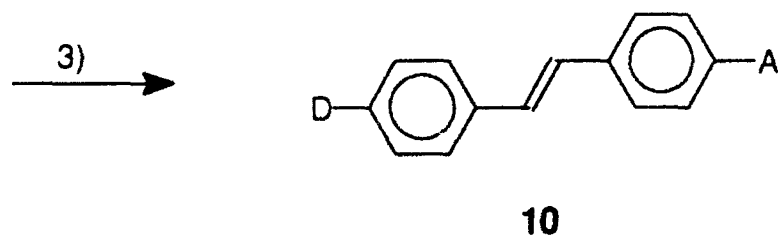
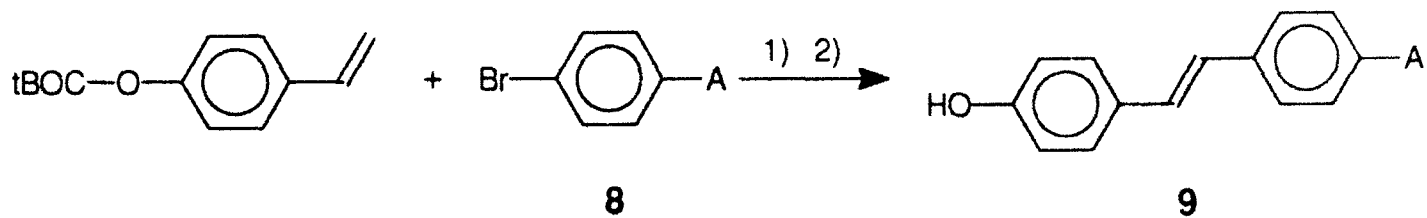
3) HCCZnCl / Pd(PPh₃)₄ / THF / rt;

4) a) *n*-BuLi / THF / -78 °C; b) ZnCl₂ / -78 °C; c) Pd(PPh₃)₄ / 0 °C;

5) *p*-I-C₆H₄-SO₃Ph / rt or *p*-Br-C₆H₄-SO₂NBu₂ / reflux;

6) *p*-MeS-C₆H₄-Br / reflux or *p*-Me₂N-C₆H₄-I / rt;

SCHEME 2



8,9,10	D	A
a	EtO	SO ₃ Ph
b	EtO	SO ₂ NBu ₂
c	EtO	SO ₂ NPh ₂
d	PrO	SO(NH)Me

1) Pd(OAc)₂ / P(o-tolyl)₃ / Et₃N / MeCN / rt;

2) NaOMe / MeOH / rt;

3) K₂CO₃ / RBr / DMF / rt;