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New Sulfonyl-Containing Materials for Nonlinear Optics: Semiempirical Calculations, Synthesis, and Properties

Abraham Ulman,* Craig S. Willand, Werner Köhler, Douglas R. Robello,
David J. Williams, and Laura Handley

Contribution from the Corporate Research Laboratories, Eastman Kodak Company, Rochester,
New York 14650-2109. Received January 24, 1990

Abstract: In this study we describe semiempirical calculations, synthesis, ground-state dipole moment measurements, and measurements of molecular second-order hyperpolarizability coefficients (β) for new stilbene and azobenzene derivatives containing a methylsulfonyl group as the electron acceptor. We show that theoretical calculations can be used to predict the *trends* for molecular hyperpolarizabilities between similar compounds and that these gas-phase calculations underestimate β values, probably as a result of the valence basis set used in the calculations. Whereas the sulfone group has been demonstrated to give molecular hyperpolarizabilities somewhat less than those of similar nitro compounds, the difference becomes less as the degree of conjugation is increased. The increased transparency in the visible spectrum and the synthetic flexibility may make sulfonyl compounds important for some applications.

Introduction

The growing need for fast and efficient optical devices has made nonlinear optics (NLO) an area on the frontier of science today and has generated great interest in second-order NLO materials. In such materials, an external stimulus produces a sudden, nonlinear modulation of light passing through the material. These materials generate three wave interactions, which are important physical phenomena that have many applications such as second harmonic generation (SHG), frequency up and down conversion, parametric applications, and electrooptic modulation.¹

All of these applications require materials with high nonlinearity, high optical damage threshold, and high linear optical quality. Four major categories of nonlinear optical materials are receiving attention: electrooptic crystals (inorganic and organic),^{2,3} bulk semiconductors,³ polymeric organic materials,⁴ and molecular

assemblies.⁵ Each category exhibits a different mix of advantages and disadvantages.

A number of inorganic materials, e.g., KDP, KTP, LiNbO₃, LiIO₃, and borate crystals,² are readily available on the market for parametric effects. However, these materials are very difficult to fabricate and are not easily integrated with semiconductor materials into monolithic circuits.

In recent years, much research has been directed to *organic* NLO materials because of several important advantages they possess.⁶ For example, the NLO response of many organic materials is extremely rapid (approaching *femtoseconds*) because the effects occur primarily through electronic polarization. In contrast, NLO effects in most liquid crystal materials operate via reorientation of whole molecules, and NLO effects in many inorganic materials operate through lattice distortions, which are comparatively slow processes. In addition, organic NLO materials offer simple processing techniques which are compatible with

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existing technologies for the fabrication of integrated optical or electrooptical devices.

In spite of the potential advantages, useful organic NLO materials have not yet been developed because the necessary molecular and macroscopic characteristics have only recently begun to be understood. However, because bulk NLO properties in organic materials arise directly from the constituent molecular nonlinearities, it is possible to decouple molecular and supramolecular contributions to the NLO properties. One can then semiquantitatively predict relative macroscopic nonlinearities based on theoretical analyses of the individual molecules.⁷ Reliable predictions of this kind are vital for the efficiency of a program aimed toward developing new organic materials with tailored NLO properties.

It is by now well-known that molecules containing electron-donor and electron-acceptor groups separated by a large conjugated π -framework possess large values of the second-order molecular hyperpolarizability, β .⁶ However, while nitro and polycyanovinyl groups have been widely studied as acceptor groups in NLO, the sulfonyl group has not received much attention despite its strong acceptor properties. (For example, its σ_p and σ^- are +0.72 and +1.05, respectively, while for the nitro group these values are +0.79 and +1.24, respectively.)⁸ In addition, the sulfonyl group is *bifunctional*, a feature which permits greater freedom in the design of compounds for specific applications and allows more flexibility for synthetically tailoring the physical properties.

This paper summarizes the theoretical analysis of some new molecules with the methylsulfonyl group as the electron-acceptor group, describes the syntheses of new stilbene and azobenzene systems, and presents the measurements of their optical spectra, ground-state dipole moments, and molecular hyperpolarizability coefficients, β . We compare theoretical and experimental results and comment on the potential usefulness of these *chromophores* as components for NLO materials. The incorporation of sulfonyl-containing chromophores into polymers and the NLO properties of the resulting materials will be discussed in our forthcoming paper.⁹

Experimental Section

NMR spectra were obtained on a GE QE-300 instrument at 300 MHz for proton and 75 MHz for ¹³C spectra in CDCl₃ solutions (unless otherwise specified), and shifts are referenced to TMS internal standard. All chemical shifts (δ) are in parts per million (ppm), and coupling constants are in hertz (Hz) units. UV-visible spectra were recorded on a Perkin Elmer Lambda 7 instrument. Melting points are not corrected. Elemental analyses were performed by the Analytical Technology Division, Eastman Kodak Company. All new materials had satisfactory elemental analyses.

Ground-State Dipole Moment Measurements. Solutions with different mole fractions from $x_D = 0$ (pure solvent) to $x_D \approx 3 \times 10^{-3}$ were prepared by using high quality solvents (Spectro Grade, Eastman Kodak Company). Compound X and XI were measured in carbon tetrachloride, *m*-xylene, toluene, and chloroform. The dielectric constants of the solutions were measured with a commercial dipole meter (DMO1, Kahlsico) at a fixed frequency of 2 MHz. The gold-plated sample cell (DFL2, Kahlsico) was equipped with a water jacket, and the temperature of the sample was maintained at 25 ± 0.05 °C. Refractive indices were measured with a Bausch & Lomb refractometer.

Hyperpolarizability Measurements. Hyperpolarizability measurements were performed by using electric-field-induced second-harmonic generation (EFISH). A series of various concentration solutions (less than 30 mg/mL) of the material to be studied in chloroform were placed in a specially designed, wedge-shaped cell similar to those described in refs 10 and 11. Pulses of 1064-nm light (10 ns duration) from a 10-pps Quanta Ray DCR Nd:YAG laser were focused into a 1-m path length cell containing 400 psi of hydrogen. The 1907-nm light pulses generated through stimulated Raman scattering were recollimated and separated from the input beam by using a dispersing prism. The 1907-nm beam was then passed through a half-wave plate/polarizer combination to control the polarization and light intensity, and then the beam was lightly

focused into the sample cell synchronous to the application of a high-voltage pulse (~ 20 kV/cm). The energy incident on the sample was maintained below 5 mJ per pulse. The second harmonic light (953 nm) produced was separated from the fundamental by a monochromator and measured by using a photomultiplier tube and gated integrator. The second harmonic intensity was monitored while translating the sample cell perpendicular to the beam. The resulting Maker fringes were numerically fitted to find their amplitude and coherence length.

4-(Diallylamino)benzaldehyde. A mixture of 25.0 g (2 mol) of 4-fluorobenzaldehyde (Aldrich), 19.6 g (0.2 mol) of diallylamine (Aldrich), 21.3 g (2 mol) of sodium carbonate, 150 mL of hexamethylphosphoramide (HMPA, Aldrich), 0.2 g of hydroquinone, and 4 drops of tripropylmethylammonium chloride was heated under nitrogen with stirring at 110 °C for 113 h. The reaction mixture was cooled and poured into 1.5 L of water, and the resulting solution was extracted with toluene (4 \times 300 mL). The combined extracts were washed with water (3 \times 250 mL) and dried (MgSO₄), and the solvent was removed at reduced pressure. The brown residue was fractionally distilled in vacuo to provide 22.3 g (55%) of a pale yellow oil: bp 128–142 °C (0.16 mmHg); ¹H NMR 3.99 (m, 4 H), 5.18 (m, 4 H), 5.80 (m, 2 H), 6.7 (d, $J = 8.8$, 2 H), 7.70 (d, $J = 8.8$, 2 H).

4-(Dibutylamino)benzaldehyde. A 20-mL sample of *N,N*-dimethylformamide (DMF, Kodak) cooled to 0 °C was treated dropwise with 7.47 g (49 mmol) of phosphorus oxychloride (Kodak). The resulting orange solution was stirred at 0 °C for 1 h and at 25 °C for 1 h, and then *N,N*-dibutylaniline (Kodak) was added slowly. The solution mixture was heated at 90 °C for 6 h, then cooled, and poured onto 50 g of ice. A brown oil separated which was taken up in dichloromethane. The extract was washed with saturated aqueous bicarbonate and then with water containing a little ammonium chloride, and the organic layer was dried (MgSO₄). The solvent was removed under reduced pressure, and the residue was distilled in vacuo to yield 6.65 g (58%) of a yellow liquid: bp 145–165 °C (3 mmHg) ¹H NMR 0.93 (t, $J = 7.3$, 6 H), 1.33 (m, 4 H), 1.56 (m, 4 H), 3.30 (t, $J = 7.7$, 4 H), 6.60 (d, $J = 8.8$, 2 H); 7.66 (d, $J = 8.8$, 2 H); 9.65 (s, 1 H); ¹³C NMR 13.7, 20.0, 29.1, 50.6, 110.5, 124.3, 132.0, 152.4, 189.6.

4-(Methylmercapto)benzyl Chloride. In a 500-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser topped with a Drierite tube was placed 200 mL of dry (molecular sieves 4Å) toluene and 154 g (1 mol) of 4-(methylmercapto)benzyl alcohol (Aldrich). Thionyl chloride (80 mL, 1.1 mol, Kodak) was added dropwise with stirring, and a deep blue color formed immediately. When the addition of the thionyl chloride was completed, the reaction mixture was heated to 80 °C and stirred for 2 h. The mixture was then cooled to room temperature, and the toluene and excess thionyl chloride were evaporated under reduced pressure. The product was distilled in vacuum at 105 °C/0.5 mmHg to yield 169 g (93%) of water clear liquid: ¹H NMR 2.49 (s, 3 H), 4.57 (s, 2 H), 7.28 (AB, $\Delta\nu = 2.2$, $J_{AB} = 8.3$, 4 H).

Diethyl 4-(Methylmercapto)benzyl Phosphonate. In a 500-mL, two-necked flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser was placed 183 g (1.1 mol) of distilled triethyl phosphite (Kodak). The phosphite was heated at reflux, and 160 g (0.94 mol) of 4-(methylmercapto)benzyl chloride was added dropwise with stirring, at such a rate that a gentle reflux was maintained. When the addition was completed, the reaction was refluxed for an additional 2 h. The mixture was cooled to 25 °C, and the product mixture was fractionally distilled under vacuum to yield 229 g (89%) of water clear, viscous liquid: bp 142–145 °C/0.025 mmHg; ¹H NMR 1.27 (t, $J = 7.2$, 6 H), 2.49 (s, 3 H), 3.13 (d, $J = 21.6$, 3 H), 4.04 (quintet, $J = 7.6$, 4 H); 7.23 (s, 4 H).

Diethyl 4-(Methylsulfonyl)benzyl Phosphonate. In a 2-L, round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was placed 500 mL of glacial acetic acid (Kodak) 174 g (0.6 mol) of diethyl (methylmercapto)benzyl phosphonate. To this stirred solution was added 171 g (1.5 mol) of H₂O₂ (30% in water, Kodak), and the reaction mixture was refluxed for 2 h. The water and acetic acid were evaporated under reduced pressure, and the residue was distilled at 214–216 °C/2 \times 10⁻⁴ mmHg to yield 121 g (66%) of very viscous liquid which solidified on standing: ¹H NMR 1.23 (t, $J = 9.6$, 6 H), 3.01 (s, 3 H), 3.19 (d, $J = 22.2$, 2 H), 4.02 (quintet, $J = 7.4$, 4 H), 7.66 (AB, $\Delta\nu = 155$, $J = 8.1$, 4 H).

4-(Dimethylamino)-4'-(methylsulfonyl)stilbene. In a dry 250-mL, three-necked, round-bottomed flask equipped with a sealed stirrer, a nitrogen inlet, and a reflux condenser topped with a Drierite tube were placed, under nitrogen, 100 mL of glyme (1,2-dimethoxyethane, Aldrich Gold Label) and 2.8 g (0.07 mol) of NaH (Aldrich, 60% in mineral oil). The suspension was stirred for 1 min. To the suspension was added 7.49 g (0.05 mol) of (*N,N*-dimethylamino)benzaldehyde (Kodak), and the mixture was stirred for 5 min to ensure complete dissolution. To this solution was added 15.3 g (0.05 mol) of diethyl 4-(methylsulfonyl)benzyl

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phosphonate in 40 mL of glyme, and the reaction mixture was refluxed with vigorous stirring for 2 h. The very bright yellow solution was poured over 200 g of crushed ice under nitrogen. Any residue that remained in the flask was mixed with ice-cold water under nitrogen, and the solid thus formed was washed into the ice mixture. The yellow solid was collected by filtration, washed with cold water, and air dried. Recrystallization from a 1:1 mixture of absolute ethanol (Kodak) and dry (NaOH) pyridine (Kodak) yielded 9.97 g (66%) of bright yellow crystals: mp 242–243 °C; $^1\text{H NMR}$ (ppm) 3.01 (s, 6 H), 3.06 (s, 3 H), 7.05 (AB, $\Delta\nu = 83$, $J_{AB} = 16.2$, 2 H), 7.08 (AB, $\Delta\nu = 217$, $J_{AB} = 8.6$, 4 H), 7.74 (AB, $\Delta\nu = 77$, $J = 8.2$, 4 H).

4-(Diallylamino)-4'-(methylsulfonyl)stilbene. The above procedure was repeated by using 13.5 g (0.0675 mol) of (*N,N*-diallylamino)benzaldehyde and 20.6 g (0.0675 mol) of diethyl 4-(methylsulfonyl)benzyl phosphonate. Recrystallization from absolute methanol (Kodak) yielded 18.2 g (78%) of bright yellow crystals: mp 101–102 °C; $^1\text{H NMR}$ 3.07 (s, 3 H), 3.99 (d, br, $J = 4.5$, 4 H), 5.18 (d, $J = 3.6$, 2 H), 5.23 (s, 2 H), 5.89 (m, 2 H), 7.05 (AB, $\Delta\nu = 83$, $J_{AB} = 16.2$, 2 H), 7.07 (AB, $\Delta\nu = 211$, $J_{AB} = 8.7$, 4 H); 7.76 (AB, $\Delta\nu = 78$, $J_{AB} = 8.3$, 4 H).

4-(Dibutylamino)-4'-(methylsulfonyl)stilbene. The above procedure was repeated by using 2.50 g (10.7 mmol) of 4-(dibutylamino)benzaldehyde, 3.27 g (10.7 mmol) of diethyl 4-(methylsulfonyl)benzylphosphonate. Two crystallizations from methanol gave 2.35 g (57%) of pure compound: mp 112–4 °C; $^1\text{H NMR}$ 0.96 (t, $J = 7.3$, 6 H), 1.4 (m, 4 H), 1.6 (m, 4 H), 3.05 (s, 3 H), 3.30 (t, $J = 7.5$, 4 H), 6.62 (d, $J = 8.6$, 2 H), 6.86 (d, $J = 16.2$, 1 H), 7.16 (d, $J = 16.2$, 1 H), 7.39 (d, $J = 8.6$, 2 H), 7.59 (d, $J = 8.3$, 2 H), 7.85 (d, $J = 8.3$, 2 H); $^{13}\text{C NMR}$ 14.0, 20.4, 29.5, 44.7, 50.8, 111.6, 121.1, 123.4, 126.3, 127.7, 128.4, 133.0, 137.5, 144.1, 148.6.

4-(Dibutylamino)-4'-nitrostilbene. A mixture of 5.00 g (21 mmol) of 4-(dibutylamino)benzaldehyde, 4.27 g (24 mmol) of 4-nitrophenylacetic acid (Kodak), 1.80 g (21 mmol) of piperidine (Kodak), and 50 mL of xylenes was heated with stirring at reflux for 20 h with continuous removal of water by using a Dean-Stark apparatus. The mixture turned dark red. Approximately half of the xylenes was distilled, 30 mL of heptane was added, and the residue was cooled to –30 °C. Red crystals separated which were collected and recrystallized from toluene/heptane to yield 2.81 g (37%) of a red solid: mp 117–119 °C; $^1\text{H NMR}$ 0.96 (t, $J = 7.3$, 6 H), 1.37 (m, 4 H), 1.58 (m, 4 H), 3.30 (t, $J = 7.6$, 4 H), 6.62 (d, $J = 8.8$, 2 H), 6.86 (d, $J = 16.2$, 1 H), 7.18 (d, $J = 16.2$, 1 H), 7.36 (d, $J = 8.7$, 2 H), 7.52 (d, $J = 8.8$, 2 H), 8.16 (d, $J = 8.7$, 2 H). $^{13}\text{C NMR}$ 14.0, 20.3, 29.4, 50.7, 111.5, 120.8, 123.1, 124.1, 125.9, 128.6, 133.8, 145.2, 145.8, 148.8.

4-(Methylsulfonyl)aniline. A mixture of 10.0 g (52.5 mmol) of 4-chlorophenyl methyl sulfone (Lancaster) and 50 mL of anhydrous liquid ammonia was heated in a glass-lined high-pressure reactor at 200 °C for 24 h. Excess ammonia was vented, and the residual solid was extracted with dichloromethane. The extract was washed with water, dried (MgSO_4), and concentrated at reduced pressure to produce a crude solid. After recrystallization from ethanol/water, 6.6 g (74%) of product was obtained: mp 133–134 °C (lit.¹² 135–6 °C); $^1\text{H NMR}$ (DMSO- d_6) 3.01 (s, 3 H), 6.08 (s, 2 H), 6.63 (d, $J = 8.6$, 2 H), 7.5 (d, $J = 8.7$, 2 H).

4-(Dibutylamino)-4'-(methylsulfonyl)azobenzene. To a stirred, ice-cooled suspension of 2.99 g (17.5 mmol) of 4-(methylsulfonyl)aniline in 20 mL of 50% aqueous HCl was added dropwise 1.33 g (19.2 mmol) of sodium nitrite in 10 mL of water. The rate of addition was controlled to maintain the temperature of the reaction below 5 °C. The solution became homogeneous after a few minutes. *N,N*-Dibutylaniline (3.80 g, 21.0 mmol, Kodak) was added dropwise at 3.5 °C, and the red solution thus formed was stirred for 30 min. Sodium acetate dihydrate (10 g) was added, and the mixture was stirred 1 h at 3 °C and 16 h at 23 °C. The precipitated product was filtered, washed with water, and air dried. After two crystallizations from methanol, 4.00 g (59%) of pure orange granular solid was obtained: mp 88–90 °C; $^1\text{H NMR}$ 0.98 (t, $J = 7.3$, 6 H), 1.4 (m, 4 H), 1.6 (m, 4 H), 3.07 (s, 3 H), 3.37 (t, $J = 7.7$, 4 H), 6.68 (d, $J = 9.1$, 2 H), 7.86 (d, $J = 9.0$, 2 H), 7.97 (AB, $\Delta\nu = 21.1$, $J_{AB} = 8.5$, 4 H); $^{13}\text{C NMR}$ 13.9, 20.3, 29.5, 44.6, 51.0, 111.2, 122.7, 126.1, 128.3, 139.6, 143.2, 151.6, 155.6.

4-(Dibutylamino)-4'-nitroazobenzene. A stirred suspension of 12.7 g (53.6 mmol) of *p*-nitrobenzenediazonium tetrafluoroborate (Kodak) in 50% (v/v) aqueous acetic acid was treated dropwise with 10.0 g (48.7 mmol) of *N,N*-dibutylaniline at 3–5 °C. The dark red mixture was stirred at 3–5 °C for 2 h and then at 23 °C for 16 h. The mixture was cooled in ice and made basic (pH = 8) by the addition of concentrated aqueous ammonia. The precipitated product was filtered, washed with

water, and air dried. The product was recrystallized from methanol/pyridine and then from toluene/heptane to yield 10.7 g (62%) of maroon crystals: mp 119–121 °C; $^1\text{H NMR}$ 0.98 (t, $J = 7.3$, 6 H), 1.41 (m, 4 H), 1.64 (m, 4 H), 3.89 (t, $J = 7.7$, 4 H), 6.71 (d, $J = 9.1$, 2 H), 7.90 (m, 4 H), 8.32 (d, $J = 9.0$, 2 H); $^{13}\text{C NMR}$ 13.9, 20.3, 29.5, 51.1, 111.3, 122.5, 124.6, 126.3, 143.4, 147.2, 151.7, 157.0.

Results and Discussion

Semiempirical Calculations. We have performed a series of semiempirical quantum mechanical calculations of the molecular hyperpolarizabilities by using two different schemes: the finite-field (FF) and the sum-over-state (SOS) methods. Under the FF method, the molecular ground-state dipole moment μ_g is calculated in the presence of a static electric field E . The tensor components of the molecular polarizability α and hyperpolarizability β are subsequently calculated by taking the appropriate first and second (finite difference) derivatives of the ground-state dipole moment with respect to the static field and using

$$(\mu_g)_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k \quad (1)$$

In the SOS method, one uses an expression for the second-order hyperpolarizability β of the second-harmonic generation process derived from second-order perturbation theory:¹³

$$\beta_{ijk} = \frac{1}{4\hbar^2} \sum_P \sum_{e,e'} \frac{\langle g|\bar{\mu}_i|e\rangle \langle e|\bar{\mu}_j|e'\rangle \langle e'|\bar{\mu}_k|g\rangle}{(\omega_{eg} - 2\omega)(\omega_{e'g} - \omega)} \quad (2)$$

where ijk are molecular Cartesian coordinates and ω is the incident frequency. $|g\rangle$ denotes the molecular ground state; $|e\rangle$, and $|e'\rangle$ are excited states of the system having transition frequencies given by ω_{eg} and $\omega_{e'g}$, respectively. The summation over P generates the six terms by permutation of the pairs $\{(-2\omega, i); (\omega, j); (\omega, k)\}$. The dipole difference operator $\bar{\mu}$ is defined as

$$\bar{\mu}_i = \mu_i - \langle g|\mu_i|g\rangle \quad (3)$$

where μ_i is the dipole moment operator. The accuracy of these types of calculations are strongly dependent on the formalism employed in deriving the ground- and excited-state properties. Clearly the best correlation between theory and experiment should be obtained at the ab initio level. A number of such investigations have been published for small molecules at the coupled Hartree-Fock¹⁴ and uncoupled Hartree Fock levels.^{15,16} However, similar analyses involving larger molecules (more than 20 heavy atoms) are not feasible due to the time and expense required to perform the calculations. In contrast, more approximate semiempirical algorithms such as INDO and CNDO can be implemented much more efficiently and are therefore more suited to these types of calculations. The quality of the results from semiempirical procedures however depends on the atomic orbital (AO) basis set used as well as the parameterization of the AO interactions. We have chosen to use a valence basis set for the following reasons: (a) Valence basis set calculations have been shown to be fairly successful in predicting molecular structure and nonlinear optical properties.^{14,17–21} (b) There is insufficient experimental data to implement a properly parameterized cal-

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Table I. Theoretical Dipole Moments and Second-Order Hyperpolarizabilities for Selected Methylsulfonyl and Nitro Compounds ($\lambda = 1907$ nm)

Compound	μ_g (D) ^a	SOS-S ^b	β_z (10^{-30} esu) SOS-S/D ^c	FF ^d
I 	7.68	1.3 (1.1)	5.3 (0.2)	1.6
II 	7.33	11.3 (9.7)	4.2 (3.9)	10.3
III 	8.68	2.4 (1.8)	1.6 (0.9)	3.1
IV 	7.88	11.6 (13.0)	5.6 (5.4)	14.7
V 	9.47	5.5 (2.87)	3.2 (1.6)	9.1
VI 	9.25	13.4 (7.54)	12.3 (6.44)	24.8
VII 	8.62	42.5 (35.0)	15.7 (15.5)	62.1
VIII 	9.70	18.0 (11.6)	13.0 (8.9)	27.8
IX 	9.94	41.8 (35.1)	19.8 (19.8)	59.4

^aDipole moments calculated by using the AM1 semiempirical method (1D = 10^{-18} esu). ^bSum-over-state method using only singly excited configurations (numbers in parentheses are β_{zzz}). ^cSum-over-state method using both singly and doubly excited configurations (numbers in parentheses are β_{zzz}). ^dFinite-field method ($\omega = 0$).

calculation by using an extended basis set which includes diffuse polarization functions for our molecules.

For this work, the molecular structures derived by using an AM1 semiempirical method²² served as input for an INDO SCF procedure,²³ which generated the electronic ground state. The FF calculations were performed by using these ground states as a starting point in further SCF iterations where a static field term was explicitly included in the Hamiltonian. The excited states used in the SOS calculations were derived from configuration interaction (CI) of states formed from single- and double-electron promotions from the 10 highest occupied to 10 lowest unoccupied molecular orbitals. (Note: The summation in eq 2 over the vibrational subspace of each electronic state is approximated as unity as is valid for all off-resonance processes.) The dipole moment matrix and transition energies corresponding to these CI states were calculated and inserted directly into eq 2.

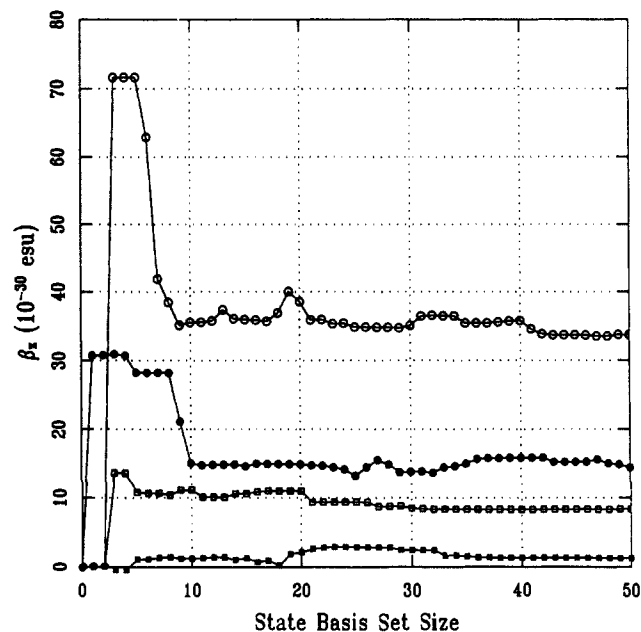
Formally, eq 2 requires knowledge of the complete state basis set (SBS). Realistically only a limited number of states can be used thereby requiring a truncation of the summation at some finite SBS size. Our results indicate that a SBS derived from the excited states mentioned above is more than sufficient for our purpose; adequate convergence of the hyperpolarizability is typically obtained within the first few excited states.

The experimental methods utilized here, as is generally the case for electric-field poling, measure the z-component of the vector component of the hyperpolarizability, β_z (eq 4)

$$\beta_z = \frac{1}{3} \sum_{i=xyz} (\beta_{zii} + \beta_{izi} + \beta_{iiz}) \quad (4)$$

where z is defined to be parallel and in the direction of the ground-state dipole μ_g .

The theoretically predicted values for μ_g and β_z of various nitro- and sulfonyl-containing compounds are listed in Table I.

**Figure 1.** A comparison of β_z as a function of the basis set size for molecules III (■), IV (□), VI (●), VII (○) ($\lambda = 1907$ nm).

Fundamentally both the SOS and FF methods should give similar results for the static second-order hyperpolarizability ($\omega = 0$). In fact, both methods predict similar trends in the hyperpolarizabilities for the molecules studied here. However, the FF method consistently predicts larger magnitudes for β_z than the SOS method. This is particularly true for the SOS calculations where doubly excited states have been included. Transitions requiring two-electron promotions are not formally allowed and subsequently cannot directly contribute to eq 2. However, promotions of this type decrease the singly excited character of the excited-state configurations yielding smaller transition moments and diluted molecular hyperpolarizabilities. Discussion of the relative accuracies of these methods will be continued in the section discussing EFISH results.

We started the analysis of the sulfonyl group as an acceptor with the calculation of 4-(methylsulfonyl)aniline (I), which is an analogue of *p*-nitroaniline (II), and their methylated derivatives (III and IV, respectively). We have found that while the ground-state dipole moments are comparable for the nitro and sulfone derivatives (Table I), the β coefficients are different in magnitude and depend on the method of calculation (Table I).

Since the hyperpolarizability of a given molecule is a function of the donor and the acceptor properties and nature of the conjugation path between them, we turned to the biphenyl system and analyzed the 4-amino-4'-(methylsulfonyl)biphenyl (V). The calculated ground-state dipole moment of this molecule is smaller than expected for such an increase in the distance between the donor and the acceptor. Thus, although the biphenyl compound has a large π system located between the electron donor and acceptor, its calculated hyperpolarizability is substantially less than that of the stilbene analogue (VI) and only slightly larger than that of substituted aniline (III, Table I). Steric interactions among the inner phenyl hydrogens cause the rings to be nonplanar and therefore reduce the electronic coupling between the sulfone and amino groups. On the other hand, analogous stilbenes are nearly planar giving rise to a longer effective conjugation length. Hence, biphenyl compounds are in general poorer candidates for nonlinear optics in so much as stilbene molecules are only slightly larger in volume but display a much larger nonlinear response.

We have calculated μ_g and β_{zzz} for 4-(dimethylamino)-4'-(methylsulfonylstilbene (VI) and compared these data with values for 4-(dimethylamino)-4'-nitrostilbene (DANS, VII). We have also included the azo derivatives VIII and IX in the comparison (Table I). Calculated values of β_z for III, IV, VI, and VII as a function of basis set size are shown in Figure 1. It is evident that in all of these cases there is a single excited state that provides

(22) See, for example: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902 and references therein.

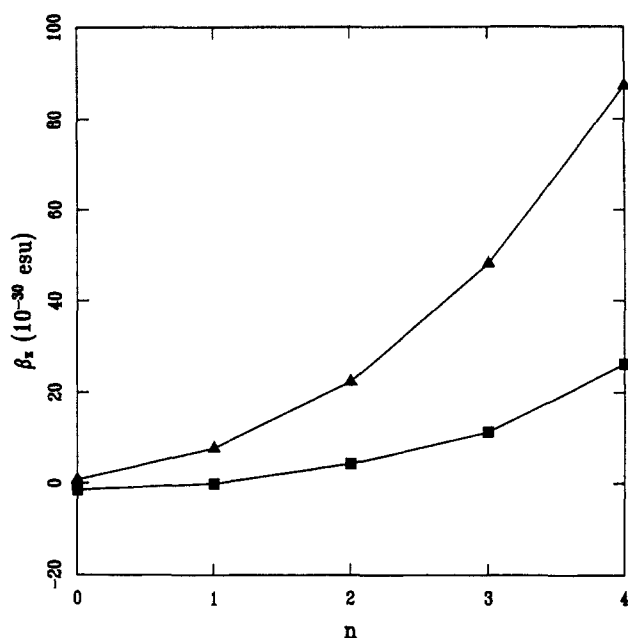


Figure 2. Calculated values (FF) of β_z for $\text{H}_2\text{N}-(\text{CH}=\text{CH})_n-\text{NO}_2$ (▲), and $\text{H}_2\text{N}-(\text{CH}=\text{CH})_n-\text{SO}_2-\text{CH}_3$ (■).

the largest contribution to the hyperpolarizability. This contribution is the diagonal term ($e = e'$) involving the amino-to-acceptor charge transfer. The other significant contributions stem from off-diagonal coupling of higher lying excited states to the charge-transfer state. One would expect therefore, as was noted above, that the details of the charge-transfer interaction would strongly influence the nonlinear optical properties. Moreover, for both the phenyl and stilbene molecules the nitro group gives higher β_z values than the sulfonyl group, which is consistent based on the differing σ values.

Our calculations predict only minor differences between the ground-state dipole moments for molecules containing nitro electron acceptors versus those possessing methylsulfonyl. In contrast, the hyperpolarizabilities behave much differently in that calculated β_z for the aminonitrostilbenes is about twice that of the (aminosulfonyl)stilbenes and the nitroanilines are more than 5 times more nonlinear the sulfonylanilines. The hyperpolarizabilities appear to be very sensitive to the details of the electron donor-acceptor interaction and hence accentuate the differences in the σ values for nitro and methylsulfonyl.

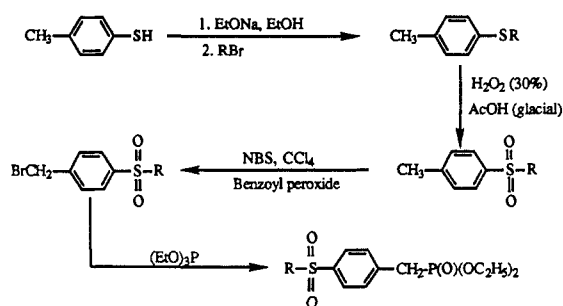
An interesting observation is that the differences between the nitro and sulfonyl electron-accepting properties have less of an impact on the nonlinearity for the more highly conjugated stilbene compounds than they do in the case of the aniline systems. A similar effect can also be seen in substituted polyenes. The calculated results for β_z of $\text{A}(\text{CH}=\text{CH})_n\text{NH}_2$ ($\text{A} = \text{NO}_2, \text{SO}_2\text{CH}_3$) are shown in Figure 2 as a function of polyene chain length n . As expected, the hyperpolarizability increases as the number of double bonds increases. However, just as is the case for the substituted aminostilbenes and anilines mentioned above, the relative nonlinearity $\beta_{z(\text{nitro})}/\beta_{z(\text{sulfonyl})}$ shows a downward trend as the degree of conjugation increases having values of 5.3, 4.3, and 3.3 for $n = 2, 3$, and 4, respectively. Apparently there is a "saturation" phenomena associated with the impact of the electron-acceptor properties on the hyperpolarizability; the nonlinearity of small molecules is strongly dependent on the electron-acceptor strength, whereas this dependency is weaker in larger, more conjugated systems. This has important consequences in the design of molecules for nonlinear optics. The choice of electron acceptors in the case of small molecules is largely restricted to those groups with large σ values; selection in highly conjugated systems can be made on the basis of other characteristics such as synthetic flexibility and optical absorption without drastically affecting the hyperpolarizability.

The calculations predict that azobenzene derivatives have nearly identical dipole moments and molecular hyperpolarizabilities as

the stilbenes. Selection of compounds for use in specific applications can therefore be based on linear optical properties (absorption) and photochemical stability requirements without sacrifice of nonlinear optical response.

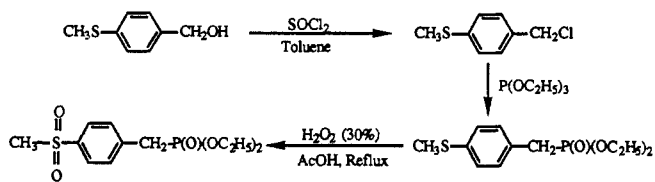
The theoretical models discussed above indicate that the sulfonyl group, although slightly weaker in electron-acceptor strength, is indeed a viable alternative to the nitro group. In particular, sulfonyl derivatives of stilbene and azobenzene display large molecular hyperpolarizabilities and can be used as bifunctional chromophores for the construction of materials with nonlinear optical properties.

Synthesis. The development of a general synthetic route for the sulfonyl-substituted stilbene and azobenzene requires that the different future material embodiments be considered. Of course, it is desirable to have one general route that can be easily adapted to different needs and to use the same starting materials in the preparation of different derivatives. Although examples presented here only have a methylsulfonyl group, we have prepared a variety of other sulfonyl-containing azobenzene and stilbene derivatives. The following sequence of reactions is suggested as a general synthetic route.

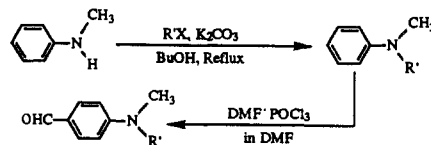


The "sulfonyl side" can be prepared by first reacting *p*-thiocresol with appropriate alkyl halide and oxidizing the resulting thioether to the corresponding sulfone. This product can be brominated with *N*-bromosuccinimide (NBS), and the resulting benzyl bromide can be converted to the corresponding phosphonate by the Arbuzov reaction with triethyl phosphite.

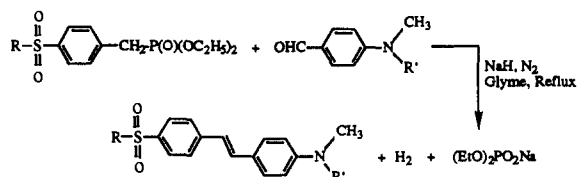
The following sequence of reactions was used in the preparation of diethyl 4-(methylsulfonyl)benzyl phosphonate:



The "amino side" can be prepared by first reacting *N*-methylaniline with 1 equiv or aniline with 2 equiv of the appropriate alkyl halide. The resulting compounds were used in the synthesis of azobenzene derivatives (see below). 4-(Dialkylamino)benzaldehyde derivatives were prepared by formylation of the aniline derivative (Vilsmeier reaction). Alternatively, the



(dialkylamino)benzaldehyde could be synthesized by condensing *p*-fluorobenzaldehyde with the appropriate secondary amine. The final connection between the "sulfonyl side" and the amine side was carried out by the Horner-Emmons reaction:



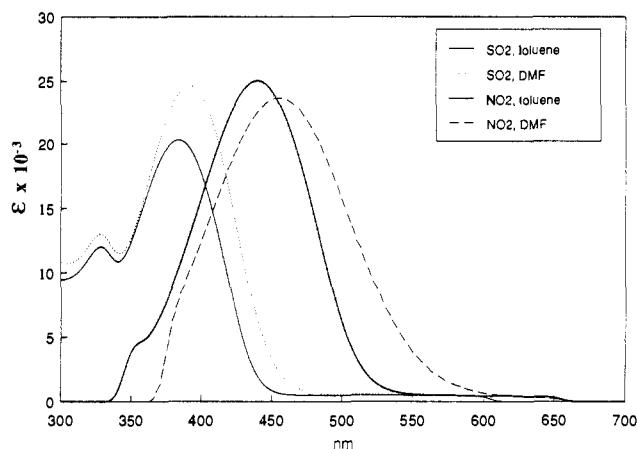
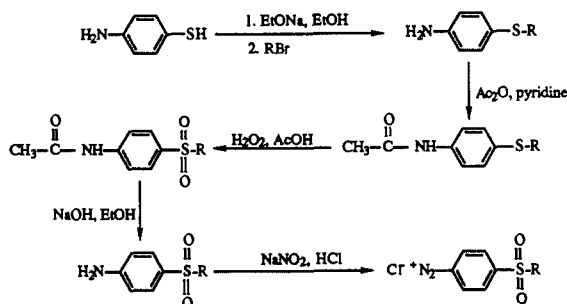
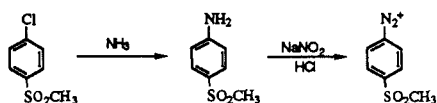


Figure 3. Optical spectra in toluene and in DMF of 4-(dibutylamino)-4'-nitrostilbene and of 4-(dibutylamino)-4'-(methylsulfonyl)stilbene.

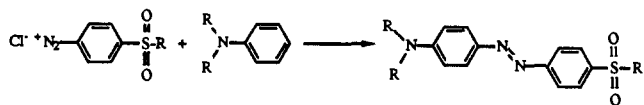
The starting material in a general synthesis of azobenzene derivatives is 4-aminothiophenol. Alkylation as described above, followed by protection of the amine group and oxidation, gives the desired sulfone. Hydrolysis of the amide with sodium hydroxide yields the free amine, which can then be diazotized with nitrous acid in acidic solution.



4-(Methylsulfonyl)aniline was synthesized by reaction of 4-chlorophenyl methyl sulfone with excess ammonia at elevated temperature.



The aniline derivative is added at this stage to the diazonium salt:



Optical Spectra. The optical spectra of the stilbene and azobenzene derivatives were studied in different solvents to establish the solvatochromic shifts of the new sulfonyl-containing chromophores and to compare them to those found for the nitro analogues. Figure 3 shows the spectra in toluene and in DMF of 4-(dibutylamino)-4'-nitrostilbene, and of 4-(dibutylamino)-4'-(methylsulfonyl)stilbene, and Figure 4 shows the spectra in the same solvents but of 4-(dibutylamino)-4'-nitroazobenzene and 4-(dibutylamino)-4'-(methylsulfonyl)azobenzene. Table II summarizes the results.

The most important feature of the spectra is the large blue shift of the sulfones vs the nitro derivatives, i.e., 53 nm (3098 cm^{-1}) for the stilbene and 30 nm (1400 cm^{-1}) for the azobenzene derivatives, in toluene. These large blue shifts suggest that sulfonyl compounds are more transparent in the visible region than their nitro analogues, a property which is crucial when considering the requirements for second-harmonic generation and other parametric processes in the visible spectrum.

If we compare $\Delta\lambda$ values ($\Delta\lambda = \lambda_{\text{DMSO}} - \lambda_{\text{toluene}}$) for the four dyes under study we get 35 nm (1428 cm^{-1}) and 27 nm (1269

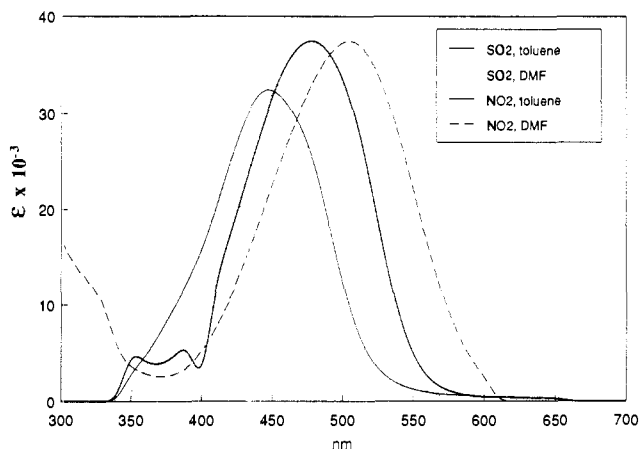


Figure 4. Optical spectra in toluene and in DMF of 4-(dibutylamino)-4'-nitroazobenzene and of 4-(dibutylamino)-4'-(methylsulfonyl)azobenzene.

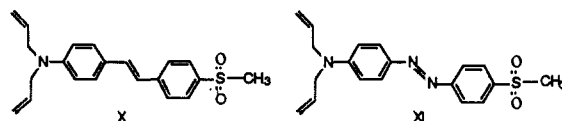
Table II. Optical Spectra of (Dibutylamino)stilbene and Azobenzene Chromophores

acceptor	type	λ_{max}^a nm ($\epsilon \times 10^{-4}$), $\text{mol}^{-1}\text{ cm}^{-1}$					
		toluene	CHCl_3	CH_2Cl_2	acetone	DMF	DMSO
NO ₂	N=N	478	498	500	492	504	513
		3.89	4.39	4.37	4.12	3.72	2.19
NO ₂	CH=CH	441	452	453	444	455	463
		2.56	2.96	2.91	3.00	2.43	2.46
CH ₃ SO ₂	N=N	448	461	464	455	469	475
		3.31	3.68	4.08	4.36	3.54	3.69
CH ₃ SO ₂	CH=CH	388	391	390	389	390	395
		2.73	2.51	2.33	2.59	2.42	2.33

^aAll reported λ_{max} and ϵ values are at 1×10^{-5} M concentrations.

cm^{-1}) for the nitro- and methylsulfonylazobenzene derivatives, respectively, and 22 nm (1077 cm^{-1}) and 7 nm (457 cm^{-1}) for the nitro- and methylsulfonylstilbene derivatives, respectively. Further examination reveals that the difference in $\Delta\lambda$ between the two stilbene derivatives is 15 nm (620 cm^{-1}), while that in the case of the azobenzene derivatives is 8 nm (159 cm^{-1}). Thus, two interesting conclusions can be drawn from this data: (a) the bathochromic shift is not only a function of the donor and acceptor groups but also of the intermediate π -system between them; and (b) while the measured hyperpolarizability coefficients for the stilbene and azobenzene sulfonyl derivatives are very similar (see below), their solvatochromism behavior is different, and therefore solvatochromism is not an accurate prediction of β .

Measurements of Ground-State Dipole Moments. The measurement of ground-state dipole moments may help to establish the validity of the theoretical calculations. We therefore measured two representative compounds, X and XI (see below), where diallyl derivatives were used to increase solubility in nonpolar solvents (e.g., CCl_4).



The dipole moments were determined from the concentration dependence of the dielectric constant and the refractive index of the solutions in the low concentration limit (mole fraction ca. 0.001).

Osipov proposed a formula to calculate the dipole moment of a polar substance in a polar solvent and proved its applicability.^{24,25}

(23) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111; **1976**, *42*, 223; **1979**, *53*, 21, and references therein.

(24) Minkin, V. I.; Osipov, O. A.; Zhdanov, Y. A. *Dipole Moments in Organic Chemistry*; Plenum Press: New York, 1970.

(25) Osipov, O. A.; Panina, M. A. *Zh. Fiz. Khim.* **1958**, *32*, 2287.

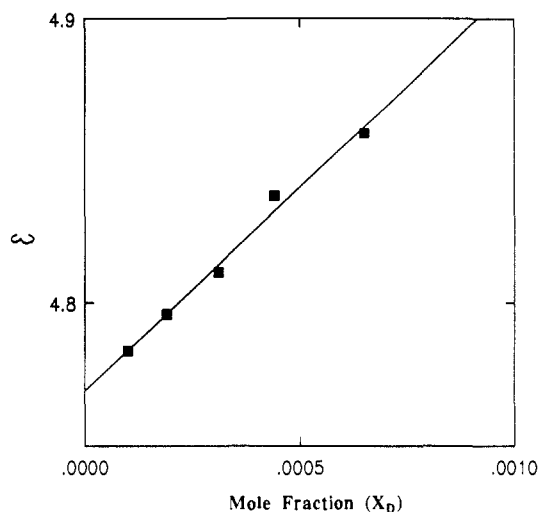


Figure 5. ϵ as a function of concentration of X in CHCl_3 .

In this case the molar orientation polarization of the solution ($P_{\text{solu}}^{\text{or}}$) can be written as

$$P_{\text{solu}}^{\text{or}} = \frac{4}{3} \pi N \frac{\mu_S^2(1-x_D) + \mu_D^2 x_D}{3kT}$$

$$= \frac{M_S(1-x_D) + M_D x_D}{\rho} \left[\frac{(\epsilon-1)(\epsilon+2)}{8\epsilon} - \frac{(n^2-1)(n^2+2)}{8n^2} \right] \quad (5)$$

where μ_S and μ_D are the ground-state dipole moments of the solvent (subscript S) and the dye (subscript D), M_S and M_D are their molecular weights, and x_D is the mole fraction of the dye. The quantities ρ , ϵ , and n are the density, dielectric constant, and refractive index, respectively, of the solution. T is the temperature, k is Boltzmann's constant, and N is Avogadro's number. The molar orientation polarization of the dye, P_D^{or} , can be calculated from eq 5:

$$\frac{4}{3} \pi N \frac{\mu_D^2}{3kT} = P_D^{\text{or}} = \frac{P_{\text{solu}}^{\text{or}} - P_S^{\text{or}}}{x_D} + P_S^{\text{or}} \quad (6)$$

$P_S^{\text{or}} = 4/3 \pi N \mu_S^2 / 3kT$ is the orientation polarization of the solvent and given by eq 5 in the case $x_D = 0$. For low dye concentrations we can use a linear relationship of $P_{\text{solu}}^{\text{or}}$ in x_D and get

$$P_D^{\text{or}} = \left. \frac{dP_{\text{solu}}^{\text{or}}}{dx_D} \right|_{x_D=0} + P_S^{\text{or}} \quad (7)$$

which together with eq 5 gives

$$P_D^{\text{or}} = P_S^{\text{or}} \left[\frac{1}{f_S} \left(\frac{E_S^2 + 2}{8\epsilon_S^2} \frac{\partial \epsilon}{\partial x_D} - \frac{n_S^2 + 2}{8n_S^4} \frac{\partial n^2}{\partial x_D} \right) - \frac{1}{\rho_S} \frac{\partial \rho}{\partial x_D} + \frac{M_D}{M_S} \right] \quad (8)$$

The subscript s refers to the values of the pure solvent and $f_S = P_S^{\text{or}} \rho_S / M_S$. $\partial \epsilon / \partial x_D$ and $\partial n^2 / \partial x_D$ were determined by linear regression of ϵ and n^2 as a function of dye concentration for typically five different solutions of mole fraction less than 10^{-3} . In all cases, the linear approximation was fully justified within the experimental error. Figure 5 shows, as an example, ϵ as a function of concentration for X in chloroform. For molecules with large dipole moments, like the ones discussed in this paper, the contribution of $\partial \rho / \partial x_D$ can be neglected since even the extreme assumption of $\partial \rho / \partial x_D = 1 \text{ g/cm}^3$ changes the value of μ_D by only 0.4%. Similarly, the term proportional to $\partial n^2 / \partial x_D$ contributes less than 4% to the determined dipole moment and can thus also be neglected in a reasonable approximation, leaving the concentration dependence of the dielectric constant as the only experimental parameter. It is important to emphasize, however, that these

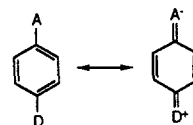
Table III. Measured Dipole Moments (in Debye) for X and XI in Various Solvents

	μ_X	μ_{XI}	μ_{XI}/μ_X
carbon tetrachloride	7.2	8.0	1.11
toluene	6.9	7.3	1.06
<i>m</i> -xylene	7.0	7.6	1.09
chloroform	7.7	8.3	1.08

approximations do not hold for molecules with low dipole moments, comparable to the ones of the solvent molecules.

The measured dipole moments for X and XI in different solvents are summarized in Table III. First, the experimental values of μ vary from solvent to solvent with a trend to higher values for more polar solvents. This may be partly due to the approximations mentioned above. It is also important to note that no attempt was made to account for the nonspherical shape of the dye molecule. We believe that this approximation is justified, since the local field factor used to calculate the hyperpolarizabilities in the EFISH experiment for the product $\mu\beta$ involves similar approximations. Thus, the effective dipole moment determined in these experiments, in the respective solvent, and not the dipole moment in vacuo is the quantity of interest and should be used in the calculations of β from EFISH experiments.

From a chemical point of view, however, it is reasonable that the measured dipole moment increases with solvent polarity, simply because in these conjugated systems the intramolecular charge transfer from the electron donor to the electron acceptor is also enhanced with the increasing solvent polarity. An intramolecular electron transfer from the donor to the acceptor gives a quinonic charge-separated structure which is more stable in more polar solvents and hence contributes more to the overall dipole moment of the dye.



Second, the ratio μ_{XI}/μ_X is always roughly the same, about 1.1, both in the experiments and in the calculations for the sulfonyl-containing materials. This result, which has also been found for a number of other dyes not discussed in this report, is important because it indicates that theoretical calculations do predict the correct trend in dipole moments. Thus, a reliable evaluation of dipole moments of proposed dyes can be carried out before they are actually synthesized.

We have also measured the ground-state dipole moment of DANS (VII), in CHCl_3 , and obtained the value 7.6 D. This, indeed, was an encouraging result since it further supported the credibility of our molecular design approach that was developed to speed up the search for new NLO materials.

β Measurements. Both theoretical analysis and dipole moment measurements indicated that sulfonyl-substituted compounds may have β coefficients similar in magnitude to their nitro analogues. Therefore, we have measured β for several sulfonyl- and nitro-substituted compounds by using electric-field-induced second-harmonic generation method (EFISH).¹⁰⁻¹¹ In this experiment, one measures an effective third-order nonlinearity Γ_{EFISH} for a solution containing the compound of interest, given by

$$\Gamma_{\text{EFISH}} = f_0 f_\omega^2 f_{2\omega} \sum_{\text{components}} N \left[\frac{(\mu_g)_z \beta_z}{5kT} + \gamma_{el} \right] \quad (9)$$

where N is the number density, kT is the thermal energy, and the summation is over all the components of the solution. γ_{el} is the effective third-order hyperpolarizability for the pure electronic four-wave mixing process $\omega + \omega + 0 = 2\omega$. This quantity can be determined by examining the temperature behavior of Γ_{EFISH} or can be approximated from the results of four-wave mixing experiments. However, the magnitude of γ_{eff} is typically less than one-tenth that of the β_z term in the case of second-order NLO materials and was therefore neglected. The local field factor f

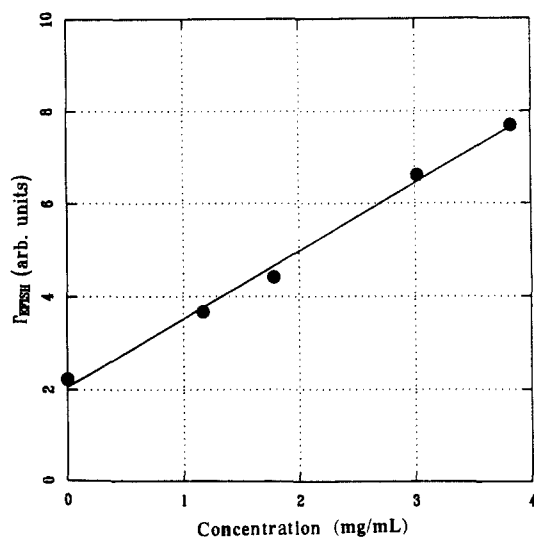


Figure 6. Γ_{EFISH} versus concentration for 4-(dimethylamino)-4'-nitroazobenzene in chloroform ($\lambda = 1907$ nm).

relates the externally applied electric fields to that present at the molecular site. These local field factors can be approximated by²⁶

$$f_0 = \frac{\epsilon_0(\epsilon_\infty + 2)}{\epsilon_\infty + 2\epsilon_0} \quad (10)$$

$$f_\omega = \frac{n_\omega^2 + 2}{3} \quad (11)$$

where ϵ_0 is the static dielectric constant, ϵ_∞ is the dielectric constant for frequencies faster than the dipole relaxation, and n_ω is the index of refraction at frequency ω . We assumed that the dielectric constant and indices of refraction are identical with that of the pure solvent; the error introduced by this assumption is small compared to the other errors for the concentration ranges used here. The experiment was performed by measuring Γ_{EFISH} as a function of chromophore concentration (Figure 6), performing as least-squares analysis of the data, extracting $(\mu_g)_z\beta_z$ by using eq 9, and assuming Γ_{EFISH} (chloroform) = 0.88×10^{-13} esu.¹⁰

The results from EFISH experiments are listed in Table IV along with the FF predictions. We note that our measured values for 4-(dimethylamino)-4'-nitrostilbene (DANS) and 4-(dimethylamino)-4'-nitroazobenzene are consistent with previously published work.^{27,28} The theoretical predictions discussed previously show an excellent correlation with the actual measured values for $(\mu_g)_z\beta_z$. As predicted the nonlinearities of nitro-containing compounds are larger than that of the corresponding sulfones with the relative differences between the two diminishing with increased conjugation. Also, the nonlinearities of the azobenzene derivatives are nearly identical with that of the stilbene compounds. While the overall trends in the theoretical predictions

Table IV. Second-Order Hyperpolarizabilities for Sulfonyl and Nitro Compounds

Compound	$(\mu_g)_z\beta_z$ (10^{-48} esu)	
	Experimental ^a	Calculated ^b
■ <chem>CN(C)c1ccc(cc1)S(=O)(=O)C</chem>	26	26.9
IV <chem>CN(C)c1ccc(cc1)[N+](=O)[O-]</chem>	143	116
X <chem>CN(C)/C=C/c1ccc(cc1)/C=C/c2ccc(cc2)S(=O)(=O)C</chem>	573	247
XII <chem>CN(C)/C=C/c1ccc(cc1)/C=C/c2ccc(cc2)[N+](=O)[O-]</chem>	1150	535
XIII <chem>CN(C)/C=C/c1ccc(cc1)/N=N/c2ccc(cc2)S(=O)(=O)C</chem>	512	270
XIV <chem>CN(C)/C=C/c1ccc(cc1)/N=N/c2ccc(cc2)[N+](=O)[O-]</chem>	1270	549

^aAll measurements are in CHCl_3 . ^bCalculated from FF values of β_z in Table I.

and the experimental data are similar, the magnitude of $(\mu_z)\beta_z$ are comparable for the anilines but differ by a factor of two for the stilbenes. This is most likely a result of the valence basis set used in our calculations. The introduction of diffuse polarization functions would afford the potential for larger charge-transfer interactions than is possible within the valence basis and hence larger hyperpolarizabilities for highly nonlinear molecules. Future work will be concerned with such calculations.

Theoretically the SOS and FF methods should yield similar results for the static second-order hyperpolarizability ($\omega = 0$) since both are at similar levels of approximation. However the SOS method requires information about many states of the system, while the FF method demands much more detailed information about one particular state (ground state). Evidently, the particular semiempirical algorithms implemented here are better suited toward the latter as the FF predictions are consistently closer to the actual experimental values than those of SOS method.

Conclusions

In this study we have described theoretical calculations, syntheses, optical spectra, ground-state dipole moment measurements, and measurements of molecular second-order hyperpolarizability coefficients (β) for new stilbene and azobenzene derivatives containing a methylsulfonyl group as the electron acceptor. We have shown that theoretical calculations can be used to predict the ratio of molecular hyperpolarizabilities between similar compounds and that these gas-phase calculations underestimate β , probably as a result of the valence basis set used in the calculations.

Whereas the sulfone group has been demonstrated to produce lower molecular hyperpolarizabilities than those of nitro groups, the difference becomes less as the degree of conjugation is increased. One would therefore expect that this difference will decrease further in more highly conjugated systems. The increased visible spectrum transparency and the synthetic flexibility may make these sulfonyl compounds important for some applications.

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(27) Katz, H. E.; Singer, K. D.; Sohn, J. E.; Dirk, C. W.; King, L. A.; Gordon, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 6561.

(28) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B* **1989**, *6*, 1339.