dissolved in $CDCl_3$ and submitted to NMR analysis. The results are given in Table II.

For quantitative analysis, a ca. 0.4 M solution of dioxirane **1** in a 33:67 solvent mixture of $CDCl_3/CCl_4$, which contained the internal standard (the $CHCl_3$ impurity in the $CDCl_3$ solvent for ^1H NMR and $FCCl_3$ for ^{19}F NMR), was submitted to NMR analysis prior to pyrolysis. Afterward, 0.5 mL of this solution was pyrolyzed and subsequently the pyrolysate again submitted to NMR analysis. The ratios of the electronic integrals of the starting dioxirane to the standard and of the final ester **3a** to the standard were the same within experimental error.

As a control experiment, ca. 0.5 M solution of dioxirane **1** in a 67:33 $CCl_4/CDCl_3$ solvent mixture, contained in a permanently sealed, 5-mm NMR tube under argon gas, was irradiated at $\lambda > 300$ nm by means of a mercury high-pressure arc at -5 °C for 10 min. After completion of the reaction, the photolysate solution was pyrolyzed under the same conditions as above, and the pyrolysate analyzed by ^1H NMR. All the pyrolysis products of the dioxirane **1** were found to be stable under the pyrolysis conditions.

3,3,3-Trifluoromethyl acetate (3b) was characterized directly in the photolysate of dioxirane **1** (as mixture with ester **3a**) in 67:33 $CCl_4/CDCl_3$. ^1H NMR (400 MHZ): δ 2.18 (s). ^{13}C NMR (100 MHz): δ 20.7 (s), 119.2 (q, $J_{CF} = 265.6$ Hz), 162.1 (s). ^{19}F NMR (84 MHz, $CFCl_3$): δ -58.3 (s). IR: 1824.3 cm^{-1} (C=O). GC-MS (70 eV): m/z (%) 128 (12.9) [M^+], 97 (1.4) [CF_3O^+], 69 (100) [CF_3^+], 59 (46.2) [CH_3COO^+], 43 (41.3) [CH_3CO^+]; GC (OV O1, 60-m capillary column, film thickness 0.25 μm, i.d. 0.32 mm, isotherm 45 °C, $T_{inj} = 150$ °C, $T_{det} = 200$ °C, N_2 pressure = 0.4 kg/cm^2); $R_t = 7.75$ min.

Acknowledgment. We thank Degussa AG (Hanau, Germany) for a generous gift of trifluoroacetone and Caroate. Financial support by the Deutsche Forschungsgemeinschaft (SFB 347 *Selektive Reaktionen Metall-aktivierter Moleküle*), the Fonds der Chemischen Industrie, and the Stifterverband is gratefully appreciated. We thank the A. von Humboldt Foundation for postdoctoral fellowships to R.M. (1989–1990) and M.E.G.N. (1988–1990) and are much indebted to Dr. Scheutzow (Institute of Organic Chemistry) and to Dr. Buchner (Institute of Inorganic Chemistry) for the NMR measurements and helpful discussions.

Registry No. 1, 115464-59-0; **3a**, 431-47-0; **3b**, 74123-20-9; **3c**, 79-20-9.

The Electronic Structure and Second-Order Nonlinear Optical Properties of Donor–Acceptor Acetylenes: A Detailed Investigation of Structure–Property Relationships

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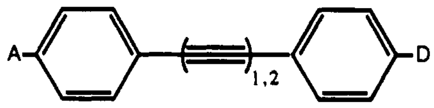
Abstract: A series of donor–acceptor acetylene compounds was synthesized in which systematic changes in both the conjugation length and the donor–acceptor strength were made. The effect of these structural changes on the spectroscopic and electronic properties of the molecules and, ultimately, on the measured second-order molecular hyperpolarizabilities (β) was investigated. It was found that increases in the donor–acceptor strength resulted in increases in the magnitude of β. For this class of molecules the increase is dominated by the energy of the intramolecular charge-transfer transition, while factors such as the ground to excited-state dipole moment change and the transition-moment integral are much less important. Increasing the conjugation length from one to two acetylene linkers did not result in an increase in the value of β; however, β increased sharply in going from two acetylenes to three. This increase is attributed to the superposition of several nearly isoenergetic excited states.

The use of organic materials for nonlinear optics applications is an area of considerable recent activity. Interest in these materials is due primarily to their inherent synthetic flexibility which, in principle, permits the "engineering" of molecular properties that will maximize particular nonlinear optical characteristics.[1] For this to be realized it is necessary to understand in detail how and to what extent changes in the electronic structure of a molecule, brought about by synthetic modification, affect the molecular second- and third-order nonlinear polarizabilities. This is required if successful "engineering" of these properties is to be accomplished.

We present here a detailed study of the relationship between the electronic structure and the microscopic second-order nonlinear polarizability for the series of donor–acceptor phenylacetylene compounds having the general structure shown below (where D and A are an electronic donor and acceptor group respectively).



For this series, systematic changes in the conjugation length and in the donor–acceptor group can be readily accomplished with the effect of these changes on the second-order hyperpolarizability determined. From this, an understanding of which changes result in the most significant enhancement of the hyperpolarizability can be deduced.

This series of compounds was also screened for SHG (second harmonic generation) activity. SHG is a macroscopic second-order nonlinear optical property that requires, in crystalline materials, not only significant molecular hyperpolarizabilities but also

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[1] (a) *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; Royal Chem. Society. (b) *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society; Washington, DC, 1983.

0002-7863/91/1513-7658$02.50/0

noncentrosymmetric crystal packing. A number of the materials were SHG active with several showing high conversion efficiencies relative to a urea standard.

Experimental Section

Spectroscopy. Absorption spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were acquired as solid-state diffuse reflectance spectra on an Analect 6160 FTIR.

The ground-to-excited-state dipole moment change, $\Delta\mu$, was determined from the solvatochromism of the relevant absorption band by means of the Lippert–Mataga equation[2]

$$\bar{\nu}_{\text{abs}} = \bar{\nu}^{g}_{\text{abs}} + C_1\frac{n^2 - 1}{2n^2 + 1} + C_2\left[\frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \qquad (1)$$

where $\bar{\nu}_{\text{abs}}$ is the frequency (cm^{-1}) of the transition in a particular solvent, and D and n are the dielectric constant and refractive index of the solvent, respectively. The intercept, $\bar{\nu}^{g}_{\text{abs}}$, is the energy of the transition in the gas phase, and $C_2 = 2\mu_g\Delta\mu/hca^2$; where μ_g is the ground-state dipole moment, h and c are Planck's constant and the speed of light, respectively, a is the Onsager radius, and $\Delta\mu$ is the dipole moment change. The constant, C_2, was determined from a least-squares fit of eq 1 to the absorption maximum of the ICT band in approximately 16 different solvents. The dipole moment change, $\Delta\mu$, was calculated from C_2 with the measured value of the ground-state dipole moment and a value of the Onsager radius which was estimated from crystal structure data as the volume of an ellipse whose long axis was taken as the donor-to-acceptor length of the molecule and whose short axis was taken as the in-plane width of the molecule at the largest point (e.g., oxygen-to-oxygen distance for the nitro group). An Onsager radius of 6.4 Å was determined for the diphenylacetylenes containing nitro or cyano acceptors and 6.5 Å for all other acceptor groups; similarly 6.7 Å was used for diphenylbutadiynes containing nitro or cyano acceptors, and 6.8 Å was used for all others.

Nonlinear Optical Measurements. The methodology for determination of the ground-state dipole moment, μ, and the hyperpolarizability, β, have been described previously.[3] Very briefly, measurements are made of the density, refractive indices, dielectric constants, the THG (third harmonic generation) and EFISH (electric field induced second harmonic generation) amplitudes, and the coherence lengths on graded concentration solutions which allows the calculation of the desired parameters. THG and EFISH measurements were performed with 1.91 μm as fundamental radiation, obtained by Raman shifting in H_2 gas the output of a Q-switched Nd-YAG laser. A specially designed "single interface" sample cell equipped with electrodes was used for THG and EFISH amplitude determination. The coherence lengths were determined in a separate wedged cell. Toluene was used as a reference liquid. The desired molecular properties were calculated with Onsager local fields and the infinite dilution limit.

Powder SHG efficiencies were measured relative to a urea standard at 1064 and 1907 nm with an experimental method reported previously.[4]

Synthesis. Diethylamine, triethylamine, and pyridine were obtained from Baker, distilled from CaH_2, and stored under an inert atmosphere. *p*-Iodoaniline, *p*-bromobenzonitrile, *p*-iodonitrobenzene, *p*-bromothioanisole, *p*-bromoanisole, *p*-bromobenzoic acid, *p*-bromoacetophenone, *p*-bromobenzophenone, cuprous iodide, and 2-methyl-3-butyn-2-ol were acquired from Aldrich and used as received. Dichlorobis(triphenylphosphine)palladium(II) was purchased from Strem Chemical and used as received. (Trimethylsilyl)acetylene was acquired from Petrarch Systems and used as received. *p*-Aminophenylacetylene,[5] *p*-cyanophenylacetylene,[5] *p*-(bromomethyl)benzoate[6] and *p*-bromophenylmethylsulfone[7] were synthesized by literature methods. The synthesis and characterization of *p*-amino-*p*′-nitrodiphenylacetylene, diphenylbutadiyne, and diphenylhexatriyne have been previously reported.[4]

Table I. Reaction Condition for the Synthesis and Purification of Donor–Acceptor Diphenylacetylenes

A	D	solv/ temp[a] (°C)/time (h)	chromatography
SO_2CH_3	NH_2	triethylamine/rt/4	1:1 CCl_2H_2:toluene/silica
CO_2CH_3	NH_2	diethylamine/rt/4	3:1 CCl_2H_2:toluene/silica
CO_2CH_3	SCH_3	diethylamine/rt/4	toluene/silica
$C(O)CH_3$	SCH_3	diethylamine/rt/8	CH_2Cl_2/silica
$C(O)CH_3$	NH_2	diethylamine/rt/8	THF/silica
CN	SCH_3	triethylamine/rt/4	CH_2Cl_2/silica
CN	NH_2	diethylamine/rt/4	CH_2Cl_2/silica
CO_2Ph	NH_2	triethylamine/rt/8	CH_2Cl_2/silica

[a] Room temperature is rt.

***p*-Ethynylthioanisole.** To 250 mL of degassed triethylamine containing *p*-bromothioanisole (25 g) and 2-methyl-3-butyn-2-ol (11 g) was added $PdCl_2P(C_6H_5)_2$ (0.35 g) and CuI (0.1 g). The solution was refluxed for 6 h under an inert atmosphere at which point the solvent was removed, and the crude oily product was triturated with petroleum ether until it solidified. The solid was dissolved in toluene, filtered to remove ammonium salts, and poured into a round-bottom flask equipped with a short path length distillation head. The isopropyl alcohol protecting group was removed with sodium hydride by the literature method.[6] After deprotection the toluene was evaporated, and the crude oil was vacuum distilled to give 8 g (44%) of *p*-ethynylthioanisole. *p*-Ethynylthioanisole decomposes appreciably at room temperature. A satisfactory elemental analysis was not obtained: IR 3287 cm^{-1} (≡C—H), 2106 cm^{-1} (C≡C), 1090 cm^{-1} (Ph—S).

Donor–Acceptor Diphenylacetylenes. Diphenylacetylenes with varying donor–acceptor groups were all synthesized by means of the dichlorobis(triphenylphosphine)palladium/cuprous iodide coupling reaction of Hagihara.[5] Terminal phenylacetylenes with the desired donor group, D-C_6H_4-C≡CH, are coupled with iodo- or bromobenzenes containing the desired acceptor group, AC_6H_4X (X = I or Br), under an inert atmosphere in either diethyl- or triethylamine. The resulting product is purified by chromatography after removal of the amine solvent. The reaction conditions, solvent, and chromatography data for all of the compounds reported here are summarized in Table I, while analytical data are summarized in Table II. A typical synthesis for a donor–acceptor diphenylacetylene is given below.

***p*-(Thiomethyl)-*p*′-nitrodiphenylacetylene.** *p*-Ethynylthioanisole (2.1 g, 14.8 mmol) and *p*-iodonitrobenzene (3.5 g, 14.1 mmol) were added to a Schlenk flask containing thoroughly degassed diethylamine (100 mL). To the flask were added $PdCl_2P(C_6H_5)_2$ (0.35 g) and CuI (0.1 g), and the reaction was stirred under a nitrogen purge at room temperature for 4 h. At the end of 4 h the reaction mixture was poured into water, and the resulting flocculent yellow precipitate was filtered and dried at room temperature. The crude product was chromatographed on silica gel with toluene as the elutant. The second bright yellow band yielded 1.52 g (40% yield) of the desired product.

Donor–Acceptor Diphenylbutadiynes. Donor–acceptor diphenylbutadiynes are made by the Glaser-type coupling of terminal phenylacetylenes containing the desired donor and acceptor group.[8] A typical synthesis is given below.

***p*-Amino-*p*′-cyanodiphenylbutadiyne.** *p*-Aminophenylacetylene (0.50 g) and *p*-cyanophenylacetylene (0.54 g) were dissolved in dried distilled pyridine. Freshly precipitated cuprous chloride (0.50 g) was added, and oxygen was bubbled through the stirred solution with a syringe needle. After an hour the solution was poured into water, and the resultant precipitate was gravity filtered and allowed to dry. The precipitate was dissolved in a minimum of methylene chloride (20 mL), filtered, and put on a silica gel column where it was further eluted with methylene chloride. The second pale yellow band yielded 0.036 g (4%) of *p*-amino-*p*′-cyanodiphenylbutadiyne.

Alkylation of *p*′-Cyano- and *p*-Amino-*p*′-nitrodiphenylacetylenes. Methylation of aminonitro- and aminocyanodiphenylacetylenes was carried out under mild conditions which afforded a quantity of both the mono- and dimethylated derivatives of each compound for the purposes of this study.

***p*-(*N*,*N*-Dimethylamino)- and *p*-(*N*-Methylamino)-*p*′-cyanodiphenylacetylene.** *p*-Amino-*p*′-cyanodiphenylacetylene (0.25 g) and methyl iodide (0.4 g) were refluxed in ethanol (200 mL) in the presence of anhydrous sodium carbonate (0.3 g) under an inert atmosphere for 24 h. The solution was filtered, and the solvent was removed by rotary evaporation. The resulting residue was chromatographed on silica gel (6 cm × 70 cm column) with toluene as the elutant. Three primary yellow bands separated the first containing the dimethylamino derivative (0.04 g, 15% yield), the second containing the methylamino derivative

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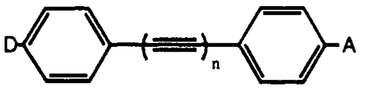
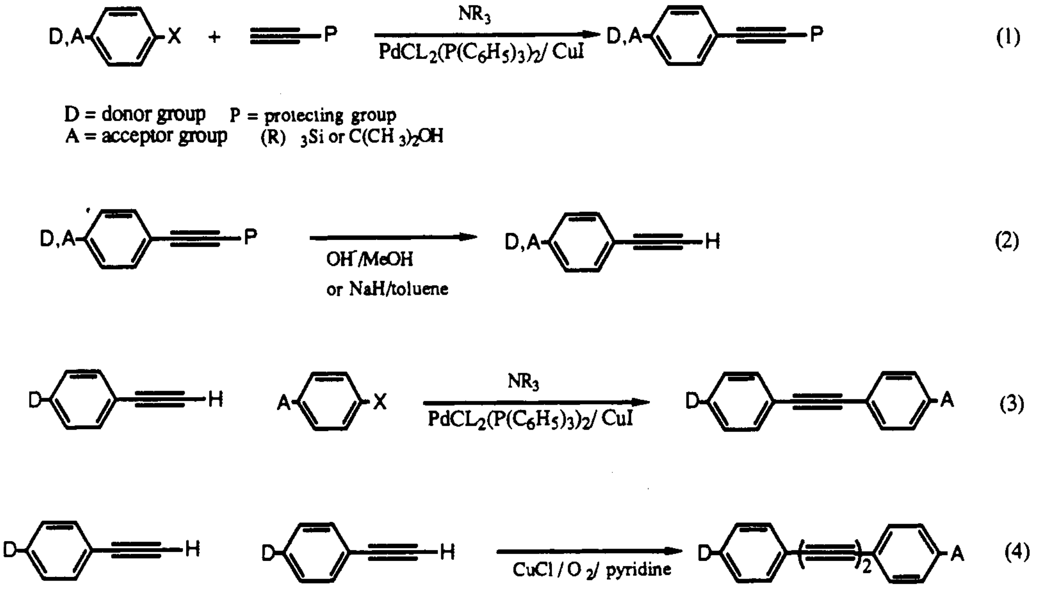
Table II. Analytical Data for the Series of Donor-Acceptor Diphenylacetylenes



				elemental analyses		
n	A	D	yield (%)	expected	found	infrared spectra
1	SO_2CH_3	NH_2	32	66.40/4.84/5.16	65.60/4.79/5.06	3456, 3388 (δ NH), 2212 (δ C$\equiv$C), 1288 (ν SO)
1	CO_2CH_3	NH_2	50	76.48/5.21/5.57	77.21/5.20/5.53	3457, 3366 (ν NH), 2209 (ν C$\equiv$C), 1700 (ν CO)
1	CO_2CH_3	SCH_3	73	72.31/5.00/0.00	72.15/4.94/0.24	2214 (ν C$\equiv$C), 1715 (ν CO)
1	$C(O)CH_3$	SCH_3	41	76.66/5.30/0.00	76.38/5.29/<0.1	2217 (ν C$\equiv$C), 1669 (ν CO)
1	$C(O)CH_3$	NH_2	40	81.68/5.57/5.95	79.14/5.66/5.78	3412, 3343 (ν NH), 2208 (ν C$\equiv$C), 1671 (ν CO)
1	C(O)Ph	NH_2	46	84.82/5.08/4.71	84.34/5.34/4.92	3454, 3346 (ν NH), 2211 (ν C$\equiv$C), 1643 (ν CO)
1	CN	SCH_3	54	77.08/4.45/5.62	77.03/4.40/5.49	2224 (ν C$\equiv$N), 2212 (ν C$\equiv$C)
1	CN	NH_2	49	82.55/4.62/12.83	81.65/4.41/12.30	3456, 3369 (ν NH), 2227 (ν C$\equiv$N), 2209 (ν C$\equiv$C)
1	CN	$NH(CH_3)$	19	82.90/5.21/12.06	81.22/4.79/11.82	3379 (ν NH), 2227 (ν C$\equiv$N), 2209 (ν C$\equiv$C)
1	CN	$N(CH_3)_2$	15	82.9/5.73/11.37	82.28/5.83/11.30	2222 (ν C$\equiv$N), 2207 (ν C$\equiv$C)
1	NO_2	$NH(CH_3)$	19	71.42/4.79/11.10	71.07/4.83/11.10	3418 (ν NH), 2199 (ν C$\equiv$C), 1504, 1327 (ν NO_2)
1	NO_2	SCH_3	46	66.90/4.12/5.20	66.63/4.13/5.04	2212 (ν C$\equiv$C), 1514, 1339 (ν NO_2)
2	CN	SCH_3	10	79.09/4.06/5.12	78.82/3.90/4.97	2226 (ν C$\equiv$N), 2212 (ν C$\equiv$C)
2	CN	NH_2	4	84.28/4.16/11.56	83.61/4.41/11.83	3461, 3369 (ν NH), 2229 (ν C$\equiv$N), 2202 (ν C$\equiv$C)
2	NO_2	SCH_3	3	69.61/3.78/4.78	69.63/3.94/4.56	2207 (ν C$\equiv$C), 1515, 1342 (ν NO_2)

Scheme I



(0.05 g, 19% yield) and final band containing unreacted starting material (0.10 g).

***p*-(*N*,*N*-Dimethylamino)- and *p*-(*N*-Methylamino)-*p*′-nitrodiphenylacetylene.** The alkylation of *p*-amino-*p*′-nitrodiphenylacetylene (0.25 g) was carried out in an identical fashion with a 2.5-fold excess of methyl iodide. The reaction conditions and purification procedure were identical with those used above resulting in 0.05 g (19%) of the methylamino derivative and 0.01 g (4% yield) of the dimethylamino derivative.

Results and Discussion

Synthesis. The general route for the synthesis of donor-acceptor diphenylacetylene and diphenylbutadiyne molecules is shown in Scheme I. This scheme utilizes two fundamental reactions; the $PdCl_2(P(C_6H_5)_3)_2/CuI$-catalyzed substitution of bromo- or iodobenzenes by terminal acetylenes and Glaser-type coupling (Cu(I)) of terminal acetylenes to produce diacetylenes.[5,8]

The terminal-substituted phenylacetylenes, required as precursors, are prepared by reacting trialkylsilyl- or isopropyl alcohol-protected acetylenes with the bromo- or iodobenzene containing the desired donor or acceptor group (reaction 1). Removal of the silane or isopropyl alcohol group, with hydroxide or sodium hydride, respectively, yields the desired terminal acetylene (reaction 2).[6,9]

As a general synthetic approach, terminal phenylacetylenes are made with the desired donor group as the substituent. The donor-acceptor diphenylacetylenes are then synthesized by reacting a donor-substituted phenylacetylene with a bromo- or iodobenzene containing the desired acceptor. This reaction is relatively clean, and the donor-acceptor molecules are easily separated by chromatography (reaction 3).

The diphenylbutadiyne donor-acceptor molecules are synthesized by the coupling of donor and acceptor terminal acetylenes with a CuCl catalyst (Glaser coupling) (reaction 4).[8] The reaction produces a mixture of products yielding not only the desired donor-acceptor molecule but also donor-donor and acceptor-acceptor diphenylbutadiynes; in all cases reported here the desired product was easily separated by column chromatography.

Nonlinear Optical Properties. The nonlinear optical properties of bulk materials manifest themselves in phenomena such as the electrooptic (Pockels) effect and second harmonic generation (SHG), which arise from second-order susceptibilities, and degenerative four-wave mixing and frequency tripling which arise from third-order susceptibilities.[10] The degree to which a material

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exhibits macroscopic second- and third-order nonlinear optical properties is dependent upon the microscopic nonlinear polarizabilities of the constituent molecules as well as on their arrangement in the bulk material.[11]

The origin of macroscopic nonlinear optical phenomena is given by the familiar expansion of the bulk polarization of the material as a power series of the applied electric field strength (eq 2), where the coefficients $\chi_{IJ}{}^{(1)}$, $\chi_{IJK}{}^{(2)}$, and $\chi_{IJKL}{}^{(3)}$, the first-, second-, and third-order susceptibilities, respectively, are tensorial quantities whose indices, *IJK*..., refer to the coordinate system of the bulk material, and whose elements are determined by its structure.[11,12]

$$P = \chi_{IJ}^{(1)} E + \chi_{IJK}^{(2)} E^2 + \chi_{IJKL}^{(3)} E^3 + \ldots \qquad (2)$$

On a microscopic level, a similar expression can be written for the polarizability of a molecule in an applied electric field (eq 3), where α_{ij}, β_{ijk}, and γ_{ijkl} are the first-, second-, and third-order

$$P_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \ldots \qquad (3)$$

polarizabilities, respectively, with the i,j,k,l indices referring to the molecular coordinate system and $E_{i,j,k...}$ referring to components of the applied field.[11,13] Like the macroscopic susceptibilities, the molecular hyperpolarizabilities are also tensorial quantities determined by the geometry and electronic structure of the molecule: the second-order hyperpolarizability, β, with which we are primarily concerned here is a third-rank tensor, while γ is a fourth ranked one.

The relationship between the macroscopic second-order susceptibility and the microscopic second-order hyperpolarizability for molecules in a crystal lattice with an ordered gas (no intermolecular interactions) approximation has been developed fully by Zyss.[14]

Microscopic Second-Order Nonlinear Optical Properties. Measurements of electric field induced second harmonic generation (EFISH) provide a direct measure of the molecular hyperpolarizability, β.[13a,15] This measurement, which is described in the Experimental Section, yields a scalar quantity which is the projection of the vector invariant of the second-order hyperpolarizability tensor onto the ground-state dipole moment of the molecule, $\beta\cdot\mu$.[13a,16] If the molecular axis is taken as the *z* axis, then dividing out the dipole moment yields the *z* projection of the tensor (eq 4).[17] For linear molecules in which the transition moment lies

$$\beta_z = \beta_{zzz} + \tfrac{1}{3}(\beta_{zyy} + \beta_{zxx} + 2\beta_{xxz} + 2\beta_{yyz}) \qquad (4)$$

along the molecular axis, which is the case for the donor–acceptor acetylenes, the contribution from the off diagonal tensor elements is minimal, yielding $\beta_z \approx \beta_{zzz}$.

The relationship between the electronic structure of the molecule and the second-order molecular hyperpolarizability tensor, as derived from time dependent perturbation theory, is given in eq 5.[14] This expression, which gives the tensor elements of β_{ijk}, is

$$\beta_{ijk}^{2\omega} = \frac{1}{2\hbar}\sum_{\mathrm{p,q}}\left(\mu_{0\mathrm{p}}^{i}(\mu_{\mathrm{pq}}^{i}\mu_{\mathrm{q}0}^{k} - \mu_{\mathrm{pq}}^{k}\mu_{\mathrm{q}0}^{j})\frac{\omega_{\mathrm{p}}\omega_{\mathrm{q}} + 2\omega^2}{(\omega_{\mathrm{p}}^2 - 4\omega^2)(\omega_{\mathrm{q}}^2 - \omega^2)} + \mu_{0\mathrm{q}}^{k}\mu_{\mathrm{pq}}^{i}\mu_{\mathrm{q}0}^{j}\frac{\omega_{\mathrm{p}}\omega_{\mathrm{q}} + \omega^2}{(\omega_{\mathrm{p}}^2 - \omega^2)(\omega_{\mathrm{q}}^2 - \omega^2)}\right) \qquad (5)$$

a sum over all of the electronic states of the molecule, where ω_{p} or ω_{q} is the energy gap between the excited state "p" or "q" and the ground state, e.g., $\omega_{\mathrm{p}} = (E_{\mathrm{p}} - E_{\mathrm{g}})/\hbar$, μ_{pq}^{i} is the matrix element of the dipole operator between states p and q, and ω is the frequency of the incident laser.

Assuming that only the lowest energy excited state makes a significant contribution to the value of β, a simple expression involving only this state and the ground state can be derived by keeping only the first term in the series and assuming simple one-dimensional behavior ($i = j = k$). This is the familiar two-state model (eq 6) which expresses β in terms of measurable spectroscopic and photophysical parameters and which has been shown to give reasonable estimates of β for a number of organic molecules.[14,18] In this expression ω_1 is the energy gap, $(E_e - E_g)/\hbar$, between the ground and excited state, ω is the frequency of the incident (laser) light beam, $\Delta\mu_1$ is the dipole moment change between the ground state and the excited state, and m_1 is the transition moment for the optical transition between the two states.

$$\beta = \frac{3\Delta\mu_1 m_1^2}{2\hbar^2}\,\frac{\omega_1^2}{(\omega_1^2 - 4\omega^2)(\omega_1^2 - \omega^2)} \qquad (6)$$

Spectroscopic and Excited-State Properties. As discussed, the value of β, the second-order hyperpolarizability, is a function of (eq 6) spectroscopic and excited-state properties of the molecule. Specifically, the value of the second-order hyperpolarizability is proportional to the dipole moment change between the ground and excited state and the intensity (transition moment integral) of the transition to that excited state and is approximately inversely proportional to the square of the energy of that transition. Therefore, in order to understand how structural changes affect the magnitude of β, it is necessary to understand the effect of these changes on the excited-state properties.

We have previously reported some aspects of the spectroscopy and photophysics of the series of *p*-amino-*p*′-nitrodiphenylacetylenes.[19] The spectroscopic properties observed for those molecules are general for all of the donor–acceptor acetylenes reported here. The absorption spectra for this class of molecules are all characterized by an intense broad low-energy transition which is assigned to the intramolecular charge-transfer transition (ICT) resulting from excitation from the donor to the acceptor group. This absorption band is solvatochromic, which is characteristic of a large dipole moment change between the ground and the excited state; in addition, the molecules also show a highly solvatochromic emission from this state.[2] It is worth noting that while this broad absorption band is principally composed of the ICT transition it may also contain weaker transitions to other excited states as is observed for *p*-nitroaniline.[20] It is reasonable to assume that the ICT band, due to its intensity and large dipole moment change, will dictate the magnitude of the second-order hyperpolarizability.

In addition to the broad ICT band, an intense transition lying to higher energy is also observed in these molecules; this band is nominally assigned as a "$\pi \rightarrow \pi^*$" type of transition.[19] This transition, while generally less solvatochromic than the ICT band, has an appreciable excited-state dipole moment for many of the molecules. This suggests that, in fact, this band has some charge-transfer character and may be more accurately described as the promotion of an electron from a π bonding level to an orbital localized on the acceptor group. This spectral band, as with the ICT band, may not represent a pure transition but may be composed of several transitions, especially in the longer, more highly conjugated members of the series.

Figure 1 shows solution spectra for three different molecules with varying donor–acceptor groups; as would be expected, the position of the ICT band is sensitive to the nature of the donor and acceptor group. The $\pi \rightarrow \pi^*$ transition shows up as a distinct, relatively intense band to higher energy of the ICT band for

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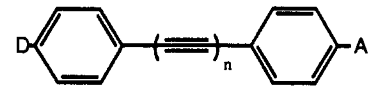
Table III. Spectroscopic and Nonlinear Optical Properties of Donor-Acceptor Diphenylacetylenes



n	A	D	λ_{max} ($\epsilon \times 10^{-4}$)[a]	f[b]	$\lvert m_1 \rvert^2$[c] (10^{-35} esu)	μ_g[d] (10^{-18} esu)	$\Delta\mu$[e] (10^{-18} esu)	β[a] (10^{-30} esu)
1	SO_2Me	NH_2	338 (3.3)	0.53	3.8	6.5	6.6	13
1	CO_2Me	SMe	328 (3.3)	0.65	4.5	2.9	4.4	8
1	CO_2Me	NH_2	337 (2.3)	0.40	2.9	3.8	10.6	15
1	C(O)Me	SMe	332 (3.1)	0.47	3.3	3.7	4.6	9.8 ± 2
1	C(O)Me	NH_2	336 (2.4)	0.42	3.0	3.3	12.6	12
1	CN	SMe	326 (3.1)	0.52	3.6	4.0	8.0	15
1	CN	NH_2	343 (2.9)	0.49	3.6	5.2	4.3	20
1	CN	NHMe	361 (2.8)	0.40	3.1	5.7	3.5	27
1	CN	NMe_2	373 (2.0)	0.28	2.2	6.1	3.1	29
1	COPh	NH_2	352 (1.3)	0.26	2.0	3.7	9.9	19
			271 (1.1)[f]	0.31	1.8		5.0	
1	NO_2	OMe	347 (2.0)	0.42	3.1	4.4	6.2	14
			255 (1.6)[f]	0.39	2.1		6.0	
1	NO_2	SMe	358 (2.2)	0.50	3.8	4.0	5.4	20
			281 (2.0)[f]	0.40	2.4		2.1	
1	NO_2	NH_2	379 (2.1)	0.47	3.8	5.5	9.5	24
			274 (2.2)[f]	0.63	3.7		5.7	
1	NO_2	NHMe	400 (2.4)	0.51	4.3	5.7	7.7	46
			285 (2.6)[f]	0.65	3.9		6.0	
1	NO_2	NMe_2	416 (1.8)	0.37	3.3	6.1	5.7	46
			294 (2.1)[f]	0.49	3.1		4.9	
2	CN	SMe	368 (2.9)	1.1[g]		3.7	2.8	17 ± 2
2	NO_2	SMe	371 (2.1)	0.54	3.1	3.9	3.5	17
2	NO_2	NH_2	384 (1.8)	0.37	3.0	6.3	8.5	28 ± 2

[a] Chloroform solvent. [b] Oscillator strength. [c] Transition dipole moment integral between the ground and the excited state: $m_1 = \langle g|er|e \rangle$, calculated from the oscillator strength. [d] Ground-state dipole moment. [e] Dipole moment change between the ground and the excited state determined from solvatochromism of the absorption band: $\Delta\mu = \mu_{ex} - \mu_g$. [f] Wavelength maximum for the high-energy "$\pi \rightarrow \pi^*$" transition. [g] More than one discrete transition associated with this spectral band.

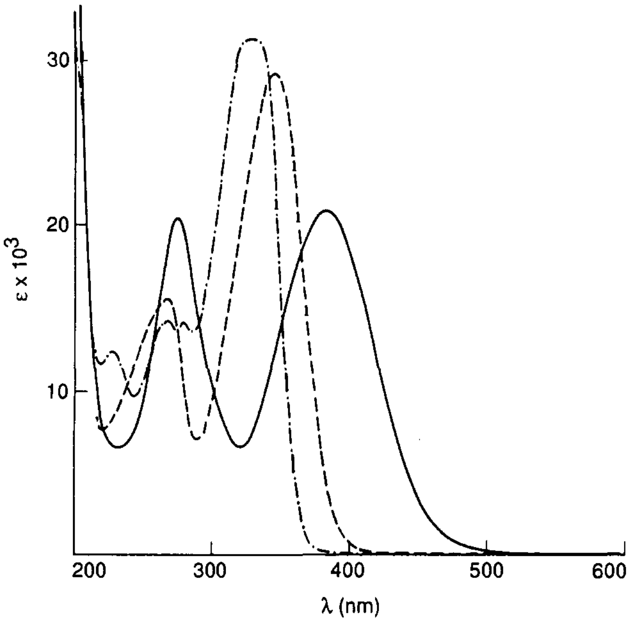


Figure 1. Electronic absorption spectra of *p*-amino-*p*′-nitrodiphenylacetylene (—), *p*-amino-*p*′-cyanodiphenylacetylene (‒‒), and *p*-(methylthio)-*p*′-cyanodiphenylacetylene (‒·‒) in acetonitrile solution.

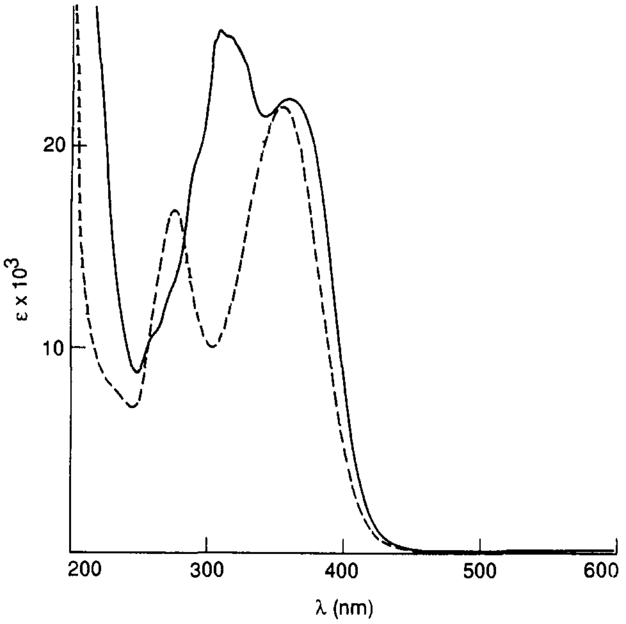


Figure 2. Electronic absorption spectra of *p*-(methylthio)-*p*′-nitrodiphenylacetylene (‒‒) and *p*-(methylthio)-*p*′-nitrodiphenylbutadiyne (—) in acetonitrile solution.

molecules of strong-to-moderate donor-acceptor strength. For weak donor-acceptor groups, such as the methylthio-cyano pairing shown in Figure 1, the ICT band occurs at an energy sufficiently high as to overlap the $\pi \rightarrow \pi^*$ band obliterating the distinction between the two bands.

The effect of changes in the conjugation length on the electronic spectra for a given donor-acceptor pair has been reported previously for the amino-nitro series.[19] It was observed that the energy *and* the intensity of the ICT transitions is relatively invariant as the conjugation length increases. However, the high-energy $\pi \rightarrow \pi^*$ transitions move progressively to lower energy until, for some molecules such as *p*-amino-*p*′-nitrodiphenylhexatriyne and *p*-(methylthio)-*p*′-cyanodiphenylbutadiyne, they directly overlap the ICT transition forming a broad asymmetric band. Figure 2 shows this trend for the methylthio-nitro series. It is clear from this figure that the ICT band is relatively constant (λ_{max} = 356 and 360 nm, respectively, for the diphenylacetylene and diphenylbutadiyne molecules), while the $\pi \rightarrow \pi^*$ transition moves to lower energy (λ_{max} = 279 and 311 nm, respectively) as the conjugation length increases.

The spectroscopic and excited-state properties for the series of donor-acceptor acetylenes are given in Table III which also contains data on the magnitude of the second-order hyperpolarizability obtained from EFISH measurements. From this data the relative effects of systematic changes in the donor–acceptor pairs and in the conjugation length on the electronic structure of the molecules, and therefore on the second-order hyperpolarizability, can be determined.

Donor–Acceptor Group Effects. The energy of the ICT transition provides a relative ordering of the donor–acceptor "strength". For a fixed donor group (NH_2) the acceptor groups can be ordered $NO_2 > CN > C(O)OCH_3 \geq SO_2CH_3 \geq C(O)CH_3$, whereas for a fixed acceptor (NO_2) the ordering $N(CH_3)_2 > NHCH_3 > NH_2 > CH_3S > CH_3O$ is applicable. This ordering scheme is, at best, approximate as various donor–acceptor pairs couple differently across the conjugated framework.

The square of the transition-moment integral ($|m_1|^2$),[21] which is the quantity of interest with respect to β, is large and relatively constant for the ICT transition of all of the molecules reported here, with no systematic variation occurring with changes in the donor–acceptor strength. For example, a strong donor–acceptor pairing such as amino–nitro, with a relatively large value of β, has approximately the same oscillator strength as the amino/sulfone pairing which is much weaker and has a small value of β. Overall, the magnitude of the transition moment squared varies by slightly more than a factor of 2 over the entire range of compounds, while the magnitude of β varies by more than a factor of 5. This and the lack of significant linear correlation between the magnitude of β and the square of the transition-moment integral (as predicted by eq 6) suggest that $|m_1|^2$ does not play a dominant role in dictating the range of values for β. The only systematic trend occurs in the alkylation of the amine donor group in which the transition moment appears to decrease slightly as the amine is alkylated. It is interesting that the magnitude of β *increases* progressively with alkylation suggesting that other factors dominate the value of this quantity.

The dipole moment change, $\Delta\mu$, between the ground state and the ICT state and, where the spectral bands are clearly resolved, between the ground state and the $\pi \rightarrow \pi^*$ transition are reported in Table III. As discussed in the Experimental Section, these values were determined from the solvent shifts of the relevant absorption bands with the Lippert-Mataga equation. For the molecules reported here those with methylthio and methoxy donors give excellent fits to the Lippert–Mataga equation and, therefore, accurate values of $\Delta\mu$. For molecules containing the amine donor a good deal more scatter in the data is observed, undoubtedly due to specific interactions of the amine group with the solvent, yielding more uncertainty in the values of $\Delta\mu$. Regardless, valid observations can be made concerning trends in the effect of structural changes on the dipole change. The dipole moment change does not correlate well with the donor–acceptor strength or with the magnitude of β for these molecules. For example, for the diphenylacetylenes the CH_3S donor group has a much larger dipole moment change with the cyano acceptor (8.0 D) than with the nitro acceptor (5.4 D) even though the cyano group is a much weaker acceptor and has a lower hyperpolarizability (15×10^{-30} vs 20×10^{-30} esu, respectively). Similarly, the amine donor shows a large dipole moment change with the nitro acceptor (9.5 D), a more modest change with the cyano acceptor (4.3 D), and relatively large changes for the carboxylate or the ketone acceptor (15 and 12 D, respectively), while the value of β gets progressively smaller as the donor–acceptor strength decreases. The alkylation of the amine donor results in an increase in the ground-state dipole moment with a concomitant decrease in the dipole moment change. For the diphenylacetylene with the cyano acceptor the dipole moment change goes from 4.3 D for the primary amine to 3.1 D for the tertiary amine. Similarly for the nitro acceptor $\Delta\mu$ goes from 9.5 to 5.7 D.

Taken as a whole, the dipole moment changes observed for donor–acceptor acetylenes cannot be easily predicted based on the energy or intensity of the ICT band. Large dipole moment changes occur for relatively weak donor–acceptor pairs indicating that the amount of charge transferred in the excited state is somewhat independent of the energy between the states. It also suggests that the excited- and ground-state dipole moments are independent of each other so that molecules with small dipole moments in the ground state may have relatively large excited-state dipole moments resulting in a large change between the two. What is also significant is that the overall range of $\Delta\mu$ (Table III) varies by approximately a factor of 4 at the extremes with most molecules having dipole moment changes falling within a factor of 3 of each other, while the magnitude of β varies by more than a factor of 5 for the series. This and, more importantly, the lack of significant linear correlation between the dipole moment change and the magnitude of β (eq 6) suggest that the effect of $\Delta\mu$ on β is not pronounced.

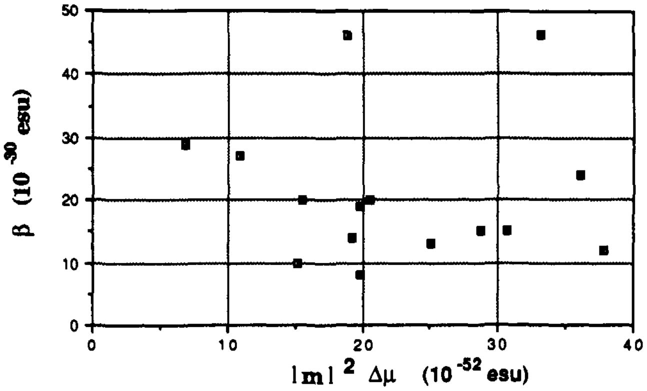


Figure 3. Plot of the second-order hyperpolarizability (β) and the product of the transition-moment integral squared and the dipole moment change, $|m_1|^2\Delta\mu$, for the series of donor–acceptor diphenylacetylenes.

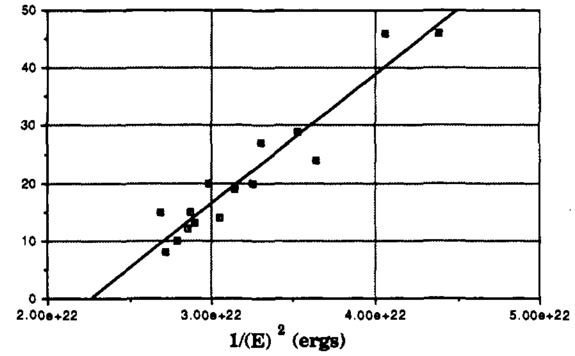


Figure 4. Plot of the second-order hyperpolarizability (β) and the inverse of the square of the frequency ($1/E^2$) of the ICT band for the series of donor–acceptor diphenylacetylenes.

Finally, it is the product, $\Delta\mu|m_1|^2$, for which β is predicted (eq 6) to vary linearly. For the series of donor–acceptor diphenylacetylenes this product varies from 6.8×10^{-53} to 37.8×10^{-53} esu with an average value of 22.5 (±.9) $\times 10^{-53}$ esu over the entire range of molecules. Figure 3 shows that, while the range of values observed for the $\Delta\mu|m_1|^2$ product can encompass the variations observed in β, there is no significant linear correlation between the two quantities. In short, the $\Delta\mu|m_1|^2$ product does not significantly dictate trends observed in the value of β.

It is clear, however, from the data in Table III that, among the series of diphenylacetylenes, the magnitude of β increases with decreasing ICT energy with strong donor–acceptor combinations such as the dimethylamino–nitro pair having the largest values of β while weaker pairs such as the methylthio–cyano pair having the smallest values. By using the two-state limit of the perturbation expression (eq 6) and assuming $\omega_1 \gg \omega$ and that the dipole moment changes and transition moment integrals are relatively constant then β should approximately scale with the square of the inverse of the frequency of the transition. A plot of β vs $1/\omega_1^2$ for the ICT transition of the diphenylacetylene series (Figure 4) shows a very high degree of linearity indicating that, at least for

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[21] The square of the transition dipole-moment integral $|m_1|^2$ is calculated from the oscillator strength, f, by the relationships given in ref 2, pp 109–113.

Table IV. Contributions to the Magnitude of β from the ICT and $\pi \rightarrow \pi^*$ Transitions for Selected Donor-Acceptor Diphenylacetylenes

A	D	$\beta_{\mathrm{ICT}}^{\mathrm{calc}}$ ($\times 10^{30}$ esu)	$\beta_{\pi\rightarrow\pi^*}^{\mathrm{calc}}$ ($\times 10^{30}$ esu)	$\beta_{\mathrm{total}}^{\mathrm{calc}}$ ($\times 10^{30}$ esu)	β^{exp} ($\times 10^{30}$ esu)
NO_2	OCH_3	10.5	3.5	14.0	14
NO_2	SCH_3	12.0	1.8	13.8	20
NO_2	NH_2	24.3	6.7	31.0	24
NO_2	$N(H)(CH_3)$	25.8	8.2	34.0	46
NO_2	$N(CH_3)_2$	15.9	5.6	21.5	46
C(O)Ph	NH_2	10.9	2.8	13.7	19

this class of molecules, the energy of the ICT transition dominates the magnitude of β, while variables such as the transition moment and the dipole moment change play a less significant role.

The effect of alkylating the amine group is interesting and provides additional insight into the relative importance of the energy, transition moment, and dipole moment change on the value of β. Methylation of the amine group results in an increase in donor-acceptor strength with a concomitant increase in β. For the series of primary, secondary, and tertiary amines with cyano acceptors β undergoes a modest increase (from 20 to 29 ($\times 10^{-30}$ esu)) for the series, while the same series with the nitro acceptor goes from 24×10^{-30} to 46×10^{-30} esu with increasing alkylation. However, for both series the transition moment and the dipole moment change tends to decrease with alkylation but these effects are more than compensated for by the energy of the optical transition.

Several interesting observations about the applicability of the simple two-state model emerge from the plot in Figure 4. As discussed, the expression given in eq 6 is obtained by keeping only the first term (first excited state) in the summation of the total perturbation expression (eq 5). Implicit in this assumption is that the first term is much larger than the terms resulting from the higher excited states and, therefore, will dominate the magnitude of β. As the excellent correlation seen in Figure 4 suggests, this assumption is reasonable for the donor-acceptor acetylenes reported here in which the energy of the intense ICT band does clearly dominate the changes in the magnitude of β. However, to obtain the simple form of eq 6 the high-energy terms are arbitrarily set equal to zero. In fact, as is evidenced by the nonzero intercept of Figure 4, these higher energy terms are not zero though they are slowly varying (constant) relative to the dominant first excited-state term. The slope obtained from the least-squares fit of the data in Figure 4 yields a $\Delta\mu|m_1|^2$ product of 14.8×10^{-52} esu which, given the assumption of a constant transition moment and dipole moment change inherent in the calculation, represents some average value for this product. The $\Delta\mu|m_1|^2$ product obtained from this fit does agree, within an order of magnitude, with the average value of this product (2.3×10^{-52}) calculated from Table III for all of the diphenylacetylenes.

Clearly, as the energy *difference* between the first excited state and the higher excited states decreases (as occurs with increasing conjugation length) the low-energy term may cease to dominate and the simple two-state model will no longer be applicable.

In light of this discussion it is worth considering to what extent the $\pi \rightarrow \pi^*$ transitions contribute to the magnitude of β for these molecules even though they lie at higher energy than the ICT band. For many of the donor-acceptor diphenylacetylenes this transition is both intense and, in many cases, possesses a large dipole moment change (Table III). An estimate of the contribution to the magnitude of β from both the ICT band and the $\pi \rightarrow \pi^*$ transition can be made by using eq 6 and the spectroscopic properties listed in Table III for both of the transitions (Table IV). The calculations suggest that, for some donor-acceptor pairs, the high energy $\pi \rightarrow \pi^*$ band can contribute significantly (up to 25%) to the total magnitude of β. Table IV also compares the total calculated value of β (the sum of the contributions from *both* excited states) to the experimentally determined values. The calculated quantities agree reasonably well with the experimentally determined ones with the contribution due to the $\pi \rightarrow \pi^*$ transition significantly improving the agreement for most of the molecules.[22]

Table V. EFISH Measurements of the Nonlinear Optical Properties of Donor-Acceptor Diphenylacetylenes in *N*-Methylpyrrolidone

donor	acceptor	no. of acetylenes	$\mu\beta$ (esu)
NH_2	NO_2	1	22×10^{-47}
NH_2	NO_2	2	24×10^{-47}
NH_2	NO_2	3	41×10^{-47}
NH_2	CN	1	10×10^{-47}
NH_2	CN	2	11×10^{-47}

Conjugation Length Effects. The effect of increases in the conjugation length on the excited state and spectroscopic properties of the molecules can be determined from the data in Table III. As previously reported, the intensity and energy of the ICT band are relatively insensitive to changes in the conjugation length.[19] For the amino-nitro donor-acceptor pair the square of the transition moment integral drops slightly, from 3.8×10^{-35} to 3.0×10^{-35} esu with the addition of one acetylene, while the energy of the band is relatively invariant. A similar trend is observed for the methylthio-nitro and amino-cyano series in going from one acetylene bridge to two.

In general, increasing the length of the molecules does not result in an increase in the excited-state dipole moment or in the dipole moment change. This is somewhat surprising as increasing the distance between the donor and the acceptor is a common approach for increasing the magnitude of β. On the basis of a simple point-dipole approximation an increase of ≈20% in the dipole moment is expected in going from diphenylacetylene to diphenylbutadiyne which have a 12.5- and 15-Å donor-to-acceptor distance, respectively. For the amino-nitro donor-acceptor pair the *ground-state* dipole moment does increase by 20%; this is consistent with a constant amount of charge being transferred (≈0.09 e) making the change proportional to the change in length of the molecule. The *excited-state* dipole moment is, however, the same for both molecules (≈15 D) which results in a decrease in the dipole moment change! This seems to imply, at least for this donor-acceptor pair, that *less* total charge is transferred to the acceptor in the excited state as the conjugation length increases. For the methylthio-nitro donor-acceptor pair both the ground and the excited-state dipole moments are relatively invariant with length, resulting in no increase in the dipole moment change. These trends may be due to a greater delocalization of charge over the molecule as the energy gap between the π and π^* molecular orbitals decreases with increasing conjugation length.

The invariance of the factors discussed above results in β being relatively constant with the increase in conjugation length of the molecule. For the methylthio-nitro diphenylacetylene and diphenylbutadiyne molecules β is, within experimental error, constant at 20×10^{-30} and $17 \pm 2 \times 10^{-30}$ esu, respectively. Similarly in the methylthio-cyano acetylenes, β has values of 15×10^{-30}–$17 \pm 2 \times 10^{-30}$ esu as the number of acetylenes increases from one to two.

For the amino-nitro series three different conjugation lengths corresponding to the diphenylacetylene, diphenylbutadiyne, and the diphenylhexatriyne are available for comparison. For the diphenylacetylene and diphenylbutadiyne molecules β shows behavior similar to that observed in the other donor-acceptor pairs with relatively constant values for β of 24×10^{-30} and $28 \pm 2 \times 10^{-30}$ esu, respectively. To compare the entire series it is necessary to compare values of the product $\mu\cdot\beta$ as the relative insolubility of the *p*-amino-*p'*-nitrodiphenylhexatriyne molecule required the use of a polar solvent (*N*-methylpyrrolidone) which prevented an accurate determination of the ground-state dipole moment. The values of the product $\mu\cdot\beta$ (Table V) are relatively constant for the diphenylacetylene and the diphenylbutadiyne at 22×10^{-47} and 24×10^{-47} esu, respectively, while for the diphenylhexatriyne $\mu\cdot\beta$ increases sharply to 41×10^{-47} esu. As the data in Table III indicates, the ground-state dipole moment varies slowly with increasing conjugation length for all of the molecules reported. This suggests that the large increase seen in the $\mu\cdot\beta$ product is due primarily to an increase in β itself. A reasonable estimate of the ground-state dipole moment can be made from a simple

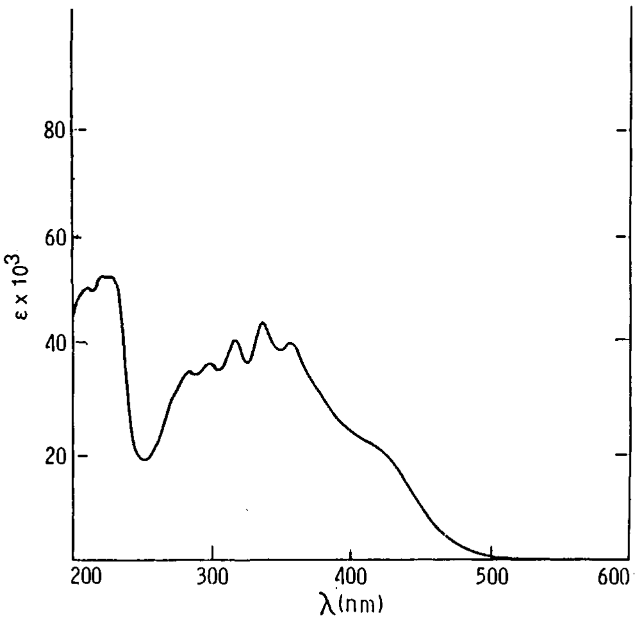

Figure 5. Electronic absorption spectrum of *p*-amino-*p'*-nitrodiphenylhexatriyne in acetonitrile solution.

point-dipole approximation. As discussed previously, the ground-state dipole moment of the amino–nitro donor–acceptor series scales very well to a point-dipole approximation with 0.09 of a unit charge transferred. With a donor-to-acceptor distance of 17.5 Å the dipole moment for the diphenylhexatriyne is predicted to be 7.6 D, which yields a value for β of 53 × 10^{-30} esu.

The explanation for the sharp increase in β is not immediately obvious, especially in light of the modest changes observed in going from one to two acetylene linkers in other molecules in the series. However, changes in the electronic structure of the molecule, which are reflected in the absorption spectra (Figure 4) as the conjugation length increases, suggest the origin of the increase. As discussed previously, the ICT band ($\approx$ 380 nm ($\epsilon \approx 10^4$)) is relatively constant for the series while the high energy $\pi \rightarrow \pi^*$ transition occurs at 275 nm for the diphenylacetylene and 320 nm for the diphenylbutadiyne. The $\pi \rightarrow \pi^*$ transition for this particular series of molecules is intense and is accompanied by a reasonably large excited-state dipole moment change ($m_1 = 3.7 \times 10^{35}$ esu and $\Delta\mu$ = 5.7 D for the amino–nitrodiphenylacetylene). As previously discussed, the contribution of this state to the magnitude of β is significant and will become more significant as its energy drops and becomes equal to that of the ICT state.

In the case of the *p*-amino-*p'*-nitrodiphenylhexatriyne molecule, the electronic spectrum is comprised of a large intense transition in which the ICT band appears as a low-energy shoulder (Figure 5). The entire band has an oscillator strength of 2.0, which suggests that it is composed of a number of transitions including the ICT band as well as several $\pi \rightarrow \pi^*$ bands. It is reasonable to attribute the large increase that occurs in the magnitude of β for the diphenylhexatriyne molecule to the additive two-level contributions of all of these essentially isoenergetic states.

Macroscopic Nonlinear Optical Properties: Second Harmonic Generation. One macroscopic phenomenon that originates from the microscopic second-order hyperpolarizability is frequency doubling or second harmonic generation (SHG). This phenomenon involves the doubling in frequency of an incident laser line. For example, the 1064-nm fundamental of a Nd:YAG is doubled to yield light at 532 nm.[10,11]

However, for this effect to be observed at all in solid crystalline materials it is necessary for the molecules to pack in a noncentrosymmetric space group.[14] Noncentrosymmetric packing prevents the hyperpolarizability tensor elements of the molecules from cancelling each other as light propagates through the crystal. Implicit in this condition is that molecules, regardless of the value of β, yield no SHG signal if they do not crystallize in an appropriate space group.

Table VI. Second Harmonic Generation Efficiencies for Donor–Acceptor Acetylene Compounds

			SHG efficiency (relative to urea)[a] (nm)	
donor	acceptor	n	1064	1907
NH_2	NO_2	1	0.2	0.4
NH_2	NO_2	2	0.05	0.07
NH_2	NO_2	3	0.03	0.7
NH_2	CN	1	0.23	0.08
NH_2	CN	2	0.4	0.3
NH_2	CO_2CH_3	1	120, 114, 68[b]	120, 71[b]
NH_2	CO_2CH_3	2	16, 15[b]	34, 22[b]
CH_3S	NO_2	1	65, 49[b]	200, 159[b]
CH_3S	NO_2	2	0.2	0.6
CH_3S	CN	2	0.7	0.04
NH_2	$COCH_3$	1	39, 38[b]	102
CH_3S	$COCH_3$	1	10, 15[b]	15

[a] Values less than 0.05 are not statistically significant. [b] Multiple determinations on different batches of material.

The entire series of molecules were screened for their SHG activity with the Kurtz powder method.[23] The efficiencies (relative to a urea standard) of those molecules found to be SHG active are shown in Table VI. The importance of the crystallographic space group is apparent from the data. One of the highest SHG efficiencies was measured for the amino–carboxylate diphenylacetylene molecule which has an efficiency of 120 times urea but a molecular hyperpolarizability of 15 × 10^{-30} esu. By comparison, the amino–nitro series has very small SHG efficiencies but the largest values of β. The space group of the amino–carboxylate diphenylacetylene is $P2_1$ which is noncentrosymmetric, while the amino–nitro series all crystallized in centrosymmetric space groups.[7] In principle, centrosymmetric materials such as the amino–nitro series should give *no* measurable SHG signal at all. The existence of measurable SHG signals with values as high as 0.2 × urea emanating from bulk microcrystalline samples of these materials has been attributed to noncentrosymmetric, SHG active, crystal phases of the molecules that "contaminate" the bulk material.[7]

Summary and Conclusions

In general, a number of conclusions about the effect of structural changes on the magnitude of the second-order molecular hyperpolarizability for this class of molecules can be drawn. Overwhelmingly, the value of β is dominated by the energy of the ICT band with strong donor–acceptor pairs producing large values of β primarily because they have low-energy absorption bands. The effect of the transition moment and dipole moment change on the value of β was uncorrelated and less predictable. The transition moment was large for all of the molecules investigated and relatively independent of donor–acceptor strength or changes in the length of the molecule. The dipole moment change, $\Delta\mu$, varied over a significant range; however, this variation did not scale uniformly with changes in donor–acceptor strength. Weak donor–acceptor combinations frequently had large dipole moment changes, while stronger pairs actually showed smaller changes. Furthermore, as the conjugation length increased the dipole moment change actually decreased—a trend that is somewhat counterintuitive. Taken together, this suggests that engineering large dipole moment changes into a molecule in order to increase β may not be straightforward, at least for acetylene-bridged compounds. One particularly interesting suggestion from this study was the origin of the large value of β achieved for the amino–nitro diphenylhexatriyne molecule. The degree to which

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(22) Calculations of β for organic molecules with the two-state model (eq 6) have been performed by a number of workers (e.g., ref 18) who, in general, report values closer to the experimentally determined values than our results reported in Table IV. Our calculations were performed to illustrate the contribution of the higher energy state to the total magnitude of β and were not an attempt to duplicate the experimental results.

(23) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.

the superposition of electronic states in long conjugated molecules contributes to large second-order hyperpolarizabilities is worthy of further investigation.

While these conclusions apply strictly to the acetylene-linked donor–acceptor pairs investigated here, a comparison to other donor–acceptor molecules indicates that many of these observations may be general. A recent study of donor–acceptor benzene and stilbene compounds indicates that, within a series, the value of β is dominated by the energy of the ICT transition.[3a] In comparing totally different molecules it is clear that other factors, such as dipole moment change and transition moment, play a significant role. In general, the donor–acceptor benzenes had smaller values of β than either the stilbene or acetylene derivatives for similar ICT band energies. Furthermore, the stilbene-linked donor–acceptor pairs have larger β values than the acetylene linkers. This is due to the greater degree of conjugation inherent in the ethylene-linked π system. The acetylene group, which possesses a short carbon–carbon bond (a constraint imposed by the in-plane π bond), does not overlap as well with the π system on the phenyl groups as the ethylene bridge. This is reflected in the position of the ICT band which is at lower energy for the stilbene than for the acetylene linker (402 vs 381 nm respectively for the amino–nitro donor–acceptor pair). Likewise the β value is larger for the stilbene than the acetylene (24×10^{-30} vs 40×10^{-30} esu, respectively, for the amino–nitro derivatives). It is worth noting than the very large value of β observed for the amino–nitro stilbene relative to the diphenylacetylene analogue is due not only to the lower ICT transition energy but also to a larger dipole moment change; this suggests that factors such as $\Delta\mu$ are more important in going from one class of molecules to another and that they are within a homologous series.

Acknowledgment. This work was performed in part by the Jet Propulsion Laboratory, California Institute of Technology, as part of its Center for Space Microelectronics Technology, which is supported by the Strategic Defense Initiative Organization, Innovative Science and Technology Office through an agreement with the National Aeronautics and Space Administration.

Structure and Mesophases of Hexacyclen Derivatives

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Received March 28, 1991.

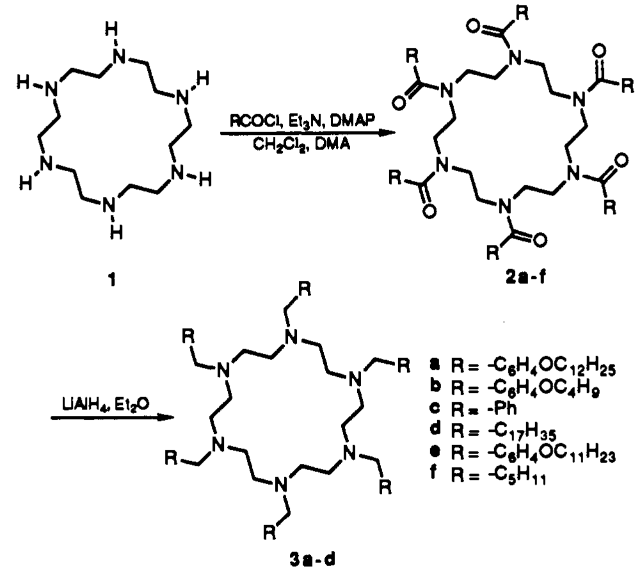
Abstract: A variety of hexacyclen derivatives with aliphatic substituents have been prepared and characterized via X-ray diffraction, calorimetry, thermogravimetric analysis, and computer simulations. A subset of these compounds (**2a** and **2e**) are seen to display a liquid crystalline mesophase, while others transform directly from the crystalline to the isotropic liquid phase. The merits of tubular and smectic liquid crystalline models for the mesophase structure are discussed.

1. Introduction

It is generally considered that the liquid crystalline phases formed by a mesogenic compound are primarily determined by the geometry of the constituent molecules; traditional prolate molecules form layered smectic phases or nematic phases, while highly oblate "discotic" molecules[1,2] form columnar or discotic nematic phases. Although the majority of discogenic molecules studied have flat, rigid cores with six or more flexible aliphatic tails, columnar-phase formation is possible with a remarkable degree of molecular nonplanarity and asymmetry.[2] Accordingly, when Lehn et al. found[3] that the hexakis(p-(n-dodecyloxy)benzoyl) derivative of hexasubstituted azacrown[18]-N_6 (**2a**) (Scheme I) exhibited mesogenic behavior, the most natural hypothesis was that a columnar structure was formed. This hypothesis was strengthened by microscopic and X-ray observations of samples oriented by shearing or slow cooling on a glass substrate. Furthermore, the structural representation in Scheme I exhibits an intriguing, albeit small, open space in the center of the molecule, leading to the description of the mesophase structure as "tubular": consisting of a hexagonal disordered columnar phase ("D_{hd}") with *hollow* columns.

Several subsequent studies of **2a** and related compounds[4-7] were essentially consistent with those of Lehn et al., although phase-transition temperatures were found to vary from laboratory to laboratory. It has been suggested[6] that these variations arise from differing amounts of water in the highly hygroscopic samples. It is also seen that mesophase formation is quite sensitive to tail structure;[5] in particular, only substituents consisting of proximal aromatic residues with aliphatic tails result in mesophase formation.

Scheme I



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