

First Hyperpolarizabilities of 1,3,5-Tricyanobenzene Derivatives: Origin of Larger β Values for the Octupoles than for the Dipoles

Sang Hae Lee,^[a] Jo Ryoung Park,^[a] Mi-Yun Jeong,^[a] Hwan Myung Kim,^[a] Shaojun Li,^[a] Jongwon Song,^[b] Sihyun Ham,^{*,[b]} Seung-Joon Jeon,^{*,[a]} and Bong Rae Cho^{*,[a]}

A series of donor–acceptor substituted stilbene and diphenylacetylene derivatives and their octupolar analogues have been synthesized and the linear and nonlinear optical properties (β) studied by both experiments and theoretical calculation. The λ_{max} of the dipoles increases with the conjugation length and is always larger when the C=C bond is used, instead of the C≡C bond, as the conjugation bridge. Although the λ_{max} values of the octupoles show no clear trend, they are much larger than those of the dipoles. The $\beta(0)$ values of the dipoles increase with conjugation length and as the conjugation bridge is changed from the C≡C to C=C bond. This increase is accompanied by an increase in

either λ_{max} or the oscillator strength. Similarly, the $\beta(0)$ values of the octupoles increase with the conjugation length and with a change in the donor in the order: $NEt_2 < N(i\text{-amyl})Ph < NPh_2$. Moreover, β_{yyy}/β_{zzz} ratios are in the range of 1.6–3.9 and decrease with the conjugation length. β values calculated by the finite-field and sum-over-states methods are in good agreement with the experimental data. Also, there is a parallel relationship between the calculated β values and bond length alternation (BLA). From these results, the origin of the larger β values for octupoles than for dipoles is assessed.

Introduction

There is much interest in the development of organic nonlinear optical (NLO) materials for possible applications in electro-optic devices. The most intensively studied NLO chromophores are donor–acceptor substituted dipolar molecules.^[1] While such studies have led to a detailed understanding of the relationship between the chromophore structure and the NLO properties, it has become apparent that the dipoles have certain limitations. One such problem is the difficulty associated with aligning the dipoles non-centrosymmetrically in the solid state to achieve a maximum bulk effect.

More recently, octupolar molecules with three-fold symmetry have been developed as alternative NLO chromophores.^[2–6] An advantage of such molecules in comparison to the more conventional dipolar molecules is the fact that the second-harmonic response of octupoles does not depend on the polarization of the incident light because it is more isotropic than that of the dipolar NLO molecules.^[2d] Also, the two-dimensional octupoles favor the formation of non-centrosymmetric crystals, which is important for practical applications.^[5] Moreover, there is a design strategy for the synthesis of octupoles with large first hyperpolarizabilities.^[7] According to the VB-3CT model, the β value of two-dimensional octupoles increases gradually with the extent of charge transfer. Hence, the β values of such molecules could be significantly enhanced by simultaneously increasing the donor–acceptor strength, the charge-transfer ability of the conjugation bridge, and the conjugation length. Accordingly, various derivatives of subphthalocyanine, truxenone,

1,3,5-tris[(*p*-styryl)phenyl]benzene, 1,3,5-tricyano-2,4,6-tris(ethynyl)benzene, 1,3,5-tris(ethynyl)-2,4,6-triazine, triphenylamine, and hexa-substituted donor–acceptor benzene derivatives have been synthesized and their structure–property relationship investigated.^[2–4] Recently, we reported that 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives and their dendrimers show modest to very large first hyperpolarizabilities.^[4b,f,g] The most interesting result from this study is that 1,3,5-tricyano-2,4,6-tris(*p*-diethylaminostyryl)benzene produces a non-centrosymmetric crystal, which exhibits one of the largest second-harmonic generations (SHG) known in the literature.^[5b] Moreover, octupolar molecules showed modest to large enhancement in the first hyperpolarizability compared to dipolar molecules.^[3f,4f] However, the origin of this enhancement has not been clearly established.

[a] Dr. S. H. Lee, J. R. Park, Dr. M.-Y. Jeong, H. M. Kim, Dr. S. Li, Prof. S.-J. Jeon, Prof. B. R. Cho
Molecular Optoelectronics Laboratory
Department of Chemistry and Center for Electro- and Photo-Responsive Molecules
Korea University, 1-Anamdong, Seoul, 136-701 (Korea)
Fax: (+82) 2-3290-3121
E-mail: chobr@korea.ac.kr

[b] J. Song, Prof. S. Ham
Department of Chemistry, Sookmyung Women's University
140-742 Chungpa 2-dong, Seoul, 136-701 (Korea)

Supporting information for this article is available on the WWW under <http://www.chemphyschem.org> or from the author.

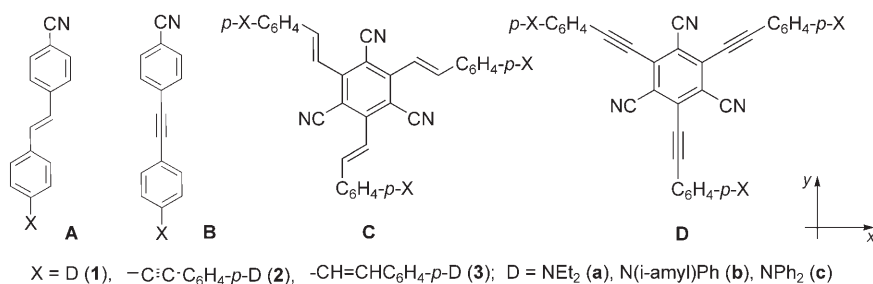
Here, we have synthesized a series of donor–acceptor substituted dipolar compounds (**A**, **B**) and their octupolar analogues (**C**, **D**) and studied the linear and nonlinear optical properties by experiments and theoretical calculations. The effects of conjugation bridge, conjugation length, donor, and molecular symmetry on the linear and nonlinear optical properties of **A–D** have been studied. From these results, the origin of the larger β values for the octupoles than for the dipoles is assessed.

Results and Discussion

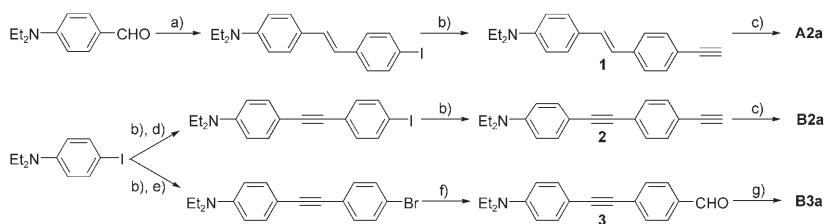
Synthesis

Compounds **A1a**, **A3a**, **C1a**, **C3a**, and **C3c** were available from a previous study.^[4b,f] Synthesis of **A2a**, **B2a**, and **B3a** is summarized in Scheme 2. All dipolar compounds were synthesized from **1–3** by using Sonogashira coupling and the Horner–Wittig reaction.

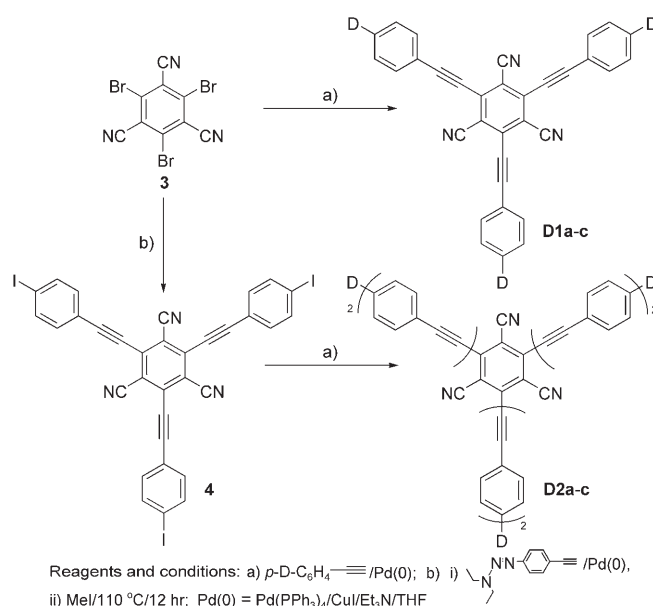
The octupolar molecules **C2a** and **C2c** were synthesized by the Horner–Wittig reaction between 1,3,5-tricyano-2,4,6-tris-[(diethoxyphosphoryl)methyl]benzene and appropriate benzaldehyde derivatives, as reported.^[4b,f] Synthesis of **D1a–c** and **D2a–c** is shown in Scheme 3. All compounds were prepared by the Sonogashira coupling between 1,3,5-tribromo-2,4,6-tricyanobenzene (**3**) or 1,3,5-tricyano-2,4,6-tris(*p*-iodophenylethynyl)benzene (**4**) and substituted phenylacetylenes.^[7] The structures of the new compounds were unambiguously confirmed by ¹H, and ¹³C NMR spectroscopy, IR spectroscopy, and elemental analysis. **D1a** was previously synthesized by a similar procedure starting from 1,3,5-trichloro-2,4,6-tricyanobenzene.^[3e] Although one of the C-13 NMR peaks was reported to be miss-



Scheme 1. Structures of **A–D**.



Scheme 2. Reagents and conditions: a) (EtO)₂P(O)CH₂C₆H₄-p-I/LDA/THF from -78°C to rt, b) TMSacetylene/Pd(II)/KOH/MeOH at rt, c) CN-C₆H₄-p-I/Pd(II); d) 1,4-diiodobenzene/Pd(II), e) 4-iodobromobenzene/Pd(II), f) *n*BuLi/THF from -78°C to rt; g) (EtO)₂P(O)CH₂C₆H₄-p-CN/LDA/THF from -78°C to rt; Pd(II) = PdCl₂(PPh₃)₂/CuI/THF/Et₃N.



Scheme 3. Synthesis of **D1a–c** and **D2a–c**.

ing, the ¹H NMR spectrum, the UV spectrum, and the melting point are consistent with our results.

Structures of **A–D**

We performed geometry optimizations for the dipolar compounds (**A**, **B**) and their octupolar analogues (**C**, **D**) with ab initio molecular-orbital theory at the RHF/6-31G level using the Gaussian 98 program.^[8] Vibrational frequency calculations were executed to verify the identity of each stationary point as a minimum at the same level. The torsion angles of **A1a–A3a** and **C1a–C3a** are summarized in Table 1. The corresponding data for **B1–3a** and **D1–3a** are summarized in Table S1 of the Supporting Information.

The torsion angles between the phenyl groups linked by the C=C bonds (ϕ_3, ϕ_6) are in the range $33\text{--}40^\circ$, indicating that they are significantly distorted by the steric effect. For comparison, the calculated ϕ_3 value of 36.1° for **C1a** is significantly larger than that of 26.7° observed in the crystal.^[5b] This indicates that the molecule is more planar in the crystal where the stacking interaction is important.

The ϕ_1 value decreases from 160° to 135° from **A1a–A3a** to **C1a–C3a**. This is because the C=C bonds are located between the two CN groups in the latter,

Entry	Cmpd.	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
1	A1a	161.0	167.1	−33.1	–	–	–
2	A2a	159.6	162.1	−40.3	0.0	0.0	0.0
3	A3a	160.0	163.7	−38.0	161.6	165.3	34.6
4	C1a	135.6	−164.0	36.1	–	–	–
5	C2a	135.8	−163.8	35.3	0.0	0.0	0.0
		(−44.1)	(−164.1)	(35.3)	(0.0)	(0.0)	(0.0)
6	C3a	134.3	−158.1	32.7	161.3	165.7	36.3
		(−45.1)	(−158.8)	(32.7)	(161.3)	(165.8)	(36.6)

[a] ϕ_1 – ϕ_6 are the torsion angles between the cyanophenyl group (Ph1) and C=C or C≡C (π), π and the second phenyl group (Ph2), Ph1 and Ph2, Ph2 and π , π and the third phenyl group (Ph3), and Ph2 and Ph3, respectively.

which increases the steric effect. When the steric effects are similar, the torsion angles are also similar. Note that the absolute values of ϕ_1 and ϕ_2 for **A1a–A3a** are similar to ϕ_2 of **C1a–C3a** and ϕ_4 and ϕ_5 of **B3a** and **C3a** (Tables 1 and S1). Furthermore, **C1a** has C_3 symmetry. As the conjugation length is increased to **C2a** and **C3a**, the structures are more distorted and the C_3 symmetry is broken. In contrast, the phenyl groups linked to the C≡C bond are nearly coplanar regardless of the molecular symmetry (**A2a**, **B1a–B3a**, **C2a**, and **D1a–D2c**) (Tables 1 and S1). Also, the D_3 symmetry of **D1a** is maintained in **D2a**.

Absorption Spectra

Figure 1 shows that the λ_{\max} values of **A1a** and **A2a** are nearly the same, whereas that of **A3a** is red-shifted by 24 nm (1472 cm^{-1}) from **A2a** (Table 2). This indicates a more efficient intramolecular charge transfer (ICT) in **A3a** than in **A2a**, and that the C=C bond is a more effective conjugation bridge than the C≡C bond. Consistently, the λ_{\max} value of **B1a** is blue-shifted from **A1a** by 18 nm (1190 cm^{-1}). In addition, the λ_{\max} values of **B1a** and **B2a** are almost the same, and that of **B3a** is red-shifted by 26 nm (1668 cm^{-1}) compared to **B2a** (Table 2). Inter-

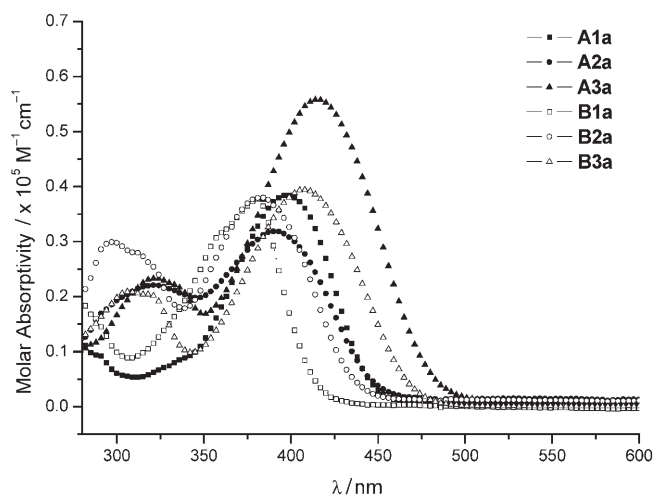


Figure 1. Molar absorptivity spectra for **A1a–A3a** and **B1a–B3a**.

estingly, the λ_{\max} value of **B3a** is red-shifted by 16 nm (1000 cm^{-1}) from **A2a**, even though the donor/acceptor and the conjugation bridge are the same (Table 2). This may be due to the fact that the C≡C bond is more electron-deficient than C=C and enhances the acceptor strength of **B3a** while reducing the donor strength of **A2a**. However, the larger λ_{\max} value of **A3a** compared to **B3a** suggests that this effect is not as important as the nature of the conjugation bridge.

A similar result is observed for the octupolar molecules (Figure 2). λ_{\max} of **C2a** is blue-shifted from that of **C1a** by 35 nm (1632 cm^{-1}), despite the extended conjugation. When the second conjugation bridge is changed from C≡C (**C2a**) to the more efficient C=C bond (**C3a**), the shorter-wavelength band decreases and λ_{\max} increases (Figure 2).

As observed for **B1a** and **B2a**, λ_{\max} of **D1a** and **D2a** are the same, indicating that the factors affecting λ_{\max} are more or less the same regardless of the molecular symmetry for the ethynyl derivatives (Figures 1 and 2). Also, the shorter-wavelength bands in **D1a** and **D2a** are nearly identical to the charge-transfer (CT) bands of *p*-diethylaminophenylacetylene (**1'**) and 4-(*p*-diethylaminophenylethynyl)phenylacetylene (**2**), indicating that they are due to the localized absorption (Figure S2).

The octupoles show large bathochromic shifts ranging from 54 to 104 nm (3089 to 5655 cm^{-1}) from their dipolar analogues (Table 3). This indicates that these octupoles are not just three molecules of dipoles arranged in a symmetrical way but the extension of the latter sharing the central phenyl group, so that an efficient π -orbital overlap is possible to enhance the ICT. Moreover, the λ_{\max} values of **D1a** and **D2a** are red-shifted by more than 100 nm (5474 cm^{-1}) from their dipolar analogues, whereas **C1a**, **C2a**, and **C3a** show smaller red shifts. This is as expected because the more planar the molecule is, the more effective the π -orbital delocalization will be.

First Hyperpolarizabilities of Dipolar Molecules

The β values were measured at 1064 nm by the hyper-Rayleigh scattering (HRS) method.^[49,9,10] To determine the β values accurately, the pure HRS signal was obtained by subtracting the two-photon-excited fluorescence (TPF) from the total signal intensity, followed by the correction for the self-absorption. In all cases, an average of 200 signals was used for the calculation (see the Experimental Section for details).

Table 2 shows that the $\beta(0)$ values of **A1a–A3a** are in the range: $(49\text{--}150) \times 10^{-30}$ esu. They increase with the conjugation length and as the conjugation bridge is changed from C≡C to C=C, that is, **A1a** < **A2a** < **A3a**. Note that the increase is accompanied either by a larger oscillator strength (**A1a** < **A2a**) or by a larger λ_{\max} (**A2a** < **A3a**), as predicted by the two-level model

Entry	Cmpd.	$\lambda_{\max}^{[a]}$ [nm]	$10^{-4}\epsilon^{[b]}$ [molL ⁻¹ cm ⁻¹]	$f^{[c]}$	$\beta^{[d,e]}$ [10 ⁻³⁰ esu]	$\beta(0)^{[e,f]}$ [10 ⁻³⁰ esu]	$\beta_{zzz}^{[g]}$ [10 ⁻³⁰ esu]	BLA ^[h]	$\sqrt{\langle \beta_{HRS}^2 \rangle}^{[i,j]}$
1	A1a ^[4f]	398	3.84	0.62	130	49	118	-0.13890	19
2	A2a	392	3.20	0.82	201	79	191	-0.13850	24
3	A3a ^[4f]	416	5.58	1.1	457	150	362	-0.13850	30
4	B1a	380	3.76	0.62	–	–	112 ^[j]	-0.23450	18
5	B2a	382	3.81	0.80	224	95	229	-0.23445	29
6	B3a	408	3.94	0.56	351	123	297	-0.23350	31

[a] Absorbance maximum. [b] Molar extinction coefficient. [c] Oscillator strength estimated by the relationship: $f = 4.319 \times 10^{-9} \epsilon \nu_{1/2}$. [d] Determined at 1064 nm. [e] Estimated uncertainty: $\pm 15\%$. [f] Corrected at $\lambda \rightarrow \infty$ using a two-level model.^[11] [g] Calculated from the relationship: $\langle \beta^2 \rangle = (6/35)\beta_{zzz}^2$ for 1D chromophores.^[12] [h] Bond length alternation of the conjugation bridge nearest to the cyanophenyl group. [i] Calculated by using the finite-field method.^[8] [j] Estimated by assuming that the experimental ratio of β_{zzz} for **A1a** and **B1a** is the same as the calculated value.

Entry	Cmpd.	$\lambda_{\max}^{[a]}$ [nm]	$10^{-4}\epsilon^{[b]}$ [molL ⁻¹ cm ⁻¹]	$f^{[c]}$	$\beta^{[d,e]}$ [10 ⁻³⁰ esu]	$\beta(0)^{[e,f]}$ [10 ⁻³⁰ esu]	$\beta_{yyy}^{[g]}$ [10 ⁻³⁰ esu]	β_{yyy}/β_{zzz}	BLA ^[h]	$\sqrt{\langle \beta_{HRS}^2 \rangle}^{[i,j]}$
1	C1a ^[4f]	481	10.3	1.7	1732	252	408	3.5	-0.13590	33 (19)
2	C2a	446	7.00	1.9	1372	336	544	2.8	-0.13579	43 (28)
3	C2c	417	8.00	2.2	933	394	638	–	-0.13535	44
4	C3a ^[4f]	480	10.2	2.3	2350	348	564	1.6	-0.13546	41 (45)
5	C3c	450	11.0	2.5	1697	396	642	–	-0.13520	39
6	D1a	484	14.0	1.7	2001	273	442	3.9	-0.22800	44 (31)
7	D1b	479	13.0	1.5	1861	281	455	–	-0.21960	39
8	D1c	480	10.8	1.4	2028	300	486	–	-0.21870	47
9	D2a	483	7.02	1.4	2787	389	630	2.8	-0.19870	71 (35)
10	D2b	466	7.65	1.5	2010	378	612	–	-0.19880	69
11	D2c	456	8.58	1.5	1687	365	591	–	-0.19880	64

[a–e],[h] See Table 2 for the footnotes. [f] Corrected at $\lambda \rightarrow \infty$ using a three-level model. [g] Calculated from the relationship: $\langle \beta^2 \rangle = (8/21)\beta_{yyy}^2$ for D_3 chromophores.^[12] [i] Calculated using the finite-field method unless otherwise noted.^[8] [j] The numbers in the parenthesis are calculated by the sum-over-states method (β_{SOS}).^[13]

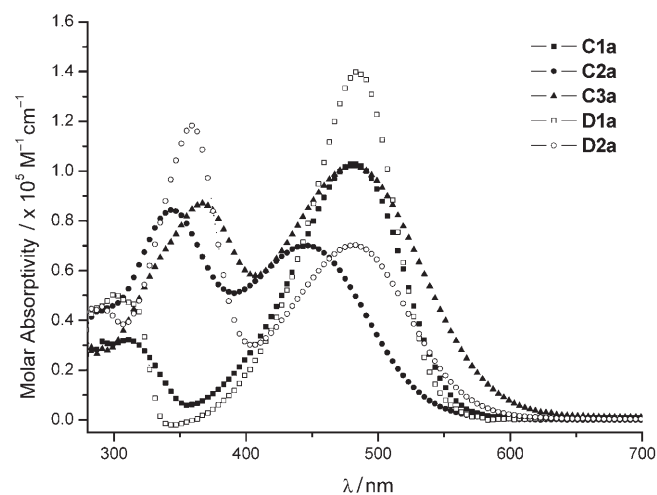


Figure 2. Molar absorptivity spectra for **C1a–C3a**, **D1a**, and **D2a**.

(see below).^[11] A similar result is observed for **B1a–B3a**, that is, **B2a** < **B3a**, although the experimental value of β for **B1a** is not available because the measurement was hampered by the two-photon-excited fluorescence. Here again, λ_{\max} increases by the same order and the oscillator strength is larger for **B2a**

than for **B1a** (Table 2). Interestingly, the $\beta(0)$ values for **A1a–A3a** and **B1a–B3a** are not very much different, probably because the λ_{\max} values and the oscillator strength are similar for the two series of compounds.

First Hyperpolarizabilities of Octupolar Molecules

The first hyperpolarizability of a D_3 symmetric molecule can be expressed by the three-level model [Eq. (1)], where μ_{10} is the transition moment between the ground and degenerate first excited CT state, μ_{12} is the transition moment connecting the degenerate excited states, ω_{10} is the CT energy and ω is the energy of the incident laser light (Figure 3).^[2a] The equation is identical to that of the two-level model of molecular nonlinearity for the dipoles if μ_{12} is substituted by $(\mu_2 - \mu_1)$, where μ_1 and μ_2 are the dipole moments in the ground and in the first excited CT state, respectively.^[11]

$$\beta_{yyy} = \frac{1}{\hbar^2} \times \frac{\mu_{10}^2 \mu_{12}}{\omega_{10}^2} \times \frac{\omega_{10}^4}{(\omega_{10}^2 - 4\omega^2)(\omega_{10}^2 - \omega^2)} \quad (1)$$

The $\beta(0)$ values of **C1a–C3a** gradually increase from 252×10^{-30} esu to 348×10^{-30} esu in the order: **C1a** < **C2a** < **C3a** (Table 3). For the change from **C1a** to **C2a**, λ_{\max} is blue-shifted

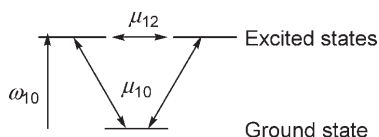


Figure 3. Transitions between the ground and excited states.

by 35 nm (1632 cm^{-1}), whereas the oscillator strengths, which are proportional to the square of the transition moment (μ_{10}^2), are similar. Therefore, the large increase in $\beta(0)$ from **C1a** to **C2a** can be explained if μ_{12} is larger for **C2a** than for **C1a** [Eq. (1)]. On the other hand, the small increase in the $\beta(0)$ from **C2a** to **C3a** is consistent with the modest increase in λ_{max} and oscillator strength.

When the conjugation bridge is changed from C=C (**C1a**) to C≡C (**D1a**), $\beta(0)$ remains similar—probably because λ_{max} and oscillator strength are almost the same (Table 3). For comparison, the value of $\beta_{\text{yyy}} = 442 \times 10^{-30}$ esu for **D1a** is larger than the literature value of 257×10^{-30} esu determined under similar conditions.^[3e] At present, the origin of this dichotomy is not clear. The $\beta(0)$ value of **D1a** increases significantly as the conjugation length increases to **D2a**, despite the similarity in λ_{max} and oscillator strength. Here again, a larger μ_{12} value for **D2a** than for **D1a** is required to explain this result [Eq. (1)].

The $\beta(0)$ values of **C2a,c** and **C3a,c** increase as the donor is changed from NEt_2 to NPh_2 (Table 3). Similarly, those of **D1a-c** increase with the donor in the order: $\text{NEt}_2 < \text{N(i-amy)Ph} < \text{NPh}_2$. Because λ_{max} decreases and the oscillator strengths remain nearly the same, this result could be explained if μ_{12} increases in the same order [Eq. (1)]. On the other hand, the gradual decrease in the $\beta(0)$ for **D2a-c** by a weaker donor is consistent with the shorter λ_{max} .

Theoretical Study

The first hyperpolarizabilities of **A1a–D2c** have been calculated by the finite-field method with the HF/6-31G Hamiltonian (see the Experimental Section for details).^[8] The results are included in Tables 2 and 3 along with the bond-length alternation (BLA), which is defined as the difference between the C=C or C≡C bond length of the conjugation bridge and the average length of the two C–C bonds connected to it. In this section, the BLA values of the conjugation bridge nearest to the cyanophenyl group are used in the discussion.

For dipolar molecules, the calculated values show the general trend of increasing β with respect to the conjugation length, which is in excellent agreement with the experiment, although the calculated values are much smaller. Octupolar molecules show similar results, except that the β values of **C1–C3** are significantly smaller than **D1–D2**. This may be because the former values are underestimated by their distorted structures in the gas phase (see above). Moreover, there are qualitatively linear relationships between β and BLA for both series of compounds (**C1–C3** and **D1–D2**). As BLA increases, the charge-transfer character of the excited electronic state would increase, and consequently, β becomes large.^[6]

For **C1a**, **C2a**, **C3a**, **D1a**, and **D2a**, the β values have also been calculated by the sum-over-states (SOS) method (β_{SOS}).^[13] The β_{SOS} can be expressed by using Equation (2):

$$\beta = \sum_n \sum_s \frac{1}{2\hbar(\omega_n - \omega_1)(\omega_{sg} - \omega_1 - \omega_2)} \frac{M_{gn}^i M_{ns}^j M_{sg}^k}{\omega_n - \omega_1} \quad (2)$$

where g refers to the ground state and n and s are various excited states with $\omega_{ng} = \omega_n - \omega_g$. M_{gn} is the transition dipole matrix element between $|g\rangle$ and $|n\rangle$, and M_{ns} denotes the transition (if $n \neq s$) or the permanent dipole moment (if $n = s$) of the excited state. This equation is essentially the same as Equation (1), except that more excited states are included.

Table 3 shows that there is parallel increase in β_{SOS} and BLA for both series of octupoles (**C1–C3** and **D1–D2**). Hence, the gradual increase in the calculated β_{SOS} with the octupolar structure variation can be attributed to a smaller CT energy, a larger transition dipole matrix element between the ground and excited states, and a larger transition or permanent dipole moment of the excited state [Eq. (2)]. Moreover, β_{SOS} is almost linearly proportional to the experimental value $\beta(0)$ (Table 3). In contrast, there is no relationship between BLA and λ_{max} , probably because the calculation has been conducted in the gas phase, and spectral data are obtained in tetrahydrofuran (THF) solution. Nevertheless, because the λ_{max} values and the oscillator strengths of the octupoles are scattered, the gradual increase in $\beta(0)$ with the conjugation length can, at least in part, be attributed to the transition or permanent dipole moment of the excited state.

Origin of the Larger $\beta(0)$ Values for the Octupoles than for the Dipoles

Comparison of the $\beta(0)$ values reveals that octupoles show much larger first hyperpolarizabilities than dipoles. According to tensor addition calculations, the $\beta_{\text{xyy}} = -\beta_{\text{yyy}}$ value of a D_3 symmetric molecule is 3/4 of the β_{zzz} value of its dipolar analogue if subchromophore interactions are negligible.^[2b] In case of triarylamine derivatives, the $\beta_{\text{zzz}}(\text{dipole})/\beta_{\text{yyy}}(\text{octupole})$ ratios of 0.94–1.0 have been reported.^[3c,f] For comparison, the corresponding ratios for **C1a**, **C2a**, **C3a**, and **D2a** calculated by using the relationships $\langle \beta^2 \rangle = (6/35)\beta_{\text{zzz}}^2$ and $\langle \beta^2 \rangle = (8/21)\beta_{\text{yyy}}^2$ for 1D and D_3 chromophores are 3.5, 2.8, 1.6, and 2.8, respectively.^[12]

As seen in Tables 2 and 3, λ_{max} is red-shifted by 83 nm (4336 cm^{-1}) and the oscillator strength increases by a factor of 2.7 from **A1a** to **C1a**. Although it is not possible to compare the values of μ_{12} of **C1a** and of μ_{2-1} of **A1a** with existing data, the large ratio of $\beta_{\text{yyy}}/\beta_{\text{zzz}} = 3.5$ calculated for **C1a** can be attributed to the smaller CT energy and the larger transition moment between the ground and excited states [Eq. (1)]. Similar changes in λ_{max} [$\Delta\lambda_{\text{max}} = 104\text{ nm}$ (5655 cm^{-1})] and the oscillator strength (2.7-fold) are observed from **B1a** to **D1a**, which therefore leads to a similar ratio of 3.9. As stated above, the large bathochromic shifts in the λ_{max} of the octupoles in comparison to the dipoles has been ascribed to the efficient π -or-

bit overlap between the three dipolar units sharing the central phenyl group. Because the transition moment is expected to increase with ICT, the origin of large β_{yyy}/β_{zzz} ratios can be attributed to the efficient π -orbital overlap. Consistently, the calculated BLA and β are larger for the octupoles than for the dipoles, probably for the same reason (Tables 2 and 3). In addition, the ratio decreases in the order: **C1a** > **C2a** > **C3a**, indicating that this effect becomes less important as the conjugation length increases. Interestingly, the β_{yyy}/β_{zzz} ratios calculated by the finite field method show a similar trend, although the absolute magnitudes are much smaller.

Conclusions

We have studied linear and nonlinear optical properties of a variety of newly synthesized dipolar and octupolar molecules. The $\beta(0)$ values of dipoles increase with conjugation length and as the conjugation bridge is changed from $C\equiv C$ to $C=C$ bond. The $\beta(0)$ values of the octupoles also increase with the conjugation length, but are relatively insensitive to the nature of the conjugation bridge. Except for **D2a–c**, $\beta(0)$ increases as the donor is changed in the order: $NEt_2 < N(i\text{-amyl})Ph < NPh_2$. Moreover, β values calculated by the finite-field and SOS methods show similar trends with the experimental data. Furthermore, β_{yyy}/β_{zzz} ratios are in the range: 1.6–3.9 and decreases with the conjugation length. The origin of the larger β values for octupoles than for dipoles has been attributed to the efficient π -orbital overlap between the three dipolar units sharing the central phenyl group. Furthermore, this result suggests an interesting possibility that β values of octupoles can be significantly enhanced in comparison to dipoles, if they are designed to have maximum π -orbital delocalization to enhance the ICT. Secondly, the shorter the conjugation length, the larger the value of β_{yyy}/β_{zzz} . Thirdly, the use of an *N*-Ph substituent in the donor should be a plus.

Experimental Section

Measurement of the First Hyperpolarizability by Hyper-Rayleigh Scattering Method: The β values were measured at 1064 nm by hyper-Rayleigh Scattering (HRS) method using an Nd:YAG laser (Continuum Powerlite II 8000, 10 Hz, 9.3-ns pulse width).^[49,9,10] Solutions of increasing concentrations ($c = 5 \times 10^{14}$ – 2×10^{17} molecules mL⁻¹) of **A–D** in THF were cleaned through 0.2- μ m Millipore filters to remove microscopic particles. The emitted photons from the sample cuvette were collected at the right angle and collimated to the monochromator by two lenses, while changing the wavelength in 0.1-nm increments to obtain the HRS and two-photon fluorescence spectra. As shown in Figure 4, all of the chromophores emitted a sharp HRS signal at 532 nm along with the broad two-photon fluorescence (TPF) when excited by 1064-nm laser photons. To determine the β values accurately, the total HRS and TPF intensity was measured by averaging 200 laser pulses in the range: 528–536 nm.

The fluorescence intensity was subtracted from the total signal intensity to obtain the pure HRS signal (Figure 4, inset).^[10a] The octupoles also have absorption bands at 532 nm (Figures 1, 2, S1, and S2). The HRS intensity was further corrected for self-absorption by using Equation (3):^[10b]

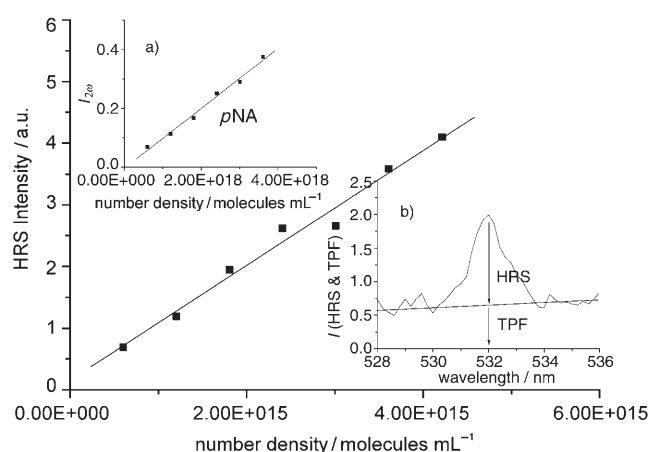


Figure 4. Plot of I_{2w} versus number density for **D2b** in THF at 1064 nm. The solid lines (—) represent the linear squares fit through the experimental data. Inset: a) The same plot for *p*-nitroaniline; b) HRS and TPF spectrum of **D2b** ($c = 1.2 \times 10^{15}$ molecules mL⁻¹) obtained by averaging 200 laser pulses in the range: 528–536 nm. The HRS intensity was obtained by subtracting the TPF intensity from the total signal intensity.

$$I_{2w}(\text{obs}) = I_{2w}(\text{true})e^{-\sigma I N} \quad (3)$$

where $I_{2w}(\text{obs})$ and $I_{2w}(\text{true})$ are the intensity of the second-harmonic light detected after absorption and that actually generated, respectively, $\sigma = 1000\varepsilon \ln(10)/N_A$, where N_A is Avogadro's number and ε is the molar absorptivity expressed in units of $M^{-1} \text{cm}^{-1}$, I is the path length of the scattering cell, and N is the number density of the chromophore.^[10b] The corrected HRS intensities were plotted against the number density (N_c) of chromophores in Figure 4. The β values of the chromophores were calculated using *p*-nitroaniline ($\beta_{st} = 21.4 \times 10^{-30}$ esu) as the external reference.^[10c] According to the external-reference method, β can be calculated by using Equation (4):

$$\beta_c = \beta_{st} \sqrt{m_c/m_{st}} \quad (4)$$

where β_c and β_{st} are the chromophore and standard effective molecular hyperpolarizabilities, respectively, and m_c and m_{st} are the slopes of the plots in Figure 4 for the chromophores and the standard, respectively. The estimated uncertainty for this measurement is $\pm 15\%$.

Theoretical Calculations: All calculations, for geometry optimization and configuration interaction, were performed using the Gaussian 98 software package.^[8] We performed the geometry optimizations for dipolar compounds (**A**, **B**) and their octupolar analogues (**C**, **D**) with ab initio molecular orbital theory at the RHF/6-31G level using the Gaussian 98 program.^[8] Vibrational frequency calculations were executed to verify the identity of each stationary point as a minimum at the same level. The first hyperpolarizabilities of **A1a–D2c** have been calculated by the finite-field method with the HF/6-31G Hamiltonian.^[8] To make direct comparisons of the HF/6-31G-calculated β ($\sqrt{\langle \beta_{HRS}^2 \rangle}$) with the experimental values, the following depolarization ratios were applied.^[10] For dipolar compounds, the orientationally averaged quantity, $\sqrt{\langle \beta_{HRS}^2 \rangle} = \sqrt{\langle \beta_{zzz}^2 \rangle} = \sqrt{6\beta_{zzz}^2/35}$, where β_{zzz} is the [zzz] tensor element with the molecular *z* axis being one of the rotation axes, was obtained. For octupolar compounds, $\sqrt{\langle \beta_{HRS}^2 \rangle} = \sqrt{\langle \beta_{yyy}^2 \rangle} = \sqrt{8\beta_{yyy}^2/21}$ was obtained for comparison where β_{yyy} is the [yyy] tensor element with the molecular *y* axis representing the largest hyperpolarizability.

The SOS calculation was performed by using configuration interaction (CI) with single excited configurations (SCI) only. This level of theory has been generally accepted to be adequate for computing first hyperpolarizability. The summations over excited states used in the SOS expressions generated from CI calculations are in general infinite. In practice, one usually truncates these sums after apparent convergence has been reached. It is generally accepted that the first hyperpolarizability β converges rapidly with the number of lower excited states.^[14] In this SOS calculation, the lowest CI energy states were included.

Supporting Information for this article is available. This information includes synthesis of dipolar and octupolar molecules, representative torsion angles in the optimized (6-31G) structures of **B1a–B3a** and **D1a–D2c**, molar absorptivity spectra for **C2c**, **C3c**, **D1b**, **D2b**, and **D2c**, and normalized absorption spectra for **D1a**, *p*-diethylaminophenylacetylene (**1**), **D2a**, and 4-(*p*-diethylaminophenylethynyl)-phenylacetylene (**2**).

Acknowledgments

This work is supported by KOSEF (project number: 2004-02141) and CRM-KOSEF. J.R.P., H.M.K., and S.L. were supported by the BK21 program. We thank KISTI supercomputing center for the computer time.

Keywords: dipoles • donor–acceptor systems • hyperpolarizability • octupoles • structure–property relationships

- [1] a) P. N. Prasad, D. J. William, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, **1991**; b) J. Zyss, *Molecular Nonlinear Optics: Materials, Physics and Devices*; Academic Press, Boston, **1994**; c) G. A. Lindsay, K. D. Singer, *Polymers for Second-Order Nonlinear Optics*, ACS Symposium Series 601, American Chemical Society: Washington, DC, **1994**; d) L. R. Dalton, W. H. Steier, B. H. Robinson, C. Zhang, A. Ren, S. Garner, A. Chen, T. Londergan, L. Irwin, B. Carlson, L. Fifield, G. Phelan, C. Kincaid, J. Amend, A. Jen, *J. Mater. Chem.* **1999**, *9*, 1905; e) H. T. Uyeda, Y. Zhao, K. Wostyn, I. Asselberghs, K. Clays, A. Persoon, M. J. Therien, *J. Am. Chem. Soc.* **2002**, *124*, 13 806; f) B. J. Coe, L. A. Jones, J. A. Harris, B. S. Brunshawig, I. Asselberghs, K. Clays, A. Persoon, *J. Am. Chem. Soc.* **2003**, *125*, 862.
- [2] a) M. Joffre, D. Yaron, R. J. Silbey, J. Zyss, *J. Chem. Phys.* **1992**, *97*, 5607; b) J. Zyss, I. Ledoux, *Chem. Rev.* **1994**, *94*, 77; c) C. J. Dhnauld, I. Ledoux, I. D. W. Samuel, J. Zyss, M. Bourgault, H. Le Bozec, *Nature* **1995**, *374*, 339; d) S. Brasselet, Zyss, *J. Opt. Soc. Am. B* **1998**, *15*, 257; e) B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux, J. Zyss, *J. Am. Chem. Soc.* **1998**, *120*, 12 808; f) J. Zyss, I. Ledoux, S. Volkov, V. Chernyak, S. Mukamel, G. P. Bartholomew, G. Baza, *J. Am. Chem. Soc.* **2000**, *122*, 11 956; g) J. Brunel, I. Ledoux, J. Zyss, M. Blanchard-Dsce, *Chem. Commun.* **2001**, 923; h) K. Sénéchal, O. Maury, H. L. Bozec, I. Ledoux, J. Zyss, *J. Am. Chem. Soc.* **2002**, *124*, 4560.
- [3] a) R. Wortman, C. Glania, P. Krämer, R. Mastchiner, J. J. Wolff, S. Kraft, B. Treptow, E. Barbu, D. Längle, G. Görlitz, *Chem. Eur. J.* **1997**, *3*, 1756; b) C. Lambert, G. Nöll, E. Schämzlín, K. Meerholz, C. Bräuchle, *Chem. Eur. J.* **1998**, *4*, 512; c) C. Lambert, W. Gaschler, E. Schämzlín, K. Meerholz, C. Bräuchle, *J. Chem. Soc. Perkin Trans. 2* **1999**, 577; d) J. J. Wolff, R. Wortman, *Adv. Phys. Org. Chem.* **1999**, *32*, 121; e) J. J. Wolff, F. Siegler, R. Mastchiner, R. Wortman, *Angew. Chem.* **2000**, *112*, 1494; *Angew. Chem. Int. Ed.* **2000**, *39*, 1436; f) C. Lambert, W. Gaschler, G. Nöll, M. Weber, E. Schämzlín, C. Bräuchle, K. Meerholz, *J. Chem. Soc. Perkin Trans. 2* **2001**, 964.
- [4] a) B. R. Cho, S. J. Lee, S. H. Lee, K. H. Son, Y. H. Kim, J.-Y. Doo, G. J. Lee, T. I. Kang, Y. K. Lee, M. Cho, S.-J. Jeon. *Chem. Mater.* **2001**, *13*, 1438; b) B. R. Cho, S. B. Park, S. J. Lee, K. H. Son, S. H. Lee, M.-J. Lee, J. Yoo, Y. K. Lee, G. J. Lee, T. I. Kang, M. Cho, S.-J. Jeon, *J. Am. Chem. Soc.* **2001**, *123*, 6421; c) B. R. Cho, M. J. Piao, K. H. Son, S. H. Lee, S. J. Yoon, S.-J. Jeon, M. Cho, *Chem. Eur. J.* **2002**, *8*, 3907; d) B. R. Cho, K. Chajara, H. J. Oh, K. H. Son, S.-J. Jeon, *Org. Lett.* **2002**, *4*, 1703; e) B. R. Cho, Y. H. Kim, K. H. Son, Y. H. Kim, S.-J. Jeon, *Bull. Korean Chem. Soc.* **2002**, *23*, 1253; f) M. J. Lee, M. Piao, S. H. Lee, M.-Y. Jeong, K. M. Kang, S.-J. Jeon, *J. Mater. Chem.* **2003**, *13*, 1030; g) H. C. Jeong, M. J. Piao, S. H. Lee, M.-Y. Jeong, K. M. Kang, G. Park, S.-J. Jeon, B. R. Cho, *Adv. Funct. Mater.* **2004**, *14*, 64; h) G. Park, B. R. Cho, *J. Phys. Org. Chem.* **2004**, *17*, 169; i) G. Park, B. R. Cho, *J. Phys. Org. Chem.* **2005**, *18*, 264.
- [5] a) V. R. Thalladi, S. Brasselet, H.-C. Weiss, D. Bläser, A. K. Katz, H. L. Carrell, R. Boese, J. Zyss, A. Nangia, G. R. Desiraju, *J. Am. Chem. Soc.* **1998**, *120*, 2563; b) V. Le Floch, S. Brasselet, J.-F. Roch, J. Zyss, B. T. Cho, S. H. Lee, S.-J. Jeon, M. Cho, K. S. Min, M. P. Suh, *Adv. Mater.* **2005**, *17*, 196.
- [6] a) Y.-K. Lee, S.-J. Jeon, M. Cho, *J. Am. Chem. Soc.* **1998**, *120*, 10921; b) W.-H. Lee, H. Lee, J.-A. Kim, J.-H. Choi, M. Cho, S.-J. Jeon, B. R. Cho, *J. Am. Chem. Soc.* **2001**, *123*, 10658.
- [7] C. Lahiri, J. L. Thompson, J. S. Moore, *J. Am. Chem. Soc.* **2000**, *122*, 11 315.
- [8] M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chem, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. P. Stewart, M. HeadGordon, C. Gonzalez, J. A. Pople, *Gaussian 98*, Gaussian Inc., Pittsburgh, **1998**.
- [9] E. Hendricks, K. Clay, A. Persoons, *Acc. Chem. Res.* **1998**, *31*, 675.
- [10] a) N. W. Song, T.-I. Kang, S. C. Jeong, S.-J. Jeon, B. R. Cho, D. Kim, *Chem. Phys. Lett.* **1996**, *261*, 307; b) O. K. Song, J. N. Woodford, C. H. Wang, *J. Phys. Chem. A* **1997**, *101*, 3222; c) J. N. Woodford, A. A. Pauley, C. H. Wang, *J. Phys. Chem. A* **1997**, *101*, 1998.
- [11] J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664.
- [12] a) S. J. Cyvin, J. E. Rauch, J. C. Decious, *J. Chem. Phys.* **1965**, *43*, 4083; b) R. Bersohn, Y.-H. Pao, H. L. Frisch, *J. Chem. Phys.* **1966**, *45*, 3184.
- [13] a) J. Ward, *Rev. Mod. Phys.* **1965**, *37*, 1; b) J. Ward, G. H. C. New, *Phys. Rev.* **1969**, *185*, 57.
- [14] D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195.

Received: May 18, 2005

Published online on December 2, 2005