J. Am. Chem. Soc. **2001,** *123,* 6421−6422

1,3,5-Tricyano-2,4,6-tris(vinyl)benzene Derivatives with Large Second-Order Nonlinear Optical Properties

Bong Rae Cho,* Soon Bong Park, Seung Jae Lee,
Kyung Hwa Son, Sang Hae Lee, Myung-Ja Lee, Jun Yoo,
Yun Kyong Lee, Geon Joon Lee, Tae Im Kang,
Minhaeng Cho, and Seung-Joon Jeon*

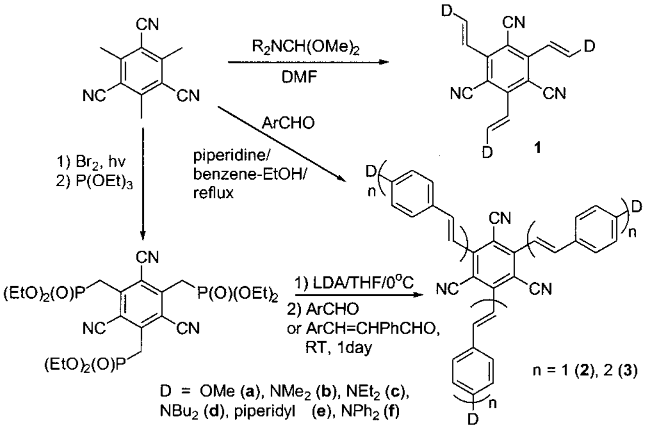
Molecular Opto-Electronics Laboratory
Department of Chemistry and Center for
Electro- and Photo-Responsive Molecules
Korea University, 1-Anamdong, Seoul 136-701, Korea

Received July 13, 2000
Revised Manuscript Received January 2, 2001

Application of the nonlinear optical materials to the optical and optoelectronic devices requires large second-order nonlinear optical property and thermal stability.[1,2] Much effort has been focused to optimize the physical properties of the donor−acceptor dipoles in order to meet these criteria. While there has been a great progress in improving these properties, it has become apparent that the dipolar molecules have certain limitations. One such problem is the difficulty associated with aligning the dipoles noncentrosymmetrically in the solid sate to achieve maximum bulk effect [$\chi^{(2)}$]. Because the dipoles favor antiparallel pairing in the solid state to nullify bulk nonlinearity, various approaches including crystallization, poled polymer, Langmuir−Blodgett film, and self-assembly technique have been employed to overcome the attractive forces between the dipoles.[3] Recently, Dalton and Steier reported that dipole-based polymers can be fabricated to an electrooptic modulator with huge bandwidth acceptance and low modulation voltage, which is the major breakthrough in this area.[1]

An alternative approach to overcoming this difficulty would be to use the octupolar compounds with three-fold symmetry.[4] These compounds are of particular interest not only because they exhibit moderate to very large β, but because they are less prone to relaxation due to the lack of the ground-state dipole moment, once they are assembled to exhibit large bulk nonlinearity. The challenge is the macroscopic organization of the two-dimensional octupoles in noncentrosymmetric assemblies. Because the electric poling method is not applicable to these octupolar molecules with zero permanent dipole moment, optical poling has been explored to tackle this problem.[5] A straightforward solution to this problem would be the spontaneous arrangement of the NLO chromophores in the solid state. Planar octupoles with three-fold symmetry appear particularly attractive for this purpose. We recently suggested that, by using a simple three-state model, the first hyperpolarizability of the octupolar molecules increases as the extent of charge transfer from the peripheral donor to central acceptor is increased.[6,7] This prediction was confirmed by carrying out both semiempirical and ab initio quantum chemistry calculations of crystal violet derivatives and other types of octupolar molecules. These observations provide a firm basis for the design and synthesis of the planar octupoles with large β values. Here we show that octupolar compounds containing three donor−acceptor dipoles within a molecule not only show large first hyperpolarizability and high thermal stability, but also exhibit significant second harmonic generation (SHG) in the powder state.

Scheme 1



The synthesis of the octupolar compounds is shown in Scheme 1. Compounds **1b**, **1c**, **1**, **2a**, **2c**, and **2e** were prepared by refluxing tricyanomesitylene with *N*-formylamine dimethylacetal or substituted benzaldehyde. Compounds **2f** and **3d**−**f** were synthesized in 61−86% yields by the Wittig reaction of 1,3,5-tricyano-2,4,6-tris[(diethoxyphosphoryl)methyl]benzene with *p*-diphenylaminobenzaldehyde or 4-(*p*-dialkylaminostyryl)benzaldehyde.

The β values of the octupoles were measured at 1560 nm by Hyper-Rayleigh Scattering (HRS) method.[8] To avoid complications due to the multiphoton excitation, the excitation wavelength was shifted to 1560 nm with the OPO laser (Continuum Surelite OPO, 5 ns pulses), which was pumped by 355 nm third harmonic of the Nd:YAG laser (Continuum SL-II-10, Q-switched,10 Hz).[9] The possibility of the multiphoton fluorescence was examined by irradiating the solutions of **2a**, **2f**, **3d**, and **3e** whose $\lambda_{\text{cut-off}}$ values are larger than others, at 1560 nm under the same condition. For all compounds, the spectra showed one sharp HRS signal at 780 nm without fluorescence background (Figures S1-4 in the Supporting Information). This result strongly negates such possibility. Furthermore, the observed signal showed strictly quadratic dependence on laser intensity, demonstrating that it is the HRS signal that we are observing (Figure S5 in the Supporting Information). It is well established that the dominant β tensor component of the dipolar compounds is β_{zzz}.[3] For the octupolar compounds, the nonzero tensor elements are β_{yyy}, β_{yxx}, β_{xyx}, and β_{xxy}.[4,6] Here, the molecular *y*-axis is assumed to be one of the three C$_2$-axis. We have measured the sum of orientationally averaged hyperpolarizabilities, $\langle\beta^2{}_{ZZZ}\rangle$ and $\langle\beta^2{}_{XZZ}\rangle$, by using the HRS method, where the incident beam travels in the X-direction and the scattered light is measured in the Y-direction. More specifically, $\langle\beta^2{}_{ZZZ}\rangle = (24/105)\beta^2{}_{yyy}$ and $\langle\beta^2{}_{XZZ}\rangle = (16/105)\beta^2{}_{yyy}$.[8] The HRS signal of the CHCl$_3$ solution of the compounds was collected and the β was calculated by using the internal reference method.[8] In this method the solvent is the reference and the β value of CHCl$_3$ is -0.49×10^{-30} esu.[10]

The results of UV−vis absorption and second-order nonlinear optical measurements are summarized in Table 1. For all

---

(1) (a) Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science*, **2000**, *288*, 119. (b) Dalton, L. R.; Steier, W. H.; Robinson, B. H.; Zhang, C.; Ren, A.; Garner, S.; Chen, A.; Londergan, T.; Irwin, L.; Carlson, B.; Fifield, L.; Phelan, G.; Kincaid, C.; Amend, J.; Jen, A. *J. Mater. Chem.* **1999**, *9*, 1905.

(2) Zyss, J.; Ledoux, I. *Chem. Rev.* **94**, 77−105 1994.

(3) (a) Marder, S. R.; Perry, J. W. *Science*, **1994**, *263*, 1706. (b) Saadeh, H.; Wang, L.; Yu, L. *J. Am. Chem. Soc.* **2000**, *122*, 546.

(4) (a) Zyss, J. *Nonlinear Opt.* **1991**, *1*, 3. (b) Joffre, M.; Yaron, D.; Silbey, R. J.; Zyss, J. *J. Chem. Phys.* **1992**, *97*, 5607. (c) Zyss, J. *J. Chem. Phys.* **1993**, *98*, 6583. (d) Blanchard-Desce, M.; Baudin, J.-B.; Jullien, L.; Lorne, R.; Ruel, O.; Brasselet, S.; Zyss, J. *Opt. Mater.* **1999**, *12*, 333. (f) Thalladi, V. R.; Brasselet, S.; Weiss, H.-C.; Bläser, D.; Katz, A. K.; Carrell, H. L.; Boese, R.; Zyss, J.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 2563.

(5) Brasselet, S.; Zyss, J. *Opt. Lett.* **1997**, *22*, 1464.

(6) Lee, Y.-K.; Jeon, S.-J.; Cho, M. *J. Am. Chem. Soc.* **1998**, *121*, 10921.

(7) Lee, H.; An, S.-Y.; Cho, M. *J. Phys. Chem. B* **1999**, *103*, 4992.

(8) Hendrickx, E.; Clay, K.; Persoons, A. *Acc. Chem. Res.* **1998**, *31*, 675.

(9) Stadler, S.; Dietrich, R.; Bourhill, G.; Brauchle, Ch. *Opt. Lett.* **1996**, *21*, 251.

10.1021/ja0025595 CCC: $20.00

Table 1. Selected Optical Data and Thermal Stability for the Octupolar Compounds

entry	D	compd	λ_{max} (nm, ϵ)	$\lambda_{cut-off}$ (nm)	β (10^{-30} esu)	$\beta(0)$[a] (10^{-30} esu)	T_d^i/°C[b]
1	NMe_2	**1b**	389 (105,100)	455	35	25	340
2	piperidyl	**1e**	396 (113,000)	474	25	17	319
3	OMe	**2a**	388 (41,800)	478	20	14	385
4	NEt_2	**2c**	493 (82,200)	560	121	65	390
5	piperidyl	**2e**	468 (74,900)	565	118	69	418
6	NPh_2	**2f**	488 (101,700)	568	223	124	422
7	NBu_2	**3d**	499 (82,200)	633	219	116	340
8	piperidyl	**3e**	461 (47,400)	576	178	108	402
9	NPh_2	**3f**	468 (80,300)	558	184	107	404

[a] Corrected at $\lambda \rightarrow \infty$ using a three-level model.[4b] [b] Determined by thermal gravimetric analysis (TGA).

compounds the $\lambda_{cut-off}$, the wavelength at which the transmittance is 95%, is shorter than 650 nm. The λ_{max} increases when the conjugation length is increased from **1** to **2**, but remains nearly constant by a further increase in the conjugation (entries 2, 5, and 8). On the other hand, $\beta(0)$ increases gradually as the donor strength (entries 3−5) and the conjugation length are increased (entries 2, 5, and 8). The change of β with the octupolar structural variation is consistent with our theoretical prediction.[6,7] Moreover, the steeper increase in β than λ_{max} indicates an improved transparency-nonlinearity tradeoff for the octupoles compared with the dipoles, in which both β and λ_{max} increase monotonically with the conjugation length.[11,12] We have also measured the β values for dipolar 4-cyanostilbene derivatives, in which MeO, Et_2N, and piperidine are substituted at the 4′-position under the same condition. The values of $\beta(0)$ are 4, 10, and 11 $\times$ 10^{-30} esu, respectively. The $\beta(0)$ values of the octupoles are 3−6-fold larger than those of the corresponding dipoles, indicating that the former has larger $\beta(0)$ per molecular weight. Recently, a very large $\beta(0)$ was reported for the acetylene analogue of **2c**.[13] The result is somewhat surprising because the donor−acceptor dipoles with acetylenic bridging units usually yield smaller NLO responses than the corresponding ethylenic structures.[14] Finally, these octupoles show very high thermal stability as indicated by their initial decomposition temperatures (T_d^i) ranging from 319 to 422 °C.[15]

The $\chi^{(2)}$ values of the powdered samples of the octupoles were measured by the second harmonic with evanescent wave (SHEW) method.[16] Among the compounds we synthesized, the SHG efficiencies of **1b**, **2c**, **2f**, and **3f** were determined because they showed good crystallinity required for the measurement. The powder samples were packed into a sample holder and pushed in contact with the hemi cylindrical prism of SF59 glass (n_{780}=1.8955, n_{1560}=1.9253). The sample holder was rotated to scan the incidence angle and the detection part was rotated independently with coincidence of a rotational center. The incident-angle-dependent second harmonic was detected at the same excitation wavelength used in the HRS measurement. The reliability of this method was confirmed by measuring the d coefficients of the powder sample of *m*-nitroaniline (mNA). Because of the uncertainty in the refractive index measurement, the figure of merit (M)[17] which is proportional to the second harmonic generation efficiency was estimated.

The powder sample of **1b** showed no SHG. On the other hand, the M/M_{mNA} values for the powder samples of **2c**, **2f**, and **3f** are found to be 3.4, 0.36, 2.1, respectively. The value of M/M_{mNA} for **2c** indicates that the SHG value of this compound is approximately 45-fold larger than that of urea.[18] Although the origin of the significant bulk nonlinearity observed for these compounds is currently under investigation, it is believed that they form noncentrosymmetric crystals spontaneously during precipitation.

In conclusion, we have synthesized a series of octupolar NLO molecules **1**−**3**. They show large first hyperpolarizability, high thermal stability, and significant SHG in the powder state. The spontaneous arrangement of the octupolar NLO molecules in the solid sate to produce bulk nonlinearity may ultimately lead to electrooptic devices without electric poling.

Acknowledgment. This work is supported by a National Research Laboratory Grant by Korea Ministry of Science and Technology and CRM-KOSEF. S.H.L., M.-J.L., and Y.K.L. were supported by BK21 scholarship.

Supporting Information Available: General experimental procedures and ^1H and ^{13}C NMR and elemental analyses of all new compounds, contribution of multiphoton fluorescence to the HRS signal, and the quadratic dependence of the HRS signal on laser intensity (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

JA0025595

---

(10) Kazjar, F.; Ledoux, I.; Zyss, J. *Phys. Rev. A.* **1987**, *36*, 2210.

(11) Blanchard-Desce, M.; Alain, V.; Bedworth, P. V.; Marder, S. R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, S.; Wortmann, R. *Chem. Eur. J.* **1997**, *3*, 1091.

(12) Andraud, C.; Zabulon, T.; Collet, A.; Zyss, J. *Chem. Phys.* **1999**, *245*, 243.

(13) Wolff, J. J.; Siegler, F.; Matschiner, R.; Wortman, R. *Angew. Chem., Int. Ed.* 2000, *39*, 1436.

(14) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.

(15) One of the reviewers pointed out that the photochemical stability of the NLO molecules is also important. Although we did not measure the photochemical stabilities of compounds **1**−**3** quantitatively, they were stable in the solid- and solution states for at least one year under room light. In addition, both the HRS and SHG data were reproducible when the same experiments were repeated with the same sample for several times.

(16) Kiguchi, M.; Kato, M.; Kumegawa, N.; Taniguchi, Y. *J. Appl. Phys.* **1994**, *75*, 4332.

(17) The figure of merit is defined by $M = d^2/n_{2\omega}(n_\omega)^2$, where n_ω and $n_{2\omega}$ are the refractive index at frequency ω and 2ω, respectively.

(18) Dmitriev, V. G. Gurzadyan, G. G. Nikogosyan, D. N. *Handbook of Nonlinear Optical Crystals*; Springer-Verlag: Berlin, 1991; pp 120−121.