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Octupolar Crystals for Nonlinear Optics: 1,3,5-Trinitro-2,4,6-tris(styryl)benzene Derivatives

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There has been extensive research into developing organic nonlinear optical materials for high-performance electro-optic devices.[1,2] The most thoroughly studied nonlinear optical (NLO) chromophores are the donor−acceptor substituted conjugated polyenes. One of the most important drawbacks of the dipolar compound is that they must be aligned parallel to the applied electric field to exhibit second-harmonic generation (SHG, $\chi^{(2)}$). Because the dipoles tend to align antiparallel to each other in the solid state, various approaches including crystallization, poled polymer, Langmuir−Blodgett film, and self-assembly technique have been employed to overcome the dipolar intermolecular interactions.[3] However, all these methods have met with limited success.

A fundamentally different approach for overcoming this difficulty would be to use the octupolar compounds as an alternative NLO molecule.[4] Because they have no permanent dipole moments, the octupolar supramolecules, if synthesized,[5] would be less prone to reorientational relaxation, which is the detrimental factor for the dipolar molecules favoring undesired antiparallel pairing.

Various compounds, such as triaminotrinitrobenzene,[6] 2,3,6,7,10,11-hexastyryl-1,4,5,8,9,12-hexaazatriphenylene,[7] tris(*trans*-4,4′-diethylaminostyryl-2,2′-bipyridine)-ruthenium complexes,[8] 2,4,6-tris[4-(*N*,*N*-diethylamino)-phenyethynyl]-1,3,5-triazine,[9] subphthalocyanine,[10] tris-alkynylruthenium complexes,[11] tris[5-(oligothienyl)]-methyl cations,[12] tricyanovinyl-substituted triphenylamines,[13] and tris-1,3,5-(4-*N*,*N*-diethylaminophenyethynyl)-2,4,6-tricyanobenzene[14] have been shown to exhibit significant β values. We reported that, unlike the donor−acceptor dipoles whose β value increases to a maximum value and then decreases as the bond-length alternation increases,[15] the β values of the octupolar molecules increase gradually as the extent of the charge transfer is increased.[16] This result provides a firm basis for the design and synthesis of planar octupoles with large β values. However, there have been little experimental studies regarding the structure−property relationship of the octupolar molecules.

The most representative dipolar nonlinear optical chromophore is 4-diethylamino-4′-nitrostilbene.[1,2] We now have synthesized 1,3,5-trinitro-2,4,6-tristyrylbenzenes **2** in which three stilbene moieties are incorporated within a single molecule, and their smaller analogues **1** and triple-bond derivatives **3**, as shown in Figure 1. The first hyperpolarizabilities (β), powder SHG efficiencies, and thermal stabilities of these compounds were determined. Comparison of the results with the corresponding dipolar compounds reveals the relative assets and drawbacks of the dipolar and octupolar molecules as the NLO molecules.

The octupolar NLO molecules **1** and **2** were synthesized by the condensation of the 2,4,6-trinitromesitylene

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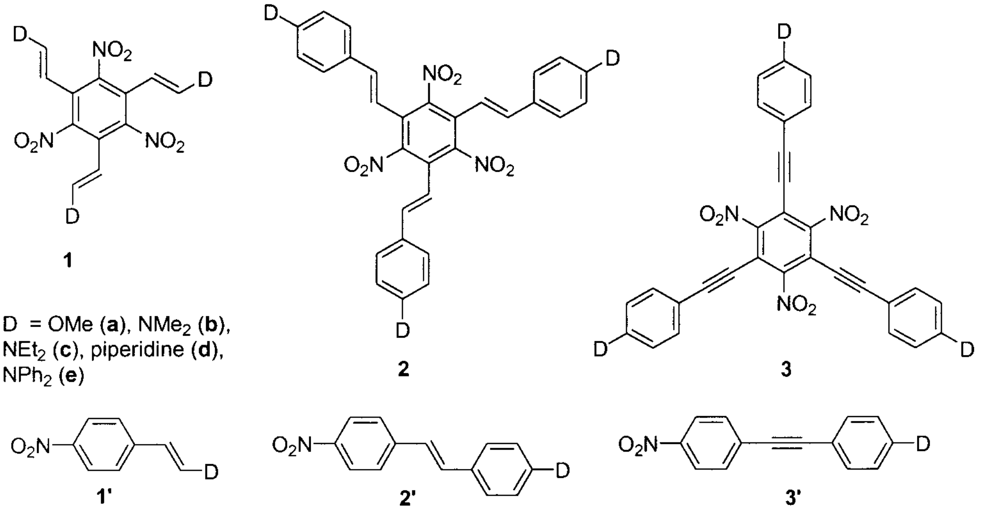

Figure 1. Structures and labeling scheme for the octupoles and the dipoles investigated in this study.

with dimethylacetal of *N*,*N*-dialkyl-*N*-formylamine or substituted benzaldehydes.[17] Compounds **3c** and **3d** were prepared by the reaction between substituted phenylacetylides with 1,3,5-trichloro-2,4,6-trinitrobenzene.

The β values of the octupoles were measured by the Hyper-Rayleigh Scattering (HRS) method at 1360 nm.[18] The powder SHG efficiencies of **2c**, **2d**, **2e**, and **3c**, which showed good crystallinity required for the measurement, were determined by the second harmonic with evanescent wave (SHEW) method.[19] An advantage of this method is that the measured powder SHG efficiency is independent of the average particle size and coherence length because the phase-matched directional SHG is detected through the total reflection geometry. Because of the uncertainty in the refractive index measurement, the figure of merit (M),[20] which is proportional to the square of the second-harmonic generation efficiency, was estimated. The initial decomposition temperatures (T^{i}_{d}), where the first slope change occurs in the TGA thermogram, were determined as reported previously.[7]

The optical and thermal properties of **1-3** are summarized in Table 1. For all compounds, the $\beta(0)$ value increases as the aryl substituent is made more electron donating, reaching at the maximum value with the *para*-piperidyl group as the donor. Similarly, the values of $\beta(0)$ are larger for the octupoles with more extended π-orbital conjugation. The results are consistent with our theoretical model that the β values of the octupolar molecules increase as the extent of the charge-transfer character increases.[16] As commonly observed for the donor−acceptor dipoles, the $\beta(0)$ values are larger for **2** than **3** apparently due to the more efficient charge-transfer ability of the double bond than the triple bond.[1e] To confirm the octupolar symmetry of the molecules in solution, we measured the depolarization ratio $D = \langle\beta_{ZXX}^2\rangle/\langle\beta_{XXX}^2\rangle$, where $\langle\beta_{ZXX}^2\rangle$ and $\langle\beta_{XXX}^2\rangle$ are the components of $\langle\beta^2\rangle$ measured for the detection polarization perpendicular and parallel to the excitation polarization, respectively. A D value of **2c** was found to be 0.58, which is close to the theoretical value of 0.67 calculated for a pure octupolar molecule.[21] Finally, these molecules show high thermal stability as indicated by their T^{i}_{d} ranging from 210 to 310 °C.

Table 1. Optical Properties and Thermal Stability of Octupoles and Corresponding Dipoles

entry	compd	D	$\lambda_{max}{}^{a}$ (ϵ)	$\lambda_{cut\ off}{}^{a}$	$\beta^{b,c}$	$\beta(0)^{b-d}$	T^{i}_{d}/°C^{e}
1	**1b**	NMe$_2$	394 (11,800)	480	40	24	230
2	**1d**	piperidyl	399 (25,000)	488	80	48	210
3	**2a**	OMe	340 (41,600)	430	48	34	265
4	**2c**	NEt$_2$	428 (53,000)	554	116	63	278
5	**2d**	piperidyl	405 (41,700)	515	151	89	256
6	**2e**	NPh$_2$	424 (63,000)	555	141	78	280
7	**3c**	NEt$_2$	406 (79,400)	462	46	27	310
8	**3d**	piperidyl	388 (72,500)	466	72	47	306
9	**1b′**	NMe$_2$	441 (20,000)	503	43	22	
10	**1d′**	piperidyl	442 (11,200)	529	30	16	
11	**2a′**	OMe	378 (25,600)	466	66	42	
12	**2c′**	NEt$_2$	450 (28,200)	548	85	43	
13	**2d′**	piperidyl	424 (25,500)	532	97	53	
14	**3c′**	NEt$_2$	426 (22,100)	536	33	18	
15	**3d′**	piperidyl	402 (20,000)	536	45	27	

[a] nm. [b] 10^{-30} esu. [c] The experimental uncertainty on β is of the order of 10−15%. [d] Corrected at $\lambda \rightarrow \infty$ using a three-level model.[22] [e] Initial decomposition temperature determined by thermal gravimetric analysis (TGA) (see text).

For comparison, we have also measured the optical properties of the dipolar analogues **1′**−**3′** under the same condition (Table 1). To our surprise, the λ_{max} values of **1**−**3** were blue-shifted compared with those of the corresponding dipoles. Although the $\beta(0)$ values of the former are slightly larger, $\beta(0)$ per molecular weight is smaller than the latter. The result may be attributed to the structures of **1-3**. The molecular structures of **1b**, **2c**, and **3c** in chloroform solution were calculated by the ab initio method (HF/6-31G) using the self-consistent reaction field (SCRF) (Figure S1 in the Supporting Information).[23] The same level of calculations was done for their corresponding dipolar molecules (**1b′**, **2c′**, and **3c′**). The NO$_2$ groups of **1b**, **2c**, and **3c** are nearly

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perpendicular to the phenyl rings and the angles between the central ring and the peripheral vinyl or styryl moieties are in the range of 40°−47°, 49°−60°, and 3°−13°, respectively. On the other hand, **1b′**, **2c′**, and **3c′** are nearly planar except that the angle between the two phenyl groups of **2c′** is about 38°. These ab initio calculation results clearly indicate that **1**−**3** are significantly more distorted than the corresponding dipolar compounds. Therefore, the conjugation between the peripheral donors and central acceptors of **1**−**3** is interrupted so that the extent of the charge transfer is diminished, which would in turn decrease both $\lambda_{\max}$ and β. However, in terms of transparency-nonlinearity tradeoff, the octupoles are superior to the corresponding dipoles.

The β values of 1,3,5-trinitro-2,4,6-tris(styryl)benzene derivatives are about 10-fold larger than 1,3,5-tri-(isopropylamino)-2,4,6-trinitrobenezene and comparable to 1,3,5-tris(*p*-diethylaminophenyl)-2,4,6-triazine and subphthalocyanine.[9,10] On the other hand, they are an order of magnitude smaller than that of the most efficient octupolar compound reported in the literature, $\mathrm{Ru}^{\mathrm{II}}$[tris(4,4′-*p*-dibutylaminostyryl-2,2′-bipyridine)] of which β was found to be 740×10^{-50} esu.[8] Nevertheless, the most crucial result of the present report is the fact that the powder samples of **2** and **3** exhibit significant SHG efficiencies. The values of effective M/M_{mNA} are found to be 5.8, 0.63, 0.20, and 0.48, for **2c**, **2d**, **2e**, and **3c**, respectively, indicating that the SHG values are approximately (3−75)-fold larger than that of urea.[24] Although the origin of the significant bulk nonlinearity is currently under investigation, it is apparent that they produce noncentrosymmetric crystals spontaneously during precipitation. Moreover, the lack of correlation between the powder SHG and β for this series of compounds underlines the importance of the molecular orientations in the former. To our knowledge, this is the first example of octupolar NLO materials, which exhibit large SHG in the solid state.

In conclusion, we have synthesized a series of octupolar NLO molecules **1-3**. The β values of these molecules increase gradually as the donor strength and the conjugation length are increased. The result is in contrast to that of push−pull polyenes in which the β values show nonlinear dependence on the donor−acceptor strength.[15] Moreover, these compounds are thermally stable up to 310 °C and exhibit moderate β(0) and significant SHG values in the powder state [$M/M_{\mathrm{mNA}} = 0.2-5.8$]. The spontaneous formation of noncentrosymmetric crystals to produce bulk nonlinearity may ultimately lead to electro-optic devices without electric poling.

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Supporting Information Available: Synthesis of 1,3,5-trinitro-2,4,6-tris(styryl)benzene derivatives, measurement of β by the Hyper-Rayleigh Scattering (HRS) method, measurement of SHG by the evanescent wave (SHEW) method, structure optimization by the ab initio method, and the molecular structures of **1b**, **2c**, and **3c** in chloroform, optimized by ab initio calculations using the self-consistent reaction field (SCRF) method (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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