JOURNAL OF
Materials
CHEMISTRY
Communication

Nonlinear optical properties of dehydrobenzo[18]annulenes: expanded two-dimensional dipolar and octupolar NLO chromophores

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Received 7th August 2001, Accepted 31st August 2001
First published as an Advance Article on the web 25th September 2001

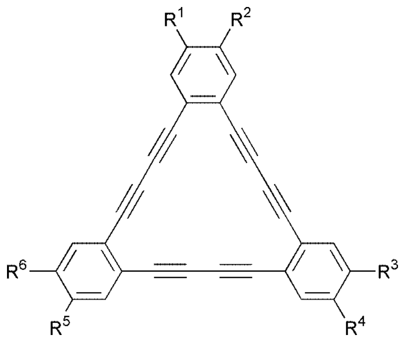
The optical and second-order nonlinear optical response of a series of donor–acceptor substituted dehydrobenzo[18]annulenes is reported. The resultant β values, determined by the HRS method, are comparable or superior to that for DANS.

Interest in organic compounds for second-order and third-order nonlinear optical (NLO) applications has increased steadily during the past two decades.[1–5] The major advantages of these materials over their inorganic counterparts include similar or better off-resonance susceptibilities, fast nonlinear response times, small relative permittivities, and lower costs. However, the most attractive and significant feature of organic NLO materials is the ability to tune the physical properties of such materials to enhance a specific NLO effect merely by manipulation of its chemical structure. This ability also allows researchers to incorporate functional groups which are important for materials processing and device formation. Typical NLO chromophores studied are one-dimensional, conjugated π-systems with donor (D) and acceptor (A) moieties as terminal substituents. The first hyperpolarizability (β) can attain high values for such D–A systems, which is desirable for second-order NLO properties.[6] Optimizing the β values of these dipolar NLO chromophores is subject to a trade-off between efficiency and transparency[6] and is limited by the unidirectional dipole moment. Recently it has been suggested that non-dipolar two-dimensional (octupolar) NLO chromophores can circumvent this problem.[7] These chromophores, especially those with three-fold symmetry, afford a higher β value coupled with enhanced transparency in the visible region as compared to 1-D dipolar structures.[8] Several groups have explored 2-D chromophores and shown that they are very promising NLO candidates.[9] Contrary to 1-D chromophores such as *p*-nitroaniline (pNA), non-dipolar NLO chromophores with multiple D–A substituents generally show several significant tensor elements of β. This allows new NLO processes through efficient coupling of electric fields of different polarization.

Despite the aforementioned attributes, 2-D NLO molecules are relatively rare compared to their 1-D dipolar counterparts. This is because their design and synthesis is non-trivial, involving simultaneous increase of conjugation in two dimensions. We have been investigating a class of 2-D macrocycles, namely dehydrobenzo[18]annulenes (DBAs),[10] for some time and recently became interested in the nonlinear optical properties of these compounds. Similar to the pioneering studies of Diederich *et al.* on donor–acceptor substituted tetraethynylethenes,[9d,11] our annulenic system is uncommon in that we can easily "tune" the substitution pattern of the DBA chromophore for maximum NLO behavior using a straightforward synthetic scheme developed in our laboratory.[12] By virtue of a stepwise route used for DBA construction, we are able to place donor and acceptor substituents in predetermined positions, thus "engineering" the DBA macrocycle to possess a dipole moment dependant upon the different substituents on the phenyl rings. In addition, the macrocycle is locked into a planar conformation[12,13] which increases the overall π conjugation and thus should translate into better NLO efficiency. We report in this paper studies on a new series of expanded dipolar and octupolar 2-D NLO chromophores based on the dehydrobenzo[18]annulene skeleton (DBAs **1–6**, Table 1), compounds which exhibit high hyperpolarizabilities.

Illustrative of the synthetic technique is the assembly of octupolar DBA **5** (Scheme 1). Selective and sequential Sonogashira cross-coupling to diiodobenzene **7**[14] gave the requisite regioisomeric triynes **8** and **9**. These triynes in turn were attached sequentially to a third equivalent of **7** using an *in situ* desilylation/alkynylation reaction protocol,[13a,15] thus generating asymmetrically functionalized α,ω-polyyne **10**.

Table 1 Dehydrobenzo[18]annulenes (DBAs) used in this study



DBA	R^1	R^2	R^3	R^4	R^5	R^6
1	NO_2	H	H	H	H	NBu_2
2	NO_2	NBu_2	H	H	H	H
3	NO_2	H	H	NBu_2	H	H
4	NO_2	NBu_2	H	NBu_2	NO_2	H
5	NO_2	NBu_2	NO_2	NBu_2	NO_2	NBu_2
6	H	H	H	H	H	H

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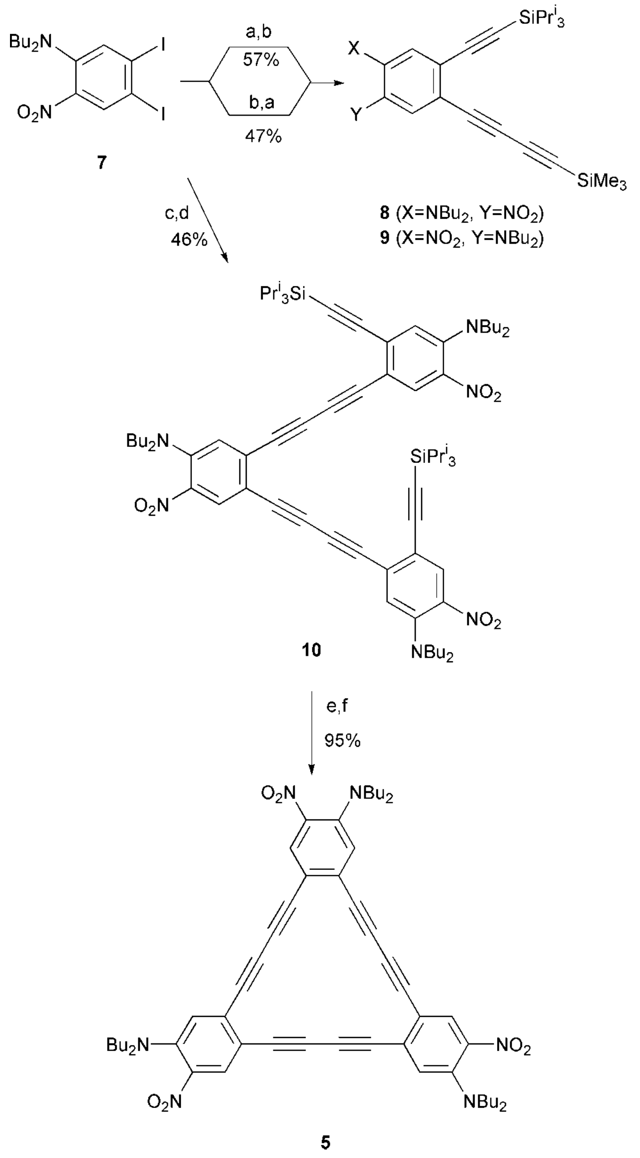
DOI: 10.1039/b107182n



Scheme 1 *Reagents*: a) $Pr^i_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; b) $Me_3SiC{\equiv}CC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; c) **8**, aq. KOH, $PdCl_2(PPh_3)_2$, CuI, Et_3N; d) **9**, aq. KOH, $PdCl_2(PPh_3)_2$, CuI, Et_3N; e) Bu_4NF, EtOH, THF; f) CuCl, $Cu(OAc)_2 \cdot H_2O$, pyridine.

Fluoride-induced protiodesilylation followed by Cu-mediated intramolecular cyclization furnished C_{3h}-symmetric **5** as the sole product in *ca.* 20% overall yield. It is noteworthy that the traditional cyclooligomerization approach, while several steps shorter, gave an *inseparable* 1 : 2 mixture of **5** and its regioisomeric DBA in *ca.* 30% yield.

The first hyperpolarizability (β) of five substituted DBAs (**1–5**)[12] along with the parent hydrocarbon **6**[16] was measured utilizing the hyper Rayleigh scattering (HRS) technique.[17] The HRS method is advantageous for our studies as it permits evaluation of the β value of non-dipolar and octupolar 2-D chromophores in liquid isotropic solutions. The β values of DBA solutions in $CHCl_3$ were determined using the external standard method (ESM),[18] which involved measuring HRS from two series of solutions—one of the DBA and the other of a NLO chromophore with an accurately known β value. For our studies, 4-dimethylamino-4′-nitrostilbene (DANS) was used as the reference sample, which in turn was checked against another standard chromophore, disperse red (DR1).

The intensity of the HRS radiation, $I(2\omega)$, from a binary NLO chromophore–solvent solution is given by

$$I(2\omega) = K(\rho_s\beta_s^{2} + \rho_c\beta_c^{2})I^2(\omega) \qquad (1)$$

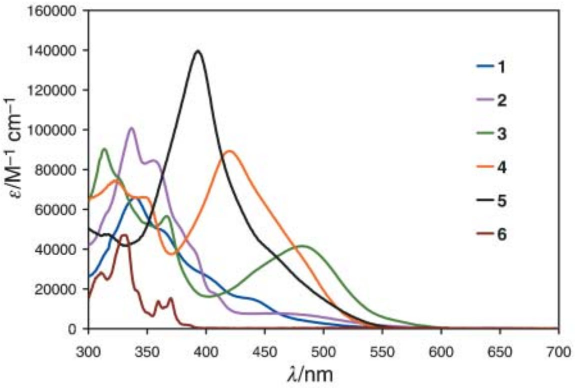


Fig. 1 Electronic absorption spectra of DBAs **1–6**.

where $I(\omega)$ is the intensity of the fundamental light and K is a constant determined by the scattering geometry, local field factors at ω and 2ω, and other optical and instrumental quantities. The quantities (ρ_s, β_s) and (ρ_c, β_c) are the (concentration, first hyperpolarizability) of the solvent and chromophore molecules, respectively. $I(2\omega)/I^2(\omega)$ *versus* ρ_c plots were constructed for each solution series and the slopes were obtained. The ratio of the slopes is then β_c^2/β_{st}^2, where β_{st} is the β value of the standard chromophore (DANS) and β_c is the β value of the DBA chromophore.

For NLO chromophores, it is absolutely essential to tune the structure for maximum NLO behavior. Our electronic "tuning" of the DBA skeleton is reflected in the linear optical properties, *i.e.*, the electronic absorption spectra of **1–6**, as depicted in Fig. 1. DBA **6**, which possesses three-fold symmetry, has λ_{max} at 397 nm and $\lambda_{cut\text{-}off}$ at 450 nm, and therefore is essentially transparent at 532 nm (18 800 cm^{-1}), enabling non-resonant HRS measurements at $\lambda = 1064$ nm. The λ_{max} and $\lambda_{cut\text{-}off}$ of cycles **1–5**, which are substituted at various positions with donor and acceptor groups, are at somewhat longer wavelengths.

All DBAs showed a quadratic dependence of the scattered light on the intensity of the incident 1064 nm light. Using macrocycle **5** as a typical example, Fig. 2 depicts a plot of the square of its intensity of fundamental light *versus* the HRS intensity. The quadratic dependence (*i.e.*, straight line) demonstrates that the scattered light is due to a second-order effect. The HRS signals of all the DBAs were confirmed to be free of background fluorescence by separately measuring the fluorescence spectra of these chromophores. None of the DBAs used in this study showed any detectable fluorescence near or at the same wavelength as the HRS signal.

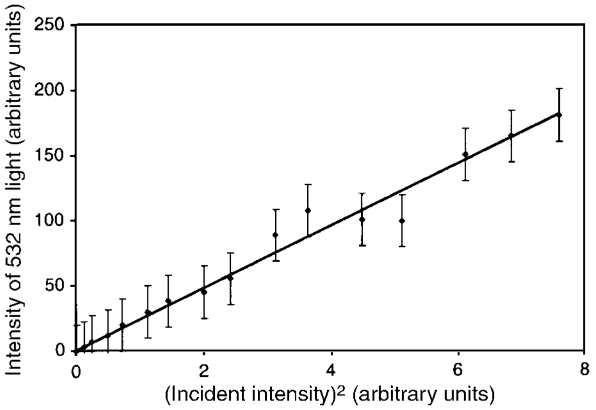


Fig. 2 Intensity of the frequency-doubled light plotted *versus* the square of the incident (1064 nm) light intensity for DBA **5**.

The DBA solutions displayed constant and intense HRS

Table 2 First hyperpolarizability (β) values for DBAs **1–6** in $CHCl_3$ as measured using ESM of HRS

DBA	λ_{max}/nm	$\beta_{expt}/10^{-28}$ esu	$\beta_0{}^a/10^{-28}$ esu	$(\beta_0/M)_{rel}{}^b$
1	338	12.5	6.6	1.4
2	355	12.8	6.3	1.3
3	480	21.2	3.1	0.7
4	418	15.0	4.9	0.9
5	392	4.2	1.7	0.3
6	329	3.8	1.7	0.5
DANS[c]	438	16.0	2.4	=1

[a] β_0 is the first hyperpolarizability after dispersion correction. [b] $(\beta_0/M)_{rel}$ is the normalized NLO figure of merit for the DBAs relative to DANS where M is the molecular mass of the corresponding chromophores. [c] Reference 18.

signals as compared to DANS solution. Table 2 gives the experimental β values[19] of the DBAs when the measurements were carried out with 10^{-6} M $CHCl_3$ solutions. As compared to DANS, the corrected β_0 values of DBAs **1–5** are similar in magnitude or even two to three times larger. The parent DBA **6**, possessing no substituents and being totally transparent in the visible region, also exhibits a commensurate β_0 value. A more interesting analysis is the optical transparency of the DBA solutions *versus* NLO activity based on the figure of merit. Compared to a variety of similarly active chromophores,[1d] the transition wavelengths of the DBA macrocycles are generally 25–50 nm higher in energy, which translates into better overall optical transparency. Finally, it is noteworthy that DBA **1**, the most promising of the systems studied in Table 2, packs in a *noncentrosymmetric* pattern in the solid state.[12] Such an arrangement will be obligatory if DBAs or other organic systems are to find use as viable NLO materials for incorporation in devices such as high-speed optical switches.[20]

The large β values of the DBAs make these planar 2-D chromophores very promising candidates for second-order NLO applications. To our knowledge, these are among the most active organic NLO chromophores reported to date, and present a novel structural motif for designing NLO-active molecules with greater optical transparency. Based on these results, we are conducting an inclusive study of all other DBAs available in our lab to probe the structure–property relationship for second-order NLO properties. In addition, our ability to tune easily the electronic properties of the DBA skeleton, as well as to incorporate easily polarizable functionalities such as thiophenes,[21] will permit us to design even more active NLO chromophores. These results will be detailed in future reports.

Acknowledgements

This research was supported by the National Science Foundation and The Camille and Henry Dreyfus Foundation (Teacher-Scholar Award to M.M.H.). J.J.P. acknowledges the ACS Division of Organic Chemistry for a Graduate Fellowship, sponsored by Organic Syntheses.

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