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First hyperpolarizabilities of dipolar photoconductive chromophores: an approach toward monolithic molecular materials for photorefractivity

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Abstract

Second-order optical nonlinearities of a series of dipolar photoconductive chromophores have been investigated by semiempirical quantum chemical calculations using time-dependent Hartree–Fock formalism in conjunction with PM3 parameter and experimental evaluation of the first molecular hyperpolarizability (β). A linear correlation between the measured and calculated β values was observed, and the structure–property relationship discussed in terms of the structural variation. It was noted that the optical nonlinearities of the dipolar photoconductive molecules with carbazole, indole, or indoline as donor units are large enough for the electrooptic and photorefractive applications. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

With the growing need of materials for photonics technologies, a large number of dipolar organic molecules have been investigated theoretically and experimentally [1]. These push–pull molecules, composed of electron donor and acceptor end groups interacting through a conjugating segment, are of considerable interest for their large first hyperpolarizabilities (β) leading to the second-order nonlinear optical (NLO) property. In particular, the combination of the electrooptic (EO) Pockels effect of these dipolar molecules with the photoconductivity, which can be provided either by the separate molecules or by the integration into the push–pull molecular structure, makes them one of the best candidates for photorefractive (PR) materials [2,3]. Among several combination strategies investigated to date, the integration approach, i.e., the use of monolithic molecule with two different functionalities within a single molecular system, is considered to be more ideal, and intensive studies have been carried out for low molecular weight organic glass and polymeric systems [4–7]. Thus, the molecular

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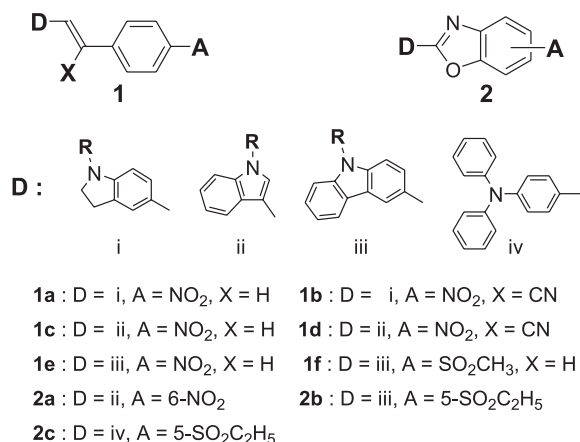*E-mail address:* parksy@plaza.snu.ac.kr (S.Y. Park).

Fig. 1. Chemical structures of dipolar photoconductive chromophores examined in this study. Donor segment **D**, acceptor **A**, and substituent **X** are denoted above for each chromophore. **R** is 2-hydroxyethyl (**1a**, **1d**), 2-methacryloyloxyethyl (**1b**), 6-methacryloyloxyhexyl (**1c**), 2-ethylhexyl (**1e**, **1f**, and **2a**), or 6-hydroxyhexyl (**2b**).

level investigation of the second-order optical nonlinearity of such class of photoconductive NLO chromophores is very important for the design of monolithic photorefractive materials.

In this work, we first report the hyperpolarizabilities of a series of dipolar photoconductive chromophores (Fig. 1), which are promising monolithic molecular materials for photorefractivity. Molecular structures of these chromophores are characterized by the integration of photoconductive moiety, i.e., carbazole, indole, indoline, or triphenylamine as the push group of NLO chromophore, which is connected to the conventional acceptors where the conjugated bridge is stilbene or 2-arylbenzoxazole type. The latter structure provides better thermal and photochemical stability with presumably enhanced photoconductivity to the monolithic molecules. Large photorefractivity of our monolithic chromophore was recently proved by two-beam coupling. [1] In

order to correlate the second-order optical nonlinearities of the chromophores to the molecular structure, we investigated the β values using hyper-Rayleigh scattering (HRS) method and semi-empirical calculation.

2. Experimental

The general synthetic methodologies for the dipolar photoconductive chromophores are depicted in Scheme 1 (**D** and **A** are indicated in Fig. 1). Stilbene and cyanostilbene linkages were formed by Wadsworth–Emmon's reaction or Knoevenagel reaction of **D**-CHO with acceptor-substituted benzyl phosphate, phenylacetic acid, or phenylacetonitrile. Benzoxazole ring was formed by oxidative ring closure of phenolic Schiff's base, which was obtained from **D**-CHO and acceptor-substituted o-aminophenol, catalyzed by the oxidizing agent, lead(IV) acetate. The detailed synthetic procedures and photoconductivities of these compounds were and are to be reported by us in the literature [8–10]. HRS measurements were performed with the fundamental radiation of 1064 nm at room temperature in chloroform or methanol depending on the solubility of each compound [11]. Since a fused quartz cell generally gives an SHG intensity which is more intense than the hyper-Rayleigh signal, glass cuvettes were used as the solution-holding cells. A Nd:YAG laser (10 Hz, 3–8 ns pulse width) was used as an excitation source, which was filtered by a long pass filter to remove the second-harmonic component at 0.53 mm. The scattered signal at 90° was filtered at the second-harmonic frequency and directed to a photomultiplier tube. A boxcar integrator was used to process the signal. The measured values were converted to the corresponding nonresonant ones at zero frequency (β_0) using the two-state approximation [12]. Because no correction was applied to the effect of two-photon absorption-induced fluorescence (TPF), where the femtosecond pulsed laser is needed, we obtained only the relative β_0 values, not the exact intrinsic values, for the similar structures studied in this work. Semi-empirical quantum chemical calculation was carried out using MOPAC 97 program [13]. We

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[1] 9-(2-Ethyl-hexyl)-3-[2-(4-methanesulfonyl-phenyl)vinyl]-9H-carbazole (**1f**) formed an optically clear molecular glass with $T_g = 25°C$, which showed large two-beam coupling gain coefficient without any auxiliary (≈ 70 cm^{-1} at 633 nm under the electric field of 100 V/μm).
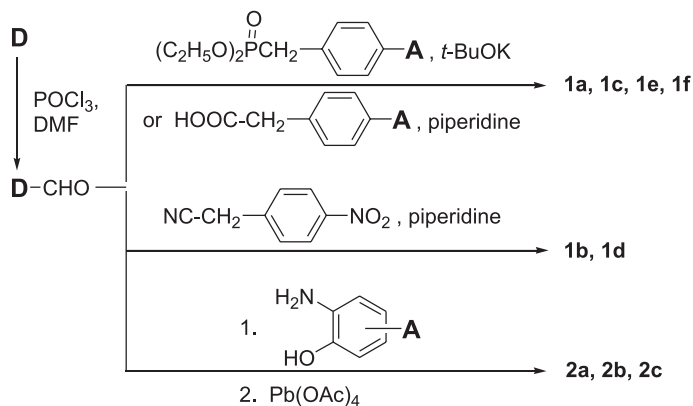
Scheme 1.

employed the PM3 procedure for geometry optimization in the ground state, and predicted β_0 values based on the time-dependent Hartree–Fock (TDHF) approach, following the method given in the literature [14]. For simplicity of calculation, substituent **R** in Fig. 1 was set to methyl in all the compounds since the calculation with the elongated alkyl chain showed only a small deviation of β values (about 5%) for a similar system [15].

3. Results and discussion

Rotation of the photoconductive donor segments except triphenylamine around the C–C bond between donor segment and vinyl or benzoxazole group yields a different, nondegenerate conformation, as shown in Fig. 2, for the two representative chromophores **1e** and **2a**. Torsional angle potential shown in Fig. 2 illustrates that two planar conformations of almost equal energy (**A** and **B**) are preferred. The rotational energy barriers for **1e** and **2a** are 2.3 and 3.8 kcal/mol, respectively, and at room temperature (at 298 K, $RT \approx 0.6$ kcal/mol), we expect a reasonable conformational flexibility about this dihedral, but not a completely free rotation. On this basis, for all chromophores, we fixed the geometries at the position of minimum energy, i.e., **A** conformation in Fig. 2, for the prediction of β_0 values.

The determined β_0 values for dipolar photoconductive chromophores are summarized in
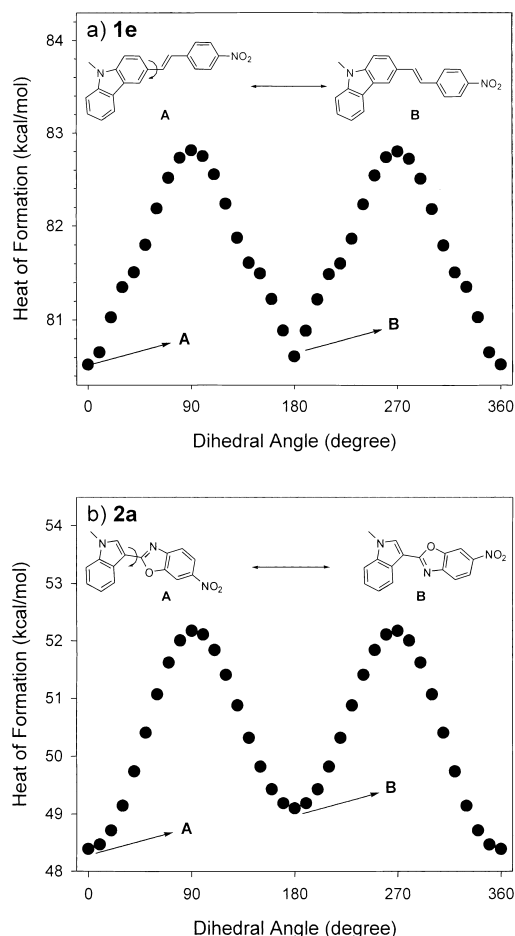

Fig. 2. Torsional angle potential for (a) **1e** and (b) **2a** about the C–C bond indicated by arrows.

Table 1
Absorption maxima and hyperpolarizabilities (β) of dipolar photoconductive chromophores

Compound	λ_{max} (nm)[a]	β^{b} ($\times 10^{-30}$ esu)	$\beta_{0,expt}{}^{c}$ ($\times 10^{-30}$ esu)	$\beta_{0,calcd}$ ($\times 10^{-30}$ esu)
1a	430 (MeOH)	401	116	34.0
1b	461 (CHCl$_3$)	498	101	27.4
1c	420 (MeOH)	430	137	35.3
1d	422 (MeOH)	407	127	26.9
1e	414 (MeOH)	430	143	33.8
1f	358 (CHCl$_3$)	129	63	23.9
2a	384 (CHCl$_3$)	220	92	24.2
2b	344 (MeOH)	119	62	16.5
2c	376 (CHCl$_3$)	142	62	17.2

[a] Solvents for UV–VIS absorption and HRS experiment are given within parentheses.
[b] Determined by HRS measurement using 1064 nm radiation.
[c] Static nonresonant values corrected by the two-level model.

Table 1. The measured values ($\beta_{0,expt}$) are plotted against the calculated values ($\beta_{0,calcd}$) in Fig. 3. There exists a linear correlation between the calculated and experimental β_0 values ($\beta_{0,expt} \approx 3.80\beta_{0,calcd}$). Although solvent effect is not significant, the measured values in methanol tend to be slightly larger than that in chloroform when considering the trend of the calculated β_0 values for homologues (**1d**–**2a**, **1f**–**2b**). This solvent effect can be explained by the simple prediction that the charge-separated resonance structure of the homologues would be slightly more stabilized in a more polar solvent [16]. For all the chromophores,
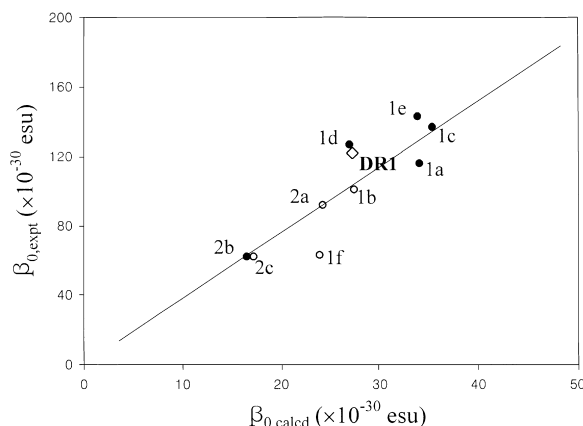

Fig. 3. Linear correlation between the calculated and experimental β_0 values, i.e., $\beta_{0,calcd}$ and $\beta_{0,expt}$. Open and solid circles indicate the results obtained in chloroform and methanol, respectively. **DR1** is the reference material, or 4-(p-nitrophenyl-azo)-N,N-dimethylaniline.

the difference between $\beta_{0,calcd}$ and $\beta_{0,expt}$ may be due to the different conformations and electronic states in solution (HRS) and in isolated gas phase (calculation) [14]. It might also be affected by other nonlinear mechanisms, such as TPF, which is the well-known problem of HRS using 1064 nm radiation [17]. By any means, a qualitative discussion for the calculated and experimental β_0 values is considered to be reliable from the fact that the result for the reference material, 4-(p-nitrophenyl-azo)-N,N-dimethylaniline (disperse red 1, **DR1**) determined in the same calculation and measurement system agrees well with the linear correlation in Fig. 3. Compared with the result of **DR1**, it is concluded that the photoconductive dipolar compounds examined here possess sufficiently large β values for photorefractivity.

The structure–property relationship can be discussed with the structural dependence of the calculated β values for homologous chromophores. Fig. 4 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **1a**, **1c**, and **1e**. It clearly illustrates the redistribution of electronic charge in the excited state through the π-conjugation pathway to form intramolecular charge transfer resonance structure. Since the structural variation of the donor segment, i.e., idoline, idole, and carbazole, affects the β value (Table 1), their charge distribution was calculated in order to determine the electron-donating ability. Table 2 summarizes the Mulliken charge and dipole moment in the ground and first excited states

HOMO   LUMO
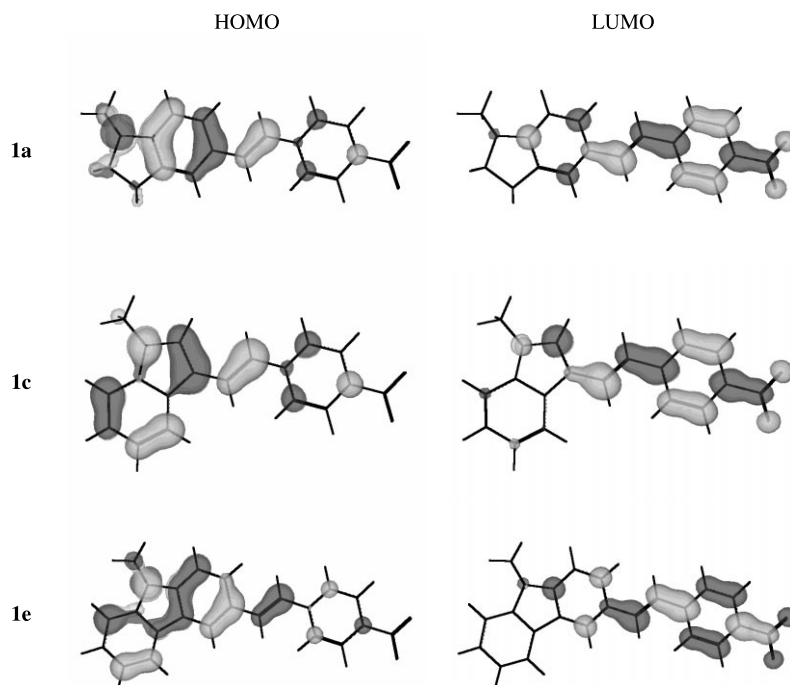
Fig. 4. Sketches of HOMO and LUMO for **1a**, **1c**, and **1e**.

of stilbene chromophores. The negative charge in the acceptor part (part N; see the footnote b of Table 2) of a totally neutral molecule indicates the charge transfer even in the ground state. In the excited state, its absolute values and the dipole moments increase significantly, manifesting the charge redistribution, as predicted above by the

orbital diagram. Although the variation of the net charge in part N is not so large for the chromophores with the same acceptor (**1a**, **1c**, and **1e**), **1c** exhibits the largest degree of charge separation, while it is almost equal for **1a** and **1e**. The change of charge in part N between the ground and excited states also shows the same tendency. On this

Table 2
Calculated Mulliken charges, dipole moments (μ) in the ground and the first excited singlet states, and transition energies (E_g)

Compound	Ground state		Excited state		$E_{g,calcd}$ (nm)
	Charge[a] in N[b]	μ_g (D)	Charge[a] in N[b]	μ_e (D)	
1a	−0.048	7.46	−0.208	9.59	372
1c	−0.060	8.87	−0.241	10.79	388
1e	−0.047	7.68	−0.209	10.23	374
1f	−0.036	7.42	−0.153	9.11	364
2a		8.97		11.65	372
2b		6.85		8.74	356

[a] The unit is the elementary electric charge (e).
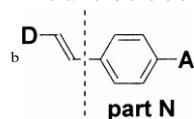
basis, it can be concluded that the order of electron-donating ability is carbazole $\leqslant$ indoline $<$ indole, and the $\beta_{0,calcd}$ increases in that order. Concerning the effect of electron-accepting ability, dipole moment, net charge in part N and their changes between the two electronic states are larger in **1e** (nitro) than in **1f** (sulfone), indicating that the nitro group is more electron-withdrawing than the sulfone group. Thus, as acceptor strength increases from sulfone to nitro (**1f** $\rightarrow$ **1e**), β is enhanced with the decreased, more optimal bond length alternation (BLA) [18–20]. The enhanced aromaticity due to the heteroaromatic benzoxazole moiety tends to decrease the absorption maxima and β values (**1c** $\rightarrow$ **2a**, **1f** $\rightarrow$ **2b**). The calculated transition energies in Table 2 also confirm that the excitation of benzoxazole derivatives **2a** and **2b** requires a higher energy than that of stilbene analogues. This tendency can be explained by the fact that an additional aromatic delocalization energy limits the excitation, i.e., the intramolecular charge separation [21,22]. Since the β_0 value is proportional to E_g^{-3} according to the two-state model [12], the decrease in E_g gives rise to the decrease in β_0.

When a cyano group is incorporated into stilbene (**1a** $\rightarrow$ **1b**, **1c** $\rightarrow$ **1d**), planarity of the conjugated architecture in the optimized geometry is remarkably reduced by the steric repulsion, where the dihedral angles for **1b** and **1d** are calculated to be about 45°. This distortion from planarity causes the reduced extent of π-orbital conjugation and thus the reduced β values, as interpreted for β-nitrostyrene derivatives [16].

4. Conclusions

In conclusion, we found a linear correlation between the β values determined by the PM3 calculation and HRS measurement with dipolar photoconductive molecules and discussed the structure–property relationship in terms of the structural variation. It was also shown that the photoconductive NLO chromophores shown in this work have sufficient second-order optical nonlinearity and thus are good candidates for photorefractive molecular materials.

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