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7. To obtain the minimum energy structure, molecular dynamics and molecular mechanics calculations were carried out with the CVFF force field⁸ and the DISCOVER simulation package of MSI.⁹ Molecular dynamics was run at 800 K for 1000 ps with 1 fs time step, and the resulting trajectory analyzed. Of 1,000 conformers obtained in the dynamics simulation, the lowest energy structure was selected, and then the energy minimization with conjugate gradient algorithm⁹ was performed on this structure to a gradient norm of less than 0.001 kcal/mol per Å.
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First-Order Hyperpolarizabilities of α -Cyano-p-nitrostilbene Derivatives

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Received April 25, 1996

It has been clearly established that π donor-acceptor compounds with small CT energy and large differences between the ground- and excited-state dipole moments as well as large oscillator strength can exhibit large molecular second-order optical nonlinearities.^{2,8-11} The β value can be expressed as eq. 1, where ΔE is the energy of the molecular charge transfer, $h\nu$ and $2h\nu$ are the energies of the fundamental and second harmonic waves, f is the oscillator strength, and $\Delta\mu$ is the difference between the ground- and excited state

Table 1. Linear and Nonlinear Optical Properties of Various Stilbene Derivatives

Compound	λ_{max} , nm ^a	10^{30} β , esu ^b	10^{30} $\beta(0)$, esu ^c
Ia	370 ^d	56 ^e	46 ^e
IIa	368	0 ^f	0
IIb	382	0 ^f	0
IIIb	386	77	32
Ic	437 ^d	84 ^e	63 ^e
IIc	488 ^e	399 ^e	50

^aSolvent was methanol except otherwise noted. ^bMeasured by Hyper-Rayleigh scattering with 1064 nm fundamental radiation in methanol except otherwise noted. ^cCalculated by using the two-level model.¹⁵ ^dSolvent was CHCl₃. ^eLiterature values determined by EFFISH in CHCl₃.¹³ ^fSmall scattering was detected. ^gSolvent was DMSO.

dipole moments.¹²

$$\beta = \frac{3e^2\hbar^2}{2m} \frac{\Delta E f \Delta\mu}{[\Delta E^2 - (2h\nu)^2][\Delta E^2 - (h\nu)^2]} \quad (1)$$

One of the most well known NLO chromophores is the stilbene derivatives. Thus disubstituted stilbenes with various donor-acceptor pairs exhibit the β value of $19\text{--}73 \times 10^{-30}$ esu in CHCl₃.¹³ We were interested in learning whether a cyano substituent at either of the olefinic carbons of this compound might enhance the molecular hyperpolarizability (β). It was expected that the cyano group would change not only the dipole moment but the ΔE and f values, which would in turn change the β values. Accordingly, we have synthesized compounds IIa-c and IIIb and compared their β values with those for the stilbene derivatives I.

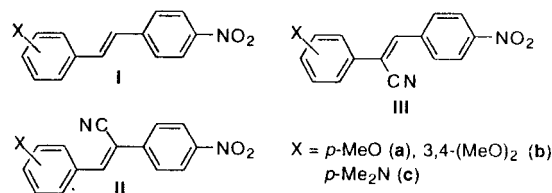


Table 1 compares the β values of the various stilbene derivatives. In general, the β values are always smaller for the α -cyanostilbenes than for the stilbenes. Comparison of the absorption maxima reveals that they are almost the same for Ia and IIa, whereas that for Ic is significantly shorter than IIc. Hence it is difficult to explain the smaller β values for the α -cyanostilbene derivatives only in terms of the λ_{max} values. On the other hand, the result can readily be interpreted with the difference between the ground and the excited state dipole moments. A semiempirical calculation has revealed that the ground state dipole moments for Ic and IIc are almost the same.¹⁴ However, the excited state dipole moment is significantly smaller for the former due to the increased charge transfer from the dimethylamino to the cyano group (Figure 1). Accordingly, the difference between the ground and the excited state dipole moments ($\Delta\mu$) for IIc is smaller than that for Ic by approximately 14%. This would predict that the β value should be smaller for the former

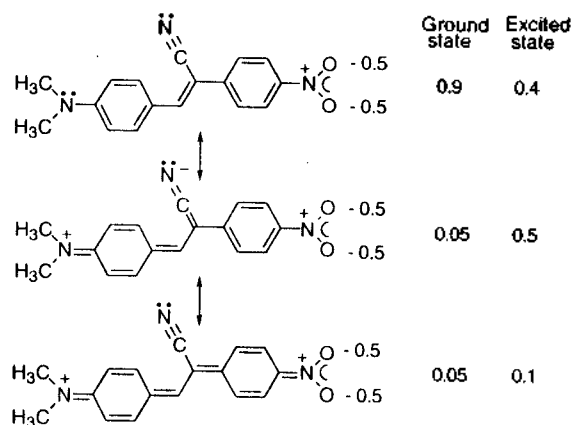


Figure 1. Resonance structures of **IIc** and relative abundance in ground state and excited state¹⁴.

(eq. 1), as observed.

The importance of the difference between the ground state and the excited state dipole moments in determining the molecular hyperpolarizability is also demonstrated by the much larger β value for **IIIb** than for **IIb**. Since the cyano group in the former cannot be in resonance with the para methoxy substituent, the excited state charge transfer from the donor to the cyano group in **IIIb** is not expected to be as efficient as in **IIb** (*vide supra*). This would predict that the $\Delta\mu$ should be larger for the former to enhance the β value (eq. 1). On the other hand, the λ_{max} for **IIIb** and **IIb** are almost the same. Therefore, the larger β value observed for **IIIb** can most reasonably be attributed to the larger difference between the ground state and the excited state dipole moments.

In conclusion, the present results reveal that the β values of the α -cyano-*p*-nitrostilbene derivatives are significantly smaller than those for the stilbene derivatives apparently due to the smaller difference between the ground and the excited state dipole moments.

Experimental

Substituted α -cyano-*p*-nitrostilbene derivatives **IIa-c** were synthesized in reasonable yields by reacting *p*-nitrobenzyl cyanide (1.6 g, 10 mmol), KOH (0.7 g, 12 mmol), and 1 equiv of substituted benzaldehyde in 50 mL ethanol by known procedure.¹⁶ Compound **IIIb** was prepared by the same procedure using 3,4-dimethoxybenzyl cyanide and *p*-nitrobenzaldehyde. The physical and spectroscopic data for **IIa-c** and **IIIb** were consistent with the proposed structures.

The λ_{max} values and extinction coefficients have been mea-

sured with a Varian 3E UV-VIS spectrophotometer. The β values of **IIa-c** and **IIIb** have been determined by hyper-Rayleigh scattering using 1064 nm light as the fundamental wave as reported previously.¹⁷

Acknowledgment. This research was supported in part by OCRC-KOSEF and Basic Science Research Institute Program, Ministry of Education, 1995 (Project No. BSRI-95-34 06). CHW acknowledges partial financial support from the NSF Material Division (DMR9112993).

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