Amine Donors in Nonlinear Optical Molecules:
Methyl and Phenyl Substitution Effects on the First Hyperpolarizability

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The effects of amine donors (**a**:NH_2, **b**:NMe_2, **c**:NMePh, **d**:NPh_2) and conjugation length on the molecular hyperpolarizabilities of a series of dipolar molecules have been theoretically investigated by using CPHF/6-31G method. The first hyperpolarizabilities (β) of *p*-nitrobenzene derivatives increase with the donor in the order, NH_2 < NMe_2 < NMePh < NPh_2, whereas slightly different order is observed in more conjugated derivatives, *i.e.*, NH_2 < NPh_2 < NMe_2 < NMePh. The result has been attributed to the extent of charge transfer and torsion angle. Moreover, the results show that "non-traditional" π-conjugation effect exists in small compounds and decreases as the conjugation length between donor and acceptor increases.

Key Words : Molecular hyperpolarizability, Nonlinear optical, Amine donor, N-Substitution effects, *Ab initio*

Introduction

Organic materials exhibiting large nonlinear optical (NLO) response has become a focus of current research due to their potential applications in various photonic technologies.[1,2] Most organic NLO materials are push-pull π-conjugated systems, in which donor and electron acceptor groups are bound to the opposite ends of the highly delocalized π-electron bridges. One of the most important research objectives in this area has been the optimization of molecular structures to obtain large NLO responses. The structure-NLO property relationship studies of the dipolar molecules reveal that the most important factors controlling the β are the molecular planarity, conjugation length, and donor/accepter strength.[1a,1b,2-4]

Among the most extensively utilized electron donors in organic NLO materials are the amino groups. The NLO enhancement effect of the *N*-alkyl substituent at the amino group in typical organic push-pull dipolar compounds is well established.[5] Recently, by using the theoretical calculations and the EFISH measurements. McMahon*et al.* reported that the *N*-phenyl substitutent at the amine group increases the molecular hyperpolarizability of the *p*-nitroaniline derivatives.[6] The result has been attributed to the increased π-conjugation by the *N*-phenyl group in a "non-traditional" manner, where the additional π-electron unit lie outside of the donor-acceptor framework. It was also proposed that this "non-traditional" substitution pattern of π-conjugation might provide new possibilities concerning the design of efficient NLO chromophores.

In this work, we have studied the effects of various substituted amino groups and the conjugation length on the molecular hyperpolarizabilities of **1-4** by ab initio method (Chart 1). We were interested in learning whether such "non-
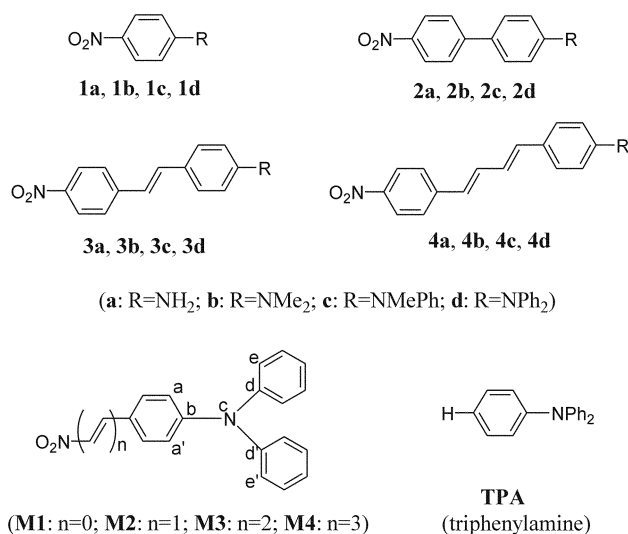

(a: R=NH_2; b: R=NMe_2; c: R=NMePh; d: R=NPh_2)

(M1: n=0; M2: n=1; M3: n=2; M4: n=3)   TPA (triphenylamine)

Chart 1

traditional" effect is operating in more complex compounds, which might be more interesting to organic materials chemists. We now report that the effect indeed exists in small compounds and decreases as the conjugation length between donor and acceptor increases.

Computational Method

The molecules in Chart 1, are fully optimized at Hartree-Fock level using 6-31G basis set in *Gaussian* 98 program.[7] The tensor components of the static first hyperpolarizabilities are analytically calculated by using the coupled perturbed Hartree-Fock (CPHF) method. The intrinsic hyperpolarizability $\beta_{\parallel}$ is given by magnitude of the vector component of the hyperpolarizability (β);[8] $|\beta_{\parallel}| = (\beta_x^2 - \beta_y^2$

$+ \beta_z^2)^{1/2}$, where β_x, β_y and β_z are the vector components of the hyperpolarizability tensor in the direction of the x, y and z molecular axes, respectively.

Results and Discussion

Table 1 contains the calculated values of the first hyperpolarizability ($\|\beta\|$), HOMO-LUMO energy separation (ΔE), torsion angles around the amine donors and total charge density at the donor-π-spacer-acceptor. The first hyperpolarizability ($\|\beta\|$) values of **1-4** are in the range of (9-105) $\times 10^{-30}$ esu, and increase with the conjugation length.[1a,1b,2-4] For a given donor, the ΔE always decreases with the conjugation length (Table 1). Hence the larger $\|\beta\|$ values for more extended compounds can readily be attributed to the smaller ΔE.

The $\|\beta\|$ values of **1** increase with the change in the donor in the order, $NH_2 < NMe_2 < NMePh < NPh_2$. This is consistent with McMahon's result obtained by AM1/FF or ZINDO/SOS method. It shows that the effectiveness of the donors in enhancing the $\|\beta\|$ increases in the same order, *i.e.*, N-phenyl group increases the $\|\beta\|$ more than the N-methyl group, and the "non-traditional" conjugation effect of the former seems to be operating. In contrast, the $\|\beta\|$ values of **2-4** increase with the donor in the order, $NH_2 < NPh_2 < NMe_2 < NMePh$.[9] As shown in Figure 1, this order is general for **2-4** and the largest $\|\beta\|$ calculated for **1d** appears to be an exception. Moreover, it is entirely different from their

relative electron-donating abilities, *i.e.*, $NPh_2 < NH_2 < NMePh < NMe_2$ (vide infra). Therefore, this result seems to indicate that the special effect of the N-phenyl group observed in **1d** disappears as the conjugation length increases, whereas that of NMePh always exists in **1-4**. This conclusion is supported by the Mulliken charge analysis and the torsional angles as discussed below.

The Mulliken charge analysis reveals that the total charges of nitro group (Z_{NO2}) and amine donor (Z_{amine}) are negative, whereas those of the π-spacer (Z_{spacer}) are positive (Table 1). This suggests that significant amount of the electronic charges are transferred from the spacer to the donor and acceptor. For all compounds, Z_{amine} decreases monotonically in the order, $NH_2 > NMe_2 > NMePh > NPh_2$, probably because of the polarizability effect. The concomitant increase in the Z_{spacer} with the same donors reveals that the major part of the enhanced electron density is originated from the spacer. Hence, the relative electron-donating ability of the donors can best be assessed by comparing Z_{NO2}, which is the total electron density transferred from the spacer and amino groups, not Z_{amine} (vide supra). As shown in Table 1, there is small but clear trend in Z_{NO2} with different donors, *i.e.*, $NPh_2 < NH_2 < NMePh < NMe_2$, indicating that the electron-donating ability increases in this order. A possible explanation for the smaller differences between Z_{NO2} values may be the unfavorable polarizability effect due to the smaller size of the nitro group than the spacer and the donor. Moreover, the absolute value of Z_{NO2} decreases significantly from **1** to **2**

Table 1. $\|\beta\|$, HOMO-LUMO Energy Separation, Torsion Angles, and Total Charge of Acceptor-π-spacer-donor Calculated by CPHF/6-31G method.

	$\|\beta\|^a$		ΔE^b	$\phi 1^c$	$\phi 2^d$	Z_{NO2}^e	Z_{spacer}^f	Z_{amine}^g
1a	9.01	10[h]	0.37685	0.0	-	-0.631466	0.868111	-0.236645
1b	12.8	13[h]	0.36367	0.1	-	-0.637593	0.922515	-0.284922
1c	15.4	-	0.36661	0.0 (0.0)	90.7	-0.636633	0.942306	-0.305673
1d	18.0	24[h]	0.34774	20.2	62.3 (62.2)	-0.628188	0.948310	-0.320122
2a	23.1	-	0.32872	0.3	-	-0.606618	0.866734	-0.260116
2b	28.8	-	0.31974	0.9	-	-0.607862	0.922873	-0.315011
2c	31.8	-	0.32232	6.7 (3.1)	82.3	-0.607574	0.942697	-0.335123
2d	27.9	-	0.31008	36.2	51.2 (51.1)	-0.602405	0.948695	-0.346290
3a	51.7	-	0.30517	0.3 (0.1)	-	-0.609434	0.869278	-0.259844
3b	63.0	-	0.29877	0.4 (0.2)	-	-0.610288	0.925348	-0.315060
3c	68.0	-	0.30081	2.5 (1.4)	87.5	-0.610050	0.946193	-0.336143
3d	59.5	-	0.29523	36.5 (36.3)	51.0 (50.5)	-0.605637	0.953433	-0.347796
4a	83.1	-	0.29010	0.0 (0.0)	-	-0.609544	0.871186	-0.261642
4b	97.7	-	0.28533	0.1 (0.0)	-	-0.610029	0.927522	-0.317493
4c	105	-	0.28681	0.0 (0.0)	90.6	-0.610022	0.948724	-0.338702
4d	88.2	-	0.28522	38.4 (37.7)	50.3 (49.3)	-0.606432	0.956743	-0.350311
M1[i]	18.0	-	0.34775	20.2	62.3 (62.2)	-0.628188	0.948310	-0.320122
M2	41.0	-	0.31872	26.0 (25.3)	58.4 (57.4)	-0.572301	0.901998	-0.329697
M3	69.2	-	0.30043	30.8 (30.1)	55.0 (54.0)	-0.571149	0.909601	-0.338452
M4	101	-	0.28781	34.4 (33.8)	52.6 (51.7)	-0.570125	0.914407	-0.344282
TPA	0.005	-	0.39341	45.9	45.9	-	-	-0.359835

[a]10^{-30} esu. [b]$\Delta E = E_{lumo} - E_{homo}$ (a.u.). [c]Torsion angle, degree (°), (a-b-c-d, a'-b-c-d'). [d]Torsion angle, degree (°), (b-c-d-e, b-c-d'-e'). [e]Total charge of NO$_2$-acceptor. [f]Total charge of π-spacer. [g]Total charge of amine-donor. [h]β_μ values using EFISH experiment at 1907 nm in chloroform (see ref. 6). [i]M1 is same as **1d**.

and remains nearly the same for further changes in the conjugation length. It appears that the extent of charge transfer from the donor to the acceptor decreases exponentially with the distance between them. However, it should be noted that the calculated $\beta\|$ for 1-4 cannot be explained with extent of charge transfer alone.

As expected, the HOMO-LUMO energy gap (ΔE) decreases monotonically as the conjugation length increases (Table 1). Hence, the gradual increase in $\|\beta\|$ with the conjugation length can readily be attributed to the smaller ΔE (vide supra). For all compounds, ΔE decreases with the donor in the order, NH_2 > $NMePh$ > NMe_2 > NPh_2. In contrast, $\|\beta\|$ of 1 and 2-4 increase in the order, NH_2 < NMe_2 < $NMePh$ < NPh_2, and NH_2 < NPh_2 < NMe_2 < $NMePh$, respectively. Therefore, it seems difficult to attribute the substituent effect on $\|\beta$ to ΔE.

The torsion angles (ϕ1) for **1a**, **b-4a**, **b** ($R - NH_2$, NMe_2) are close to zero, indicating that the amino groups are coplanar with the Ar group, where Ar is the aryl group directly bound to the donor. This is not unexpected because it would allow efficient charge transfer from the donor to the acceptor, by which the compounds could be stabilized. When $R = NMePh$ (**1c-4c**), ϕ1 ranges from 0.0 to 6.7, whereas ϕ2 from 82.3 to 90.7, respectively. This indicates that the N-Ar is planar, *i.e.*, Ar is coplanar with the nitrogen atom of the donor, and the phenyl substituent at the amino group is nearly orthogonal to the N-Ar plane, probably because of the steric effect. As the size of the donor group increases to $R - NPh_2$ (**1d**), ϕ1 increases and ϕ2 decreases (Table 1). This is again due to the steric effect (vide infra). Moreover, when the conjugation length is increased from 1 to 4, ϕ1 increases from 20.2 to 38.4, whereas ϕ2 decreases from 62.3 to 50.3, respectively. This result can readily be attributed to the balance between the charge transfer and the steric effect. If the N-Ph groups are coplanar with the Ar group, the compounds could be stabilized by the charge transfer from the donor to the acceptor, but destabilized by the steric hindrance. In **1d**, where the distance between the donor and acceptor is the shortest, the maximum stabilization is obtained by retaining the smallest ϕ1 value, probably because the charge transfer effect is most important. When the conjugation length increases, the extent of charge transfer decreases (vide supra) and the steric effect becomes more important. This is expected to increase ϕ1. Also, if ϕ1 increases, ϕ2 should decrease to minimize the steric effect. However, it should noted that ϕ1 is always smaller than ϕ2 regardless of the conjugation length.

Interestingly, the effect of substituent on $|\beta|$ can be explained with the torsion angle. Figure 1 shows that the $\|\beta\|$ values of **1a-d** increase in the order, NH_2 < NMe_2 < $NMePh$ < NPh_2, which is consistent with the literature data, *i.e.*, NH_2 < NMe_2 < NPh_2.[6] The larger value of $\|\beta\|$ for NPh_2 has been attributed to the participation of N-Ph moiety in the excited state, *i.e.*, a larger change in dipole moments between the ground state and the excited state ($\Delta\mu$).[6] Similar explanation can be applied to the larger $\|\beta\|$ for $NMePh$ than NMe_2. Hence, if the "non-traditional" method of increasing the
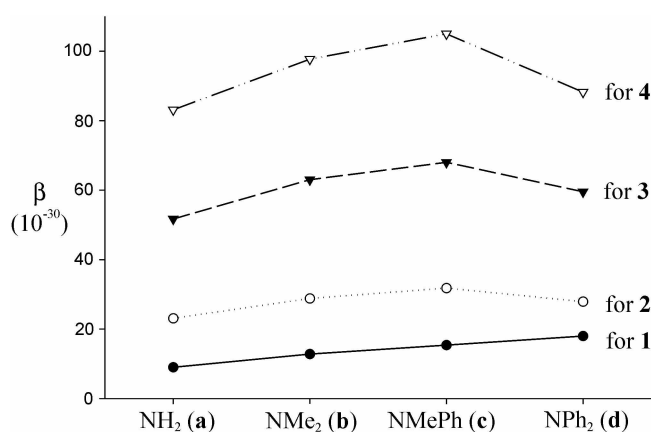

Figure 1. Plots of β values with amine donors.

conjugation is the result of the phenyl group participation in the excited state to increase $\Delta\mu$, such effect seems to exist in **1c**, **d**. On the other hand, the $\|\beta$ values of 2-4 increase in the order, NH_2 < NPh_2 < NMe_2 < $NMePh$. It appears that the special effect due to the N-phenyl group still exists in $NMePh$, but not in NPh_2. A possible explanation for this dichotomy might be the larger ϕ1 values for NPh_2 than others. As shown in Table 1, the ϕ1 values for the latter are sufficiently small to allow efficient charge transfer from the donor to the acceptor. In case of $NMePh$, the special effect could exist in all compounds (**1-4**) because ϕ1 is always small and the charge transfer from the donor to the acceptor is possible. Although ϕ2 value for this donor are close to 90 (vide supra), the phenyl group should be able to participate, at least in part, in the "non-traditional" conjugation, probably because ϕ2 is expected to decrease as the N-Ph bond is extended in the excited state. This is why compounds with R $- NMePh$ show the largest β in 2-4, despite that it is second to the NMe_2 in terms of the electron-donating ability (vide supra). On the other hand, **1d** has the smallest ΔE in this series. Also, ϕ1 of **1d** is 20.2, which is small enough for the efficient charge transfer and partial extension of the "non-traditional" π-conjugation (vide supra). Combination of these two factors would make **1d** the most efficient NLO chromophores among **1a-d**, as observed by McMahon *et al.*[6] When the conjugation length is increased, ϕ1 increases concomitantly and the special effect of NPh_2 group disappears. Note that the extension of π-conjugation by "non-traditional" manner is not possible without the charge transfer. However, $\beta\|$ values of **2d-4d** are larger than **2a-4a** probably because of the smaller ΔE.

To provide supporting evidences for the above conclusions, we have studied model compounds **M1-M4** by the same method (Table 1). The result shows that the extent of charge transfer, ϕ2, and ΔE decrease, whereas ϕ1 and $\|\beta\|$ increase with the conjugation length. All of these data are entirely consistent with the above conclusion. Additional evidence is provided by the results from N,N-diphenyl-p-nitroaniline. Figure 2 shows that the extent of charge transfer and $|\beta$ decrease as the torsion angle between the N-phenyl and p-nitroaniline moieties increases. This result is again consistent.
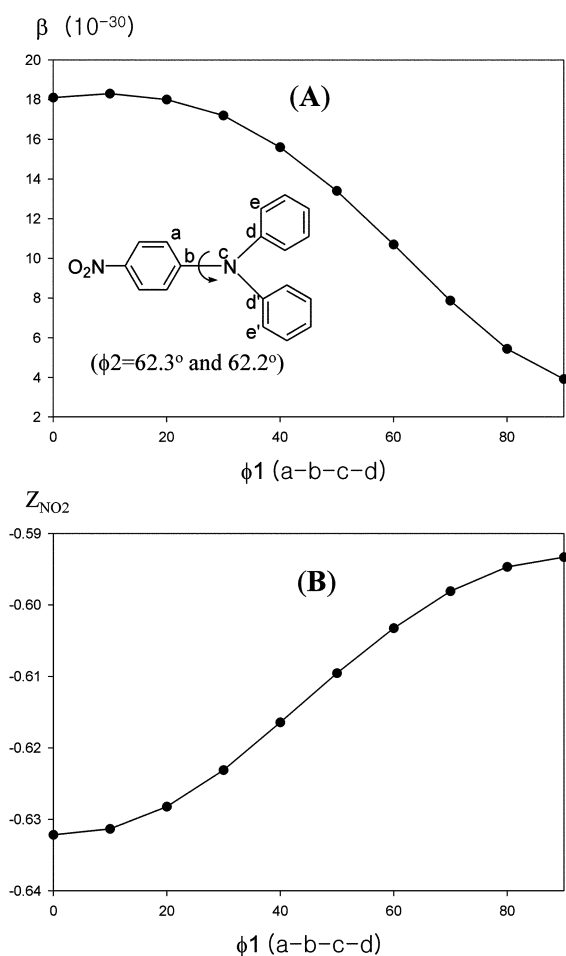
β (10^{-30})

(A)

O$_2$N—
a
b—c—N
e
d
d'
e'

(ϕ2=62.3° and 62.2°)

ϕ1 (a-b-c-d)

Z$_{NO2}$

(B)

ϕ1 (a-b-c-d)

Figure 2. Plots of β (A) and Z$_{NO2}$ (B) against torsion angle ϕ1 (a-b-c-d).

It is interesting to note that ϕ2 − 20 is the threshold for the disappearance of the special effect in both **1-4** and *N,N*-diphenyl-*p*-nitroaniline.

Conclusion

In this work, we have studied the effects of amine donors (a:NH$_2$, b:NMe$_2$, c:NMePh, d:NPh$_2$) and the conjugation length on the first hyperpolarizabilities of **1-4** using CPHF/

6-31G method. The β values increase with the donor in the order, NH$_2$ < NMe$_2$< NMcPh < NPh$_2$ in **1**, and NH$_2$ < NPh$_2$ < NMe$_2$ < NMcPh in **2-4**. In contrast, the relative electron-donating ability of the donors is NPh$_2$ < NH$_2$ < NMcPh < NMe$_2$. The apparent dichotomy has been attributed to the extent of charge transfer and torsion angle. Moreover, the results show that "non-traditional" π-conjugation effect indeed exists in small compounds and decreases as the conjugation length between donor and acceptor increases. These results would provide useful design strategy for the synthesis of efficient non-linear optical materials.

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8. ||β|| is also commonly referred to as β$_{vec}$. The calculated values were converted into electrostatic units (1 a.u. 8.6398 × 10^{-33} esu).
9. Using the same calculation method as shown in this report. a similar trend has been observed in *trans*-stilbene derivatives with amino donor and cyano acceptor group: that is. NMePh > NMe$_2$ > NPh$_2$. Cho. B. R. and Park. G.. unpublished results.