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First hyperpolarizabilities of triazine derivatives. *Ab initio* studies and Hammett correlation

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ABSTRACT: First hyperpolarizabilities (β) of triazine derivatives were studied by the *ab initio* method (HF/6–31G). The β values of these molecules increase with a stronger donor and as the conjugation length increases, probably because the electronic charge becomes more delocalized and the HOMO–LUMO energy gap (ΔE) and the bond length alternation (BLA) decrease with variation of the chromophore structure. Also, the susceptibility of β to the donor strength is found to be larger for a more elongated substrate. Noteworthy is the excellent linear relationship between β and BLA and also the gas-phase substituent constants (σ^{+}_{gas}). This result may serve as a useful guideline for the design of two-dimensional octupoles with large first hyperpolarizabilities. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: non-linear optical materials; octupole; triazine; first hyperpolarizability; *ab initio*; Hammett correlation

INTRODUCTION

There is much interest in non-linear optical (NLO) materials owing to their potential application in various photonic technologies.[1] To develop useful NLO materials, it is important to synthesize efficient NLO molecules with large first hyperpolarizabilities and assemble them non-cetrosymmetrically in the solid state to achieve significant second harmonic generation. The most extensively investigated NLO molecules are donor–acceptor substituted dipolar compounds. One of the most important achievements in this area is the development of opto-electronic devices with large electro-optic coefficients.[1b] Recently, octupolar molecules with threefold symmetry have received much attention as alternative NLO molecules.[2–5] Advantages of such molecules over more conventional dipolar molecules include the following: (i) the second harmonic responses of octupolar molecules do not depend the polarization of the incident light because they are more isotropic than the dipolar NLO molecules;[2d] (ii) the coupling of excited states can lead to enhanced non-linearity at virtually no cost of transparency;[2f] and (iii) owing to the lack of ground-state dipole moment, two-dimensional octupoles may favor the formation of non-centrosymmetriccrystals, which is important for practical applications.[3] Various derivatives of subphthaocyanine, 1,3,5-trinitro-2,4,6-tristyrylbenzene, 1,3,5-tricyano-2,4,6-tristyrylbenzene, 1,3,5-tricyano-2,4,6-triethynylbenzene, triphenylamine and truxenone have been synthesized and structure–property relationship studies have been reported.[2–5]

In this work, we studied the first hyperpolarizabilities of triazine derivatives **1**–**3** by the *ab initio* method. The results show that **1**–**3** exhibit significant first hyperpolarizabilities and that their β values show a linear relationship with both bond length alternation (BLA) and gas-phase substituent constants (σ^{+}_{gas}). In this series, the acceptor is the central triazine and the donors are the *para*-substituted phenyl group (Ph—R) at the periphery, which are connected by conjugation bridges. The conjugation length varied from $n = 0$ to 2, where n is the number of C═C bonds between the triazine and Ph—R.

RESULTS AND DISCUSSION

Structures of 1–3

The structures of **1**–**3** were fully optimized at the Hartree-Fock level using the 6–31G basis set in the g98 program.[6] The bond length, dihedral angle and charge density of **1**–**3** are summarized in Table 1. For all derivatives, the dihedral angles between the central triazine moiety and the peripheral phenyl groups are $<7.3°$ indicating that **1**–**3** are nearly planar. The length of the single bond ($r1$, $r3$, $r5$) decreases and that of double bond ($r2$, $r4$) increases

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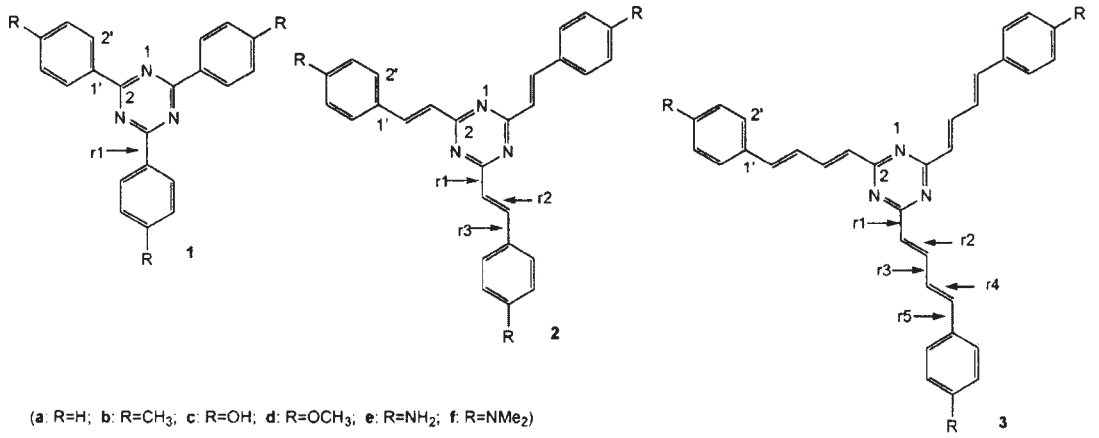

monotonically with a stronger donor and as the number of conjugated double bond increases (Table 1). Consequently, the BLA, calculated by subtracting the average double bond length from that of single bond, i.e. $(r1 + r3)/2 - r2$ for **2** and $(r1 + r3 + r5)/3 - (r2 + r4)/2$ for **3**, decreases in the same order (Table 2).

Table 1 gives the Mulliken charge densities of **1**–**3**. In **1a**, the negative charge is delocalized on the nitrogen atoms of the triazine ($z1$) and phenyl (Z_{Ph}) groups, whereas the positive charge is on the carbon atoms of triazine ($z2$) and *para*-H (Z_R). When the donor is changed to a stronger one, $z1$ decreases and $z2$ increases gradually. The sum of $3(z1 + z2)$ is the total charge density at the triazine ($Z_{triazine}$), which decreases in the same order, indicating a gradual increase in the electron density at triazine as the donor is changed to a stronger one. On the other hand, the positive charge at Ph—R is delocalized between Ph and R. When R is changed from H (**1a**) to Me (**1b**), Z_{Ph} increases, i.e. the charge density at Ph decreases, and Z_R decreases, i.e. that on the donor increases, probably because the carbon atom in Me is more electronegative than H. A further change to **1c**–**f** slightly increases Z_{Ph} and decreases Z_R. Note that Z_R of **1c** and **d** is more negative than that of **1e** and **f**, i.e. the more electronegative the atom is, the higher the charge density at R becomes. However, the total charge density at Ph—R decreases with a stronger donor, indicating a gradual increase in the electronic shift from Ph—R to triazine (see above).

When the conjugation length is increased from $n = 0$ (**1**) to $n = 1$ (**2**), both $Z_{triazine}$ and $Z_{Ph—R}$ decrease without affecting Z_R, and the electronic charge on the spacer (Z_{spacer}) has a large positive value. This indicates that the charge density is shifted primarily from the spacer to triazine and Ph, triazine and Ph have more negative charge and the electron is more delocalized. A further increase in the conjugation length to $n = 2$ (**3**) increases Z_{spacer} slightly without affecting $Z_{triazine}$, and shifts a small amount of negative charge to Ph—R. Since the number of carbons in the spacer increases from **2** to **3**, the average charge density on each carbon atom in the spacer is much smaller in **3** than **2**. This indicates a greater electron delocalization in **3**. Similarly, when the donor is changed to a stronger one, Z_{spacer} decreases and $Z_{Ph—R}$ increases, as observed in **1**. Here again, a stronger donor induces a greater charge delocalization. These results reveal that the electronic charge is more delocalized as the donor strength and the conjugation length increase.

Finally, the HOMO–LUMO energy gap (ΔE) and the BLA, defined by the difference between the single and double bond lengths, decrease with variation of the chromophore structure (Table 2). Therefore, it may be concluded that the more delocalized the electronic charge is, the smaller ΔE and BLA become in this series of compounds.

First hyperpolarizability

The first hyperpolarizabilities of the triazine derivatives were calculated using the following relationships:[7]

$$\|\beta\| = [\|\beta_{J=1}\|^2 + \|\beta_{J=3}\|^2]^{1/2}$$
$$\|\beta_{J=1}\|^2 = 3/5[(\beta_{XXX} + \beta_{XYY})^2 + (\beta_{YYY} + \beta_{YXX})^2]$$
$$\|\beta_{J=3}\|^2 = 2/5(\beta_{XXX}^2 + \beta_{YYY}^2 + 6\beta_{YXX} + 6\beta_{XYY}^2 - 3\beta_{YXX}\beta_{YYY} - 3\beta_{XYY}\beta_{XXX})$$

The tensor components of the static first hyperpolarizabilities were calculated analytically by using the coupled perturbed Hartree–Fock (CPHF) method.[8] The calculated $\|\beta\|$ values of the triazine derivatives are summarized in Table 2 along with the Hammett substituent constants (σ^+).[9]

The first hyperpolarizability of a D_3 symmetric molecule can be expressed by a three-level model:

$$\beta_{YYY} = \frac{1}{\hbar^2} \times \frac{\mu_{01}^2 \mu_{12}}{\omega_{01}^2} \times \frac{\omega_{01}^4}{(\omega_{01}^2 - 4\omega^2)(\omega_{01}^2 - \omega^2)} \quad (1)$$

where μ_{01} is the transition moment between the ground and degenerate first excited charge-transfer (CT) state, μ_{12} is the transition moment connecting these degenerate

Table 1. Structural properties of triazine derivatives **1–3**

Compound	$r1$[a]	$r2$[a]	$r3$[a]	$r4$[a]	$r5$[a]	ϕ[b]	$z1$[c]	$z2$[d]	$z_{triazine}$[e]	Z_{spacer}[f]	Z_{Ph}	Z_R	$Z_{Ph—R}$[g]
1a	1.47319	—	—	—	—	0.008	−0.629264	0.514448	−0.344449	–	−0.272108	0.616557	0.344449
1b	1.47098	—	—	—	—	0.014	−0.633555	0.517472	−0.348249	–	0.212481	0.135768	0.348249
1c	1.46820	—	—	—	—	0.015	−0.641557	0.525449	−0.348324	–	1.454884	−1.10656	0.348324
1d	1.46809	—	—	—	—	0.007	−0.642091	0.524803	−0.351864	–	1.508164	−1.1563	0.351864
1e	1.46426	—	—	—	—	0.004	−0.652888	0.528307	−0.373742	–	1.166412	−0.79267	0.373742
1f	1.46407	—	—	—	—	0.005	−0.651287	0.527111	−0.372530	–	1.33902	−0.96649	0.372530
2a	1.45787	1.33206	1.47004	—	—	0.124	−0.634157	0.475405	−0.476254	0.460824	−0.597977	0.613407	0.015430
2b	1.45741	1.33253	1.46846	—	—	0.087	−0.636536	0.476209	−0.480981	0.452268	−0.103819	0.132532	0.028713
2c	1.45702	1.33277	1.46696	—	—	0.061	−0.638685	0.477764	−0.482763	0.448833	1.14677	−1.11284	0.033930
2d	1.45689	1.33296	1.46657	—	—	0.057	−0.639385	0.477788	−0.484761	0.442713	1.203818	−1.16177	0.042048
2e	1.45573	1.33432	1.46368	—	—	0.013	−0.645249	0.479606	−0.496929	0.408469	0.88264	−0.79418	0.088460
2f	1.45569	1.33441	1.46329	—	—	0.082	−0.645379	0.479521	−0.497574	0.409746	1.053848	−0.96602	0.087828
3a	1.45595	1.33424	1.45337	1.33513	1.47078	7.268	−0.630799	0.471982	−0.476451	0.501869	−0.635576	0.610158	−0.025418
3b	1.45571	1.33448	1.45297	1.33554	1.46937	0.543	−0.632171	0.472379	−0.479374	0.487239	−0.136768	0.128903	−0.007865
3c	1.45565	1.33450	1.45280	1.33563	1.46840	0.047	−0.632606	0.472677	−0.479787	0.485397	1.11176	−1.11737	−0.005610
3d	1.45556	1.33461	1.45267	1.33580	1.46800	0.028	−0.633188	0.472763	−0.481275	0.476568	1.171247	−1.16654	0.004707
3e	1.45498	1.33525	1.45166	1.33696	1.46548	0.015	−0.636524	0.476349	−0.480524	0.430194	0.84756	−0.79723	0.050330
3f	1.45494	1.33532	1.45156	1.33708	1.46498	0.015	−0.636728	0.473629	−0.489296	0.430143	1.028403	−0.96925	0.059153

[a] Bond lengths (Å).
[b] Dihedral angle (°) between triazine and phenyl groups (<1-2-1′–2′).
[c] Atomic charge of N on triazine.
[d] Atomic charge of C on triazine.
[e] Total charge of triazine.
[f] Total charge of the spacer.
[g] Total charge of the phenyl group.

Table 2. Hammett σ^+, llβll, HOMO–LUMO energy gap (ΔE) and BLA of triazine derivatives

			1 ($n=0$)		**2** ($n=1$)			**3** ($n=2$)		
	R	σ^{+a}_{gas}	llβll[b]	ΔE[c]	llβll[b]	BLA[d]	ΔE[c]	llβll[b]	BLA[d]	ΔE[c]
a	H	0.00	14.3	0.39042	33.0	0.13189	0.35607	59.3	0.12534	0.33210
b	CH_3	0.33	21.3	0.38404	43.6	0.13040	0.35193	74.1	0.12434	0.32869
c	OH	−0.55	25.9	0.37889	50.1	0.12922	0.34836	82.4	0.12388	0.32618
d	OCH_3	−0.80	29.6	0.38192	56.1	0.12877	0.35034	91.0	0.12354	0.32769
e	NH_2	−1.19	41.1	0.36653	75.6	0.12538	0.33739	120	0.12127	0.31653
f	$N(CH_3)_2$	−1.73	53.6	0.35779	93.3	0.12508	0.33091	143	0.12099	0.31186

[a] Substituent constants in gas phase.[9b]
[b] 10^{-30} esu.
[c] $\Delta E = E_{Lumo} - E_{Homo}$ (a.u.).
[d] $(r1 + r3)/2 - r2$ for **2**, $(r1 + r3 + r5)/3 - (r2 + r4)/2$ for **3**.

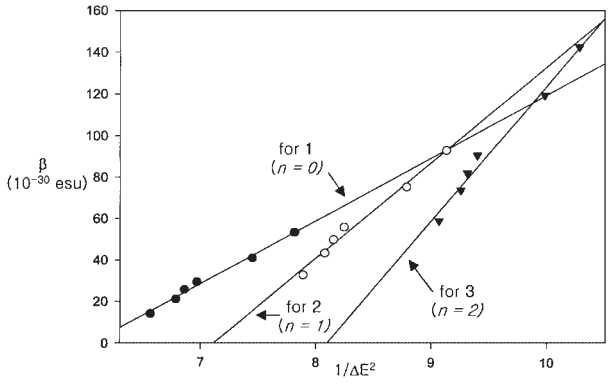

Figure 1. Plots of β against $1/\Delta E^2$: (•) **1**; (○) **2**; (▼) **3**

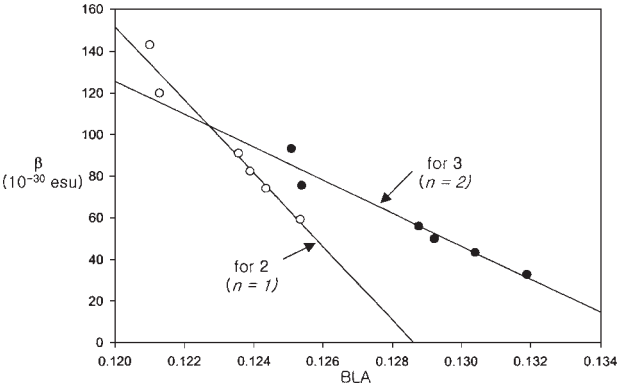

Figure 2. Plots of β against BLA: (•) **2**; (○) **3**

excited states, ω_{01} is the CT energy and ω is the energy of the incident laser light.[2a]

Table 2 shows that the first hyperpolarizability values of **1–3** are in the range $(14–143) \times 10^{-30}$ esu. The β values of **1–3** increase with a stronger donor and increased conjugation length. Figure 1 shows that the plots of β of **1–3** against $1/\Delta E^2$ are linear, as predicted by Eqn (1). The excellent linearity in these plots indicates that μ_{01}, μ_{12} and the resonance correction term in Eqn (1) are more or less the same in this series of compounds. In addition, the slope of the plot increases with the conjugation length, apparently because of the smaller ΔE for more extended molecule (Table 2). Similar straight lines are also obtained when the β values of **2** and **3** are plotted against BLA (Fig. 2). It is well established that the β value of a dipolar molecule increases until it reaches a maximum value and then decreases as the BLA decreases from a large positive value towards a negative value.[10] On the other hand, the β values of octupolar molecules have been shown to increase gradually with change in the BLA.[4a] Hence the linear relationship between β and BLA observed for triazine derivatives is not without precedent. Moreover, the slope of this plot is much steeper when $n = 2$ than when $n = 1$, owing to the smaller differences between the BLA of **3a–f** than of **2a–f** (Table 2). This result underlines the importance of increasing the conjugation length to design two-dimensional octupoles with large β values in this series of compounds.

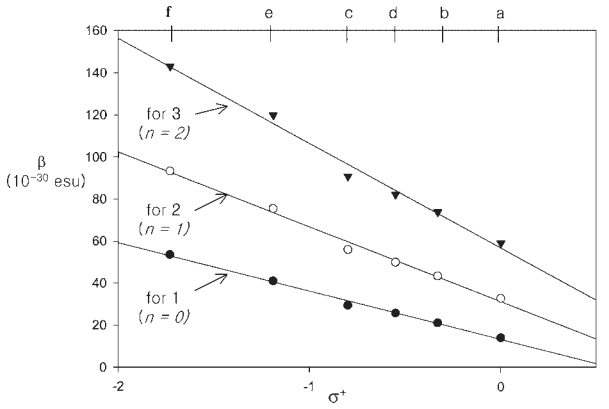

Figure 3. Plots of β against gas-phase substituent constants (σ^+_{gas}) (•) **1**; (○) **2**; (▼) **3**

Recently, we reported[4b] that the β values of crystal violet derivatives could be correlated with the Hammett equation by using the Brown–Okamoto constants (σ^+).[9a] Similarly, excellent linearity is observed in the plots of β against gas-phase substituent constants (σ^+_{gas}) for **1–3** (Fig. 3). Interestingly, the σ^+_{gas} values show a better correlation with the β values than the Brown–Okamoto constants in the Hammett plots (plots not shown). As stated above, the first hyperpolarizability of the two-dimensional octupole is inversely proportional to the CT energy [Eqn (1)].[2a] It is also found that the CT

energy decreases gradually with a stronger donor (Table 2). Since the σ^{+}_{gas} values are a measure of the electron-donating ability of the aryl substituent, the linear relationship between β and σ^{+}_{gas} is not unexpected. Moreover, the slope of the plot increases with the conjugation length (**1** < **2** < **3**), as observed in Figs 1 and 2, i.e. the longer the conjugation length, the more pronounced the substituent effect becomes.

As stated above, BLA has been extensively employed to explain the structure–NLO property relationship, because it is a qualitative measure of the extent of charge transfer. Also, BLA can be quantitatively determined by x-ray crystallography or calculated by using the *ab initio* method. However, both methods require significant effort. On the other hand, σ^{+}_{gas} values are readily available in the literature and familiar to most chemists.[9b] The results presented in this paper provide additional evidence that σ^{+}_{gas} values can be used in place of BLA to explain the structure–NLO property relationship.

CONCLUSION

We have studied the first hyperpolarizability of the triazine derivatives by the *ab initio* method. All of the derivatives are planar and show significant β values. The first hyperpolarizabilities of these molecules increase with a stronger donor and increased conjugation length. The susceptibility of β to the donor strength is larger for a more elongated substrate. Noteworthy is the excellent linear relationship between β and BLA and also σ^{+}_{gas}. This result may serve as a useful guideline for the design of two-dimensional octupoles with large first hyperpolarizability.

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