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First hyperpolarizabilities of 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives: *ab initio* studies and Hammett correlation

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ABSTRACT: First hyperpolarizabilities (β) of the 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives were studied by an *ab initio* method (HF/6–31G). The β values of these molecules increase with increase in donor strength, reaching a maximum value of 262×10^{-30} esu with an oxyanion as the donor. Also, the electronic charge is more delocalized, and the HOMO–LUMO energy gap (ΔE) and the bond length alternation (BLA) decrease with the same variation of the donor. Noteworthy is the excellent linear relationship between β and $1/\Delta E^2$ and $\sigma_{\mathrm{gas}}{}^{+}$. These results 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; first hyperpolarizabilities; *ab initio*; Hammett correlation

INTRODUCTION

There is substantial research effort into the design and synthesis of organic materials exhibiting a large second-order non-linear optical (NLO) response because of their potential application in telecommunications, optical computing and optical signal processing.[1] Applications of such materials require a large second-order non-linear optical property and thermal stability. Much effort has been focused on optimizing the physical properties of donor–acceptor dipoles to meet these criteria. Recently, octupolar molecules with threefold symmetry have been developed as alternative NLO chromophores.[2–4] An advantage of such molecules in comparison with the more conventional dipolar molecules is that the second harmonic response of octupoles does not depend on the polarization of the incident light because they are more isotropic than dipolar NLO molecules.[2d] Moreover, two-dimensional octupoles favor the formation of non-centrosymmetric crystals, which is important for practical applications.[5] In this context, various derivatives of subphthalocyanine, 1,3,5-trinitro-2,4,6-tris(styryl)benzene, 1,3,5-tricyano-2,4,6-tris(styryl)benzene, 1,3,5-tricyano-2,4,6-tris(ethynyl)-benzene, triphenylamine and truxenone derivatives have been synthesized and their structure–property relationships have been investigated.[2–4]

Recently, we reported a theoretical study on the first hyperpolarizability (β) of a series of triazine derivatives.[6] The β values of these molecules increased with increase in donor strength and increased conjugation length. Noteworthy was the excellent linear relationship between β and bond length alternation (BLA) and $\sigma_{\mathrm{gas}}{}^{+}$. These results suggest an interesting possibility that $\sigma_{\mathrm{gas}}{}^{+}$ values can be used in place of BLA to explain the structure–NLO property relationship.

In this work, we studied the first hyperpolarizabilities of 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives **A**–**G** by an *ab initio* method. In these molecules, the acceptor is CN and the donors are the *para*-substituent (X) at the peripheral phenyl groups, which are linked by the styryl moieties. This series of compounds is of particular interest because the experimental values of β for MeO (**D**) and NEt_2 derivatives have been reported.[3c] Moreover, the latter has been shown to produce non-centrosymmetric crystals with large $\chi^{(2)}$. We calculated the β, BLA, and HOMO–LUMO energy gap (ΔE) of these molecules and compared them with the geometric parameters. The main objectives of this research were (i) to provide a detailed understanding of the substituent effect on the β values, (ii) to assess whether the linear relationship between β and $\sigma_{\mathrm{gas}}{}^{+}$ reported for the triazine

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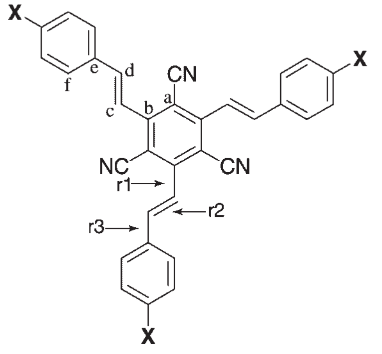
derivatives is general for octupolar molecules and (iii) to find a new donor for the octupoles with very large β.



A: **X** = -H
B: -CH$_3$
C: -OH
D: -OCH$_3$
E: -NH$_2$,
F: -NMe$_2$
G: -O$^-$

RESULTS AND DISCUSSION

Structures of A–G

The structures of **A**–**G** were fully optimized at the Hartree–Fock level using the 6–31G basis set in the Gaussian 98 program.[7] Table 1 summarizes the bond lengths, dihedral angles and charge densities of **A**–**G**. The dihedral angles ($d1$) between the central phenyl group and the C═C bond are in the range 33–45 °, whereas those between the peripheral phenyl and the latter range from 0 to 24 °. For comparison, the corresponding angles for the 2,4,6-tris-(styryl)-1,3,5-triazine derivatives, where the steric effect is expected to be negligible, are nearly zero.[6] This indicates that the structures of **A**–**G** are significantly distorted and the distortion is more pronounced in the core, probably because the C═C bonds have more severe steric interaction with the CN than with the phenyl group at the periphery. As the donor is changed to a stronger one, $d1$ remains relatively constant, whereas $d2$ decreases, i.e. a stronger donor increases the planarity where the steric effect is less important. Moreover, the lengths of the single bonds ($r1$, $r3$) decrease and that of the double bond ($r2$) increases with increase in donor strength (Table 1). Consequently, the BLA calculated by subtracting the average double bond length from that of a single bond, i.e. $(r1 + r3)/2 - r2$ decreases in the same order (Table 2). Interestingly, the BLA of **A**–**F** are larger than those for the triazine derivatives, despite the greater extent of charge transfer (CT) (see below).[6] This can be attributed to their distorted structures (see above).

The Mulliken charge density for **A**–**F** reveals that the negative charge is delocalized on the tricyanophenyl group ($Z_{3CN\text{-}Ph}$), whereas the positive charge is on the C═C bond (Z_{CHCH}) and peripheral aryl group ($Z_{Ar\text{-}X}$). This indicates a significant CT from the peripheral styryl to the tricyanophenyl group in the core. When the donor is changed to a stronger one, Z_{CN} decreases significantly and Z_{Ph} increases slightly. Also, the sum of these two, i.e. $Z_{3CN\text{-}Ph} = 3Z_{CN} + Z_{Ph}$, and Z_{CHCH} decrease simultaneously. On the other hand, the total charge density at the ArX group, i.e. $3Z_{Ar\text{-}X} = 3Z_{Ar} + 3Z_X$, of **A**–**F** increases gradually with the same variation of the donor, although no clear trend is evident in Z_{Ar} and Z_x. The results indicate that more electronic charge is shifted from the ArX to the tricyanophenyl and C═C groups as the donor is changed to a stronger one. It should be noted that the large negative charge at the ArX of **G** is not an anomaly but occurs because the donor is an oxyanion; hence the same explanation can be applied. Moreover, the extent of CT from the donor to the acceptor in **A**–**F** is much larger than observed in the triazine derivatives, apparently because of the much stronger acceptors in the former. Finally, ΔE decreases with increase in donor strength. It appears that the more delocalized the electronic charge is, the smaller ΔE and BLA become in this series of compounds. Similar results were observed for the triazine derivatives, except that ΔE was somewhat larger.[6]

Table 1. Structural properties of **A**–**G**

Compound	$r1^{a}$	$r2^{a}$	$r3^{a}$	$d1^{b}$	$d2^{c}$	$3Z_{CN}{}^{d}$	$Z_{Ph}{}^{e}$	$Z_{3CN\text{-}Ph}{}^{f}$	$3Z_{CHCH}{}^{g}$	$3Z_{Ar}{}^{h}$	$3Z_{X}{}^{i}$	$3Z_{Ar\text{-}X}{}^{j}$
A	1.47776	1.33091	1.47348	45.49	−24.07	−0.72195	−0.05722	−0.77917	0.72557	−0.56682	0.62043	0.05361
B	1.47722	1.33158	1.47165	44.95	−21.31	−0.72996	−0.05681	−0.78677	0.71628	−0.07279	0.14328	0.07049
C	1.47684	1.33185	1.47051	44.78	−21.88	−0.73424	−0.05274	−0.78698	0.71729	1.17593	−1.10623	0.0697
D	1.47669	1.33204	1.47024	44.72	−21.83	−0.73676	−0.05358	−0.79034	0.71202	1.23168	−1.15346	0.07822
E	1.4751	1.33402	1.46584	43.18	−15.39	−0.75931	−0.05174	−0.81105	0.67166	0.92153	−0.78220	0.13933
F	1.47493	1.33423	1.46527	43.05	−14.32	−0.76075	−0.05229	−0.81304	0.67108	1.09147	−0.94953	0.14194
G	1.46329	1.35253	1.44145	33.68	0.30	−0.94391	−0.02253	−0.96644	0.33529	0.06747	−2.43632	−2.36885

[a] Bond lengths (Å).
[b] Dihedral angle (°) between tricyanophenyl and vinyl groups (∠a–b–c–d).
[c] Dihedral angle (°) between vinyl and peripheral aryl groups (∠c–d–e–f).
[d] Total atomic charge on the tricyano groups.
[e] Atomic charge on the central phenyl group.
[f] Total atomic charge on the tricyanophenyl group in the core ($Z_{3CN\text{-}Ph} = 3Z_{CN} + Z_{Ph}$).
[g] Total atomic charge on the three vinyl groups.
[h] Total atomic charge on the three aryl groups at the periphery.
[i] Total atomic charge on the three aryl substituents at the periphery.
[j] Total atomic charge on the three ArX groups at the periphery ($3Z_{Ar\text{-}X} = 3Z_{Ar} + 3Z_X$).

Table 2. Hammett σ^+, $||\beta||$, HOMO–LUMO energy gap (ΔE) and BLA of **A**–**G**

Compound	X	$\sigma_{gas}{}^{+a}$	$\vert\vert\beta\vert\vert^b$	BLA[c]	ΔE^d
A	H	0.00	27.7	0.14471	0.347
B	CH_3	−0.33	38.3	0.14286	0.341
C	OH	−0.55	44.4	0.14183	0.338
D	OCH_3	−0.80	49.5	0.14143	0.335
E	NH_2	−1.19	74.3	0.13645	0.320
F	$N(CH_3)_2$	−1.73	93.5	0.13587	0.314
G	O^-	−2.3[e]	262	0.12714	0.271

[a] Substituent constants in gas phase.[10b]

[b] 10^{-30} esu.

[c] $(r1+r3)/2-r2$.

[d] $\Delta E = E_{LUMO}-E_{HOMO}$ (a.u.).

[e] Brown–Okamoto constants.[10a]

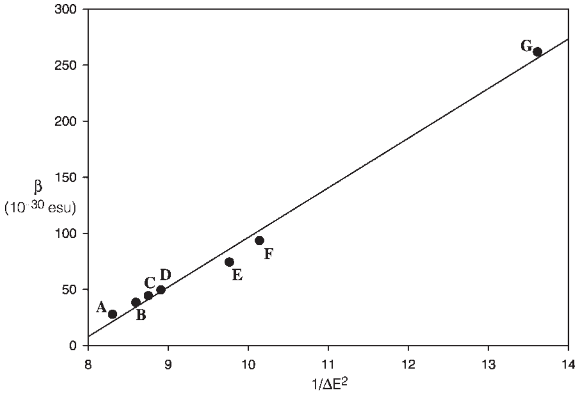


Figure 1. Plot of β against $1/\Delta E^2$

First hyperpolarizability

The first hyperpolarizabilities of **A**–**G** were calculated by using the following relationships:[8]

$$||\beta|| = (||\beta_{J=1}||^2 + ||\beta_{J=3}||^2)^{1/2}$$

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

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

The tensor components of the static first hyperpolarizabilities were calculated analytically by using the coupled perturbed Hartree–Fock (CPHF) method.[9] The calculated $||\beta||$ values for **A**–**G** are summarized in Table 2.

The first hyperpolarizability of a D_3 symmetric molecule can be expressed by the 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 state and degenerate first excited CT state, μ_{12} is the transition moment connecting these degenerate excited states, ω_{01} is the CT energy and ω is the energy of the incident laser light.[2a]

Table 1 shows that the β values of **A**–**G** increase monotonically with increase in donor strength, reaching a maximum value of 262×10^{-30} esu. For comparison, the experimental values of $\beta(0)$ for **D** and the NEt_2 derivative are 14×10^{-30} and 65×10^{-30} esu, respectively.[3c] Although the absolute values are significantly different from the theoretical result, the trend is consistent. In addition, the β values of **A**–**F** are smaller than those of the triazine derivatives, despite the smaller ΔE and greater extent of CT (see above).[6] This result underlines the importance of planarity in determining β.

Figure 1 shows that the plots of β of **A**–**G** vs $1/\Delta E^2$ are linear. 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. As expected, β increases gradually as BLA decreases (Fig. 2). The non-linear relationship between β and BLA is not without precedent. In the case of dipolar NLO molecules, β first increases until it reaches a maximum and then decreases as BLA decreases.[1c] For crystal violet derivatives, the plot of β vs BLA was found to be a curve. Hence the straight line observed in the plot of β vs BLA for triazine derivatives[6] seems to be an exception and can be attributed to the fact that the difference in BLA is very small (0.00681 for triazine vs 0.01757 for **A**–**G**). Whatever might be the explanation, this provides additional support for the previous conclusion that the β value of an octupolar molecule increases as BLA decreases.[4a]

Figure 3 shows plots of β against gas-phase substituent constants ($\sigma_{gas}{}^+$).[4b,10b] The plot is linear with an excellent correlation, if **G** is excluded. Although the corresponding plots for the triazine derivatives did not show any deviation this was because the oxyanion was not included.[6] The large positive deviation for **G** could be

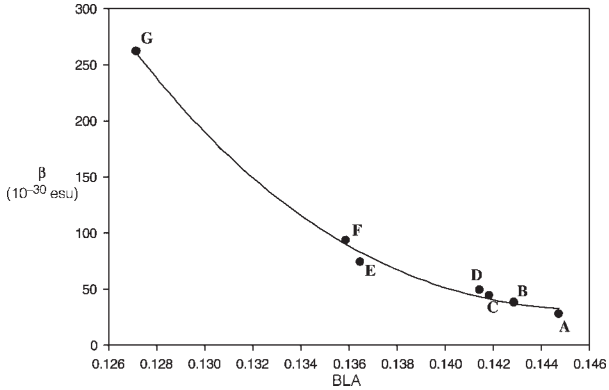


Figure 2. Plot of β against bond length alternation (BLA)

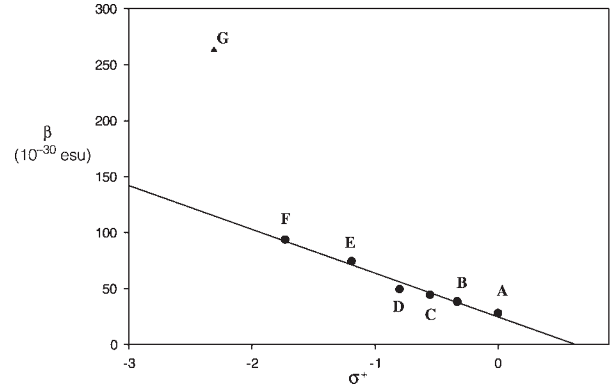


Figure 3. Plot of β against substituent constants (σ^+). The data for **G** are not included in the plot

explained if $\sigma_{\text{gas}}{}^+$ for the oxyanion is much larger than the Brown–Okamoto constant (σ^+).[10a] Note that we have used σ^+ in the Hammett plot because $\sigma_{\text{gas}}{}^+$ for the oxyanion is not available in the literature. Since the oxyanion cannot be stabilized by solvation in the gas phase, more charge density would be shifted to the electron-deficient center. The net result of this effect would be to increase the electron-donating ability of the oxyanion much more in the gas phase ($\sigma_{\text{gas}}{}^+$) than in solution (σ^+). Also, this may be why the β value of **G** is approximately three times larger than **F**, despite the modest difference in the σ^+ values.[10a] Consistently, the structural parameters including the dihedral angle, extents of CT, BLA and ΔE show remarkable changes from **F** to **G**. Finally, this suggests an interesting possibility that octupolar molecules with very large β could be designed by using the oxyanion as the donor.

We have previously reported that the β values of crystal violet and triazine derivatives could be correlated with σ^+ and $\sigma_{\text{gas}}{}^+$ values.[4b,6] The excellent linearity in Fig. 3 provides additional evidence that the structure–NLO property relationship of octupolar molecules could be explained with the Hammett equation. Considering that the Hammett substituent constants are readily available in the literature, the use of the substituent constants would significantly facilitate the design of octupolar molecules with large first hyperpolarizabilities.

CONCLUSION

We have studied the first hyperpolarizabilities of the 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives **A**–**G** by an *ab initio* method. The first hyperpolarizabilities of **A**–**G** increase with increase in donor strength and as BLA decreases. An excellent linear relationship is observed between β and $1/\Delta E^2$ and $\sigma_{\text{gas}}{}^+$. In addition, it is found that the oxyanion is an unusually strong donor. This result may provide a useful design strategy for the synthesis of two-dimensional octupoles with very large first hyperpolarizabilities.

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