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Chromophore Environmental Effects in Saltlike Nonlinear Optical Materials. A Computational Study of Architecture/Anion Second-Order Response Relationships in High-β Stilbazolium Self-Assembled Films

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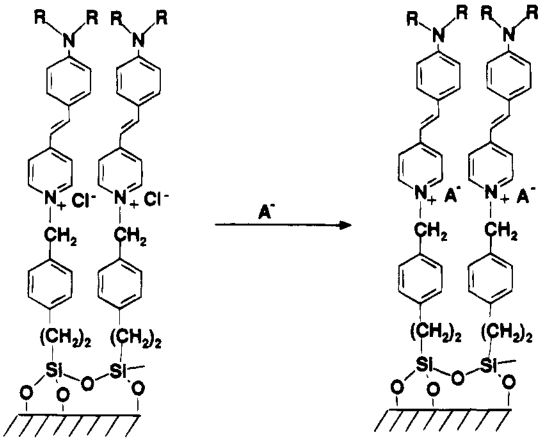
The very large cation–anion environmental effects on second-order nonlinear optical response observed in self-assembled stilbazolium monolayer ion-exchange experiments are investigated theoretically using the ZINDO/SOS quantum chemical formalism. Ion pairs consisting of the 4′-(dimethylamino)-*N*-methyl-4-stilbazolium cation with chloride, iodide, and *p*-aminobenzenesulfonate counteranions in differing mutual orientations, are examined as models to relate calculated ion pair hyperpolarizabilities to anion-exchange-induced changes in macroscopic linear optical and nonlinear optical response. Calculated hyperpolarizabilities depend strongly on the relative cation–anion packing configuration. In accord with anion exchange experiments, enhancements of the second-order nonlinear optical response on passing from Cl^- to I^- and *p*-aminobenzenesulfonate can be related to likely displacement of the bulkier I^- and *p*-aminobenzenesulfonate anions from more closely packed structural arrangements originally produced as a consequence of the self-assembly process.

Introduction

Intrisically acentric self-assembled multilayers containing high-hyperpolarizability stilbazolium chromophores (Scheme 1)[1] represent an alternative approach to poled polymers and Langmuir–Blodgett films for the construction of robust, highly efficient second-order nonlinear optical (NLO) materials.[2,3] The saltlike nature of the chromophoric constituents in these multilayer materials affords an unusual opportunity to tailor the microstructural architecture and optical properties by ion exchange (metathesis) of the stilbazolium counteranion (A^- in Scheme 1) using anions of varying size, shape, and hyperpolarizability. It has been demonstrated[4] that the chloride counterion in such self-assembled monolayers is accessible to exchange (~60%) with anions such as iodide, *p*-aminobenzenesulfonate (TS^-), and ethyl orange. Moreover, polarized second harmonic generation (SHG) measurements (at 1064 nm) reveal ion-exchange-induced increases in second-order NLO response, $\chi^{(2)}_{zzz}$, of +34%, +25%, and +44% for I^-, TS^-, and ethyl orange, respectively, without significant changes in the average chromophore tilt angle with respect to the surface normal.[4] It is therefore unlikely

Scheme 1



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that the observed $\chi^{(2)}_{zzz}$ enhancements result from stilbazolium orientational reorganization effects. Rather, they must reflect changes in chromophore local environment,[5] i.e., changes in specific chromophore cation–anion interactions.

Such poorly understood NLO "salt effects", first noted by Meredith,[6] are doubtless operative in high-$\chi^{(2)}_{zzz}$ stilbazolium-containing Langmuir–Blodgett films[7] and in numerous NLO-active acentric, saltlike crystal structures.[8,9] The observed NLO response of the latter systems is known to be strongly dependent on the cation–anion packing motif and the nature of the exchangeable anion.[8,9] However, the relative NLO contributions of packing architecture and anion identity to the macroscopic $\chi^{(2)}_{zzz}$ response cannot be unambiguously disentangled using the experimental data at hand and are thus not well-understood.

In this context, it would be of fundamental interest to explore theoretically the dependence of NLO response in chromophoric ion pairs to changing the nature and packing arrangement of the constituent species. In this contribution, we present a theoretical analysis, using the proven ZINDO/SOS quantum chemical formalism,[5,10–12] of NLO-active chromophoric stilbazolium cation–anion pair systems as a function of packing architecture and counteranion characteristics (Figure 1). The 4′-(dimethylamino)-*N*-methyl-4-stilbazolium cation (SBZ^+) has been selected as a model to relate the calculated molecular hyperpolarizability tensor to NLO response in sequentially varied self-assembled chromophore structures. The results are then discussed in the context of recently acquired experimental SHG/ion exchange data.[4]

Theoretical Methods

The all-valence INDO/S (intermediate neglect of differential overlap) method,[13] in connection with the sum-over excited particle–hole–states (SOS) formalism,[14] was employed. Details of the computationally-efficient ZINDO-SOS-based method for describing second-order molecular optical nonlinearities have been reported elsewhere.[10] The INDO/S model has been successfully used for the description of molecular linear[13] and nonlinear[10,11] optical responses as well as for the linear and nonlinear optical properties of various intermolecular interactions,[5,12,15] including those involving charged chromophores.[10a] Moreover, the use of Slater orbitals renders the formalism appropriate for describing long-range interactions. Standard parameters and basis functions were used. In the present approach, the closed-shell restricted Hartree–Fock formalism was adopted, and the monoexcited configuration interaction (MECI) approximation was employed to describe the excited states. In all calculations, the lowest 180 energy transitions between SCF and MECI electronic configurations were chosen to undergo CI mixing and were included in the SOS. This SOS truncation was found to be sufficient for a complete convergence of the second-order response in all cases considered.

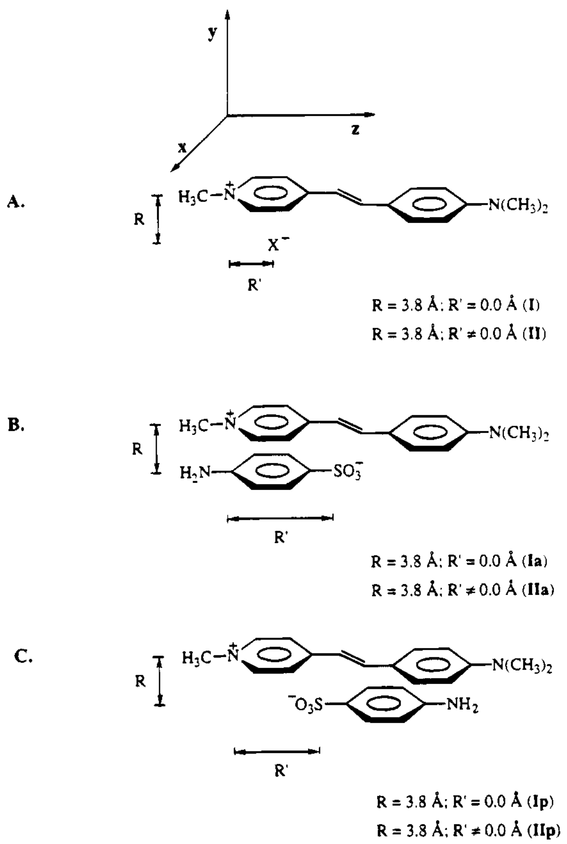

Figure 1. Molecular geometries of SBZ^+ (4′-(dimethylamino)-*N*-methyl-4-stilbazolium) chromophore ion pairs with halides (X^-) and the *p*-aminobenzenesulfonate (TS^-) anion examined computationally: (A) SBZ^+X^- (X^- = Cl, I); (B) SBZ^+TS^- in antiparallel arrangement; (C) SBZ^+TS^- in parallel arrangement.

In the case of the SBZ^+I^- ion pair and, in general, for SBZ^+–halide distances smaller than 3.8 Å, the calculations indicate that chromophore–anion interactions give rise to very weak (oscillator strengths

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smaller than 0.04) low energy intermolecular halide → chromophore charge-transfer (CT) transitions (in the 500–1000 nm region), analogous to those observed in electron donor–acceptor complexes.[12,16] As a consequence, spurious resonant enhancement of hyperpolarizability values (less than 10% of the total hyperpolarizability) is predicted for some laser input frequencies at these energies. In those cases, the calculated hyperpolarizability values were corrected, for each laser frequency, by removing the two-level contributions associated with these low energy CT transitions (eq 1, vide infra).

Molecular and Ion Pair Geometries

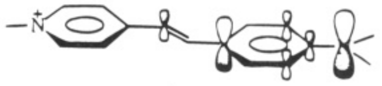
Metrical parameters for calculations on SBZ^+X^- (X = Cl, I) and SBZ^+TS^- ion pairs were taken from published crystallographic data,[8,17,18] assuming a planar SBZ^+ geometry. Several cation–anion packing arrangements were considered (Figure 1). In the case of halide salts (Figure 1A), the anion was first placed above the SBZ ring (**I**). Starting from this structure and holding the $SZB^+ \cdots X^-$ (R) distance fixed at 3.8 Å, a number of configurations (**II**) were generated by translation (R′) of the anion along the z axis. For the SZB^+TS^- ion pair, two different cofacial structures were considered. In the first (Figure 1B), the SZB^+ and TS^- molecular dipoles (μ_z is the principal vector component) are in an antiparallel (**a**) arrangement and, starting from a $N^+ \cdots SO_3^-$ (TS^-) superimposed structure (**Ia**), a number of slipped conformations (**IIa**) were generated by translation (R′) of the anion along the z axis. In the second configuration (Figure 1C), parallel (**p**) arrangements of SZB^+ and TS^- molecular dipoles were investigated. In analogy to arrangement **a**, conformations **Ip** and **IIp** were generated.

Results and Discussion

4′-(Dimethylamino)-*N*-methyl-4-stilbazolium Ion. The calculated second-order hyperpolarizability, β_{zzz} (where β_{zzz} is the dominant tensor component along the molecular CT axis), of the isolated SBZ^+ chromophore is 778×10^{-30} cm^5 esu^{-1} at $\hbar\omega = 1.17$ eV. Within the framework of the two-state model (eq 1),[2] the NLO

$$\beta_t = \frac{3e^2}{2}\,\frac{\hbar\omega_{ge} f \Delta\mu_{ge}}{[(\hbar\omega_{ge})^2 - (\hbar\omega)^2][(\hbar\omega_{ge})^2 - (2\hbar\omega)^2]} \qquad (1)$$

response may be related to the nature of the frontier molecular orbitals (MOs) involved in the two-state process in terms of the energy, $\hbar\omega_{ge}$, oscillator strength, f, and dipole moment change, $\Delta\mu_{ge}$, associated with the lowest CT optical transition. The SBZ^+ chromophore possesses a strong ($f = 1.12$) low-energy CT transition ($\lambda_{max} = 472$ nm) accompanied by a strong dipole moment variation between the ground and excited state ($\Delta\mu_{ge} = 17$ D). Analysis of the mixing coefficients of the CI expansion indicates that the HOMO and LUMO orbitals are mainly involved in the transition. As expected, the HOMO (**1**) is principally localized on both the nitrogen atom of the donor ($N(CH_3)_2$) group and over the adjacent aromatic ring. The LUMO (**2**) is essentially localized over the pyridinium acceptor ring. Moreover, the positive charge of the SZB^+ ion is localized primarily (51%) on the pyridinium ring, thus leading to a low energy LUMO and, hence, resulting in a low-energy CT transition.



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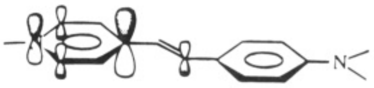

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Chromophoric 4′-(Dimethylamino)-*N*-methyl-4-stilbazolium Cation–Anion Pairs. We first consider SZB^+X^- salts with the goal being to understand how cation–anion orientations influence the SZB^+ NLO response. The crystal structure of SZB^+I^- consists[17] of stacked chromophoric layers in which the iodide anion lies above the plane of the pyridinium ring with a $N^+ \cdots I^-$ distance of 3.82 Å, representing the shortest crystallographic contact between the iodide and non-hydrogen atoms. This result, when contrasted with structural data on related pyridinium halide salts,[19] indicates that a wide variety of SZB^+ cation–anion packing motifs should be possible. This diversity therefore suggests that the relatively “flexible” molecular architecture of the self-assembled layers can readily accommodate different packing arrangements of the counteranion and, hence, different chromophore–anion interactions as the size and shape of the anion are varied. In the present investigation, we consider packing arrangements in which the halide anion lies above the SBZ^+ ring plane (Figure 1A).[20]

We initially consider the SZB^+Cl^- ion pair. When the Cl^- anion is first placed 3.8 Å above the stilbazolium chromophore (structure **I**), the charge polarization within the pyridinium ring is enhanced by ~60%, resulting in a combined energetic stabilization of the bonding and destabilization of related antibonding (including the LUMO) MOs associated with the pyridinium ring. Therefore, the formation of the neutral ion pair is accompanied by a blue-shift (versus the isolated SBZ^+ chromophore) of the lowest energy CT transition ($\lambda_{max} = 397$ nm) and, hence, a diminution of β_{zzz} (159×10^{-30} cm^5 esu^{-1} at $\hbar\omega = 1.17$ eV).[21]

Translation of the Cl^- anion along the y axis (structure **I**, $R = 3.8 \pm 0.5$ Å) results in sizable changes

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[16] (a) Although no intermolecular (halide → chromophore) CT transitions have been detected in the present self-assembled stilbazolium films,[1] simpler pyridinium iodide salts, in which the positive charge is strongly localized on the pyridinium nitrogen atom, are classically considered to be electron donor–acceptor (or charge-transfer) complexes.[16b,c] (b) See, for example: Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: New York, 1969; Chapter 3. (c) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Dekker, Inc.: New York, 1979; Chapter 6.

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[20] Calculations in which the halide lies coplanar with the molecular ring indicate generally smaller hyperpolarizability values. For example, calculated hyperpolarizability values for SZB^+Cl^- (Cl^- in-plane; $R = 3.8$ Å) are ~20% smaller than those calculated for structure **I** (Table 1).

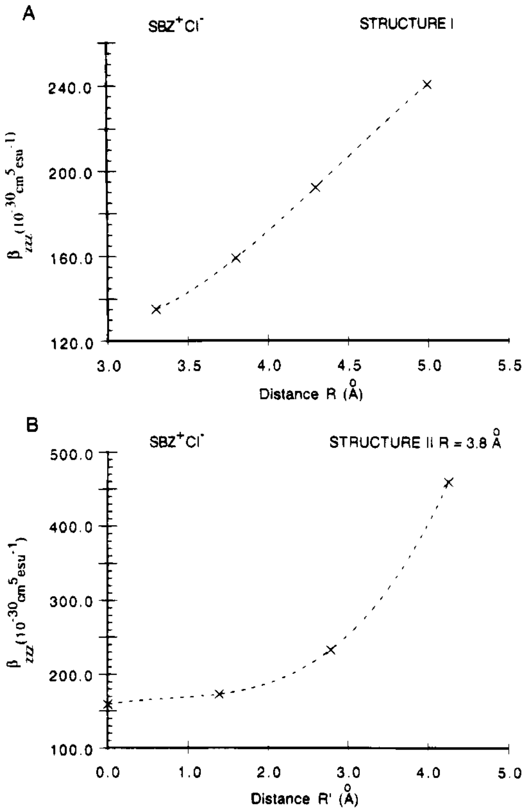

Figure 2. Variation of the calculated β_{zzz} hyperpolarizability tensor component ($\hbar\omega$ = 1.17 eV) with (A) R coordinate, (B) R' coordinate, in the SBZ$^+$Cl$^-$ ion pair.

Table 1. Computed Dipole Moment, Linear Optical Spectroscopic, and Nonlinear Optical Properties[a] of SBZ$^+$–Halide and *p*-Aminobenzenesulfonate Ion Pairs

		Cl$^-$ (R = 3.8 Å)	
R' (Å)[b]	0.0	1.39	2.78
μ_z (D)	8.8	2.6	−3.2
λ_{max} (nm)	397	401	417
$\Delta\mu_{ge}$ (D)	15.3	15.6	16.1
β_{zzz} (0.65)	68	74	88
β_{zzz} (1.17)	159	173	233
		I^- (R = 3.8 Å)	
R (Å)[b]	0.0	1.39	2.78
μ_z (D)	8.7	2.6	−3.1
λ_{max} (nm)	397	400	417
$\Delta\mu_{ge}$ (D)	15.2	15.6	15.8
β_{zzz} (0.65)[c]	80	83	85
β_{zzz} (1.17)[c]	173	195	224
		TS$^-$ (Structure **a**, R = 3.8 Å)	
R' (Å)[b]	0.0	1.39	2.78
μ_z (D)	2.3	−3.3	−8.7
λ_{max} (nm)	390	403	424
$\Delta\mu_{ge}$ (D)	14.4	13.1	15.3
β_{zzz} (0.65)	63	73	98
β_{zzz} (1.17)	140	174	275
		TS$^-$ (Structure **p**, R = 3.8 Å)	
R' (Å)[b]	0.0	1.39	2.78
μ_z (D)	14.2	7.9	2.2
λ_{max} (nm)	400	397	405
$\Delta\mu_{ge}$ (D)	12.9	11.2	13.1
β_{zzz} (0.65)	56	57	66
β_{zzz} (1.17)	124	120	155

[a] All hyperpolarizability data are in units of 10^{-30} cm^5 esu^{-1}. [b] The 1.39 and 2.78 Å (R') distances correspond to the position of the X$^-$ or TS$^-$ anion atoms over the centroid of the pyridinium ring and over the C(1) carbon atom, respectively. [c] Hyperpolarizability values corrected for contributions due to intermolecular CT transitions (see text).

(±17%) in the calculated hyperpolarizability (Figure 2A). This effect can be associated with the shift of the lowest energy CT transition (±10 nm) due to differing polarization (induced by the anion) of the positive charge delocalized over the pyridinium ring. In particular, greater β_{zzz} values are associated with larger z-axis displacements (red-shifts of the CT transition) and vice versa. The greatest increases in β_{zzz} values (Table 1, Figure 2B) are associated with the displacement (R') of the chloride anion from the pyridinium acceptor portion of the chromophore toward the donor $-N(CH_3)_2$ group, along the z (CT) axis (structure **II**). This is a consequence of increased $\Delta\mu_{ge}$ values (due to the reduced ground-state dipole moment, μ_z, along the CT axis) and red-shifting of the lowest energy CT transition (due to the reduced energy gap between the relevant MOs). The largest (resonant) β_{zzz} values are associated with the configuration in which the chloride anion closely approaches the $-N(CH_3)_2$ donor substituent ($R' \geq 4.25$ Å).

Calculations on the SBZ$^+$I$^-$ ion pair provide similar results in terms of calculated λ_{max}, $\Delta\mu_{ge}$, and β_{zzz} values, once similar cation–anion spatial arrangements are adopted (Table 1). The present results and the experimental ion-exchange data therefore argue that[4] the observed increase in $\chi^{(2)}_{zzz}$ values upon exchange of chloride for iodide counteranion in the self-assembled structures cannot arise from different NLO response mechanisms or from SBZ$^+$ reorientational effects. Rather, these results show that $\chi^{(2)}_{zzz}$ enhancements of this magnitude can easily arise from different cation–anion packing configurations. In particular, the larger $\chi^{(2)}_{zzz}$ values are consistent either with larger SBZ$^+\cdots$I$^-$ distances vis-à-vis the original SBZ$^+\cdots$Cl$^-$ contacts or with greater displacements of the iodide ion along the R′ coordinate (structure **II**), relative to the most energetically stable, proximate N$^+\cdots$Cl$^-$ pairs. Such a structural regime could easily arise when larger I$^-$ ions replaced smaller Cl$^-$ ions in a cationic matrix originally formed/self-assembled to accommodate the latter. Note that calculations on the configuration in which the I$^-$ is translated 2.8 Å along the R' coordinate results in a 20 nm red-shift (relative to R' = 0) of the CT transition, as well as in a 40% increase of the β_{zzz} value (224 × 10^{-30} cm^5 esu^{-1} at $\hbar\omega$ = 1.17 eV). These results can be compared to an experimentally observed Cl$^-$ → I$^-$ red-shift of ~20 nm (for full substitution) and $\chi^{(2)}_{zzz}$ increases of ~34%.[4]

Let us now consider the case of SBZ$^+$TS$^-$ ion pairs. Among the possible geometrical arrangements, those arising from cofacial conformations in which the SBZ$^+$ and TS$^-$ molecular dipoles are aligned in parallel and antiparallel arrangements have been considered (Fig-

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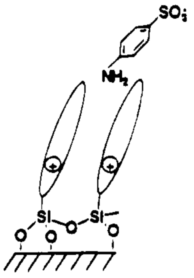
(21) Note that the present calculated hyperpolarizabilities may underestimate experimental values because matrix environmental effects are not completely taken into account. These effects induce[11] a red-shift of the lowest energy CT transition (SZB$^+$Cl$^-$: λ_{max} (calc) = 397 nm; λ_{max} (exptl) = 490 nm) in a manner analogous to solvation effects.[11] Moreover, the quadratic dependence of hyperpolarizability on the energy of the first excited (CT) state argues that such red-shifts are an important mechanism[11] for increases in hyperpolarizability on passing from isolated ion pairs to self-assembled layers. We are presently preparing a manuscript that will discuss these effects in greater detail.

ures 1B,C). The calculated β_{zzz} values for arrangement **Ia** (R = 3.8 Å), as well as all related parameters, are similar to those obtained for the halide analogues (Table 1). By analogy to the aforementioned halide salts, increased β_{zzz} values parallel the TS^- translation along R′ (structures **IIa**), as a consequence of red-shifts of the CT excitation. As expected, on switching to parallel SBZ^+TS^- configurations, smaller β_{zzz} values, compared to the **a** analogues, are predicted (Table 1). This is essentially a consequence of smaller $\Delta\mu_{ge}$ values due to the larger ground-state dipole moment (μ_z) along the CT axis, associated with the parallel arrangement of the SBZ^+ and TS^- molecular dipoles (Table 1). In addition, smaller (relative to the antiparallel arrangements) red-shifts also contribute to the smaller hyperpolarizability. Although parallel dipole arrangements of the SBZ^+ and TS^- ions should be less favored on electrostatic energetic grounds, the spatial orientation of self-assembled chromophores and the energetics associated with surface ion exchange experiments, suggest that these arrangements cannot ruled out (e.g., **3** vs **4**).



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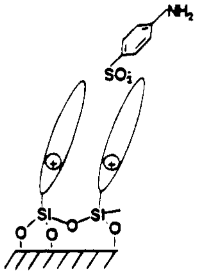

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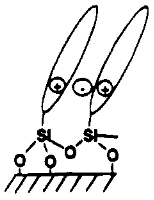
Conclusions

Analysis of the present computational data in light of the results of ion-exchange experiments in chromophoric stilbazolium self-assembled thin films suggests that large hyperpolarizability and hence $\chi^{(2)}_{zzz}$ enhancements on passing from chloride, to iodide and *p*-aminobenzenesulfonate counterions can be understood on the basis of differing, plausible anion−cation packing configurations. In particular, larger SBZ^+X^- distances or larger lateral displacements of the bulkier I^- and *p*-aminobenzenesulfonate anions (e.g., **6**) relative to the most energetically stable, spatially proximate N^+−small anion configurations (**5**), account well for the observed linear optical displacements and $\chi^{(2)}_{zzz}$ enhancements.



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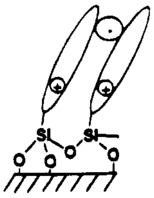

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