

# Charge Distribution and Second-Order Nonlinear Optical Response of Charged Centrosymmetric Chromophore Aggregates. An ab Initio Electronic Structure Study of *p*-Nitroaniline Dimers

Santo Di Bella,<sup>\*,†</sup> Giuseppe Lanza,<sup>†</sup> Ignazio Fragalà,<sup>\*,†</sup> Shlomo Yitzchaik,<sup>\*,‡</sup> Mark A. Ratner,<sup>\*,‡</sup> and Tobin J. Marks<sup>\*,§</sup>

Contribution from the Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 8, 95125 Catania, Italy, Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel, and Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60208-3113

Received October 7, 1996<sup>⊗</sup>

**Abstract:** This contribution presents a quantum chemical investigation of the nonlinear optical response of charged centrosymmetric aggregates of the archetypical chromophore *p*-nitroaniline using an ab initio supermolecular approach. Localized hole states, responsible for aggregate nonlinearity, are predicted to be more stable than delocalized states. The calculated aggregate hyperpolarizabilities are consistently larger than in the isolated chromophore, and the mechanism giving rise to the nonlinearity is essentially “intramolecular” in nature. The aggregate formation is predicted to stabilize the positive charge and to enhance the nonlinearity. Moreover, the calculations reveal that a (formally) centrosymmetric charged aggregate can possess a substantial dipole moment the principal axis of which is oriented *perpendicular* to the principal hyperpolarizability tensor; the dipole moment arises because electron localization breaks the charge distribution symmetry. These results explain a number curious features of chromophoric polymer films which are electric field poled with an “in-plane” electrode geometry.

## Introduction

Poled polymer films containing large hyperpolarizability chromophores<sup>1</sup> are attractive candidates as second-order nonlinear optical (NLO) materials in diverse optoelectronic technologies.<sup>2</sup> Poling involves the application of an electric field to the polymer film which causes partial alignment of the NLO-active chromophores and induces an acentric microstructure. Corona poling and contact poling result in optically uniaxial films which can exhibit large second-order nonlinearities,  $\chi^{(2)}$ , dominated by the  $\chi_{xxx}^{(2)}$  tensor term, where *x* is the direction *parallel* to the applied field (perpendicular to the plane of the polymer film).<sup>1</sup>

Recent studies have argued<sup>3–6</sup> that a different poling mechanism is operative when nonuniform electric fields, in an “in-

plane” poling geometry (field in the plane of the film), are applied to chromophore-doped polymer films. In such cases, a strong nonlinear optical response is observed *perpendicular* to the applied field,  $\chi_{zzz}^{(2)}$ , which is  $\sim 1$ – $2$  orders of magnitude larger than the measured  $\chi_{xxx}^{(2)}$  response (parallel to the applied field).<sup>6</sup> Moreover, it has been demonstrated on the basis of linear optical absorption and emission spectroscopy that NLO dye molecules dispersed in polymer matrices can form aggregates even at low chromophore number densities<sup>7</sup> and that neutral monomeric and dimeric chromophore molecules tend to align parallel to the electric field in mesomorphic matrices<sup>8</sup> (negligible macroscopic alignment is found in isotropic polymers). Studies of  $\chi^{(2)}$  dependence on poling field show that the tensor components parallel to the dc field scale linearly with the magnitude of the field, as expected; however, the orthogonal component,  $\chi_{zzz}^{(2)}$ , scales exponentially and exhibits I–V behavior typical of charge injection processes in dielectric materials.<sup>8</sup> Additionally, the decay of  $\chi_{zzz}^{(2)}$  after cessation of poling approximately parallels the discharge current flow, illustrating the intimate relationship between trapped charge and the optical nonlinearity normal to the dc field. Additional evidence for asymmetric charge injection and the creation of a charge gradient normal to the film plane has been recently provided by pyroelectric measurements,<sup>9</sup> and in the accompanying contribution,<sup>6</sup> creation of charged chromophoric species is demonstrated by electron spin resonance spectroscopy, revealing the formation of nitrogen-centered radical cations in poled samples.

In this intriguing context, it is of fundamental interest in designing and understanding optimized second-order NLO materials as well as alternative poling geometries to explore

<sup>†</sup> Università di Catania.

<sup>‡</sup> The Hebrew University of Jerusalem.

<sup>§</sup> Northwestern University.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, December 15, 1996.

(1) (a) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31. (b) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155.

(2) For recent reviews of NLO materials and their applications see, for example: (a) Burland, D. M., Ed. *Optical Nonlinearities in Chemistry. Chem. Rev.* **1994**, *94*, Issue 1. (b) *Molecular Nonlinear Optics: Materials, Physics, and Devices*; Zyss, J., Ed.; Academic Press: Boston, MA, 1993. (c) Prasad, N. P.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (d) *Materials for Nonlinear Optics: Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (e) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vols. 1 and 2.

(3) Yitzchaik, S.; Berkovic, G.; Krongauz, V. *J. Appl. Phys.* **1991**, *70*, 3949.

(4) Yitzchaik, S.; Krongauz, V.; Berkovic, G. *Nonlinear Optics* **1993**, *4*, 265.

(5) Cohen, R.; Berkovic, G.; Yitzchaik, S.; Krongauz, V. *Mol. Cryst. Liq. Cryst.* **1994**, *240*, 169.

(6) Yitzchaik, S.; Di Bella, S.; Lundquist, P. M.; Wong, G. K.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 3091 (preceding paper in this issue).

(7) Yam, R.; Cohen, R.; Berkovic, G. *Nonlinear Opt.* **1995**, *11*, 311.

(8) Yitzchaik, S.; Cabrera, I.; Buchholtz, T.; Krongauz, V. *Macromolecules* **1990**, *23*, 707.

(9) Donval, A.; Berkovic, G.; Yilmaz, S.; Bauer-Gogonea, S.; Wirges, W.; Gerhard-Multhaupt, R. *Opt. Commun.* **1996**, *123*, 195.

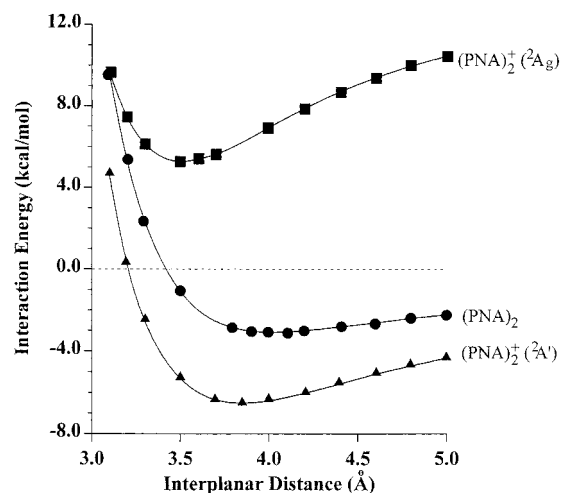
theoretically the NLO response of charged (open-shell) chromophore aggregates and to relate the calculated hyperpolarizabilities,  $\beta(-2\omega; \omega, \omega)$ , to those of the corresponding neutral and charged monomers. In this contribution, we present the first theoretical analysis, using an ab initio supermolecular approach,<sup>10</sup> of the NLO properties of a positively charged chromophore aggregate. We focus on centrosymmetric dimers formed from monomeric units of the archetypical donor-acceptor chromophore molecule *p*-nitroaniline (PNA). We emphasize that the goal of this initial investigation is to probe the effects of the charge distribution and chromophore aggregation on  $\beta(-2\omega; \omega, \omega)$ . Therefore, the analysis is necessarily limited to simple PNA model dimers, thus allowing a semi-quantitative ab initio treatment, which is precluded in the case of larger dye molecules. These systems are the subject of the accompanying contribution.<sup>6</sup> Importantly, the present results argue that a simple, dimeric cationic (charge injected) aggregate, even if centrosymmetric, can exhibit a substantial dipole moment and second-order response consistent with SHG data for "in-plane" poled films.<sup>6</sup>

### Theoretical Methods

Calculations were performed using the restricted Hartree-Fock (RHF) method for the closed-shell states and the unrestricted Hartree-Fock (UHF) method for the open-shell states. Symmetry-adapted (SA) and symmetry-broken (SB) UHF calculations were performed in the case of the charged  $(\text{PNA})_2^+$  dimer. In SA calculations, each molecular orbital (MO) was required to have either g or u inversion symmetry ( $C_{2h}$  symmetry). SB calculations were carried out without any restriction that each MO is of g or u symmetry ( $C_s$  symmetry). The double- $\zeta$  Dunning basis set (DZV) was used for all atoms.<sup>11</sup> SCF interaction energies were corrected for basis set superposition error (BSSE)<sup>12</sup> (average value 1.2 kcal/mol), evaluated by using the function counterpoise of Boys and Bernardi.<sup>13</sup> Interaction energies were also evaluated using second-order Møller-Plesset (MP2) perturbation theory, which is a size-consistent method.<sup>10</sup> The static hyperpolarizability tensor components were computed analytically via electric-field derivatives of the total energy following a coupled perturbative Hartree-Fock (CPHF) approach.<sup>14</sup> Calculations were performed by using the HONDO-8<sup>15</sup> and GAUSSIAN-92<sup>16</sup> programs on IBM ES/9000 and Cray-C90 systems.

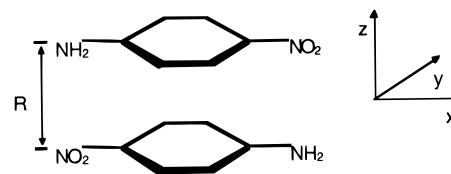
### Molecular Geometries

Geometrical parameters for calculations on the monomeric PNA molecule were taken from the published ab initio optimized  $C_{2v}$  structure.<sup>17</sup> In all dimeric structures studied, the molecular geometries were constructed assuming PNA planar monomers. Calculations on neutral and charged PNA dimers were performed in a centrosymmetric cofacial ( $C_{2h}$ ) arrangement, in which the molecular dipoles ( $\mu_x$  is the principal vector component) are in an antiparallel arrangement, by varying the



**Figure 1.** Potential energy curves showing SCF interaction energies for the centrosymmetric  $(\text{PNA})_2$ ,  $(\text{PNA})_2^+ (^2A_g \text{ state})$ , and  $(\text{PNA})_2^+ (^2A' \text{ state})$  dimers.

### Chart 1



interplanar distance ( $R$ ) in the range 3.0–5.0 Å (Chart 1). It will be seen that calculations on the centrosymmetric geometry are most informative, since they demonstrate that charge injection (cation radical formation) can generate a structure with a substantial dipole moment (susceptible to orientation in a poling field) and hyperpolarizability. In the present investigation, no effects due to the relaxation of monomer geometries or to counteranions are considered.

### Results and Discussion

Let us first consider the case represented by two monomeric units of neutral PNA brought together in a centrosymmetric cofacial conformation. Figure 1 shows the dependence of the computed interaction energy on the interplanar separation ( $R$  in Chart 1) between the two chromophore molecules. The potential energy curve indicates a shallow minimum in the vicinity of 3.8 Å and repulsive interaction energies for  $R < 3.5$  Å. As expected, intermolecular interactions in the neutral  $(\text{PNA})_2$  dimer are mainly governed by dipolar interactions,<sup>18</sup> and the dimer MOs can be related to the simple combination of monomer-related MOs. Of course, due to the centrosymmetry of the system, a vanishing molecular ground-state dipole moment and a vanishing second-order nonlinearity are calculated for such a conformation.

The removal of one electron from the HOMO ( $22a_g$ ) of the neutral centrosymmetric  $(\text{PNA})_2$  dimer (SA calculations;  $R = 3.5$  Å), leads to the formation of a  $^2A_g$   $(\text{PNA})_2^+$  electronic state. This represents a *delocalized* hole state since the loss of the electron is equally shared by the two PNA units (Figure 2A). In analogy to the neutral  $(\text{PNA})_2$  dimer, ionization results in a vanishing molecular ground-state dipole moment and second-order nonlinearity. The removal of one electron from any of the next three lower frontier  $(\text{PNA})_2$  MOs ( $22a_u$ ,  $14b_u$ , and  $14b_g$ , respectively) similarly results in delocalized  $(\text{PNA})_2^+$  states

(10) Chalasinski, G.; Szczesniak, M. M. *Chem. Rev.* **1994**, *94*, 1723.

(11) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter 1.

(12) van Duijneveldt, F. B.; van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873.

(13) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

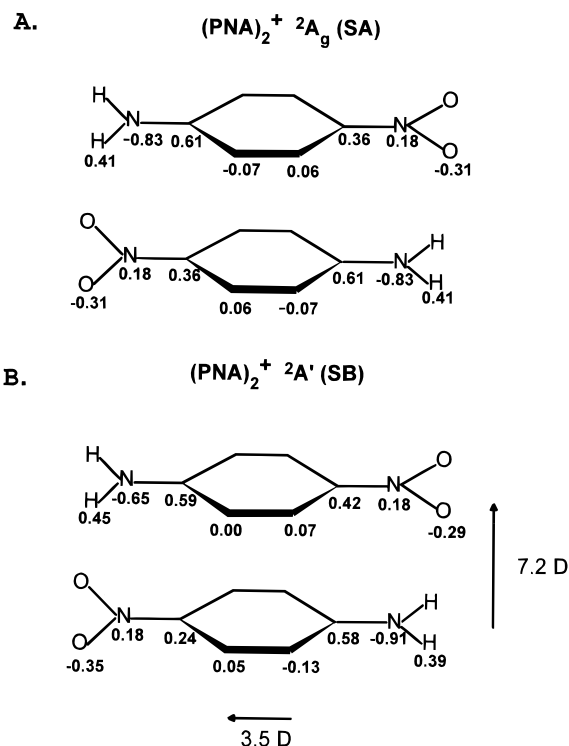
(14) (a) Dykstra, C. E.; Jasienski, P. G. *Chem. Phys. Lett.* **1984**, *109*, 388. (b) Karna, S. P.; Dupuis, M. *J. Comput. Chem.* **1991**, *12*, 487.

(15) Dupuis, M.; Farazdel, A.; Karna, S. P.; Maluendes, S. A. In *MOTTEC-90: Modern Techniques in Computational Chemistry*; Clementi, E., Ed.; ESCOM: Leiden, The Netherlands, 1990; Chapter 6.

(16) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. J.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN-92*; Gaussian Inc.: Pittsburgh, PA, 1992.

(17) Karna, S. P.; Prasad, P. N.; Dupuis, M. *J. Chem. Phys.* **1991**, *94*, 1171.

(18) Di Bella, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 5849.



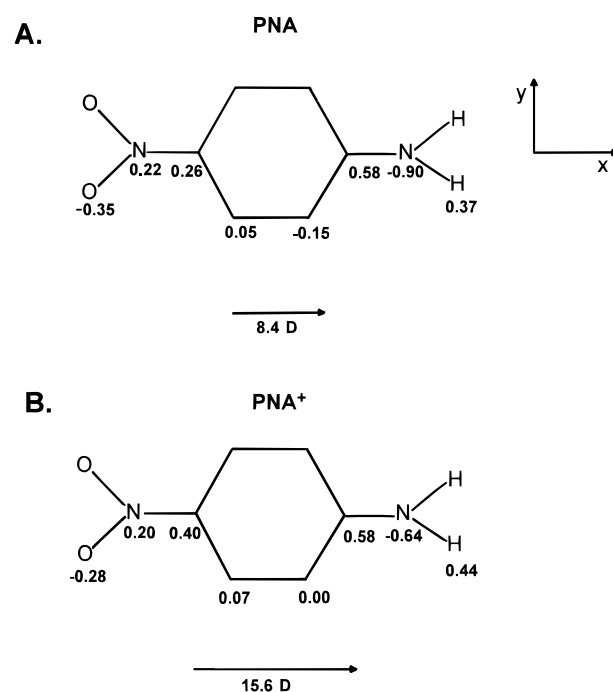
**Figure 2.** SCF charge distribution and ground state dipole moment for the delocalized  $^2A_g$  (A) and the localized  $^2A'$  (B) states of the  $(\text{PNA})_2^+$  dimer (the coordinate system is shown in Chart 1).

which lie higher in energy than the  $^2A_g$  ground state. However, by relaxing the requirement that the ionized electron belong to orbitals either of g or u symmetry (SB calculations), we obtain a second solution to the UHF equations.<sup>19</sup> In particular, the removal of one electron from the HOMO (44a') results in a localized  $^2A'$   $(\text{PNA})_2^+$  state<sup>20</sup> (Figure 2B). The pronounced charge localization ( $\sim 99\%$  in one PNA unit) in this  $^2A'$  state results in an unsymmetrical charge distribution between the two PNA units (Figure 2B), close to those evaluated for isolated neutral and charged PNA molecules (Figure 3), and in a net dipole moment<sup>21</sup> (7.2 D) along the intermolecular ( $z$ ) axis, and a smaller value ( $-3.5$  D) along the intramolecular ( $x$ ) axis (Table 1). Actually, very similar  $(\text{PNA})_2^+$  dipole moment values are calculated even using correlated MP2 wave functions (Table 1). These features are suggestive of a nonvanishing second-order nonlinearity (vide infra). Moreover, the  $(\text{PNA})_2^+$  positive charge is mainly localized (75%) on the  $>C-NH_2$  group of one PNA unit (Figure 2B) and the calculated spin density on the  $-NH_2$  group is 0.36. These findings are in very good agreement with ESR spectroscopic experiments on in-plane

(19) There are two equivalent solutions of this type, one in which the electron is removed from one PNA unit and the second in which it is removed from the other unit.

(20) (a) For a general discussion of hole localized vs delocalized states, see, for example: Sawatzky, G. A.; Lenselink, A. *J. Chem. Phys.* **1980**, *72*, 3748. Logan, J.; Newton, M. D.; Noell, J. O. *Int. J. Quantum Chem. Symp.* **1984**, *518*, 213. (b) Examples of the energetic preference for localized states have been found in the case of the ionization energy of inner-shell hole states in  $O_2^+$ ,<sup>20c</sup> in  $nd^{-1}$  ionizations of various metal clusters,<sup>20d</sup> and in mixed valence inorganic complexes.<sup>20e</sup> (c) Ågren, H.; Bagus, P. S.; Roos, B. O. *Chem. Phys. Lett.* **1981**, *82*, 505. (d) See, for example: Tomonari, M.; Tatewaki, H.; Nakamura, T. *J. Chem. Phys.* **1986**, *85*, 2875. Newton, M. D. *Chem. Phys. Lett.* **1982**, *90*, 291. (e) Newton, M. D. *Int. J. Quantum Chem. Symp.* **1980**, *514*, 363.

(21) Formally, the computation of dipole moment is not gauge-invariant for a charged system. That is, the calculated value will differ depending on where the axis origin is placed. One common although entirely arbitrary choice is to locate the origin at the center of mass (e.g.: Geertsen, J.; Scuseria, G. *J. Chem. Phys.* **1989**, *90*, 6486). We have made this choice for all computations reported here.



**Figure 3.** SCF charge distribution and ground state dipole moment of the PNA (A) and  $\text{PNA}^+$  (B) molecules.

poled poly(methyl methacrylate) thin films containing dispersed DANS [4-(*N,N*-dimethylamino)-4'-nitrostilbene] chromophore molecules.<sup>6</sup> These experiments indicate the formation of a  $N(\text{CH}_3)_2$ -centered cation radical species when the poling field is applied. These results suggest that the basic picture deduced from the present calculations holds in far more computationally demanding DANS aggregates.

MP2 interaction energies of both the delocalized ( $^2A_g$ ) and the localized ( $^2A'$ ) state of the  $(\text{PNA})_2^+$  supermolecule indicate bonded states (interaction energies  $\sim 7$ – $16$  kcal/mol) in the physically relevant interplanar separation region of  $3.5$ – $4.5$  Å (Table 2). Qualitative (SCF) potential energy curves, in the larger ( $3.0$  and  $5.0$  Å) range of interplanar distances, are reported in Figure 1. They indicate a flat minimum near  $3.5$  Å in the case of the delocalized ( $^2A_g$ ) state, which shifts to larger interplanar distances ( $\sim 3.8$  Å) on passing to the localized  $(\text{PNA})_2^+ \ ^2A'$  state (Figure 1). On the comparison of both SCF and MP2 interaction energies, it can be inferred that, for distances  $\leq 3.5$  Å, the delocalized  $(\text{PNA})_2^+$  state is favored, while for larger ( $> 3.5$  Å) distances, the localized state is more stable. Thus, at larger interplanar distances, aggregate formation stabilizes the hole-localized state and the localization is favored essentially because the drop in energy resulting from delocalization is no longer large enough to dominate the stabilization derived from charge polarization on a single PNA molecule. Newton<sup>22</sup> observed similar behavior in calculations on mixed valence binuclear complexes of iron. Analogously to the  $(\text{PNA})_2$  dimer, intermolecular interactions in the localized  $(\text{PNA})_2^+ \ ^2A'$  state are mainly governed by dipolar interactions further reinforced (more so than in the symmetrically charged dimer) by the larger charge separation. The  $^2A'$  MOs can be related to slightly perturbed, monomer PNA and  $\text{PNA}^+$  MOs.

Static hyperpolarizability tensor components  $\beta_{ijk}$  of the  $(\text{PNA})_2^+$  dimer ( $^2A'$  state) are reported in Table 1 using the same coordinate system as in Chart 1 and are compared with corresponding data for the monomeric PNA and  $\text{PNA}^+$  chromophores. In view of the necessarily semiquantitative nature of the present calculated hyperpolarizabilities (the prodigious

(22) Logan, J.; Newton, M. D. *J. Chem. Phys.* **1983**, *78*, 4086.

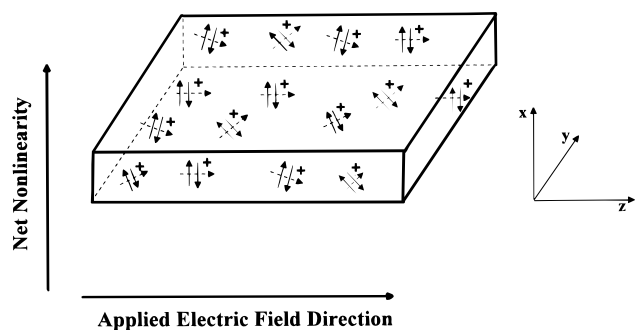
**Table 1.** SCF-Calculated Dipole Moment ( $\mu$ , D) and Static Hyperpolarizability ( $\beta_{ijk}(-2\omega;\omega,\omega)$ ,  $10^{-30}$  esu) Tensor Components of PNA, PNA<sup>+</sup>, and (PNA)<sub>2</sub><sup>+</sup> (<sup>2</sup>A' State)<sup>b</sup>

molecule	$\mu_x$	$\mu_y$	$\mu_z$	$\beta_{xxx}$	$\beta_{yyy}$	$\beta_{yyy}$	$\beta_{xxz}$	$\beta_{xzz}$	$\beta_{zzz}$
PNA	8.41 (7.3)	0.0	0.0	6.10	-1.03	0.0	0.0	-0.05	0.0
PNA <sup>+</sup>	15.6 (11.6)	0.0	0.0	-12.58	-0.65	0.0	0.0	-0.11	0.0
(PNA) <sub>2</sub> <sup>+</sup>	-3.5 (-0.9)	0.0	7.2 (6.8)	13.03	-0.30	0.0	-1.26	0.78	-1.83

<sup>a</sup> Values in parentheses refer to calculated MP2 data. <sup>b</sup> Coordinate system shown in Chart 1.

**Table 2.** Calculated MP2 Interaction Energies (kcal/mol) for the Delocalized (<sup>2</sup>A<sub>g</sub>) and Localized (<sup>2</sup>A') States of (PNA)<sub>2</sub><sup>+</sup> at Various Interplanar Distances

R (Å)	3.5	3.8	4.5
<sup>2</sup> A <sub>g</sub>	15.4	12.1	6.9
<sup>2</sup> A'	14.2	15.9	14.5

**Scheme 1**

computational requirements necessitate incomplete basis sets and neglect of correlation effects),<sup>23</sup> we focus on informative trends rather than on absolute hyperpolarizability values.<sup>24</sup> In analogy to the PNA monomer,  $\beta_{xxx}$  is found to be the principal tensor component in the <sup>2</sup>A' (PNA)<sub>2</sub><sup>+</sup> dimer. The magnitude is approximately 2 times larger than in PNA. The  $\beta_{zzz}$  tensor, parallel to the intermolecular  $z$  axis, is about 1 order of magnitude smaller than  $\beta_{xxx}$ . The remaining non-zero tensor components have smaller values. In analogy to previously analyzed cofacial eclipsed PNA aggregates,<sup>18</sup> these results point to an “intramolecular” mechanism governing the second-order nonlinearity in the (PNA)<sub>2</sub><sup>+</sup> dimer. In the context of “in-plane” poled polymer film experiments,<sup>3–6</sup> the present results provide support for a picture in which charged aggregate chromophores are preferentially oriented with the intermolecular ( $z$ ) axes (direction of the largest dipole moment) *parallel to the poling field* direction, while the charge gradient normal to the applied field leads to a preferential charge trapping along the intramolecular ( $x$ ) axes, thus orienting largest second-order nonlinearity

(23) Sim, F.; Chin, S.; Dupuis, M.; Rice, J. E. *J. Phys. Chem.* **1993**, *97*, 1158.

(24) Currently, for technical reasons, it is computationally prohibitive for us to perform hyperpolarizability calculations for such large (PNA)<sub>2</sub><sup>+</sup> systems using extensive basis sets and including electron correlation effects.

tensor ( $\beta_{xxx}$ ) *perpendicular to the applied field* (Scheme 1), in good agreement with experiment.<sup>3–6</sup>

Finally, it is also instructive to note that, in terms of the  $\beta_{xxx}$  tensor, the second-order nonlinearity of the (PNA)<sub>2</sub><sup>+</sup> dimer is slightly larger than that of the PNA<sup>+</sup> monomer. This is because the second-order response of the (PNA)<sub>2</sub><sup>+</sup> dimer along the intramolecular charge transfer axis ( $\beta_{xxx}$ ) results from  $\beta_{xxx}$  contributions of the interacting PNA and PNA<sup>+</sup> fragments. Thus, the asymmetric (PNA)<sub>2</sub><sup>+</sup> charge distribution not only stabilizes the hole formation but also “switches on” the second-order NLO response and enhances the molecular optical nonlinearity.

## Conclusions

The results of this investigation indicate that the formation of charged centrosymmetric aggregates as would be produced by charge injection in an “in-plane” poling experiment can lead to species with substantial dipole moments and microscopic second-order NLO responses consistently larger and oriented in a different direction with respect to major axis of the dipole moment than in isolated, neutral PNA chromophores. Furthermore, for sufficiently large interplanar separation, localized (PNA)<sub>2</sub><sup>+</sup> states, which are responsible for the aggregate optical nonlinearity, are predicted to be more stable than delocalized states. The mechanism governing the nonlinearity of such aggregates is still “intramolecular” in nature, resulting in a net nonlinearity along the molecular charge transfer axis which is about one order of magnitude larger than that along the intermolecular axis. The aggregation formation is expected to stabilize the hole localized state and to enhance the nonlinearity; nuclear relaxation, which we have not included, should also enhance the charge localization.

Work is in progress to further investigate the frequency dependence of NLO response of charged dye aggregates.

**Acknowledgment.** This work was supported by the Consiglio Nazionale delle Ricerche (CNR, Rome), the National Science Foundation through the Northwestern Materials Research Center (Grant DMR 9120521), and by the Air Force Office of Scientific Research (Contract 94-0169). The CINECA computer center (Casalecchio di Reno, BO, Italy) is gratefully acknowledged for providing a computational grant.

JA963490X