Conformational effects on optical charge transfer in the emeraldine base form of polyaniline from electroabsorption measurements and semiempirical calculations

Lavanya L. Premvardhan,a) Sebastian Wachsmann-Hogiu,b) Linda A. Peteanu,c) and David J. Yaron
Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213
Pen-Cheng Wang, Wei Wang, and Alan G. MacDiarmid
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104
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The electroabsorption (Stark) spectrum of the emeraldine base form of polyaniline (EB) in a polymethyl methacrylate (PMMA) matrix at room temperature is presented. For the lowest-energy (1.98 eV) band, the absolute value of the change in dipole moment (\(\Delta \mu\)) is 6.1 D and the trace of the change in polarizability (\(\text{Tr} \Delta \alpha\)) is 200 Å³. Similar values were obtained for the corresponding electronic transition of a five-ring oligomer of EB that is symmetrically terminated with phenyl rings, also in a PMMA matrix. In order to understand the origin of the substantial value of \(|\Delta \mu|\) measured for these nominally symmetric species, a series of calculations were performed in which the geometries of model oligomers were varied in a systematic fashion and resulting effects on the values of \(|\Delta \mu|\) were determined. Numerous low-energy conformers were identified by this method having substantial values of \(|\Delta \mu|\), suggesting that the large \(|\Delta \mu|\) measured experimentally results from conformational heterogeneity. Our findings suggest that Stark spectroscopy is a useful probe of structural disorder in this technologically important polymer in the solid state. © 2001 American Institute of Physics. [DOI: 10.1063/1.1388559]

I. INTRODUCTION

Electroabsorption (Stark-effect) spectroscopy has proven to be an invaluable tool for investigating the electronic properties of conjugated polymers. From these studies, important physical parameters such as the magnitude of the change in the dipole moment (\(|\Delta \mu|\)) and the trace of the change in polarizability (\(\text{Tr} \Delta \alpha\)) between the ground state and the excited state of interest can be extracted from the field-induced changes in the absorption spectrum. The value of \(|\Delta \mu|\) reflects the extent of charge transfer for a particular electronic state, while the extent of electron delocalization may be correlated to \(\Delta \alpha\). These two parameters are probes both for structural disorder of the polymer itself and large asymmetric local fields in its environment. For example, in polaryizable symmetric conjugated polymers, it is common to measure large values of \(|\Delta \mu|\) that arise from conformational disorder and/or the asymmetry of the fields in the solid state. In addition, comparison of the measured and calculated values of \(|\Delta \mu|\) and \(\Delta \alpha\) for a given electronic transition can frequently aid in determining its orbital nature. This is of particular use for the emeraldine base (EB) form of polyaniline (Fig. 1) because there has been controversy in the literature concerning the assignment of the lowest-lying electronic state.12–17

1. The absorption spectrum of EB consists of a high-energy transition (3.78 eV) that is likely of \(\pi-\pi^*\) origin and a low-energy feature (1.98 eV) for which several assignments exist in the literature.12–17 We report the properties of these two electronic states of EB within a poly(methyl methacrylate) (PMMA) matrix. Our experiments indicate that there is a significant increase in charge separation (a substantial \(|\Delta \mu|\) upon excitation into the low-energy band, though ideally, in the infinite-chain limit, the symmetric polymer should exhibit a \(\Delta \mu\) of zero. Similar values are measured for the lowest-energy state of a five-ring symmetrically terminated oligomer of EB (oEB) as well (Fig. 2). The asymmetry in these species implied by their nonzero \(\Delta \mu\)’s may arise due to a number of sources including conformational disorder and/or inhomogeneous local fields in the molecular environment.4,5

To our knowledge, the majority of the published electronic-structure calculations that have probed the effect of geometric disorder on the properties of EB and related molecules have focused primarily on the impact of varying ring torsion angles on the oscillator strength and excitation energies of the electronic transitions.13,17–21 Here, we use computational methods to investigate geometrical effects on the charge-transfer properties of EB as probed by the values of \(\Delta \mu\). A direct comparison of this quantity with our experimental measurements, reported here, provides a useful and experimentally straightforward probe for the structural disorder present in film samples of the polymer.

a)Department of Biophysics, Vrije Universiteit (Amsterdam), The Netherlands.
b)On leave from the National Institute of Laser, Plasma, and Radiation Physics, Bucharest-Magurele, Romania.
c)Electronic mail: peteanu@andrew.cmu.edu
II. EXPERIMENT

A. Synthesis of nondoped polyaniline (EB)

The synthesis of EB follows that outlined in Ref. 22. An aqueous solution of (NH₄)₂S₂O₈ was added slowly to a solution of aniline dissolved in 1 M aqueous HCl solution. After 1 h, the precipitate which had formed was removed by filtration, washed repeatedly with 1 M aqueous HCl solution, and dried under dynamic vacuum for ~48 h. The material thus obtained is emeraldine hydrochloride. The emeraldine hydrochloride was converted into EB by stirring with a 0.1 M solution of NH₄OH for several hours. The material was dried under dynamic vacuum for 48 h, pulverized by a mortar and pestle to a fine powder, and further dried under dynamic vacuum for another 48 h. The oligomer of EB used in these experiments, oEB, was produced by a new method outlined in Ref. 23. Figure 2 shows the two positional isomers that may be present in our sample of oEB.

B. Sample preparation and instrumentation

We prepared the EB–PMMA blend samples in a similar fashion as reported previously for the doped form of polyaniline24 with NMP (N-methyl-2-pyrrolidinone) replacing chloroform as the solvent. However, because the boiling point of NMP is high (~200 °C), evaporation by exposure to the atmosphere is very slow. We also found that, as NMP evaporated, the EB molecules tended to migrate away from the surface of the electrode. To circumvent this problem, we prepared a highly viscous solution of EB in NMP containing 1–2 mg of EB, ~1.3 g of PMMA, and ~5 mL of NMP. A few drops of this highly viscous blend solution were then placed on two ITO or inconel coated slides and placed in an oven at ~50 °C for 10–15 h to evaporate the solvent. We used this relatively low temperature to evaporate NMP because we found that, if the samples containing a significant amount of NMP are kept for over an hour at temperatures greater than 80 °C, the sample changes color, indicating that the electronic properties of the polymer have been altered. Once the residual NMP has evaporated through the heating process, the slides were then clamped together and heated in the oven at 140 °C for 10–15 min. Following this step, there was no further change in the absorption spectrum of the sample. A similar methodology was used to prepare the oEB–PMMA blend films. The samples used for the electroabsorption measurements had absorbances of between 0.2 and 0.7 optical density. In order to obtain the absorption spectra, blanks consisting of PMMA alone were made by the same procedures outlined previously.

In order to determine the magnitude of the field applied across the sample, its thickness was obtained both from the interference patterns in the transmission of the sample in the near IR (900–2000 nm) using a value of 1.49 for the refractive index of PMMA and by using a micrometer. The films were typically found to be between 50 and 180 μm thick with errors of ±10 μm. The instrumentation has been previously described in detail.25 The spectra were measured in transmission mode with a resolution of 5 nm.

C. Calculations

Molecular geometries were obtained using the AM1 semiempirical quantum chemistry method within MOPAC-6.26 Following Libert et al.,16 we constrained the para carbon atoms of the phenyl rings, which are those bonded to the nitrogen atoms, to be coplanar. Without application of this constraint, the chain exhibited a very low-energy bowing, or gentle curving, of the backbone. This in turn caused the geometry optimization to be slowly convergent and led to undesirable variance in the resulting structures. Moreover, one would expect such a motion to be frozen out in solid-state samples.

Electronic properties of the ground and excited states were obtained via singles configuration interaction (SCI) calculations on the INDO Hamiltonian, including all excitations between the 25 highest filled and 25 lowest unfilled molecular orbitals. The INDO calculations were done using both ARGUS™27 and our own implementation. Comparison of these two implementations showed agreement. The dipole moments and transition moments were obtained by direct evaluation of the dipole operator matrix elements. The magnitude and the sign of the vectorial difference of the ground- and excited-state dipole moments are reported.

FIG. 1. Emeraldine base (EB).

FIG. 2. The two possible positional isomers of the five-ring EB oligomer (oEB) used in this work. The top isomer is referred to as the symmetric isomer and the bottom is the asymmetric isomer in the text.
II. DATA FITTING METHOD

The analysis of the electroabsorption data follows the standard procedure as outlined by Liptay.\textsuperscript{28} Essentially, the change in absorption due to the application of an external electric field is fit to the weighted sum of zeroth, first, and second derivatives of the zero-field absorption spectrum. The overall change in absorbance caused by the application of an electric field is described by

\[
\Delta A(\tilde{\nu}) = \hat{F}^2 \left[ a_x(A(\tilde{\nu})) + b_x \frac{\tilde{\nu}}{15h} \frac{\partial}{\partial \tilde{\nu}} \left( A(\tilde{\nu}) \right) + c_x \frac{\tilde{\nu}^2}{30h^2} \frac{\partial^2}{\partial \tilde{\nu}^2} \left( A(\tilde{\nu}) \right) \right].
\]

(1)

The \( A(\tilde{\nu}) \) term represents the unperturbed absorption as a function of wave number, \( \tilde{\nu} \), and \( \hat{F} \) represents the field at the sample in V/cm. This effective field includes the enhancement of the applied field due to the cavity field of the matrix. The subscript \( \chi \) represents the angle between the direction of the applied electric field and the electric field vector of the polarized light. Each of the coefficients in Eq. (1), \( a_x \), \( b_x \), and \( c_x \), represent the magnitude of the contributions of the zeroth, first, and second derivative of the absorption spectrum, respectively, to the electroabsorption spectrum. These are related to molecular parameters by the following equations at the magic angle (\( \chi = 54.7^\circ \)),

\[
\begin{align*}
\alpha_{54.7} &= \frac{1}{30|m|^2} \sum_{i,j} 10A_{ij}^2 + \frac{1}{15|m|^2} \sum_{i,j} 10m_iB_{ij}, \\
b_{54.7} &= \frac{1}{|m|^2} \sum_{i,j} 10m_iA_{ij}\Delta\mu_j + \frac{5}{2} \text{Tr}\Delta\alpha, \\
c_{54.7} &= 5|\Delta\mu|^2.
\end{align*}
\]

(2)-(4)

The symbols \( \Delta\alpha \) (a second-order tensor) and \( \Delta\mu \) represent the polarizability tensor and the dipole moment vector, respectively. Information about the difference in charge distribution between the ground and excited state is contained in \( |\Delta\mu| \). The difference in polarizability between the ground and excited states is \( \Delta\alpha \). We measure \( \text{Tr}\Delta\alpha \), the trace of this tensor. This term is the sum of \( \Delta\alpha_{xx} \), \( \Delta\alpha_{yy} \), and \( \Delta\alpha_{zz} \), and does not itself contain any directional information. The transition moment is represented by \( \tilde{m} \) (\( \tilde{m} \) is a unit vector in this direction) and the tensors \( A \) and \( B \) represent the transition polarizability and transition hyperpolarizability, respectively. These describe the effect of \( \hat{F} \) on the molecular transition moment: \( \tilde{m}(\hat{F}) = \tilde{m} + A \cdot \hat{F} + B \cdot (\hat{F} \times \hat{F}) \). The indices \( i \) and \( j \) in these tensor components [Eqs. (2) and (3)] correspond to the axes of the fixed coordinate system of the molecule. Generally, \( A \) and \( B \) can be neglected for strongly allowed transitions. Information regarding \( |\Delta\mu| \) for the molecule is contained in the \( c_{54.7} \) term [Eq. (4)]. If the orientation of the dipoles of the molecules in the matrix is isotropic and fixed, there will be an equal number of molecules oriented parallel and antiparallel to the applied field at all times. These molecules will be stabilized or destabilized, respectively, to an equal extent by the applied field. An overall broadening of the absorption spectrum will result if the excited state dipole moment is different from that of the ground state. This field-induced broadening gives rise to a contribution to the electroabsorption spectrum that is proportional to the second derivative of the unperturbed absorption spectrum. For a more detailed discussion of these effects, see Refs. 28 and 29.

The coefficients, \( a_x \), \( b_x \), and \( c_x \), are extracted by means of a linear least-squares fit of the electroabsorption signal to the sum of the derivatives of \( A(\tilde{\nu}) \). Deviations between the fit obtained using a single set of \( a_x \), \( b_x \), and \( c_x \) parameters and the experimental electroabsorption spectrum indicate that there is more than one transition (electronic or vibronic) underlying the absorption band having different electro-optical properties (\(|\Delta\mu|\) and/or \( \Delta\alpha \)) and/or that multiple ground-state conformers with differing properties are present.

\[\text{FIG. 3. The low-energy absorption bands of oEB and EB are contained in (a) and (b). Panels (c) and (d) contain the electroabsorption spectrum (solid line) and the fit to the spectrum (dashed line) of oEB and EB, respectively. Panels (e) and (f) show the individual contributions of the zeroth derivative (dotted), first derivative (crosses), and second derivative (triangles) of the absorption spectrum to the line shape of the electroabsorption spectra which are reproduced in solid lines for comparison. The electroabsorption signals are normalized to the square of the applied field.}\]
TABLE I. Electronic properties for the electronic transitions of EB and oEB.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Charge-transfer band</th>
<th>π−π* band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tr Δμ</td>
<td>Energy</td>
</tr>
<tr>
<td>EB</td>
<td>200±20</td>
<td>16 000</td>
</tr>
<tr>
<td>oEB</td>
<td>240±70</td>
<td>17 100</td>
</tr>
</tbody>
</table>

*The values of the Tr Δμ and |Δμ| are extracted from the fits shown in Figs. 3 and 4. The dipole moments are in debye, the polarizabilities in Å³, and the absorption maxima are in cm⁻¹.

IV. RESULTS

A. Electroabsorption of the low-energy transition of EB and oEB

The absorption and electroabsorption spectra of oEB and EB in PMMA at room temperature are contained in Fig. 3. The absorption spectra of the two species [(a) and (b), respectively] are very similar with maximum of the oligomer spectrum lying ~0.1 eV to higher energy than that of the polymer. The electroabsorption spectra (solid lines) and fits (dashed lines) for both species are shown in panels (c) and (d). The two electroabsorption spectra are also quite similar in shape though the fit to the spectrum of the oligomer is of somewhat higher quality than that of the polymer. We will return to this point in the Discussion Section. In the remaining panels, the fits are decomposed into their zeroth-, first-, and second-derivative contributions (see Sec. III). The values of |Δμ| and Tr Δμ for oEB and EB derived from these fits are remarkably similar (Table I), demonstrating experimentally that calculations on the oligomer, such as those reported here, should be expected to reproduce the electronic properties of the polymeric species as well.

B. Electroabsorption of the high-energy transition of EB

The second prominent transition in EB, at 30 500 cm⁻¹ (3.78 eV), has been assigned to a π−π* state localized on the benzenoid rings. The absorption spectra and fits to this band are shown in Fig. 4. Figure 4(a) contains the absorption spectrum in the region between 22 600 cm⁻¹ (2.8 eV) and 36 300 cm⁻¹ (4.5 eV). The fit [dashed line in Fig. 4(b)] to the electroabsorption spectrum [solid line in Fig. 4(b)] is obtained in the region between 22 600 (2.8 eV) and 33 600 cm⁻¹ (4.17 eV). At higher energies, the signal to noise of the absorption spectrum is poor so that it is not possible to obtain a good fit to the electroabsorption signal in this region. For the remainder of the spectrum, however, a good fit is achieved and the corresponding electronic properties are reported in Table I. No studies were performed on the corresponding band of oEB.

C. Computational results

Our initial studies were performed on a series of oligomers of EB that are from three to six rings in length (Scheme 1 and Table II) generated using the constrained AM1 method (see Sec. II). All the species shown have dihedral angles between phenyl rings of magnitude 45°±5°. These alternate in sign such that the overall structure is nonhelical. Of the structures shown, the one that we consider to be the best model of EB is that denoted ApQpA (Scheme I) because it contains the full repeat unit of the polymer (ApQp) but is symmetrically terminated by a second phenyl-amino group (denoted as A) to mimic the symmetry of the long-chain polymeric species. Nevertheless, calculations were performed as a function of chain length to determine if and how the properties reported depend on this parameter. In the section following, calculations on both possible isomers of the specific oligomer used in the experimental study (oEB, Fig. 2) will also be described.

For the low-energy band of the EB oligomers in Table II, the two important observations can be summarized as follows. First, the excitation energy of all the oligomers falls within ~300 cm⁻¹ of one another, demonstrating the relatively localized character of the electronic states that has been noted previously. This is also consistent with comparison of the Mulliken charges on each atom of the EB oligomers in their respective ground and excited states (data not shown). These results demonstrate that, in symmetric structures such as those in Table II, ~0.25|e| of charge is injected into the quinoid (Q) from each of the two adjoining phenyl ring, so that 95% of the change in the distribution of charge is localized in the central pQp moiety regardless of chain length. For less symmetric structures having nonzero values of Δμ, such as those discussed in the following paragraphs, the relative amounts of charge injected into the quinoid from the two adjoining phenyls changes though the

\[
p\text{Qp}: \text{NH}_2(\text{C}_6\text{H}_4)\text{N}=(\text{C}_6\text{H}_4)\text{N}=(\text{C}_6\text{H}_4)-\text{NH}_2
\]

\[
\text{ApQp} \quad H\{-\text{NH}(\text{C}_6\text{H}_4)\text{NH}(\text{C}_6\text{H}_4)\text{N}=(\text{C}_6\text{H}_4)\text{N}=(\text{C}_6\text{H}_4)\}\text{-NH}_2
\]

\[
\text{ApQpA} \quad H\{-\text{NH}(\text{C}_6\text{H}_4)\text{NH}(\text{C}_6\text{H}_4)\text{N}=(\text{C}_6\text{H}_4)\text{N}=(\text{C}_6\text{H}_4)\}\text{-NH}(\text{C}_6\text{H}_4)\text{-NH}_2
\]

\[
\text{ApQpAA} \quad H\{-\text{NH}(\text{C}_6\text{H}_4)\text{NH}(\text{C}_6\text{H}_4)\text{N}=(\text{C}_6\text{H}_4)\text{N}=(\text{C}_6\text{H}_4)\}\text{-NH}(\text{C}_6\text{H}_4)\text{-NH}(\text{C}_6\text{H}_4)\text{-NH}_2
\]

Scheme I. Labeling scheme for the structures discussed in the text.
The absorption band of the emeraldine base (EB) of polyaniline in the region of the high-energy ($\pi-\pi^*$) transition. (b) The electroabsorption spectrum (solid) and the fit to the spectrum (dashed). (c) The individual contributions of the zeroth (dotted), first (crosses), and second derivative (triangles) of the absorption spectrum to the line shape of the electroabsorption spectrum which is reproduced (solid line) for comparison.

The second important observation is that the ground-state dipole moments ($\mu_0$) and the values of $\Delta \mu$ are essentially zero for all structures in Table II, regardless of chain length. The latter result represents a significant discrepancy with our experimental results on the EB polymer. To reconcile theory and experiment, we postulated that lower symmetry structures present in the polymer film could cause the charge transfer that characterizes the low-energy band to become asymmetric, leading to a significant $\Delta \mu$. A distribution of such structures could exist in an amorphous environment such as that of neat films or in the solid-state solutions used here, in contrast to the single geometry one might find in a crystal. This is the case provided that the asymmetric structures lie close enough in energy to the symmetric structure to be populated due to solid-state interactions that are not accounted for in the gas-phase geometry minimization.

However, generating an ensemble of geometries that accurately mimics those present in amorphous samples is a difficult challenge that would require detailed knowledge of both the solid-state packing forces and the glass formation kinetics. Here, we use an alternative approach to generate a representative collection of low-energy structures of the five-ring oligomer model of EB (ApQpA, Scheme I) and of both possible isomers of oEB (Fig. 2). The latter calculations were performed to facilitate a more direct comparison with species that were measured experimentally in this study and to explore the consequence of structural isomerism on the electronic properties of these systems. To mimic the effects of solid-state packing, we assume that these forces will tend to twist the various phenyl rings away from their minimum energy positions, while leaving the nitrogen atoms free to find their minimum energy locations. We therefore constrained the dihedral angles between adjacent phenyl rings (i.e., C6–C7–C11–C16 of Fig. 1) to specific values and optimized the remainder of the structure. Both the ApQpA oligomer and the two isomers of oEB have five phenyl rings and therefore four dihedral angles. These dihedrals were varied from 45° to 65° in increments of 10°, with alternating signs such that the structure was nonhelical, generating a total of 81 structures. The number of structures found having heats of formation ($H^f$) within 5 kcal/mol of the global

sum of the two remains $\sim 0.5 e$. This highly localized nature of the low-energy charge-transfer transition in EB again supports the use of oligomers as good model systems for calculating the electronic properties of the polymeric species.

The electronic properties of polyaniline oligomers are given in parentheses. The dipole moments are in debye, and the correlation coefficients ($R$) between the dipole moments of CT1 with CT2 and with the $\pi-\pi^*$ states are reported (see the text). We report the mean value of each property obtained from the number of structures shown as well as its standard deviation.

The correlation coefficients ($R$) between the dipole moments of CT1 with CT2 and with the $\pi-\pi^*$ states are reported (see the text). We report the mean value of each property obtained from the number of structures shown as well as its standard deviation.

### Table II. Electronic properties of polyaniline oligomers

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\mu_0$</th>
<th>Charge-transfer transition</th>
<th>$\pi-\pi^*$ transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQp</td>
<td>0.01</td>
<td>22.082 (0.72)</td>
<td>0.11</td>
</tr>
<tr>
<td>ApQp</td>
<td>1.60</td>
<td>22.072 (0.80)</td>
<td>0.95</td>
</tr>
<tr>
<td>ApQpA</td>
<td>0.26</td>
<td>22.033 (0.92)</td>
<td>1.00</td>
</tr>
<tr>
<td>ApQpAA</td>
<td>1.57</td>
<td>22.311 (0.90)</td>
<td>0.24</td>
</tr>
</tbody>
</table>

*Transition energies, ground-state dipole moments ($\mu_0$), and difference dipole moments ($\Delta \mu$) were obtained from INDO1/SCI calculations on structures optimized using AM1. The dipole moments are in debye, and the absorption maxima are in cm$^{-1}$. The calculated oscillator strengths for each transition ($f$) are given in parentheses.

### Table III. Electronic properties of EB oligomers averaged over an angular ensemble of structures

<table>
<thead>
<tr>
<th></th>
<th>ApQpA</th>
<th>oEB symmetric isomer</th>
<th>oEB asymmetric isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy CT1 state</td>
<td>22.698±358</td>
<td>22.839±281</td>
<td>23.114±356</td>
</tr>
<tr>
<td>Energy CT2 state</td>
<td>23.837±179</td>
<td>23.785±199</td>
<td>24.857±121</td>
</tr>
<tr>
<td>Energy $\pi-\pi^*$ state</td>
<td>31.329±660</td>
<td>31.310±637</td>
<td>31.547±639</td>
</tr>
<tr>
<td>CT1–CT2 energy gap</td>
<td>1139±32</td>
<td>946±34</td>
<td>1742±377</td>
</tr>
<tr>
<td>$\Delta \mu$ CT1 state</td>
<td>4.9±3.6</td>
<td>5.0±3.1</td>
<td>12.0±1.1</td>
</tr>
<tr>
<td>$\Delta \mu$ CT2 state</td>
<td>4.8±3.4</td>
<td>5.0±2.9</td>
<td>9.1±1.4</td>
</tr>
<tr>
<td>$\Delta \mu$ $\pi-\pi^*$ state</td>
<td>2.6±1.9</td>
<td>2.2±1.4</td>
<td>4.5±3.0</td>
</tr>
<tr>
<td>$\sigma$ (of CT1 and CT2)</td>
<td>0.98</td>
<td>0.97</td>
<td>0.71</td>
</tr>
<tr>
<td>$\sigma$ (of CT1 and $\pi-\pi^*$)</td>
<td>0.48</td>
<td>0.24</td>
<td>0.16</td>
</tr>
<tr>
<td>$f$ of CT1</td>
<td>0.53±0.2</td>
<td>0.47±0.16</td>
<td>0.41±0.18</td>
</tr>
<tr>
<td>$f$ of CT2</td>
<td>0.01±0.02</td>
<td>0.02±0.03</td>
<td>0.08±0.05</td>
</tr>
<tr>
<td>$f$ of $\pi-\pi^*$</td>
<td>1.5±0.2</td>
<td>1.5±0.2</td>
<td>1.2±0.4</td>
</tr>
<tr>
<td>Number of structures</td>
<td>63</td>
<td>73</td>
<td>72</td>
</tr>
</tbody>
</table>
minimum was 63 for ApQpA, 73 for the symmetric oEB isomer, and 72 for the asymmetric isomer. For all three species, the averages over each property calculated for these lowest-energy structures are reported as the mean followed by the standard deviation (Table III).

For all three oligomers, the transition energy of the lowest-energy state (CT1 in Table III) exhibits a very small standard deviation of \( \sim 360 \text{ cm}^{-1} \) or less. Therefore, the energy of this state varies only weakly between the various structures, as was found earlier for oligomers of various lengths. In contrast, \( \Delta \mu \) varies strongly with geometry in both ApQpA and the symmetric isomer of oEB, while the asymmetric oEB isomer exhibits a substantial \( \sim 12 \pm 1.1 \text{ D} \) \( \Delta \mu \) that is relatively constant for all geometries probed. The large \( \Delta \mu \)'s calculated for the asymmetric isomer of oEB reflect the effect on electron donor strength of H termination versus NH$_2$ termination of the phenyl ring adjacent to the quinoid. That is to say, similar calculations on the analogous isomer in which the structure is terminated by NH$_2$ groups instead of hydrogen yield \( \Delta \mu \)'s of 6.1\( \pm \)3.5 D (data not shown) which are similar to the values obtained for ApQpA. In all cases, the values of \( \Delta \mu \) for the \( \pi-\pi^* \) transition are roughly half that of the charge-transfer transition, which is in reasonable agreement with the ratio between the experimentally observed \( \Delta \mu \)'s of these two bands in EB (Table I).

All three oligomers exhibit a second much weaker transition lying \( \sim 1200 \text{ cm}^{-1} \) above the first excited state. This state is referred to as CT2 in Table III. Due to this small splitting, both bands would be expected to underlie the experimental absorption bandwidth. The average transition moments to the lower and upper states are such that the lower state carries two orders of magnitude more intensity than the upper state. The \( \Delta \mu \)'s of these two states are highly correlated in ApQpA and in the symmetric oEB isomer, though not in the asymmetric oEB isomer (Fig. 5 and Table III). In other words, a structure having a large \( \Delta \mu \) for one state will have a large \( \Delta \mu \) for the other. In contrast, a much weaker correlation is seen between the values of \( \Delta \mu \) in the charge-transfer and \( \pi-\pi^* \) states in all cases. Similar results were obtained when the constraint that the para carbon atoms remain coplanar was removed.

A possible rationale for the correlation observed in ApQpA and the symmetric oEB isomer is that the torsional distortions lead to large mixing between the first two excited states. In the symmetric structure, neither state has a large \( \Delta \mu \) but there is a large transition moment between the two states. State mixing would convert this transition moment to \( \Delta \mu \)'s. Furthermore, if the mixing involved only the first two excited states, their values of \( \Delta \mu \) would be equal. This would then account for the high degree of correlation (R) observed in Fig. 5 for ApQpA and reported in Table III for the symmetric isomer of oEB as well. Interestingly, this correlation is much weaker (\( R = 0.78 \)) for the asymmetric oEB isomer (Table III).

However, there are a number of indications that mixing also occurs with higher excited states. For instance, mixing of the first two excited states causes the higher energy of the two, which is "dark" in the symmetric structure, to borrow intensity from the "bright" state at lower energy. If mixing were limited to these two states, the transition moment to the upper state would then be correlated with the \( \Delta \mu \) of the lower state. This correlation is rather weak for both species, suggesting that significant mixing occurs with higher excited states. In addition, the sum of the intensities to the first two excited states would be conserved if mixing were to occur exclusively between them. For ApQpA and the symmetric isomer of oEB, the average sum of these intensities is 58%–61% of that present in the symmetric structure. This also indicates that the state mixing is not limited only to the two first excited states.

V. DISCUSSION

Stark-effect spectroscopy is an effective tool to determine the nature of electronic transitions because it yields the magnitude and spatial extent of charge separation and/or charge transfer in the excited state compared to that of the ground state for the molecular system under study. It is also a particularly sensitive probe of disorder-induced charge transfer in nominally symmetric molecular systems. Here we will compare our electroabsorption results for electronic transitions of EB in a PMMA matrix to theoretical models that have been previously published\(^1,2,13,17,19,31\) and to our own calculations reported here. Specific attention will be paid to two aspects of EB photophysics: the orbital assignment of the low-energy transition and the role of molecular and/or environmental asymmetry affecting the observed charge-transfer properties.

A. Charge-transfer properties of the low-energy transition

The assignment of the low-energy transition in EB to charge transfer from the \( \pi \) orbital of each of the two surrounding benzenoid rings to the central quinoid \( \pi \) orbital was originally put forward by Duke and Conwell\(^13\) and by Stafström et al.\(^31\) Though a second assignment of this band, due to Kim et al.,\(^14\) is to an \( n-\pi^* \) state, both our calculations here and the most recent study of Libert et al.\(^16\) concur...
B. Models for asymmetry-induced charge transfer

It is well known that EB can adopt a variety of conformations (tight versus expanded coil, etc.) depending on solvent and other environmental conditions, and it is this conformational disorder that is emphasized in the work. We will now consider other mechanisms that may contribute to $|\Delta \mu|$ and argue that these mechanisms, though present, are unlikely to predominate. A large $|\Delta \mu|$ can result from asymmetry in the local field experienced by the polymer, provided the ground state and excited state have very different polarizabilities, i.e., $\Delta \alpha$ is large. This is the interpretation given to the large $\Delta \mu$ observed in the nominally symmetric polymers polydiacetylene and MEH-PPV. For instance, in MEH-PPV, a $\Delta \mu$ of $\sim 50$ D was measured for a $\Delta \alpha$ of $\sim 8000$ Å. This value of $\Delta \mu$ is consistent with an asymmetry in the local field of $2 \times 10^6$ V/cm. However, using the value of 200 Å$^3$ for $\Delta \alpha$ of EB measured in this work, we estimate that a net asymmetry of $\sim 9 \times 10^6$ V/cm in the local field would be necessary in order to generate the $\Delta \mu$ measured for this system. In other words, the required asymmetry is approximately as large the solvent field itself and is a factor of 4–5 larger than the strength of the fields required to generate the $\Delta \mu$’s that have been measured for polydiacetylene and related compounds. This comparison suggests that symmetry in the local solvent fields may contribute to the value of $|\Delta \mu|$ measured for EB but is not likely to be its sole source. Another potential contributor to $|\Delta \mu|$ is the presence of chemical defects and aggregate formation. However, we argue that both of these effects are smaller in the oligomer than in the polymer. While branching points and other chemical defects are expected to be present in the polymer, such defects are not expected in the oligomer. Also, while EB exhibits a tendency to form aggregates in our PMMA films, the formation of aggregates was less obvious in the films made from the oligomer as determined by visual inspection. The one defect that may be present in both the oligomer and the polymer is that of positional isomers such as are shown in Fig. 2. Interestingly, the calculated values of $\Delta \mu$ calculated for the asymmetric isomer of oEB (bottom, Fig. 2) are roughly a factor of 2 larger than experiment, indicating that this species does not predominate in our samples. In summary, the fact that the similar values of both $|\Delta \mu|$ and $\Delta \alpha$ observed for the polymer (EB) and oligomer (oEB) samples argues against chemical defects and aggregation playing a dominant role.

Another striking similarity between EB and oEB is that both exhibit noticeable deviations between their electroabsorption spectra and the corresponding fits, although the deviation is somewhat less pronounced for the oligomer. This suggests that these samples have similar heterogeneity in the molecular parameters ($|\Delta \mu|$ and $\Delta \alpha$) within their low-energy absorption bands. Note that this heterogeneity is much more readily seen in the fits to the electroabsorption spectrum than in the absorption spectrum itself because the position of the absorption maximum is relatively insensitive to conformation, while $|\Delta \mu|$ is strongly dependent on conformation. That a similar degree of heterogeneity is observed in EB and oEB suggests that the conformational disorder may also be similar in these two systems, validating our use of short oligomers to model the conformational subspace available to the polymer.

In summary, our results demonstrate that Stark spectroscopy and particularly the measurement of $|\Delta \mu|$ is a highly sensitive probe of structural disorder in polymeric systems, especially for molecules such as EB, for which the optical band gap is only weakly dependent on structure due to the highly localized character of the optical transition.

VI. CONCLUSIONS

The electronic properties of the emeraldine base (EB) form of polyaniline in a PMMA film have been determined via electroabsorption and the measured asymmetry in charge transfer has been correlated to structural asymmetry with INDO1/SCI calculations. The electronic properties measured for the low-energy charge-transfer band at 1.98 eV are $|\Delta \mu| = 6.1$ D and $\Delta \alpha = 200$ Å$^3$ and it is found by calculation to be localized within the benzenoid–quinoid–benzenoid moiety of the structure, in agreement with previous work. Similar results are obtained for a five-ring oligomer of EB.

The substantial $|\Delta \mu|$ measured for this nominally symmetric polymer is indicative of geometric disorder in the structure. Calculations of $\Delta \mu$, performed as a function of varying the molecular geometry of various end-capped monomers, demonstrate that the asymmetry in charge transfer is highly sensitive to molecular structure.

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