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DFT and experimental study of *N*,*N*′-bis(3′-carboxy,4′-aminophenyl)-1,4-quinonediimine, a carboxyl substituted aniline trimer

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ABSTRACT

Density functional calculations were performed on N,N'-bis(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine, a carboxylic acid substituted aniline trimer. Results of the calculations were compared to experimental properties of the herein synthesized trimer, as well as to the properties of the anthranilic acid/ aniline co-polymer reported in the literature. The calculated LUMO levels for isomers of the title compound range from -4.45 to -5.05 eV. The calculated electron affinities range from 75.93 kcal mol⁻¹ to 89.04 kcal mol⁻¹ (3.29–3.86 eV). Both the LUMO levels and electron affinities are greatest in magnitude for the anti, syn isomer. The HOMO levels, on the other hand, range from -5.32 eV (for the trans, trans isomer) to -5.36 eV (syn, syn inner). In acetonitrile solvent, the zwitterionic form is calculated to be energetically preferred to the non-zwitterion. Experimental UV-vis and near-IR studies in acetonitrile and ethanol show little evidence for zwitterion formation, but those in water show strong evidence. The predicted electronic transitions for the non-zwitterion in acetonitrile solvent correspond closely to those seen at 533 and 416 nm. The zwitterion present in solvent corresponds to a trimer with the capability to "self-dope", suggesting that the trimer would be effective at corrosion inhibition in the emeraldine base form, unlike other trimers which are only effective in the emeraldine salt form. This effectiveness in the emeraldine base form would enable the material to be utilized in corrosion inhibition applications in alkaline environments where standard oligo- and polyanilines fail.

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1. Introduction

Conducting organic polymers such as polyacetylene [1], polyaniline [2], polypyrrole [3], and polythiophene [4] have stimulated numerous investigations. The importance of their discovery was recognized by the award of the Nobel Prize in chemistry to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa in 2000. Polyaniline (PANI) has been investigated for its utility in catalysis [5], composites [6], corrosion inhibition [7–9], nano-junctions [10], non-linear optics [11], nanoparticles and microtubules, and solar cells [12]. PANI exists in at least three oxidation states, called *leucoemeraldine* (the most reduced form, LEB), *emeraldine* (EB), and *pernigraniline* (the most oxidized form the next by a two electron oxidation or reduction. Interconversion of oxidation states is often readily achieved under mild conditions (Fig. 1). This ease of switching oxidation states is an important reason for the interest in polyanilines.

To become suitable for either conducting polymer and corrosion control applications, the polymer in the emeraldine oxidation state needs to become protonated by a Brønsted–Lowry acid, or reacted

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with a suitable Lewis acid – "doped" [13]. Only the doped emeraldine form of the polymer conducts, and only the doped emeraldine form is effective for corrosion inhibition. The applicability of the doped forms of the oligomer or polymer to these processes depends upon its redox properties (the enhanced electron affinity of the doped state is the key to the corrosion inhibition mechanism [7]). This interconnectivity of the acid/base properties of the polymer and its redox activity adds to the complexity of polyanilines. The base strength of the imine nitrogen atoms is often a critical factor in the utility of these materials in alkaline environments, since deprotonation renders the polymer or oligomer less able to inhibit corrosion.

The relationship between the structure and the function of aniline oligomers has been investigated [14–22]. Aniline oligomers have several advantages over the polymer. Aniline trimers are more effective in corrosion inhibition than the polymer. The trimers are easier materials to process than the polymer, since they are soluble in a wide variety of common solvents, whereas PANI is only soluble in *N*-methyl-2-pyrrolidone (NMP). Their precise chain length (monodispersity) removes the complications inherent in the polydispersity of the polymer. The presence of the carboxylate functionality on the oligomer increases the solubility, particularly in more polar solvents such as ethanol or water.



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Fig. 1. Redox states of N,N'-(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine. R1=NH₂ for leucoemeraldine and emeraldine states, and NH for pernigraniline. R2=COOH for all redox states.

Since doping is necessary for several applications, the benefit of an aniline polymer or oligomer that can self-dope is apparent. The quest for self-doping was a motivating rationale in the synthesis of poly-anthranilic acid [23] and the anthranilic acid/aniline (AA/A) co-polymers [2]. High level quantum chemical calculations are feasible on aniline trimers, whereas systematic investigation of the polymers at high level is too computationally expensive. Therefore, comparison of experimental properties of the trimers with calculations can be used to gain insight into both the trimers and the polymers.

2. Experimental methods

All reagents employed were purchased from Sigma–Aldrich and used without further purification. The anthranilic terminated aniline trimer *N*,*N*'-bis(3'-carboxy,4'-aminophenyl)–1,4-quinonediimine (hereafter *anthranilic emeraldine base trimer*, AEB) was synthesized [24] as follows. 1.00 g (0.00925 mol) of 1,4-*para*-phenylenediamine was dissolved in 200 mL of 2 M hydrochloric acid using magnetic stirring at room temperature. The solution was then cooled to approximately -5 °C by immersion of the reaction beaker in an ice/salt water solution. 2.11 g (0.0185 mol) of ammonium persulfate were added slowly. Upon color change of the solution from clear to light brown, 2.54 g (0.0185 mol) of anthranilic acid (AA) were added slowly. The stirring continued for one hour. The solution was allowed to reach room temperature, and excess 2 M ammonium hydroxide solution was added with magnetic stirring. The solution was then vacuumed filtered to recover the emeraldine base. The crude amine base product (mixed with a considerable remainder of the hydrochloride salt) was dissolved in absolute ethanol. Excess sodium carbonate was added with occasional stoppering of the flask and shaking, until there was no further evolution of carbon dioxide from reaction of the acid with the carbonate. More highly purified amine free base was removed from this mixture by Soxhlet extraction with ethanol, which was then evaporated in a fume hood. Ethanol was used in preference to acetonitrile, the anthranilic trimer being far more soluble in ethanol than in acetonitrile.

UV–vis spectra were collected in acetonitrile, dimethylsulfoxide, ethanol, or water using 1 cm quartz cuvettes on a Beckmann-Coulter DU-600 spectrophotometer. The solution concentrations were in the range of 10^{-5} – 10^{-4} M. Molar absorptivities in ethanol ranged from 12,400 L mol⁻¹ cm⁻¹ (at 330 nm) to 15,600 L mol⁻¹ cm⁻¹ (at 246 nm).

IR spectra were collected on a Thermo Scientific "Smart Performer" Attenuated Total Reflectance (ATR) attachment (diamond crystal) to a Nicolet 380 FT-IR. IR *N*,*N*-bis(3'-carboxy,4'-aminophe-nyl)-1,4-quinonediimine (ATR, cm⁻¹): v_{max} 1404, 748, 823, 1218, 1483, 1544, 1658, 2360, 3033, 3120.

Near-IR spectra were collected in water, acetonitrile, or 100% ethanol solvent, using 1 cm quartz cuvettes in a Foss 6500 system, using transmission mode. The wavelengths examines ranged from 1100 to 2500 nm, with a resolution of 2 nm. *N*,*N*'-bis(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine (ethanol, nm): λ_{max} 2114; (acetonitrile, nm): λ_{max} 1902, 1394; (water, nm): λ_{max} 1846, 1878, 1984.

¹H NMR spectra were collected on an Anasazi EPT-90 90 MHz NMR in DMSO-d₆ with 64 scans. NMR *N*,*N*'-bis(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine (DMSO-d₆, δ): 2.6 (proton on imine nitrogen), 5.5 (NH₂ protons, doublet), 6.7 (quinoid H, two doublets), 7.2 (aromatic protons at 3' position, two overlapping doublets), 7.8 (aromatic protons at 6' position, doublet), and 8.0 (aromatic protons at 5' position, multiplet).

The melting point was impossible to determine, being greater than 350 °C.

3. Computational methods

Optimized structures for each isomer of AEB (Fig. 2) were computed using the 6-31G^{*} [25] Pople-style Gaussian basis set (double ζ quality for the valence orbitals, plus one set of polarization functions on heavy atoms) and Becke's hybrid density functional B3LYP [26] within the Gaussian 03 suite of programs [27]. All electrons were included in the computations. The structures were then confirmed as true minima by frequency calculations at the B3LYP/6-31G^{*} level, zero imaginary frequencies being detected. Zero point energies were computed at B3LYP/6-31G^{*} with no scaling factors.

Single point energies for each structure were computed using the 6-311+G(2d,p) Pople-style Gaussian basis set [28]. This basis is triple ζ quality on the valence orbitals, supplemented by one set of diffuse functions and two additional *d* polarization functions on heavy atoms, and one set of *p* polarization functions on hydrogen. The computational method employed for the single point energies was the B3LYP hybrid density functional [26] within the Gaussian 03 suite of programs [27]. Tight convergence criteria were selected by use of the SCF = tight keyword option.

Different basis sets were employed in this work for geometry optimization [6-31G^{*}] and single point energy [6-311+G(2d,p)] calculations, since experience has shown that use of large basis sets is much less advantageous for geometry optimization than for energy calculation. Calculated thermochemical properties of a set of molecules (the "G2" set) for which excellent experimental values are available have been compared with the experimental values [29]. These comparisons allow an estimation of the accuracy of various density functional and basis set combinations. Results for B3LYP/6-31G^{*} optimization followed by B3LYP/6-311+G(2d,p) single point energy calculation had a mean absolute deviation from experiment of 3.2 kcal mol⁻¹, whereas results for B3LYP/6-311+G(2d,p) optimization followed by B3LYP/6-311+G(2d,p) single point energy calculation had a mean absolute deviation from experiment of 3.1 kcal mol⁻¹ – a minimal improvement in accuracy at best, at a huge increase in computational cost.

Enthalpies were calculated for the lowest energy singlet and triplet states of each isomer. Triplet energies for the EB isomers range from 16.3 kcal mol⁻¹ (0.707 eV) for the anti, syn isomer to 17.7 kcal mol⁻¹ (0.768 eV) for the syn, syn inner isomer. For each isomer, S₀ was lower in energy than T₁. For the dihydrochloride salts, the triplet energies were consistently near 10.3 kcal mol⁻¹ (0.447 eV), with the triplets (T₁) being again higher in energy than S₀, but lower than S₁. S₁ energies were predicted by CIS, TD-DFT, ZINDO/S, and Δ SCF.

Electron affinities were computed on the neutral minimum geometries (thereby giving the vertical electron affinities) using the 6-311+G(2d,p) basis and the B3LYP functional as implemented by Gaussian 03 [27] by difference of the computed energies (single point energy plus zero point correction) of the neutral molecule and the anion.

The enthalpy of the gas phase reaction between one mole of each trimer in the emeraldine oxidation state (EB) and two moles of hydrogen chloride to give one mole of the emeraldine dihydro-chloride salt (ES_2)

$$\mathsf{EB} + 2\mathsf{HCl} \to \mathsf{ES}_2 \tag{1}$$

was calculated using single point energy calculations at the B3LYP/ 6-311+G(2d,p) level of theory on B3LYP/6-31G^{*} optimized geometries. Zero-point energy and enthalpic corrections to 298.15 K were calculated using frequency calculations at B3LYP/6-31G^{*} [29(b)].

Wavelengths of electronic transitions were calculated using the Δ SCF method [30], which has already demonstrated its effectiveness in predicting electronic transitions for a number of oligoanilines [16–19,24]. For comparison purposes, the transition energies were also calculated using the Configuration Interaction Singles (CIS) method [31], Time-dependent density functional theory (TD-DFT) [32], and the ZINDO/S formalism [33] on B3LYP/6-31G^{*} optimized geometries. All methods were employed on both the zwitterionic and non-zwitterionic structures.

The effects of solvation on molecular structure and the electronic spectra were assessed by use of the Self-Consistent Isodensity Polarizability Continuum Model (SCIPCM) [34], with a model acetonitrile solvent. This solvent was chosen to allow comparison with the experimental UV–vis spectra, which were taken in acetonitrile. The emeraldine trimers were geometry optimized using B3LYP/6-31G^{*} chemistry in the model solvent (acetonitrile), and the electronic spectra predicted using the Δ SCF method with the orbital energies generated by a single-point calculation at B3LYP/ 6-311+G(2d,p) on the B3LYP/6-31G^{*} solvent optimized geometries.

Given the presence of both carboxylic acid and amine/imine groups in the oligomer, the potential for zwitterions formation was considered. Optimized structures for the emeraldine trimer zwitterions (Fig. 3) were generated in both the presence and absence of acetonitrile solvent. Acetonitrile was selected since its dielectric constant (ε = 36) is roughly halfway between vacuum (ε = 1) and water (ε = 78).

The computations were performed on the National Science Foundation HP GS1280 system at the Pittsburgh Supercomputing Center. Visualizations of molecular structures and orbitals were generated by ChemCraft [35].

4. Results and discussion

Calculations (Table 1) find the syn, syn (inner) isomer of AEB to be lowest in enthalpy, though the differences in enthalpies in the gas phase among isomers are less than 2 kcal mol⁻¹. In acetonitrile solvent, the calculated enthalpy differences are even smaller, still favoring the syn, syn (inner) structure. Assuming the isomers are Boltzmann distributed, the population of the AEB trimer at 298.15 K should be 69.9% syn, syn inner (ssi), 4.8% syn, syn outer



Fig. 2. Calculated molecular structures (*from top*) of syn-, syn- (inner) – *N*,*N*'-(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine; syn-, syn- (outer) – *N*,*N*'-(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine; anti-, syn- *N*,*N*-(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine; anti-, syn- *N*,*N*-(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine; anti-, syn- *N*,*N*-(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine; anti-, syn- syn- syn- syn- syn- syn- syn-



Fig. 3. Calculated molecular structure of the anti-, syn- N.N-(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine zwitterions, optimized at B3LYP/6-31G*.

Table 1

Relative enthalpies of anthranilic emeraldine trimers (with respect to lowest energy isomer) calculated at B3LYP/6-311+G(2d,p) on B3LYP/6-31G^{*} optimized geometries, with zero-point and enthalpic corrections to 298.15 K at B3LYP/6-31G^{*}. Solvent effects in acetonitrile modeled using SCIPCM method.

	Neutral molecule (gas phase)ª	Neutral molecule (solvent) ^a	Zwitterion (gas phase) ^a	Zwitterion (solvent) ^a
Syn-, syn- (inner)	0.000	0.000	10.122	NA
Syn-, syn- (outer)	1.602	0.892	8.792	0.000
Syn-, anti-	1.034	0.824	7.479	NA
Anti-, syn-	1.247	1.339	0.000	15.025
Anti-, anti-	1.649	NA	9.345	11.965

^a kcal mol⁻¹.

(sso), 12.3% syn, anti (sa), 8.6% anti, syn (as), and 4.4% anti, anti (aa).

Zwitterionic forms in the gas phase have a much different population distribution. The anti, syn isomer is the lowest in enthalpy by 7.5–10.1 kcal mol⁻¹, which means that if the isomers are Boltzmann distributed, the population of the AEB zwitterionic trimer at 298.15 K should be virtually all the anti, syn isomer.

Enthalpies of activation for isomerization of AEB were calculated at the B3LYP/6-311+G(2d,p) level after identifying the transition state for inversion at the imine nitrogen (transition state optimized and zero-point corrected to 298.15 K at B3LYP/6-31G^{*}). The value (19.6 kcal mol⁻¹) is virtually identical for the enthalpy of activation for isomerization calculated for the unsubstituted EB. Similarly, enthalpies of activation for rotation of AEB between syn and anti isomers (relative to the carboxyl group) were calculated after identifying the transition state for rotation of the outer amine rings (same level of theory as for isomerization). The value (2.18 kcal mol⁻¹) is only slightly larger than the enthalpy of activation for rotation calculated for the unsubstituted EB (1.88 kcal mol⁻¹).

The presence of both a carboxylic acid function and an imine suggested the potential for zwitterion formation (in polymeric parlance – "self-doping"). The possibility is enhanced by the inherent basicity of quinonediimines. The zwitterionic structures herein described are the *di*-zwitterions, with both carboxylates deprotonated, and both imine nitrogen atoms protonated. In the gas phase, the anti, syn AEB zwitterion structure is enthalpically favored by as much as 10 kcal mol⁻¹ over the other isomers. In acetonitrile solvent, the calculated preference is as much as 12 kcal mol⁻¹, though calculations for two isomers failed to converge.

Calculations reveal characteristic structural effects of the carboxylate group. In the analogous aniline EB trimer without a carboxyl substitution, *i.e.*, N,N'-bis(4'-aminophenyl)-1,4-quinonediimine, the tilt of the outer benzenoid rings with respect to the inner quinoid ring (C–C–N=C) is 39.97° for the syn isomer, and 40.36° for the anti; for the corresponding carboxylate-less dihydrochloride salt (ES₂), the ring tilt is the significantly smaller 27.46° for the syn isomer, and 25.73° for the anti. The greater conductivity of the doped emeraldine salt forms relative to the emeraldine base is often attributed in part to their greater (near) planarity.

For the AEB, the ring tilts are calculated at 39.69° (ssi), 38.27° (sso), 39.81° (sa), 39.73° (as), and 39.73° (aa). In other words, the presence of the carboxylic acid group at the 3' position on each outer ring has an almost non-existent effect on the calculated ground state geometry in the gas phase. Possible geometric/steric effects of the carboxyl on neighboring chains in the solid state were not addressed.

Calculated ring tilts for the anthranilic emeraldine salt (AES₂) were little changed from those of the unsubstituted aniline trimer – 28.90° (ssi), 28.71° (sso), 28.95° (sa), 28.63° (as), 26.75° (aa). For the AEB zwitterions, however, there is a quite substantial movement towards planarity. The calculated ring tilts drop to 18.40° (ssi), 21.58° (sso), 20.67° (sa), 18.44° (as), and 20.86° (aa)

The AEB zwitterions in the gas phase are approximately 46 kcal mol^{-1} higher in enthalpy that the non-zwitterionic forms in the gas phase. This is to be expected, since there is no mechanism for stabilization of the charge separation in the gas phase. The neutral molecules are only slightly stabilized by solvation, about 12 kcal mol^{-1} . The zwitterions, however, are greatly stabilized even by solvation in the slightly polar acetonitrile, nearly 65 kcal mol^{-1} for one isomer.

For the AES₂ dihydrochlorides in the gas phase (Table 2), calculated enthalpies show the *as* isomer as most stable – by essentially the same amount as for the zwitterions in the gas phase. The enthalpies of reaction of AEB with two moles of hydrogen chloride to yield the corresponding emeraldine disalt were computed. For each isomer, the reaction was clearly exothermic. The greatest enthalpy of reaction was found for the *as* isomer, at -3.3 kcal mol⁻¹. The enthalpies of reaction for 3',4'-diaminophenyl-1,4-quinonediimine was computed to be 16.35 kcal mol⁻¹, for 3'-hydroxy,4'-aminophenyl-1,4-quinonediimine 12.26 kcal mol⁻¹ [36]. Clearly,

Table 2Enthalpies of anthranilic emeraldine trimerdihydrochlorides calculated at B3LYP/6-311+G(2d,p) on B3LYP/6-31G* optimizedgeometries, with zero-point and enthalpiccorrections to 298.15 K at B3LYP/6-31G*, relative to anti, syn isomer.

	ΔH^{a}
Syn-, syn- (inner)	1.015
Syn-, syn- (outer)	3.095
Syn-, anti-	2.018
Anti-, syn-	0.000
Anti-, anti-	0.779

^a kcal mol⁻¹.

Table 3

Enthalpies of anthranilic pernigraniline trimers calculated at B3LYP/6-311+G(2d,p) on $B3LYP/6-31G^*$ optimized geometries, with zero-point and enthalpic corrections to 298.15 K at $B3LYP/6-31G^*$, relative to anti, anti isomer.

^a kcal mol⁻¹.

Table 4

Vertical electron affinities of anthranilic emeraldine trimers calculated at B3LYP/6-311+G(2d,p) on B3LYP/6-31G* optimized geometries, with zero-point and enthalpic corrections to 298.15 K at B3LYP/6-31G*.

	Emeraldine	Emeraldine	Emeraldine
	base ^a	dihydrochloride ^a	zwitterion ^a
Syn-, syn- (inner)	37.78	80.38	82.64
Syn-, syn- (outer)	38.84	79.13	89.04
Syn-, anti-	38.28	79.56	82.64
Anti-, syn-	38.40	79.69	75.92
Anti-, anti-	38.78	79.19	89.42

^a kcal mol⁻¹.

Table 5

LUMO levels of anthranilic emeraldine trimers calculated at B3LYP/6-311+G(2d,p) on B3LYP/6-31G^{*} optimized geometries, with zero-point and enthalpic corrections to 298.15 K at B3LYP/6-31G^{*}.

	Emeraldine	Emeraldine	Emeraldine
	base ^a	dihydrochloride ^a	zwitterion ^a
Syn-, syn- (inner)	-2.92	-4.65	-4.77
Syn-, syn- (outer)	-2.95	-4.58	-5.05
Syn-, anti-	-2.93	-4.61	-4.92
Anti-, syn-	-2.93	-4.60	-4.45
Anti-, anti-	-2.93	-4.58	-5.05

^a eV.

the imine nitrogens in AE are far weaker bases than those in aniline oligomers featuring a hydroxyl group (3'-hydroxy,4'-aminophenyl) or amino group (3',4'-diaminophenyl) in place of the carboxylate.

Table 6

Experimental and theoretical electronic transitions (in nanometers) of anthranilic emeraldine trimers calculated at B3LYP/6-311+G(2d,p) on B3LYP/6-31G* optimized geometries, with zero-point and enthalpic corrections to 298.15 K at B3LYP/6-31G*. Solvent effects in acetonitrile using SCIPCM method. CIS (at CIS/6-311+G*), TDDFT results (at B3LYP/6-311+G*) and ZINDO/S results are on B3LYP/6-31G* optimized geometries (gas phase). Experimental transitions are for mixture of isomers; results listed as "experimental" are identical for each isomer, since it was not possible to ascribe transitions to specific isomers.

	Transition ^a	Experimental	ΔSCF	Δ SCF (SCIPCM)	ZINDO	CIS	TDDFT
Syn-, syn- (inner)	$H \to L$	533	508	526	504		550
	$H-1 \to L$	416	415	424	449	380	385
	$H \rightarrow L + 1$	320	341	340	358		346
Syn-, syn- (outer)	$H \rightarrow L$	533	516	533	507		556
	$H - 1 \rightarrow L$	416	418	426	451	384	388
	$H \rightarrow L + 1$	320	344	344	358		345
Syn-, anti-	$H \rightarrow L$	533	512	530	505		552
	$H-1 \to L$	416	416	424	450	382	387
	$H \rightarrow L + 1$	320	344	344	357		345
Anti-, syn-	$H \rightarrow L$	533	517	533	511		563
	$H - 1 \rightarrow L$	416	418	425	445	384	385
	$H \rightarrow L + 1$	320	342	343	357		344
Anti-, anti-	$H \rightarrow L$	533	520	N/A	513		565
	$H-1 \to L$	416	419	N/A	447	385	386
	$H \rightarrow L + 1$	320	343	N/A	357		343

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Like other aniline trimers, AEB can be easily oxidized to the pernigraniline oxidation state (APB) by addition of concentrated hydrogen peroxide. The calculated isomeric preferences in the gas phase for this state are slightly different than for the emeraldine one. The *ssi* is the least stable pernigraniline isomer, whereas the *aa* is the most stable (Table 3).

4.1. IR spectra

The principal absorption bands in the IR are very close to those reported for the AA/A co-polymer. The trimer has a benzenoid stretch at 1483 cm⁻¹ (co-polymer at 1477 cm⁻¹), and a quinoid stretch at 1546 cm⁻¹ (1546 cm⁻¹ in co-polymer). The protonated imine stretch is found at 1157 cm⁻¹ (1124 cm⁻¹ in the co-polymer), and the C=O stretch from the carboxylate is found at 1656 cm⁻¹ (1674 cm⁻¹ in the co-polymer).

4.2. ¹H NMR

Indirect effects of the carboxyl group on the geometry of the AE trimer can be seen in the NMR. The ¹H NMR of the aniline trimer (as well as 3'-hydroxy and 3'-amino substituted aniline trimers) shows very broad resonances. This can be attributed to torsion of the outer rings relative to the central quinoid ring. For the AEB trimer, the proton resonances are at quite distinct chemical shifts, and the splitting patterns are easily deciphered – quite unlike several similar aniline trimers in the same (DMSO) solvent.

4.3. Electronic spectroscopy

Vertical electron affinities (EA) are a key index of potential utility in corrosion inhibition applications (Table 4). Unsubstituted aniline trimers (EB) have EA's of 1.428 (syn) and 1.434 (anti) kcal mol⁻¹. For the corresponding AE trimers (AEB), the EA's range from 1.638 eV for the *ssi* isomer, to 1.684 eV for the *sso* isomer. The very small range of values suggests that the primary influence of the carboxylate group is electronic, not steric. The difference in EA's between the unsubstituted trimer and AE results from the electron-withdrawing effect of the carboxyl group by resonance. As has been previously described, doping of aniline trimers leads to a very substantial increase in the electron affinity, attributable to the strong electron-withdrawing effects of hydrochloride, primarily by induction (the electronegativity of chlorine). The calculated electron affinities of the AE dihydrochlorides vary from

^a H = HOMO, L = LUMO, H – 1 = next highest occupied molecular orbital, L + 1 = next lowest unoccupied molecular orbital.

3.431 eV to 3.487 for the *ssi* isomer. This corresponds to a range of only 0.056 eV among the isomers. Surprising, the zwitterions of AE trimers, undoped by an external mineral acid, have an even greater electron affinity than the mineral-acid-doped emeraldine dihydrochloride salt. These can be as low as 3.293 eV, or as large as 3.861 eV, demonstrating that structural effects exert subtle but substantial effects on the overall electron affinity. The phenomenon of "self-doping" appears to be manifest through zwitterion formation, with the benefit of increasing the electron affinity of the oligomer beyond what could be achieved by mineral acid doping.

Unsubstituted aniline trimer dihydrochlorides have calculated LUMO's at -4.44 eV (syn isomer), or -4.42 eV (anti). The calculated LUMO levels (Table 5) for the AE dihydrochloride range from -4.58 to -4.65 eV (for the *ssi* isomer). The lower LUMO levels of the AE dihydrochlorides can be attributed to the additional with-

draw of electron density by the two carboxylic acid groups, largely though inductive effect of the oxygen atoms. The AE zwitterions, lacking the strong electron-withdrawing effect of the hydrochloride dopant, nevertheless have an even lower LUMO level than the AE dihydrochloride. The calculated levels range from -4.45 eV to -5.05 eV for the AE *aa* zwitterion isomer. The proton dopant on the imine nitrogens can be expected to withdraw far less electron density than would hydrogen chloride. Similarly, the carboxylate anion of the AE zwitterions should be less effective in withdrawing density by induction than the un-ionized carboxyl (because of the negative charge on the carboxylate). Therefore, the difference in LUMO levels must result from the substantial withdrawal of density by *resonance*. The electronic affinities of the various AE isomers closely parallel the calculated LUMO levels, suggesting that the most significant determinant of electron affin-



Fig. 4. Calculated frontier orbitals of anti-, syn- *N*,*N*'(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine at B3LYP/6-311+G(2d,p) on the B3LYP/6-31G* optimized structure: LUMO+1 (top), LUMO (*upper middle*), HOMO (*lower middle*), and HOMO-1.

ities (and therefore, corrosion inhibition) are those structural effects that "pull down" the LUMO.

Unsubstituted aniline trimer dihydrochlorides have calculated HOMO's at -6.00 eV (syn isomer), or -6.02 eV (anti). For the AE trimer hydrochlorides, the calculated HOMO values range from -6.21 eV (for the *ssi* isomer) to -6.18 (*st*). The effect of the carboxylate groups on the outer rings is to lower the HOMO, just as they lower the LUMO.

For the AEB trimers in the non-zwitterionic form, predicted electronic transitions by several methods are listed in Table 6. While there is excellent agreement between the predictions for the shortest wavelength absorption (320 nm.) and the experimental spectrum (Fig. 6), the next two absorptions are not seen in water. For the zwitterions, the shortest predicted wavelength is essentially the same as for the non-zwitterion, but the next two predicted absorptions are substantially red-shifted to 923 and 1365 nm for the ssi isomer, or 1529 nm for the as isomer. Since the as isomer is predicted to be the predominant form if conversion to zwitterions is complete, its presence in the near-IR would be evidence of zwitterion formation. In fact, the presence of a near-IR band around 1600 nm [37] or 1700 nm [38] has been cited as evidence of doping of polyaniline by Lewis or Brønsted acid. The strong near-IR band are found at 1902 nm in acetonitrile, and 1982 nm in water, with smaller bands in both solvents around 1460 nm. The ratio of the absorbance at 1982 nm to that at 1460 nm is much great for water than the ratio of 1902 nm to

1460 for acetonitrile, which suggests that the equilibrium is shifted more toward zwitterion formation in water than in acetonitrile. The near-IR bands (except for the band in water at 1982 nm) are not very broad – in sharp contrast to the situation in doped polyanilines [39]. The broadness of the relevant near-IR peaks in polyaniline has been attributed to changes in the conformations of the polymer, which conformations are not so important in the smaller sized oligomers. The expected transitions for the non-zwitterion appear in less polar, non-protic solvents such as DMSO and acetonitrile – precisely those solvents where zwitterion formation would be less expected.

For the unsubstituted aniline trimer, the primary electronic transitions observed are H (HOMO) \rightarrow L (LUMO, 544 nm) and H \rightarrow L + 1 (second lowest unoccupied molecular orbital, 277 nm). Oxygenated aniline trimers, on the other hand, show primarily a H – 1 (second highest occupied molecular orbital) \rightarrow L transition. AE shows considerable difference from either of the other two classes of aniline trimer investigated. AE shows only the H \rightarrow L + 1 transition in water, but H \rightarrow L and H – 1 \rightarrow L in other solvents. The frontier orbitals of AE are displayed in Fig. 4 (non-zwitterion) and Fig. 5 (zwitterion). This strongly suggests that zwitterion formation dominates in other solvents, and that the one transition seen in both sets of solvents is H \rightarrow L + 1, though H \rightarrow L + 1 for the non-zwitterion is much different in character from the H \rightarrow L + 1 for the zwitterions.



Fig. 5. Calculated frontier orbitals of the anti-, syn- N,N'-(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine zwitterions at B3LYP/6-311+G(2d,p) on the B3LYP/6-31G* optimized structure: LUMO+1 (top), LUMO (upper middle), HOMO (lower middle), and HOMO-1.



Fig. 6. UV-vis spectra of *N*,*N*-(3'-carboxy,4'-aminophenyl)-1,4-quinonediimine in acetonitrile, ethanol, and water solvent.

For the co-polymer [2], absorptions at greater than 600 nm decrease rapidly as the ratio of aniline to AA decreases. This is attributed to reduction of conjugation length of the co-polymer due to steric effect of AA. It could also be attributed to the appearance of the zwitterions. The UV–vis of the trimer is almost identical to that of the AA/A co-polymer. According to reference [2], the absorption at 330 nm in the co-polymer is $\pi \rightarrow \pi^*$ and "related to the extent of conjugation between adjacent phenyl rings", whereas in the trimer it seems to be an $H \rightarrow L + 1$ transition, involving intense charge transfer between the outer rings and the central quinoid ring. The authors [2] note a shift from 330 nm (in polyaniline) to 280 nm (in the AA/A 1:1 co-polymer), which they attribute to the "steric effect of the carboxylate groups in the polymer chain that causes perturbation in of the coplanarity of the π -system..."

For the trimers, the change is in the opposite direction. The aniline trimer has its $\pi \to \pi^*$ transition at 277 nm, which is shifted to 320 nm for AE. Solvent effects are mostly consistent with the nature of the transition. On changing the solvent, the absorption shifts from 329 nm (ethanol) to 331 nm (acetonitrile) to 336 nm (DMSO). The red shift on increasing polarity of the solvent is indicative of a $\pi \to \pi^*$ transition. In water, however, the transition suddenly blue shifts to 318 nm – evidence that the transition in water is different from those in the other, less polar, mostly non-protic solvents.

The intensities of the two strongest electronic transitions for the non-zwitterionic trimers were calculated using three of the same methods (ZINDO/S, CIS, and TD-DFT) that had been used to predict the wavelengths of the transitions themselves. The calculated oscillator strength for the band at 326 nm ranges from 0.26 (TD-DFT) to 1.24 (CIS). The experimental oscillator strength was calculated by plotting the molar absorptivity (in L mol⁻¹ cm⁻¹) for the bands at 242 and 326 nm as a function of frequency (in s⁻¹). Trial fits of Gaussian curves were made to each, with standard deviations of 5.0×10^{13} and 5.3×10^{13} s, respectively. The oscillator strengths therefore were 0.29 and 0.24, in reasonable agreement with the TD-DFT values.

Effect of addition of HCl to AE trimer is anomalous. Typically, there is a red-shift of all the important transitions upon addition of HCl, due to the conversion of EB to ES and then ES₂, with a progressive narrowing of the HOMO–LUMO gap. The electron-with-drawing effect of the hydrogen chloride is particularly strong at the imine nitrogen. This is usually described in the polymer case as a reduction in the exciton energy as a result of an increase in

the effective conjugation length. However, the only shift observed for the AE trimer upon addition of acid is a slight *blue* shift. This is to be expected in the AE zwitterionic case, where the imine nitrogens are *already* protonated. The only protonation events possible are at the carboxylates. Transformation of the carboxylate to a carboxyl group reduces the electron withdrawing ability of the group by resonance, which, as stated above, is largely responsible for pulling down the energy of the LUMO.

5. Conclusions

The AE trimer has be synthesized, and its experimental and theoretical investigation enables a deeper understanding of subtle electronic and steric effects in co-polymers of aniline and anthranilic acid. In non-protic solvents, the non-zwitterionic form predominates, whereas in water, the zwitterion predominates. This AE zwitterion effectively self-dopes as the emeraldine base, with LUMO levels and electron affinity even lower than those calculated for the carboxyl substituted aniline trimer dihydrochloride. Since lower LUMO levels and more negative electron affinity have been linked with superior corrosion inhibition, further investigation of these materials is warranted. The UV-vis of the trimer is almost identical to that of the AA/A co-polymer, while the IR of the trimer is very similar. For the perspective of electronic and vibrational spectroscopy, with benefit of density functional theory, N,N'bis(3'-carboxy,4'-aminophenyl)-1,4-guinonediimine is an appropriate model for the aniline/anthranilic acid co-polymer. As an appropriate (and computationally accessible) model, it gives insight into phenomena in the co-polymer which would be impossible to access directly.

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