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Effect of Substituting Oxygen for Terminal Nitrogen in Aniline Oligomers: a DFT Comparison of Hydroxyl and Amino Terminated Aniline Trimers

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Quantum mechanical density functional theory (DFT) calculations are reported for *N*,*N*′-bis(4′-hydroxyphenyl)-1,4-quinonediimine [henceforth referred to as the *hydroxyl terminated trimer*], a derivative of previously investigated aniline trimers. Calculations are also reported on all isomers, common oxidations states, and hydrochloride salts of this material. The significance of replacing terminal amino groups by hydroxyl groups is detailed. The hydroxyl terminated trimer has a calculated electron affinity larger than that of the corresponding amino terminated aniline trimer *N*,*N*′-bis(4′-aminophenyl)-1,4-quinonediimine. The electron affinity of the anti conformer of the hydroxyl terminated emeraldine base trimer is 0.059767 hartrees (37.5 kcal mol^{-1}), whereas that of the amino terminated form is 0.052728 (33.1 kcal mol^{-1}). The electron affinity of the anti conformer of the hydroxyl terminated emeraldine dihydrochloride salt trimer is 0.130546 hartrees (81.9 kcal mol^{-1}), whereas that of the amino terminated dihydrochloride salt is only 0.118972 (74.7 kcal mol^{-1}). Because previous work has suggested that a larger electron affinity in the salt form leads to improved effectiveness in the role of corrosion inhibitor, these high-level calculations suggest a new and superior material for this application.

Introduction

Polyaniline (PAni), in both oligomeric and polymeric forms, has been investigated for its utility in solar cells,[1] corrosion inhibition,[2,3] nonlinear optics,[4] composites,[5] nanoparticles and microtubules,[6] nanojunctions,[7] and catalysis.[8] PAni exists in numerous oxidation states, many of which are readily interconvertible in the requisite physical or chemical environment (Figure 1). For both conducting polymer and corrosion control applications, the polymer in the emeraldine oxidation state needs to become protonated by Brønsted-Lowry acid, or reacted with a suitable Lewis acid (i.e., “doped”).[9]

Studies have appeared that have investigated the relationships between PAni structure and function.[10−18] These studies have confirmed that aniline trimers are more effective in corrosion inhibition than the polymer. The trimers are also far more tractable materials than the polymer, because they are soluble in a wide variety of common solvents, whereas PAni is only soluble in *N*-methyl-2-pyrrolidone (NMP). It has also been shown that the electronic states of the aniline trimer sufficiently resemble those of the polymer for the trimer to be an effective model of the polymer, at least as far as electronic states are concerned.[15] The subject of quantum structure activity relationships in aniline trimers has only been lightly investigated, and further inquiry holds the promise of more rapid advance in the utilization of these materials for existing and novel applications.

Results and Discussion

Geometry optimization of the hydroxyl terminated aniline trimers at the BLYP/6-31G* level is in agreement with previous work demonstrating that aniline trimers are distinctly nonlinear and nonplanar (Figure 2). This nonplanarity (caused primarily by the sp^2 hybridization at the central imine nitrogens) leads to multiple isomers. Hydroxyl terminated aniline trimers can exist in two isomeric forms, syn and anti. Calculated isomeric preferences for amino terminated trimers have been published previously.[2,12−16] Hydroxyl terminated trimers have a very slight energetic preference for the anti conformation in the leucoemeraldine, emeraldine, and pernigraniline oxidation states, but a more pronounced preference for the syn conformation in both the mono- and dihydrochloride (“doped”) states (Table 1). The effect of solvation on the isomeric preferences was determined by SCI-PCM calculations of each isomer in acetonitrile solvent. The single point energy of the syn hydroxyl terminated emeraldine isomer in solvent was −954.546244998 hartrees, and that of the anti isomer was −954.545740654 hartrees. Therefore, the conformational preference (at least for the emeraldine oxidation state) is not altered by solvation in acetonitrile.

Calculation of the frontier orbital energies for both amino and hydroxyl terminated aniline trimers shows that hydroxyl substitution for amino at the terminal positions of the trimers pulls down the energy of each frontier orbital for the HOMO−1 up to the LUMO+1 (Figure 3). This is the expected result based upon the superior electron-withdrawing capability of oxygen relative to nitrogen, deriving from oxygen’s greater electronegativity. This effect is analogous to the even more substantial effect of hydrochloride doping at the imine nitrogens upon salt formation with the amino terminated trimers. Earlier work suggested that much of the greater corrosion inhibition effect of the salts as opposed to the amino terminated emeraldine free base could be explained by the electron-withdrawing effect of the chlorine. Therefore, investigations of those moieties that withdraw electron density are of considerable relevance to improving the corrosion inhibition of the trimers.

The effect of doping with two molecules of hydrochloride is greater than the effect of substituting both amino groups with

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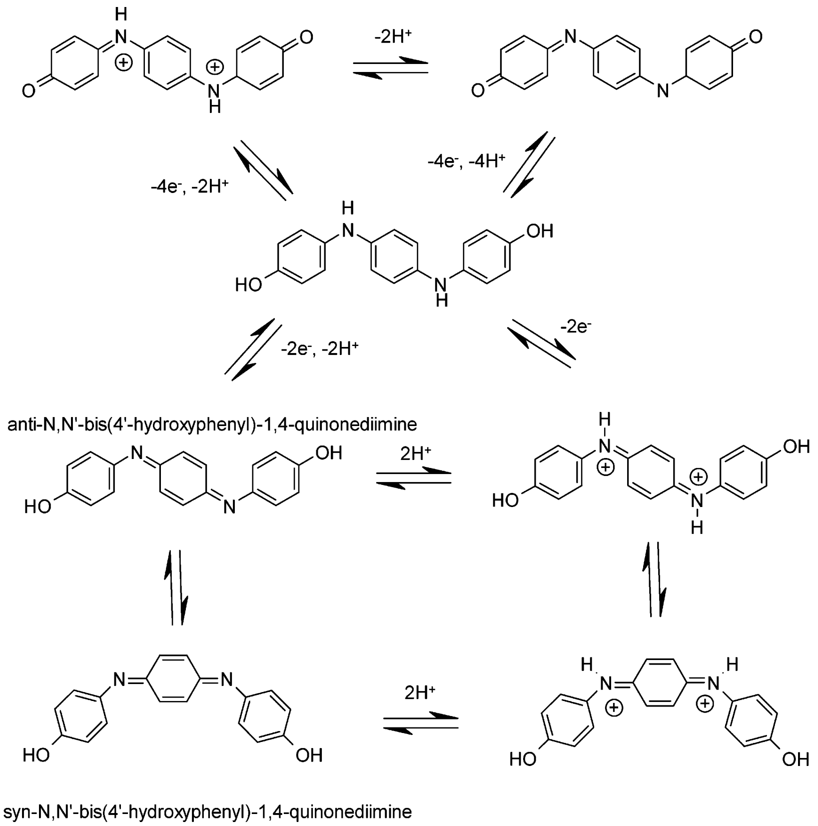

Figure 1. Molecular structure of *N*,*N*′-bis(4′-hydroxyphenyl)-1,4-quinonediimine, its redox states, its salts, and its isomers.

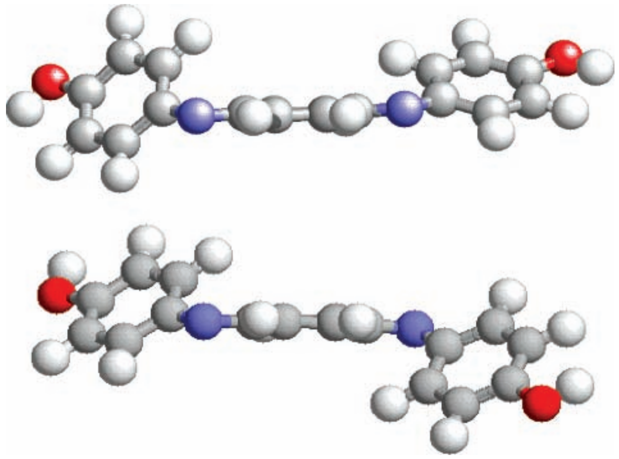

Figure 2. Molecular structure of syn (upper) and anti (lower) hydroxyl terminated aniline trimer in emeraldine oxidation state, optimized at B3LYP/6-31G*. Carbon atoms are gray, hydrogen atoms white, nitrogen atoms blue, and oxygen atoms red.

hydroxyl ones, but the effects are cumulative. Therefore, even though the hydroxyl terminated emeraldine trimer free base does not feature as dramatic a reduction of the orbital energies as does the amino terminated emeraldine *di*hydrochloride salt, the effect is essentially identical to that of the amino terminated *mono*hydrochloride salt. The hydroxyl terminated emeraldine dihydrochloride salt is the most effective at pulling down the LUMO energy of any of the species investigated in this paper. Because failure of corrosion inhibition can result from de-doping of the trimer (or parent polymer), the use of a trimer that still has a substantial electron-withdrawing effect, even under conditions under which de-doping would occur with other trimers, might be expected to offer a more effective inhibitor under real world conditions.

TABLE 1: Enthalpies of Isomers of Hydroxyl Terminated Aniline Trimers in Various Oxidation States[a]

syn[b]	anti[b]	
−955.473682	−955.473258	leucoemeraldine
−954.251070	−954.250615	emeraldine
−1415.091777	−1415.091341	emeraldine monohydrochloride
−1875.928721	−1875.928052	emeraldine dihydrochloride
−953.034638	−953.035006	pernigraniline

[a] Single point energies computed using B3LYP functional and 6-311+G(2d,p) basis set on B3LYP/6-31G* optimized geometries. Zero-point energies calculated at B3LYP/6-31G* on B3LYP/6-31G* optimized geometries without scaling. [b] Hartrees.

The frontier orbitals of each trimer were calculated at the B3LYP/6-311+G(2d,p) level from the B3LYP/6-31G* optimized geometry (Figures 4 and 5). In the HOMO, electron density is maximized primarily on the outer two rings. This is essentially the same configuration as found in the amino terminated trimer, except that the amino terminated emeraldine also has considerable density on the central ring,[15] which is absent in the hydroxyl trimer. This might be ascribed to the electron-withdrawing capability of oxygen. The calculated HOMO orbital is considerably different from what would be predicted were the trimer to be linear and planar. The electron density is *not* completely delocalized over all three rings, and the orbital symmetry is not completely π. The nonlinearity and nonplanarity cause a considerable mixing of σ and π orbitals.

The LUMO is rather similar to that found for the amino terminated trimer.[15] Almost all electron density has left the terminal hydroxyl or amino group and is found on the central ring, the imine nitrogens, or the regions of the outer rings closest to the imine nitrogens.

The HOMO−LUMO gaps for each trimer were calculated at the B3LYP/6-311+G(2d,p) level based on the B3LYP/6-31G* optimized geometries using the ΔSCF method (Table 2).

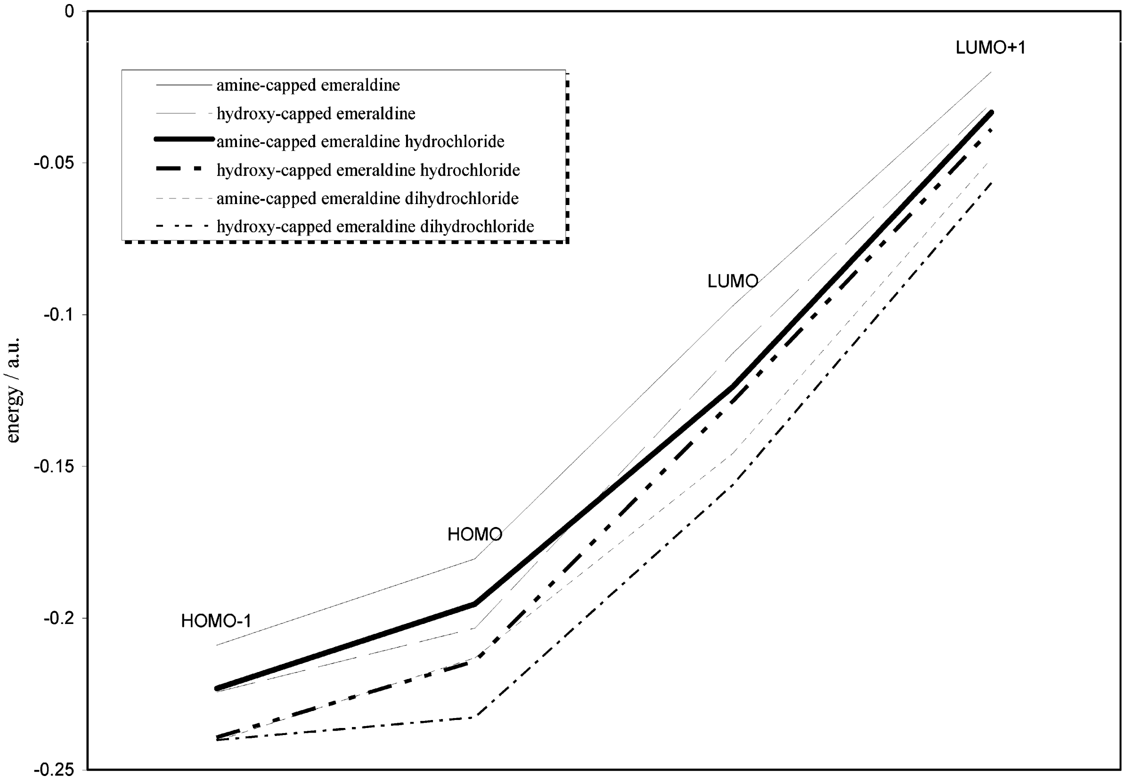

Figure 3. Energies of frontier orbitals for syn amino and hydroxyl terminated aniline emeraldine trimers, calculated at B3LYP/6-311+G(2d,p) on B3LYP/6-31G* optimized geometries.

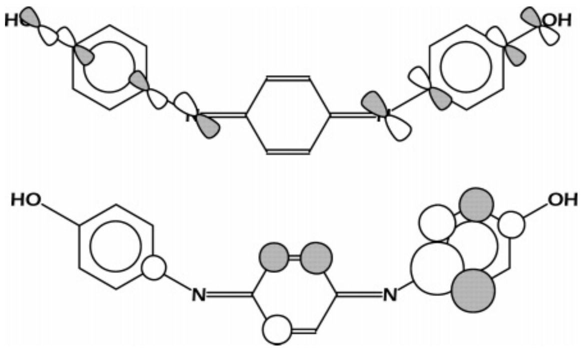

Figure 4. Highest occupied molecular orbital of syn hydroxyl terminated aniline trimer, calculated at B3LYP/6-311+G(2d,p) on the B3LYP/6-31G* optimized geometry. The molecular orbital is shown as a linear combination of atomic p orbitals (upper) and atomic s orbitals (lower). The size of the orbital is proportional to the calculated MO coefficient. Orbitals with coefficients smaller than 0.08 were omitted for clarity.

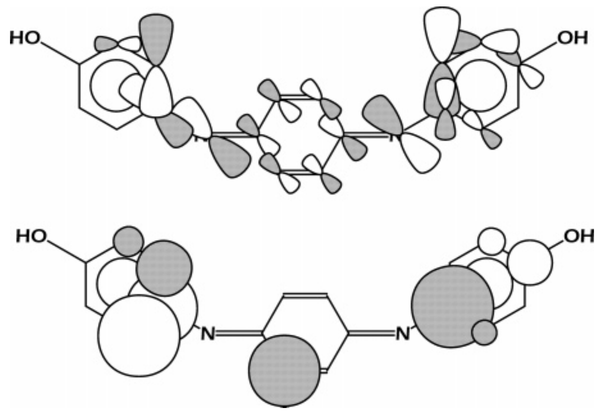

Figure 5. Lowest occupied molecular orbital of syn hydroxyl terminated aniline trimer, calculated at B3LYP/6-311+G(2d,p) on the B3LYP/6-31G* optimized geometry. The molecular orbital is shown as a linear combination of atomic p orbitals (upper) and atomic s orbitals (lower). The size of the orbital is proportional to the calculated MO coefficient. Orbitals with coefficients smaller than 0.08 were omitted for clarity.

Hydroxyl substitution minimized the band gap relative to the amino terminated trimers, particularly through pulling down of the LUMO energy.

The ΔSCF method is successful in predicting the electronic transition observed in the UV−vis spectrum collected in acetonitrile. This has been previously demonstrated for other aniline trimers.[17] Curiously, the HOMO−LUMO gap is not observed as one of the prominent bands in the spectrum. The transitions with the largest molar absorptivities are HOMO−1 → LUMO and HOMO → LUMO+1. This behavior has been observed previously, for 2-hydroxy substituted aniline trimers [formally, *N*,*N*′-bis(3′-hydroxy-4′-aminophenyl)-1,4-quinonediimine]. It appears to be a distinctive feature of hydroxyl substitution at various locations on the outer rings, whether in place of the amino group or in addition to it, that the HOMO → LUMO transition becomes much weaker than other transitions. The “exciton band”, the longest wavelength transition observable on the UV−vis spectrum, which was demonstrated to be a HOMO → LUMO transition for the unsubstituted aniline trimers,[15] becomes a HOMO−1 → LUMO transition upon substitution with oxygen.

The ΔSCF method was also applied to trimer structures optimized with the SCIPCM method to simulate the effects of solvation. Though the predicted bands are shifted by only a few nanometers relative to the gas-phase calculations, in each case the SCIPCM prediction is closer to the experimental value than the gas-phase calculation.

ZINDO/S[19] calculations of the trimer excited states yielded much poorer agreement with experiment than did the ΔSCF calculations (Table 3). This could not have been a result of an

TABLE 2: Theoretical Predictions for Electronic Transitions for Syn and Anti Isomers Using the ΔSCF Method for Hydroxyl Terminated Aniline Trimers[a]

predicted (gas)[b]	predicted (solvent)[b]	exptl[b]	transition	isomer
260	258	247	HOMO → LUMO+1	syn emeraldine
396	399	409	HOMO-1 → LUMO	syn emeraldine
475	482	*c*	HOMO → LUMO	syn emeraldine
260	259	247	HOMO → LUMO+1	anti emeraldine
396	398	409	HOMO-1 → LUMO	anti emeraldine
475	486	*c*	HOMO → LUMO	anti emeraldine

[a] Solvent predictions in solvent utilize acetonitrile. Experimental values collected using acetonitrile as solvent. [b] Nanometers. [c] Not observed.

TABLE 3: Theoretical Predictions for Electronic Transitions for Syn and Anti Isomers Using the ZINDO/S Method for Hydroxyl Terminated Aniline Trimers[a]

predicted[b]	exptl[b]	transition	isomer
346	247	HOMO → LUMO+1	syn emeraldine
440	409	HOMO-1 → LUMO	syn emeraldine
479	*c*	HOMO → LUMO	syn emeraldine
345	247	HOMO → LUMO+1	anti emeraldine
434	409	HOMO-1 → LUMO	anti emeraldine
485	*c*	HOMO → LUMO	anti emeraldine

[a] Experimental values collected using acetonitrile as solvent. [b] Nanometers. [c] Not observed.

TABLE 4: Vertical Ionization Potentials for Amino or Hydroxyl Terminated Aniline Trimers, Computed at B3LYP/6-311+G(2d,p) on B3LYP/6-31G* Optimized Geometries

amino[a]	hydroxyl[a]	
0.210811	0.220838	syn leucoemeraldine
0.210807	0.222067	anti leucoemeraldine
0.233897	0.250960	syn emeraldine
0.232465	0.250232	anti emeraldine
0.250491	0.268504	syn emeraldine monohydrochloride
0.248651	0.267287	anti emeraldine monohydrochloride
0.265693	0.284580	syn pernigraniline
0.265092	0.283760	anti pernigraniline

[a] Hartrees.

inaccurate input geometry, as the ZINDO/S calculations used the same geometry as did the gas-phase ΔSCF calculations, the B3LYP/6-31G* optimized geometry. It is likely that the ZINDO/S calculations failed at prediction for exactly the same reason that the ΔSCF method calculations were successful: the excited states of these trimers can be adequately described by a single determinant. It was impossible to make ZINDO/S predictions on the trimer salts, as there are no parameters available for chlorine.

Doping with mineral acid (specifically, hydrogen chloride) is predicted to reduce the band gap further, as has been widely demonstrated previously for amino terminated trimers, oligomers, and polymers. This suggests that hydroxyl terminated aniline trimers might be exploited in novel photonic applications.

The vertical ionization potentials were calculated for each amino or hydroxyl terminated trimer, in each possible oxidation state, using the B3LYP/6-311+G(2d,p) level of theory on B3LYP/6-31G* optimized geometries (Table 4). As might be expected, the presence of oxygen in place of nitrogen causes a substantial increase of the ionization potential of the trimer. The general trends for the various oxidation states of the hydroxyl terminated trimer parallel those for the amino terminated ones. Vertical electron affinities were calculated, also at the B3LYP/6-311+G(2d,p) level of theory (Table 5). The hydroxyl terminated trimers have consistently greater (more negative, therefore more favored) electron affinities than the amino terminated ones. This suggests that the tendency of oxygen to stabilize the anion by withdrawal of electron charge is more important than its tendency to release electron density through resonance. The hydroxyl terminated emeraldine dihydrochloride salt has a greater electron affinity than any comparable amino terminated trimer, whether base or salt. This suggests that the hydroxyl terminated trimer might have enhanced effectiveness in corrosion inhibition.

TABLE 5: Vertical Electron Affinities for Amino or Hydroxyl Terminated Aniline Trimers, Computed at B3LYP/6-311+G(2d,p) on B3LYP/6-31G* Optimized Geometries

amino[a]	hydroxyl[a]	
−0.021435	−0.018097	syn leucoemeraldine
−0.022348	−0.017554	anti leucoemeraldine
0.052450	0.059347	syn emeraldine
0.052728	0.059767	anti emeraldine
0.089606	0.098305	syn emeraldine monohydrochloride
0.088873	0.097927	anti emeraldine monohydrochloride
0.119220	0.111056	syn emeraldine dihydrochloride
0.118972	0.130546	anti emeraldine dihydrochloride
0.078471	0.095823	syn pernigraniline
0.077904	0.095225	anti pernigraniline

[a] Hartrees.

TABLE 6: Energy of Reaction for Amino or Hydroxyl Terminated Aniline Trimers[a]

amino[b]	hydroxyl[b]	
−9.3671	−7.5134	syn emeraldine monohydrochloride
−14.4941	−12.6655	syn emeraldine dihydrochloride
−11.9062	−7.5249	anti emeraldine monohydrochloride
−18.8149	−12.5310	anti emeraldine dihydrochloride

[a] The reactions are emeraldine base (EB) plus hydrogen chloride to give emeraldine monohydrochloride salt (ES), or emeraldine monohydrochloride salt (ES) plus hydrogen chloride to give emeraldine dihydrochloride salt (ES_2). Energies computed on B3LYP/6-31G* optimized structures at the B3LYP/6-311+G(2d,p) level of theory, with zero-point energies computed at B3LYP/6-31G*, unscaled. [b] kcal/mol.

The energy change upon reaction with hydrogen chloride dopant was calculated at the B3LYP/6-311+G(2d,p) level of theory for both the amino and hydroxyl terminated emeraldine free bases (Table 6). This was done to assess the Brønsted−Lowry base strength of each of the trimers. In each case, the energy of the resulting salts was calculated on the relaxed, optimized geometries. The free base forms of the trimers are generally ineffective at corrosion inhibition, just as the free base form of polymeric polyaniline is both nonconducting and ineffective in corrosion inhibition. Therefore, it is important to predict the tendency of the trimer to become de-doped by loss of the hydrogen chloride acid to a stronger base. The hydroxyl terminated trimer appears to be about as strong a base as the amino terminated one. No attempt was made to correct for entropy effects or, more importantly, the effects of solvation. Therefore, although the calculations cannot be expected to account for all effects, the general suggestion is that hydroxyl terminated trimers should be at least as effective in resisting de-doping as the amino terminated ones.

A final consideration can be noted. Aniline trimers have found use as corrosion inhibitors as substitutes for chromium, which is known to be carcinogenic in the Cr(VI) oxidation state. Aromatic amines are also environmentally suspect. Amines are prone to oxidation, and many amines are suspected of carcinogenicity.[20] On the other hand, phenols, though capable of acute toxicity in high doses, are also known to be potent antioxidants.[21] It remains to be seen whether phenol-terminated aniline trimers might prove to be not only superior at corrosion inhibition but also more environmentally friendly.

Experimental Methods

All reagents employed in the syntheses were purchased from Aldrich and used without further purification. Amino terminated aniline trimers were synthesized by established methods.[15] The hydroxyl terminated aniline trimers [*N*,*N*′-bis(4′-hydroxyphenyl)-1,4-quinonediimine] were synthesized by adaptation of these methods (Figure 1). A 1 g (0.00925 mol) quantity of 1,4-phenylenediamine was dissolved in 200 mL of 2 M hydrochloric acid using magnetic stirring. The solution was then cooled to approximately −5 °C by immersion of the reaction beaker in ice/salt water solution. A 2.11 g (0.0185 mol) amount of ammonium persulfate was added slowly. Upon color change of the solution from clear to light brown, 1.74 g (0.0185 mol) of phenol was added slowly. The mixture was then allowed to react for 1 h. After the solution was allowed to reach room temperature, excess 2 M ammonium hydroxide solution was added with magnetic stirring. The solution was then vacuumed filtered to recover the amine base. Reaction with ammonium hydroxide solution is not entirely effective in neutralizing all hydrochloric acid. Therefore, the crude amine base product was dissolved in acetonitrile. Excess sodium carbonate was added 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 acetonitrile, which was then evaporated in a fume hood.

UV−vis spectra were collected in acetonitrile using 1 cm quartz cuvettes on a Beckmann-Coulter DU-600 spectrophotometer. IR spectra were collected on a “Smart Performer” attenuated total reflectance (ATR) attachment to a Nicolet 380 FT-IR. IR (ATR, cm^{-1}) $\nu_{\max}$ 1399, 669, 692, 706, 753, 829, 1167, 1231, 1292, 1433, 1505, 1510, 1557, 1564, 2808, 3037, 3122. ^{1}H NMR were collected on a 90 MHz Anasazi NMR in DMSO-d_6: 4H at 6.8 δ (on central ring); 4H at 7.27 δ (meta to hydroxyl group); 4H at 7.9 δ (ortho to hydroxyl group); 2H at 6.6 δ (phenolic). Due to rapid exchange, the phenolic proton peak at 6.6 was very weak. Mp > 350 °C.

Computational Methods

Optimized structures for each compound or isomer were computed using the 6-31G* Pople-style Gaussian basis set [double ζ quality for the valence orbitals, plus one set of polarization functions on heavy atoms] and the B3LYP hybrid density functional[22] within the Gaussian 03 suite of programs.[23] All electrons were included in the computations. The structures were confirmed as true minima by frequency calculations at the B3LYP/6-31G* level, and the appropriate zero point energies were also computed. No scaling factors were employed.

Single point energies for each structure were computed using the 6-311G+(2d,p) Pople-style Gaussian basis set [triple ζ quality for the valence orbitals, one set of diffuse functions, two additional d polarization functions on heavy atoms, and one set of p polarization functions on hydrogen] and the B3LYP hybrid density functional[22] within the Gaussian 03 suite of programs.[23]

Ionization potentials and electron affinities were computed on the neutral minimal geometries (thereby giving the vertical ionization potential or electron affinities) using the 6-311+G-(2d,p) basis and the B3LYP functional within Gaussian 03.[23] Wavelengths of electronic transitions were calculated using the ΔSCF method,[24] which has already demonstrated its effectiveness in predicting transitions for a number of oligoanilines.[12−16] Transition energies were also calculated using the ZINDO/S formalism[19] on B3LYP/6-31G* optimized geometries.

The effects of solvation on molecular structure and the electronic spectra were assessed use of the self-consistent isodensity polarizability continuum model (SCIPCM),[25] 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 the B3LYP/6-31G* model chemistry, and the electronic spectra predicted using the ΔSCF method with the orbital energies generated by a single-point calculation at B3LYP/6-311+G(2d,p) on the B3LYP/6-31G* optimized geometries.

The computations were performed on the National Science Foundation HP GS1280 system at the Pittsburgh Supercomputing Center.

Conclusions

Aniline trimers have been found to be effective in a wide range of applications, having superior solubility to polyaniline, and being more effective at corrosion inhibition. Density functional theory has proven effective in predicting the optical and electrochemical properties of aniline trimers. Using these same methods, it was possible to accurately predict the electronic spectrum for hydroxyl terminated aniline trimers. These trimers are also predicted to possess greater electron affinity than the amino terminated ones, and it is this electron affinity that has been positively correlated in previous studies with corrosion inhibition effectiveness. In addition, the manufacture of these trimers from phenols, as opposed to amines, offers the potential for a reduction in harm to the environment.

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Supporting Information Available: Optimized structures of the amino and hydroxyl terminated trimers in various oxidation states. This material is available free of charge via the Internet at http://pubs.acs.org.

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