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Synthesis, characterization, and computational study of *N*,*N*'-bis (2',4'-dihydroxyphenyl)-1.4-quinonediimine, a hydroxyl-capped three-ring quinonediimine with sterically hindered substituent on outer rings

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ABSTRACT

Density functional calculations were performed on *N*,*N'*-bis (2',4'-dihydroxyphenyl)-1.4-quinonediimine, a hydroxyl-terminated quinonediimine with an additional meta-hydroxyl substituent on each outer ring. Results of the calculations were compared to experimental properties of the herein synthesized compound. The calculated LUMO levels for isomers of the title compound range from -2.764 to -3.279 eV. The calculated electron affinities range from 1.398 to 1.989 eV. Both the LUMO levels and electron affinities are greatest in magnitude for the syn, anti isomer. The HOMO levels, on the other hand, range from -5.383 eV (for the anti, anti isomer) to -5.541 eV (syn, anti). The predicted electronic transitions for the molecule in ethanol solvent correspond closely to those seen at 580 and 254 nm. The isomers vary widely in energy, leading to a marked preference for the syn, syn (outer) isomer – a direct result of the steric effect of the hydroxyl group at the 2' position.

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1. Introduction

Conducting polymers derived from polyaniline (PAni) have been widely investigated [1]. Unfortunately, PAni has low solubility in most common organic solvents, leading to interest in aniline oligomers [2,3]. Aniline oligomers that are amino-terminated at each end share many properties with PAni. They can be easily interconverted between multiple oxidation states just as can PAni, and the same names are commonly assigned to these redox states – leucoemeraldine for the most reduced state, emeraldine for the intermediate oxidation state, and pernigraniline for the most oxidized state. The oligomers are effective at corrosion control, and they are most effective when doped by mineral acids when in the emeraldine form, just as polyaniline is most effective at corrosion control when doped with mineral acids in the emeraldine form.

The smallest amino-terminated oligomer of aniline that possesses three distinct oxidation states is the one with three aromatic rings. This oligomer can be easily synthesized by reaction of *p*-phenylene diamine with (substituted) anilines, with the *p*-phenylene diamine molecule becoming the central quinoid ring, and the substituted anilines forming the outer benzenoid rings. A substituted quinonediimine is thus formed, which is analogous to an amino-capped aniline oligomer in the emeraldine redox state. A variety of modifications can been made to the outer rings of the oligomer by replacing aniline or a substituted aniline by any aromatic compound possessing a sufficiently strong activating group for electrophilic aromatic substitution and an open *para* position for attack by the *p*-phenylenediamine. A novel quinonediimine (Fig. 1) has been synthesized from resorcinol, the properties of which are herein investigated. The synthesis utilizes resorcinol to generate *meta*-substituted hydroxyl groups on the outer rings of the oligomer. Previous reports have described mono-substituted [2i] or ortho-substituted hydroxyl-capped [2j] quinonediimines. Resorcinols (which feature *meta*-substituted hydroxyl groups) are an interesting class of organic molecule, some members of which are important natural products [4]. In addition, resorcinols have found use in synthetic and crystal engineering applications [5].

2. Experimental methods

All reagents employed were purchased from Sigma–Aldrich and used without further purification. The resorcinol terminated quinonediimine *N*,*N'*-bis (2',4'-dihydroxyphenyl)-1,4-quinonediimine (hereafter *resorcinol quinonediimine*, RQD) was synthesized [2] 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

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Fig. 1. Redox states of N,N'-(2',4'-dihydroxyphenyl)-1,4-quinonediimine. R1=OH for leucoemeraldine and emeraldine states, and O for pernigraniline.

water solution. 4.22 g (0.0185 mol) of ammonium persulfate were added slowly. Upon color change of the solution from clear to light brown, 2.04 g (0.0185 mol) of resorcinol were added slowly. The stirring continued for 1 h. 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 resorcinol quinonediimine being more soluble in ethanol than in acetonitrile.

UV-vis spectra were collected in acetonitrile, chloroform, dimethylsulfoxide, ethanol, or methanol using 1 cm quartz cuv-

ettes on a Beckmann–Coulter DU-600 spectrophotometer. The solution concentrations were in the range of 10^{-5} – 10^{-4} M.

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 (2',4'-dihydroxy-phenyl)-1,4-quinonediimine (ATR, cm⁻¹): v_{max} 1078, 800, 968, 1279, 1416, 1497, 1574, 2808, 3026, 3151, 3336. Vibrational frequencies were calculated at B3LYP/6-31G* on B3LYP/6-31G* optimized geometries. Frequencies were then scaled using the widely used 0.9945 scale factor [6].

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

3. Computational methods

Optimized structures for each isomer of RQD in the emeraldine redox state (Fig. 2) were computed using the 6-31G^{*} [7] Pople-style



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

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 [8] within the Gaussian 03 suite of programs [9]. 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 [10]. 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 [8] within the Gaussian 03 suite of programs [9]. Tight convergence criteria were selected by use of the SCF = Tight keyword option. This option is standard when diffuse functions are utilized.

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 reliable experimental values are available have been compared with the experimental values [11]. 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 quinonediimine isomers range from 12.71 kcal mol⁻¹ for the syn, syn (outer) isomer to 20.58 kcal mol⁻¹ for the syn, syn (inner) isomer. For each isomer, S_0 was lower in energy than T_1 . For the dihydrochloride salts, the triplet energies were calculated in range from 6.79 kcal mol⁻¹ for the syn, syn (outer) isomer to 17.37 kcal mol⁻¹ for the syn, syn (inner) isomer, with the triplets (T_1) being again higher in energy than S_0 , but lower than S_1 . The splitting between S_0 and T_1 was consistently smaller for the dihydrochloride salts than for the emeraldine bases, but the same two isomers in each case exhibited the maxima and minima. S_1 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 [9] 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 quinonediimine in the emeraldine oxidation state (EB) and two moles of hydrogen chloride to give one mole of the emeraldine dihydrochloride salt (ES₂)

$$EB + 2HCl \rightarrow ES_2 \tag{1}$$

was calculated using single point energy calculations at the B3LYP/ 6-311 + G(2d,p) level of theory on B3LYP/6-31G^{*} optimized geometries (Fig. 3). Zero-point energy and enthalpic corrections to 298.15 K were calculated using frequency calculations at B3LYP/6-31G^{*} [11b].

Wavelengths of electronic transitions were calculated using the Δ SCF method [12], which has already demonstrated its effectiveness in predicting electronic transitions for a number of oligoanilines [2]. For comparison purposes, the transition energies were also calculated using the Configuration Interaction, Singles (CIS) method [13], Time-dependent density functional theory (TD-DFT) [14], and the ZINDO/S formalism [15] on B3LYP/6-31G* optimized geometries. All methods were employed on each structure.

The effects of solvation on molecular structure and the electronic spectra were assessed by use of the Self-Consistent Isodensity Polarizability Continuum Model (SCIPCM) [16], with a model acetonitrile solvent (Fig. 4). This solvent was chosen to allow comparison with the experimental UV–vis spectra, which were taken in acetonitrile. The quinonediimines 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



Fig. 3. Calculated molecular structures (*from top*) of syn-, syn- (inner) – *N*,*N*⁻(2',4'dihydroxyphenyl)-1,4-quinonediimine dihydrochloride; syn-, syn- (outer) – *N*,*N*-(2',4'-dihydroxyphenyl)-1,4-quinonediimine dihydrochloride; anti-, syn- *N*,*N*'-(2',4'-dihydroxyphenyl)-1,4-quinonediimine dihydrochloride; anti-, syn- *N*,*N*'-(2',4'-dihydroxyphenyl)-1,4-quinonediimine dihydrochloride; and anti-, anti-*N*,*N*'-(2',4'-dihydroxyphenyl)-1,4-quinonediimine dihydrochloride; and anti-, anti-*N*,*N*'-6-31G*.

orbital energies generated by a single-point calculation at B3LYP/6-311 + G(2d,p) on the B3LYP/6- $31G^*$ solvent optimized geometries.

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 [17].

4. Results and discussion

Calculations (Table 1) find the syn, syn (outer) isomer of RQD to be lowest in enthalpy. Unlike other quinonediimines investigated [2], the differences in enthalpies in the gas phase among isomers is very large, up to nearly 15 kcal mol⁻¹. In acetonitrile solvent, the calculated enthalpy differences are somewhat smaller, still favoring the syn, syn (outer) structure. However, only two structures could be successfully calculated. The SCIPCM algorithm has difficulties with irregularly shaped molecules. The presence of the hydroxyl group at the 2' position causes the solvent cavity created by the method to be sufficiently ill-shaped to cause the method to abort. Assuming the isomers are Boltzmann distributed, the population of RQD in the gas phase at 298.15 K should be more than 99.99% syn, syn outer (sso), with syn, syn inner (ssi); syn, anti (sa); anti, syn (as); and anti, anti (aa) each less than 0.01% each.

The non-linearity and non-planarity of the three rings in the quinonediimine lead to important structural effects. If there are no substituents at the 2', 3', 5', and 6' positions, there are only two isomers, one with the rings on the same side of the central quinoid ring (syn), or with the rings on opposite sides (anti). The syn conformer belongs to point group $C_{2\nu}$, and the anti isomer belongs to C_i . With a substituent at the 2' position (as in RQD), there are five isomers. The *ssi* and *sso* isomers belong to the point group $C_{2\nu}$, whereas the *aa* isomer belongs to C_i . The two remaining isomers belong to group C_1 .

Enthalpies of activation for isomerization of RQD 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 (17.365 kcal mol⁻¹) is less for the enthalpy of activation for isomerization calculated for the unsubstituted EB (19.622 kcal mol⁻¹). Similarly, enthalpies of activation for rotation of RQD between syn and anti isomers (relative to the hydroxyl group nearest the imine nitrogen, the 2' position) were calculated after identifying the transition state for rotation of the outer amine rings (same level of theory as for isomerization). The value (0.741 kcal mol⁻¹) is again less than the enthalpy of activation for rotation calculated for the unsubstituted EB (1.876 kcal mol⁻¹).

Calculations reveal characteristic structural effects of the hydroxyl group at the 2' position. In the analogous phenol quinonediimine without a carboxyl substitution, i.e., *N*,*N*'-bis (4'hydroxyphenyl)-1,4-quinonediimine ["phenol quinonediimine"], the tilt of the outer benzenoid rings with respect to the inner quinoid ring (C--C-N=C) is 43.82° for the syn isomer, and 43.03° for the anti; for the corresponding dihydrochloride salt (ES₂) without the hydroxyl group at the 2' position, the ring tilt is the somewhat smaller 36.08° for the syn isomer, and 33.22° 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, and we see this pattern for the phenol emeraldine.

For the RQD, the ring tilts are calculated at 50.29° (ssi), 31.11° (sso), 48.94° (sa), 49.67° (as), and 29.85° (aa). In other words, the presence of the hydroxyl group at the 2' position on each outer ring has a very large effect on the calculated ground state geometry in the gas phase. The effect is greatest in precisely those isomers where the hydroxyl group is in the greatest proximity to the imine nitrogen atom. Possible geometric/steric effects of the hydroxyl on neighboring chains in the solid state were not addressed.

Calculated ring tilts for the resorcinol emeraldine salt (RES₂) are much large than those of the unsubstituted phenol quinonediimine -44.66° (ssi), 36.66° (sso), 44.29° (sa), 44.13° (as), 43.78° (aa). If we



Fig. 4. Calculated molecular structures (from top) of syn-, syn- (outer) – N,N'-(2',4'-dihydroxyphenyl)-1,4-quinonediimine dihydrochloride and anti-, syn- N,N'-(2',4'-dihydroxyphenyl)-1,4-quinonediimine dihydrochloride in acetonitrile solvent, optimized at B3LYP/6-316* using the SCIPCM method.

Table 1

Relative enthalpies of RQD (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.

	Gas phase (kcal mol ⁻¹)	Solvent (kcal mol ⁻¹)
Syn, syn (inner)	14.247	N/A
Syn, syn (outer)	0.000	0.000
Syn, anti	6.225	N/A
Anti, syn	14.847	10.041
Anti, anti	8.156	N/A

Table 2

Enthalpies of RQD dihydrochlorides 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 lowest enthalpy syn, syn (outer) isomer.

	ΔH (kcal mol ⁻¹)
Syn, syn (inner)	18.226
Syn, syn (outer)	0.000
Syn, anti	10.086
Anti, syn	18.408
Anti, anti	10.467

Table 3

Enthalpies of RQD in the pernigraniline redox state 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.

	ΔH (kcal mol ⁻¹)	
Syn, syn (inner)	17.691	
Syn, syn (outer)	0.000	
Syn, anti	7.232	
Anti, syn	15.203	
Anti, anti	6.430	

consider a ring tilt of 36.08° to be typical for hydroxyl-terminated quinonediimines (i.e., those with an hydroxyl group at the 4' position, but no other ring substitutions, as in phenol quinonediimine), then the steric effect of the hydroxyl substituent at the 2' position accounts for approximately 8° of the tilt.

For the RES_2 dihydrochlorides (Table 2) in the gas phase, calculated enthalpies show the *sso* isomer as most stable. Next highest are the *sa* and *aa* isomers. The *ssi* and *as* isomers are very much

Table 4

Calculated and experimental ATR-IR vibrational frequencies of syn, syn (outer) RQD on B3LYP/6-31G^{*} optimized geometries. Calculated frequencies were scaled by 0.9945 [6].

Calculated (cm ⁻¹)	Experimental (cm ⁻¹)	Assignment
806	800	Quinoid stretch
1125	1078	C—H wagging
1302	1279	C—H wagging, 2′-OH wagging
1420	1416	C—H wagging on benzenoid rings
1523	1497	C=N symmetric stretch
1596	1574	C=N asymmetric stretch
N/A	2808	C—H stretch
3178	3026	C—H stretch for between OH
		groups
3217	3151	C—H stretch
3461	3336	2'-OH stretch

Table 5

Vertical electron affinities of RQD 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°.

	Base (eV)	Dihydrochloride (eV)		
Syn, syn (inner)	1.398	3.298		
Syn, syn (outer)	1.989	3.697		
Syn, anti	1.971	3.713		
Anti, syn	1.425	3.324		
Anti, anti	1.758	3.546		

Table 6

HOMO/LUMO levels of RQD 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*.

	HOMO base (eV)	HOMO base (eV) HOMO dihydrochloride (eV)		LUMO dihydrochloride (eV)	
Syn, syn (inner)	-5.466	-6.221	-2.764	-4.545	
Syn, syn (outer)	-5.402	-6.512	-3.265	-4.911	
Syn, anti	-5.541	-6.452	-3.279	-4.930	
Anti, syn	-5.389	-6.142	-2.774	-4.556	
Anti, anti	-5.383	-6.212	-3.057	-4.760	

Table 7

Predicted and experimental electronic transitions of various isomers of RQD in nanometers. Since it is impossible to determine the relative populations of the isomers in solution, the same "experimental" wavelengths are listed for each isomer.

Isomer	Experimental	Transition	ΔSCF	TD-DFT	CIS	ZINDO/S
Syn, syn (inner)	580	$H \rightarrow L$	459	544		476
	N/A	$H - 1 \rightarrow L$	408	329		453
	254	$H \rightarrow L + 1$	253	282	239	
Syn, syn (outer)	580	$H \rightarrow L$	580	566		541
	N/A	$H-1 \rightarrow L$	410	404	396	458, 377
	254	$H \rightarrow L + 1$	276	295	237	
Syn, anti	580	$H \rightarrow L$	548	613		519
	N/A	$H - 1 \rightarrow L$	434	500		466, 367
	254	$H \rightarrow L + 1$	266	282		
Anti, syn	580	$H \rightarrow L$	474	552		487
	N/A	$H - 1 \rightarrow L$	405	328	377	443
	254	$H \rightarrow L + 1$	261	281	240	
Anti, anti	580	$H \rightarrow L$	533	567		520
	N/A	$H - 1 \rightarrow L$	410	482	370	448
	254	$H \rightarrow L + 1$	271	336	240	

the highest in enthalpy. The enthalpies of reaction of RQD with two moles of hydrogen chloride to yield the corresponding dihydrochloride salt were computed. For each isomer, the reaction was clearly exothermic. The most favorable (lowest) enthalpy of reaction was found for the *sso* isomer, at -14.55 kcal mol⁻¹. The *aa* isomer had the next most favorable enthalpy of reaction at -12.24 kcal mol⁻¹, with the remaining three isomers clustered around -10.5 kcal mol⁻¹. The equivalent reaction for phenol quinonediimines has enthalpy of reaction of -13.85 kcal mol⁻¹ (syn) and -13.72 kcal mol⁻¹ (anti). For the 3',4'-dihydroxy quinonediimine (the one with ortho hydroxyl groups on the outer rings), the enthalpies of reaction range from -9.71 kcal mol⁻¹ to -13.07 kcal mol⁻¹. The favorable enthalpy for reaction for the sso isomer of RQD with HCl can be attributed to two factors. First, the sso isomer both the base and dihydrochloride salts of RQD has its hydroxyl substituent (2' position) optimally located to min-



Fig. 5. UV-vis spectra of N,N'-(2',4'-dihydroxyphenyl)-1,4-quinonediimine in acetonitrile.

imize steric hindrance with the inner quinoid ring. Secondly, the dihydrochloride salt is partially stabilized by a hydrogen-bonding interaction between the hydroxyl group and the hydrochloride.

Like other quinonediimines, RQD can be easily oxidized to the pernigraniline oxidation state by addition of concentrated hydrogen peroxide. The calculated isomeric preferences in the gas phase for this state are exactly the same as for the emeraldine base. The *sso* is the lowest enthalpy isomer, followed by the *sa* and *aa* relatively close to each other, with *ssi* and *as* very much higher in energy, exactly as for the RQD and the RQD dihydrochloride (Table 3).

4.1. IR spectra

The compound has a benzenoid stretch at 1497 cm⁻¹, and a quinoid stretch at 1574 cm⁻¹. The presence of two, symmetry distinct hydroxyl groups at each end of the molecule leads to a very broad absorption from about 2800 to 3400 cm⁻¹. Assignments in this region are also complicated by intermolecular hydrogen bonding (Table 4).

4.2. Electronic spectroscopy

Vertical electron affinities (EA) are a key index of potential utility in corrosion inhibition applications (Table 5). Unsubstituted phenol quinonediimines have EA's of 1.615 (syn) and 1.434 (anti) eV. For the corresponding resorcinol quinonediimines (RQD), the EA's range from 1.398 eV for the *ssi* isomer, to 1.989 eV for the *sso* isomer. The range of values among the isomers is noticeably greater than for other quinonediimines studied. The trend in electron affinity appears to be inversely related to the enthalpy of the isomer – the more enthalpically stable the isomer, the greater the electron affinity. The hydroxyl substituent at the 2' position distorts the planarity of the molecule, and thereby affects the electronics.

The greater EA of RQD (for those isomers for which the EA is greater) results from the electron withdrawing effect of the hydroxyl groups by resonance. The effects of the electronegativity of the oxygen atoms of the 2'-hydroxyl group on the electron affinity should be essentially independent of conformation, leaving resonance as the primary cause of the increased EA.

The doping of aniline oligomers generally 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 RQD dihydrochlorides vary from 3.298 eV (ssi) to 3.713 for the *sa* isomer. This corresponds to a range of 0.415 eV among the dihydrochloride isomers. For the related phenol quinonediimine dihydrochlorides, they are 3.022 eV (syn), 3.552 eV (anti), a range of 0.53 eV. Clearly, though the steric hindrance of the hydroxyl group has a substantial effect on the EA of the resorcinol quinonediimine, it has comparatively little effect on the EA of the corresponding dihydrochloride salts.

The trend in electron affinities for the RQD dihydrochlorides is unusual. It does not inversely parallel the trend in enthalpies, as do the electron affinities of the resorcinol quinonediimine bases.

The phenol quinonediimine dihydrochloride has calculated LU-MO's at -4.278 eV (syn isomer), or -4.768 eV (anti). The calculated LUMO levels (Table 6) for the RQD dihydrochlorides range from -4.545 (*ssi* isomer) to -4.930 eV (for the *sa* isomer). The lower LUMO levels of the RQD dihydrochlorides can be attributed to the slight additional withdrawal of electron density by the two additional 2' position hydroxyl groups, largely though inductive effect of the oxygen atoms. The electronic affinities of the various RQD isomers closely parallel the calculated LUMO levels, suggesting that the most significant determinant of electron affinities (and therefore, corrosion inhibition) is the "pulling down" of the LUMO.

Unsubstituted phenol quinonediimine dihydrochlorides have calculated HOMO's at -6.048 eV (syn isomer), or -6.378 eV (anti). For the RQD dihydrochlorides, the calculated HOMO values range from -6.452 eV (for the *sa* isomer) to -6.142 (*as*). The additional hydroxyl groups on the outer rings lower the HOMO, just as they lower the LUMO.

For RQD, predicted electronic transitions by several methods are listed in Table 7, with the experimental spectrum in Fig. 5. The longest wavelength absorption is predicted exactly by the Δ SCF method for the *sso* isomer, which is expected to be the predominate isomer. The next predicted absorption is not seen in solution. The third longest wavelength predicted by Δ SCF is in good agreement with the actual experimental result. TD-DFT gives reasonably good predictions of the longest and shortest wavelengths, ZINDO/S gives poorer results, and CIS does not even predict a band longer than 396 nm.

For the unsubstituted aniline quinonediimine, the primary electronic transitions observed are H (HOMO) \rightarrow L (LUMO, 544 nm)



Fig. 6. Calculated frontier orbitals of the syn-, syn- (outer) N,N-(2',4'-dihydroxy-phenyl)-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.

and $H \rightarrow L + 1$ (second lowest unoccupied molecular orbital, 277 nm). Oxygenated amino-terminated quinonediimines, on the other hand, show primarily a H - 1 (second highest occupied molecular orbital) \rightarrow L transition. RQD acts more like the unsubstituted amino-terminated quinonediimine than the hydroxyl-terminated one, even though both RQD and the hydroxyl-terminated quinonediimine are "oxygenated". The effect of amino and hydroxyl substitutions on the character of the most intense electronic transitions is very subtle, as seen by comparison among such trimers with the substituents slightly rearranged. The frontier orbitals of RQD are displayed in Fig. 6.

5. Conclusions

The resorcinol quinonediimine has been synthesized, and its experimental and theoretical investigation enables a deeper understanding of subtle electronic and steric effects in amino- and hydroxyl-terminated quinonediimines. The hydroxyl group at the 2' position exerts two distinct effects on the compound. On one hand, it reinforces the electron withdrawing effect of the hydroxyl group at the 4' position by electronegativity, while it counteracts its withdrawal of electron density by resonance. On the other hand, it destabilizes any isomers in which it closely approaches the imine nitrogen, so that if the isomers are Boltzmann distributed, at room temperature all molecules should be in the enthalpically favored sa isomer. This suggests that structural factors could be used to more efficiently engineer quinonediimines with desired electronic properties.

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