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Halogen-Capped Aniline Trimers. Away from the Polyaniline Paradigm by Isosteric Replacement of Amino Groups: A Theoretical Study

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Halogen-capped aniline trimers represent an important class of molecules that are no longer appropriate models for polyaniline, but they can nevertheless be expected to demonstrate useful properties in their own right. Such molecules are herein investigated by DFT (density functional theory) calculations of important thermodynamic parameters and are compared and contrasted to the parameters of amino-capped aniline trimers. The implications for the utility of such materials in corrosion control/inhibition are highlighted.

Introduction

Isosterism[1] is the replacement of one functional group in a molecule by another of "similar" electronic structure. The systematic investigation of such replacements has been a fruitful source of ideas for rational drug design.[2] By the Grimm hydride replacement law,[3] there is an equivalence among the halogens and between a halogen and hydrogen, since they most frequently demonstrate a valency of one. Similarly, there is a correspondence between hydrogen and the amino group. By transitivity, one can establish a correspondence between the amino group and the halogens. This correspondence is the inspiration for the present study.

Polyaniline (PAni) is a π-conjugated polymer widely studied for its electrical conduction and corrosion inhibition properties. Unfortunately, it is poorly soluble in most common solvents, thereby hampering experimental investigations and limiting its commercial exploitation. Aniline oligomers, particularly trimers, are soluble in a wide range of common solvents. Though they are no longer capable of electrical conduction, the trimers are even more effective in corrosion inhibition than the parent polymer. There is also experimental and theoretical evidence that the aniline trimer is an adequate minimalist embodiment of the electronic chromophore[4] (like PAni, the trimers are brightly colored.). Just as in the polymer, the trimers can exist in three distinct oxidation states: leucoemeraldine (the most reduced), emeraldine, and pernigraniline (the most oxidized).

Halogen-capped aniline trimers represent a completely new type of compound, no longer merely an analogue of the well-studied polyaniline.[4−11] "Halogen-capped" implies that the terminal amino groups are replaced by halogen atoms. Amino-capped aniline trimers are effective and appropriate models for polyaniline, since they, like the parent polyaniline, can exist in three distinct oxidation states and possesses both amine and imine nitrogens. The trimers have distinct advantages over the polymer in their greater solubility in a wider range of solvents and their monodispersity. Once the amino-cap is removed, the similarity to polyaniline is diminished. Halogen-capped aniline trimers in the emeraldine state are no longer capable of being easily oxidized by removal of hydrogen (since they possess only imine nitrogens), so the halogen-capped trimers are effectively limited to two (rather than three) oxidation states: emeraldine and leucomeraldine. Chain elongation upon polymerization is no longer possible for the halogen-capped oligomers because of the (usual) absence of halogen catenation.

In a previous paper,[8e] we have shown that emeraldine bases (EB) are excellent electron donors. Other experimental work[12,13] has suggested that at elevated temperatures, polyaniline bases are capable of electron acceptance from metals. Emeraldine salts (monosalt, ES_1; disalt, ES_2), particularly the hydrochlorides, are extremely effective electron acceptors. This electron acceptance is believed to be essential to the mechanism of corrosion inhibition by oligo- and polyanilines.[8f] Calculation of the relevant thermodynamic parameters for halogen-capped emeraldines will allow an assessment of the possibility of a similar temperature-dependent donor/acceptor dichotomy for the halogen-capped forms. An amino-capped emeraldine trimer must usually be diprotonated (doped) to achieve its greatest electron affinity; since such protonation is strongly dependent on the local chemical environment (pH) and the actual basicity of the emeraldine itself, it would be useful to increase the electron affinity of emeraldines in their base forms. The utility of oligoanilines in corrosion control can be compromised, in neutral to alkaline solutions, by the weak basicity of the imine nitrogen atoms. Therefore, an increase in the electron affinities of oligoanilines in their neutral, base forms will be useful in extending the corrosion protection capabilities to metals exposed to more alkaline solutions.

Results and Discussion

The halogen-capped trimers can exist in both syn and anti conformations. Relative populations of each were determined by first calculating the enthalpies of each isomer, and computing the populations as a Boltzmann distribution. (Table 1) We can gain insight into the effect of the interactions of the capping groups on the stability of each isomer. For the amino-capped trimers, the syn form is energetically preferred; therefore, the

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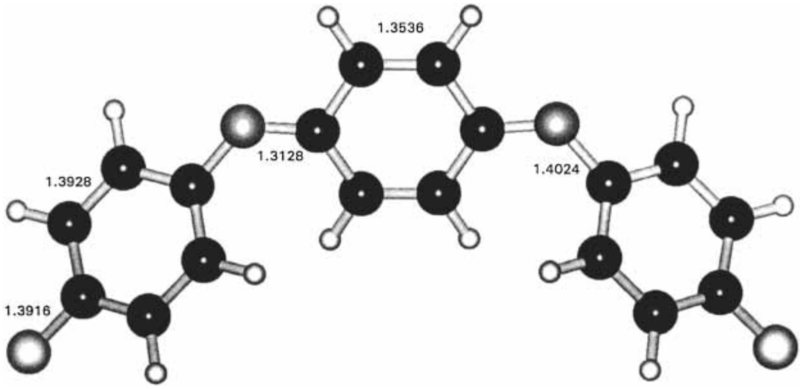

Figure 1. Molecular structure of syn fluorine-capped emeraldine trimer, optimized at B3LYP/6-31G. Carbon atoms are black spheres, nitrogen atoms are gray, halogen atoms are large white spheres, and hydrogen atoms are small white spheres.

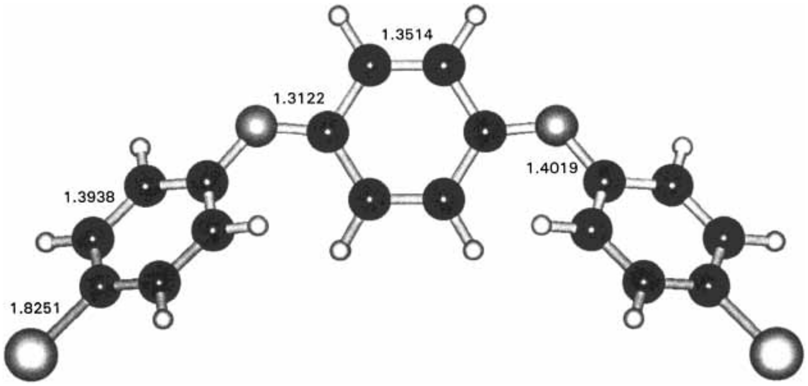

Figure 2. Molecular structure of syn chlorine-capped emeraldine trimer, optimized at B3LYP/6-31G. For color code, see Figure 1.

TABLE 1: Population Distributions in Amino- and Halogen-Capped Aniline Trimers[a]

		Boltzmann	preferred
EB	syn	1.0000	syn
EB	anti	0.8617	
F-capped EB	syn	1.0000	syn
F-capped EB	anti	0.7033	
Cl-capped EB	syn	1.0000	syn
Cl-capped EB	anti	0.7839	
Br-capped EB	syn	1.0000	syn
Br-capped EB	anti	0.7888	
I-capped EB	syn	0.4968	
I-capped EB	anti	1.0000	anti

[a] Boltzmann distributions calculated at 298 K from enthalpies of syn and anti minimum structures. Enthalpies calculated at B3LYP/6-311G(2d,p) on B3LYP/6-31G-optimized geometries (except for the iodine-capped emeraldines, which used B3LYP/3-21G on iodine).

long-range "dispersion" (dipolar, van der Waals, and London) forces must be more attractive than the electron−electron repulsive forces from the capping groups.

Many solid-state bulk properties of polymers are strongly dependent on the morphology, which is itself strongly dependent on such molecular properties as stereoregularity. For the halogen-capped trimers, the relative population of the syn isomer decreases as the atomic number of the halogen increase. For the iodine-capped trimers, the repulsive forces finally overcome the attractive forces, so the anti conformation is preferred over the syn. This is unusual even for emeraldines substituted with bulky alkyl side chains.[14] It is, however, similar to the situation in amino-capped trimers in the pernigraniline oxidation state

This similarity between iodine-capped trimers in the emeraldine state and the imino-capped aniline trimer in the pernigraniline state is stronger than appears at first glance and has been previously investigated.[15] This implies that a more substantive isosterism exists between a halogen and an imine group than between a halogen and an amino group. It also implies that isosterism is a more accurate model for short-range electronic interactions than for long-range ones such as van der Waals or London forces.

TABLE 2: Partial Charges of Amino- and Halogen-Capped Aniline Trimers[a]

		imine N	capping group
EB	syn	0.4563	0.0702
EB	anti	0.4470	0.0701
F-capped EB	syn	0.4440	0.3262
F-capped EB	anti	0.4459	0.3265
Cl-capped EB	syn	0.4416	0.1316
Cl-capped EB	anti	0.4431	0.1321
Br-capped EB	syn	0.4424	0.0246
Br-capped EB	anti	0.4438	0.0257
I-capped EB	syn	0.4415	0.2583
I-capped EB	anti	0.4377	0.2593

[a] Partial charges calculate by Mulliken population analysis during single-point calculation at B3LYP/6-311G(2d,p) on B3LYP/6-31G-optimized geometry, except for the iodine-capped emeraldines, which were optimized at B3LYP/6-31G on all atoms except iodine, for which B3LYP/3-21G was used.

Calculation of partial atomic charges (Table 2) by the Mulliken method[16] demonstrates, as might be predicted, that the iodine atoms are relatively electropositive, whereas the nitrogen atoms (of the amino cap) and the halogens of the earlier rows are electronegative. It appears that the amino group is intermediate in electronegativity between chlorine and bromine. The imine nitrogens of either the amino-capped or halogen-capped emeraldines are of virtually equivalent electronegativities. This suggests that there may not be a strong effect of the basicity of the imines, but further investigation of this point is indicated.

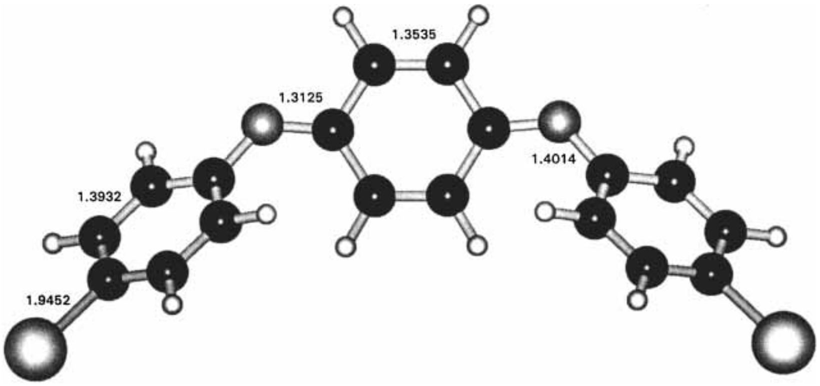

Figure 3. Molecular structure of syn bromine-capped emeraldine trimer, optimized at B3LYP/6-31G. For color code, see Figure 1.

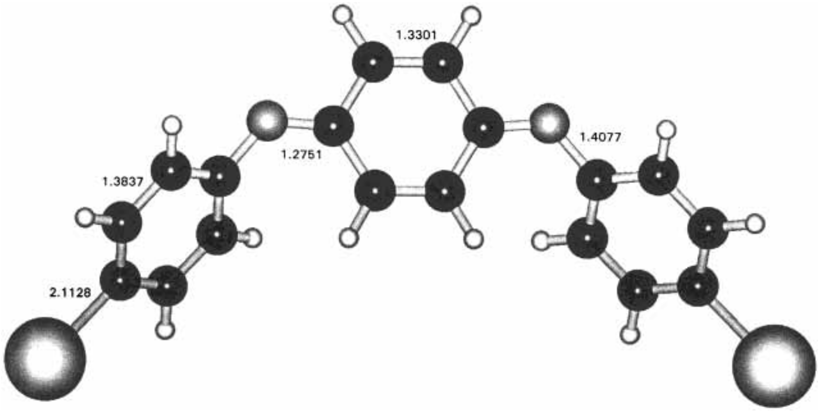

Figure 4. Molecular structure of syn iodine-capped emeraldine trimer, optimized at B3LYP/6-31G, but with 3-21G basis on iodine atoms. For color code, see Figure 1.

TABLE 3: Bond Length Alterations in Various Trimeric Anilines

		central ring	outer ring	cap−outer ring bond
EB	syn	1.3565	1.3871	1.3826
EB	anti	1.3582	1.3873	1.3823
F-capped EB	syn	1.3536	1.3928	1.3916
F-capped EB	anti	1.3550	1.3908	1.3917
Cl-capped EB	syn	1.3534	1.3973	1.8251
Cl-capped EB	anti	1.3547	1.3939	1.8254
Br-capped EB	syn	1.3535	1.3932	1.9452
Br-capped EB	anti	1.3547	1.3933	1.9455
I-capped EB	syn	1.3301	1.3837	2.1128
I-capped EB	anti	1.3549	1.3967	2.1467

[a] Bond lengths (in Å) as calculated by full geometry optimization at B3LYP/6-31G, except for the iodine-capped species, which were optimized at B3LYP/6-31G on all atoms except iodine, for which B3LYP/3-21G was used.

TABLE 4: Ionization Potentials—Vertical[a] and Adiabatic[b]

	syn[a]	syn[b]	anti[b]
EB	137.8	133.9	133.6
TTF	151.2	143.9	N/A
F-capped EB	170.0	162.2	161.4
Cl-capped EB	181.9	174.8	163.6
Br-capped EB	168.3	163.4	162.6
I-capped EB	164.0	159.5	159.0

[a] Enthalpies (in kcal mol^{-1}) calculated at B3LYP/6-311G(2d,p) on B3LYP/6-31G-optimized geometries of the appropriate neutral, without relaxation upon ionization. For the iodine-capped emeraldines, B3LYP/6-31G was used for all atoms except iodine, for which B3LYP/3-21G. ZPE was employed with enthalpic corrections to 298 at B3LYP/6-31G with a scale factor of 1.00. [b] Enthalpies (in kcal mol^{-1}) calculated at B3LYP/6-311G(2d,p) on B3LYP/6-31G-optimized geometries of the appropriate neutral or cationic species. For the iodine-capped emeraldines, B3LYP/6-31G was used for all atoms except iodine, for which B3LYP/3-21G was employed. ZPE and enthalpic corrections to 298 at B3LYP/6-31G with scale factor of 1.00 were used.

The substitution of halogen for nitrogen has little effect on the geometry of the trimer (Figures 1−4, Table 3). Even the bond angles at the imine nitrogens change very little. The most dramatic change is at the capping atom itself. The bond length of the amino-capping nitrogen to the nearest carbon is 1.3826 Å, but it is 2.1128 Å from the iodine to the nearest carbon. Even the fluorine−carbon bond is 1.3916 Å. The presence of the halogen−aromatic bond provides a wide range of synthetic possibilities, from use as Grignard reagents to substrates for Ullmann reactions.

Adiabatic ionization potentials (IP) for the amino-capped and iodine-capped emeraldines were calculated by subtracting the enthalpy of the neutral base form from the enthalpy of the (fully optimized) cation. The IP is a useful thermodynamic measure of a molecule's ability to donate an electron in the formation of charge-transfer complexes (Table 4). Vertical ionization potentials were also calculated to permit comparison with experimental data. Emeraldines are excellent electron donors.[8e] The halogen-capped emeraldines are not as effective donors as the amino-capped emeraldine, and they are less effective than the prototypical electron donor tetrathiafulvalene (TTF). Nevertheless, all of the halogen-capped emeraldines are more effective donors than iron (vertical IP of 181.5 kcal mol^{-1})[17] and should, therefore, be useful for the construction of organic charge-transfer complexes. There is no linear correlation between the electronegativity of the capping atom and the IP, which suggests that inductive donation of electron density into the outer aromatic rings by the halogen is involved.

The electron affinity (EA) was calculated for the fluorine-capped emeraldine trimer (Table 5), since it is imagined that this would be the most likely to demonstrate a dramatic change

TABLE 5: Electron Affinities of *syn*-Emeraldine Trimers and Representative Electron Acceptors[a]

	vertical	adiabatic
EB	26.5	32.7
F-capped EB	41.6	43.9
ES_1	52.3	55.3
TCNE	72.9	75.6
TCNQ	79.3	82.1
ES_2	84.4	87.7

[a] Electron affinities (in kcal mol^{-1}) were calculated at B3LYP/6-311G(2d,p) on B3LYP/6-31G-optimized geometries. ZPE and enthalpic corrections to 298 K were made at the B3LYP/6-31G level.

in EA, due to the electronegativity of fluorine. As expected, the EA of the fluorine-capped emeraldines is 30% higher than for the amino-capped emeraldine. It is not quite as strong an acceptor as the emeraldine monohydrochloride trimer (ES_1 in the table) and is much less strong than the dihydrochloride (ES_2). Nevertheless, since even the amino-capped emeraldine trimer has demonstrated evidence of electron acceptance, the fluorine-capped trimer is a good candidate for further study as an electron acceptor. Since it is almost as effective as the monohydrochloride, it might be useful in applications (e.g. corrosion control) where maintenance of the trimer in a neutralized form may not be possible, due to the high pH of the environment. Unlike ES_2, the fluorine-capped trimer is less effective an electron acceptor than the widely studied tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ). This is not necessarily a disadvantage; the intermediate nature of the donor/acceptor properties suggests that halogen-capped trimers should be considered for incorporation into novel charge-transfer complexes, as the acceptor (with TTF as the donor) or as the donor (with TCNE or TCNQ as the acceptor).

Computational Methods

All calculations were performed using the Gaussian 94[18] suite of programs. All compounds were optimized using the B3LYP hybrid density functional,[19] which has been shown previously[4] to be extremely effective in the calculation of molecular properties of oligoanilines. The 6-31G basis set was used for optimizations and zero-point corrections, except for the iodine atoms, for which the 3-21G basis set was used. Single point energies were calculated with the large B3LYP/6-311G(2d,p) set.

Conclusions

Halogen-capped emeraldine trimers are distinctly different from their amino-capped cousins and are poorer electron donors. They are, however, better electron acceptors than the amino-capped emeraldine trimer in the base form. Since theoretical models of corrosion inhibition have postulated that the strong electron acceptance by the emeraldine salt is a key feature of the mechanism, the ability to fabricate aniline oligomers that possess that feature even in their neutral base forms might be of considerable utility in practical applications. Though they are no longer appropriate models for polyaniline, these halogenated trimers may be expected to show promise in the synthesis of novel charge-transfer complexes.

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