

Substituent effects on the electrochemical oxidation of *N,N',N''*-triphenyl-1,3,5-triaminobenzenes

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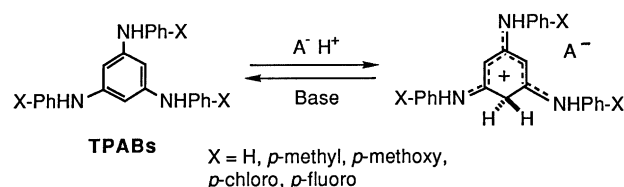
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ABSTRACT: Correlation analysis of the oxidation potentials of a series of *N,N',N''*-triphenyl-1,3,5-triaminobenzenes (TPABs) substituted at the *para* positions of the outer phenyl rings shows a linear free energy relationship with resonance-enhanced substituent parameters (σ^+). Reaction parameters (ρ^+) for oxidation of TPABs were found to be -1.53 , -1.45 and -1.34 (per substituent) in methylene chloride, acetonitrile and propylene carbonate respectively. The resonance enhancement and small magnitude of the ρ^+ values are related to a significant but weak delocalization of charge onto the outer phenyl rings in the molecular orbitals of radical cations resulting from the oxidation of TPABs. Data on the oxidation of *p*-substituted triphenylamines were treated similarly and gave a ρ^+ value of -3.27 (per substituent) in acetonitrile, greater than that for TPABs owing to a more significant delocalization of charge onto the phenyl rings in the molecular orbitals of the corresponding radical cations. To demonstrate their predictive value, these linear free energy correlations were used to estimate the oxidation potentials of similarly substituted *N,N,N',N'',N'''*-hexaphenyl-1,3,5-triaminobenzenes, which are of interest as building blocks for molecular magnetic materials. © 1998 John Wiley & Sons, Ltd.

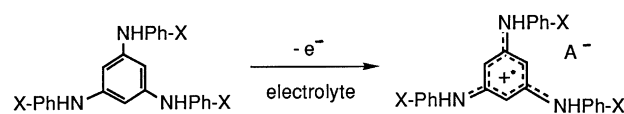
KEYWORDS: substituted 1,3,5-triaminobenzenes; electrochemistry; linear free energy correlation; substituted triphenylamines

INTRODUCTION

Several *N*-alkyl- and *N*-aryl-substituted derivatives of 1,3,5-triaminobenzene have been shown to react with electrophiles at the central aromatic ring to form stable carbocationic σ -complexes.^{1–3} These stable σ -complexes are of inherent interest and are useful as models for the intermediate steps of electrophilic aromatic substitution reactions.¹ There has been growing interest in ferromagnetic spin coupling between radical cations mediated by 1,3-diaminobenzene and 1,3,5-triaminobenzene moieties,^{4–10} especially in systems derivative of the tris (radical cation) of *N,N,N',N'',N'''*-hexaphenyl-1,3,5-triaminobenzene (HTAB), which have been shown to exhibit high spin states up to a ground state quartet in solution.^{4,5,7} It has been shown that electron-donating substituents, e.g. methoxy groups, on the outer phenyl rings of HTAB derivatives decrease the oxidation potentials and increase the stability of the resulting radical cations,^{4–6} but the magnitude of these substituent effects has not been treated quantitatively. The stability



of the cationic σ -complexes of *N,N',N''*-triphenyl-1,3,5-triaminobenzenes (TPABs) formed by protonation of the central benzene ring (Scheme 1) has been quantified and was found to exhibit a strong linear free energy relationship with respect to substituents on the outer benzene rings, especially electron donors at the *para* positions.² In principle the same substituents may influence the formation and stability of radical cations generated by oxidation of TPABs (Scheme 2). Systematic studies of the electrochemical oxidation of a series of substituted TPABs would help clarify the potential of substituents to increase the stability of the triradical cations of HTABs and may facilitate the use of HTABs



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as building blocks in the construction of molecular magnetic materials.¹¹ In this study the electrochemical oxidation of a series of *p*-substituted TPABs was studied and the results were analyzed by linear free energy correlation.

EXPERIMENTAL

All solvents were obtained commercially and used without further purification unless otherwise noted. The *p*-substituted TPABs were synthesized using literature procedures^{2,12} and were recrystallized from toluene prior to use. Simple Hückel MO calculations were carried out using the HMO program (version 2.1, J.J. Farrell and H. H. Haddon, Franklin and Marshall College, Lancaster, PA, USA) for MacIntosh computers. Cyclic voltammetry (CV) data were obtained using a Cypress Systems Omni 90 potentiostat and Yokogawa Model 3025 X-Y recorder. Cypress Systems gold (for CH₂Cl₂) or platinum (for acetonitrile and propylene carbonate) mini-electrodes (1 mm diameter) were used as working electrodes, together with a Pt wire auxiliary electrode. Several reference electrodes appropriate for the different solvents were used. Oxidation potentials are reported to 0.01 V, normalized to the potential of an aqueous Ag/AgCl (3 M KCl saturated with AgCl) reference electrode from Microelectrodes using the redox potential of ferrocene with each solvent/electrode pair for calibration purposes. An Ag/Ag⁺ reference electrode for use in acetonitrile or propylene carbonate was fabricated by immersing a clean Ag wire in a ceramic-fritted plastic sleeve containing 100 mM AgNO₃ in acetonitrile.¹⁵ An Ag/AgCl wire reference electrode for use in CH₂Cl₂ was fabricated by placing a clean Ag wire in a saturated solution of KCl and drying.¹³ The formal reduction potentials E° measured for ferrocene (10.2 mM) in acetonitrile with Bu₄NBF₄ (100 mM) as the electrolyte against the references were as follows: 0.44 V vs Ag/AgCl_(aq), 0.51 V vs Ag/AgCl_(wire), 0.01 V vs Ag/Ag⁺. For CH₂Cl₂ and acetonitrile, 1 mM TPAB (10 mM for propylene carbonate) in 100 mM electrolyte solution was scanned at 250 mV s⁻¹, beginning at 0.00 V vs the reference electrode and scanning initially in the cathodic direction. Nitrogen was

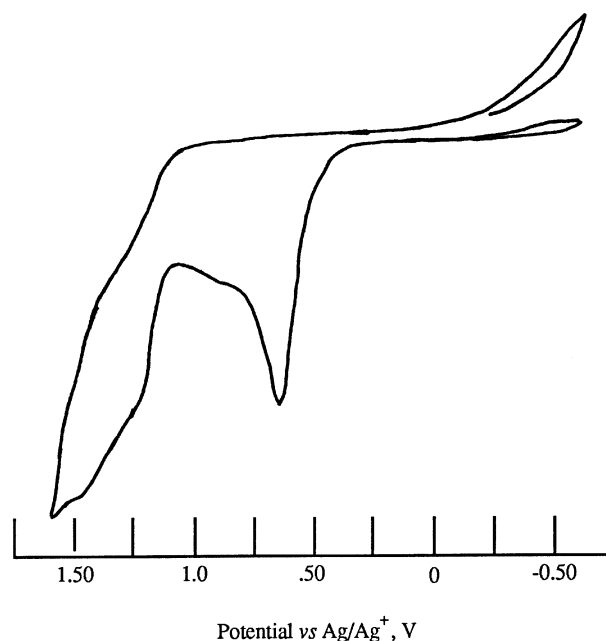


Figure 1. Typical cyclic voltammogram for TPABs. The example shown is for *N,N,N'*-tri(4-methylphenyl)-1,3,5-triaminobenzene in propylene carbonate. Conditions: 10 mM 1,3,5-tris(4-methylphenylamino)benzene; electrolyte, 100 mM Bu₄NBF₄; solvent, propylene carbonate; working electrode, Pt; auxiliary electrode, Pt wire; reference electrode, Ag/Ag⁺; initial coordinate, -0.40 V; anodic limit, 1.20 V; cathodic limit, -1.00 V; X (potential), 0.25 V cm⁻¹; Y (current), 2.5 μA cm⁻¹; scan rate, 250 mV s⁻¹

bubbled through the sample solutions for about 1 min before the cyclic voltammetry scans were run. Cyclic voltammograms were recorded with the samples at ambient temperature. Baseline scans of solvent/electrolyte were carried out to ensure the absence of artifacts in the TPAB voltammograms.

RESULTS AND DISCUSSION

The electrochemistry of TPABs in methylene chloride, acetonitrile and propylene carbonate was investigated by cyclic voltammetry. Cyclic voltammograms of *p*-substituted TPABs showed one to three non-reversible

Table 1. Electrochemical data from CV for *p*-substituted *N,N,N'*-triphenyl-1,3,5-triaminobenzenes in methylene chloride^a

Substituent	E_{pa1} (V) ^b	E_{pa2} (V) ^b	E_{pa3} (V) ^{b,c}	ΔE_{x1} (V) ^d	$\Delta \log K_x$	σ_p^+
-OCH ₃	0.68	1.28	—	0.21	3.56	-0.78
-CH ₃	0.81	1.42	—	0.08	1.36	-0.31
-F	0.85	1.55	—	0.04	0.68	-0.07
-H	0.89	—	—	0	0	0
-Cl	0.93	1.58	—	-0.04	-0.68	0.11

^a Conditions: 1 mM compound, 100 mM Bu₄NBF₄, reference electrode Ag/AgCl, working electrode Au, scan rate 250 mV s⁻¹.

^b E_{pa} in V vs Ag/AgCl_(aq).

^c Potentials were not detected within the electrochemical window of the solvent system.

^d $\Delta E_{x1} = E_{pa1H} - E_{pa1X}$.

Table 2. Electrochemical data from CV for *p*-substituted *N,N,N'*-triphenyl-1,3,5-triaminobenzenes in acetonitrile^a

Substituent	E_{pa1} (V) ^b	E_{pa2} (V) ^b	E_{pa3} (V) ^{b,c}	ΔE_{x1} (V) ^d	$\Delta \log K_x$	σ_p^+
OCH ₃	0.56	1.15	–	0.17	2.88	–0.78
CH ₃	0.65	1.30	–	0.08	1.35	–0.31
F	0.74	1.40	–	–0.01	–0.17	–0.07
H	0.73	–	–	0	0	0
Cl	0.80	1.43	–	–0.07	–1.18	0.11

^a Conditions: 1 mM compound, 100 mM Bu₄NBF₄, reference electrode Ag/Ag⁺, working electrode Pt, scan rate 250 mV s^{–1}.

^b E_{pa} V vs Ag/AgCl_(aq).

^c Potentials were not detected within the electrochemical window of the solvent system.

^d $\Delta E_{x1} = E_{pa1H} - E_{pa1X}$.

Table 3. Electrochemical data from CV for *p*-substituted *N,N,N'*-triphenyl-1,3,5-triaminobenzenes in propylene carbonate^a

Substituent	E_{pa1} (V) ^b	E_{pa2} (V) ^b	E_{pa3} (V) ^b	ΔE_{x1} (V) ^c	$\Delta \log K_x$	σ_p^+
OCH ₃	0.58	1.15	1.28	0.16	2.71	–0.78
CH ₃	0.66	1.28	1.45	0.07	1.19	–0.31
F	0.73	1.40	–	0.01	0.17	–0.07
H	0.73	1.38	1.50	0	0	0
Cl	0.80	1.43	–	–0.07	–1.18	0.11

^a Conditions: 10 mM compound, 100 mM Bu₄NBF₄, reference electrode Ag/Ag⁺, working electrode Pt, scan rate 250 mV s^{–1}.

^b E_{pa} is V vs Ag/AgCl_(aq).

^c $\Delta E_{x1} = E_{pa1H} - E_{pa1X}$.

oxidations (Fig. 1) at potentials summarized in Tables 1–3. As expected, the oxidation potentials of the *p*-substituted TPABs with electron-donating groups were lower than for those with electron-withdrawing groups. The non-reversibility of the first TPAB oxidation possibly arises from the loss of protons from the iminium-like nitrogen atoms after oxidation occurs,¹³ and thus the system is likely non-chemically reversible. To a first approximation then, the first oxidation exhibits classical EC mechanism behavior,¹³ and if the rate of chemical reaction is much faster than the rate of electrochemical reaction, the electrochemical step becomes pseudo-first-order, albeit non-reversible. This is most likely the case for our systems, as changes in scan rate over a limited range for the cyclic voltammograms have no effect on the lack of observed reduction peaks and little effect on the position of the anodic peak potential E_{pa} (even without scanning as far as to include the second oxidation potential). As long as these conditions hold for all the compounds and the transfer coefficient is the same for each compound under identical scan conditions, differences in E_{pa} should reasonably reflect free energy differences and allow for correlation using the Hammett linear free energy relationship¹⁴

$$\log K_{rel} = \rho\sigma \quad (1)$$

Correlation analysis has been applied to non-reversible electrode processes¹⁵ and only a brief description of the

derivation is given here. The polarographic half-wave potential $E_{1/2}$ is simply related to ΔG by

$$E_{1/2} = -\Delta G/nF \quad (2)$$

For a slow, irreversible electrode process (eqn (3)) the kinetic expression contains the heterogeneous rate constant k_e^o at the standard potential E^o and the half-wave potential is given by eqn (4).



$$E_{1/2} = E^o - (2.3RT/\alpha nF) \log(0.886k_e^o)(t_1/D) \quad (4)$$

Here α is the transfer coefficient, t_1 is the drop time, n is the number of electrons, F is the Faraday constant, T is the temperature in kelvins, R is the gas constant and D is the diffusion coefficient. For the difference in the half-wave potentials $(E_{1/2})_x$ caused by adding a substituent X in the *para* or *meta* position of the parent compound (X ≡ H), eqn (5) can be derived from eqn (4).

$$(\Delta E_{1/2})_x = (2.3RT/(\Delta\alpha n)_x F) \Delta \log(k_e^o)_x \quad (5)$$

$$(\Delta E_{1/2})_x = (2.3RT/nF) \Delta \log K_x \quad (6)$$

Assuming that the transfer coefficient is the same for each substituted compound, eqn (5) is equivalent to that for a reversible process (eqn (6)). If E_{pa} is measured for each substituent by cyclic voltammetry using the same scan rate, working electrode, electrolyte concentration and compound concentration, the difference in the oxidation potentials

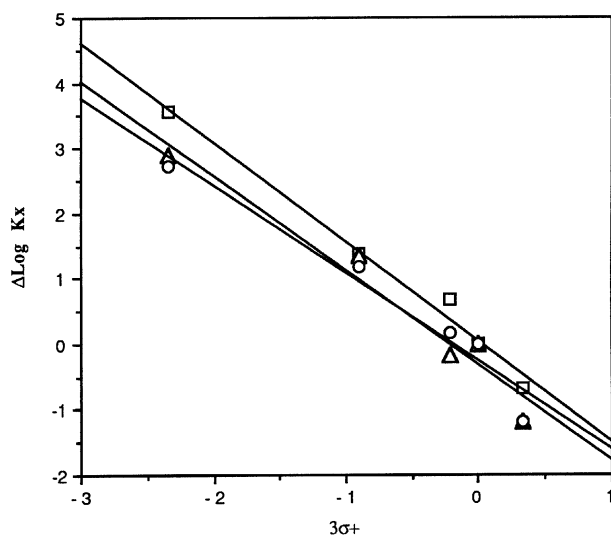


Figure 2. Hammett plots of $\Delta \log K_x$ vs $3\sigma_p^+$ for first oxidation potentials of *p*-substituted *N,N',N''*-triphenyl-1,3,5-triaminobenzenes in methylene chloride (squares, $\Delta \log K_x = 0.032 - 1.53(3\sigma_p^+)$, $R = 0.99$), acetonitrile (triangles, $\Delta \log K_x = 0.328 - 1.45(3\sigma_p^+)$, $R = 0.98$) and propylene carbonate (circles, $\Delta \log K_x = 0.260 - 1.34(3\sigma_p^+)$, $R = 0.98$)

$$\Delta E_x = E_{\text{paH}} - E_{\text{paX}} \quad (7)$$

can be substituted into eqn (6) to give eqn (8). The reaction constant ρ for the electrode process can then be determined by plotting $\Delta \log K_x$ against the substituent constants σ (eqn (9)).¹⁵

$$\Delta E_x = (2.3RT/nF) \Delta \log K_x \quad (8)$$

$$\Delta \log K_x = \rho \sigma \quad (9)$$

Values of $\Delta \log K_x$ for the first oxidation potentials of the *para*-substituted TPABs in all three solvents showed a linear relationship with respect to resonance-enhanced substituent constants σ_p^+ (Fig. 2).¹⁴ Plotting $\Delta \log K_x$ against several different σ values indicated that the best linear fit was with σ_p^+ values (e.g. correlation coefficient for simple σ values in methylene chloride, $R = 0.91$). The slopes of the Hammett plots of the first oxidation potentials of the *para*-substituted TPABs against the $3\sigma_p^+$ values gave ρ^+ as -1.53 , -1.45 and -1.34 in methylene chloride, acetonitrile and propylene carbonate respectively. The $3\sigma_p^+$ values were used to normalize for the presence of three substituents. The effect of the substituents is less in the most polar solvent, propylene carbonate, which should better stabilize the radical cations formed than the least polar solvent, methylene chloride, and values of ρ^+ appear to scale linearly with the dielectric constant of the solvent. In propylene carbonate the second oxidation potentials of the *para*-substituted TPABs also showed a linear relationship to the σ_p^+ values (correlation coefficient for σ values, $R = 0.95$) and gave a ρ^+ value of -1.81 ($R = 0.99$). The increase in ρ^+ for the second oxidation process would

be expected owing to the less stable diradical cation species.

The correlation of the oxidation potentials of the *para*-substituted TPABs with the σ_p^+ values shows that there is a resonance-enhanced substituent effect. In spite of the full positive charge developed on the TPAB upon oxidation, the correlation of oxidation potentials with σ_p^+ values was not expected. It has previously been shown that the substitution effect on the pK_a values of the protonated σ -complexes of the TPABs, which also bear a full positive charge (Scheme 1), was linear in relation to simple σ values.² The correlation between TPAB pK_a values and simple σ values was explained by the fact that once protonation of the central ring occurred, simple resonance contributors could not be drawn to delocalize the charge from the central ring onto the outer rings to allow direct interaction with the substituents. Similarly, simple resonance structures cannot be drawn to show the direct resonance stabilization of the positive charge by the *para* substituents on the outer rings of a radical cation localized in the central ring or on the nitrogen. This would suggest that there should not be a resonance-enhanced substituent effect and σ_p^+ values should not give the best linear fit. Resonance structures can be drawn to place the radical adjacent to the *para* substituents on the outer rings, which could then be stabilized by π -resonance, but this effect, if operating solely, would be relatively weak and not be expected to be very solvent-dependent. However, for the protonation of TPABs the substitution effect on the pK_a values corresponds to equilibrium free energy differences between the protonated and non-protonated species which have different electronic structures. The stabilities of the charged, protonated TPABs would be expected to contribute most to the free energy differences and the effects of the substituents are most pronounced in the protonated species. The π -system of the protonated TPABs is broken up by the protonated carbon, diminishing the π -delocalization (resonance) contribution of the substituents. Simple Hückel MO calculations showed that almost all the excess positive charge generated on protonation of TPAB remains on the inner ring and nitrogens, while the outer rings actually have a slight total negative charge, including at the *para* position. Therefore the effect of outer-ring TPAB substituents on the stability of the protonated species is largely inductive and results in a best linear correlation with simple σ values.

In contrast with the protonation of TPABs, the oxidation of TPABs involves removing an electron from the HOMO of the TPAB and in the process does not change the MOs, only the electron density distributions and the total energy of the system. Therefore whatever contribution the substituents make to the HOMO of the neutral molecule through delocalization is preserved in the SOMO of the radical cation through the intact π -system, resulting in the free energy differences and in the linear relationship between the oxidation potentials and

Table 4. Electrochemical data for *p*-substituted *N,N,N*-triphenylamine in acetonitrile

Substituent	$E_{p/2}$ (V) ^a	ΔE_{x1} (V) ^b	$\Delta \log K_x$	σ_p^+	$3\sigma_p^+$
OCH ₃	0.52	0.40	6.78	-0.78	-2.34
CH ₃	0.75	0.17	2.88	-0.31	-0.93
F	0.95	-0.03	-0.51	-0.07	-0.21
H	0.92	0	0	0	0
Cl	1.04	-0.12	-2.03	0.11	0.33
Br	1.05	-0.13	-2.20	0.15	0.45

^a $E_{p/2}$ is V vs SCE; see Ref. 17.

^b $\Delta E_{x1} = E_{p/2H} - E_{p/2x}$.

the σ_p^+ values. Indeed, simple Hückel MO calculations showed that although more than 75% of the excess positive charge generated on oxidation of TPAB remains on the inner ring and nitrogens, about 10% excess charge resides at the three *para* positions of the outer rings. The relatively small amount of excess charge on the *para* positions of the outer rings is consistent with the fact that simple resonance structures cannot be drawn to show direct resonance stabilization of the positive charge by the *para* substituents on the outer rings and is also consistent with the magnitude of ρ^+ values for TPAB oxidations, which are quite small for resonance-enhanced reactions.¹⁶

Given the above results for TPABs, we were interested in the correlation analysis of oxidation potentials of substituted triphenylamines. Several studies of the oxidation potentials of substituted triphenylamines have been reported,^{17–20} but to the best of our knowledge they have not been correlated with Hammett substituent constants. The oxidation potentials of the trisubstituted triphenylamines,¹⁷ treated as described above for the oxidation potentials of the *para*-substituted TPABs, gave values of $\Delta \log K_x$ (Table 4) which showed a linear relationship to σ_p^+ values. A Hammett plot of $\Delta \log K_x$ vs $3\sigma_p^+$ gave a ρ^+ value of -3.27 (Fig. 3). The oxidation of triphenylamines is analogous to that of the TPABs and therefore correlation of oxidation potentials with σ_p^+ values was expected. Simple Hückel MO calculations showed that about 25% of the excess positive charge resides at the three *para* positions of the phenyl rings of triphenylamine on oxidation, accounting for the larger magnitude of ρ^+ relative to that for the TPABs.

The predictive value of the linear correlations presented here can be demonstrated by comparing oxidation potentials of substituted HTABs calculated using the data above with measured values.⁶ Applying the linear correlation for oxidation of substituted TPABs in dichloromethane (Fig. 2) and using $6\sigma_p^+$, calculated values of $E_{pa} = 0.72$ and 0.47 V vs Ag/AgCl_(aq) (0.70 and 0.45 V vs SCE) are obtained for the oxidation of hexa-*p*-methyl- and hexa-*p*-methoxy-substituted HTABs respectively. At first glance these values do not correlate very closely with experimental values (estimated $E^{o'}$ = 0.82 and 0.65 V vs SCE).⁶ However, HTABs have greater

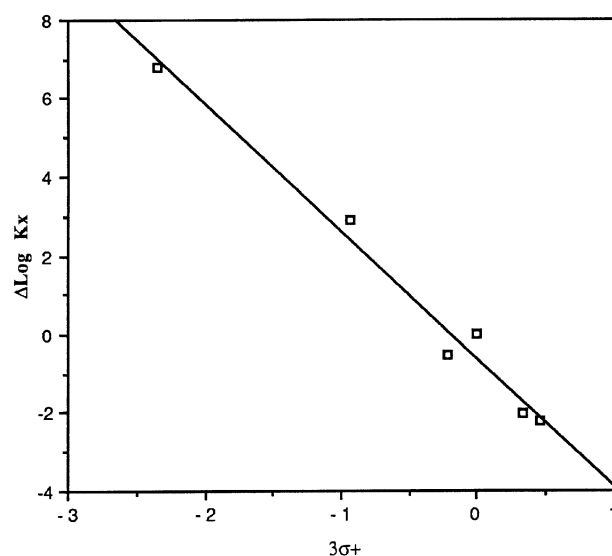


Figure 3. Hammett plot of $\Delta \log K_x$ vs $3\sigma_p^+$ for first oxidation potentials of *p*-substituted *N,N,N*-triphenylamines in acetonitrile ($\Delta \log K_x = -0.634 - 3.27(3\sigma_p^+)$, $R = 0.99$)

steric constraints than TPABs and the diphenylamino moieties are likely turned out of the plane of the central benzene ring,¹⁰ decreasing resonance interactions and increasing the oxidation potentials for the HTABs.

This can be shown by comparing the oxidation potential for non-substituted TPAB reported here ($E_{pa} = 0.87$ V vs SCE) with that of non-substituted HTAB ($E^{o'} = 0.98$ V vs SCE, average of literature values),^{6,10} which results in an increase in oxidation potential of about 0.11 V due to decreased resonance interactions. Using this value of 0.11 as an empirical correction factor and adding it to the calculated oxidation potentials for hexa-*p*-methyl- and hexa-*p*-methoxy-substituted HTABs gives $E_{pa} = 0.81$ and 0.56 V vs SCE respectively, values which agree reasonably with the experimental values. The underestimation of the calculated values and the larger discrepancy for the methoxy-substituted HTAB suggest that there may be some undetermined scaling factor, possibly due to comparing E_{pa} values with estimated $E^{o'}$ values,²¹ which needs to be applied to gain more accuracy. Dual-parameter correlations¹⁴ and higher-level calculational studies of the electronic and structural differences between TPABs and HTABs may lead to better correlations and to a better understanding of the inductive and resonance contributions of substituents toward the oxidation potentials of TPABs and HTABs and the stability of the resulting radical cations.

CONCLUSIONS

The linear free energy relationship between the oxidation potentials of substituted TPABs results from small but significant resonance effects from substituents at the *para*

positions of the outer phenyl rings. The linear correlation allows prediction of the oxidation potentials of related phenylamino-substituted compounds and may aid in the design of molecular magnetic materials based on these compounds, especially with respect to matching redox potentials in donor-acceptor complexes involving these compounds.

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