

Effect of Substitution on the Electrochemical and Xerographic Properties of Triarylamines: Correlation to the Hammett Parameter of the Substituent and Calculated HOMO Energy Level

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It has been found that both the electrochemical and xerographic properties of a series of triarylamines vary with the nature (quantified by its Hammett parameter, σ) and the frequency of substituents that make up a triarylamine. Three series of triarylamines, encompassing a total of 35 compounds, have been synthesized by Ullman condensation of an appropriately substituted aniline with an excess of an appropriately substituted iodophenylene by a published procedure [Goodbrand, H. B.; Hu, N. X. *J. Org. Chem.* **1999**, *64* (2), 670–674]. The xerographic properties, including transport properties, of a select number of compounds have been measured as solid-state solutions in polycarbonate-Z. The recorded xerographic properties varied with the measured oxidation potential ($E_{1/2}$) of the molecule, which in turn correlates to both the Hammett parameter of the substituent and the calculated HOMO energy level of the triarylamine.

Introduction

The use of arylamines as hole-transporting molecules (HTMs) within optoelectronic devices [both organic photoreceptor devices¹ and organic light emitting diodes² (OLEDs)] is well-documented. Typically, in an organic photoreceptor the arylamine is present as a solid-state solution in a polymeric binder, whereas in an OLED device it is usually a thin solid film. In either case, a constantly increasing demand on the improvement of these devices (longer life, higher efficiency, etc.) necessitates stricter control over the properties and characteristics of the HTMs that make up the device.

Among other requirements, control over the HOMO energy level of the HTM (as measured by its oxidation

potential) is desirable. This is done in order to control and affect the electrochemical events in which the electrons occupying the HOMO of the HTM participates within the optoelectronic device. A rapid and convenient method for the accurate prediction of the HOMO energy level without needing to synthesize and measure the oxidation potential of an HTM in question would be advantageous.

Since first described as a measure of the substituent effect on the pK_a of substituted benzoic acids in aqueous media, the Hammett parameter (σ) has been found to correlate to many reaction and equilibrium phenomena in organic chemistry.³ In essence, the Hammett parameter is a quantified descriptor of the ability of an organic functional group to affect the electron density distribution of an aryl group. A functional group that is electron-withdrawing has a positive Hammett parameter and a group that is electron-donating has a negative parameter.

A simple search of chemical literature will find some 10 000 references pertaining to Hammett parameters. Recently many research groups have found Hammett parameter relationships involving electrochemical events and a statistically significant number of related compounds, for example, in ruthenium(III)trisbipyridine complexes,⁴ 2-[(R-phenyl)amine]-1,4-naphthalenediones,⁵ ruthenium β -diketonate/2,6-bis(*N*-pyrazolyl)pyridine com-

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plexes,⁶ substituted anthracenes,⁷ alkynyl flavins,⁸ iron-(III)/*N*-benzoyl-*N*-salicylidenehydrazines complexes,⁹ ferrocene derivatives,¹⁰ and *N,N,N'*-triphenyl-1,3,5-triaminobenzenes.¹¹

More to the point of this paper, a person skilled in the art would say qualitatively the addition of electron-donating groups to a triarylamine will lower its oxidation potential and the addition of electron-withdrawing groups will increase its oxidation potential. However, to the best of our knowledge, no group has ever quantified the effect of substituent on the oxidation potential of triarylamines. Herein we present the quantification of the relationship between the substituent and oxidation potential of a series of triarylamines. Furthermore, since triarylamines are used as hole-transporting molecules in xerographic devices, we have measured the effect of substituent on the hole-transporting properties of selected molecules within such a device.

Experimental Section

Materials. Toluene, ethanol, and potassium hydroxide were purchased from Caledon Labs (ACS reagent grade) and used as received. 4-Iodo-*o*-xylene was purchased from Wychem Ltd., New Market, Suffolk, UK, and used as received. Filtrol-24 was purchased from Harshaw/Filtrol Partnership, Cleveland, OH, and used as received. All other chemicals and reagents were purchased from Sigma-Aldrich Canada Ltd., Mississauga, Canada, and used as received.

General Methods. All reactions were carried out in oven-dried glassware under argon atmosphere. Each reaction was followed by HPLC (RP-18, acetonitrile:methanol 1.0 mL/min: 0.2 mL/min) until the reaction was deemed complete, where convenience warranted. The final compounds were >99% pure, as determined by ¹H NMR (CDCl₃) and in-house elemental analysis.

General Synthetic and Purification Method. All triarylamines were made by Ullman condensation of an appropriately substituted aniline with 3 equiv of appropriately substituted aryl iodide in the presence of potassium hydroxide with copper(II)acetate/1,10-phenanthroline catalyst in refluxing toluene.¹²

Bis(3,4-dimethylphenyl)-3-methylphenylamine (Compound 1b). Typical Procedure. To a 2 L Erlenmeyer flask were added toluene (800 mL), *p*-toluidine (58.73 g, 0.80 mol), and 4-iodo-*o*-xylene (382.92 g, 1.65 mol). Then in order, 1,10-phenanthroline (4.60 g), copper(II)acetate monohydrate (6.40 g), and potassium hydroxide pellets (400 g) were added with vigorous stirring. The flask was fitted with a reflux condenser atop a Dean-Stark trap and set to reflux under argon bleed. The next morning (approximately 18 h, although some reactions were done in as little as 4 h) HPLC showed a completed reaction, and after cooling the solution was partitioned between dichloromethane (1 L) and water (1 L).

Typical Purification Method. The organic phase was removed and the residue taken up in toluene (2 L) and treated with a mixture of Filtrol-24 (288 g, an acid leached benonite

clay) and acidic alumina (196 g) at 75 °C. The solution was filtered by gravity while hot, and the absorbents were washed with hot toluene (200 mL). The absorbent treatment was repeated. The toluene was removed to yield a yellow liquid that could be dissolved in hot ethanol. On cooling the ethanol gave an off-white crystalline powder. Repeated recrystallization from ethanol gave a white crystalline powder, compound **1b** (149.10 g, 59%). All other compounds (except **1p**, which was always obtained as a yellow oil) could also be recrystallized from ethanol. Yields for other compounds were in the range 30–60%.

Series 1 Triarylamines. **1a**, R = phenyl; calcd for C, 87.66; H, 7.69; N, 4.65; found, C, 87.92; H, 7.38; N, 4.47; $E_{1/2} = +0.880$ V; $\sigma = 0$. **1b**, R = 4-methylphenyl; calcd for C, 87.57; H, 7.99; N, 4.44; found, C, 87.29; H, 7.88; N, 4.47; $E_{1/2} = +0.820$ V; $\sigma = -0.17$. **1c**, R = 4-phenylphenyl; calcd for C, 89.08; H, 7.21; N, 3.71; found, C, 88.92; H, 7.10; N, 3.70; $E_{1/2} = +0.856$ V; $\sigma = -0.01$. **1d**, R = 4-*tert*-butylphenyl; calcd for C, 87.34; H, 8.74; N, 3.92; found, C, 88.53; H, 8.63; N, 4.09; $E_{1/2} = +0.814$ V; $\sigma = -0.197$. **1e**, R = 4-*sec*-butylphenyl; calcd for C, 87.34; H, 8.74; N, 3.92; found, C, 88.36; H, 8.72; N, 4.12; $E_{1/2} = +0.810$ V; $\sigma = -0.197$. **1f**, R = 4-*n*-butylphenyl; calcd for C, 87.34; H, 8.74; N, 3.92; found, C, 87.21; H, 8.86; N, 3.95; $E_{1/2} = +0.812$ V; $\sigma = -0.151$. **1g**, R = 4-fluorophenyl; calcd for C, 82.73; H, 6.94; N, 4.39; found, C, 82.30; H, 7.15; N, 4.52; $E_{1/2} = +0.912$ V; $\sigma = 0.062$. **1h**, R = 3-fluorophenyl; calcd for C, 82.73; H, 6.94; N, 4.39; found, C, 83.01; H, 6.89; N, 4.62; $E_{1/2} = +0.981$ V; $\sigma = 0.337$. **1i**, R = 2-fluorophenyl; calcd for C, 82.73; H, 6.94; N, 4.39; found, C, 82.10; H, 6.69; N, 4.42; $E_{1/2} = +0.991$ V. **1j**, R = 2,4-difluorophenyl; calcd for C, 78.31; H, 6.27; N, 4.15; found, C, 77.53; H, 5.82; N, 4.24; $E_{1/2} = +1.016$ V. **1k**, R = 4-methoxyphenyl; calcd for C, 83.34; H, 7.60; N, 4.23; found, C, 82.71; H, 7.22; N, 4.12; $E_{1/2} = +0.735$ V; $\sigma = -0.268$. **1l**, R = 3-methoxyphenyl; calcd for C, 83.34; H, 7.60; N, 4.23; found, C, 81.32; H, 7.56; N, 4.18; $E_{1/2} = +0.824$ V; $\sigma = 0.115$. **1m**, R = 2-methoxyphenyl; calcd for C, 83.34; H, 7.60; N, 4.23; found, C, 82.53; H, 7.05; N, 4.35; $E_{1/2} = +0.844$ V. **1n**, R = 4-phenoxyphenyl; calcd for C, 85.46; H, 6.92; N, 3.56; found, C, 86.36; H, 6.80; N, 3.73; $E_{1/2} = +0.800$ V; $\sigma = -0.32$. **1o**, R = 4-bromophenyl; calcd for C, 69.48; H, 5.83; N, 3.68; found, C, 69.36; H, 5.42; N, 3.61; $E_{1/2} = +0.938$ V; $\sigma = 0.232$. **1p**, R = 4-chlorophenyl; oil elemental analysis not possible; $E_{1/2} = +0.943$ V; $\sigma = 0.227$. **1q**, R = 3-trifluoromethylphenyl; calcd for C, 74.78; H, 6.00; N, 3.79; found, C, 75.80; H, 6.08; N, 3.92; $E_{1/2} = +1.021$ V; $\sigma = 0.43$.

Series 2 Triarylamines. **2a**, R = phenyl; calcd for C, 87.87; H, 7.01; N, 5.12; found, C, 86.95; H, 7.04; N, 5.12; $E_{1/2} = +0.974$ V; $\sigma = 0$. **2b**, R = 4-methylphenyl; calcd for C, 87.66; H, 7.69; N, 4.65; found, C, 87.51; H, 7.23; N, 4.59; $E_{1/2} = +0.844$ V; $\sigma = -0.17$. **2c**, R = 4-*tert*-butylphenyl; calcd for C, 87.22; H, 9.15; N, 3.63; found, C, 86.79; H, 9.30; N, 3.75; $E_{1/2} = +0.837$ V; $\sigma = -0.197$. **2d**, R = 4-fluorophenyl; calcd for C, 77.65; H, 5.54; N, 4.53; found, C, 77.85; H, 5.40; N, 4.50; $E_{1/2} = +1.021$ V; $\sigma = 0.062$. **2e**, R = 4-methoxyphenyl; calcd for C, 79.25; H, 6.95; N, 4.20; found, C, 79.28; H, 6.45; N, 4.18; $E_{1/2} = +0.690$ V; $\sigma = -0.268$. **2f**, R = 3-methoxyphenyl; calcd for C, 79.25; H, 6.95; N, 4.20; found, C, 74.56; H, 6.32; N, 3.74; $E_{1/2}$ = not reversible; $\sigma = 0.115$. **2g**, R = 3-trifluoromethylphenyl; calcd for C, 64.55; H, 4.19; N, 3.42; found, C, 66.66; H, 3.86; N, 3.56; $E_{1/2} = +1.252$ V; $\sigma = 0.43$.

Series 3 Triarylamines. **3a**, triphenylamine; calcd for C, 88.13; H, 6.16; N, 5.71; found, C, 87.80; H, 5.65; N, 5.77; $E_{1/2} = +1.126$ V; $\sigma = 0$. **3b**, tritoylamine (tri(4-methylphenyl)amine); calcd for C, 87.76; H, 7.36; N, 4.87; found, C, 88.16; H, 6.98; N, 4.88; $E_{1/2} = +0.867$ V; $\sigma = -0.17$. **3c**, tri(4-fluorophenyl)amine; calcd for C, 72.24; H, 4.04; N, 4.68; found, C, 72.35; H, 3.68; N, 4.79; $E_{1/2} = +1.138$ V; $\sigma = 0.062$. **3d**, tri(4-methoxyphenyl)amine; calcd for C, 75.20; H, 6.31; N, 4.18; found, 74.62; H, 5.79; N, 4.32; $E_{1/2} = +0.654$ V; $\sigma = -0.268$.

Electrochemical Characterization. Cyclic voltammograms were recorded on a BAS 100B electrochemical workstation in dichloromethane solution containing 1 M Bu₄NClO₄ at a scan rate of 100 mV/s. All compounds were scanned in the range -0.5 to 1.2 V. All oxidation potentials ($E_{1/2,ox}$) are relative

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to Ag/AgCl and were corrected using decamethylferrocene as an internal reference ($E_{1/2,red} = -0.012$ V).

Electrophotographic Device Fabrication. It was determined that the simplest method for evaluating the xerographic properties of the triarylaminines was to incorporate a select number of them into a standard dual layer photoreceptor. The dual layer photoreceptor device was comprised of an aluminumized Mylar substrate with a thin ($\sim 1 \mu\text{m}$) charge-generation layer and a thick ($\sim 25 \mu\text{m}$) charge-transport layer.^{13,19} The charge-generation layer was comprised of a type V hydroxy gallium phthalocyanine (HOGaPC) pigment dispersed into a styrene vinyl pyridine block copolymer, while the charge transport layer was comprised of 40 wt % triarylamine dispersed in a polycarbonate-Z binder. The charge-transport layer was coated, from a chlorobenzene solution, using a film applicator with a blade gap specifically selected to yield a final film thickness of $25 \mu\text{m}$. The film was dried at 115°C for 60 min.

Electrophotographic Device Measurements. All of the xerographic discharge measurements were performed with a flat plate xerographic scanner. The flat plate scanner is a standard xerographic evaluation tool and has been used extensively in the characterization of new photoreceptor materials. The instrumentation details of the scanner have been discussed, in detail, in numerous publications.¹³ The flat plate scanner is designed to provide the user with a reasonable understanding of a photoreceptor's performance in an actual xerographic machine.

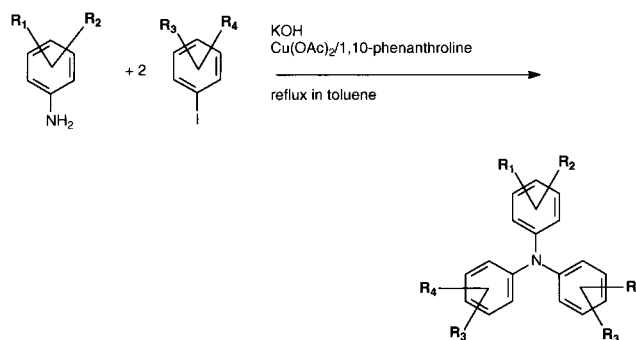
Perhaps the most pertinent experiment recorded with the flat plate scanner is the photoinduced discharge curve (PIDC). A single PIDC provides a considerable amount of information concerning a photoreceptor device. The key PIDC parameters that were used to characterize the triarylaminines are background potentials after exposure and the residual potential after erase. In this study, the devices were charged to -800 V and then exposed with 780 nm incident light to ensure efficient photogeneration of charge carriers in the phthalocyanine-based generation layer and erased with 600 – 800 nm light.

The carrier mobility of the select number of triarylaminines was also measured using a conventional time-of-flight apparatus. In this technique, a sheet of carriers is injected through the bulk and its drift under the influence of a DC electric field is time-resolved.¹⁹ However, the poor performance of certain samples made it extremely difficult to record reliable transients for all the studied triarylaminines. This will be discussed in greater detail further in the paper. It should also be noted that the samples used for TOF were only $\sim 15 \mu\text{m}$ thick.

Results and Discussion

Synthesis. A series of triarylaminines have been synthesized by one-step Ullman condensation of a

Scheme 1. One-Step Synthesis of Substituted Triarylaminines



substituted aniline with excess of substituted arylidide (Scheme 1), using a procedure adapted from Goodbrand and Hu.¹² Each triarylamine was obtained in yields ranging from 30% to 60% after purification with absorbents and their purity established at $>99\%$ by elemental analysis, ^1H NMR, and HPLC.

The triarylaminines can be grouped into three distinct categories. Compounds in series **1** have varying substituent on only one aryl ring, while the other two are *o*-xylyl moieties (Figure 1). Whereas, series **2** have identical substituents on two of the three aryl rings, the other being *o*-xylyl (Figure 2), and series **3** have identical substituents on all three aryl rings (Figure 3). In each case the nature of the substituent was chosen so as to span a wide range of Hammett parameters from strong electron withdrawing groups (for example, *m*-CF₃, compounds **1q** and **2g**) and strong electron donating groups (for example, *p*-OCH₃, compounds **1k** and **2e**). Furthermore, several compounds with ortho-substituents were synthesized (for example, compounds **1i**, **1j**, and **1m**), although no Hammett parameters are available to investigate the effect of ortho-substitution on the oxidative behavior of the series **1** triarylaminines.

It is worth noting that although a wide variety of substituents are represented in this study, the syntheses of several triarylaminines with other substituents were attempted but failed. For example, the attempted condensation of *N,N*-dimethyl-1,4-phenylene diamine, 2,4-dimethoxyaniline, 3,4-methylenedioxyaniline, or 4-trifluoromethylaniline with 4-iodo-*o*-xylene produced no triarylamine product. Similarly, the attempted condensation of pentafluoroaniline or 4-aminoacetophenone with 4-iodo-*o*-xylene resulted in a vigorous reaction, yielding, in both cases, an intractable dark brown mass.

Electrochemical Characterization. A cyclic voltammogram (CV) of each triarylamine was obtained in dichloromethane solution containing tetrabutylammonium perchlorate as the supporting electrolyte and using decamethylferrocene as the internal reference (Figure 4). The half-wave reduction potential ($E_{1/2,red}$) of decamethylferrocene was established to be -0.012 V vs Ag/AgCl by comparison to the well-known hole-transport material TPD, which has an established first half-wave oxidation potential ($E_{1/2,ox}^1$) of 0.805 V vs Ag/AgCl.¹⁴ All oxidation potentials are reported as half-wave oxidation potentials and were calculated as the average between the peak oxidation potentials ($E_{peak,ox}$).

Each triarylamine studied exhibited a single reversible oxidation over the range 0.654 V (compound **3d**) to 1.252 V (compound **2g**, Table 1). A compound is said to

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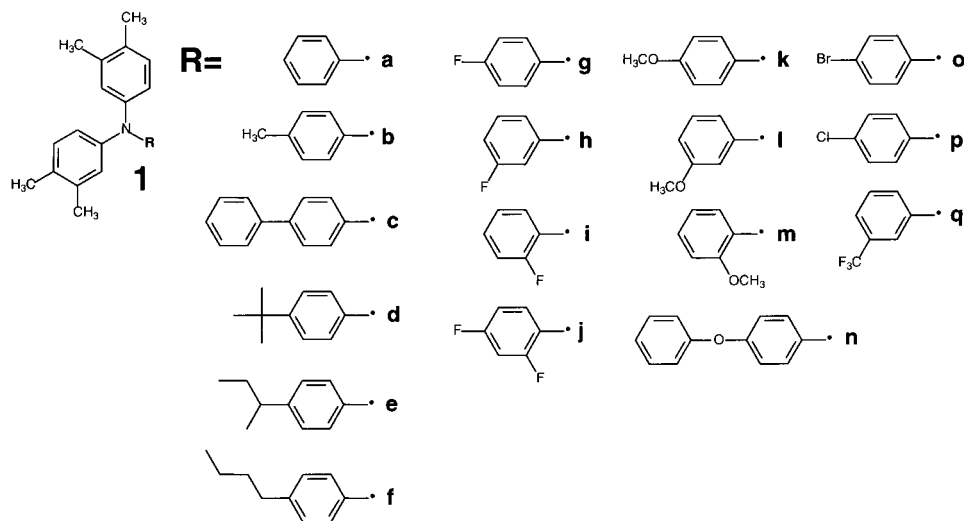


Figure 1. Series 1 triarylamines.

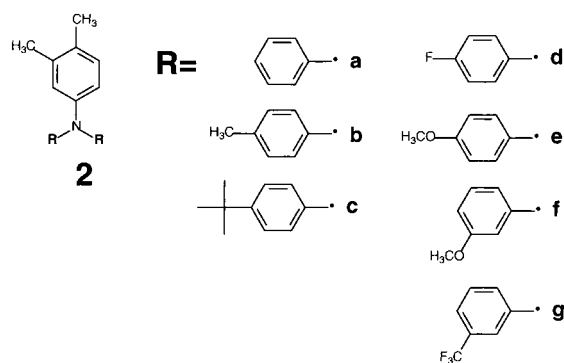


Figure 2. Series 2 triarylamines.

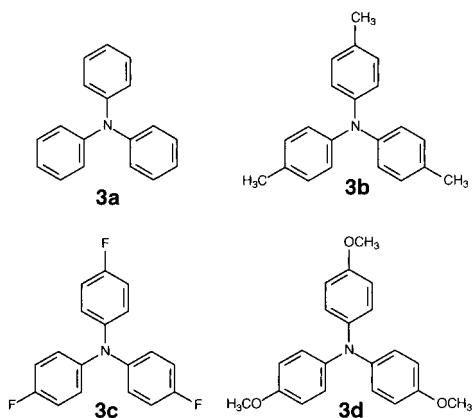


Figure 3. Series 3 triarylamines.

have a reversible oxidation potential if it shows a superimposable CV over at least six complete cycles during the measurement. A typical CV is shown in Figure 4 (compound **1k**).

A plot of oxidation potential ($E_{1/2,ox}$) versus Hammett parameter (σ), for the compounds in series 1–3 for which Hammett parameters are known, indicates that there is indeed a strong dependency of the oxidation potential on the nature of the substituents around the triarylamine molecular backbone (Figure 5). One might expect a correlation between σ and the peak oxidation potential difference ($\Delta E_{peak,ox}$, a measure of the difference between the oxidation and back reduction events), but we have found no such correlation.

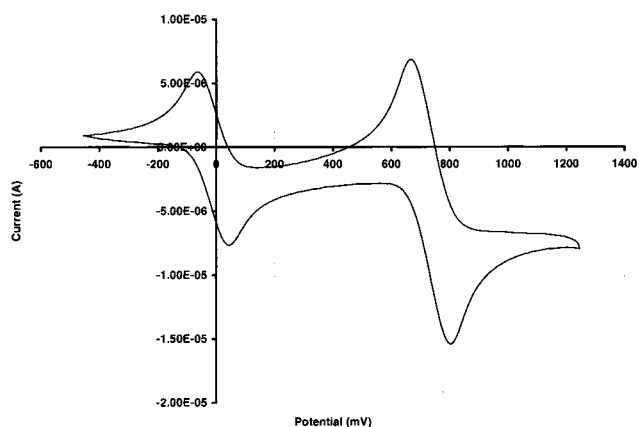


Figure 4. Cyclic voltammogram (CV) of compound **1k** with decamethylferrocene internal reference.

As expected, the presence of an electron-donating group around the triarylamine backbone reduces the oxidation potential, and the presence of an electron-withdrawing group does the opposite. The slope of the Hammett plot (ρ) indicates the sensitivity of this relationship, which increase proportionally with the number of aryl rings bearing substituents. For series 1 triarylamines (one ring bearing a substituent) $\rho = 0.319$, for series 2 triarylamines $\rho = 0.745$, and for series 3 $\rho = 0.966$.

There are no Hammett parameters available for ortho-substituents. One might expect the effect on oxidation potential of ortho-substitution to be similar in magnitude to para-substitution, because of resonance effects through the aryl ring. However, we have found this not to be the case. Rather, ortho-substitution produced a sizable increase in oxidation potential compared to para-substitution. This is the case for both triarylamines bearing electron-withdrawing fluorine atoms (**1g–j**) and triarylamines bearing electron-donating methoxy groups (**1k–m**). Molecular modeling shows that in each case of ortho-substitution (**1i** and **1m**) the aryl rings of the triarylamine are at a higher twist angle than the para-substituted equivalents (**1g** and **1k**). A higher twist angle promotes a state of lower conjugation between the aryl rings that make up the triarylamine and hence a higher oxidation potential. While a steric argument can be used to explain why a higher twist

Table 1. Physical Characteristics of Series 1–3 Triarylaminines Used in This Study^a

compd	substituent	mp (°C)	T_g (°C)	Hammett parameter (ρ)	oxidation potential ($E_{1/2}$, V vs Ag/AgCl)	HOMO energy (eV)		
						AM1 calcd	PM3 calcd	STO-3G calcd
1a	<i>p</i> -H	107.0	0.4	0	0.880	7.7966	8.1786	
1b	<i>p</i> -Me	117.8	5.1	0.17	0.820	7.7434	8.1284	
1c	<i>p</i> -phenyl	118.0	36.3	0.01	0.856	7.7712	8.1303	
1d	<i>p</i> - <i>tert</i> -butyl	81.4	26.0	0.197	0.814	7.7446	8.1372	
1e	<i>p</i> - <i>sec</i> -butyl	92.6	1.4	0.197	0.810	7.7479	8.1324	
1f	<i>p</i> - <i>n</i> -butyl	57.1	12.6	0.151	0.812	7.7424	8.1445	
1g	<i>p</i> -F	118.0	1.6	0.062	0.912	7.8916	8.3052	5.1798
1h	<i>m</i> -F	101.0	no	0.337	0.981	7.9551	8.3550	
1i	<i>o</i> -F	113.0	2.3	na	0.991	8.0425	8.3068	
1j	di- <i>o</i> - <i>p</i> -F	114.8	n.o.	na	1.016	8.1496	8.4362	
1k	<i>p</i> -OMe	122.0	3.8	0.268	0.735	7.7130	8.0970	5.0158
1l	<i>m</i> -OMe	130.1	1.3	0.115	0.824	7.8178	8.1633	
1m	<i>o</i> -OMe	92.1	7.4	na	0.844	7.8853	7.9946	
1n	<i>p</i> -phenoxy	99.1	14.9	0.32	0.800	7.9061	8.2721	
1o	<i>p</i> -Br	137.2	16.3	0.232	0.938	7.9459	8.3209	5.2689
1p	<i>p</i> -Cl	oil	oil	0.227	0.943	7.9032	8.2384	
1q	<i>m</i> -CF ₃	117.1	1.7	0.43	1.021	8.0805	8.5042	5.3844
2a	di- <i>p</i> -H	113.1	9.6	0	0.974	7.8735	8.2546	
2b	di- <i>p</i> -Me	105.7	1.5	0.17	0.844	7.7605	8.1540	
2c	di- <i>p</i> - <i>tert</i> -butyl	121.5	36.0	0.197	0.837	7.7564	8.1678	
2d	di- <i>p</i> -F	77.0	11.1	0.062	1.021	8.0503	8.5119	
2e	di- <i>p</i> -OMe	85.5	1.2	0.268	0.690	7.7069	8.0900	
2f	di- <i>m</i> -OMe	88.9	10.6	0.115	nr			
2g	di- <i>m</i> -CF ₃	80.9	12.5	0.43	1.252	8.4356	8.8457	
3a	tri-H	135.2	cryst	0	1.126			
3b	tri-Me	120.2	cryst	0.17	0.867			
3c	tri-F	125.8	cryst	0.062	1.138			
3d	tri-OMe	97.5	8.0	0.268	0.654			

^a no = not observed; na = not available; nr = not reversible; oil = compounds isolated as an oil; cryst = compound isolated as crystals.

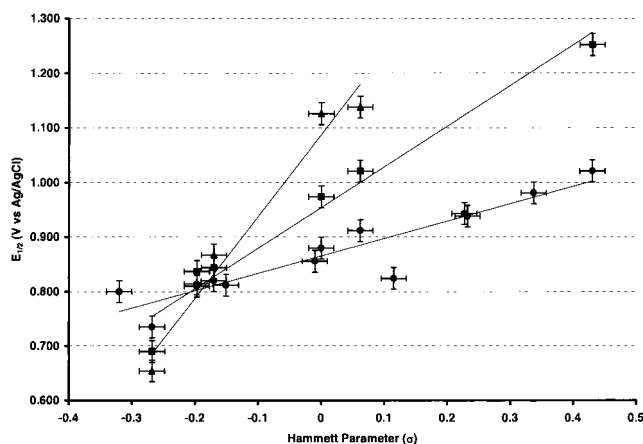


Figure 5. Oxidation potential ($E_{1/2,ox}$, V vs Ag/AgCl) vs Hammett parameter (ρ) for series 1 (●, $\rho = 0.319$), series 2 (■, $\rho = 0.746$), and series 3 (▲, $\rho = 1.498$) triarylaminines.

angle exists in the ortho-substituted methoxylated compound **1m**, it cannot be used to explain why this is the case with the fluorinated compound **1i**, because the steric size of a fluorine atom is approximately the same as a hydrogen atom. Therefore, one explanation for the twisting of the triarylamine structure for compounds **1i** may be an electrostatic repulsion between the *o*-fluorine atom and the other two aryl rings.

The effect of substitution of the triarylamine has also been shown to be accumulative. Compound **1j** is both ortho- and para-substituted with fluorine atoms and its possess a proportionally higher oxidation potential compared to compounds **1g** and **1i**.

Molecular Modeling. On the basis of these results it would be of interest to establish a correlation of oxidation potential ($E_{1/2}$) and calculated HOMO energy level. This would allow the use of molecular modeling

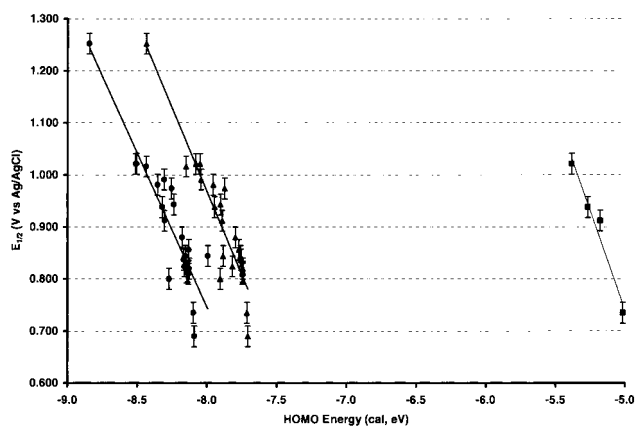


Figure 6. Oxidation potential ($E_{1/2,ox}$, V vs Ag/AgCl) vs HOMO energy (cal, eV) for selected series 1 and series 2 triarylaminines calculated using AM1 (▲, $\rho = -0.58$) and PM3 (●, $\rho = -0.64$) semiempirical methods and STO-3G (■, $\rho = -0.75$) ab initio method.

to predict the oxidation potential of triarylaminines when suitable Hammett parameters do not exist.

The HOMO energy of each series 1 and 2 triarylamine was calculated using both the AM1 and PM3 semiempirical methods as implemented in HyperChem ver 5.1.¹⁵ Additionally, four compounds (**1g**, **1k**, **1o**, and **1q**) were selected¹⁶ and their HOMO energies were calculated using the STO-3G ab initio method also as implemented in HyperChem ver 5.1.¹⁷

When the measured oxidation potentials ($E_{1/2}$) are plotted against the calculated HOMO energies, a reasonable correlation is found (Figure 6): the deeper the HOMO, the higher the oxidation potential of the triarylamine. When a comparison is drawn between the AM1 and PM3 semiempirical methods, it can be seen that although the absolute values for the HOMO energy

level that each method calculates are different, the sensitivity of the relationship (φ) is nearly the same.

Due to the extended computation time required for ab initio level calculations, the HOMO energy levels of only a few compounds from series **1** were calculated using an STO-3G basis set. Again, the calculated energy levels correlated as expected to the measured oxidation potentials of the triarylamine. The slope of the plot (φ) is nearly equivalent to that obtained using semiempirical methods; however, the calculated HOMO energies are significantly shallower than predicted by semiempirical methods. In fact, the HOMO energy values calculated using the STO-3G basis set are more in line with the HOMO energy levels of 5.2–5.5 eV expected for compounds of this type.¹⁸

It then seems that if one is interested in the trend of correlation to experimental results then calculation at the semiempirical method is sufficient. However, if the absolute value of the HOMO energy level is necessary, then calculation at least the STO-3G Ab Initio level is required.

Xerographic Properties. The primary theme of this work is to understand the relative influence of the triarylamine (within a given series) on photoreceptor device performance. Device performance is a function of three main factors: charge generation, charge injection, and charge transport. It is often difficult to isolate the influence of each of these factors on device performance. However, since hydroxy gallium phthalocyanine (HOGaPC) is constant as the photoconductor in all our devices, it can be assumed that charge generation will not be the dominant factor affecting the relative performance.¹⁹ Since it is the hole-transport molecules that are changing, it can be assumed that charge transport (mobility and trapping) and charge injection will be the dominant factors affecting device performance. Both the injection efficiency and carrier mobility are known to be strongly influenced by the energy levels of the hole-transport molecule.²⁰

Figure 7 is a single time-resolved discharge curve for six photoreceptors containing one of the following series **1** triarylamine (**1c**, *p*-phenyl; **1e**, *p*-*sec*-butyl; **1g**, *p*-F; **1k**, *p*-Ome; **1o**, *p*-Br; **1q**, *m*-CF₃) at an exposure of 1.6 ergs/cm² and an erase of 70 ergs/cm². Both the expose and erase are flash exposures for approximately 50 and 150 ms, respectively. As can be observed from the plot, there is a drastic difference in photoreceptor performance. The most interesting characteristics are the shape (slope) of the curve at the onset of expose and erase and the residual potential after erase. The triarylamine with a Hammett parameter below 0.0 (**1c**, **1e**, **1k**) all behaved in similar and favorable manner. These PIDCs all possessed a steep slope after expose and erase and a low residual voltage after erase. There appears to be no major transport or injection limitations. There is some variation from sample to sample; however, as stated previously, we are looking for trends and not absolute values. In contrast, the triarylamine with a Hammett parameter greater than 0.0 (**1g**, **1q**, **1o**) all behaved in an unfavorable manner; the larger the

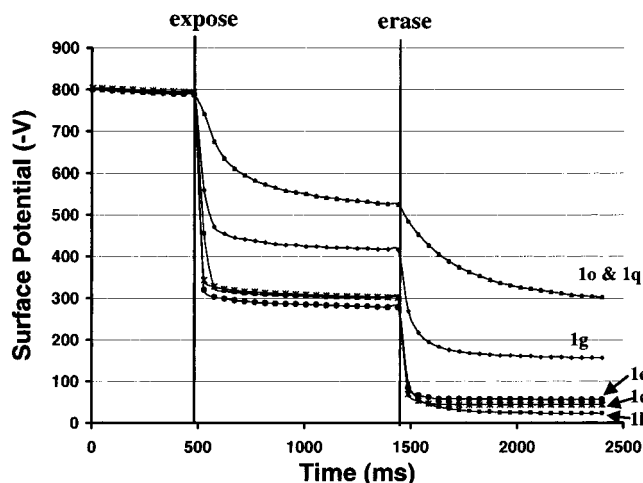


Figure 7. A single photoinduced discharge curve for six photoreceptors containing the following series **1** triarylamine (**1c**, *p*-phenyl; **1e**, *p*-*sec*-butyl; **1g**, *p*-F; **1k**, *p*-Ome; **1o**, *p*-Br; **1q**, *m*-CF₃) at an exposure of 1.6 ergs/cm² and an erase of 70 ergs/cm².

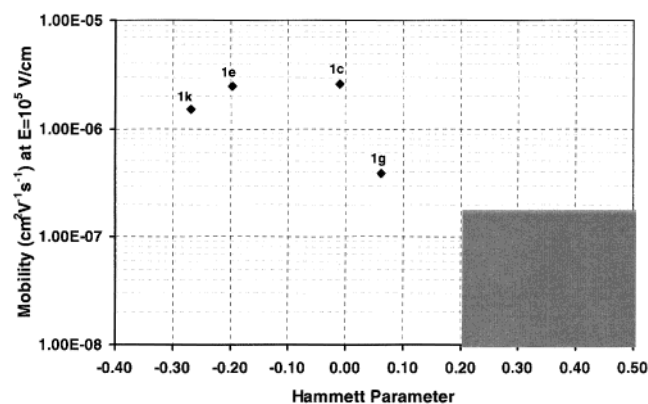


Figure 8. A plot of carrier mobility at an electric field of 10⁵ V/cm vs Hammett parameter for compounds **1c** (*p*-phenyl), **1e** (*p*-*sec*-butyl), **1g** (*p*-F), **1k** (*p*-OMe), **1o** (*p*-Br), and **1q** (*m*-CF₃). The shaded area broadly defines the mobility of triarylamine **1o** and **1q**.

Hammett parameter, the less desirable the performance. The device with triarylamine **1g** ($\sigma = 0.062$) has a slower discharge and higher residual potential when compared to the triarylamine with a Hammett parameter below 0.0. The performance further deteriorates (slower discharge and high residual potential) for the devices containing triarylamine **1q** and **1o**. It should be noted that the residual potential after erase also remained high in experiments with both a prolonged time period for recording the erase potential and a dramatically increased erase light intensity. Therefore, from the PIDC experiments it is observed that charge-transport layers possessing triarylamine with a Hammett parameter below 0.0 could efficiently discharge with a HOGaPc-based CGL, while charge-transport layers possessing triarylamine with a Hammett above 0.0 were unable to discharge efficiently with a HOGaPc-based CGL.

Plots of percent discharge versus exposure also illustrated the previously described dependence of behavior on the triarylamine Hammett parameter. All of the triarylamine possessing a Hammett parameter below 0.0 behave in a similar and favorable manner, while all of the triarylamine possessing a Hammett

(20) (a) Pai, D. M.; Springett, B. E. *Rev. Mod. Phys.* **1993**, *65*, 163. (b) DiPaola-Baranyi, G.; Hsiao, C. K.; Hor, A. M. *J. Imag. Sci.* **1990**, *34*, 224. (c) Pai, D. M.; Yanus, J. *Photogr. Sci. Eng.* **1983**, *27*, 14. (d) Stolka, M.; Yanus, J. F.; Pai, D. M. *J. Phys. Chem.* **1984**, *88*, 4707.

parameter above 0.0 behave in a less than favorable manner, with performance deteriorating with increasing Hammett parameter.

In an attempt to further elucidate the fundamental nature of the differences in device performance, the carrier mobility was measured using TOF. Figure 8 is a plot of carrier mobility at an electric field of 10^5 V/cm vs Hammett parameter. The triarylaminines with a Hammett parameter below 0.0 all possess mobility in the low 10^{-6} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, while the triarylaminines with a Hammett parameter above 0.0 possess mobility in the range of 10^{-7} to $\sim 10^{-8}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. Due to the high degree of dispersion of triarylaminines **1q** and **1o**, it was extremely difficult to record a reliable transient for these devices. Therefore, instead of a discrete point, the general area on the graph, which includes **1q** and **1o**, has been highlighted.

From the data presented in Figures 7 and 8, it can be determined that the Hammett parameter is a useful property for indicating the relative performance of triarylaminines. If the Hammett parameter was greater than 0.0, the triarylaminines possessed poor xerographic properties, including transport properties. The xerographic properties seem to deteriorate with an increas-

ing Hammett parameter. Triarylaminines possessing a Hammett parameter below 0.0 possessed favorable xerographic properties, including transport properties. However, the subtle difference between these samples (having $\sigma < 0.0$) is difficult to predict solely on the Hammett parameter.

Conclusions

On the basis of the selected compounds, which were chosen to span a wide range of Hammett parameters (σ), we have shown that the relative xerographic performance of the triarylamine can be understood by examining the substituents that make up the triarylamine. It follows that the xerographic properties can also be partially understood by considering the oxidation potential (either measured or calculated using molecular modeling) of the triarylamine in question. In general we have found that the presence of electron-withdrawing substituents (having Hammett parameter $\sigma > 0$) drastically hinder the performance of the triarylamine as a hole-transporting material in a xerographic device.

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