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Substituent effects on the redox properties and structure of substituted triphenylamines. An experimental and computational study

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ABSTRACT

The peak oxidation potentials of a series of polysubstituted triphenylamines were found to be highly linearly correlated (R=0.995) with their ionization potentials as computed by density functional theory. The computations, as well as confirming previous experiments demonstrating the planar geometry of such substances around the central nitrogen atom, also demonstrate substantial resonance interactions between the central nitrogen atom and a nitro group located *para* or *ortho* to it; no such interaction is involved in the corresponding amine cation radicals. On the other hand, a methoxy group located *para* to the central nitrogen atom interacts strongly with the central nitrogen in the cation radical, but *not* in the neutral amine.

1. Introduction

Steckhan and co-workers reported the synthesis of a series of brominated triphenylamines and showed that these substances are excellent electrocatalysts for oxidative transformation of a variety of organic substrates.[1] Our interest was aroused recently in this class of substances in connection with our studies on the anodic oxidation of electronegatively substituted alkenes[2] and other such substrates bearing one or more strong electron-withdrawing substituents. We have found that the polybromotriphenylamines of Steckhan and co-workers[1,9] are not useful electrocatalysts for anodic oxidation of electronegatively substituted substrates.[2,4] This is apparently because the differences between the oxidation potentials of the catalyst and that of such substrates are too great. Our aim recently has therefore been to develop triarylamine electrocatalysts of substantially higher oxidation potential and to explore the use of these substances as electrocatalysts for the oxidation of difficultly oxidized organic substrates.[3,4] In connection with this goal, we felt that computation could provide a valuable adjunct to these studies by guiding the design of promising new triarylamine electrocatalysts. That is, it would be useful to be able to predict in advance whether a triphenylamine containing a given combination of ring substituents is likely to have a high enough oxidation potential to be useful before embarking upon a proposed synthesis of it. The traditional way to do this would be to construct a plot of the experimental oxidation potentials of a series of substituted triphenylamines versus the sum of the Hammett constants of the substituents. If the data proved to be well correlated (correlation coefficient close to unity), then the oxidation potential of an unknown triphenylamine could be predicted with reasonable accuracy using the Hammett values of the substituents on it. Linear correlations of this type with excellent correlation coefficients have been observed for the reduction of many classes of substituted arenes.[5] A number of attempts to construct such correlations for oxidative processes have also been reported.[6–9] However, we recently reported a better procedure for correlating and predicting the effects of ring substituents upon reduction potential.[10] The experimental reduction potentials of a set of 100 benzylideneacetophenones (so-called ‘chalcones’), bearing anywhere from one to four ring substituents, were measured by linear sweep voltammetry (LSV). Simultaneously, their electron affinities were computed by density functional theory (DFT). A plot of reduction potential versus electron affinity for the 100 chalcones was found to afford an excellent linear correlation (R=0.969), with a standard deviation of 22 mV between the experimental and computed reduction potentials.[10] A plot of reduction potentials versus Hammett substituent constants afforded a linear correlation, but with greater scatter of points about the line (R=0.953). Similar attempts to construct correlations between Hammett constants and the oxidation potentials of a series of related compounds have been reported.[6–9] If we could show a good correlation between the oxidation potentials of a series of known substituted triphenylamines

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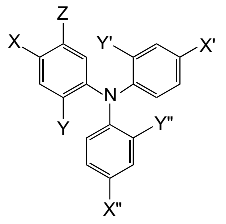
and their computed ionization potentials, the correlation line could be used to point our synthetic efforts in the direction of promising candidates. We wish to report the results of our attempts to develop such a correlation and, at the same time, to extend our previous computational efforts on cathodic systems[10] into the anodic arena. The ionization potentials of a series of substituted triphenylamines (**1a**–**u**) were computed by DFT[11] and their oxidation potentials were measured by LSV in acetonitrile. The quality of the correlation between the two properties was assessed, together, for comparison, with that of a similar correlation of the oxidation potentials with Hammett substituent constants.[5,10] At the same time, instructive information on the effects of substituents upon the triarylamine structure was found by examining the optimized geometries of both the neutral and cationic species.



1a, X = X' = X" = Y = Z = H
b, X = X' = X" = OMe
c, X = X' = X" = Me
d, X = X' = X" = Br
e, Z = NO_2
f, Y = NO_2
g, X = NO_2
h, X = X' = X" = Me; Y = Y' = NO_2
i, X = X' = NO_2
j, X = Y' = NO_2; X' = X" = Br
k, X = X' = X" = Me; Y = Y' = Y" = NO_2
l, X = X' = NO_2; X" = Y" = Br
m, X = X' = X" = NO_2
n, X = X' = Me; X" = Y = Y' = NO_2
o, X = X" = Y" = Br; X' = Y = NO_2
p, X = X' = X" = Cl
q, X = X' = X" = Cl; Y = NO_2
r, X = X' = X" = Cl; Y = Y' = NO_2
s, X = X' = X" = Cl; Y = Y' = Y" = NO_2
t, X = X' =X" = $SCH_2CH_2CH_3$
u, X = X' =X" = $SO_2CH_2CH_2CH_3$
v, X = OCH_3
w, X = Br
x, X = X' = Br

2. Experimental

2.1. General

^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury Vx 300 MHz pulsed field gradient spectrometer. Chemical shifts for the NMR spectra are reported in parts per million with the solvent (^{1}H: CD_3CN, δ 1.94 (5); ^{13}C: $CDCl_3$, δ 77.23(3)) as the internal standard. An Agilent Technologies 6890N Gas Chromatograph with an HP-5 column coupled to a 5973N MS Detector was used for measurement of mass spectra. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, GA. Cyclic voltammetry with electronic iR compensation was carried out using a CH Instruments (Austin, TX) Model 650-A electrochemistry system.

2.2. Sources of triphenylamines

All compounds are either commercially available (**1a**–**e**), were described in earlier papers (**1g**–**o**),[3,4,12,13] or were synthesized in the course of the present work (**1f**, **p**–**u**). Compounds **1v**–**x** were examined computationally but were not synthesized.

2.2.1. *2-Nitrotriphenylamine (**1f**)*

4-Nitrotriphenylamine (**1g**) can be prepared by treatment of triphenylamine (**1a**) with a limited quantity of $Cu(NO_3)_2\cdot 2.5H_2O$ in acetic anhydride.[3,12] We have since found that **1g** is accompanied by a small amount of the 2-isomer (**1f**), which can be separated by repeated chromatography: mp 103–105 °C (lit.[13] 102–103 °C); ^{1}H NMR (300 MHz, CD_3CN): δ=7.82 (dd, *J*=8.1 and 1.2 Hz, 1H), 7.60 (dt, *J*=8.0 and 1.5 Hz, 1H), 7.31 (t, *J*=7.8 Hz, 1H), 7.2–7.4 (m, 5H), 7.05 (t, *J*=7.5 Hz, 2H), 6.96 (d, *J*=7.5 Hz, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): δ=146.7, 145.8, 141.3, 133.7, 129.9, 129.6, 126.2, 124.4, 123.8, 123.4; MS: *m*/*z* (%): 291 (20), 290 (100), 244 (43), 243 (42), 242 (25), 241 (25), 166 (17). We have also prepared **1f** in low yield by the copper-catalyzed Ullmann reaction of 2-bromonitrobenzene with diphenylamine.[13]

2.2.2. *4,4′,4″-Trichlorotriphenylamine (**1p**)*

This compound was prepared using a procedure described by Patil and co-workers.[14] 1-Chloro-4-iodobenzene (2.73 g, 11.5 mmol) and 4-chloroaniline (0.696 g, 5.5 mmol) were dissolved in dry toluene (35 mL). Copper(I) iodide (38.1 mg, 3.6 mol %) and 2,2′-bipyridyl (31.5 mg, 3.6 mol %) were added to the solution, and the reaction vessel was placed in an oil bath heated to 115 °C. Potassium *tert*-butoxide (1.85 g, 16.5 mmol) was added, and then the vessel was sealed and purged with N_2. After 5 h, the reaction was allowed to cool to rt. Solids were removed by vacuum filtration, and solvent was removed by rotary evaporation. The product was dissolved in CH_2Cl_2 (30 mL) and washed with 0.1 M aqueous $NaHSO_3$ (2×30 mL), followed with distilled H_2O (1×30 mL). Purification by flash chromatography using silica with hexane as the eluent, followed by recrystallization from 95% EtOH, yielded **1p** (853 mg; 44%): mp 144–146 °C (lit.[15] 148–149 °C); ^{1}H NMR (300 MHz, CD_3CN): δ=7.28 (d, *J*=9.0 Hz, 6H), 7.01 (d, *J*=8.7 Hz, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ=145.9, 129.8, 128.6, 125.4; MS: *m*/*z* (%): 353 (3), 351 (33), 349 (100), 347 (100), 311 (14), 277 (21), 75 (11). Anal. Calcd for $C_{18}H_{12}Cl_3N$: C, 62.01; H, 3.47. Found: C, 61.86; H, 3.35.

2.2.3. *4,4′,4″-Trichloro-2-nitrotriphenylamine (**1q**)*

$Cu(NO_3)_2\cdot 2.5H_2O$ (0.25 g) was added to a solution of 4,4′,4″-trichlorotriphenylamine (**1p**) (200 mg, 0.574 mmol) in acetic anhydride (40 mL), and the mixture was stirred for 3 h. The reaction was quenched with distilled water (75 mL), and extracted with dichloromethane (3×10 mL). After washing with saturated aqueous $NaHCO_3$ (150 mL), the organic layer was separated, washed with H_2O (10 mL), and dried over Na_2SO_4. Purification by flash chromatography using silica with 2:1 hexanes/benzene as the eluent, followed by recrystallization from 95% EtOH, yielded **1q** (87 mg; 33%): mp 102–104 °C; ^{1}H NMR (300 MHz, CD_3CN): δ=7.89 (d, *J*=2.7 Hz, 1H), 7.61 (dd, *J*=8.7 and 2.4 Hz, 1H), 7.30 (d, *J*=8.7 Hz, 1H), 7.27 (d, *J*=8.7 Hz, 4H), 6.96 (d, *J*=8.7 Hz, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): δ=145.7, 144.6, 139.1, 134.2, 130.9, 130.3, 130.0, 129.6, 126.4, 124.5; MS *m*/*z* (%): 398 (5), 396 (36), 394 (100), 392 (100), 345 (21), 311 (48), 275 (19), 241 (15), 75 (10). Anal. Calcd for $C_{18}H_{11}Cl_3N_2O_2$: C, 54.92; H, 2.82. Found: C, 54.68; H, 2.80.

2.2.4. *4,4′,4″-Trichloro-2,2′-dinitrotriphenylamine (**1r**)*

$Cu(NO_3)_2\cdot 2.5H_2O$ (0.50 g) was added to a solution of 4,4′,4″-trichlorotriphenylamine (**1p**) (200 mg, 0.574 mmol) in acetic anhydride (40 mL), and the mixture was stirred overnight. The reaction was quenched with distilled water (75 mL), and extracted with dichloromethane (3×10 mL). The organic solution was washed with saturated aqueous $NaHCO_3$ (150 mL), washed