Tetrahedron 65 (2009) 2408–2414

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

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

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A R T I C L E I N F O

Article history:
Received 13 August 2008
Received in revised form 22 December 2008
Accepted 6 January 2009
Available online 14 January 2009

Keywords:
Substituent effects
Triphenylamines
Oxidation potentials
Ionization potentials

A B S T R A C T

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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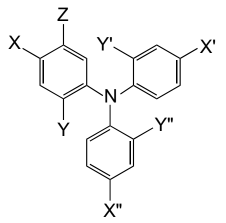
doi:10.1016/j.tet.2009.01.023

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 $Cu(NO_3)_2\cdot2.5H_2O$ 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**)*

$Cu(NO_3)_2\cdot2.5H_2O$ (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**)*

$Cu(NO_3)_2\cdot2.5H_2O$ (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 once with H_2O (10 mL), and dried over Na_2SO_4. Purification by flash chromatography using silica with 9:1 hexanes/ethyl acetate as the eluent, followed by recrystallization from 95% EtOH, yielded **1r** (92 mg; 36%): mp 168–170 °C; ^1H NMR (300 MHz, CD_3CN): δ=7.80 (d, J=2.4 Hz, 2H), 7.52 (dd, J=8.7 and 2.4 Hz, 2H), 7.26 (d, J=8.7 Hz, 2H), 7.17 (d, J=9.3 Hz, 2H), 6.73 (d, J=8.7 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): δ=145.1, 143.4, 137.6, 134.5, 131.5, 130.9, 130.3, 130.1, 126.2, 123.0; MS: m/z (%): 441 (32), 439 (100), 437 (100), 359 (20), 347 (14), 309 (27), 275 (25), 239 (10), 75 (9). Anal. Calcd for $C_{18}H_{10}Cl_3N_3O_4$: C, 49.29; H, 2.30. Found: C, 48.95; H, 2.19.

*2.2.5. 4,4′,4″-Trichloro-2,2′,2″-trinitrotriphenylamine (**1s**)*

Nitration was carried out by the procedure of Uemura and co-workers.[16] Sodium nitrite (625 mg, 9 mmol) was added to a solution of 4,4′,4″-trichlorotriphenylamine (**1p**) (349 mg, 1 mmol) in trifluoroacetic acid (100 mL), upon which the solution turned deep blue and then green in color. The mixture was sealed with a rubber septum and stirred overnight. After 20 h, H_2O (100 mL) was added to the orange-brown solution and the reaction mixture was then cooled in ice. While stirring, NaOH pellets (50+ g) were added very slowly (*exothermic*) until the solution turned red litmus paper blue. The product was extracted with CH_2Cl_2 (3×10 mL) and washed thoroughly with H_2O to yield **1s** (350 mg; 72%): mp 302–303 °C; ^1H NMR (300 MHz, CD_3CN): δ=7.96 (d, J=2.4 Hz, 3H), 7.61 (dd, J=8.7 and 2.4 Hz, 3H), 7.22 (d, J=9.0 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ=144.1, 136.9, 134.5, 132.3, 129.7, 126.6; MS: m/z (%): 486 (33), 484 (96), 482 (100), 345 (24), 311 (52), 309 (74), 289 (34), 287 (49), 264 (35), 238 (25), 69 (28). Anal. Calcd for $C_{18}H_9Cl_3N_4O_6$: C, 44.70; H, 1.88. Found: C, 44.81; H, 1.94.

*2.2.6. 4,4′,4″-Tripropanesulfonyltriphenylamine (**1u**)*

4,4′,4″-Tris[propylthio]triphenylamine (**1t**) was prepared by the method described by Chen and co-workers for 4,4′,4″-tris[methylthio]triphenylamine.[17a] The propyl analog was prepared to improve solubility properties. Potassium propylmercaptide was prepared by adding 1-propanethiol (734 mg, 9.6 mmol) to a solution of KO*t*-Bu (1.081 g, 9.6 mmol) in MeOH (17 mL). The solvent was removed by rotary evaporation and heated until dry. The mercaptide and 4,4′,4″-tribromotriphenylamine (**1d**) (516 mg, 1.1 mmol) were placed in a reaction vessel sealed with a rubber septum and purged with N_2. DMF (20 mL) was injected into the reaction vessel and the solution was heated to 125 °C and stirred overnight. The solvent was removed by rotary evaporation. The residue was dissolved in a 50:50 mixture of CH_2Cl_2 and hexane and the solution was washed with saturated aqueous NH_4Cl and then successively with water and brine, and dried over Na_2SO_4. Purification by flash chromatography using silica with 3:1 hexanes/CH_2Cl_2 as the eluent yielded **1t** (183 mg; 35%): mp 47–49 °C; ^1H NMR (300 MHz, CD_3CN): δ=7.25 (d, J=8.1 Hz, 2H), 6.95 (d, J=7.8 Hz, 2H), 2.87 (t, J=7.1 Hz, 2H), 1.62 (sextet, J=7.3 Hz, 2H), 1.00 (t, J=7.5 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ=145.9, 131.2, 130.4, 124.6, 36.9, 22.9, 13.6; MS: m/z (%): 467 (M^+,100), 424 (39). Purification of **1t** to analytical purity was difficult because of its high solubility and low mp, hence it was used directly in the next step. Oxidation of **1t** was carried out by the procedure of Trost and Curran.[17b] To a solution of OXONE® (2.368 g, 7.7 mmol) in EtOH (70 mL) and H_2O (30 mL) was added 0.2 mmol of **1t** (100 mg), and the mixture was stirred overnight. The mixture was diluted with water and extracted with dichloromethane (3×50 mL). The combined organic layers were washed with water and brine and then dried over Na_2SO_4. Purification by flash chromatography with 19:1 dichloromethane/ethyl ether as eluent, followed by recrystallization from 95% EtOH, yielded **1u** (81 mg, 81%): mp 210–212 °C; ^1H NMR (300 MHz, CD_3CN): δ=7.80 (d, J=8.4 Hz, 2H), 7.30 (d, J=9.0 Hz, 2H), 3.13 (t, J=7.7 Hz, 2H), 1.68 (sextet, J=7.5 Hz, 2H), 0.98 (t, J=7.4 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ=150.5, 135.2, 130.3, 124.7, 58.2, 16.7, 13.2. Anal. Calcd for $C_{27}H_{33}NS_3O_6$: C, 57.52; H, 5.90. Found: C, 57.49; H, 5.88.

2.3. Voltammetry

Cyclic voltammograms of compounds **1a**–**u** were measured at a scan rate of 0.1 V/s at a glassy carbon working anode and platinum wire counter electrode in acetonitrile containing 0.1 M lithium perchlorate. Potentials were measured versus a Ag/0.1 M $AgNO_3$ reference electrode. The potential of this electrode is +0.350 V versus SCE and −0.030 V versus Fc/Fc^+. Adams and co-workers showed that the cation radicals of triphenylamines containing at least one *para*-unsubstituted site are unstable on the cyclic voltammetric time scale because they rapidly dimerize.[8,18] Such compounds therefore exhibit irreversible voltammetric behavior. For this reason, anodic peak potentials were recorded for all substances (Table 1).

2.4. Computational method

The energies of both the neutral species and the cation radicals of substances **1a**–**x** were computed[11] by density functional theory employing the B3LYP hybrid functional[19] and the 6-31G(d) basis set, which includes d-orbital polarization functions on all second row and higher atoms (C, N, O, S, Cl, Br). This procedure was chosen in an effort to achieve both reasonable accuracy and acceptable computation times. The geometries of both the neutral amine and its corresponding cation radical were optimized at the B3LYP/6-31G(d) level separately; this was necessary because certain aspects of the geometry change upon one-electron oxidation. Each structure was verified as a true minimum by

Table 1
Substituent effects on oxidation and ionization potentials of substituted triphenylamines

Compound	E_{ox}[a]	I.P.[b]	$\Sigma\sigma$[c]	$\Sigma\sigma^n$[d]	$\Sigma\sigma^+$[e]
1a	0.54	4.77	0	0	0
1b	0.25	4.35	−0.804	−0.45	−1.94
1c	0.40	4.61	−0.510	−0.51	−0.768
1d	0.78	5.02	0.696	0.78	0.0750
1e	0.84	5.03	0.710	0.778	0.674
1f	0.83	5.07	0.778	0.81	0.740
1g	0.88	5.16	0.778	0.81	0.740
1h	0.96	5.35	1.05	1.11	1.15
1i	1.08	5.45	1.56	1.62	1.35
1j	1.17	5.54	2.09	2.14	1.53
1k	1.28	5.61	1.82	1.92	1.45
1l	1.31	5.73	2.02	2.14	1.58
1m	1.33	5.78	2.33	2.43	2.22
1n	1.33	5.72	1.99	1.92	1.71
1o	1.37	5.80	2.25	2.4	1.55
1p	0.79	5.02	0.681	0.72	0.105
1q	1.00	5.29	1.46	1.53	0.845
1r	1.25	5.60	2.24	2.34	1.59
1s	1.56	6.94	3.11	3.15	2.33
1t	0.36	4.49	0.00	0.15	−0.492
1u	1.15	5.58	2.04	2.19	2.24
1v	NM[f]	4.61	−0.268	−0.15	−0.648
1w	NM[f]	4.85	0.232	0.26	0.025
1x	NM[f]	4.93	0.464	0.52	−0.050

[a] Oxidation potential in volts versus Ag/0.1 M $AgNO_3$ in CH_3CN/0.1 M $LiClO_4$.

[b] Ionization potential in eV computed at the density functional B3LYP/6-31G(d) level.

[c] Sum of Hammett constants of ring substituents.

[d] Sum of van Bekkum, Verkade, and Wepster σ^n constants of ring substituents.[22]

[e] Sum of σ constants of ring substituents.

[f] Not measured.

ensuring the absence of imaginary vibrational frequencies. The ionization potential (I.P.) (in eV) is then, by definition, the energy of the cation radical minus that of the neutral species. The solvation energies of both neutral amine and cation in acetonitrile, computed using the polarized continuum (PCM) method,[20] were included in the computations. Even though ionization potentials are normally measured in the vapor phase, the correlation between the computed value and the experimental (solution) oxidation potential was expected to provide a more realistic comparison with the experiment when the I.P. computation includes solvation effects, since the cation radicals should be strongly solvated by the donor solvent (acetonitrile). In this connection, it is important to note that we are not attempting to compute ionization potentials per se; rather, we simply need a conveniently computable parameter that correlates well with the experimental oxidation potentials.

3. Results and discussion

3.1. Substituent effects on oxidation potential

A plot of the experimental voltammetric peak oxidation potentials (E_p) versus the computed I.P.'s exhibited an excellent linear correlation between these properties (R=0.995) (Fig. 1). Analogous plots of E_p versus Hammett σ,[21] σ^n,[21a,22] and σ^+[21a] showed somewhat more scatter (Figs. 2–4), and thus the correlations exhibited were not as good as the correlation with computed I.P., suggesting the presence of resonance effects with some of the triphenylamines. The correlation between the experimental data and each of the four parameters can be expressed as Eqs. 1–4, together with their correlation coefficients (R).

$$E_p^{ox} = -3.190 + 0.789\text{I.P.} \quad R = 0.995 \tag{1}$$

$$E_p^{ox} = 0.542 + 0.346\sum\sigma \quad R = 0.981 \tag{2}$$

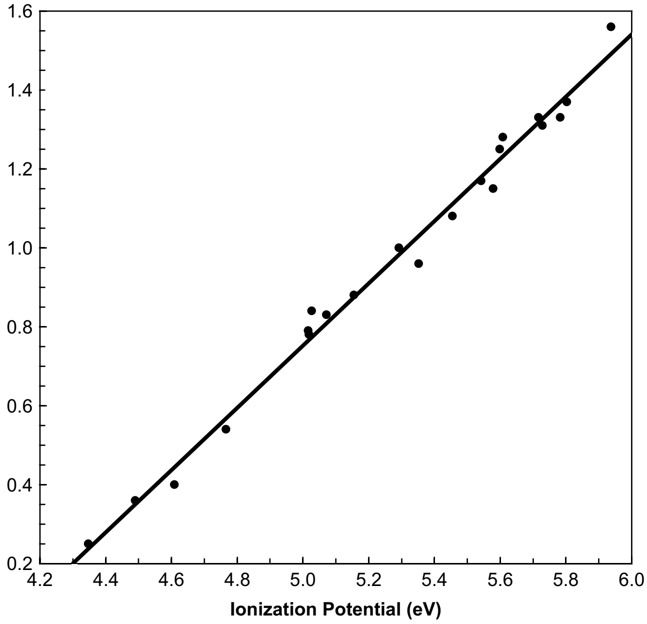


Figure 1. Plot of experimental oxidation potentials of a series of substituted triphenylamines versus their ionization potentials computed by density functional theory at the B3LYP/6-31G(d) level.

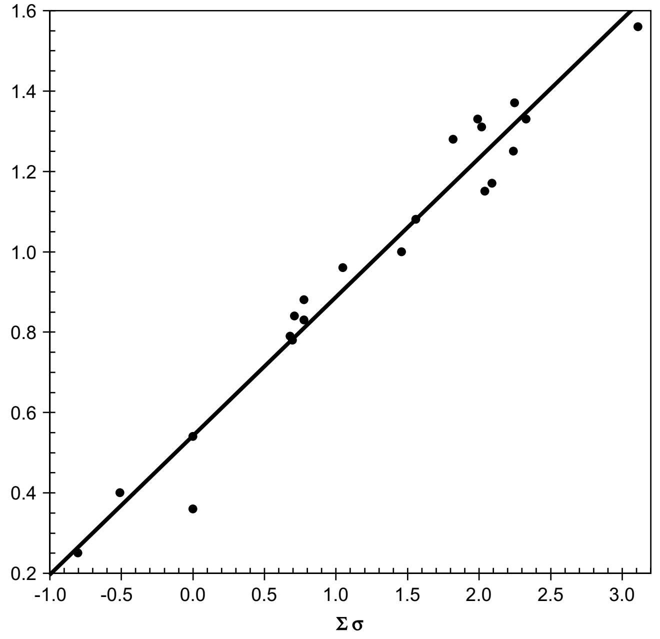


Figure 2. Plot of experimental oxidation potentials of a series of substituted triphenylamines versus the sum of the Hammett constants ($\Sigma\sigma$) of the substituents.

$$E_p^{ox} = 0.512 + 0.347\sum\sigma^n \quad R = 0.973 \tag{3}$$

$$E_p^{ox} = 0.692 + 0.317\sum\sigma^+ \quad R = 0.945 \tag{4}$$

The decrease in R as one proceeds through Eqs. 1–4 confirms the visual impression of increasing scatter as one proceeds through Figures 1–4. Our previous study of substituent effects on the voltammetric reduction potentials of a series of 100 benzylideneacetophenones (chalcones) produced the same result, i.e., the best correlation (R=0.962) was observed between computed electron

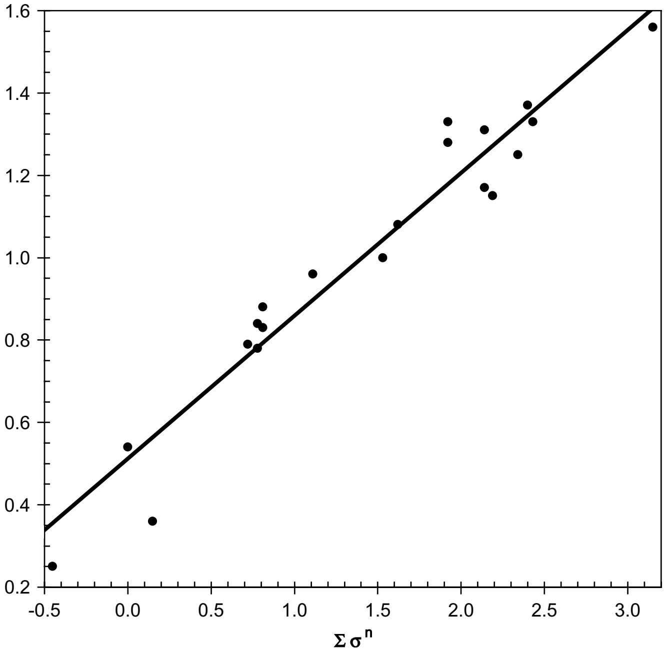


Figure 3. Plot of experimental oxidation potentials of a series of substituted triphenylamines versus the sum of the σ^+ constants ($\Sigma\sigma^+$) of the substituents.

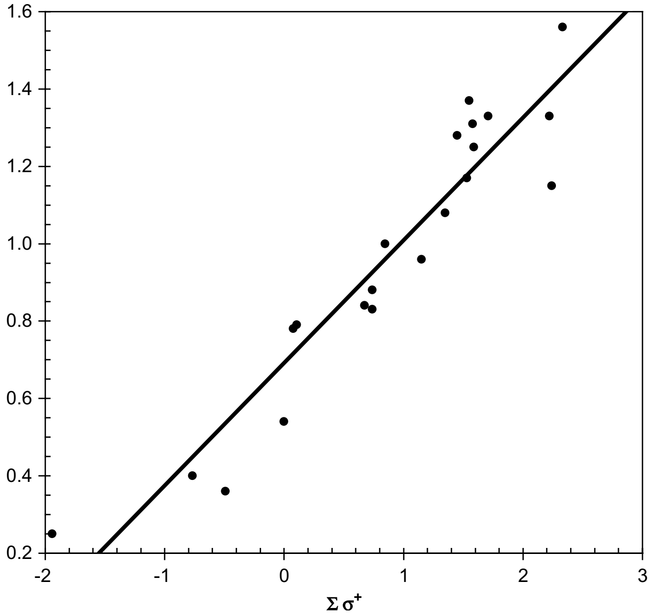


Figure 4. Plot of experimental oxidation potentials of a series of substituted triphenylamines versus the sum of the σ^n constants ($\Sigma\sigma^n$) of the substituents.

affinities, followed by Hammett σ values and the BVW σ^n parameters.[10] In general, the reason for the poorer correlation between Hammett values and any type of voltammetric data is the fact that the experimental redox potential is related to the free energy difference between the neutral species and its corresponding anion or cation radical, whereas the substituent constants α and σ are derived from measurements on the neutral compound. Similarly, σ^+ is derived from measurements of the effect of the substituent on a charged species. In contrast, the computation of either electron affinity or ionization potential involves computing the energy of both the neutral substance and its charged counterpart; the effect of the substituent on *both* species is incorporated into the final values. This procedure therefore emulates the experimental measurement more realistically. However, to gain this advantage, it is necessary to carry out the computation at a sufficiently rigorous level that one can be assured that the computed energies of both species are reliable. We showed in our earlier study that computations at the density functional B3LYP/6-31G(d) level satisfy this criterion; the semi-empirical AM1 and PM3 methods were not as good as Hammett values at correlating reduction potentials.[10] As noted above, the same premise underlies our inclusion of solvation into the computation in the present work, because the cation radicals should be particularly responsive to solvent effects. Solvation energies of mono-charged ions in polar solvents are typically in the range 35–45 kcal/mol, whereas those of neutral species are generally less than 10 kcal/mol.[23] The poorer correlation with σ^n probably arises from resonance effects upon the structures of the neutral and/or cation radical (see Section 3.2).

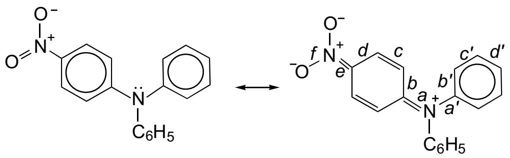
3.2. Substituent effects on molecular geometry

An electron diffraction study has shown that the three rings in triphenylamine are equivalent in the gas phase at 160 °C.[24] Quantum chemical computations at the HF/6-31G* level,[24] X-ray crystallographic[25] measurements, and both IR and Raman spectra[26] agree that the molecule is planar or nearly so at the central nitrogen atom. Advantage has been taken of this in the past to study the dynamics of interconversion of the various conformations by variable temperature measurements.[27] Our computations agree with the experimental data in showing that in the parent triphenylamine (**1a**) the three phenyl groups are equivalent and oriented in a propeller-type geometry, i.e., they are rotated by 48° from the hypothetical planar structure. In general, the central nitrogen atom is almost planar, allowing for maximum orbital overlap with the *pi*-system.

Certain substituents in **1a**-**x**, i.e., nitro and methoxy, are capable of interacting strongly by resonance with *pi*-systems to which they are attached. Such substituents on the triarylamine core structure may affect the geometry of the system as a result of resonance interaction with the central nitrogen atom when they are located either *ortho* or *para* to it. This effect should be particularly important in (a) neutral triphenylamines bearing a nitro group at the 4- or 2-position and (b) triphenylamine cation radicals bearing a methoxy group in the 4- or 2-position. 4- and 2-Nitrosubstituted triphenylamines are highly colored, which strongly indicates an electronic interaction of the nitro group with the central nitrogen atom. The geometry optimizations carried out in the course of the I.P. computations provide a way to assess the magnitude of these effects upon structure. Tables 2 and 3 present illustrative data for several triphenylamines in which resonance effects are operative.

3.3. Effect of the nitro group

Comparison of columns 2 and 3 of Table 2 reveals that introduction of a nitro group at position 3 (*meta* to the central nitrogen) has little effect upon the geometry of the molecule. However, introduction of the nitro group at the 4-position (*para*) has a very significant effect. The quinoid structure (**2b**) should be a significant contributor to the resonance hybrid in triphenylamines substituted at the 4-position by the strongly electronegative nitro group (**2a**). Evidence for this is readily found in the computed geometries of these substances; 4-nitrotriphenylamine (**1g**) itself is exemplary. To the extent that the polar quinoid structure makes a contribution to the overall structure of the neutral compound, bonds *a* and *c* of **1g** should be shorter than *a*′ and *c*′ of the unsubstituted rings, and bonds *b* and *d* should be longer than *b*′ and *d*′. Indeed, as shown in Table 2, bond *a* is shorter than *a*′ by 0.047 Å while *c* is shorter than *c*′ by 0.030 Å; at the same time *b* and *d* are lengthened by 0.016 and 0.004 Å, respectively. Further, bond *e* should be shorter than the corresponding bond in 3-nitrotriphenylamine (**1e**) and bond *f* should be longer. The computations support all of these expectations. Bond alternation causes the range of ring bond lengths from shortest to longest to be much greater (0.039 Å) in **1g** than in the parent compound (**1a**) (0.012 Å). The 2-nitro analog (**1f**) exhibits bond alternation but to a lesser degree than **1g**. The computed structure shows the reason for this: the nitro group is twisted 35° out of the plane of the ring to which it is attached, apparently because of unfavorable steric interactions with the nearby unsubstituted ring, thus reducing its resonance interaction with the central nitrogen atom. It is interesting to note the effect of increasing nitro group substitution upon structure: bond lengths *a*–*d* in the trinitro derivative (**1m**) are almost the same as in the parent (**1a**), with greatly reduced bond alternation. This presumably is because all three of the nitro groups are competing for the electron pair on the central nitrogen atom, so that each ring exhibits only a share of the resonance effect.



2a **2b**

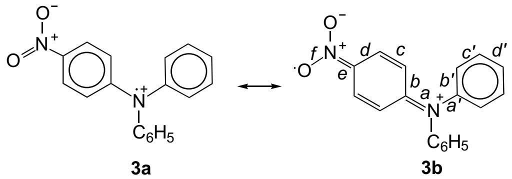
The radical cations (**3**) corresponding to these nitro compounds present a different situation. The radical cation is produced by

Table 2
Substituent effects on bond lengths (in Å) of substituted neutral triphenylamines

Bond[a]	**1a**	**1e**	**1f**	**1g**	**1i**	**1m**	**1w**	**1x**	**1d**	**1v**	**1b**
a	1.423	1.407	1.408	1.388	1.408	1.417	1.414	1.418	1.421	1.426	1.423
b	1.405	1.404	1.415	1.418	1.411	1.407	1.407	1.406	1.405	1.403	1.411
c	1.393	1.393	1.401	1.382	1.386	1.388	1.393	1.394	1.394	1.393	1.393
d	1.396	1.395	1.388	1.402	1.399	1.397	1.394	1.394	1.394	1.402	1.401
e	NA[b]	1.460[c]	1.460[d]	1.439	1.439	1.456	1.922	1.921	1.920	1.369	1.370
f	NA[b]	1.230[c]	1.235[d]	1.241	1.237	1.235	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
a′	1.423	1.429	1.424	1.435	1.407	1.417	1.426	1.418	1.421	1.419	1.423
a″	1.423	1.428	1.427	1.436	1.440	1.417	1.426	1.428	1.421	1.419	1.423
b′	1.400	1.404	1.404	1.402	1.411	1.408	1.404	1.405	1.405	1.405	1.411
b″	1.405	1.403	1.403	1.402	1.400	1.407	1.404	1.404	1.405	1.405	1.411
c′	1.395	1.395	1.395	1.395	1.386	1.387	1.395	1.394	1.394	1.394	1.393
c″	1.395	1.395	1.395	1.396	1.396	1.388	1.395	1.395	1.394	1.394	1.393
d′	1.398	1.397	1.398	1.398	1.399	1.396	1.398	1.394	1.394	1.398	1.401
d″	1.398	1.397	1.398	1.398	1.398	1.397	1.398	1.398	1.394	1.398	1.401
e′	NA[b]	NA[b]	NA[b]	NA[b]	1.450	1.456	NA[b]	1.920	1.920	NA[b]	1.370
e″	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]	1.456	NA[b]	NA[b]	1.920	NA[b]	1.370
f′	NA[b]	NA[b]	NA[b]	NA[b]	1.237	1.235	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
f″	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]	1.235	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]

[a] Letters refer to bond identifiers in structures **2** and **4**.
[b] Not applicable.
[c] Nitro group is *meta* to central nitrogen atom.
[d] Nitro group is *ortho* to central nitrogen atom.

removal of an electron from the lone pair on the central nitrogen atom. This should reduce the contribution from the quinoid structure to the resonance hybrid. In fact, a quinoid contributing structure (**3b**) would have to involve donation of an electron in the opposite sense, i.e., from an oxygen atom of the nitro group to the central nitrogen, which should be a relatively minor but probably real[28] contributor to the resonance hybrid due to the higher electronegativity of oxygen. Thus the bond lengths in the ring bearing the nitro group should be close to those in the unsubstituted ring. The computations bear out this expectation remarkably well: (a) the respective computed bond lengths in the radical cations of 4-nitro- and 3-nitrotriphenylamine are essentially identical (Table 3); (b) the range of computed ring bond lengths is only 0.012 Å, and (c) the Mulliken charges are almost identical in the neutral (−0.46) and cation (−0.41), demonstrating that structure **3b** does not contribute to the structure of 4-nitrotriphenylamine cation radical. Furthermore, the Mulliken charge on the central nitrogen atom of the neutral amine (−0.66) is reduced compared to that on the cation radical (−0.55), demonstrating that the electron is lost from an orbital delocalized over the entire molecule but with the principal contributor having the unpaired electron on nitrogen.



3a **3b**

3.4. Effect of the methoxy group

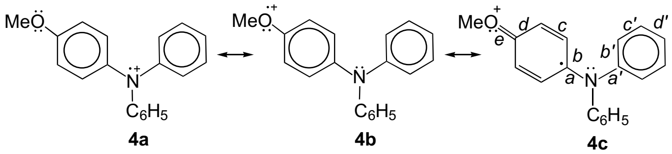
The methoxy group interacts strongly with electron-withdrawing groups located *ortho* and *para* to it on an aromatic ring, as evidenced by its large σ^+ value.[21] Oxidation of a 4-methoxytriphenylamine to the cation radical should therefore result in substantial electron donation from the unshared electron pair on oxygen (see structure **4b**). It will be noted, therefore, that **4b** is isoelectronic with a benzyl radical and that quinoidal structure **4c** will be a significant contributor to the hybrid. This should result in substantial bond alternation, with bonds *c* and *e* becoming shorter and bonds *b* and *d* longer than in the neutral species. Once again, the computations verify this expectation (structure **1v**, Tables 2 and

Table 3
Substituent effects on bond lengths (in Å) of substituted triphenylamine cation radicals

Bond[a]	**1a**	**1e**	**1f**	**1g**	**1i**	**1m**	**1w**	**1x**	**1d**	**1v**	**1b**
a	1.413	1.420	1.408	1.419	1.419	1.411	1.407	1.418	1.413	1.396	1.410
b	1.411	1.403	1.415	1.408	1.408	1.411	1.408	1.405	1.407	1.418	1.411
c	1.389	1.388	1.401	1.388	1.388	1.386	1.389	1.393	1.389	1.379	1.384
d	1.401	1.395	1.388	1.396	1.396	1.397	1.396	1.394	1.397	1.413	1.409
e	NA[b]	1.47[c]	1.46[d]	1.469	1.471	1.473	1.897	1.921	1.894	1.341	1.349
f	NA[b]	1.231[c]	1.23[d]	1.231	1.231	1.231	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
a′	1.414	1.410	1.424	1.409	1.418	1.412	1.418	1.418	1.413	1.421	1.410
a″	1.414	1.409	1.427	1.409	1.400	1.412	1.418	1.428	1.413	1.421	1.410
b′	1.411	1.413	1.404	1.413	1.408	1.412	1.405	1.405	1.407	1.407	1.411
b″	1.411	1.413	1.403	1.413	1.418	1.412	1.405	1.403	1.407	1.407	1.411
c′	1.389	1.388	1.395	1.388	1.388	1.386	1.390	1.394	1.389	1.391	1.384
c″	1.389	1.388	1.395	1.388	1.388	1.386	1.390	1.395	1.389	1.391	1.384
d′	1.401	1.402	1.398	1.402	1.396	1.395	1.399	1.393	1.397	1.399	1.409
d″	1.401	1.402	1.398	1.402	1.404	1.404	1.399	1.398	1.397	1.399	1.409
e′	NA[b]	NA[b]	NA[b]	NA[b]	1.231	1.473	NA[b]	1.921	1.894	NA[b]	1.349
e″	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]	1.470	NA[b]	NA[b]	1.894	NA[b]	1.349
f′	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]	1.231	NA[b]	NA[b]	NA[b]	NA[b]	NA
f′	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]	1.231	NA[b]	NA[b]	NA[b]	NA[b]	NA

[a] Letters refer to bond identifiers in structures **2** and **4**.
[b] Not applicable.
[c] Nitro group is *meta* to central nitrogen atom.
[d] Nitro group is *ortho* to central nitrogen atom.

3). In contrast to **1g**, bond *a* of the 4-methoxy derivative **1v** is actually slightly *longer* than bond *a*′ of the neutral compound, probably because of repulsion between the two electron pairs *para* to each other on the nitrogen and oxygen atoms. Otherwise the bond lengths in the substituted ring differ very little from those in the unsubstituted ring or in the parent compound **1a**. But in the cation radical of **1v**, bond alternation is evident: e.g., bonds *a* and *c* are much shorter than either bonds *a*′ and *c*′ or the corresponding bonds of **1a**, and bonds *b* and *d* are longer than the same bonds in the unsubstituted rings and in **1a** cation radical. Because of bond alternation, the range of computed ring bond lengths is much larger (0.039 Å) in the substituted ring of the cation radical than in the same ring of the neutral form (0.010 Å).



4a **4b** **4c**

4. Summary

The density functional computations reveal a strong resonance interaction between the central nitrogen atom of triphenylamines with nitro groups located *para* and *ortho* to it in the neutral amine and with methoxy groups located *para* to it in the amine cation radical. The experimental oxidation potentials are highly correlated (R=0.995) with ionization potentials computed by density functional theory.

Acknowledgements

Financial support was provided by the National Science Foundation under grant #CHE-0438474 and by Wesleyan University. L.K.S. was the recipient of a sabbatical leave from Fairfield University.

References and notes

1. Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.
2. Halas, S.; Okyne, K.; Fry, A. J. *Electrochim. Acta* **2003**, *48*, 1837.
3. Mayers, B. T.; Fry, A. J. *Org. Lett.* **2006**, *8*, 411.
4. Wu, X.; Davis, A. P.; Fry, A. J. *Org. Lett.* **2007**, *9*, 5633.
5. Zuman, P. *Substituent Effects in Organic Polarography*; Plenum: New York, NY, 1967.
6. Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124.
7. Amthor, S.; Noller, B.; Lambert, C. *Chem. Phys.* **2005**, *316*, 141.
8. Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498.
9. Dapperheld, S.; Steckhan, E.; Brinkhaus, K. H. G.; Esch, T. *Chem. Ber.* **1991**, *124*, 2557.
10. Hicks, L. D.; Fry, A. J.; Kurzweil, V. C. *Electrochim. Acta* **2004**, *50*, 1039.
11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision D.01*; Gaussian,: Wallingford, CT, 2004.
12. Wu, X.; Dube, M. A.; Fry, A. J. *Tetrahedron Lett.* **2006**, *47*, 7667.
13. Forrest, J. *J. Chem. Soc.* **1960**, 581.
14. Patil, N. M.; Kelkar, A. A.; Chaudhari, R. V. *J. Mol. Catal. A* **2004**, *223*, 45.
15. Walter, R. I. *J. Am. Chem. Soc.* **1955**, *77*, 5999.
16. Uemura, S.; Toshimitsu, A.; Okano, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1076.
17. (a) Chen, B.; Lee, S.; Venkatamaran, D.; DiSalvo, F.; Lobkovsky, E.; Nakayama, M. *Cryst. Growth Des.* **2002**, *2*, 101; (b) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 1287.
18. Nelson, R. F.; Adams, R. N. *J. Am. Chem. Soc.* **1968**, *90*, 3925.
19. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
20. Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.
21. (a) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, NY, 1972; pp 145–153; (b) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, NY, 1978; pp 439–540.
22. van Bekkum, H.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 815.
23. Fry, A. J. *Tetrahedron* **2006**, *62*, 6558.
24. Naumov, V. A.; Samdal, S.; Naumov, A. V.; Gundersen, S.; Volden, H. V. *Russ. J. Gen. Chem.* **2005**, *75*, 1956.
25. Sobolev, A. N.; Belsky, V. K.; Romm, I. P.; Chernikova, N. Y.; Gurianova, E. N. *Acta Crystallogr., C* **1985**, *41*, 967.
26. Rodionov, A. N.; Rucheva, N. I.; Rogozhin, K. L.; Shigorin, D. N. *J. Appl. Spectrosc.* **1974**, *20*, 409.
27. Hellwinkel, D.; Melan, M.; Degel, C. R. *Tetrahedron* **1973**, *29*, 1895.
28. The value of the σ^+ substituent constant of the nitro group is slightly smaller (0.740) than its σ value (0.778), demonstrating a slight mitigation of its powerful inductive electron-withdrawing effect by resonance when it is *para* to an atom bearing a positive charge and able to conjugate with it as in **3a**.