^{13}C NMR Study of *ortho*-, *meta*- and *para*-Substituted Phenyldiphenylamines: Substituent Effect Correlations

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The ^{13}C chemical shifts of 11 substituted triphenylamines have been determined and the assignment of these resonances made using intensities, ^{1}H and ^{19}F couplings and predictions from bond additivity relationships. ^{13}C chemical shifts at carbons bearing the substituent and at carbons *ortho* to the substituent correlated reasonably well with the *Q* parameter. A multiple regression analysis of chemical shifts with the field and resonance parameters of Swain and Lupton and the *Q* parameter produced significantly better correlations than those obtained when *Q* was omitted for these positions. ^{13}C chemical shift correlations for carbons *meta* and *para* to the substituent were not significantly better than when *Q* was omitted. Significant correlations were obtained between field and resonance parameters and ^{13}C chemical shifts of C-*o* and C-*p*, and C-*i*, C-*o*, C-*m* and C-*p* of the non-substituent bearing phenyl rings in *ortho*- and *para*-substituted phenyldiphenylamines, respectively.

Considerable interest has been exhibited[1–4] in establishing correlations between ^{1}H, ^{13}C and ^{19}F NMR chemical shifts and systematic variations in the molecular structures of monosubstituted and *ortho*-, *meta*- and *para*-disubstituted benzenes. The basic assumption made in these correlations is that ^{1}H, ^{13}C and ^{19}F chemical shifts reflect the electronic environment of the observed atoms.[5] Inductive effects, resonance effects, electronegativity of the substituent, steric factors and magnetic anisotropy of substituents have developed[2–9] as theoretical or empirical parameters which can be correlated with chemical shifts. Spiesecke and Schneider[2] reported that correlations of Hammett's σ with ^{13}C chemical shifts of monosubstituted benzenes held up well only for the *para* position. Maciel and Natterstad[9] correlated Taft's reactivity resonance parameters,[10] σ_R and $\sigma_R{}^\circ$, and ^{13}C chemical shifts in monosubstituted benzenes and Hinton and Layton[11] correlated σ_R and ^{13}C chemical shifts for the *para* position of a series of *para*-substituted bromobenzenes. Taft's divided substituent constants, σ_I and $\sigma_R{}^\circ$, and the ^{13}C chemical shifts of seven *ortho*-substituted aromatic systems, I, were correlated using the multiple linear regression Eqn (1), by Yoder and co-workers.[6] Correlations at

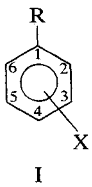
$$\delta_X - \delta_H = \rho_I\sigma_I + \rho_R\sigma_R{}^\circ + C \qquad (1)$$

ortho-carbons and ring carbons bearing the substituent were significantly improved when the parameter *Q*, defined by Hruska, Hutton and Schaefer,[4,12] was added to Eqn (1). An experimental method for determining *Q* values has been developed by Smith and Roark.[13]

A unified correlation of substituent effects with ^{1}H, ^{13}C and ^{19}F chemical shifts in aromatic and olefinic systems was reported by Smith and Proulx.[7] Chemical shifts in these systems were found to be correlated well by linear multiple regression analysis with the Swain and Lupton[14] field and resonance parameters $\mathcal{F}$ and $\mathcal{R}$, and the semiempirical parameter *Q*. Values of *a*, *b*, *c*, *d*, the correlation coefficient *r*, the average deviation and the range of chemical shifts for each carbon position were determined for homologous series of aromatic compounds using Eqn (2).

$$\delta = a\mathcal{F} + b\mathcal{R} + cQ + d \qquad (2)$$

We have been investigating the ^{13}C chemical shifts of a series of *mono*-substituted phenyldiphenylamines, phosphines and arsines[15] in order to study the usefulness of bond additivity in making ^{13}C chemical shift assignments and to test the use of the unified correlation of substituent effects of ^{13}C chemical shifts. The results of this investigation for triphenylamine and 11 of its derivatives are reported herein. The numbering sequence of the triphenylamine derivatives is given in II.



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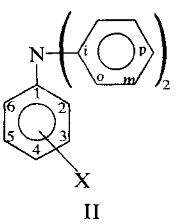

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EXPERIMENTAL

Triphenylamine was obtained from Pfaltz and Bauer and used without further purification. The ^{13}C NMR spectrum of triphenylamine in a 1:1 (v:v) solution of d_6-acetone (Wilmad) and dichloromethane gave chemical shifts which differed from literature[16] values due to the use of a different solvent. Literature procedures[17-20] were followed in the syntheses of *o*-chloro-, *o*-nitro-, *o*-amino- and *p*-fluorophenyldiphenylamines. The Ullman reaction,[21] as modified by Nelson and Adams,[14] was used to synthesize *p*-bromo- and *p*-nitrophenyldiphenylamine,[19] and the new compounds *o*-fluoro-, *o*-bromo-, *o*-iodo, *m*-bromo- and *p*-chlorophenyldiphenylamine. All reactions were conducted in a 500 ml 3-neck flask fitted with a mechanical stirrer, a Dean Stark trap, a reflux condenser and a nitrogen purge. Starting materials for the reactions were obtained commercially and used without further purification. Finely powdered anhydrous potassium carbonate was used to take up hydrogen iodide liberated in the condensation reaction. The copper catalyst was prepared according to the procedure described by Kleiderer and Adams.[22] Reaction mixtures were heated at reflux in *o*-dichlorobenzene or nitrobenzene and stirred vigorously. Reaction progress was monitored using gas chromatographic analysis by measuring loss of diphenylamine and concomitant formation of the appropriate product. After the reactions were complete the products were filtered while hot through a Buchner funnel to remove inorganic materials. The filtrate was vacuum distilled to separate the solvent and reaction products. A summary of the reaction conditions for new compounds is given in Table 1. Elemental and mass spectral data for compounds recrystallized from ethanol are given in Table 2. (Microanalytical determinations were performed by Galbraith Laboratories, Knoxville, TN. Mass spectrometric analyses were performed using either a Dupont 21-590F low resolution mass spectrometer or a Hewlett Packard 5930 Quadrupole mass spectrometer.)

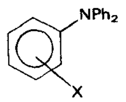
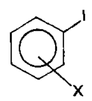
Determinations of ^{13}C chemical shifts of triphenylamine and monosubstituted triphenylamines were made using a Varian CFT-20 NMR spectrometer operating at 20 MHz and a probe temperature of *c.* 37 °C. d_6-Acetone was used as a deuterium lock and as a secondary internal reference with final chemical shifts being referenced to TMS. A flip angle of 19° and an acquisition time of 1.023 s for 8 K data were employed for acquisition of approximately 8000 transients. Broad band proton noise decoupled spectra were obtained for *c.* 20% (w/v) solutions of the compounds in 1:1 (v:v) d_6-acetone/methylene chloride solution using 8 mm tubes. Chemical shift values were reproducible to better than ±0.02 ppm.

DISCUSSION

The ^{13}C chemical shift assignments given in Table 3 were made on the basis of peak intensities, similarities of ^{13}C chemical shifts for closely related compounds, nuclear Overhauser enhancement considerations, off-resonance experiments, bond additivity predictions[11] and carbon–fluorine coupling constants. The numbering and lettering sequence used to identify the positions of the carbon atoms in the substituted and non-substituted phenyl rings of the triphenylamine derivatives described in this discussion are given by II.

First, ^{13}C chemical shift assignments were made for the four magnetically non-equivalent carbon atoms of the two non-substituted phenyl rings. These resonances were clearly distinguishable from peaks due to the carbons of the substituted phenyl ring in each spectrum on the basis of their intensities, as illustrated in Fig. 1, and on the basis of the constancy of the chemical shift values in each spectrum for *meta*- and *para*-substituted triphenylamine derivatives in order

Table 1. Summary of reaction conditions for synthetic procedures

		Ph_2NH mass (moles)	K_2CO_3 mass (moles)	Cu mass (moles)	Product mass (moles)[c] (% yield)	Reflux[a] time (hrs)	b.p. (°C)
o-Fluoro	25.0 g (0.113)	19.1 g (0.113)	15.6 g (0.113)	7.2 g (0.113)	20.5 g (0.078) (69%)	187	155°/1.3 mm
o-Bromo[e]	55.0 g (0.192)	32.8 g (0.194)	26.8 g (0.194)	12.3 g (0.194)	40.1 g (0.124) (69%)	96	165°/0.3 mm
o-Iodo	20.0 g (0.061)	10.3 g (0.061)	6.3 g (0.046)	3.0 g (0.047)	12.1 g (0.033) (53%)	96	155°/0.2 mm
m-Bromo[e]	17.5 g (0.062)	10.3 g (0.061)	8.5 g (0.062)	3.9 g (0.062)	7.2 g (0.022) (36%)	72	193°/2.5 mm
p-Bromo[e]	19.8 g (0.070)	11.8 g (0.070)	9.8 g (0.071)	4.5 g (0.071)	11.1 g (0.034) (49%)	48	185°/2.5 mm
p-Nitro	25.0 g (0.100)	16.9 g (0.100)	13.8 g (0.100)	6.5 g (0.100)	16.5 g (0.057) (57%)	48[b]	[d]
p-Chloro	20.0 g (0.084)	14.2 g (0.084)	11.6 g (0.084)	5.3 g (0.084)	10.5 g (0.040) (47%)	48	130°/0.3 mm

[a] Solvent used was *ortho*-dichlorobenzene.
[b] Solvent used was nitrobenzene.
[c] Product was recrystallized from ethanol.
[d] This product was obtained by recrystallization from ethanol after the solvent was stripped from the reaction mixture.
[e] Product was recrystallized from 2-propanol.

Table 2. Analytical data for X-phenyldiphenylamines[22]

Compound	Parent ion peak	C(%) Found	C(%) Req'd	H(%) Found	H(%) Req'd	N(%) Found	N(%) Req'd	Halogen (%) Found	Halogen (%) Req'd	m.p. Exp.	m.p. Lit.	Ref.
o-Fluorophenyldiphenylamine $C_{18}H_{14}NF$	263	81.94	82.09	5.16	5.32	5.51	5.32	7.23	7.22	98		This work
o-Chlorophenyldiphenylamine $C_{18}H_{14}NCl$	279, 281	76.90	77.27	5.72	5.05	4.84	5.01	12.42	12.67	200[a]	202[a]	17
o-Bromophenyldiphenylamine $C_{18}H_{14}NBr$	323, 325	66.65	66.68	4.49	4.35	4.25	4.32	24.49	24.65	63		This work
o-Iodophenyldiphenylamine $C_{18}H_{14}NI$	371	58.39	58.24	3.90	3.80	3.68	3.77	34.02	34.18	83		This work
o-Nitrophenyldiphenylamine $C_{18}H_{14}N_2O_2$	290	73.91	74.46	5.00	4.87	9.42	9.65			99	98	18
o-Aminophenyldiphenylamine $C_{18}H_{16}N_2$	260	82.87	83.04	6.21	6.20	10.61	10.76			148	145	19
m-Bromophenyldiphenylamine $C_{18}H_{14}NBr$	323, 325	66.34	66.68	4.69	4.35	4.25	4.32	24.43	24.65	92		This work
p-Fluorophenyldiphenylamine $C_{18}H_{14}NF$	263	81.91	82.09	5.34	5.32	5.18	5.32	7.26	7.22	102	101	20
p-Chlorophenyldiphenylamine $C_{18}H_{14}NCl$	279, 281	77.31	77.27	4.97	5.05	5.02	5.01	12.59	12.67	107	108	20
p-Bromophenyldiphenylamine $C_{18}H_{14}NBr$	323, 325	66.74	66.68	4.50	4.35	4.31	4.32	24.28	24.65	112	113[b]	This work
p-Nitrophenyldiphenylamine $C_{18}H_{14}N_2O_2$	290	74.61	74.46	5.09	4.87	9.57	9.65			144	141[b]	This work

[a] Values are for boiling point at 1 mm of Hg.

[b] M.p. values are for this compound as synthesized by the procedure of Ref. 20.

of increasing field strength C-*i*, C-*m*, C-*o* and C-*p* as shown in Fig. 2. The ^{13}C chemical shifts for C-*m* remained the most constant for the series of triphenylamine derivatives, whereas those for C-*p* were further downfield than for C-*o* of *ortho*-substituted derivatives. This order is inverted in comparison to that observed for triphenylamine and *meta*- and *para*-substituted triphenylamine derivatives. It is apparently due to a steric or a magnetic anisotropic effect on the diphenylamine group when placed *ortho* to the variable substituent. Assignment of ^{13}C chemical shifts for *ipso*-positions were supported by the observation that C-*i* resonances had lower intensities than C-*p* resonances. This is in accord with the relative intensities of

Table 3. Observed and predicted ^{13}C chemical shifts for substituted phenyldiphenylamines in ppm

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-*i*	C-o	C-m	C-p	Method
Triphenylamine	147.8	123.9	129.1	122.6			147.8	123.9	129.1	122.6	exp.
							147.9	121.2	129.1	122.5	Ref. 16
o-Fluoro	134.3	158.7	116.7	124.9	126.2	129.3	147.2	122.0	128.9	122.3	exp.
	133.5	159.0	114.8	123.5	124.7	124.8					pred.
o-Chloro	143.8	132.7	131.0	126.9	130.9	128.1	146.9	121.7	128.8	121.9	exp.
	148.0	129.6	129.3	124.1	127.4	125.4					pred.
o-Bromo	145.2	123.4	140.7	127.3	134.2	131.5	147.8	121.6	128.8	121.8	exp.
	150.9	117.8	132.1	124.4	127.7	125.7					pred.
o-Iodo	148.7	99.9	140.7	127.6	131.3	129.8	146.8	121.8	128.8	121.8	exp.
	156.9	89.5	138.2	124.5	128.2	125.8					pred.
o-Nitro	140.5	145.8	125.6	124.6	133.5	129.8	146.3	122.8	129.1	123.2	exp.
	142.7	143.6	124.0	123.7	135.5	125.0					pred.
o-Amino	131.4	144.5	116.2	127.1	118.2	129.9	146.8	120.9	128.9	121.4	exp.
	134.0	143.2	115.3	123.2	118.1	124.5					pred.
m-Bromo	149.7	125.1	122.4	124.7	130.5	121.3	147.1	124.7	129.4	123.6	exp.
	149.6	126.9	123.0	125.6	130.9	122.5					pred.
p-Fluoro	143.9	126.3	115.8	158.7			147.8	123.4	129.1	122.4	exp.
	143.6	125.7	115.9	157.2							pred.
p-Chloro	146.6	124.5	129.0	126.8			147.3	124.2	129.2	123.1	exp.
	146.1	125.4	129.3	128.3							pred.
p-Bromo	146.8	124.8	132.1	114.3			147.4	124.5	129.4	123.4	exp.
	146.4	125.7	132.1	116.5							pred.
p-Nitro	153.4	125.7	125.0	139.9			145.6	126.5	129.8	117.6	exp.
	154.2	125.0	124.0	142.3							pred.

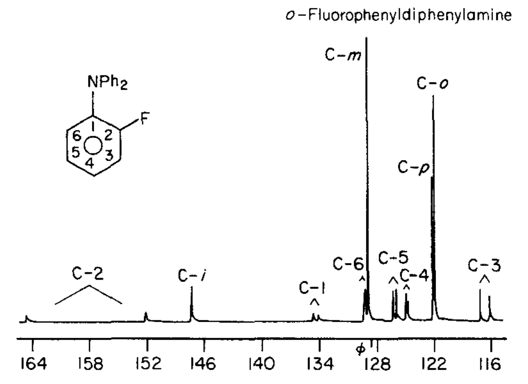


Figure 1. ^{13}C NMR spectrum of o-fluorophenyldiphenylamine.

the two positions based on predictable differences in nuclear Overhauser enhancements. Furthermore, carbon atoms assigned to C-*i* positions were not bonded to hydrogen, as shown by off-resonance spectra.

Next, the usefulness of bond additivity[11,23–25] for the assignments of the ^{13}C chemical shifts for C-1 through C-6 of the substituted phenyl rings was examined. With this method ^{13}C chemical shift differences between a mono-substituted compound and its parent unsubstituted compound are expressed by $\Delta\delta_X$, as shown in Eqn (3) for each ring carbon denoted by *k*. The additivity rule can be stated as Eqn (4) for disubstituted compounds containing X and Y substituents. Agreement between

$$\Delta\delta_X^{(k)} = \delta_X^{(k)} - \delta_H^{(k)} \tag{3}$$

$$\delta_{XY}^{(k)} = \delta_H^{(k)} + \Delta\delta_X^{(k)} + \Delta\delta_Y^{(k)} \tag{4}$$

calculated values based on Eqn (4) and experimentally observed ^{13}C chemical shifts has been generally good for *meta*- and *para*-substituted aromatic compounds and poor for *ortho*-substituted compounds.[23]

Values of $\Delta\delta_X^{(k)}$ were obtained from ^{13}C chemical shifts of benzene and monosubstituted benzene compounds as *c.* 20% (w/v) in 1:1 (v:v) d_6-acetone/methylene chloride solution and agreed with literature values,[2] with small differences being ascribed to different solvent conditions. Assignments of ^{13}C chemical shifts for *meta*- and *para*-substituted compounds using bond additivity was straightforward, as illustrated by the data of Table 3. However, assignment of *ortho*-substituted compounds was not, as illustrated by the differences between the observed ^{13}C chemical shifts of C-1 through C-6 and those calculated by bond additivity. Although the ^{13}C chemical shift assignments using bond additivity were made in such a way as to minimize the sum of the deviations between experimental and calculated shifts, assignments of C-4, C-5 and C-6 were less certain for *ortho*-derivatives. The mean deviations between experimental chemical shifts and those calculated from bond additivity were 0.8 ppm for both *meta*- and *para*-substituted aromatics, whereas the mean deviation for *ortho*-substituted compounds was 3.4 ppm. Mean deviations were greatest at C-1, C-2 and C-6 for the *ortho*-substituted phenyldiphenylamines and increased with size when the substituents were halogens. Intramolecular hydrogen bonding did not appear to be a perturbing factor in the assignment of C-1 through C-6 in the case of *ortho*-aminophenyldiphenylamine. The accuracy of the calculated ^{13}C chemical shifts for C-1 through C-6 improved as the distance between the position of the observed carbon and the substituent increased. This was in agreement with the conclusion that interactions between ring carbons and substituents decreased rapidly and bond additivity was more accurate as substituents were placed further apart in a series of 1,4-phenylene derivatives.[25]

Further evidence supporting ^{13}C chemical shift assignments of *ortho*- and *para*-fluorophenyldiphenylamine was obtained from the observed magnitudes of ^{13}C—^{19}F coupling constants given in Table 4. In aromatic compounds containing fluorine, one-bond ^{13}C—^{19}F coupling constants[26] are approximately

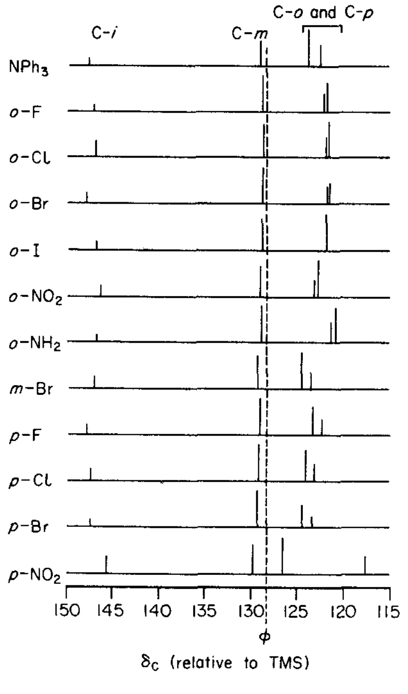
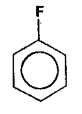
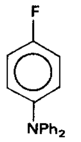
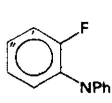


Figure 2. ^{13}C chemical shifts of the *ipso*-, *ortho*-, *meta*- and *para*-carbons for the two non-substituted phenyl groups in the triphenylamine derivatives.

Table 4. A comparison of ^{13}C—^{19}F coupling constants[a] of *ortho*- and *para*-fluorophenyldiphenylamine with fluorobenzene[b]

^{13}C—^{19}F Coupling constants (Hz)			
J(CF)	244.0	241.8	250.0
J(CCF)	21.5	22.7	10.7
J(CCCF)	7.9	7.9	1.8
J(CCCCF)	2.9	2.8	7.7
J(C′CF)			19.6
J(C″C′F)			3.8

[a] Compounds were *c.* 20% in 1:1 (v:v) d_6-acetone/methylene chloride solution.
[b] Taken from Ref. 26.

250 Hz. These decrease rapidly with increased number of bonds to c. 3 Hz for four-bond separations. This order of decreasing J(CF) values with increasing number of intervening bonds was observed for *para*-fluorophenyldiphenylamine and supported the ^{13}C chemical shift assignments based on the bond additivity method. In *ortho*-fluorophenyldiphenylamine only J(CF) and J(C'CF) exhibited values expected for one- and two-bond coupling, respectively. The breakdown in similarity of ^{13}C—^{19}F coupling constants for the remainder of the ring carbons was indicative of differences in the electronic distribution in the ring. This is apparently due to the electronegativity and the steric interaction of substituents when placed *ortho* to each other in the aromatic ring. As additional evidence for ^{13}C chemical shift assignments for C-1 and C-2, off-resonance spectra were obtained for all compounds. The non-hydrogen bearing aromatic carbons were unequivocally assigned from these data. The relationships between the Q parameter of Hruska, Hutton and Schaefer[4] and the ^{13}C chemical shifts of the C-1 through C-6 ring carbons were examined in order to gain further insight into the nature of *ortho*-substituent interactions. Plots of Q versus ^{13}C chemical shifts of C-1 to C-3 for *ortho*-substituted phenyldiphenylamines and of C-3 and C-4 for *para*-substituted phenyldiphenylamines resulted in the linear relationships shown in Figs 3 and 4, respectively, whereas the remaining ring carbons gave poor correlations. The correlation coefficient of the least squares line is given for each graph. These plots exhibit a behavior similar to that of plots for *ortho*-substituted phenols[7] and *ortho*-substituted fluorobenzenes.[27] Substituent effects at C-1 and C-3 in *ortho*-substituted compounds operate in the opposite sense to that at C-2, and the substituent effects at C-4 in *para*-substituted compounds operate in the opposite sense to those at C-3.

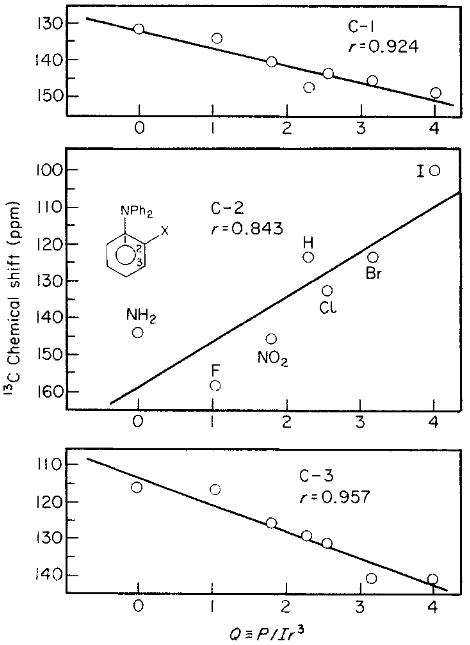


Figure 3. The ^{13}C chemical shifts at C-1 to C-3 for *ortho*-substituted phenyldiphenylamines plotted against Q with the corresponding correlation coefficient also shown.

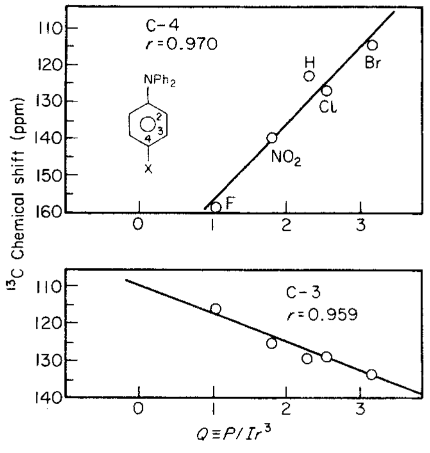


Figure 4. The ^{13}C chemical shifts at C-3 and C-4 for *para*-substituted phenyldiphenylamines plotted against Q with the corresponding correlation coefficient also shown.

Smith and Proulx[8] interpreted this behavior as indicating that factors other than electron density were important because the effects were not predicted by calculations[2] of electron density. It is evident that further theoretical calculations of substituent effects on the ^{13}C chemical shifts of aromatic compounds will have to account for this behavior in addition to effects due to σ or π electron density.

Both *ortho*- and *para*-substituted phenyldiphenylamines afforded a test of the correlatability of ^{13}C chemical shifts with field and resonance parameters of Swain and Lupton[14] and the Q parameter using Eqn (2). The quality of the correlations for the disubstituted ring, both with and without the use of the Q parameter, is illustrated by the results given in Table 5. That the special factor measured by Q is important is demonstrated by the improved quality of the linear regression fit. Values of the correlation coefficients and the average deviations between experimentally observed ^{13}C chemical shifts and those calculated from results of regression analysis support this conclusion. The Q parameter is most significant at C-1, C-2 and C-3 in *ortho*-substituted phenyldiphenylamines and at C-3 and C-4 in *para*-substituted phenyldiphenylamines. In agreement with the results of previous work,[7,27] the coefficient of Q for the carbon bearing the variable substituent is negative in value and opposite in sign compared to the carbon atoms *ortho* to the substituent.

The *ortho* series was particularly interesting because the diphenylamine moiety is larger than groups tested previously with this relationship. Steric effects for *ortho*-substituted phenyldiphenylamines could be reflected either in the quality of the correlation or in the values of the coefficient of the Q parameter. Values of c, the coefficient of Q, obtained in this study for *ortho*- or *para*-substituted triphenylamine derivatives were not greatly different compared to those previously reported for *ortho*- and *para*-substituted aromatic compounds.[7,27]

The correlatability of the ^{13}C chemical shifts of C-*i*, C-*o*, C-*m* and C-*p* with Q and the field and resonance parameters of Swain and Lupton[14] for *ortho*- and *para*-substituted triphenylamine derivatives was also

Table 5. Constants and correlation coefficients of $a\mathcal{F}+b\mathcal{R}+cQ+d$ of C-1 through C-6 for *ortho*- and *para*-substituted phenyldiphenylamine compounds from linear regression analysis[a]

Position	*a*	*b*	*c*	*d*	*r*	Average deviation	Range
			ortho-substituted phenyldiphenylamines				
C-1	−6.37	9.98	4.22	138.50	0.998	0.3	17.3
	−4.91	20.41		148.50	0.707	3.8	
C-2	18.94	11.98	−15.50	157.16	0.952	5.1	58.8
	13.55	−26.39		119.81	0.362	13.1	
C-3	−1.23	−3.31	7.69	112.36	0.962	2.1	24.5
	1.44	15.72		130.89	0.446	7.2	
C-4	2.56	−8.05	0.92	120.88	0.914	0.6	5.0
	2.88	−5.78		123.08	0.733	1.0	
C-5	3.94	9.51	1.87	124.78	0.976	0.7	16.0
	4.59	14.15		129.29	0.899	1.9	
C-6	5.72	−8.06	0.29	123.45	0.897	0.9	7.6
	5.83	−7.34		124.15	0.887	0.9	
			para-substituted phenyldiphenylamines				
C-1	2.64	17.24	−0.003	147.76	0.999	0.1	9.5
	2.64	17.24		147.78	0.999	0.1	
C-2	1.49	−1.26	−0.71	125.48	0.967	0.2	2.4
	1.75	−1.74		123.73	0.778	0.5	
C-3	−1.87	9.05	7.16	112.85	0.998	0.3	16.3
	−4.49	13.94		130.55	0.476	4.4	
C-4	8.86	−15.09	−19.76	168.00	0.999	0.2	44.4
	16.13	−28.60		119.13	0.461	11.9	

[a] The coefficient of multiple regression is given under *r*. The chemical shift ranges and the average deviations are given in ppm and *d* is based on ^{13}C chemical shifts found in Table 3 referenced to TMS. The second set of values for each carbon position are the results from linear regression with *c* equal to zero.

Table 6. Constants and correlation coefficients of $a\mathcal{F}+b\mathcal{R}+d$ of C-*i*, C-*o*, C-*m* and C-*p* for *ortho*- and *para*-substituted phenyldiphenylamine compounds from linear regression analysis[a]

Position	*a*	*b*	*d*	*r*	Average deviation	Range
		ortho-substituted phenyldiphenylamines				
C-*i*	−0.834	0.634	147.68	0.519	0.4	1.5
C-o	−1.52	3.98	123.75	0.931	0.3	3.0
C-*m*	−0.173	0.38	129.09	0.662	0.1	0.3
C-*p*	0.002	1.87	122.52	0.818	0.3	1.8
		para-substituted phenyldiphenylamines				
C-*i*	−1.51	−3.33	147.81	0.998	0.04	2.2
C-o	1.69	4.83	123.91	0.994	0.1	3.1
C-*m*	0.50	0.99	129.10	0.971	0.04	0.7
C-*p*	−3.06	−8.86	122.88	0.903	0.8	5.8

[a] The coefficient of multiple regression is given under *r*. The chemical shift ranges and the average deviations are given in ppm and *d* is based on ^{13}C chemical shifts found in Table 3 referenced to TMS.

examined.† Although the range of ^{13}C chemical shifts was smaller than for C-1 through C-6, significant correlations were determined using the two-part correlation given by Eqn (5). The quality of the correlations is illustrated by the results given in Table 6. These correlations

$$\delta = a\mathcal{F} + b\mathcal{R} + d \qquad (5)$$

appeared to be significant only for C-*o* and C-*p* in *ortho*-substituted phenyldiphenylamines whereas ^{13}C shifts at all four positions, C-*i*, C-*o*, C-*m* and C-*p*, correlated well in the *para*-phenyldiphenylamine series. The correlatability of the ^{13}C chemical shifts for carbons in the non-substituent bearing phenyl rings appears to be mainly due to field and resonance effects which are transmitted through nitrogen. That correlations are considerably poorer for *ortho*-substituted derivatives in comparison to *para*-derivatives indicates that the steric effect of the substituent disrupts the transmission of magnetic and electronic interactions between substituent and non-substituent bearing phenyl rings.

This investigation has shown that bond additivity is a reliable method for making ^{13}C chemical shift assignments in singly substituted phenyldiphenylamine compounds and that these assignments appear to be supported by the consistency of the results of ^{13}C chemical shift results when correlated to Eqn (2) as proposed by Smith and Proulx.[7] That this series of compounds shows a good correlation extends the application of the unified correlation method.

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† Correlations of the ^{13}C chemical shifts for C-*i*, C-*o*, C-*m* and C-*p* with Swain and Lupton field and resonance parameters were undertaken at the suggestion of a referee.

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