g) of polymeric material was obtained by elution with pure ether.

The third fraction is further chromatographed on silica gel impregnated with 5% $AgNO_3$ with pentane–benzene (3:2) as eluent. A first fraction (1.1 g) was recrystallized twice from hexane to give 0.25 g of pure **7** (mp 200–202 °C). A second fraction (0.6 g) of tetraphenylethane was obtained followed by 2.2 g of slightly yellow crystals which could be shown to be a mixture of diadducts.

Thermal Rearrangement of 2. A solution of 0.25 g of **2** in 10 mL of diglyme was sealed in a Pyrex tube after degassing by the freeze–thaw method. After being heated to 220 °C for 30 h, the tube was cooled and opened, and the contents were poured into 40 mL of water. The structure was extracted with 60 mL of benzene and the benzene solution washed several times with water. Crystallization from this benzene solution yielded 0.22 g of **6** (mp 103–106 °C).

Acid-Catalyzed Isomerization of 2. A solution of 0.1 g of **2** in 15 mL of CCl_4 with 0.1 mL of CF_3COOH was refluxed for 0.5 h. The solvent was washed with water and dried over sodium sulfate. Crystallization yielded 0.04 g of **6** (mp 103–106 °C).

Hydrogenation of 6. A solution of 0.1 g of **6** in 15 mL of heptane was hydrogenated at 3 atm of H_2 over 0.1 g of PtO for 15 h. Filtration and evaporation of solvent yielded 0.09 g of oily crystals from which 0.05 g of hydrogenated product could be obtained after crystallization from hexane (mp 133–134 °C).

Reaction of 1 with Triphenyl(bromodifluoromethyl)phosphonium Bromide in Tetrahydrofuran at Room Temperature. To a solution of 2.7 g of triphenylphosphine in 15 mL of absolute tetrahydrofuran was added 2.7 g of dibromodifluoromethane. After the rapid exothermic formation of the phosphonium salt ceased, stirring was continued for 40 min, at which point 1.6 g of **1** was added rapidly, followed by 2.6 g of KF. Stirring was maintained at room temperature for 120 h, and the mixture was filtered and washed with fresh tetrahydrofuran. The solvents were evaporated at reduced pressure, 30 mL of pentane was added, and the mixture was allowed to stay in a refrigerator for 1 h. The mixture was then filtered and evaporated to yield 2.25 g of an oily material which could be chromatographed on silica gel with heptane as eluent. The first fraction contained 0.32 g of recovered **1** and isomerized **1** (**15**) in the ratio 35:65. Gas chromatography on a 3-ft SE-30 column at 105 °C separated the components. A second fraction contained a mixture of **10** and **11** in the ratio 88:12 as revealed by gas chromatography on a 10-ft, 5% Dexil column operated at 180 °C. Further elution of the column with pentane–ether (80:20) yielded **13** and **14.**

Reaction of 1 with Triphenyl(bromodifluoromethyl)phosphonium Bromide in Tetrahydrofuran under "Superdry" Conditions. Before the reaction, triphenylphosphine was dried at 60 °C and 0.5 torr for 4 h. KF was dried at 250 °C and 2 torr for 4 h, and tetrahydrofuran was freshly distilled. The reaction was carried out in a carefully closed vessel.

To a solution of 1.1 g of triphenylphosphine in 10 mL of THF freshly distilled from LAH was added 0.9 g dibromodifluoromethane. After the rapid exothermic formation of phosphonium salt, the stirring was continued for 40 min, at which time 0.47 g of **1** followed by 0.93 g of KF was added. Stirring was maintained at room temperature for 200 h. Analysis by gas chromatography on a 10-ft, 5% Dexil column at 180 °C showed **15** (14%), **1** (18%), **11** (1%), **10** (56%), and diadduct **12** (11%).

Reaction of 1 with Triphenyl(bromodifluoromethyl)phosphonium Bromide in Acetonitrile at Room Temperature. To a solution of 2.2 g of triphenylphosphine in 25 mL of freshly distilled acetonitrile was added 1.8 g of dibromodifluoromethane. After rapid formation of the phosphonium salt, stirring was continued for 30 min, and 1.0 g of **1** and 1.8 g of KF were added. Stirring was maintained in the carefully closed flask for 30 h. Gas chromatography on a 10-ft, 5% Dexil column at 180 °C showed **1** (17%), **10** (59%), **12** (19%), and 5% of an unknown compound.

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Registry No. 1, 770-14-9; **2**, 73367-56-3; **3**, 73395-34-3; **4**, 73367-57-4; **6**, 73367-58-5; **7**, 73367-59-6; **10**, 73367-60-9; **11**, 73367-61-0; **12**, 73367-62-1; **13**, 73367-63-2; **14**, 702-81-8; **15**, 59039-27-9; diphenyldiazomethane, 883-40-9; triphenyl(bromodifluoromethyl)phosphonium bromide, 58201-66-4.

Nonadditive Carbon-13 Nuclear Magnetic Resonance Substituent Shifts in 1,4-Disubstituted Benzenes. Nonlinear Resonance and Shift–Charge Ratio Effects[1]

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Meta and para carbon-13 substituent chemical shifts are reported for fourteen series of para-disubstituted benzenes (p-C_6H_4Y) at high dilution in deuteriochloroform. Series with one substituent (Y) fixed and the other one variable (p-X) have been examined for each of the following substituents: NMe_2, NH_2, OMe, F, Cl, Br, Me, H, CF_3, CN, CO_2Et, COMe, CHO, and NO_2. The substituent effects are strongly nonadditive; the fixed group Y substantially changes the para carbon substituent chemical shifts (C_p-SCS). The results are interpreted in terms of the local π-electron density at the para carbon. Through the use of theoretical calculations of π electronic charges and dual substituent parameter methods, the common Y group is shown to exert two major influences on C_p-SCS values. First, the Y group gives rise to a characteristic sensitivity effect, called the shift–charge ratio (SCR), which is the C_p-SCS value divided by the corresponding para X substituent induced π charge at carbon. Values of the SCR are found to range from ~125 to 250 ppm/e. Second, the π-electron delocalization of the para X substituent may be either enhanced (conjugative effect) or reduced (repulsive π-electron saturation), depending upon the "electron demand" exerted by the Y group. These resonance effects are accurately described by a nonlinear relationship with the $\sigma_R{}^0$ value of the para substituent, involving an "electron-demand" parameter, ϵ, for the Y group. The meta carbon C_m-SCS data offer further confirmation of these effects as well as show that small resonance effects operate at the meta positions which are of opposite sign to those for the corresponding para positions. The detailed analysis obtained with the present results was made possible through the use of a broad range of substituent electronic properties, the relatively high sensitivity of the C_p-SCS measurements, and the use of very dilute solutions of a relatively inert solvent, $CDCl_3$.

Carbon-13 chemical shift measurements have been used extensively for studying the electronic properties of aromatic systems.[3] Since ^{13}C substituent chemical shifts (SCSs) for fixed distant sites are related to electronic ef-

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fects and can now be measured with very good precision, a useful means is provided for reexamining and extending our knowledge of the way in which substituents interact. In particular, we wished to examine the effects of the trans quinoidal interactions of 1,4-disubstituted benzenes and to use the measurements to test and extend the application of generalized substituent effect treatments.[4,5] It has been established in a preliminary report that large nonadditive effects are observed in these systems.[6]

The ^{13}C chemical shifts of a number of benzene systems have been reported in the literature.[7] However, most of these data have been measured under a wide variety of concentration and solvent conditions with an insufficient number of substituents and hence are unsatisfactory for our work.[8] To obtain accurate results, we have minimized solvent and concentration effects and used a comprehensive range of substituents. Specifically, meta and para SCS values have been determined for 1,4-disubstituted benzenes having 14 substituents (X) of widely varying electronic properties within complete series involving the same substituents as fixed groups (Y); cf. structure I. The weakly interacting solvent $CDCl_3$ has been used, and measurements were made at low concentrations. The results of this work provide new insights into the quantitative nature of electronic interactions.

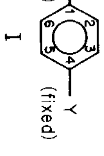

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Table I. Carbon-13 Substituent Chemical Shifts of Carbon Atom 4 for 1,4-Disubstituted Benzenes in Deuteriochloroform[a]

	4-substituent (Y)													
X[c]	NMe_2	NH_2	OMe	F	Cl	Br	Me	H	CF_3	CN	COOEt	COMe	NO_2	CHO
NMe_2	−6.56	−8.35	−7.48	−7.20	−12.43	−13.93	−11.76	−11.69	−12.82	−15.11	−13.15	−11.79	−11.10	−11.36
NH_2	−5.78	−7.67	−6.83	−6.54	−11.12	−12.27	−10.10	−9.80	−10.61	−12.54	−10.44	−9.32	−9.13	−8.94
OMe	−4.88	−6.35	−5.68	−5.63	−8.74	−9.67	−7.96	−7.68	−7.77	−8.48	−7.62	−6.80	−6.76	−6.41
F	−3.15	−3.86	−3.84	−4.07	−5.15	−5.96	−4.56	−4.39	−4.17	−3.81	−3.74	−3.54	−3.84	−3.41
Cl	−1.61	−1.36	−1.36	−1.60	−1.71	−2.17	−1.65	−1.90	−1.54	−1.59	−1.60	−1.70	−1.82	1.56
Br	−1.12	−0.83	−0.89	−1.05	−1.07	−1.41	−1.12	−1.50	−0.90	−1.13	−1.16	−1.26	−1.21	−1.31
Me	−1.79	−2.52	−2.28	−1.82	−3.21	−3.40	−3.15	−3.05	−2.79	−3.14	−2.72	−2.43	−2.14	−2.23
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CF_3	1.55	3.13	2.48	1.79	3.88	3.96	4.18	3.67	3.35	3.69	3.20	2.62	1.70	2.28
CN	1.79	4.22	3.24	2.14	5.24	5.51	5.78	4.35	3.91	4.31	3.79	2.77	1.75	2.33
COOEt	2.57	4.47	3.64	2.79	4.89	5.34	5.53	4.42	3.62	3.88	3.64	3.06	2.23	2.82
COMe	2.72	4.86	3.84	2.82	5.14	5.83	5.92	4.67	3.71	3.93	3.74	3.11	2.09	2.57
NO_2	3.42	6.21	5.05	3.38	7.07	7.52	8.06	6.18	5.29	5.94	5.39	4.37	2.77	3.69
CHO	3.64	6.27	5.05	3.66	6.74	7.28	7.62	6.07	5.00	5.29	4.66	4.13	2.87	3.64
δ H[b]	150.59	146.22	159.52	162.82	134.24	122.44	137.83	128.31	130.62	112.35	130.45	137.00	148.26	136.37

[a] Positive shifts are downfield relative to the hydrogen substituent in parts per million; resolution 0.05 ppm. [b] Chemical shifts corresponding to the hydrogen substituent relative to Me_4Si in parts per million. [c] The 1-substituent.

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Table II. Carbon-13 Substituent Chemical Shifts of C-3,5 for 1,4-Disubstituted Benzenes in Deuteriochloroform[a]

	4-substituent (Y)													
X[c]	NMe_2	NH_2	OMe	F	Cl	Br	Me	H	CF_3	CN	COOEt	COMe	NO_2	CHO
NMe_2	2.74	1.50	1.11	0.06	0.21	0.19	0.55	0.74	1.14	1.24	1.65	2.04	2.63	2.19
NH_2	2.89	1.59	0.89	0.27	0.43	0.49	0.68	0.88	1.49	1.63	2.04	2.23	2.86	2.61
OMe	2.02	1.24	0.86	0.41	0.66	0.72	0.87	0.88	1.72	1.88	1.94	2.04	2.40	2.24
F	1.32	0.89	0.89	1.37	1.28	1.42	1.24	1.13	2.44	2.58	2.52	2.38	2.83	2.49
Cl	1.18	1.12	1.32	1.37	1.20	1.28	1.31	1.40	1.61	1.28	1.41	1.12	1.43	1.17
Br	1.44	1.59	1.82	1.86	1.57	1.65	1.80	1.71	1.70	1.32	1.51	1.31	1.55	1.22
Me	0.54	−0.14	−0.11	−0.47	−0.40	−0.25	−0.10	−0.09	−0.05	−0.12	0.00	−0.15	0.05	−0.05
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CF_3	−1.30	−0.97	0.08	0.62	0.47	0.58	0.29	0.40	0.73	0.60	0.44	0.10	0.61	0.20
CN	−1.32	−0.74	0.84	1.48	1.01	1.14	0.78	0.70	0.95	0.70	0.53	0.14	0.81	0.15
COOEt	−2.01	−1.31	−0.40	0.04	−0.01	0.05	−0.05	−0.09	0.14	0.11	−0.10	−0.34	0.00	−0.19
COMe	−2.11	−1.46	−0.25	0.23	0.09	0.34	0.14	−0.09	0.44	0.41	0.24	0.00	0.39	0.00
NO_2	−2.15	−1.75	0.12	1.07	0.89	1.12	0.73	0.93	1.57	1.40	1.16	0.83	1.41	0.78
CHO	−1.76	−1.04	0.43	0.99	0.76	0.92	0.78	0.63	0.88	0.80	0.68	0.19	0.78	0.39
δ H[b]	35.64	38.05	36.85	38.30	51.61	54.46	51.98	51.30	48.17	55.02	52.47	51.45	46.45	52.66

[a] Positive shifts are downfield relative to the hydrogen substituent in parts per million; resolution 0.05 ppm. [b] Chemical shifts corresponding to the hydrogen substituent relative to the center peak of Me_4Si. [c] The 1-substituent.

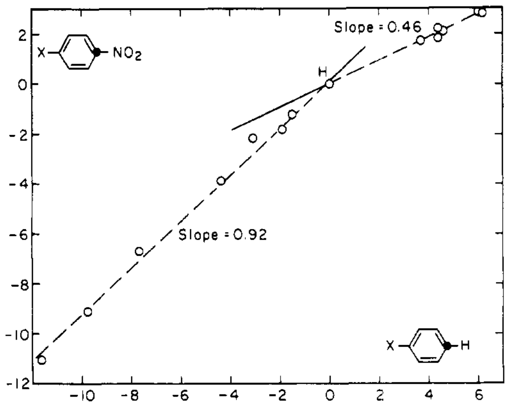

Figure 1. C_p-SCS for para-substituted nitrobenzenes plotted against the corresponding C_p-SCS for monosubstituted benzenes.

Experimental Section

All new compounds were obtained commercially or were prepared by using standard methods. Samples were made up in 10-mm NMR tubes at a concentration of 2–4% (w/v) except for the aldehyde set which was run at 6% (w/v). Spectra were proton noise decoupled and were recorded on a JEOL PFT-100 NMR spectrometer at 25 MHz. Chemical shifts were measured relative to the center peak of deuteriochloroform which was also used as an internal lock. The $CDCl_3$ reference peak is 77.01 ppm from Me_4Si. 8K data points were collected over a spectral width of 5000 Hz, resulting in a resolution of 0.05 ppm.

Results

Tables I and II give the C-13 chemical shifts of carbon atoms 4 (para) and 3,5 (meta), respectively, for the complete series of 1,4-disubstituted benzenes in 3% (w/v) $CDCl_3$. For all the series, positive values denote that the C-13 chemical shift for the compound with the substituent X is at lower field than the corresponding unsubstituted compound (X = H) and vice versa.

The chemical shifts of all the ring positions, relative to Me_4Si, can be calculated from the data in Tables I and II. Table III gives the ipso chemical shifts relative to the unsubstituted para carbon atom of the monosubstituted benzene. This table is useful in showing the ranges in ipso shifts and the way that the ipso shift is modified by para substituents. Except for the ipso shift of 2.26 for CF_3, the data in these tables agree to within a few tenths of a part per million with available literature values measured under similar conditions[9] but differ (in the order of 1 ppm) where data were obtained at high concentrations or in different solvents.[7] Other authors have also noted the discrepancy in the ipso-CF_3 shift.[10]

Discussion

Relationship between Corresponding C_p-SCS Values in Monosubstituted and 1,4-Disubstituted Benzenes. If additivity prevailed, the presence of the common group, Y, would have little or no effect on the Cp-SCS of the para X substituent. This is not the case. Additivity requires that all the data in the horizontal rows of Tables I and II be constant. Contrary to the general literature axiom of additive aromatic carbon shifts, variations of up to 8 ppm are found in these tables. That is, the common substituent, Y, exerts significant control over the Cp-SCS values of the substituent X.

The influence of the common Y group can be shown graphically by plotting the para carbon substituent (X) chemical shifts against the corresponding series of monosubstituted benzenes (Y = H) (see Table I). For Y = NO_2, a π-electron-accepting substituent, this results in the plot shown in Figure 1. The plot shows a crude monotonic relationship which can be roughly represented as bilinear. For the π-acceptor substituents X (positive C_p-SCS values

Table III. Carbon-13 Substituent Chemical Shifts of C-1 for 1,4-Disubstituted Benzenes in Deuteriochloroform[a]

X^b	4-substituent (Y)													
	NMe_2	NH_2	OMe	F	Cl	Br	Me	H	CF_3	CN	COOEt	COMe	NO_2	CHO
NMe_2	27.41	26.31	25.09	23.53	22.58	22.67	23.56	22.28	20.44	19.73	20.44	20.34	19.48	19.85
NH_2	21.25	20.05	19.26	18.44	18.46	18.58	18.45	17.91	17.64	17.79	17.96	18.11	17.91	18.11
OMe	35.43	34.18	33.23	31.76	31.76	31.82	31.99	31.21	30.30	30.12	30.43	30.39	30.04	30.19
F	39.00	37.77	36.57	34.84	34.82	34.97	35.75	34.51	32.90	32.31	32.88	32.67	31.67	32.10
Cl	5.20	4.61	4.89	5.17	6.13	6.37	5.78	5.93	6.42	6.84	6.41	6.41	6.78	6.50
Br	−8.11	−8.34	−7.85	−7.44	−6.13	−5.78	−6.21	−5.87	−5.31	−4.70	−4.95	−4.70	−4.57	−4.66
Me	9.45	9.22	9.25	9.34	9.78	9.90	9.42	9.52	10.29	10.95	10.63	10.78	11.36	11.07
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CF_3	1.18	1.50	2.23	2.53	2.68	2.91	2.58	2.31	2.26	1.88	1.51	1.36	1.39	1.24
CN	−19.83	−18.71	−16.76	−15.38	−15.65	−15.59	−16.05	−15.96	−15.68	−16.00	−16.50	−16.69	−16.24	−16.74
COOEt	0.67	1.50	2.21	2.79	2.45	2.74	2.48	2.14	1.94	1.59	1.36	1.22	1.31	0.73
COMe	8.59	9.11	9.59	9.54	8.90	8.93	9.33	8.69	7.91	7.12	7.33	7.14	6.84	5.97
NO_2	20.54	20.63	20.89	20.50	20.04	20.24	20.88	19.95	18.25	17.36	17.76	17.38	16.50	16.75
CHO	8.39	8.92	9.34	9.04	8.27	8.25	8.89	8.06	6.93	6.05	6.46	6.75	5.53	5.63

[a] Positive shifts are downfield relative to the hydrogen substituent in parts per million; resolution 0.05 ppm. [b] The 1-substituent.

in Figure 1) the slope is 0.46, whereas for the π donors it is 0.92. The smaller slope for π-acceptor substituents is explicable in terms of π-repulsive saturation interactions[13] with the π acceptor Y = NO_2, compared to enhancements due to conjugation between this group and π-donor substituents. If this were the only effect, however, the slope for π-acceptor substituents would be less than unity while that for the π-donor substituents would be greater than unity. The common NO_2 group reduces the sensitivity of the ipso carbon SCS's to electron density changes. This reduced sensitivity gives slopes which are less than 1 for both π-acceptor and π-donor substituents.

The reverse situation applies if Y is a π-donating group. Here the slope of the rough bilinear relationship is greater for the π-acceptor substituents than for π-donor substituents, in accord with donor–acceptor conjugation for the former and π saturation for the latter.

The C_p-SCS are mainly determined by the paramagnetic shielding term ($\sigma^A{}_{para}$) which has the three contributions shown in eq 1. For monosubstituted benzenes, the con-

$$\sigma^A{}_{para} = k(\Delta E^{-1})\cdot\langle r^{-3}\rangle\cdot\Delta q_\pi \qquad (1)$$

stant (k), the mean excitation energy term (ΔE^{-1}), and the effective size of the 2p orbital term ($\langle r^{-3}\rangle$) apparently combine to give a proportionality constant between C_p-SCS and the para C excess π charge density which we hereafter refer to as the shift charge ratio (SCR). By use of π-electron densities calculated by the Gaussian-70 method,[11] the SCR for monosubstituted benzenes is 189 ppm/e. The above behavior noted for the 1,4-disubstituted benzene C_p-SCS may be explained in terms of charges induced by the common substituent Y in all of the terms of eq 1. If the changes induced by Y in the ΔE^{-1} and $\langle r^{-3}\rangle$ terms are approximately independent of changes induced by the para X substituted in the Δq_π term, then the observed C_p-SCS may be explained by two effects: (1) the influence of Y on π charge delocalized to the para C position by the substituent X and (2) a modified SCR characteristic of the common Y group. In the following sections we explore (in this order) the evidence favoring such a simplified interpretation.

Theoretical Evidence for π Electron Conjugation and Saturation Interactions. We have carried out calculations for para-disubstituted benzenes by the Gaussian-70 method[12] of the effects of common Y groups on the total π electronic charge delocalized by para substituents. The results are given in Table IV. In each series, π-electron donation is seen to increase (increasingly negative number) in the familiar (σ_R) order, i.e., $CH_3 < F < OH < NH_2$; likewise, π-electron withdrawal increases in a σ_R order, i.e., $CF_3 < CN < NO_2 < CHO$. However, as the common Y group becomes increasingly π-electron withdrawing, π donation from the p-X substituent increases, and π-electron withdrawal decreases (compare horizontal rows of Table IV). Similarly, as Y becomes increasingly π-electron donating, π-electron withdrawal by the para X substituent increases, and π-electron donation decreases.

The theoretical calculations therefore support the view that there is significant π-electron saturation as well as conjugative interactions between the X and Y substituents. We turn next to analysis of the experimental values of

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[11] W. J. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.*, 12, 159 (1976).

[12] (a) QCPE, program no. 236; W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969); (b) W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, 94, 1496 (1972).

[13] A. J. Hoefnagel, M. A. Hoefnagel, and B. M. Wepster, *J. Am. Chem. Soc.*, 98, 6194 (1976).

Table IV. Total π Charges Delocalized by Para X Substituents in a Series of XPbY Having the Indicated Fixed Y Group as Obtained by STO-3G Calculations

	Y							
X	NO_2	CN	CHO	H	F	OH	NH_2[a]	$\sigma_R{}^0$
NH_2[a]	−0.139	−0.133	−0.128	−0.120	−0.117	−0.113	−0.108	(−0.55)[b]
OH	−0.115	−0.111	−0.107	−0.102	−0.099	−0.096	−0.092	(−0.42)[c]
F	−0.086	−0.084	−0.081	−0.078	−0.076	−0.074	−0.071	−0.31
CH_3	−0.011	−0.010	−0.009	−0.008	−0.008	−0.007	−0.006	−0.13
H	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00
CF_3	0.009	0.010	0.011	0.012	0.012	0.014	0.015	0.08
CN	0.014	0.017	0.020	0.023	0.025	0.029	0.033	0.08
NO_2	0.020	0.026	0.028	0.031	0.034	0.038	0.044	0.15
CHO	0.022	0.024	0.030	0.033	0.036	0.041	0.046	0.22

[a] For coplanar conformation. [b] For $N(CH_3)_2$. [c] For OCH_3.

Table V. DSP Analysis of C_p-SCS Data for 1,4-Disubstituted Benzenes in Dilute $CDCl_3$ Solutions[a]

Y	ρ_I	ρ_R	SD	*f*
NMe_2	1.9	12.6	0.25	0.07
NH_2	5.0	17.8	0.67	0.14
OMe	3.7	15.5	0.50	0.12
F	1.8	14.0	0.28	0.07
Cl	5.4	23.8	0.26	0.04
Br	5.5	26.3	0.32	0.04
Me	6.6	23.3	0.55	0.09
H	4.6	21.5	0.17	0.03
CF_3	3.9	21.4	0.61	0.10
CN	4.5	24.3	1.01	0.15
CO_2Et	3.9	21.3	0.71	0.12
COMe	2.8	18.8	0.66	0.13
NO_2	1.1	17.1	0.87	0.19
CHO	2.2	17.7	0.75	0.16

[a] σ_I and $\sigma_R{}^0$ values given in ref 5.

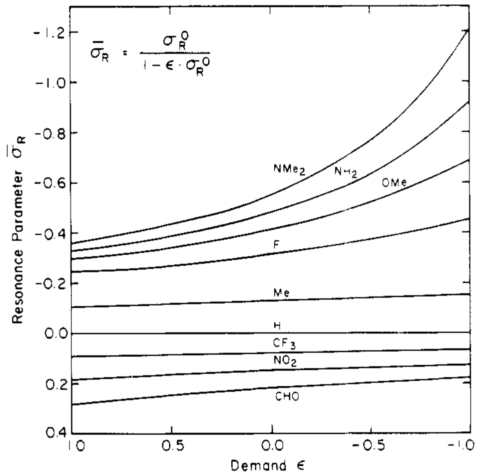

Figure 2. Variation in the resonance parameter ($\bar{\sigma}_R$) with electron demand (ϵ) for some representative substituents as given by eq 3.

C_p-SCS by the dual substituent parameter (DSP) method as a means of gaining further evidence for this view.

Relationship between C_p-SCS's and Electronic Substituent Constants Using the DSP Equation. The C-SCS values for para carbons of monosubstituted benzenes in dilute carbon tetrachloride solution correlate well with charge densities from ab initio molecular orbital theory using the STO-3G minimal basis set.[11] It was shown that both the π charges and the C-SCS values are controlled by two substituent interaction mechanisms: (1) the delocalization of π electronic charge between the substituent and the meta and para carbons[14] and (2) the substituent-induced polarization (without delocalization) of the benzene π electrons.[15] Either or both of these interactions modify the carbon atoms' π charge densities. Contributions from the former are well correlated by the resonance effect parameter, $\sigma_R{}^0$, and contributions from the latter by the inductive or dipolar substituent effect parameter, σ_I. The π-electron delocalization term is the major contributor to most C_p-SCS values.

The inductive and resonance contributions to C_p-SCS's can be estimated by using the DSP equation (eq 2).[4,5] For

$$C_p\text{-SCS} = \rho_I\rho_I + \rho_R\sigma_R{}^0 \qquad (2)$$

the C_p-SCS's of 1,4-disubstituted benzenes, the results of DSP analyses using the $\sigma_R{}^0$ (NMR) scale[5] are shown in Table V.

The goodness of fit parameter f = SD/rms provides a critical index of the success of eq 2 in describing the C_p-SCS values for each series. With the $\sigma_R{}^0$ (NMR) scale for treating chemical shifts, it has been recently shown[5] that f = 0.06 or less is required for an acceptable fit for a data set with a critical selection of substituents. It is indeed significant that only the series with Y = H, Cl, and Br, which are noninteracting or weakly interacting substituents, meet this criteria (cf. Table V). The results of Table V show that f progressively increases as the π-donating or -accepting ability of the Y group increases.

The results in Table V, therefore, provide evidence that the DSP equation (eq 2) is inadequate for accurately describing the C_p-SCS for 1,4-disubstituted benzenes. We next investigate whether this inadequacy results from the failure to take into account both enhancement and saturation effects resulting from X–Y interactions.

Nonlinear Substituent Resonance Effects. The theoretical results in Table IV suggest that the effective resonance parameter, $\bar{\sigma}_R$, should become smaller in magnitude when X and Y are both π donors or both π acceptors but should increase in magnitude when one is a π donor and the other is a π acceptor. Further, the π-electron effect of a para substituent in a given series should be related through its $\sigma_R{}^0$ value to its response to the "electron demand" imposed by the common Y group. For simplicity, the electron demand may be taken to be a characteristic constant, ϵ, for each Y group. Once evaluated by correlation analysis, the relationship of ϵ values to the

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(14) R. T. C. Brownlee and R. W. Taft, *J. Am. Chem. Soc.*, **92**, 7007 (1970); **90**, 6537 (1968).

(15) W. F. Reynolds, I. R. Peat, M. H. Freedman, and J. R. Lyerla, *Can. J. Chem.*, **51**, 1857 (1973); (b) W. F. Reynolds, *Tetrahedron Lett.*, 675 (1977); (c) S. K. Dayal, and R. W. Taft, *J. Am. Chem. Soc.*, **95**, 5595 (1973); (d) J. Fukunaga and R. W. Taft, *ibid.*, **97**, 1612 (1975); (e) M. J. Shapiro, *J. Org. Chem.*, **41**, 3197 (1976); (f) R. T. C. Brownlee, G. Butt, M. P. Chan, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 1486 (1976); (g) R. D. Topsom, *Prog. Phys. Org. Chem.*, **12**, 1 (1976); (h) W. F. Reynolds and G. K. Hamer, *J. Am. Chem. Soc.*, **98**, 7296 (1976); (i) D. F. Ewing, S. Sotheeswaran, and K. J. Toyne, *Tetrahedron Lett.*, 2041 (1977); (j) G. L. Anderson, R. C. Parish, and L. M. Stock, *J. Am. Chem. Soc.*, **93**, 6984; (1971); (k) W. Adcock and T. H. Khor, *J. Am. Chem. Soc.*, **100**, 7797 (1978).

Table VI. DSP-NLR (Eq 4) Analysis of C_p-SCS Data for 1,4-Disubstituted Benzenes in Dilute $CDCl_3$ Solutions

Y	ρ_I	ρ_R	ϵ	SD	f (=SD/rms)
NMe_2	1.6	13.7	0.25	0.16	0.05
NH_2	4.1	21.0	0.56	0.28	0.06
OMe	3.1	17.8	0.45	0.26	0.06
F	1.7	14.7	0.14	0.26	0.07
Cl	5.3	24.2	0.05	0.26	0.04
Br	5.4	26.7	0.05	0.32	0.04
Me	6.0	25.9	0.34	0.26	0.04
H	4.5	21.9	0.06	0.15	0.03
CF_3	4.6	18.0	−0.42	0.16	0.03
CN	5.5	18.5	−0.60	0.29	0.04
COOEt	4.6	17.3	−0.48	0.27	0.05
COMe	3.4	15.3	−0.49	0.29	0.06
NO_2	1.8	12.2	−0.72	0.16	0.03
CHO	2.9	13.5	−0.60	0.29	0.06

$\sigma_R{}^0$ and σ_I values of Y can be readily ascertained. We have found that eq 3 gives an effective resonance parameter,

$$\bar{\sigma}_R = \sigma_R{}^0/(1 - \epsilon\sigma_R{}^0) \qquad (3)$$

$\bar{\sigma}_R$, which varies in a generally suitable way with the electron demand parameter, ϵ, imposed by the common Y group. With the use of eq 3, a nonlinear resonance effect function, all of the C_p-SCS values of Table I are described quite precisely (f = 0.06 or less).

The way in which the resonance parameter $\bar{\sigma}_R$ varies with the demand (ϵ) according to eq 3 is illustrated in Figure 2. As the demand on the substituent for π electrons becomes larger (ϵ increasingly negative), the absolute values of $\bar{\sigma}_R$ for the π donors become larger whereas $\bar{\sigma}_R$ values for π acceptors become smaller (both are dependent upon the magnitude of the $\sigma_R{}^0$ value). The converse holds as π electrons are increasingly made available to the substituent (ϵ increasingly positive).[16] The nonlinear function is similar to one described by Blagdon[17] except that we have used only one parameter (ϵ) to characterize the electron demand exerted by the common Y group on the resonance effects of the general para X substituent. The relationship between resonance effects and electron demand incorporated into Blagdon's and our equation has a general basis in the Klopman[18]–Salem[19] perturbation theorem of chemical reactivity. Happer has recently proposed a logarithmic relationship between σ_R and electron demand,[20] but this treatment is less successful than eq 3.

Relationship between C_p-SCS and Substituent Constants Using the DSP-NLR Equation. The dual substituent parameter equation into which eq 3 has been incorporated is given by eq 4. We have designated this

$$C_p\text{-SCS} = \sigma_I\rho_I + \sigma_R{}^0\rho_R/(1 - \epsilon\sigma_R{}^0) \qquad (4)$$

equation as the DSP-NLR equation (dual substituent parameter nonlinear resonance effects). Each set of chemical shift data is best fitted to give three parameters, two transmission coefficients, ρ_I and ρ_R, and the demand parameter ϵ. The results of DSP-NLR analyses of the C_p-SCS values for the 1,4-disubstituted benzene SCS's are shown in Table VI. The goodness of fit f values obtained with eq 4 are seen to be at the acceptable level of 0.06 or less including all data sets where Y is either a strong π donor or acceptor.

The extent of saturation and exaltation is measured by the sign and magnitude of the empirical demand parameter ϵ. The demand parameter ϵ is positive for all π-donor Y groups, essentially zero for Y = H, and negative for all π-acceptor Y groups. This agrees with what is expected from the π-electron interactions of X and Y. However, the ϵ values indicate that electron demand of the common group Y is not determined by its π delocalization ability alone. Except for the $N(CH_3)_2$ group, the ϵ values of Table VI are satisfactorily fitted by the DSP equation given as eq 5. The substantial inductive effect contribution in-

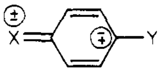
$$\epsilon = -0.9\sigma_{I(Y)} - 1.6\sigma_{R(Y)}{}^0; \qquad SD = 0.09 \qquad (5)$$

dicated by eq 5 appears to emphasize the importance of the π inductive effect in determining C_p-SCS values.[15] The inclusion of the inductive contribution in eq 5 is consistent with an analysis of para-substituent resonance effects on infrared intensities in disubstituted benzenes,[21] where the effect of electron demand of the common group was related to its σ_p value ($\sigma_R + \sigma_I$).

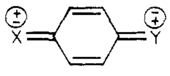
Substitution of (5) into (3) gives the effective $\bar{\sigma}_R$ value for a para X substituent in terms of its $\sigma_R{}^0$ value and the $\sigma_R{}^0$ and σ_I values of the Y group (eq 6).

$$\bar{\sigma}_{R(X)} = \frac{\sigma_{R(X)}{}^0}{1 + 1.6\sigma_{R(X)}{}^0[\sigma_{R(Y)}{}^0 + 0.56\sigma_{I(Y)}]} \qquad (6)$$

The ϵ value obtained for the NMe_2 group deviates very substantially from eq 5 (ϵ_{obsd} = 0.21; ϵ_{calcd} = 0.85). Two types of resonance forms, i and ii, represent the π inter-



i



ii

actions of the para X substituent in 1,4-disubstituted benzenes. Form i implies the development of π charge at the para carbon position, whereas the trans quinoidal form ii does not. Consequently, only i is implied to be of importance in determining the observed C_p-SCS. The deviation of the NMe_2 group from eq 5 may indicate that geometric considerations result in a relatively greater contribution from form ii in this case. It is known that the NMe_2 group tends toward greater coplanarity with the benzene ring than does the otherwise similar NH_2 group.[22] This will tend to increase the relative importance of form ii and consequently to decrease the effective ϵ value. Hydrogen bonding of $CDCl_3$ to para π electron acceptor substituents, e.g., NO_2, in this series may also increase the relative importance of form ii. Hydrogen bond donor solvents interact with *p*-nitro-*N*,*N*-dimethylaniline at the nitro oxygens.[23]

Shift–Charge Ratio. The successful fitting of all of the C_p-SCS values to eq 4, we believe, indicates that eq 3 and 6 take reasonably proper account of the electron-demand influences of the common Y groups on the π-electron delocalization and π inductive effects of para X substituents. The variations in ρ_R and ρ_I values (Table VI) from the fittings by eq 4 must therefore be largely attributed to other causes. Since the ρ_R terms are predominant, this

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[16] The relative enhancement is controlled by the term $\epsilon\sigma_R{}^0$ in the denominator of eq 3. We have replaced this by the expression $(\epsilon\sigma_R{}^0)^x$ and varied the value of x from 0.5 to 1.5 but find the best value is 1.0.

[17] D. E. Blagdon, private communication on the effect of electron demand on sigma constants, 1971.

[18] G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).

[19] L. Salem, *J. Am. Chem. Soc.*, **90**, 543, 553 (1968).

[20] D. A. R. Happer and G. J. Wright, *J. Chem. Soc., Perkin Trans. 2*, 694 (1979).

[21] R. T. C. Brownlee, D. G. Cameron, R. D. Topsom, A. R. Katritzky, and A. F. Pozharsky, *J. Chem. Soc., Perkin Trans. 2*, 247 (1974).

[22] T. Axenrod in "Nitrogen NMR", M. Witanowski and G. A. Webb, Eds., Plenum Press, London, 1973, p 272.

[23] M. J. Kamlet, E. G. Kayser, J. W. Eastes, and W. H. Gilligan, *J. Am. Chem. Soc.*, **95**, 5210 (1973).

Table VII. Shift-Charge Ratio (SCR) Values

Y	SCR[a]	SCR[b]	SCR_{av}	SCR[c]	r
NMe_2	119.0	107.0	113.0		
NH_2	181.0	153.0	167.0	179.0	0.997
OMe	153.0	130.0	142.0	157.0	0.996
F	127.0	115.0	121.0	152.0	0.995
Cl	210.0	189.0	199.0		
Br	231.0	208.0	220.0		
Me	223.0	198.0	211.0	205.0	0.996
H	(189.0)	(189.0)	(189.0)	(189.0)	0.991
CF_3	155.0	166.0	161.0	163.0	0.996
CN	159.0	180.0	170.0	183.0	0.993
CO_2Et	149.0	163.0	156.0		
COMe	132.0	147.0	140.0		
NO_2	106.0	119.0	113.0	132.0	0.982
CHO	117.0	130.0	124.0		

[a] From eq 7. [b] From eq 8. [c] From slope of correlation of C_p-SCS values vs. $\Delta q_\pi^{p\text{-}C}$.

constant for each data set should be reasonably well defined. We believe that (as noted in the discussion of Figure 1) it is indeed plausible to attribute this constant (as it differs from that for Y = H) to the effect of the Y group on the shift charge ratio (eq 7). Values of the SCR for

$$\mathrm{SCR_Y} \simeq \frac{\rho_R{}^{Y}}{\rho_R{}^{H}}\,(189\ \mathrm{ppm/e}) \qquad (7)$$

each Y group obtained in this manner are listed in the first column of Table VII. An alternate method of obtaining SCR values directly from C_p-SCS values is one which recognizes that the CF_3 and Cl substituents have essentially equal σ_I values and small $\sigma_R{}^0$ values of opposite sign. Consequently, it is reasonable to take the difference in C_p-SCS values between the CF_3 and Cl substituents in a given Y series, $(C_p\text{-SCS})_Y{}^{CF_3} - (C_p\text{-SCS})_Y{}^{Cl}$, relative to the same difference for the H series, $(C_p\text{-SCS})_H{}^{CF_3} - (C_p\text{-SCS})_H{}^{Cl}$, as a measure of the relative SCR (eq 8). Values

$$\mathrm{SCR_Y} \simeq \frac{(C_p\text{-SCS})_Y{}^{CF_3} - (C_p\text{-SCS})_Y{}^{Cl}}{(C_p\text{-SCS})_Y{}^{CF_3} - (C_p\text{-SCS})_H{}^{Cl}}\,(189\ \mathrm{ppm/e}) \qquad (8)$$

of the SCR estimated from eq 8 are listed in the second column of Table VII. Agreement between the two methods is generally satisfactory. The average value of the SCR obtained for each series is recorded in the third column of Table VII.

Theoretical Gaussian-70 ab initio calculations of the π charges at the carbon atom para to the X substituents in each series with a common Y group provide a means of confirming the SCR values. Correlations for each series have been run for the para NH_2, OCH_3, F, Me, CF_3, CN, and NO_2 substituents for C_p-SCS vs. Δq_π at the para carbon.[24] The SCR (slope) for each of these correlations and the corresponding correlation coefficient are recorded in Table VII (columns four and five). Agreement between the third and fourth column SCR values will be seen to be quite satisfactory.

It is noteworthy that SCR values may vary by as much as a factor of 2 between the Y groups of Table VII. Incomplete studies with other common Y groups suggest that even larger variations in SCR values will be found.[7h,k,q,r]

Table VIII. DSP Analysis of C_m-SCS of 1,4-Disubstituted Benzenes

series	ρ_I[a]	ρ_R	SD	f
NMe_2[b]	−1.6	−6.3	0.48	0.26
NH_2[b]	−1.1	−3.9	0.48	0.41
OMe	1.0	−1.8	0.29	0.41
F	2.1	−0.2	0.29	0.36
Cl	1.7	−0.6	0.23	0.33
Br	2.0	−0.5	0.19	0.24
Me	1.6	−1.1	0.19	0.26
H	1.6	−1.3	0.19	0.25
CF_3	2.7	−2.2	0.24	0.19
CN	2.5	−2.5	0.33	0.26
COOEt	2.2	−3.2	0.28	0.22
COMe	1.6	−3.8	0.33	0.25
NO_2[b]	2.6	−4.3	0.35	0.21
CHO	1.7	−4.1	0.34	0.23

[a] All correlations exclude Br and CHO/SCS data.
[b] DSP-NLR analysis gives ϵ, ρ_I, ρ_R, and SD values as follows: for NMe_2 series, 1.4, −0.9, −9.0, 0.24; for NH_2 series, 2.0, −0.3, −6.1, 0.27; for NO_2 series, −0.7, 2.5, −3.0, 0.29.

The concept of C-SCS values which are dependent upon variations in SCR has been referred to in the literature in qualitative terms.[7q,15i,25] For example, Toyne noted that the ipso carbon of the benzene ring in 4-phenyl-1-substituted bicyclo[2.2.2]octanes is considerably more sensitive to substituent effects than that of the para carbon and suggested, in effect, a modified shift–charge ratio.[15i] Fraenkel[25a] has studied the relationship between ^{13}C shifts and charges in arines. We note that the β-carbon (C_β-SCS) of β-substituted styrenes responds to para substituents in the phenyl ring to different extents, depending upon the common β substituent. For example, the C_β-SCS's in β-nitrostyrenes[7o] and β-fluorostyrenes[26] are much less sensitive to para substituent effects those than for the corresponding β-unsubstituted styrenes,[7h] in accord with the small SCR for the NO_2 and F series of Table VII.

It has been suggested by Lynch that the susceptibility factor increases as the ionization potential decreases.[7r] Though there is a rough trend in this direction, as there is between the ionization potential and electronegativity, for example, the correlation is poor. Lynch's suggestion must be discarded in view of the appreciably smaller SCR value for Y = NMe_2 than for NH_2, as well as the smaller value for Y = CF_3 than CN.

The variation in the ipso SCS values shown in Table III may also be understood in terms of the SCR values.[7x] The ipso shift may be thought of as the cumulative effect of the ipso substituent chemical shift in monosubstituted benzenes and a contribution from the modification of the C_p-SCS by the relative SCR. The direction of the ipso shift at C-1 in changing the C-4 substituent from NMe_2 to CHO is related to the SCR value. This shift is negative for a relative SCR < 189 (NMe_2, NH_2, OMe, etc.) and positive for the series with a relative SCR > 189 (Me, Cl, Br).[7m]

Although the ρ_I values obtained in the fittings to eq 4 do not show the same dependence on the Y group as do the ρ_R values, the trends are generally similar. That is, generally, $\rho_R/\rho_I = \lambda = 4.7 \pm 1$, indicating that the ρ_I values also reflect the same SCR values. Notable exceptions are for Y = NMe_2, F, and NO_2. In these series, there are probably also some modifications in the π inductive effects of para X substituents (compared to those for the corresponding H series).

Analysis of C_m-SCS Data for the 1,4-Disubstituted Benzenes. The C_m-SCS data of Table II have been an-

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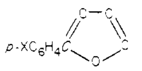
(24) We have shown that at the CNDO/2[14] and ab initio[11] STO-3G levels of approximation the para carbon in substituted benzenes has induced σ-electron-density changes which are inversely proportional to the induced π-electron-density changes at the same site. Therefore, chemical shift correlations with σ, π, or total density are of the same quality.

(25) (a) T. Tokuhiro and G. Fraenkel, *J. Am. Chem. Soc.*, **91**, 5005 (1969); (b) W. J. E. Parr and R. E. Wasylishen, *J. Mol. Struct.*, **38**, 272 (1977).

(26) W. F. Reynolds, private communication.

Table IX. Some Applications of the DSP-NLR Treatment (Eq 4) to ^{13}C and ^{19}F Side-Chain SCS

				DSP-NLR[b]				DSP (with $\epsilon = 0.00$)[b]			DSP with best fit σ_R[c]			
series	solvent	ref	n	ϵ	ρ_I	ρ_R	SD	ρ_I	ρ_R	SD	ρ_I	ρ_R	SD	scale
p-XC$_6$H$_4$*C*OMe[a]	CDCl$_3$	28	12	−1.39	−2.7	0.7	0.17	−2.7	1.9	0.30	−2.6	0.8	0.18	σ_R^+
p-XC$_6$H$_4$C*F*$_3$	CFCl$_3$	29	5	−1.03	0.1	1.4	0.15	0.1	2.9	0.28	0.1	1.0	0.16	σ_R^+
p-XC$_6$H$_4$*C*N	CDCl$_3$	28	12	−1.02	−2.8	−1.7	0.11	−2.7	−3.0	0.25	−2.7	−1.1	0.10	σ_R^+
p-XC$_6$H$_4$COC$_6$H$_4$-p-*F*	CH$_2$Cl$_2$	30	7	−0.59	2.5	2.9	0.05	2.5	3.9	0.15	2.6	2.7	0.07	σ_R(BA)
p-XC$_6$H$_4$*C*F$_3$	CDCl$_3$	28	12	−0.18	−1.7	−1.6	0.08	−2.7	−3.0	0.25	−1.7	−1.2	0.08	σ_R(BA)
C$_{10}$ 2-X-naphthalenes	CDCl$_3$	31	10	0.05	0.6	11.4	0.17	0.7	11.3	0.17	0.7	10.8	0.38	σ_R^0
p-XC$_6$H$_4$CH=*C*H$_2$	CCl$_4$	6h	10	0.06	5.4	8.7	0.18	5.4	8.5	0.24	5.3	8.1	0.22	σ_R^0
p-XC$_6$H$_4$*F*	CCl$_4$	27	11	0.21	6.1	33.3	0.35	6.7	31.1	0.54	7.4	30.6	0.42	σ_R^0
p-XC$_6$H$_4$C≡*C*H	CCl$_4$	6k	11	1.32	4.7	9.3	0.39	5.0	6.3	0.51	4.0	5.3	0.35	σ_R^-
	CDCl$_3$	6u	7	1.09	3.1	−2.9	0.17	3.4	−2.4	0.22	−3.4	−2.2	0.17	σ_R^-

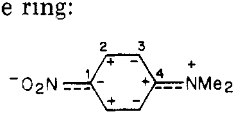
[a] Italic atom is the NMR site. [b] σ_I and σ_R^0 values from ref 5. [c] σ_I and σ_R values from ref 4.

alyzed by the simple DSP method (eq 2), and the results are shown in Table VIII. Although C$_m$-SCS data are generally an order of magnitude smaller than the corresponding C$_p$-SCS data, the SD of fit is almost the same as that for the DSP-NLR analysis of the latter.

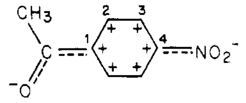
The C$_m$-SCS data for the 1,4-disubstituted benzenes are only fitted appreciably better by the DSP-NLR equation when the ρ_R value is of significant magnitude (NMe$_2$, NH$_2$, and NO$_2$). For the other series, which all have small ρ_R values, the fit is essentially the same for both DSP and DSP-NLR. The Br and CHO data were excluded from the meta correlations because of their known anisotropic contributions and large observed deviations.

The most important features of the fitting parameters obtained by the DSP, DSP-NLR and C$_m$-SCS data (Table VI) are as follows: (1) ρ_R values are opposite in sign and about one-sixth as large as those obtained from the corresponding C$_p$-SCS data; (2) when the DSP-NLR equation is effective in reducing the SD's, the values of the ϵ parameter are found to be influenced as usual by π-delocalization effects of the common group (Y), i.e., tending to be positive for the common π-donor substituents and negative for the π-acceptor substituent; (3) the opposite signs of the ρ_I and ρ_R values (except for the NH$_2$ and NMe$_2$ series) account for the unusual substituent-effect order for the C$_m$-SCS values.

All of the ρ_I values from the C$_m$-SCS data are close to 2 (except for the NH$_2$ and NMe$_2$ series). The relatively small variations from 2 are of questionable significance. This result supports the idea that the effects of Y are limited primarily to the para carbon of attachment and do not influence the meta position very much. Further, the ρ_I^m value of 2.0 corresponds to 0.4–0.5 times that of ρ_I^p obtained from C$_p$-SCS data for Y = H and other weakly interacting groups. This result agrees with that of Toyne[15i] for the C-3′ C-SCS of 4-phenyl-1-substituted bicyclo[2.2.2]octanes and that of Adcock[15k] for the corresponding F-3′ and F-4′ data, which give $\rho_I^m/\rho_I^p \simeq 0.4$ for the reduction factor of the π inductive effect acting at the meta compared to the para position. The values of ρ_R^m from the C$_m$-SCS data of Table VI behave in a manner consistent with STO-3G calculations[11] of $\Delta q_\pi^{m\text{-C}}$, namely, π-donor meta X substituents make $\Delta q_\pi^{m\text{-C}}$ positive. The results for the strong π donors Y = NMe$_2$ and NH$_2$ indicate that there are complementary resonance effects acting at the meta carbon for the strong π-acceptor substituents which result from a favorable alternation of sign of Δq_π about the benzene ring:



Thus, for example, the C-3 atom of p-nitro-*N*,*N*-dimethylaniline is relatively well shielded (cf. Table II). Likewise, the $\epsilon = -0.7$ value for Y = NO$_2$ indicates unfavorable repulsive π-electron saturation effects occur, e.g.



and consequently there is little deshielding of C-3 (cf. Table II).

Applications and Limitations of the DSP-NLR Treatment. Table IX gives the results of applying the DSP-NLR equation (eq 4) to diverse data sets of ^{19}F- and ^{13}C-SCS. The selection of data sets is based upon the following criteria: a discriminating set of substituents (meeting as close as possible minimum basis set requirements[5]); data obtained at high dilutions in aprotic solvents so as to avoid solvent and concentration effects;[5] unusual electronic properties for the data set, e.g., large or negative values of $\lambda = \rho_R/\rho_I$ or best fits to the simple DSP equation (eq 2) involving σ_R^+, σ_R^-, or $\sigma_{R(BA)}$ rather than σ_R^0 values.[4]

The structure and probe atom (italic) are given in the first column of Table IX, followed by the solvent and number of data points. The results of three types of data fitting are given: first, the DSP-NLR values of ϵ, ρ_I, ρ_R, and SD; second, the same results from eq 2 ($\epsilon = 0$) using the same σ_R^0 (NMR) values[5] as for DSP-NLR; third, the best fittings obtained from eq 2 using the substituent parameters of Ehrenson, Brownlee, and Taft[4] (based largely upon reactivities in hydroxylic media). In all appropriate cases, there are very significant improvements seen in Table IX for the SD values obtained by DSP-NLR methods as compared with DSP methods. Further, for those sets which involve best fits to σ_R^+, σ_R^-, or $\sigma_{R(BA)}$ with eq 2, the SD's obtained with DSP-NLR and σ_R^0 parameters are essentially as good or better.

The F$_p$-SCS values for substituted fluorobenzenes[27] are of particular interest. It was previously pointed out that

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a plot of these shifts vs. the corresponding C_p-SCS values for monosubstituted benzenes (both in CCl_4 at high dilutions) is approximately bilinear with a greater slope for π-acceptor than π-donor substituents (in line with the π-donor ability of the F probe atom).[11] The significant improvement in fit of F_p-CSC values with $\epsilon = +0.21$ compared to $\epsilon = 0.00$ (Table IX) is in noteworthy accord. The DSP-NLR treatment does best for systems which have large resonance to inductive proportions and which meet basis-set requirements.[5] When the contributions from resonance effects are small, the derived ϵ value becomes meaningless.

Equation 3 was chosen because of its simplicity and easily interpretable parameters. A fuller description, using a more complex function, would require additional parameters. This was specifically avoided. However, the choice of this simple function does impose some noteworthy limitations. For appropriate systems (such as Table IX) in which the demand parameter lies between -1.5 and $+1.5$, the method provides excellent results. However, for systems with greater demand, the results may become unreasonable. For example, if $\sigma_R{}^0 > 0.5$ as the demand parameter approaches 2, then σ_R approaches ∞. The simple function used in eq 3 also does not allow the resonance effects of substituents to "cross" in Figure 2. Hence, amphielectronic (e.g., phenyl) and extremely polarizable substituents (e.g., I and SMe) must be excluded when ϵ deviates from 0. The successful application of the DSP-NLR method illustrated in Table IX does not extend to most reaction-rate or equilibrium series. We believe that this is largely the result of the state changes involved and the ionic functional groups which have large and variable solvation, as well as certain protonic solvent effects on substituent parameters. Such applications are currently under further study.

Summary

The para substituent ^{13}C chemical shifts (C_p-SCS) are reported for 14 series of 1-X,4-Y-disubstituted benzenes at high dilution in deuteriochloroform solutions. The sensitivity of the C_p-SCS values to the local π charges at the para carbon is shown to be regulated by the common adjacent group, Y. For a given Y series, the ratio of the C_p-SCS value to the corresponding para X substituent induced para-carbon π charge is indicated to be approximately constant (called the shift–charge ratio, SCR). Values of SCR are found to range from ~125 to 250 ppm/e, depending upon the common group, Y.

Analysis of the C_p-SCS data by the DSP method indicates that in all series the π charge density at the para carbon is modified according to both the $\sigma_R{}^0$ and σ_I values of the para substituent, the former effect being predominant. The $\sigma_R{}^0$ dependence is taken to be the contribution from substituent π delocalization (resonance effect) and the σ_I dependence to be the contribution from the substituent dipolar field polarization of the benzene π-electron system (π inductive effect). A similar analysis of the meta carbon C_m-SCS data offers further confirmation of the secondary contributions from the π inductive effects. Further, it is shown that small resonance effects operate at the meta positions which are of opposite sign to those for the corresponding para positions.

The broad range of substituent electronic properties employed in this study, coupled with the high sensitivity of the C_p-SCS values obtained in $CDCl_3$ at high dilutions, has permitted a more detailed analysis than that provided by the simple DSP method. It is shown that the π-electron delocalization of the para X substituents may be either enhanced (conjugative effect) or reduced (repulsive π-electron saturation), depending upon the "electron demand" exerted on the common Y group. The resonance effects are shown to be nonlinear with the $\sigma_R{}^0$ value of the para substituent but are accurately described by a simple relationship involving the $\sigma_R{}^0$ parameters and an "electron-demand" parameter, ϵ, which is characteristic of a combination of the $\sigma_R{}^0$ and σ_I properties of the common group, Y. Limited applications of this DSP-NLR treatment are shown to be successful for diverse data sets of ^{19}F- and ^{13}C-SCS. Limitations of this method are discussed.

Acknowledgment. We acknowledge the contributions to this study resulting from helpful discussions with Professors R. D. Topsom, W. F. Reynolds, and Y. Tsuno. We are grateful to Dr. D. E. Blagdon[17] and Professor Y. Tsuno for providing unpublished material. Mr. G. Butt is thanked for the synthesis of some of the compounds used in this study. Dr. W. A. Sheppard's generous gift of *p*-nitro(trifluoromethyl)benzene is gratefully acknowledged. We thank La Trobe University Computer Center for computer time and valuable assistance.

Appendix. Procedures Used in Fitting the Chemical Shift Data to the Multiparameter Equations

Substituent chemical shift data (SCS) relative to the hydrogen substituent were fitted to the DSP equation (eq 1) by using a standard least-squares program which calculates ρ_I and ρ_R values by using known σ_I and σ_R constants.

The SCS data were fitted to the nonlinear eq 4 (DSP-NLR) in essentially the same way by modifying the σ_R values according to the demand (ϵ) as in eq 3. Starting with ϵ as zero, the DSP-NLR becomes a DSP equation, and the data fitting was performed as above to obtain ρ values and the standard deviation. The demand parameter ϵ was then incremented in small steps. This modifies the σ_R values which were used to fit the data in the normal way. The changes in ϵ were made until a minimum in the standard deviation of the fit in the experimental data was achieved.

Registry No. I (X = Y = NMe_2), 100-22-1; I (X = NMe_2, Y = NH_2), 99-98-9; I (X = NMe_2, Y = OMe), 701-56-4; I (X = NMe_2, Y = F), 403-46-3; I (X = NMe_2, Y = Cl), 698-69-1; I (X = NMe_2, Y = Br), 586-77-6; I (X = NMe_2, Y = Me), 99-97-8; I (X = NMe_2, Y = H), 121-69-7; I (X = NMe_2, Y = CF_3), 329-17-9; I (X = NMe_2, Y = CN), 1197-19-9; I (X = NMe_2, Y = COOEt), 10287-53-3; I (X = NMe_2, Y = COMe), 2124-31-4; I (X = NMe_2, Y = NO_2), 100-23-2; I (X = NMe_2, Y = CHO), 100-10-7; I (X = Y = NH_2), 106-50-3; I (X = NH_2, Y = OMe), 104-94-9; I (X = NH_2, Y = F), 371-40-4; I (X = NH_2, Y = Cl), 106-47-8; I (X = NH_2, Y = Br), 106-40-1; I (X = NH_2, Y = Me), 106-49-0; I (X = NH_2, Y = H), 62-53-3; I (X = NH_2, Y = CF_3), 455-14-1; I (X = NH_2, Y = CN), 873-74-5; I (X = NH_2, Y = COOEt), 94-09-7; I (X = NH_2, Y = COMe), 99-92-3; I (X = NH_2, Y = NO_2), 100-01-6; I (X = NH_2, Y = CHO), 556-18-3; I (X = Y = OMe), 150-78-7; I (X = OMe, Y = F), 459-60-9; I (X = OMe, Y = Cl), 623-12-1; I (X = OMe, Y = Br), 104-92-7; I (X = OMe, Y = Me), 104-93-8; I (X = OMe, Y = H), 100-66-3; I (X = OMe, Y = CF_3), 402-52-8; I (X = OMe, Y = CN), 874-90-8; I (X = OMe, Y = COOEt), 94-30-4; I (X = OMe, Y = COMe), 100-06-1; I (X = OMe, Y = NO_2), 100-17-4; I (X = OMe, Y = CHO), 123-11-5; I (X = Y = F), 540-36-3; I (X = F, Y = Cl), 352-33-0; I (X = F, Y = Br), 460-00-4; I (X = F, Y = Me), 352-32-9; I (X = F, Y = H), 462-06-6; I (X = F, Y = CF_3), 402-44-8; I (X = F, Y = CN), 1194-02-1; I (X = F, Y = COOEt), 451-46-7; I (X = F, Y = COMe), 403-42-9; I (X = F, Y = NO_2), 350-46-9; I (X = F, Y = CHO), 459-57-4; I (X = Y = Cl), 106-46-7; I (X = Cl, Y = Br), 106-39-8; I (X = Cl, Y = Me), 106-43-4; I (X = Cl, Y = H), 108-90-7; I (X = Cl, Y = CF_3), 98-56-6; I (X = Cl, Y = CN), 623-03-0; I (X = Cl, Y = COOEt), 7335-27-5; I (X = Cl, Y = COMe), 99-91-2; I (X = Cl, Y = NO_2), 100-00-5; I (X = Cl, Y = CHO), 104-88-1; I (X = Y = Br), 106-37-6; I (X = Br, Y = Me), 106-38-7; I (X = Br, Y = H), 108-86-1; I (X = Br, Y = CF_3), 402-43-7;

I (X = Br, Y = CN), 623-00-7; I (X = Br, Y = COOEt), 5798-75-4; I (X = Br, Y = COMe), 99-90-1; I (X = Br, Y = NO_2), 586-78-7; I (X = Br, Y = CHO), 1122-91-4; I (X = Y = Me), 106-42-3; I (X = Me, Y = H), 108-88-3; I (X = Me, Y = CF_3), 6140-17-6; I (X = Me, Y = CN), 104-85-8; I (X = Me, Y = COOEt), 94-08-6; I (X = Me, Y = COMe), 122-00-9; I (X = Me, Y = NO_2), 99-99-0; I (X = Me, Y = CHO), 104-87-0; I (X = Y = H), 71-43-2; I (X = H, Y = CF_3), 98-08-8; I (X = H, Y = CN), 100-47-0; I (X = H, Y = COOEt), 93-89-0; I (X = H, Y = COMe), 98-86-2; I (X = H, Y = NO_2), 98-95-3; I (X = H, Y = CHO), 100-52-7; I (X = Y = CF_3), 433-19-2; I (X = CF_3, Y = CN), 455-18-5; I (X = CF_3, Y = COOEt), 583-02-8; I (X = CF_3, Y = COMe), 709-63-7; I (X = CF_3, Y = NO_2), 402-54-0; I (X = CF_3, Y = CHO), 455-19-6; I (X = Y = CN), 623-26-7; I (X = CN, Y = COOEt), 7153-22-2; I (X = CN, Y = COMe), 1443-80-7; I (X = CN, Y = NO_2), 619-72-7; I (X = CN, Y = CHO), 105-07-7; I (X, Y = COOEt), 636-09-9; I (X = COOEt, Y = COMe), 38430-55-6; I (X = COOEt, Y = NO_2), 99-77-4; I (X = COOEt, Y = CHO), 6287-86-1; I (X = Y = COMe), 1009-61-6; I (X = COMe, Y = NO_2), 100-19-6; I (X = COMe, Y = CHO), 3457-45-2; I (X = Y = NO_2), 100-25-4; I (X = NO_2, X = CHO), 555-16-8; I (X = Y = CHO), 623-27-8; I (X = OH, Y = NO_2), 100-02-7; I (X = OH, Y = CN), 767-00-0; I (X = OH, Y = CHO), 123-08-0; I (X = OH, Y = H), 108-95-2; I (X = OH, Y = F), 371-41-5; I (X = Y = OH), 123-31-9; I (X = OH, Y = NH_2), 123-30-8; I (X = CH_3, Y = OH), 106-44-5; I (X = CF_3, Y = OH), 402-45-9.

5,6-Didehydro-7-bromodibenzo[*a*,*c*]cyclooctene and 5,6-Didehydro-8-*tert*-butoxydibenzo[*a*,*c*]cyclooctene as Reactive Intermediates.[1] A Convenient Synthesis of Dibenzo[*a*,*c*]cyclooctene

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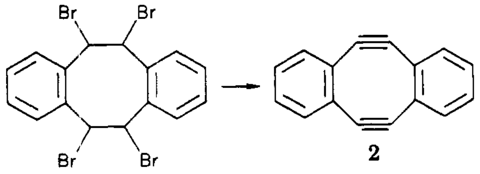
A convenient synthesis of dibenzo[*a*,*c*]cyclooctene (**8**) is described, which on bromination yielded 5,6,7,8-tetrabromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (**3**). Dehydrobromination of **3** led to 6,7-dibromodibenzo[*a*,*c*]cyclooctene (**9**), 5-*tert*-butoxy-7-bromodibenzo[*a*,*c*]cyclooctene (**11**), and 5,7-di-*tert*-butoxydibenzo[*a*,*c*]cyclooctene (**13**) via the presumed reactive intermediates 5,6-didehydro-7-bromodibenzo[*a*,*c*]cyclooctene (**10**) and 5,6-didehydro-8-*tert*-butoxydibenzo[*a*,*c*]cyclooctene (**12**). This reaction path is compatible with the observed formation of 1,4:5,8-diepoxy-1,4,5,8-tetrahydro-1,4,5,8-tetraphenyl-2,3:6,7-dibenzotetraphenylene (**14**) by dehydrobromination of the tetrabromide **3** or the dibromide **9** with potassium *tert*-butoxide in the presence of 1,3-diphenylisobenzofuran.

We have reported previously that dehydrobromination of 5,6,11,12-tetrabromo-5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**1**) with potassium *tert*-butoxide leads to 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (**2**) as a relatively stable crystalline compound.[3] It was of interest to investigate whether the analogous dehydrobromination of 5,6,7,8-tetrabromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (**3**)[4] would yield 5,6,7,8-tetradehydrodibenzo[*a*,*c*]cyclooctene (**4**), although the presence of a 1,3-diyne unit in **4** would make it very unlikely that such a compound could be isolated. We now report the results of the dehydrobromination of the tetrabromide **3**. Although there was no indication of the formation of the diacetylene **4**, evidence was obtained that 5,6-didehydro-7-bromodibenzo[*a*,*c*]cyclooctene (**10**) and 5,6-didehydro-8-*tert*-butoxydibenzo[*a*,*c*]cyclooctene (**12**) were formed as reactive intermediates.



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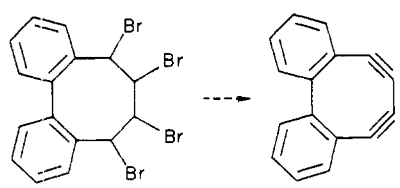

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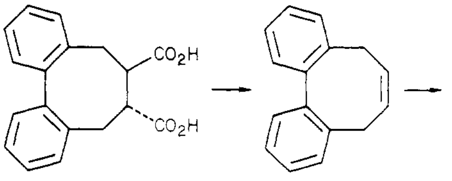
The starting material, dibenzo[*a*,*c*]cyclooctene (**8**), has been synthesized previously in ~30% yield from 5,8-dihydrodibenzo[*a*,*c*]cyclooctene (**6**) by a method involving a low-pressure pyrolysis step.[4,5] Since this is rather inconvenient experimentally, we have developed the following superior method. Decarboxylation of *trans*-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene-6,7-dicarboxylic acid



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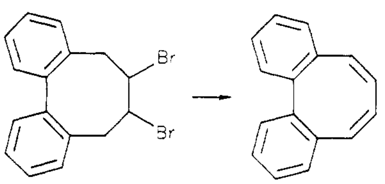

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