glycol, and a catalytic amount of *p*-toluenesulfonic acid was refluxed in 130 mL of benzene for 16 h, while H_2O was removed with a Dean–Stark water separator. In this way, 23.4 g of crystalline solid was obtained, which was used without further purification: NMR ($CDCl_3$) δ 3.9 (br s, 4 H), 2.8 (broad unresolved multiplet, 4 H), 2.3 (broad unresolved multiplet, 4 H), 1.7 (poorly resolved AB pattern, 4 H).

The monoethylene ketal **19** (5.0 g) was reduced with 0.8 g of $LiAlH_4$ in diethyl ether, providing 4.2 g of a white crystalline solid, mp 76–78 °C. Recrystallization from hexane yielded an analytical sample: mp 76.5–77.5 °C; NMR (CCl_4) δ 5.35 (d, 1 H), 3.9 (symmetrical eight-line pattern, 4 H), 3.4 (d of m, 1 H), 2.7–1.3 (complex absorption, 12 H); IR (CCl_4) 3475, 2955, 1466, 1343, 1288, 1268, 1143, 1105, 1080, 1055, 1020, 953, 937, 923 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.96; H, 7.74.

Monoethylene Ketal of 6-Hydroxyhexacyclo[6.4.2.0^{2,7}.0^{4,14}.0^{5,13}.0^{9,12}]tetradec-10-en-3-one (30). The formation of the monoethylene ketal of the dione **17** and its subsequent reduction with $LiAlH_4$ in THF proceeded unexpectionally when methods outlined above for the synthesis of **28** and **29** were used. The endo alcohol **30** obtained in this way, after recrystallization from ethyl acetate, exhibited the following: mp 119–120.5 °C; NMR (CCl_4) δ 6.2 (s, 2 H), 5.4 (d, 1 H), 4.0 (complex m, 4 H), 3.4 (d of m, 1 H), 3.0–1.5 (complex, 10 H); IR (CCl_4) 3460, 3045, 2970, 2910, 1351, 1322, 1152, 1124, 1075, 1050, 1025 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.66; H, 7.06.

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Registry No. 7a, 7172-92-1; **7b**, 4421-32-3; **7c**, 4421-33-4; **7d**, 69042-80-4; **7e**, 69028-00-8; **7f**, 69087-61-2; **8**, 31285-42-4; **10**, 2958-72-7; **12b**, 66819-91-8; **12c**, 66824-76-8; **12d**, 69087-57-6; **12e**, 69087-58-7; **12f**, 69087-59-8; **15**, 712-25-4; **16**, 69028-01-9; **17**, 71885-01-3; **18**, 58228-93-6; **19**, 62111-11-9; **21**, 66824-74-6; **22**, 69028-03-1; **23**, 69028-04-2; **24**, 69028-05-3; **25**, 69028-06-4; **28**, 58228-94-7; **29**, 69027-95-8; **30**, 71885-36-4; **31**, 69042-81-5; **32**, 69027-93-6; **33**, 69027-94-7; **34**, 69028-07-5; **36**, 71871-51-7; **37**, 69028-11-1; **38**, 69028-12-2; **39**, C = ---, 25107-14-6; **39**, C = CH_2, 704-02-9; **39**, C = $(CH_2)_2$, 71871-52-8; **39**, C = $(CH_2)_3$, 71871-53-9; **39**, C = cyclobutyl, 71871-54-0; **39**, C = cyclobutenyl, 71871-55-1; **40**, C = ---, 69027-97-0; **40**, C = CH_2, 71871-56-2; **40**, C = $(CH_2)_2$, 71871-57-3; **40**, C = $(CH_2)_3$, 71871-58-4; **40**, C = cyclobutyl, 71885-46-6; **40**, C = cyclobutenyl, 71885-45-5; **41**, C = CH_2, 71871-59-5; **41**, C = $(CH_2)_2$, 71871-60-8; **41**, C = $(CH_2)_3$, 71871-61-9; **41**, C = cyclobutyl, 71871-62-0; **41**, C = cyclobutenyl, 71871-63-1; 3-methoxy-4-oxahexacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]undecane, 69028-08-6; 1-methoxy-13-oxahexacyclo[6.4.1.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]tridecane, 69028-10-0; 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione, 51175-59-8; 1,4,4a,8a-tetrahydro-1,4-ethanonaphthalene-5,8-dione, 69685-89-8; 4a,9a-dihydro-5,9-ethenobenzocycloheptane-1,4-dione, 71885-00-2; 4a,10a-dihydro-5,10-etheno-6,8-benzocyclooctadiene-1,4-dione, 71871-64-2; *endo*-tricyclo[4.4.0.0^{2,5}]deca-3,8-diene-7,10-dione, 34231-42-0; cyclopentadiene, 542-92-7; *p*-benzoquinone, 106-51-4; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; cyclooctatetraene, 629-20-9; ethanol, 64-17-5; 1-butanol, 71-36-3.

Para Substituent Carbon-13 Chemical Shifts in Substituted Benzenes. 1. Updating the $\sigma^0_{\rm R}$ Scale and Analysis of Aprotic Solvent Effects[1a]

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The para carbon chemical shifts (C_p-SCS) for a selected series of monosubstituted benzenes have been measured in very dilute solutions of the nonpolar solvents cyclohexane and carbon tetrachloride and of the weakly polar solvent deuteriochloroform. These results provide the basis for the redefinition of $\sigma^0_{\rm R}$ values, which measure the ability of a substituent to delocalize π electrons to or from a neutral or unperturbed benzene ring. The new $\sigma^0_{\rm R}$ values are shown to make significant improvements in dual substituent parameter (DSP) correlations of appropriate data sets which are very sensitive to the effects of π electron delocalization. Applications include a definitive analysis of polar aprotic solvent induced C_p-SCS. These results offer strong support for both the new $\sigma^0_{\rm R}$ values and the basic assumptions of DSP analysis.

The $\sigma^0_{\rm R}$ scale is intended to be a quantitative measure of the ability of a substituent to delocalize π electrons into or from an unperturbed or "neutral" benzene ring.[2] The $\sigma^0_{\rm R}$ parameters have found wide application in dual substituent parameter (DSP) analysis[2d] and have been supported by the results of ab initio molecular orbital calculations.[2a] At the time the $\sigma^0_{\rm R}$ scale was developed, there were very few suitable substituent effect data for "neutral" systems. The scale was therefore heavily weighted by the ^{19}F NMR chemical shifts (F_p-SCS) of para-substituted fluorobenzenes.[2d] While F_p-SCS values are very sensitive to changes in π electron density (at or near F)[2c] and can be precisely measured at low concentrations in inert (nonpolar) solvents,[3] the F atom "probe" is a π electron donor which modifies the π electron donating or accepting ability of para substituents.[4]

With current FT instrumentation, the ^{13}C NMR chemical shifts of the para carbon atom (C_p-SCS) of monosubstituted benzenes can be obtained at high dilution in nonpolar solvents. The C_p-SCS values appear to be ideal for defining the $\sigma^0_{\rm R}$ scale since the ^{13}C "probe" is a part of the "neutral" benzene ring. Further, it is already known from measurements at higher concentrations[5] that C_p-SCS

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Table I. Substituent Chemical Shifts (C_p-SCS) for the Para Carbon of Monosubstituted Benzenes at High Dilutions (in ppm)

	solvent					
substituent	c-C_6H_{12}	CCl_4	$CDCl_3$	$(CH_3)_2CO$	$HCON(CH_3)_2$	$(CH_3)_2SO$
$N(CH_3)_2$	-11.13	-11.16	-11.69	-11.99[8a]	-12.06[8b]	-12.21[7]
NH_2	-9.98	-9.86	(-9.80)	(-11.71)[8a]		(-12.55)[7]
OCH_3	-7.77	-7.75	-7.68	-7.89[8a]	-7.81[8b]	-7.85[7]
OC_6H_5	-5.33	-5.26	-5.11	-4.99[8a]	-4.98	-4.89[7]
F	-4.52	-4.49	-4.39	-4.03[8a]	-3.73[8b]	-3.84[7]
Cl	-2.18	-2.08	-1.91	-1.55	-1.38	-1.35
Br	-1.75	-1.62[7]	-1.50	-1.08[8a]	-0.99	-0.90[7]
CH_3	-2.82	-2.89	-3.05	-3.04[8a]	-3.03[8b]	-3.04[7]
H	0.00	0.00	0.00	0.00	0.00	0.00
$SOCH_3$	1.78	2.07	(2.62)	2.29	2.32	2.35
CF_3	3.09	3.19	3.67	3.96	4.21	4.29
COC_6H_5	3.35	3.51	4.02	4.08[8a]	4.21	4.36[7]
CN	3.58	3.80	4.35	4.70[8a]	4.96[8b]	5.01[7]
$COCH_3$	3.93	4.18	(4.67)	4.58[8a]	4.70	4.83[7]
$CO_2C_2H_5$	3.99	4.12	4.42	4.68[8a]	4.78[8b]	4.90[7]
$SO_2C_6H_5$	insol	4.16	4.83	5.08[8a]	5.24	5.40[7]
SO_2CH_3	insol	4.64	(5.32)	5.12	5.19[8b]	5.31[7]
NO_2	5.20	5.53	6.15	6.58[8a]	6.82[8b]	6.95[7]
CHO	5.29	5.51	(6.07)	6.00[8a]	6.15	6.22[7]
$COCF_3$	6.43	6.66	7.09	7.65[8a]		(7.81)[7]
COCN	7.55	7.81	8.44	8.62[8a]		(8.50)[7]

[a] Values given in parentheses have been excluded from the DSP correlation because of specific solvent-substituent interaction (cf. text).

Table II. Redefined σ^0_R Values Obtained from C_p-SCS Values in Cyclohexane and Carbon Tetrachloride Solutions

	σ_I	σ^0_R
$N(CH_3)_2$	0.06	-0.55 (-0.52)
NH_2	0.12	-0.50 (-0.48)
OCH_3	0.27	-0.42 (-0.45)
OC_6H_5	0.38	-0.32
F	0.50	-0.31 (-0.34)
Cl	0.46	-0.18 (-0.23)
Br	0.44	-0.16 (-0.19)
CH_3	-0.04	-0.13 (-0.11)
H	0.00	0.00
$SOCH_3$	0.49 (0.50)	0.01 (0.00)
CF_3	0.42 (0.45)	0.08
CN	0.56	0.08 (0.13)
$SO_2C_6H_5$	0.62 (-)	0.09 (-)
SO_2CH_3	0.60 (0.59)	0.12
COC_6H_5	0.22 (-)	0.13 (-)
NO_2	0.65	0.15
$CO_2C_2H_5$	0.20 (0.30)	0.16 (0.14)
CH_3CO	0.20 (0.28)	0.16
CHO	0.27 (-)	0.22 (-)
$COCF_3$	0.50 (-)	0.23 (-)
COCN	0.66 (-)	0.26 (-)

values are satisfactorily correlated by the DSP equation, using the σ^0_R scale.[2d,e]

We have measured the C_p-SCS values for a selected series of monosubstituted benzenes at high dilution (~0.1 M or less if needed) in the nonpolar solvents cyclohexane and carbon tetrachloride and in the weakly polar solvent deuteriochloroform. The objective was to provide the basis for redefinition of σ^0_R parameters. The results involve such small modifications in σ^0_R values as to be of little concern in correlations with most of the appropriate chemical reactivity series. Nevertheless, the modified values are of significance when applied to those physical property measurements (e.g., C-SCS) which have a high dependence upon π-electron delocalization effects. It is shown that the sizable effects of polar aprotic solvents on C_p-SCS values, which appear quite anomolous from the standpoint of any single substituent parameter, are readily accounted for by the DSP treatment, using the new σ^0_R values. Further, in a future paper,[6] we will demonstrate the use of the new "inherent" σ^0_R values in delineating and studying the effects of π electronic interactions between the substituents in 1,4-disubstituted benzenes.

Experimental Section

Samples were prepared in 10-mm NMR tubes, usually at a concentration of 3% volume/volume (v/v). A concentration study showed effects on C_p-SCS values to follow a pattern similar to that observed for F NMR shifts of meta and para substituted benzenes.[3,11c] That is, the most polar solutes in the least polar solvents require the highest dilutions to obtain limiting shifts. For example, the C_p-SCS values obtained for nitrobenzene in solutions of cyclohexane of 12, 6, 3, and 1.5% v/v were 5.76, 5.50, 5.31, and 5.21 ppm, respectively. In $CDCl_3$ solutions of 3, 2, and 1% v/v, the values obtained are 6.18, 6.15, and 6.15 ppm. Consequently, in cyclohexane and carbon tetrachloride solutions, the strongly polar solutes were run at 1 to 2% v/v. For locking purposes, 5% of the perdeuterated solvent was added to c-C_6H_{12} and $HCON(CH_3)_2$. For CCl_4, a coaxial tube containing Me_2SO-d_6 was used. Shifts were measured relative to internal benzene, which was added at 1% v/v. Downfield shifts are given as positive.

Spectra were recorded on JEOL-PFT-100 and Bruker WH-90 NMR spectrometers with 8K data points and at a spectral width of 4000 Hz. Measurements from both instruments and those communicated by Professor Tsuno[8] agreed to within 0.05 ppm.

Results

The C_p-SCS values obtained in this work are given in Table I. The results in carbon tetrachloride are in generally good agreement with those obtained by Nelson, Levy, and Cargioli[5] at 10 mol % concentrations, except for the more polar solutes. The latter give limiting shifts 0.1

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Table III. Comparisons of DSP Fit of C_p-SCS in Cyclohexane, Carbon Tetrachloride, and Deuteriochloroform, Using EBT Parameters and Parameters of Table II[a]

	EBT parameters					parameters of Table II				
solvent	n	SD	f	ρ_I	ρ_R	n	SD	f	ρ_I	ρ_R
c-C_6H_{12}	14	0.56	0.10	3.62	20.15	14	0.07	0.01	3.38	20.59
c-CCl_4	15	0.51	0.10	3.96	20.28	15	0.06	0.01	3.74	20.73
$CDCl_3$	15	0.52	0.09	4.86	20.97	15	0.16	0.03	4.64	21.46

[a] The same substituents are used for each pair of comparative correlations.

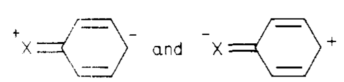
to 0.2 ppm more upfield than those reported earlier. Our results also agree within ±0.05 ppm with those obtained by Tsuno et al. at high dilutions in carbon tetrachloride and deuteriochloroform.[7] Also listed in Table I are C_p-SCS values obtained at high dilutions in acetone, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO) solutions. These are data from the literature,[7,8] except for those values which are not so designated.

Discussion

The earlier DSP treatment of C_p-SCS values for monosubstituted benzenes at 10 mol % in CCl_4 gave the following results:[2e]

$$C_p\text{-SCS} = (4.0)\sigma_I + (19.8)\sigma^0_R; \qquad \text{SD} = 0.54 \text{ ppm}; \qquad f = \text{SD/rms} = 0.099 \tag{1}$$

In eq 1, the generally predominant term $(19.8\sigma^0_R)$ has been attributed to the effect of π electron delocalization,[2] as represented by the familiar interaction forms



The secondary term $(4.0\sigma_I)$ is attributed to the effect of substituent induced polarization of the ring π electrons[9] (both π_F and π_σ effects[2f]), which occurs with no net π electron transfer between the substituent and the ring π electrons. Calculations of the para-carbon atom π charge densities for monosubstituted benzene, using ab initio molecular orbital theory at the STO-3G level, follow the same form of DSP equation and are approximately linearly related to C_p-SCS values.[2e]

Table I shows that C_p-SCS values depend strongly upon the solvent. Solute–solvent interactions lead to either modified substituent interaction or modified transmission of the substituent effect or both.[9,10] Any hope of obtaining inherent σ^0_R values from these shifts requires the use of nonpolar solvents to minimize solute–solvent interactions. We have therefore utilized σ_I values which are appropriate for hydrocarbon solvents[11] and have gone through several iterations of the C_p-SCS values in c-C_6H_{12} and CCl_4, using eq 1 in its general form (C_p-SCS = $\sigma_I\rho_I + \sigma^0_R\rho_R$) to determine whether the results converge to a precise set of σ^0_R values. This is indeed found to be the case, with σ^0_R values precise to ±0.01 or less. The values obtained are given in Table II, together with the σ_I values used. Also given in parentheses in Table II are values of σ_I and σ^0_R originally given by Ehrenson, Brownlee, and Taft[2d] (if these differ from the presently obtained values). The designation (–) indicates that no values were previously listed. Differences in the σ^0_R values are generally no greater than ±0.03 although values for Cl and CN differ by 0.05. The σ^0_R values obtained by Brownlee, Katritzky, and Topsom from IR intensity measurements of monosubstituted benzenes are also in generally good agreement.[12]

Table IV. DSP Fitting Parameters for C_p-SCS Values of Table I, Using σ_I and σ^0_R Values of Table II

solvent	π^a	ρ_I	ρ_R	λ	n	SD	f
c-C_6H_{12}	0.00	3.35	20.55	6.13	18	0.07	0.01
CCl_4	(0.19)	3.73	20.72	5.55	20	0.06	0.01
$CDCl_3$	(0.51)	4.54	21.54	4.74	15	0.11	0.02
acetone	0.68	4.95	21.81	4.41	19	0.22	0.04
DMF	0.88	5.32	21.93	4.12	17	0.27	0.05
Me_2SO	1.00	5.48	22.21	4.05	17	0.28	0.05

[a] Cf. ref 14; values in parentheses are those applicable to NMR shifts.

While the above mentioned differences in σ^0_R values are of little consequence with respect to DSP treatment of appropriate reactivity series data, there are substantial consequences with respect to physical property data sets which have a strong dependence upon π electron delocalization effects (i.e., for which $\lambda = \rho_R/\rho_I$ is 2 or greater). This point is illustrated in Table III by the comparison of the DSP fitting parameters for the C_p-SCS values in c-C_6H_{12}, CCl_4, and $CDCl_3$ obtained with the use of EBT parameters[2d] with the parameters of Table II. These fittings are based upon the substituents from Table I for which σ_I and σ^0_R values were listed by EBT.

Substituents are arranged in Table II according to increasing σ^0_R value. It is to be noted that the corresponding σ_I values do not follow this order. Indeed, a plot of σ^0_R vs. σ_I for values in Table II gives a highly scattered diagram. This high degree of noncorrelation remains true even when one considers –R π donors (negative σ^0_R values) as a separate class from +R π acceptor (positive σ^0_R value) substituents. This is a matter of crucial importance with respect to separation of inductive and resonance effects by DSP analysis.[2d] We suggest, therefore, that for the best such analysis (and, particularly, for modifications of DSP analysis) data be obtained with the following substituent basis sets: $N(CH_3)_2$ or NH_2, OCH_3, F, Cl or Br, CH_3, and H (the previously recommended basis set requirements of –R substituents[13]) plus CHO, CO_2R, or CH_3CO, as well as any two of CF_3, CN, and NO_2. The inclusion of $SOCH_3$, SO_2CH_3, or $SO_2C_6H_5$ and $COCF_3$ or COCN is also recommended for +R substituents.

Solvent Effects. Hydrogen bonding interaction between a substituent and solvent can lead to substantial

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Table V. Typical Observed and Calculated Solvent Induced C_p-SCS Values Compared with Cyclohexane Solution (in ppm)

	substituent													
	$N(CH_3)_2$		OCH_3		OC_6H_5		F		Cl		CF_3		NO_2	
solvent	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
$c\text{-}C_6H_{12}$	(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)
CCl_4	−0.03	−0.07	0.02	0.02	0.07	0.09	0.03	0.14	0.10	0.14	0.10	0.17	0.33	0.28
$CDCl_3$	−0.56	−0.47	0.09	−0.10	0.22	0.13	0.13	0.29	0.27	0.37	0.58	0.58	0.95	0.92
acetone	−0.86	−0.60	−0.12	−0.10	0.34	0.20	0.49	0.41	0.63	0.51	0.87	0.77	1.38	1.23
DMF	−0.93	−0.64	−0.04	−0.05	0.35	0.31	0.79	0.56	0.80	0.66	1.12	0.94	1.62	1.49
Me_2SO	−1.08	−0.78	−0.08	−0.12	0.44	0.28	0.68	0.56	0.83	0.68	1.20	1.02	1.75	1.63

Table VI

substituent	C_p-SCS	σ_I	σ^0_R
$C(CN)_3$	3.68[a]	0.94[b]	0.01
$Si(CH_3)_3$	0.52[c]	−0.10	0.04
SO_2Cl	6.66	0.86	0.17
SiF_3	6.13	0.45	0.22
BCl_2	6.56	0.04	0.31

[a] W. Adcock and D. P. Cox, *J. Org. Chem.*, **44** 3004 (1979). [b] Private communication from W. Adcock. [c] Private communication from W. F. Reynolds.

modifications in the electronic properties of the substituent.[5,11a] Consequently, no hydroxylic solvents are considered in this work. The solvents considered are all aprotic except for deuteriochloroform, which is only weakly protic. Likewise, with the exception of NH_2, only aprotic substituents are considered in this study. The NH_2 substituent is a hydrogen bond donor toward acetone, DMF, and Me_2SO,[5,9c] and accordingly, its C_p-SCS values in these solvents have been excluded from the correlations. Weak Lewis acid–base complexing occurs between Me_2SO and $COCF_3$ and COCN substituents,[11a] so the C_p-SCS values for these substituents are not included in the correlation analysis in Me_2SO.

The +R substituents, $SOCH_3$, SO_2CH_3, $COCH_3$, and CHO, are known to be moderately strong hydrogen bond acceptors.[5,11a] In accord with this, the C_p-SCS values for these substituents in deuteriochloroform are downfield of the corresponding values in acetone. The reverse order holds (cf. Table I) between these two solvents for all aprotic or weakly H-bond acceptor substituents, as expected for the greater polarity of the aprotic solvent, acetone. For this reason, the above substituents were excluded in correlations of the C_p-SCS in deuteriochloroform (cf. below). The −R substituents, $(NCH_3)_2$ and NH_2, are also known to be H-bond acceptor substituents.[5,11a] It was noted, however, that very satisfactory correlation analysis results are obtained with the C_p-SCS in deuteriochloroform if the NH_2 value is excluded but the $(NCH_3)_2$ value is included. It may be suggested that this follows because of steric hindrance to hydrogen bonding between the nitrogen lone pair of *N*,*N*-dimethylaniline and the $CDCl_3$.

Even with the exclusion of known specific solvent-substituent interactions, the effects of aprotic solvents on C_p-SCS values are remarkably diverse. Thus, for example, for the $N(CH_3)_2$ substituent there is a regular upfield shift in going to more polar aprotic solvents (cf. Table I). Between cyclohexane and M_2SO, the upfield solvent shift is −1.08 ppm (from −11.13 to −12.21). For the CH_3 and OCH_3 substituents, on the other hand, there is no significant solvent effect (−2.9 ± 0.1 and −7.8 ± 0.1 ppm, respectively). For the Cl, CF_3, and NO_2 substituents, for example, there is a regular downfield shift in going to more polar aprotic solvents. The magnitudes of these and of other downfield solvent induced shifts are widely variable. Between cyclohexane and Me_2SO, the solvent effects are +0.83 ppm for Cl, +1.20 ppm for CF_3, and +1.75 ppm for NO_2. Thus, the solvent induced shifts are not related to the corresponding C_p-SCS values in cyclohexane, or to any single substituent parameter, e.g., $\sigma_{(p)}$, σ_I, or σ^0_R.

The C_p-SCS values of Table I have been analyzed by the DSP equation, using the σ^0_R and σ_I values of Table II. Although the data sets in polar aprotic solvents are less precisely fitted by eq 1 than those in the nonpolar cyclohexane and carbon tetrachloride solvents, the fits are nonetheless of generally good quality (*f* is 0.02 to 0.05). The fitting parameters obtained from the correlations are given in Table IV. Both ρ_I and ρ_R values increase with increasing solvent polarity, correlating very well with the π^* values of Kamlet, Abboud, and Taft.[14] The increasing values of ρ_I are due to the increase in the π-inductive effect which results from increasing substituent–solvent dipole–dipole interaction.[10] The increasing values of ρ_R result from the increasing importance of resonance forms I and II that are induced by the substituent–solvent interactions.[15] The value of $\lambda = \rho_R/\rho_I$ decreases regularly with the solvent π^* value, showing that there are relatively greater effects of solvent polarity on the substituent induced polarization of the benzene π electrons than on π electron delocalization.[3]

The DSP equation treats remarkably well the diverse aprotic solvent induced C_p-SCS values. This is illustrated by typical results in Table V. Taking the solvent (S) induced shifts as $(C_p\text{-SCS})_S - (C_p\text{-SCS})_{c\text{-}C_6H_{12}}$, the DSP equation gives $(C_p\text{-SDS})_S - (C_p\text{-SCS})_{c\text{-}C_6H_{12}} = \sigma_I\Delta\rho_I + \sigma^0_R\Delta\rho_R$, where $\Delta\rho_I = \rho_{I(S)} - \rho_{I(c\text{-}C_6H_{12})}$ and $\Delta\rho_R = \rho_{R(S)} - \rho_{R(c\text{-}C_6H_{12})}$. The solvent induced C_p-SCS have been calculated and compared with the observed values in Table V by using the ρ_I and ρ_R values of Table IV and the σ_I and σ^0_R values of Table II. The agreement (average deviation is ±0.11 ppm for a range from −1.08 to +1.75 ppm) strongly supports the validity of DSP analysis since both *the sign* and *the magnitude* of the solvent induced C_p-SCS are strongly dependent upon the values of *both* σ^0_R and σ_I. The somewhat smaller calculated than observed values in DMF and Me_2SO are probably the result of weak Lewis acid–base interactions between these solvent molecules and substituents, e.g., CO_2R, $COCH_3$, CHO, CN, SO_2CH_3, and NO_2[11a] (as well as $COCF_3$ and COCN, as already noted). Such interaction would tend to give upfield shifted C_p-SCS and therefore reduce the ρ_I and ρ_R values.

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Appendix

C_p-SCS values in dilute carbon tetrachloride solution have been obtained for several additional substituents

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(14) M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977); J. L. Abboud, M. J. Kamlet, and R. W. Taft, *ibid.*, **99**, 8325 (1977).

(15) Cf. R. W. Taft, R. E. Glick, I. C. Lewis, I. Fox, and S. Ehrenson, *J. Am. Chem. Soc.*, **82**, 756 (1960).

which are of importance with respect to obtaining sets of π electron acceptor (+R) substituents having a high degree of nonlinearity between the σ_I and $\sigma^0{}_R$ values. Values of C_p-SCS and σ_I for these substituents and the $\sigma^0{}_R$ values defined by these results are given in Table VI.

Registry No. *N*,*N*-Dimethylaniline, 121-69-7; aniline, 62-53-3; anisole, 100-66-3; phenyl ether, 101-84-8; fluorobenzene, 462-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; toluene, 108-88-3; benzene, 71-43-2; methyl phenyl sulfoxide, 1193-82-4; α,α,α-trifluorotoluene, 98-08-8; benzophenone, 119-61-9; benzonitrile, 100-47-0; acetophenone, 98-86-2; ethyl benzoate, 93-89-0; phenyl sulfone, 127-63-9; methyl phenyl sulfone, 3112-85-4; nitrobenzene, 98-95-3; benzaldehyde, 100-52-7; 2,2,2-trifluoroacetophenone, 434-45-7; α-oxobenzeneacetonitrile, 613-90-1.

Influence of Steric Factors in the E2 Reaction. Calculation of Nonbonded Interactions and Minimum-Energy Trajectories for Base Approach in the E2 Reaction of Some Simple Alkyl Systems

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Results are presented for the evaluation of nonbonded interactions in the E2 reaction of several simple alkyl halide substrates. Minimum-energy trajectories of the base as it approaches the labile hydrogen are determined by using a Lennard–Jones 6/12 potential to describe the nonbonded interactions. These calculations are summarized as the repulsive force the base encounters when it is at its van der Waals radius from the labile hydrogen. These forces allow direct comparison of systems where isomeric reactions are possible as ratios of repulsive forces for the isomeric reaction geometries. Comparisons are made with bases of three different sizes (van der Waals radii = 3, 10, and 20 Å) and by their interactions with alkyl substrates with various alkyl substitution patterns (R = H, Me, Et, *i*-Pr, Pr, *t*-Bu, and Bu) around the E2 reaction center. These results establish a qualitative guide in succinctly stating the steric requirement of a base or departing leaving group in the E2 reaction.

Most base-promoted β-elimination reactions have been classified into the broad categories of E1, E1cB, or E2. These classifications have implied specific reaction pathways, and the general descriptions for these modes of reaction have been used to rationalize the orientational product selection for elimination reactions which yield the Hofmann and/or Saytzev alkenes.[1] Elimination reactions classified as E2, with the synchronous, antiperiplanar departure of both units of the molecule being eliminated, have been the focus of recent experimental and theoretical interest.[2] The goal of these investigations has been to understand and assess the factors which determine the product distribution in systems where there can be a selection between different isomeric E2 reaction pathways.

The base-promoted dehydrohalogenation of 2-alkyl halides is perhaps one of the most direct examples of the E2 reaction. In fact, the study of the various halide analogues in the 2-hexyl series by Bunnett has provided the foundations of the variable transition state theory.[3] In this theory, the amount of alkene character present at the transition state is specified as the determining factor in product selection. This description has been extremely successful in utilizing the relative thermodynamic stabilities of the isomeric alkene products as the primary predictors to explain qualitatively the orientational and geometrical selection between isomeric reaction pathways that are possible in these reactions. However, in several elimination reactions involving 2-alkyl halides and 2-alkyl arenesulfonates there have been product distributions reported that require the consideration of other experimental factors as modifiers to the amount of alkene character present in the transition state.[4-6] Even in the dehydrohalogenation of 2-halobutanes, changes in experimental parameters such as solvent, base size, and base strength have yielded product distributions that are inconsistent with the thermodynamic stabilities of the corresponding alkenes.[7]

One of the most obvious experimental factors that can modulate the relative free energies of isomeric reaction pathways is the distinctly different nonbonded interactions imposed by the different molecular geometries required for reactions leading to the isomeric products. These steric factors, associated with base size and the dimension and conformation of the leaving group, have been employed to explain changes in product distributions for many different systems.[7-9] Since it is the overall difference in free energy change that dictates the product selection, the steric factor must be assessed for the geometries required by each isomeric reaction pathway. Also, the change in free energy associated with steric influences is a duality of enthalpy and entropy, and even a very qualitative un-

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