(m, 1 H), 3.33 (m, 2 H), 4.18 (m, 1 H), 5.15 (t, J = 6.5 Hz, 1 H), 7.38 (m, 6 H), 7.66 (m, 4 H). Anal. Calcd for $C_{35}H_{52}O_4Si$: C, 74.42; H, 9.28. Found: C, 74.17; H, 9.20.

Allylic Alcohol 3. To a 50-mL, three-neck, round-bottom flask equipped with two addition funnels and a nitrogen inlet tube was added 5 mL of dry dichloromethane and 0.03 mL (0.024 mmol) of a 0.77 M solution of oxalyl chloride in CH_2Cl_2. The mixture was cooled to −78 °C, whereupon 0.05 mL (0.048 mmol) of a 0.94 M solution of dimethylsulfoxide in dichloromethane was added dropwise. After 2 min, 13 mg (0.023 mmol) of alcohol **23** in 5 mL of dichloromethane was added dropwise. Stirring was continued for 15 min, and 0.25 mL (0.12 mmol) of a 0.48 M solution of triethylamine in dichloromethane was added. After being stirred for 5 min at −78 °C, the mixture was warmed to room temperature, and 2 mL of water was added. The organic layer was washed again with water, dried over magnesium sulfate, and concentrated to provide 12 mg (95%) of crude aldehyde, which was used immediately and without further purification. The above crude aldehyde was dissolved in 10 mL of dichloromethane along with 12 mg (0.035 mmol) of (carbethoxymethylene)triphenylphosphorane, and the mixture was heated at reflux for 2.5 h. The solvent was removed, and the residue was flash chromatographed to afford 12 mg (90%) of the unsaturated ester **24**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.76 (d, J = 6.5 Hz, 3 H), 0.95 (d, J = 6.5 Hz, 3 H), 0.96 (d, J = 6.5 Hz, 3 H), 1.04 (s, 9 H), 1.28 (t, J = 7 Hz, 3 H), 1.55 (br s, 3 H), 1.80–2.60 (band, 5 H), 3.10 (dq, J = 6.5 Hz, 10 Hz, 1 H), 3.24 (m, 1 H), 4.16 (m, 1 H), 4.17 (q, J = 6.5 Hz, 2 H), 5.10 (t, J = 6.5 Hz, 1 H), 5.75 (dd, J = 14.9 Hz, 1.9 Hz, 1 H), 6.90 (dd, J = 14.9 Hz, 7.5 Hz, 1 H), 7.38 (m, 6 H), 7.66 (m, 4 H).

The ester **24** was immediately reduced as follows: To a 50-mL, three-neck, round-bottom flask equipped with an addition funnel and a nitrogen inlet tube was added 10 mL of dry THF and 0.1 mL (0.1 mmol) of 1 M diisobutylaluminum hydride in hexanes. The mixture was cooled to −78 °C, and 12 mg (0.019 mmol) of ester **24** in 5 mL of THF was added dropwise. Stirring was continued for 30 min, and the reaction was quenched with 10% HCl and diluted with ether. The ether layer was dried over magnesium sulfate and concentrated to give 9 mg (80%) of allylic alcohol **3**, which was spectrally identical with that prepared by Williams: IR ($CDCl_3$) 3610, 1430 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (d, J = 6.5 Hz, 3 H), 0.91 (d, J = 6.5 Hz, 3 H), 0.95 (d, J = 6.5 Hz, 3 H), 1.04 (s, 9 H), 1.10–1.75 (band, 9 H), 1.54 (br s, 3 H), 1.75–2.40 (band, 5 H), 3.11 (dq, J = 6.5 Hz, 10 Hz, 1 H), 4.17 (m, 1 H), 5.08 (t, J = 6.5 Hz, 1 H), 5.58 (m, 2 H), 7.39 (m, 6 H), 7.66 (m, 4 H).

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Empirical Correlations in Ultraviolet Spectra of Substituted Benzenes. 2. Compounds with Electron-Releasing "Parent Groups"

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The first paper[2] of this series presented an empirical procedure for estimating the position of the "primary band" in the ultraviolet absorption spectra of substituted benzenes having electron-withdrawing "parent groups". This paper extends the procedure to 424 substituted benzenes that have only electron-releasing substituents. These involve 29 electron-releasing "parent groups" and 17 of these groups serving as secondary substituents ortho, meta, or para to the parent group.

The first paper[2] of this series presented an extension of the empirical method of Scott[3] for estimating the position of the "primary band " in the ultraviolet absorption spectra of substituted benzenes having electron-withdrawing "parent groups". The present paper reports the results of applying the same purely empirical, multiple-linear-regression procedures to data on benzenes, biphenyls, and polyphenyls having only electron-releasing substituents. Again, compounds with single substituents were considered as "parent compounds" and the substituents were arranged in a priority order according to the λ_{max}'s of the parent compounds. The statistical treatment yielded empirical "base values" for the λ_{max}'s of the parent compounds and values for increments due to substituents ortho, meta, or para to the parent group. For estimation of the calculated λ_{max} of a given compound, the highest priority substituent was used as the parent group, and to the base value for that parent compound were added increments for the other substituents present.

Methods

Data. This study was based entirely on data taken from the literature.[3-6]

The "standard" solvent selected was MeOH or EtOH, but some data for aqueous solutions were used. A water-solvent correction was calculated by the same procedures used for substituent increments.

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Table I. Base Values and Substituent Increments

	base values and increments, nm (10^3 cm^{-1})				
substituent, Y	base value for PhY	ortho effect[a]	ortho increment[b]	meta increment	para increment
NPh_2	293 (34.4)	*c*	*c*	*c*	*c*
NPhAlk	292 (34.2)[d]	*c*	*c*	*c*	*c*
NHPh	279 (36.1)	−4 (0.4)	16 (−2.1)[d]	*c*	29 (−3.6)[d]
Ph-4-Ph[e]	277 (36.3)	−11 (1.9)[f]		1 (−0.1)[g]	
cyclohexeno[h]	263 (38.1)	0 (0)			
SAlk	256 (39.0)	*c*	*c*	*c*	*c*
$NAlk_2$[i]	256 (39.1)	0 (0.1)	*c*	*c*	*c*
$CH{=}CR_2$[j]	249 (40.1)	−4 (0.7)	8 (−1.2)[d]	*c*	*c*
Ph	249 (40.2)	−11 (1.9)	3 (−0.6)	1 (−0.1)	15 (−1.8)
SPh	248 (40.4)	0 (−0.1)	*c*	*c*	*c*
Ph-3-Ph[k]	248 (40.4)	−11 (1.9)[f]		1 (−0.1)[g]	
NMe_2	246 (40.6)	3 (−0.5)	−14 (2.5)[d]	8 (−1.2)[d]	25 (−3.5)
NHAlk[i]	245 (40.8)	−2 (0.3)	*c*	*c*	9 (−1.5)
NHC(O)R[l]	241 (41.4)	−2 (0.5)	−1 (2.0)	−7 (1.4)	19 (−2.5)
$CAlk{=}CR_2$[j]	241 (41.5)[d]	−8 (1.3)[d]	*c*	*c*	*c*
NHMe	240 (41.6)	3 (−0.5)	*c*	*c*	20 (−2.7)
SH	240 (41.6)	−5 (0.9)[d]	*c*	*c*	*c*
O^-	239 (42.0)	0 (0)	1 (−0.2)	6 (−1.1)	3 (−0.5)
NH_2	234 (42.7)	0 (0)	−2 (0.3)	5 (−0.8)	11 (−1.7)
Ph-2-Ph[m]	233 (42.8)	−11 (1.9)[f]		1 (−0.1)[g]	
I	227 (43.9)	0 (0)	5 (−0.8)	4 (−0.6)	12 (−2.0)
OPh	225 (44.3)	−3 (0.6)	*c*	*c*	*c*
CCl_3	224 (44.5)	1 (0.1)	*c*	*c*	12 (−2.1)
OAlk	218 (45.7)	0 (0.1)	2 (−0.4)	2 (−0.3)	6 (−0.8)
Br	216 (46.3)	−2 (0.4)	4 (−0.6)	4 (−0.7)	9 (−1.5)
OH	215 (46.3)	0 (−0.1)	4 (−0.7)	2 (−0.2)	7 (−1.0)
Cl	214 (46.6)	0 (−0.2)	2 (−0.3)	4 (−0.7)	8 (−1.4)
Alk	208 (48.0)	2 (−0.6)	1 (−0.1)	1 (−0.1)	3 (−0.6)
F	205 (48.9)	0 (0)	−1 (0.3)	−1 (0.2)	−2 (0.4)
H_2O solvent[n]					

[a] Characteristic of Y as *parent* group, with any ortho substituent. [b] Increment for Y *ortho* to a parent group. [c] Data unavailable. [d] Based on a single observation. [e] *p*-Terphenyl. [f] Ortho effect for terphenyls = ortho effect for biphenyl. [g] Meta increment for 2-, 3-, or 4-biphenylyl = *m*-Ph increment. [h] 1,2-Dihydrodnaphthalene. [i] Alk > Me. [j] R's = H or Alk. [k] *m*-Terphenyl. [l] R = Alk or NH_2. [m] *o*-Terphenyl. [n] Solvent = MeOH or EtOH unless otherwise noted. For H_2O solvent: −4 nm (0.6×10^3 cm^{-1}).

Many of the λ_{max}'s used were averages of two or more measurements.

A few of the base values and substituent increments listed in Table I are based on single observations. These λ_{max}'s and increments were not used in the statistical treatment of the data.

Mathematical Procedures. At the beginning of this study, the procedures of the first paper of this series[2] were used, involving the CDC Cyber 171 computer, Fortran programs, and SPSS[7] for the multiple-regression estimation of parameters. Later, other families of compounds were added to the data base, and the entire process was transferred to a Commodore 128 microcomputer. FORTRAN was replaced by BASIC programs, and the computations were aided by an Abacus Software Basic 128 compiler. In the multiple-regression process, the final system of linear equations was solved by a Gauss–Seidel iterative method[8] rather than by manipulation of the large matrices by the microcomputer.

Computations were performed for frequencies (10^3 cm^{-1}) as well as wavelengths.

Results and Discussion

Scope of the Study. The procedures were applied successfully to 424 substituted benzenes and polyphenyls, involving 29 electron-releasing "parent groups" and 17 of these groups serving as secondary substituents ortho, meta, or para to the parent group.

Hierarchical Arrangement of Substituents. As is evident in Table I, the substituents were finally arranged in order of decreasing calculated λ_{max}, rather than experimental[2] λ_{max} of the parent compounds.

Ortho Effect. The para-substituted compounds in this series did not show the anomalous behavior of compounds having an electron-releasing substituent para to an electron-withdrawing group.[2] On the other hand, ortho-substituted compounds having only electron-releasing substituents, especially the polyphenyls, showed anomalies. Hence, an "ortho effect" for each parent compound was included among the parameters to be evaluated. As expected, of the 26 ortho effects (in terms of wavelength) for which data were available, nearly half (10) were 0 and about half (12) were hypsochromic (indicating steric hindrance). Four, however, were bathochromic. As expected also, the polyphenyls and α-substituted styrenes showed especially large hypsochromic ortho effects.

Inclusion of ortho effects and the water-solvent correction raised to 90 the number of parameters to be evaluated.

The Styrenes. At first the styrenes were all lumped together; but discrepancies finally forced their separation into three groups: 1,2-dihydronaphthalenes, $PhCH{=}CR_2$, and $PhC(Alk){=}CR_2$. Although the unsaturated six-membered ring of 1,2-dihydronaphthalene needed separate treatment, the five-membered ring of the indenes could be treated satisfactorily as an ortho-substituted styrene.

The Polyphenyls. Similarly, the polyphenyls, all lumped together at first as substituted biphenyls, had to be separated into *p*-terphenyls, *m*-terphenyls, *o*-terphenyls, and biphenyls.

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Table II. Comparison of Observed and Calculated Absorption Positions for Selected Compounds

compd no.	compd[a]	solvent[b]	λ, nm		ref[c]	compd. no.	compd.[a]	solvent[b]	λ, nm		ref[c]
			obsd	calcd − obsd					obsd	calcd − obsd	
1	PhN(Ph)$_2$		296	-3	4b	43	PhSH		238	2	*f*
2	-4-Cl		298	3	4b	44	-3-NH$_2$		248	-3	4b
3	PhNHPh		282	-3	4b	45	PhO$^-$		238	1	5 (1)
4	-4-NMe$_2$		299	5	4b	46	PhO$^-$	H_2O	233	2	5 (2)
5	-2-NH$_2$		276	-3	4b	47	-3-O$^-$	H_2O	238	3	5 (1)
6	PhPh-4-Ph		276	1	4b	48	-2,4-(O$^-$)$_2$	H_2O	239	0	5 (11)
7	-4,4″,4‴-Ph$_3$[d]		318	4	6	49	-2,3-Cl$_2$	H_2O	241	0	5 (2)
8	-4,4″-(OH)$_2$		294	-3	5 (8)	50	PhNH$_2$		234	0	*f*
9	1,2-dihydronaphthalene		262	1	3	51	-2-NH$_2$-4-I		244	0	4b
10	-5-OH[e]		267	0	3	52	-2,4,6-I$_3$		255	1	4a
11	PhSMe		256	0	*f*	53	-2,5-(OMe)$_2$-4-Cl		241	5	4b
12	-4-Me		265	-6	4b	54	-3,4-Cl$_2$		247	-1	4b
13	PhNAlk$_2$[g]		257	-1	*f*	55	PhPh-2-Ph		233	0	5 (1)
14	-4-NH$_2$		263	4	5 (16)	56	-4,4′-(NH$_2$)$_2$[j,k]		240	4	5 (8)
15	-2-Br		260	0	5 (6)	57	-4,4″-(OH)$_2$		248	-1	5 (1)
16	PhCH=CR$_2$[h]		247	2	*f*	58	PhI		226	1	4b
17	-3,4-(OAlk)$_2$		262	-5	*f*	59	-3,5-I$_2$		232	3	4b
18	-2,6-Cl$_2$		239	6	4b	60	-3-Br		235	-4	4b
19	PhPh		247	2	4a	61	PhOPh		225	0	5 (2)
20	-4,4′-(NH$_2$)$_2$		268	3	4b	62	-2-OMe		228	-4	4b
21	-4,4′-(NH$_2$)$_2$-2,2′-Me$_2$		250	1	4b	63	PhCCl$_3$		225	-1	4b
22	-2,2′,4,4′-(OH)$_4$		255	-6	4b	64	-4-CCl$_3$-2,5-Cl$_2$		242	1	4b
23	PhSPh		250	-2	4b	65	PhOAlk		218	0	*f*
24	-4-OH-3-Me		248	8	4b	66	-3,5-(OH)$_2$		215	7	4a
25	-4-CH(OH)Ph		253	-2	4b	67	-2,4-Cl$_2$		229	-1	4b
26	PhPh-3-Ph		247	1	5 (1)	68	-3,4-Me$_2$		219	3	4b
27	-2,3″-Ph$_2$		239	2	5 (1)	69	PhOH		218	-3	3
28	m-C$_6$H$_5$(C$_6$H$_4$)$_{14}$C$_6$H$_5$		255	6	6	70	-4-OH-2,3-Me$_2$		225	-1	4b
29	PhNMe$_2$		251	-5	4b	71	-3,5-Cl$_2$		220	3	4b
30	-2-OMe		242	9	4b	72	-2,4-Alk$_2$		218	1	*f*
31	-3-OH		251	-3	5 (1)	73	PhBr	H_2O	210	2	6
32	-2,4,6-Me$_3$		258	-1	5 (1)	74	-3-Br-4-OH		223	2	4b
33	PhNHAlk[g]		248	-3	*f*	75	-4-OH		226	-3	4b
34	-4-NHEt		255	-1	5 (2)	76	PhCl	H_2O	210	0	6
35	PhNHAc/NHC(O)NH$_2$		241	0	*f*	77	-2,4,5-Cl$_3$		232	-4	4b
36	-2-NHAc		244	-6	5 (2)	78	-2-F		214	-1	4b
37	-3-NHAc		233	1	5 (1)	79	PhAlk		208	0	*f*
38	-4-Me		240	4	4a	80	-3-F		207	0	4b
39	PhCAlk=CH$_2$/CAlk=CHAlk		241	0	*i*	81	-4-F		206	0	4b
40	-2,5-Me$_2$		235	0	3	82	PhF		204	1	5 (1)
41	PhNHMe		243	-3	4b	83	-4-F		204	-1	5 (4)
42	-2-Cl		246	-1	4b						

[a] Compounds are listed in order of descending priority of parent groups and then of other substituents. [b] Solvent = MeOH or EtOH unless otherwise noted. [c] Volume number in parentheses. [d] p-Sexiphenyl. [e] OH ortho to double bond. [f] Composite: ref 4b, 5. [g] Alk > Me. [h] R's = H or Alk. [i] Composite: ref 3. [j] Note o-terphenyl used as parent compound, NH$_2$ as secondary substituent, although NH$_2$ has higher priority. [k] 4′-NH$_2$ substituent on middle ring is ignored.

As stated below in the rules for using Table I, the available data indicate that the polyphenyls should be given highest priority in the selection of a parent compound.

The p-polyphenyls have been treated in the usual way, so that the calculations yield a base value for the parent p-terphenyl and a suitable increment for each additional p-phenyl substituent. The calculated λ_{max}'s agree satisfactorily with the experimental values through p-sexiphenyl (compound 7, Table II), although the experimental λ_{max}'s may actually be approaching asymptotically a maximum value, as suggested by Jaffé and Orchin.[6]

Similarly, for the m-polyphenyls, λ_{max}'s calculated from a base value for m-terphenyl and a small increment for each additional m-phenyl substituent yield satisfactory values through the 16-ring compound (compound 28, Table II). For all these compounds, Jaffé and Orchin[6] propose a constant λ_{max} of 253 nm.

Solvent. A brief examination of data for some of these compounds in hydrocarbon or chloroform solvents disclosed no significance deviations from the data for solutions in the "standard" MeOH or EtOH. As shown in Tables I and II, however, H$_2$O solvent has a significant hypsochromic effect. This is in contrast with the slightly smaller bathochromic effect of H$_2$O solvent for compounds having an electron-withdrawing parent group.[2]

Rules for Using Table I To Estimate λ_{max}. 1. Use as parent group the substituent of highest priority in Table I.

a. Exceptions: If biphenyl or polyphenyl groupings are present, use these as parents, in the priority order p-terphenyl > m-terphenyl > o-terphenyl > biphenyl > NPh$_2$ > NHPh, etc.

b. If two or more highest priority groups of the same kind are present, use the one that gives the highest estimate of λ_{max}.

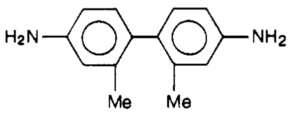
2. Add increments from Table I for other substituents ortho, meta, or para to the parent group.

a. If two or more benzene rings are present, then proceed as follows. (1) If the parent compound is biphenyl or a terphenyl, add increments for all substituents on all rings. (a) Exception: Ignore substituents on the middle ring of *o*-terphenyl. (2) If the parent compound is not biphenyl or a terphenyl, add increments for the substituents on only one benzene ring. (a) Choose the ring that gives the highest estimate of λ_{max}.

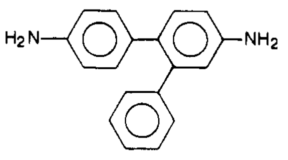
b. Include the ortho effect for the parent compound if there are ortho substituents.

c. Include the H_2O-solvent increment when appropriate.

Examples:

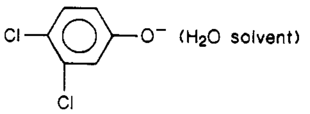


base value		249 nm		40.2×10^3 cm^{-1}
4,4′-$(NH_2)_2$:	2 × 11 =	22	2 × (−1.7) =	−3.4
2,2′-Me_2:	2 × 1 =	2	2 × (−0.1) =	−0.2
o,o′ effect:	2 × (−11) =	−22	2 × 1.9) =	3.8
calcd		251 nm		40.4×10^3 cm^{-1}
obsd		250		40.0



56

base value	233 nm	42.8×10^3 cm^{-1}	(rule 1.a.)
4-NH_2	11	-1.7	
4′-NH_2	0	0.0	(rule 2.a.(1)(a))
calcd	244 nm	41.1×10^3 cm^{-1}	
obsd	240	41.7	



base value	239 nm	42.0×10^3 cm^{-1}
3-Cl	4	−0.7
4-Cl	8	−1.4
H_2O solvent	−4	0.6
calcd	247 nm	40.5×10^3 cm^{-1}
obsd	244	41.0

Table II presents a sampling of the experimental and calculated results. For all 424 compounds, the standard deviation between calculated and experimental wavelengths was 4.16 nm (1.72% relative error). For 73 compounds, the deviation was 0 nm; for 263, 1–4 nm; for 79, 5–8 nm; and for 9, >8 nm. The maximum deviation was 12 nm.

For the calculated frequencies, the standard deviation from experimental frequencies was 0.702×10^3 cm^{-1} (1.69% relative error). For 39 compounds, the deviation was 0×10^3 cm^{-1}; for 286, $(0.1–0.7) \times 10^3$ cm^{-1}; for 93, $(0.8–1.4) \times 10^3$ cm^{-1}; for 6, $>1.4 \times 10^3$ cm^{-1}. The maximum deviation was 1.7×10^3 cm^{-1}.

The small number of deviations greater than 2 standard deviations (>8 nm or $>1.4 \times 10^3$ cm^{-1} were scattered among 321 compounds above diphenyl ether in the priority listing.

In this set of data, where the ratio of range of wavelengths to mean wavelength is comparable to the ratio of range of frequencies to mean frequency, the relative error for the calculated frequencies is nearly equal to that for the calculated wavelengths.

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