R^2 = *t*-Hx, R^3 = Hx), 42437-34-3; **6a**, 23418-81-7; **6b**, 42371-64-2; **6c**, 53535-83-4; **6d**, 42928-43-8; **6e**, 100019-68-9; **6f**, 99966-24-2; **6g**, 38050-71-4; **6h**, 99966-25-3; **7**, 6224-91-5; **8**, 100019-67-8; **10a**, 99966-26-4; **10b**, 99966-27-5; **10c**, 99966-28-6; **10d**, 99966-29-7; **10e**, 99966-30-0; **10f**, 99966-31-1; **10g**, 99966-32-2; **10h**, 99966-33-3; **12**, 38050-70-3; **13**, 99966-34-4; **14**, 99966-35-5; **15**, 18162-76-0; **16**, 99966-36-6; **17**, 99966-37-7; TMANO, 1184-78-7; 9-BBN, 280-64-8; BMS, 13292-87-0; *n*-HxOH, 111-27-3; 2-HxOH, 626-93-7; *t*-HxOH, 594-60-5; *c*-HxOH, 108-93-0; $LiCH_2SiMe_3$, 1822-00-0; 1,4-pentadiene, 591-93-5.

Supplementary Material Available: Infrared and mass spectral data for the oxaborabicyclo[3.3.2]decanes (**10**) (1 page). Ordering information is given on any current masthead page.

Empirical Correlations in Ultraviolet Spectra of Substituted Benzenes. 1. Compounds with Electron-Withdrawing "Parent Groups"

Edward J. Cowles[1]

Department of Chemistry, University of Minnesota—Duluth, Duluth, Minnesota 55812

Received July 29, 1985

The empirical method of Scott[2c] for estimating the position of the "primary band" in the ultraviolet absorption spectrum of substituted benzenes has been expanded to achieve satisfactory agreement between calculated and experimental λ_{max}'s (and ν_{max}'s) for 536 different compounds. These involve eight electron-withdrawing "parent groups" and twelve electron-releasing secondary substituents, plus six of the electron-withdrawing groups serving as secondary substituents. The procedures were able to accommodate compounds with strongly electron-releasing substituents para to strongly electron-withdrawing groups.

An empirical method[2a,b] of predicting the UV λ_{max} of polyenes and α,β-unsaturated carbonyl compounds has been valuable in confirming the structures of such organic molecules. Scott[2c] has extended the method to predict the λ_{max} of the "primary band" in the spectra of substituted benzenes (the 203-nm band of benzene itself). His work was limited to compounds having "parent groups" of the type C(O)Z and electron-releasing secondary substituents. The predicted λ_{max} of a given compound is given by eq 1,

$$\lambda_{max} = (\lambda_{max})_{parent} + \sum \Delta_i \qquad (1)$$

where $(\lambda_{max})_{parent}$ is an empirically assigned value for $C_6H_5C(O)Z$ and the Δ_i are empirically determined increments for electron-releasing secondary substituents positioned ortho, meta, or para to the parent group.

The present study was a (successful) attempt (a) to broaden the range of Scott's method with respect to both (electron-withdrawing) parent groups and secondary substituents and (b) to obtain the required parent λ_{max}'s or base values, as well as the substituent increments, by a systematic linear-regression procedure applied to the whole set of data.

Methods

Data. The study was based almost entirely on data taken from the literature, chiefly the "CRC Atlas of Spectral Data and Physical Constants for Organic Compounds"[3] and "Organic Electronic Spectral Data".[4] Spectra obtained in this laboratory were run on a Bausch and Lomb Spectronic 2000 Spectrophotometer.

The "standard" solvent selected was MeOH or EtOH, but some data for solutions in water or hydrocarbon solvents were used, and solvent corrections were calculated for these solvents, the solvent parameters being handled in the statistical treatment in the same way as substituent increments.

Many of the λ_{max}'s used were averages of two or more measurements (rounded to the nearest even number where there was a choice).

At least two examples of each type of substitution (e.g., substituent Y meta to specific parent group Q) were used.

Mathematical Procedures. Computations were done with the CDC Cyber 171 computer at the University of Minnesota—Duluth.

FORTRAN programs were used to prepare the data (including modified Wiswesser line-notation formulas) for presentation to the multiple-regression-analysis program of the "Statistical Package for the Social Sciences" (SPSS).[5] With the base values and substituent increments thus obtained, FORTRAN programs were used again for obtaining calculated values of λ_{max}'s and comparing these with the measured values.

The same calculations were performed for wavelengths converted into frequencies (10^3 cm^{-1}).

Results and Discussion

This study has been entirely empirical and is based on no assumptions concerning the nature of the electron

---

[1] University of Minnesota—Duluth

[2] (a) Fieser, L. M.; Fieser, M. "Steroids"; Reinhold: New York, 1959; pp 15–24. (b) Woodward, R. B. *J. Am. Chem. Soc.* **1941**, *63*, 1123; **1942**, *64*, 72, 76. (c) Scott, A. I. "Interpretation of the Ultraviolet Spectra of Natural Products"; Pergamon Press: New York, 1964. (d) For example: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981. Pavia, D. L.; Lampman, G. M.; Kriz, G. S. "Introduction to Spectroscopy: A Guide for Students of Organic Chemistry"; W. B. Saunders: Philadelphia, 1979. Williams, D. H.; Fleming, I. "Spectroscopic Methods in Organic Chemistry", 2nd ed.; McGraw-Hill: London, 1970.

[3] (a) "CRC Atlas of Spectral Data and Physical Constants for Organic Compounds"; Grasselli, J., Ed.; CRC Press: Cleveland, OH, 1973. (b) "CRC Atlas of Spectral Data and Physical Constants for Organic Compounds", 2nd ed.; Grasselli, J. G., Ritchey, W. M., Eds.; CRC Press: Cleveland, OH, 1975.

[4] "Organic Electronic Spectral Data", Phillips, J. P., et al., Eds.; Wiley: New York, 1946–1974; Vol. 1-16.

[5] Nie, N.; Bent, D. H.; Hull, C. H. "Statistical Package for the Social Sciences"; McGraw-Hill: New York, 1970; Chapter 15.

0022-3263/86/1951-1336$01.50/0

transitions involved in absorptions at the observed wavelengths. The observed λ_{max}'s are assumed to represent displacements of the 203-nm band in the spectrum of benzene itself. With suitable empirical modifications, the procedure was successfully applied even to compounds like *p*-nitroaniline, in which the electronic system of benzene has presumably been radically altered.

Scope of the Study. The procedures were applied successfully to 536 different substituted benzenes involving eight electron-withdrawing parent groups and twelve electron-releasing substituents, plus six of the parent groups serving as additional secondary substituents. The numerical results showed that some sets of substituents could be treated as single substituents. Thus the following sets of parent substituents could be grouped together: COOH and COOAlk; CN and $CONH_2$; SO_3H and SO_2NR_2. Likewise the following sets of secondary substituents could be grouped together: all alkyl groups or ring residues; NHC(O)Alk and $NHC(O)NH_2$; OAlk and OPh; COOH, COOAlk, CN, and $CONH_2$. For this reason, and because of averaging of λ_{max}'s, the 536 "substituted benzenes" represent more than 1000 individual λ_{max} readings.

Para-Substituted Compounds. In the first round of calculations, para-substituted compounds were treated like ortho- or meta-substituted compounds, thus yielding a constant para increment as well as constant ortho and meta increments for each electron-releasing substituent. Such treatment cannot accommodate compounds like *p*-nitroaniline, which have a strongly electron-releasing substituent para to a strongly electron-withdrawing group. (For this reason, Scott[2c] excluded the nitro group as a parent group.) When, for strongly electron-releasing para substituents, the displacement of λ_{max} from the parent λ_{max} is plotted vs. the displacement of the parent λ_{max} from the 203-nm position for benzene itself, curves are produced which can be represented by parabolic equations. Thus, for substituent Y para to parent group Q,

$$\Delta_Y = A_Y + B_Y(\Delta_Q) + C_Y(\Delta_Q)^2 \qquad (2)$$

where

$$\Delta_Y = \lambda_{max}(p\text{-}YC_6H_4Q) - \lambda_{max}(C_6H_5Q)$$

$$\Delta_Q = \lambda_{max}(C_6H_5Q) - 203\text{ nm}$$

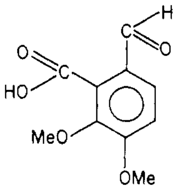
As is indicated in Table I, eq 2 was required for the following para substituents: NMe_2, O^-, NH_2, NHAc, Ph, OH, OAlk, and I. For these the same kind of treatment was needed when wavelengths were converted to frequencies. For all other substituents, constant para increments were satisfactory (as were constant ortho and meta increments for all substituents).

This special treatment of these para substituents raised to 79 the number of independent variables presented to the SPSS linear-regression program.

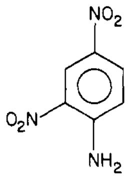
Hierarchical Arrangement of Substituents. In the first stages of this study, no more than one electron-withdrawing group was allowed in a compound. The fact that F ortho or meta, Cl meta, and Br ortho to an electron-withdrawing parent group were found to exert a hypsochromic effect suggested that the halogens here were behaving like electron-withdrawing groups. The possibility, therefore, emerged of including other electron-withdrawing substituents besides the parent group. The question of which group to use then as the parent group was settled on the basis of an early observation by Doub and Vandenbelt:[6] "Where two groups of the same type are opposed this band is displaced but slightly compared to that of the most displaced monosubstituted compound." Thus the electron-withdrawing groups should be arranged in a hierarchy according to the λ_{max} of the parent monosubstituted benzene: NO_2 > C(O)Ar > CHO > C(O)Alk > COOH = COOAlk > $CONH_2$ = CN > SO_3H = SO_2NR_2 > $AsO(OH)_2$. Then the parent group will be the group of highest priority in this series. Thus 3-methyl-5-nitrobenzoic acid will be treated as a substituted nitrobenzene instead of a substituted benzoic acid. Such a procedure successfully included many compounds containing more than one electron-withdrawing substituent. As expected, the ortho and meta increments ($\Delta\lambda$) for these groups were found to be negative. Para increments for all substituents, however, are positive.

In Tables I, II, and III the substituents are not arranged in alphabetical order: the electron-withdrawing groups are arranged in the order given above; and the electron releasing groups, in order of decreasing sums of their ortho, meta, and average para increments.

Rules for Using Table II To Estimate λ_{max}. Use as the parent group the electron-withdrawing substituent. To its base value add increments from Table II for other substituents. If two or more electron-withdrawing substituents are present, use as the parent group the one of highest priority in Table II. If two or more electron-withdrawing groups of the same kind are present, use as parent group the one that yields the highest estimate of λ_{max}. Examples:



I



base value (CHO)	246 nm		
p-OMe	+24	base value	258 nm
m-OMe	+8	*p*-NH_2	+112
o-COOH	-2	*m*-NO_2	-28
λ_{max}, calcd	276 nm	λ_{max}, calcd	342 nm
λ_{max}, exptl	285 nm[3b]	λ_{max}, exptl	336 nm[3b]
estimated λ_{max} with COOH as parent group =	243 nm	estimated λ_{max} with other NO_2 as parent group =	249 nm

Table III presents a sampling of the experimental and calculated results. For all 536 compounds, the standard deviation between calculated and experimental λ_{max}'s was 5.64 nm (2.15% relative error). For 51 compounds, the deviation was 0 nm: for 338, 1–5 nm; for 116, 6–10 nm; for 26, 11–13 nm; for 5, >13 nm. Maximum deviation = 16 nm.

For the calculated frequencies, the standard deviation from experimental λ_{max}'s was 0.717×10^3 cm^{-1} (1.86% relative error). For 29 compounds the deviation was 0×10^3 cm^{-1}: for 360, $(0.1\text{–}0.8) \times 10^3$ cm^{-1}, for 124, $(0.9\text{–}1.5) \times 10^3$ cm^{-1}, for 20, $(1.6\text{–}1.9) \times 10^3$ cm^{-1}; for 3, $>1.9 \times 10^3$ cm^{-1}. Maximum deviation = 2.1×10^3 cm^{-1}.

Of 39 deviations greater than 9 nm between experimental and calculated λ_{max}'s, 23 were negative and 16 positive. Included in these 39 compounds were the following: nitrobenzenes, 19 (12.6% of total number of nitrobenzenes examined); benzophenones, 6 (11.8%); benzaldehydes, 3 (5.0%); acetophenones, 4 (5.1%); benzoic acids, 6 (5.0%); benzenesulfonamide, 1 (2.6%). Occurrences of secondary substituents in these 39 compounds were as follows: *p*-OH, 10 (14.5% of total number of oc-

---

(6) Doub, L.; Vandenbelt, J. M. *J. Am. Chem. Soc.* **1949**, *71*, 2414.

Table I. Parameters for Calculating Para-Substituent Increments

	parent group							
	NO_2	C(=O)Ph	CHO	C(=O)Alk	COOH COOAlk	C(=O)N- H_2 CN	SO_2OH SO_2NR_2	$AsO(OH)_2$
$\Delta\lambda_0$, nm[a]	57	49	41	39	25	21	17	13
$\Delta\nu_0$, 10^3 cm^{-1} [a]	−10.8	−9.6	−8.3	−7.9	−5.4	−4.6	−3.8	−3.0

	para substituent							
	NMe_2	O^-	NH_2	NHAc	Ph	OH	OR	I
A_λ[b]	108	101	62	48	43	18	42	51
A_ν[c]	−16.3	−19.5	−10.8	−9.4	−7.9	−4.0	−8.4	−10.4
B_λ[b]	−2.4645	−3.6740	−1.2208	−0.8875	−0.3602	0.0222	−1.8533	−1.8427
B_ν[c]	−1.8135	−3.7555	−1.1102	−1.1896	−0.5096	−0.2781	−1.8690	−1.9959
C_λ[b]	0.0508	0.0767	0.0368	0.0186	0.0073	0.0060	0.0347	0.0277
C_ν[c]	−0.1443	−0.3044	−0.1131	−0.0926	−0.0308	−0.0353	−0.1549	−0.1387

[a] $\Delta\lambda_0 = (\lambda_{max})_{parent} - 203$ nm; $\Delta\nu_0 = 10^4/(\lambda_{max})_{parent} - 10^4/203$. [b] Para increment: nm = $A_\lambda + B_\lambda(\Delta\lambda_0) + C_\lambda(\Delta\lambda_0)^2$. [c] Para increment: $10^3 cm^{-1} = A_\nu + B_\nu(\Delta\nu_0) + C_\nu(\Delta\nu_0)^2$.

Table II. Base Values and Substituent Increments[c]

	parent group							
	NO_2	C(=O)Ph	CHO	C(=O)Alk	COOH COOAlk	C(=O)N- H_2 CN	SO_3H SO_2NR_2[a]	$AsO(OH)_2$
base value, nm	258	249	246	243	229	226	218	219
(base value, $10^3 cm^{-1}$)	(39.0)	(40.2)	(40.6)	(41.2)	(43.4)	(44.0)	(45.4)	(45.4)

substituent	ortho increment, nm ($10^3 cm^{-1}$)	meta increment, nm ($10^3 cm^{-1}$)	para increment, nm ($10^3 cm^{-1}$) NO_2	C(=O)Ph	CHO	C(=O)Alk	COOH COOAlk	C(=O)N- H_2 CN	SO_3H SO_2NR_2[a]	$AsO(OH)_2$
NMe_2	17 (−2.6)	2 (−0.2)	133 (−13.5)	109 (−12.2)	92 (−11.2)	89 (−11.0)	78 (−10.7)	79 (−11.0)	81 (−11.5)	85 (−12.2)
O^-	11 (−1.7)	19 (−2.6)	141 (−14.4)	105 (−11.5)	79 (−9.3)	74 (−8.8)	57 (−8.1)	58 (−8.7)	61 (−9.6)	66 (−11.0)
NH_2	19 (−2.9)	19 (−2.9)	112 (−12.0)	91 (−10.6)	74 (−9.4)	70 (−9.1)	54 (−8.1)	53 (−8.1)	52 (−8.2)	52 (−8.5)
NHC(O)Alk $NHC(O)NH_2$	22 (−3.4)	19 (−3.1)	58 (−7.4)	49 (−6.5)	43 (−5.9)	42 (−5.8)	37 (−5.7)	38 (−5.9)	38 (−6.2)	40 (−6.7)
Ph	6 (−0.9)	−7 (1.1)	46 (−6.0)	43 (−5.8)	41 (−5.8)	40 (−5.8)	39 (−6.0)	39 (−6.2)	39 (−6.4)	40 (−6.6)
$CH{=}CH_2$			40[b] (−5.6)	40 (−5.6)	40 (−5.6)	40 (−5.6)	40 (−5.6)	40 (−5.6)	40 (−5.6)	40 (−5.6)
OH	8 (−1.2)	8 (−1.2)	39 (−5.1)	33 (−4.6)	29 (−4.1)	28 (−4.0)	22 (−3.5	21 (−3.5	20 (−3.5)	19 (−3.5)
OAlk OPh	7 (−1.1)	8 (−1.2)	49 (−6.3)	35 (−4.7)	24 (−3.6)	23 (−3.3)	17 (−2.8)	18 (−3.1)	21 (−3.5)	24 (−4.2)
I	2 (−0.4)	0 (−0.2)	36 (−5.0)	27 (−4.0)	22 (−3.4)	21 (−3.3)	22 (−3.7)	25 (−4.2)	28 (−4.8)	32 (−5.7)
Br	−3 (0.5)	2 (−0.3)	14 (−2.1)	14 (−2.1)	14 (−2.1)	14 (−2.1)	14 (−2.1)	14 (−2.1)	14 (−2.1)	14 (−2.1)
Alk	2 (−0.2)	4 (−0.5)	9 (−1.4)	9 (−1.4)	9 (−1.4)	9 (−1.4)	9 (−1.4)	9 (−1.4)	9 (−1.4)	9 (−1.4)
Cl	0 (0.1)	−1 (0.1)	9 (−1.3)	9 (−1.3)	9 (−1.3)	9 (−1.3)	9 (−1.3)	9 (−1.3)	9 (−1.3)	9 (−1.3)
F	−5 (1.2)	−1 (0.3)	2 (−0.2)	2 (−0.2)	2 (−0.2)	2 (−0.2)	2 (−0.2)	2 (−0.2)	2 (−0.2)	2 (−0.2)
NO_2	−4 (0.6)	−28 (3.8	11 (−1.7)							
C(O)Ph	−4 (0.5)	−6 (0.9)	8 (−1.3)	8 (−1.3)						
CHO	−1 (0.3)	−4 (0.5)	8 (−1.1)	8 (−1.1)	8 (−1.1)					
C(O)Alk	4 (−0.3)	−6 (1.1)	8 (−1.4)	8 (−1.4)	8 (−1.4)	8 (−1.4)				
COOH COOAlk CN $CONH_2$	−2 (0.3)	0 (0)	9 (−1.4)	9 (−1.4)	9 (−1.4)	9 (−1.4)	9 (−1.4)	9 (−1.4)		
SO_3H		−4 (0.4)								

[a] The R's in SO_2NR_2 may be H, alkyl, or aryl groups. [b] The effect of a *p*-vinyl group probably parallels that of a *p*-phenyl, but, since only two *p*-vinyl compounds were available for study, the average of these two increments (43 and 37 nm) is tabulated here. [c] H_2O solvent: 3 nm (−0.5 × 10^3 cm^{-1}). Hydrocarbon or CCl_4 solvent: −2 nm (0.4 × 10^3 cm^{-1}).

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

		λ, nm		ν, 10^3 cm^{-1}		
compd[a]	Solvent[b] b	obsd	calcd − obsd	obsd	calcd − obsd	ref
PhNO$_2$		260	−2	38.5	0.5	*c*
-2-NMe$_2$-4-OH		306	8	32.7	−1.4	*d*
-3-NMe$_2$-4-OH		306	−7	32.7	1.0	*d*
-4-NMe$_2$-3-NO$_2$		367	−4	27.2	2.1	*e*
-4-O$^-$-3-NO$_2$		359	12	27.9	0.5	*f*
-4-Ar		305	−1	32.8	0.2	*c*
-3-NHAc		270	7	37.0	−1.1	*g*
-4-NHAc		314	2	31.8	−0.2	*c*
-4-NH$_2$-3,5-I$_2$		358	12	27.9	−1.3	*d*
-4-I		294	0	34.0	0	*h*
-3-OH-2-OMe-6-CHO		273	−1	36.6	0.4	*g*
-4-OH-3NO$_2$		253	16	39.5	−1.8	*f*
-3-OH-4-C(O)Ph		268	6	37.3	−0.8	*i*
-2-OH-5-CHO		254	8	39.4	−1.1	*g*
-4-OH-3,5-Br$_2$	HC	300	−1	33.3	0.4	*g*
-2-Me-5-iPr		261	3	38.3	0	*d*
-2,4,6-Me$_3$-3-NO$_2$	HC	238	3	42.0	−0.6	*g*
-2-Me-4-NO$_2$	H_2O	267	7	37.5	−0.9	*g*
-4-Me-2,3-(NO$_2$)$_2$	H_2O	239	−1	41.8	−0.3	*g*
-3-NO$_2$-4-CHO		238	0	42.0	−0.3	*g*
-2-C(O)Ph		254	0	39.4	0.1	*c*
PhC(O)Ph		252	−3	39.7	0.5	*c*
-4-Ph		290	2	34.5	−0.1	*d*
-3,3′,4,4′-(OMe)$_4$		284	8	35.2	−0.9	*g*
-2,4-(OH)$_2$-3-C(O)Ph		290	−4	34.5	0.4	*h*
-4-F	HC	246	3	40.7	−0.3	*d*
-2-C(O)Ph		254	−9	39.4	1.3	*d*
-4-C(O)Ph		263	−6	38.0	0.9	*d*
-3,3′,4,4′-(COOH)$_4$		256	2	39.1	−0.3	*d*
PhCHO		244	2	41.0	−0.4	*c*
-3-O$^-$	H_2O	267	1	37.5	0	*k*
-2-Ph		249	3	40.2	−0.5	*j*
-2-I	HC	246	0	40.7	−0.1	*g*
-2,6-(OH)$_2$-4-OEt-3-Me		295	−5	33.9	0.2	*k*
-2-CHO		252	−7	39.7	1.2	*d*
-3-CHO		244	−2	41.0	0.1	*g*
-4-CHO		254	0	39.4	0.1	*g*
PhC(O)Alk		242	1	41.3	−0.1	*c*
-2-NMe$_2$		266	−6	37.6	1.0	*k*
-3,4-(O$^-$)$_2$	H_2O	342	−3	29.2	0.1	*k*
-2-NHAc		266	−1	37.6	0.2	*k*
-2-NH$_2$		258	4	38.8	−0.5	*c*
-2,4-(OH)$_2$-5-Ac		275	−2	36.4	0.7	*g*
(1,2,3-indanetrione)		248	−1	40.3	0.6	*d*
-3-Ac	HC	235	0	42.6	0.1	*g*
-4-Ac		256	−5	39.1	0.7	*g*
PhCOOH/COOAlk		258	1	43.9	−0.5	*c*
-3-NMe$_2$		229	2	43.7	−0.5	*g*
-4-NMe$_2$-2-OH		313	2	31.9	−0.4	*d*
-2-O-	H_2O	242	1	41.3	−0.1	*k*
-3-Ph		225	−3	44.4	0.1	*d*
-2-NHC(O)NH$_2$		249	2	40.2	−0.2	*d*
-2-NH$_2$-5-OH		250	6	40.0	−0.7	*g*
-3-NH$_2$-2,4,6-Br$_3$		248	8	40.3	−0.9	*g*
-4-I		252	−1	39.7	0	*g*
-2-Br-4-COOH		241	−6	41.5	1.0	*g*
-2,4,5-Cl$_3$		233	4	42.9	−0.6	*g*
-2-F		223	1	44.8	−0.2	*g*
-3-F		225	3	44.4	−0.7	*g*
-4-F-2-COOEt		224	5	44.6	−1.1	*d*
-2,4-(COOH)$_2$	H_2O	248	−9	40.3	1.5	*g*
PhCN/C(O)NH$_2$		224	2	44.6	−0.6	*c*
-4-NH$_2$	H_2O	278	4	36.0	−0.6	*g*
-2,4,6-(OMe)$_3$		257	1	38.9	−0.2	*d*
-2-CN/C(O)NH$_2$		227	−3	44.1	0.2	*c*
PhSO$_2$OH/NH$_2$/NHAlk/NAlk$_2$		220	−2	45.5	−0.1	*c*
-3-NHAc		243	−6	41.2	1.1	*d*
-3,4-(NH$_2$)$_2$		298	−9	33.6	0.7	*d*
-3-NH$_2$-4-OMe		255	3	39.2	−0.2	*d*
-4-NH$_2$-6-Cl-3-SO$_2$NH$_2$		265	1	37.7	0	*d*
PhAsO(OH)$_2$		216	3	46.3	−0.9	*d*
-4-NHC(O)NH$_2$		257	2	38.9	−0.2	*d*

[a] Compounds are listed in order of descending priority of parent groups and then of other substituents. [b] Solvent = MeOH or 95% EtOH unless otherwise noted; HC = hydrocarbon or CCl_4. [c] Composite: reference 2c, 3a,b. [d] Reference 3b. [e] Reference 4, Vol. 4. [f] Author's data. [g] Reference 3a. [h] Reference 4, Vol. 2. [i] Reference 4, Vol. 12. [j] Reference 4, Vol. 6. [k] Reference 2c.

currences of *p*-OH); *o*-OH, 10 (12.7%); *p*-OAlk, 8 (15.1%); *m*-Alk, 8 (12.5%); *o*-OAlk, 6 (17.1%); *m*-OAlk, 6 (15.8%); *o*-Alk, 5 (7.1%); *m*-OH, 4 (12.1%); m-I,4 (44.4%); *m*-NO_2, 3 (11.5%); *o*-Ac, 3 (50.0%); H_2O solvent, 5 (12.8%); hydrocarbon solvent, 3 (10.3%). Ten other substituents occurred once or twice each. *p*-OH and *p*-OAlk substituents accounted for six of the seven negative deviations in excess of positive deviations.

The relative error for the calculated frequencies is evidently smaller than that for the calculated wavelengths. This may be so for either or both of the following reasons: (1) The range of values of the frequencies is much smaller compared with the mean frequency than is the range of wavelengths compared with the mean wavelength. (2) The use of frequencies can be expected to give better results, since frequencies are directly related to energies. (On the other hand, the users[2d] of these empirical correlations are more likely to use nm than cm^{-1}.)

The final values of the empirical base values and substituent increments depend to some extent upon the particular set of data from which they were derived. Nevertheless, these values generally changed by no more than 1 or 2 nm as new compounds were added to the data base. The largest positive substituent increment, for NMe_2 para to NO_2, has varied from 130 to 134 nm; and the largest negative increment, for the *m*-NO_2 substituent, has varied from −26 to −29 nm.

With one exception, the general pattern of substitution (1, 2, 4 vs. 1, 3, 5, etc.) appeared to be insignificant. The exception was pure 1,4-substitution (vs. 1, 4 plus additional 2-, 3-, 5-, or 6-substitution). For four substituents, O^-, OH, $C(O)NH_2$, and OAlk, "pure para" increments of 5–9 nm [(−0.8 to −1.4) × 10^3 cm^{-1}] were found. Inclusion of these caused a shift of ±1 nm in most of the other parameters and showed somewhat better agreement between calculated and experimental absorption positions, yielding standard deviations of 5.56 vs. 5.64 nm; 0.707 × 10^3 vs. 0.717 × 10^3 cm^{-1}. Since this small improvement was considered not to justify the added complexity in the estimation of λ_{max}'s, the "pure para" effects have been omitted from the final tabulation of parameters.

Future Work. Part 2 of this series is in preparation: on substituted benzenes having only electron-releasing substituents. Application of the methods to substituted naphthalenes and heterocyclic aromatic compounds also is intended.

Acknowledgment. I thank the Computer Center of the University of Minnesota—Duluth for a series of grants in support of this work.