SUBSTITUENT EFFECTS IN ELECTRONIC SPECTROSCOPY: CORRELATIONS WITH PLATT SPECTROSCOPIC MOMENTS

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Two correlation equations for the intensity of the ^1L_b band in benzene derivatives were tested: the classic theory of Platt, Eq. (*1*), and the linear modification suggested by Ballester, Eq. (*2*). A systematic and statistically correct comparison of mono- and disubstituted derivatives revealed that Eq. (*1*) holds for substituents which are not conjugated or only slightly conjugated with the benzene ring, both in the ground and in the excited state (alkyls, Cl, Br, I, CH_2X, $CHal_3$). Some symmetrical properties of the substituents might be also of importance but their spectral properties (the spectroscopic moment itself, or the spectral shift) are not decisive. The conjugated substituents deviate from Eq. (*1*) in such a sense that the cumulative substituent effect is less than predicted; a part of the deviations may be approximately described by Eq. (*2*) but an exact range of validity cannot be determined. The spectroscopic moments depend mainly on the mesomeric effect of the substituent and quite little on its inductive effect; they cannot, however, be expressed only by a combination of these two effects as determined from the ground state properties. This was demonstrated on the series of compounds $C_6H_5CH_2X$ since the correlation with σ_I constants revealed only a general trend.

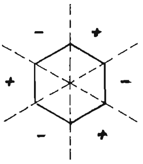
The classic theory of electronic spectra of benzene derivatives[1] assigns the secondary band to a ^1L_b transition corresponding to the $^1A_{1g} \rightarrow {}^1B_{2u}$ in unsubstituted benzene. The symmetry of the total wave function of the excited state is described as in *A*. Accordingly, a weakly perturbing substituent R situated in the position 1, at the nodal plane, modifies the charges in its proximity and contributes a finite transition moment, oriented perpendicularly to the $R-C_{(1)}$ bond. The contribution of several substituents, called their spectroscopic (or migration) moments[2], then add vectorially according to the Scheme *B*. The total molar absorptivity of the ^1L_b band depends on the square of this vector sum and includes still the vibrational absorption component ε_v. With a reasonable approximation, the integrated absorptivity can be replaced by the apparent maximum (ε_{sm}) of a smoothed absorption curve[2], averaging out the vibrational structure:

$$\varepsilon_{sm} = \varepsilon_v + (\sum_{i=1}^{6} \boldsymbol{m}_i)^2 . \qquad (1)$$

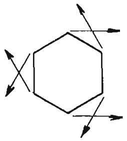
Platt[2] verified the general validity of this approximate equation on some 60 disubstituted benzenes using a constant value of $\varepsilon_v = 150$. He calculated the spectroscopic moments $\boldsymbol{m}$ for 25 substituents of moderate perturbing power. The absolute values of $\boldsymbol{m}$ are obtained most reliably from mono derivatives, but bis derivatives are necessary for determining the sign. A more sophisticated but fundamentally not different version of the theory[3] was based on true integrated absorption intensities and the term ε_v was estimated in each case individually. Although the evidence seemed convincing, Eq. (*1*) referred to as the "square law", was challenged by Ballester and his colleagues[4,5] who extended the experimental studies to polychlorinated compounds and proposed the "linear law":

$$\varepsilon_{sm} = |40 \sum_{i=1}^{6} \boldsymbol{m}_i| - 250 \qquad (2)$$

The proportionality constant of 40 makes the defined values of $\boldsymbol{m}$ close to the original ones, calculated from Eq. (*1*). Eq. (*2*) was confirmed mainly on polychloro derivatives with $\varepsilon_{sm} > 350$ and it was regarded as an empirical limiting law the rationale of which is an assumed nonlinear (S-shaped) dependence of the oscillator strength on the spectroscopic moment[5]. The square law would then accord with the lower part of this dependence (weak perturbation), the linear law with the middle part (moderate perturbation), finally a saturation of substituent effects is expected in the upper part (*e.g.* in anisoles and anilines).

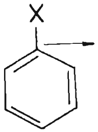


A

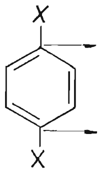


B

In our opinion the validity of equations (*1*) and (*2*) has not yet been tested on a sufficiently broad set of compounds in an statistically unobjectionable manner. The tests applied[4,5] were restricted to arbitrarily selected compounds and/or made use of plotting two quantities, which were not obtained independently. In the previous communication[6] we suggested a more efficient test of similar semiempirical theories. It consists in comparing two series of compounds with identical substituents and is independent of the individual values of empirical parameters. However, the series investigated previously[6], *meta-* and *para-*substituted benzonitriles did not allow a definite decision between Eqs. (*1*) and (*2*). A more suitable model, used already by Ballester[4], compares a monosubstituted benzene (*C*) with the corresponding 1,4-disubstituted derivative (*D*), or the 1,2-derivative (*E*) with the 1,2,4,5-derivative (*F*).



C



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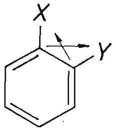

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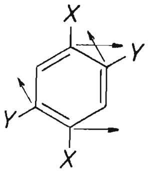


F

The second compound of each pair has always the total spectroscopic moment twice as large as the first. For their smoothed absorptivities ε_1 and ε_2 the square law, Eq. (*1*), yields the relationship:

$$\varepsilon_2 = 4\varepsilon_1 - 450 \tag{3}$$

if the vibration contributions ε_v are assumed[2] equal to 150 for either compound. A more detailed investigation[3] revealed differences 0–20% in the ε_v values which can be neglected for our purpose, in particular with higher absorptivities. According to the linear law, Eq. (*2*), the relationship between ε_1 and ε_2 should be:

$$\varepsilon_2 = 2\varepsilon_1 + 250\,. \tag{4}$$

In contradistinction to ref.[4] we carried out the experimental test by plotting directly the measured quantities ε_2 against ε_1 and included as many compounds as possible (Fig. 1). The relevant data (Table I) were selected with the only condition that the ^1L_b band is well separated in the spectrum from the ^1L_a band. Most measurements were done in nonpolar solvents since the value of ε_v is solvent dependent[2]. Nevertheless, the less soluble compounds had to be measured in methanol, ethanol, or water, but they show so strong substituent effects that the difference in solvent is of no weight.

The following conclusions can be drawn from Fig. 1. No single relationship, linear or nonlinear, is able to fit the data for all possible substituents as it would follow from the assumed nonlinear dependence of the oscillator strength on the spectroscopic moment[5]. It is true that the values of ε_{sm} are not exactly reproducible since drawing a smoothed curve by eye is a subjective procedure. But even an experi-

TABLE I

Molar Absorptivities of the Smoothed ^1L_b Band of Selected Benzene Derivatives

Substituents No	ε_{sm} (mono derivative)	ε_{sm} (bis derivative)	Solvent	References[a]
		Mono and 1,4-derivatives		
1. H	110	110	isooctane	2
2. CH_3	192	425	isooctane	7
2. C_2H_5	180	357	isooctane	7
4. i-C_3H_7	157	320	isooctane	7
5. t-C_4H_9	156	274	isooctane	7
6. c-C_5H_9	210	390	cyclohexane	7, 8
7. c-C_6H_{11}	184	370	isooctane	7
8. CH_2CN	140	185	methanol	this work
9. CF_3	350	925	isooctane	4
10. CCl_3	400	950	isooctane, cyclohexane	4
11. CHO	1 200	2 150	cyclohexane, heptane	9, this work
12. $COCH_3$	900	1 670	cyclohexane, heptane	10, this work
13. COOH	900[b]	630	hexane (+ ether)	11
14. $COOCH_3$	850	720[c]	hexane, heptane	11, this work
15. CN	560	1 450	heptane	6
16. OH	1 320	2 300	isooctane	2
17. OCH_3	1 700	2 350	cyclohexane	4
18. OCF_3	160	525	hexane	12
19. $OCOCH_3$	250	600	hexane	11
20. SCH_3	1 000	2 000	hexane	12
21. SCF_3	540	1 300	hexane	12
22. SO_2CH_3	870[d]	1 750	methanol	this work
23. SO_2CF_3	1 450[e]	2 700[e]	methanol	this work
24. SO_2NH_2	590[f]	1 200	methanol	this work
25. NH_2	1 900	3 200	isooctane, ether	5, 13
26. $N(CH_3)_2$	2 350	2 500	isooctane, cyclohexane	5
27. F	690	1 550	cyclohexane, isooctane	4
28. Cl	180	375	hexane, isooctane	2, 4
29. Br	175	430	isooctane, heptane	2, this work
30. (N)aza	2 000[g,h]	5 600[h]	cyclohexane	14
31. (N)aza	2 650[h]	5 900	water	14
32. (NH^+)azonium	5 290	7 300	water	15, 14
		1,2- and 1,2,4,5-derivatives		
33. CH_3, CH_3	235	610	isooctane	2, 4
34. CH_3, i-C_3H_7	230	570	isooctane	8
35. i-C_3H_7, i-C_3H_7	220	560	isooctane	8
36. $-(CH_2)_2-$	1 300	4 600	ethanol	7

TABLE I
(*Continued*)

Substituents No	ε_{sm} (mono derivative)	ε_{sm} (bis derivative)	Solvent	References [a]
37. —$(CH_2)_3$—	1 040	3 700	ethanol	7
38. —$(CH_2)_4$—	465	1 450	ethanol	7
39. CN, CN	1 530	3 200	methanol	this work
40. CCl_3, Cl	800	1 900	cyclohexane	4
41. Cl, Cl	250	870	hexane, cyclohexane	2, 4
42. (N), CH_3	2 400[g]	5 700	cyclohexane	2, 14
43. (N), CH_3	3 560	6 840	water	15, 14
44. (N), (N)	1 300[h]	2 150	cyclohexane	14
45. (N), (N)	1 090	2 840	water	14
46. (NH^+), CH_3	6 630	8 080	water	15, 14
		Derivative of hexachlorobenzene		
47. Cl	225[i]	225[i]	cyclohexane	4
48. H	400	870	cyclohexane	4
49. CH_2Cl	600	1 450	cyclohexane	4
50. $CHCl_2$	1 000	2 300	cyclohexane	4
51. CCl_3	1 430	3 030	cyclohexane	4
52. *E*-C_3Cl_5	750	1 750	cyclohexane	4
53. COCl	700	1 750	cyclohexane	4

[a] Secondary references reporting the smoothed values are generally preferred to the sources of original spectral data; [b] ref.[2] reports 990; [c] this value based on our determination seems preferable to the literature[11] report ($\varepsilon = 1\,800$) with respect to the preceding data for carboxylic acids; [d] the spectrum agrees well with ref.[16] (in ethanol); [e] the agreement with ref.[12] is only fair; [f] the spectrum agrees well with ref.[17] (in ethanol); [g] at variance with ref.[18]; [h] there is a considerable difference against ref.[2]; [i] the band is not well separated from the ^1L_a band, compare ref.[19].

mental error of 10%, as shown in Fig. 1, is by far smaller than the observed scatter of points. In the case of very strongly perturbing substituents, even the assignment of bands is not quite sure and was sometimes challenged[5]. However, such substituents, *e.g.* $N(CH_3)_2$ or OCH_3, deviate strongly in any case and are of little importance for the adherence to one or the other straight line.

The only possibility how to achieve validity of the Platt relationship is evidently to define with more precision its range of validity. Platt originally restricted this range according to spectroscopic criteria[2], essentially to compounds with $\varepsilon_{sm} < 2000$; it means that *e.g.* substituents $COCH_3$, COOR, SO_2CH_3, SO_2NH_2, CN are still admitted even in disubstituted derivatives, CHO and OCH_3 for mono derivatives only. In Petruska's version[3] all these substituents were excluded by the requirement that the frequency shift by the substitution is less than 1 500 cm^{-1}; thus only substituents R, Hal, CH_2X, and $CHal_3$ practically remained. Our results accord merely with the latter restriction, but the range of validity should be, in our opinion, defined in chemical rather than in spectroscopic terms: only non-conjugated or very slightly conjugated substituents are admitted. For example, the substituents F, CN, SO_2NH_2 deviate clearly from Eq. (*3*) although ε_{sm} is only intermediate; the substituent 1,2-$(CH_2)_2$-raises a much higher absorptivity but Eq. (*3*) is still fulfilled. It is difficult to decide *a priori* which substituents are conjugated only slightly since even the conjugation in the excited state may be of importance. Certainly many substituents appear as conjugated which were found very little conjugated in the ground state according to their effects on the dissociation constants[20] (SO_2X, CN, NO_2). As result the square law[2], Eq. (*1*) or (*3*), holds for alkyl groups of any kind and for substituents CH_2CN, CF_3, CCl_3, Cl, Br (but not F), remarkably enough also for $OCOCH_3$, even the substituents OCF_3, SCF_3, and CN deviate but slightly. The adherence

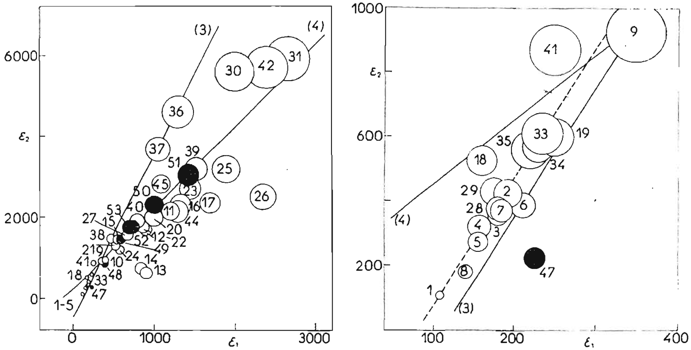


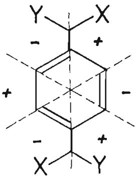
FIG. 1 *A* *B*

Experimental Test of the Equations (*3*) and (*4*); *A* the Whole Range, *B* the Left Bottom Part Enlarged

The smoothed absorptivities of the ^1L_b band are plotted on the *x*-axis for the monoderivatives (ε_1), on the *y*-axis for the bis derivatives (ε_2); a 10% error is shown. Black points correspond to derivatives of hexachlorobenzene, numbering see Table I. The full lines correspond to Eqs (*3*) and (*4*) respectively, the broken line to Eq. (*3*) with a modified value $\varepsilon_v = 110$.

to Eq. (*3*) would be better if the constant 450 (*i.e.* $3\varepsilon_v$) were replaced by 330; this is true in particular for the alkyl substituents (broken line in Fig. 1*B*). The value of $\varepsilon_v = 150$ was determined empirically[2] as an averaged one; for little perturbing substituents the value of 110, immediately derived from measurement on benzene, is to be preferred. From the remaining points, deviating from Eq. (*3*), a group can be selected following the linear law[4], Eq. (*4*). Among them the derivatives of hexachlorobenzene, on which Ballester has essentially based his law[4], play an important part but their behaviour is difficult to understand in terms of conjugation in the classic sense. The more difficult is to find any common feature for the remaining substituents following ing the linear law: SCF_3, CN, F, 1,2-$(CN)_2$, aza (in H_2O). Some points are situated between the square and linear laws, for some others their appurtenance cannot be determined with certainty, and finally some points deviate strongly even from the linear law. It seems that additional laws could be formulated for small subgroups, *e.g.* the points SO_2NH_2, SO_2CH_3, and SO_2CF_3 are situated on a common line, together with CHO and $COCH_3$. Two of the outliers, OCH_3 and $N(CH_3)_2$, are noted for a strong conjugation, while no explanation can be offered for a similar behaviour of COOH and $COOCH_3$.

For most of the named groups still another cause of deviation, hitherto overlooked, comes into consideration. The simple theory assumes that the substituent is located in the nodal plane of the wave function (see *A*), but this cannot hold for unsymmetrical coplanar groups. The pertinent *para* derivatives exist in two conformations *G* and *H*, populated approximately equally, of which only *G* has a spectroscopic moment twice as large as the monoderivative. The presence of *H* diminishes ε_{sm} of the *para* derivative and could be responsible for a part of deviations in Fig. 1. From this point of view it is significant that the substituents 1,2-$(CH_2)_2$ and 1,2-$(CH_2)_3$- produce so strong perturbation and at the same time obey so closely the square law: Due to their steric arrangement the C-atoms are strongly deflected from the nodal plane but only one conformation *J* of the bis derivative is possible. In conclusion there seem to be only one relationship with a broader and defined range of validity, *viz.* Eq. (*1*); the deviations of the remaining substituents may be discussed and explained in individual cases but no further general regularity is apparent.



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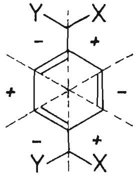

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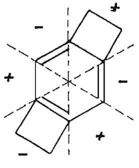

J

The second point at issue within the Platt theory[2] concerns the meaning of the spectroscopic moments ***m***, *i.e.* their relation to the chemical properties. According to Platt they are related to the mesomeric effect[2], according to Petruska to the inductive effect[3], the latter term being evidently used in another sense than usual in organic chemistry. The relation to the inductive effect was contradicted by Bollester and coworkers[4]. The correlation of ***m*** with σ_I and σ_R constants yielded the equation[21]

$$m = -17{\cdot}8\sigma_I - 62{\cdot}7\sigma_R^{BA} \quad (s = 1{\cdot}79,\ n = 7)\,. \tag{5}$$

Although the correlation is close, it has not the relevancy given to it[21] since the set of substituents was rather arbitrarily restricted. We repeated the calculations for several sets with the original values[22] of σ_I and σ_R^{BA} and came to the conclusion that the substituents used were: H, CH_3, F, Cl, Br, OCH_3 and CF_3 ($s = 1{\cdot}65$, $r = 0{\cdot}996$). We do not see. however, the reason why just these substituents were selected. Even a better correlation is obtained when OCH_3 was replaced by CN:

$$m = -18{\cdot}2\sigma_I - 67{\cdot}4\sigma_R - 0{\cdot}69 \quad (s = 0{\cdot}71,\ r = 0{\cdot}999,\ n = 7)\,. \tag{6}$$

TABLE II

Molar Absorptivities of the Smoothed ^1L_b Band of Benzyl Derivatives

Substituent X in $C_6H_5CH_2X$	ε_{sm}		Spectroscopic moment[a] ***m***		$\sigma_I(X)$ (ref.[23])
	in heptane	in methanol	heptane	(methanol)	
H	186[b]	205	9	(9)	0
$CONH_2$	—	195	—	(—9)	0·27
COOH	138	160	—5	(—7)	0·32
$COOC_2H_5$	155	190	—7	(—9)	0·34
CN	142	140	—6[c]	(—5)	0·57
SiH_3	245	—	12	—	(—0·13)[d]
NH_2	148	165	6	(7)	0·12
$NHCOCH_3$	—	178	—	(—8)	0·26
NO_2	340	415	—15	(—18)	0·76
OH	130	152	±4[c]	(±6)	0·25
SO_2CH_3	—	215	—	(—10)	0·59
SO_2NH_2	—	330	—	(—15)	0·44
Cl	—	—	—13[e]	—	0·47
I	—	—	—12[f]	—	0·39

[a] Calculated from Eq. (*1*) with $\varepsilon_\upsilon = 110$ for either solvent, the sign of ***m*** is mostly only estimated; [b] ref.[7] reports 192 in isooctane; [c] ref.[25] reports —10 for CH_2CN and —3 for CH_2OH, solvent not given; [d] σ_I for $Si(CH_3)_3$ determined from dissociation constants was preferred to σ_I for SiH_3 from ^{19}F-NMR spectroscopy[23]; [e] data of ref.[2]; [f] ref.[25], solvent not given.

On the other hand, any more extended correlation is significantly worse. For these extensions we used the best σ_I and σ_R values now available[23], for the latter those determined from IR intensities on benzene monoderivatives were preferred; however, the differences between individual values are irrelevant for the following conclusions. For a set of slightly perturbing substituents (H, CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, c-C_6H_{11}, F, Cl, Br, CH_2Cl, CH_2I, $CHCl_2$, CCl_3, CF_3) we obtained the correlation:

$$m = -14{\cdot}0\sigma_I - 87{\cdot}8\sigma_R - 6{\cdot}18 \qquad (7)$$

$$(s = 4{\cdot}62,\ r = 0{\cdot}922,\ n = 14)$$

which is not significantly different from a more extended one (in addition OH, OCH_3, OCF_3, $OCOCH_3$, SCF_3, C≡CH, CHO, $COCH_3$, COOH, $COOCH_3$, CN, SO_2CH_3, SO_2NH_2):

$$m = -16{\cdot}7_{\sigma I} - 90{\cdot}2\sigma_R - 5{\cdot}09 \quad (s = 5{\cdot}57,\ r = 0{\cdot}954,\ n = 27)\,. \qquad (8)$$

Eqs (*7*) and (*8*) represent very rough correlations and in addition the inductive terms are statistically almost insignificant. From all correlations were excluded the substituents: NH_2 and $N(CH_3)_2$ strongly perturbing, I the $\sigma^* \leftarrow n$ absorption of which might be not accounted for exactly[24], and some further ones the σ constants of which are not quite reliable.

Using a more direct approach we investigated the importance of the inductive effect on benzyl derivatives $C_6H_5CH_2X$ (Table II). The substituents CH_2Cl and CH_2I deviated markedly from Eq. (*7*) but we expected that the non-inductive effects are constant within the whole series, in particular their mesomeric effect was assumed

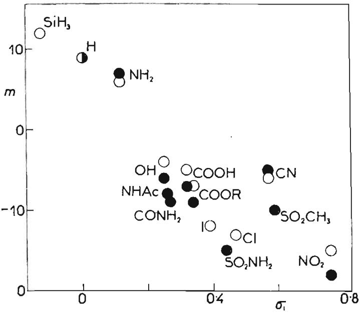

FIG. 2

Dependence of the Spectroscopic Moment *m* of Group CH_2X on the Inductive Effect of the Substituent X (σ_I)

○ Measured in n-heptane, ● measured in methanol.

to be small and constant if not exactly zero[20]. The spectroscopic moments of the CH_2X groups are plotted in Fig. 2 against the σ_I constants of X. Although a trend is evident, a single line cannot be drawn. Note that the sign of m was mostly estimated on the basis of values[2,25] for CH_2Cl and CH_2I, but even some misassigned signs (CH_2OH or CH_2NH_2) would not change the general picture. A possible explanation would be in some effects operating in the excited state and not involved in the σ constants, another one could refer to conformational effects. The stable conformation of benzyl chloride has the C—Cl bond in a perpendicular plane to the benzene ring[26], hence the chlorine atom is in the nodal plane of the wave function (Scheme *A*). Similar position can be assumed for all substituents CH_2X with an axially symmetrical group X. In fact the groups SiH_3, H, CN, NO_2, and the moderately unsymmetrical NH_2 would define a straight line in Fig. 2 with a reasonable accuracy, the deviations of Cl and I had to be explained in terms of excited state properties referring to the *d*-orbitals. Similarly the best correlation achieved, Eq. (*6*), involved only symmetrical substituents. (But CCl_3 would deviate.)

In conclusion we may state that the spectroscopic moments are controlled primarily by the mesomeric effect in the classic sense, as documented by significant correlations with σ_R and by high regression coefficients in Eqs (*5*)–(*8*). The inductive effect is much less important and can be observed only in selected series, otherwise it is obscured by other effects.

EXPERIMENTAL

Materials. Most of the compounds were commercially available and/or well-known except 1,4-bis(methylsulfonyl)benzene[27], phenyl trifluoromethyl sulfone[28], 1,4-bis(trifluoromethylsulfonyl)benzene[29], and 1,2,4,5-tetracyanobenzene[30].

Spectral measurements. The UV spectra were recorded on Unicam SP 800 B, Zeiss Specord UV-VIS, and Zeiss VSU 1 spectrometers at two concentrations within the range 10^{-4}—10^{-3}M. The molar absorptivities were read off from the smoothed absorption curves drawn by eye as described previously[6].

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