---

# New Linear Law and Effects Relating the Ultraviolet Spectra of Substituted Benzenes and the Migration (Spectroscopic) Moment[1]

BY MANUEL BALLESTER,[2] JUAN RIERA,[2] AND LEONARD SPIALTER[3]

RECEIVED MARCH 23, 1964

Ultraviolet absorption spectra in the region of 40,000 cm.$^{-1}$ (250 m$\mu$) were obtained with high reproducibility (better than 5% precision in molar absorptivity) for more than 100 benzene derivatives. These compounds, ranging from mono- to persubstitution, contained methyl, fluoro, chloro, bromo, iodo, methoxy, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, perchloroethyl, chlorocarbonyl, perchlorovinyl, and/or perchlorostilbyl substituents alone or in combination. The molar absorptivities observed, ranging from 100 to 3000, correlate much better with a here-proposed linear function of the moment obtained by vectorial addition of substituent contributions (of the Sklar "migration moment" type or the Platt "spectroscopic moment" type) rather than the currently accepted "square law." The effect of *ortho* substituents is successfully accounted for in terms of ring distortion and resonance inhibition and leads to the concept of a "constellation migration moment."

## Introduction

The near-ultraviolet absorption spectrum of a simple benzene derivative consists of two band systems: the secondary band, centered in the unsubstituted benzene at about 40,000 cm.$^{-1}$ (250 m$\mu$), and the primary bands, at higher wave numbers.[4] The former is by far the better known and the most studied. It is due to the $^1A_{1g} \rightarrow {}^1B_{2u}$ or $^1L_b$ transition.[5] In the vibrationless, undistorted benzene this transition is forbidden.

Sklar has shown[6] that there are two separable contributions to the intensity of absorption in the secondary band: the *migrational* absorption, due to the electronic perturbation caused by the substituents, and the *vibrational* absorption, due to the symmetry-breaking atomic motions. The former is obtained simply by subtracting the latter from the total absorption.

The relevant migrational transition moment of a polysubstituted benzene is supposed to be an additive property of the substituents. Consequently, to every substituent a *migration moment* (Sklar) (or, equivalently, *spectroscopic moment* in the Platt[8] nomenclature) is assigned.

The migration moment of a substituent is a vector in the plane of the benzene ring and perpendicular to

the bond axis. Its direction is reversed when the substituent is shifted to the next benzene carbon atom. The modulus (or intensity) of the migration moment vector can be calculated from the integrated absorptivity of the secondary band by means of expression 1,

$$\left( \sum_{i=1}^{6} \mathbf{m}_i \right)^2 = k \int (\epsilon - \epsilon_v) d\nu \qquad (I)$$

where $\epsilon$ and $\epsilon_v$ are the observed maximum and the vibrational absorptivities, respectively, at frequency $\nu$, $k$ is a factor which can be considered constant, and $\mathbf{m}_i$ is the migration moment of the $i$-substituent. The summation indicated is vectorial addition.

If one assumes that the half-width and shape of the "smoothed" secondary band[10] are constant, then the integrated absorptivity is proportional to $\epsilon_{max}$ and, hence, expression I can be replaced by the simpler and more convenient expression II[11]

$$\left( \sum_{i=1}^{6} \mathbf{m}_i \right)^2 = k'(\epsilon_{max} - \epsilon_v) \qquad (II)$$

*where $\epsilon_{max}$ represents the observed maximum absorptivity of the smoothed curve, and $k'$ is a proportionality constant.*

The migration moments of different substituents may vary not only in magnitude but also in sign (or direction). Their sign and value indicate, respectively, the direction and value of the resonance effect of the substituent. The migration moment of hydrogen is zero. The inductive effect seems to be relatively unimportant.[12]

(1) Part of this work has been presented before the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 11-15, 1962. This paper includes portions of the thesis submitted by J. Riera in partial fulfillment of the requirements for the degree of Doctor in Sciences (University of Barcelona). One of the authors (M. B.) spent 1 year as Visiting Research Associate at ARL, 1961–1962.

(2) Sección de Química Orgánica Teórica, Departamento de Química Orgánica, Patronato "Juan de la Cierva" de Investigación Técnica, Universidad de Barcelona, Spain.

(3) Chemistry Research Laboratory, ARL, Wright–Patterson Air Force Base, Ohio.

(4) L. Doub and J. M. Vanderbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(5) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 246, 299.

(6) A. L. Sklar, *Rev. Mod. Phys.*, **14**, 232 (1942). See also ref. 7-9.

(7) (a) H. Conrad-Billroth, *Z. physik. Chem.*, **B25**, 135 (1934); (b) A. L. Sklar, *J. Chem. Phys.*, **10**, 135 (1942); (c) Th. Förster, *Z. Naturforsch.*, **2a**, 149 (1947).

(8) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

(9) J. Petruska, *ibid.*, **34**, 1111, 1120 (1961).

(10) The secondary band usually has a vibrational structure with maxima and shoulders. The "smoothed" curve is obtained by averaging them out so that the over-all shape and integrated absorptivity are preserved. This can usually be reproduced within acceptable limits.

(11) The validity of such substitution has been checked for over 70 carefully selected benzene derivatives. The data fit the expression

$$\int \epsilon d\nu = 3240 \epsilon_{max}$$

where $\epsilon$ is the molar absorptivity at frequency $\nu$. The deviations from this expression are within 10%.

(12) Petruska, by comparison of the intensity with the frequency shifts, has concluded that the migration moment arises principally from the inductive effect.[9] The low value of the moment for $NH_3^+$,[4,12] the parallelism with

## Results and Discussion

**The Square Law.**—Although the Sklar–Förster theory permits one to predict certain trends concerning the variation of the secondary band absorptivity with type and nature of substitution, Ballester, *et al.*, have reported[16] that the calculated quantitative values can on occasion be seriously divergent from the experimental ones.

It has been assumed[6,7b] that the vibrational contribution to the absorptivity on the secondary band varies insignificantly with the position, and relatively little with the nature and number, of the substituents. Platt assumed the vibrational absorptivity ($\epsilon_v$) was equal to 150 units, *i.e.*, 40 units greater than that of benzene itself.

In Table I the maximum absorptivities of 15 substituted benzenes with theoretically predicted zero resultant migration moment are listed. These absorptivity values should, therefore, be $\epsilon_v$ for these compounds. The vibrational contribution, although it seems to increase with the number of substituents, their masses, and bond strength in many cases, can indeed, as will be seen later, be assumed constant.

### TABLE I

OBSERVED VALUES OF $\epsilon_{max}$ (SMOOTHED $^1A_{1g} \rightarrow {}^1B_{2u}$ BAND) FOR MOLECULES WITH THEORETICALLY ZERO RESULTANT MIGRATION MOMENT

| Derivative | $\epsilon$ |
|---|---|
| Benzene | 110[a] |
| Mesitylene | 180[b] |
| Hemimellitene | 170[c] |
| 1,3,5-Trifluorobenzene | 125[d] |
| 1,3,5-Trichlorobenzene | 160 |
| 1,3,5-Triisopropylbenzene | 180[e] |
| 1,3,5-Tri-*t*-butylbenzene | 170[f] |
| 1,3,5-Tris(trifluoromethyl)benzene | 140[g] |
| 2H,4H,6H-Nonachloromesitylene | 235[h] |
| Hexamethylbenzene | 225[i] |
| Hexafluorobenzene | 200 |
| 2,4,6-Trichloromesitylene | 180[h] |
| Hexaethylbenzene | 215[j] |
| Hexachlorobenzene | 225[k] |
| $\alpha$-H,$\alpha'$-H,$\alpha''$-H-Nonachloromesitylene | 310[h] |

[a] A.P.I. Project 44, Shell Development Co., 1945, p. 40. [b] *Ibid.*, Shell Development Co., 1947, p. 164. [c] *Ibid.*, Shell Development Co., 1947, p. 162. [d] *Ibid.*, Duke University, 1953, p. 495. [e] *Ibid.*, Standard Oil Co., 1955, p. 620. [f] *Ibid.*, Standard Oil Co., 1955, p. 622. [g] C. D. Cooper and F. W. Noegel, *J. Chem. Phys.*, **20**, 1903 (1952). [h] M. Ballester, J. Castañer, and E. Guardiola, *Anales real soc. españ. fís. quím.* (Madrid), **56B**, 723 (1960). [i] M.C.A. Research Project, Allied Chemical Corp., 1961, p. 36. [j] A.P.I. Project 44, Sinclair Research Laboratories, Inc., 1952, p. 488. [k] M. Ballester and J. Castañer, *J. Am. Chem. Soc.*, **82**, 4259 (1960).

The best comprehensive test for the Sklar–Förster theory is presented in Fig. 1. Thirteen pairs of homosubstituted benzenes have been selected. The second molecule of each pair should have a resultant migration moment twice as large as that of the first. Ac-

Taft's $\sigma_R$,[13] the hyperconjugation of the alkyl groups,[15] and the sharp decrease of the moment with the angle between the plane of the benzene ring and that of the groups OCH$_3$, NHR, NR$_2$, and CO$_2$R (inhibition of resonance by *ortho* substituents)[14] show however that the intensity of the secondary band due to the substituents is a resonance effect.

(13) D. Peters, *J. Chem. Soc.*, 4182 (1957).

(14) M. Ballester and J. Riera, forthcoming paper.

(15) M. Ballester and J. Riera, *Tetrahedron*, in press.

(16) M. Ballester and J. Castañer, *J. Am. Chem. Soc.*, **82**, 4259 (1960); M. Ballester, J. Castañer, and E. Guardiola, *Anales real soc. españ. fís. quím.* (Madrid), **56B**, 723 (1960).
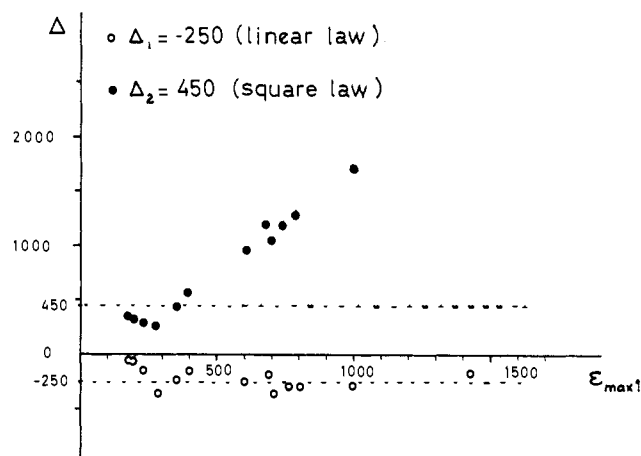


Fig. 1.—$\epsilon_{max_1}$ increasing: chlorobenzene–*p*-dichlorobenzene, toluene–*p*-xylene, *o*-xylene–durene, benzotrifluoride–*p*-bistrifluoromethylbenzene, benzotrichloride–*p*-bistrichloromethylbenzene, $\alpha$-H,$\alpha$-H-hexachlorotoluene–$\alpha$-H,$\alpha$-H,$\alpha'$-H,$\alpha'$-H-hexachloro-*p*-xylene, fluorobenzene–*p*-difluorobenzene, perchlorobenzoyl chloride–perchloroterephthaloyl chloride, perchloropropenylbenzene–perchloro-*p*-dipropenylbenzene, 2H-heptachlorotoluene–2H,5H-octachloro-*p*-xylene, $\alpha$-H-heptachlorotoluene–$\alpha$-H-$\alpha'$-H-octachloro-*p*-xylene, perchlorotoluene–perchloro-*p*-xylene.

cordingly, the migrational absorptivity should be four times as great. This means that the defined difference $\Delta_2 \equiv 4\epsilon_{max_1} - \epsilon_{max_2}$ should be equal to $4\epsilon_{v_1} - \epsilon_{v_2}$. Assuming, with Platt, that $\epsilon_{v_1} = \epsilon_{v_2} = 150$, $\Delta_2$ should be a constant, equal to 450. That such is not the case can be seen in Fig. 1, curve. Therefore, *the square law* (expression I), *one of the basic features of the Sklar–Förster theory, increases too rapidly with the resultant migration moment to account properly for the observed absorptivities.*

**The Linear Law.**—If the migrational absorptivity were a linear function of the resultant migration moment, $\Sigma m_i$, the defined difference $\Delta_1 \equiv 2\epsilon_{max_1} - \epsilon_{max_2}$ should be constant. In Fig. 1 this is shown to be so within the limits of experimental uncertainty. The linear law has been checked successfully for all of the benzene derivatives available, including those with combinations of different substituents and varying relative positions.

The best linear expression is

$$\epsilon_{max} = 40 \sum_{i=1}^{6} m_i - 250 \qquad (III)$$

where the proportionality constant has been set arbitrarily equal to 40, so that the empirical migration moments defined by eq. III are numerically close to Platt's spectroscopic moments.

In the present study the compounds with absorptivities smaller than 350 units have usually been omitted since obviously their respective vibrational and migrational contributions to the absorption become comparable in magnitude below this value. Moreover, the linear expression has a negative ordinate intercept which would imply physically meaningless negative vibrational absorptivities. The linear law must, therefore, be regarded as an empirical one valid only above that limit. In general, the use of any equation disregarding the poorly known nature of the variations of the vibrational contribution with structure,[15] as the square law also does, is essentially meaningless below this limit.

Table II

Molar Absorptivity Maximum of the $^1A_{1g} \rightarrow {}^1B_{2u}$ Band (Smoothed Curve)

| Configuration | 1 | 2 | 3 | 4 | 5 | 6 | Obsd. (solvent)[r] | Calcd.[s] |
|---|---|---|---|---|---|---|---|---|
| | $CH_3$ | ... | ... | $CH_3$ | ... | ... | 450[a] (oct) | 470 |
| | $CH_3$ | $CH_3$ | ... | $CH_3$ | ... | ... | 450[b] (oct) | 438 |
| | $CH_3$ | $CH_3$ | ... | $CH_3$ | $CH_3$ | ... | 610[c] (oct) | 610 |
| | F | ... | ... | ... | ... | ... | 690 (cyh) | 690 |
| | F | F | ... | ... | ... | ... | 690 (cyh) | 690 |
| | F | ... | F | ... | ... | ... | 625[d] (oct) | 690 |
| | F | ... | ... | F | ... | ... | 1550[e] (oct) | 1630 |
| | F | F | ... | F | ... | ... | 1300[f] (oct) | 1375 |
| | F | F | F | F | F | ... | 700 (cyh) | 690 |
| | Cl | ... | ... | Cl | ... | ... | 375[g] (oct) | 326 |
| | Cl | Cl | ... | Cl | ... | ... | 500 (cyh) | 498 |
| | Cl | Cl | ... | Cl | Cl | ... | 870 (cyh) | 870 |
| | Cl | Cl | Cl | Cl | Cl | ... | 400 (cyh) | 310 |
| | $CF_3$ | ... | ... | ... | ... | ... | 350[h] (oct) | 338 |
| | $CF_3$ | ... | $CF_3$ | ... | ... | ... | 350 (cyh) | 338 |
| | $CF_3$ | ... | ... | $CF_3$ | ... | ... | 925[i] (oct) | 926 |
| | $CCl_3$ | ... | ... | ... | ... | ... | 400[j] (oct) | 350 |
| | $CCl_3$ | ... | $CCl_3$ | ... | ... | ... | 400 (cyh) | 350 |
| | $CCl_3$ | ... | ... | $CCl_3$ | ... | ... | 950[k] (cyh) | 950 |
| | $CH_3$ | F | ... | ... | ... | ... | 680 (cyh) | (680) |
| | $CH_3$ | ... | F | ... | ... | ... | 625 (cyh) | 570 |
| | $CH_3$ | ... | ... | F | ... | ... | 1050 (cyh) | 1050 |
| | $CH_3$ | ... | ... | Cl | ... | ... | 400[l] (oct) | 398 |
| | F | Cl | ... | ... | ... | ... | 850 (cyh) | (850) |
| | F | ... | Cl | ... | ... | ... | 700 (cyh) | 582 |
| | F | ... | ... | Cl | ... | ... | 980 (cyh) | 978 |
| | F | ... | ... | Br | ... | ... | 800 (cyh) | (800) |
| | $CF_3$ | F | ... | ... | ... | ... | 1250 (cyh) | (1250) |
| | $CF_3$ | ... | F | ... | ... | ... | 1100[m] (hep) | 1086 |
| | $CF_3$ | ... | ... | F | ... | ... | 235 (cyh) | <350 |
| | $CF_3$ | Cl | ... | ... | ... | ... | 780 (cyh) | 778 |
| | $CF_3$ | ... | Cl | ... | ... | ... | 550 (cyh) | 522 |
| | $CF_3$ | ... | ... | Cl | ... | ... | 230 (cyh) | <350 |
| | $CF_3$ | Cl | ... | ... | Cl | ... | 1075 (cyh) | >948 |
| | $CCl_3$ | Cl | ... | ... | ... | ... | 800 (cyh) | 798 |
| | $CCl_3$ | ... | Cl | ... | ... | ... | 635 (cyh) | 534 |
| | $CCl_3$ | ... | ... | Cl | ... | ... | <300 (cyh) | <350 |
| | $CCl_3$ | ... | Cl | Cl | ... | ... | 560 (cyh) | >330 |
| | $CCl_3$ | Cl | ... | Cl | ... | ... | 415 (cyh) | <686 |
| | $CCl_3$ | Cl | Cl | Cl | Cl | ... | 800[k] (cyh) | 798 |
| | $CCl_3$ | Cl | Cl | ... | Cl | Cl | 2070[k] (cyh) | 1990 |
| | $CCl_3$ | Cl | Cl | Cl | Cl | Cl | 1430[k] (cyh) | 1430 |
| | $CCl_2$ | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | 1400[k] (cyh) | (1400) |
| | $CCl_3$ | Cl | ... | $CCl_3$ | Cl | ... | 1900[k] (cyh) | 1846 |
| | $CCl_3$ | Cl | Cl | $CCl_3$ | Cl | Cl | 3030[k] (cyh) | 3110 |
| | $CHCl_2$ | F | ... | ... | ... | ... | 1350 (cyh) | (1350) |
| | $CHCl_2$ | ... | ... | F | ... | ... | 270 (cyh) | ... |
| | $CHCl_2$ | Cl | ... | ... | ... | Cl | 950 (cyh) | 998 |
| | $CHCl_2$ | Cl | Cl | ... | Cl | Cl | 1600[n] (cyh) | 1558 |
| | $CHCl_2$ | Cl | Cl | Cl | Cl | Cl | 1000[k] (cyh) | 998 |
| | $CHCl_2$ | Cl | $CHCl_2$ | Cl | Cl | Cl | 1000 (cyh) | 998 |
| | $CHCl_2$ | Cl | Cl | $CHCl_2$ | Cl | Cl | 2300[o] (cyh) | 2246 |
| | $CH_2Cl$ | Cl | Cl | Cl | Cl | Cl | 600[k] (cyh) | 598 |
| | $CH_2Cl$ | Cl | Cl | $CH_2Cl$ | Cl | Cl | 1450[o] (cyh) | 1446 |
| | $C_2Cl_5$ | Cl | Cl | Cl | Cl | ... | 1000[o] (cyh) | (1000) |
| | $C_2Cl_5$ | Cl | Cl | Cl | Cl | Cl | 1900[k] (cyh) | (1900) |
| **Configuration** | | | | | | | | |
| ... | $CCl{=}CCl_2$ | Cl | Cl | Cl | Cl | ... | 825[p] (cyh) | (825) |
| ... | $CCl{=}CCl_2$ | Cl | Cl | Cl | Cl | Cl | 1000[p] (cyh) | (1000) |
| cis | $CCl{=}CClCCl_3$ | Cl | Cl | Cl | Cl | Cl | 750[n] (cyh) | 750 |
| trans | $CCl{=}CClCCl_3$ | Cl | Cl | Cl | Cl | Cl | 750[n] (cyh) | 750 |
| cis,anti,cis | $CCl{=}CClCCl_3$ | Cl | Cl | $CCl{=}CClCCl_3$ | Cl | Cl | 1800[n] (cyh) | 1750 |
| cis,syn,cis | $CCl{=}CClCCl_3$ | Cl | Cl | $CCl{=}CClCCl_3$ | Cl | Cl | 1700[n] (cyh) | 1750 |
| cis,anti,trans | $CCl{=}CClCCl_3$ | Cl | Cl | $CCl{=}CClCCl_3$ | Cl | Cl | 1800[n] (cyh) | 1750 |
| trans,trans | $CCl{=}CClCCl_3$ | Cl | Cl | $CCl{=}CClCCl_3$ | Cl | Cl | 1750[n] (cyh) | 1750 |
| cis | $CCl{=}CClC_6HCl_4$ | Cl | Cl | Cl | Cl | ... | ~800[q] (cyh) | (800) |
| trans | $CCl{=}CClC_6HCl_4$ | Cl | Cl | Cl | Cl | | ~800[q] (cyh) | (800) |

TABLE II (*Continued*)

| | 1 | 2 | 3 | 4 | 5 | 6 | Obsd. (solvent)[r] | Calcd.[s] |
|---|---|---|---|---|---|---|---|---|
| *cis* | $CCl=CClC_6Cl_5$ | Cl | Cl | Cl | Cl | Cl | $1050^q$ (cyh) | (1050) |
| *trans* | $CCl=CClC_6Cl_5$ | Cl | Cl | Cl | Cl | Cl | $\sim900^q$ (cyh) | (900) |
| ... | COCl | Cl | Cl | Cl | Cl | Cl | $700^n$ (cyh) | 730 |
| ... | COCl | Cl | Cl | COCl | Cl | Cl | $1750^n$ (cyh) | 1710 |

[a] A.P.I. Project 44, Shell Development Co., 1945, p. 45.  [b] *Ibid.*, Shell Development Co., 1947, p. 163.  [c] *Ibid.*, Shell Development Co., 1953, p. 538.  [d] *Ibid.*, Duke University, 1953, p. 492.  [e] *Ibid.*, Duke University, 1953, p. 493.  [f] *Ibid.*, Duke University, 1953, p. 494.  [g] *Ibid.*, Sinclair Air Research Laboratory, Inc., 1952, p. 460.  [h] *Ibid.*, Duke University, 1949, p. 299.  [i] C. D. Cooper and F. W. Noegel, *J. Chem. Phys.*, **20**, 1903 (1952).  [j] A.P.I. Project 44, Duke University, 1949, p. 303.  [k] M. Ballester and J. Castañer, *J. Am. Chem. Soc.*, **82**, 4259 (1960).  [l] A.P.I. Project 44, California Research Corp., 1945, p. 118.  [m] C. H. Miller and H. W. Thompson, *J. Chem. Phys.*, **17**, 845 (1949).  [n] M. Ballester and J. Castañer, to be published.  [o] M. Ballester, J. Castañer, and E. Guardiola, *Anales real soc. españ. fis. quim.* (Madrid), **56B**, 723 (1960).  [p] M. Ballester, J. Castañer, J. M. Codina, and F. Lluch, *ibid.*, **56B**, 197 (1960).  [q] M. Ballester, C. Molinet, and J. Rosa, *Tetrahedron*, **6**, 109 (1959).  [r] Solvents: cyh, cyclohexane; oct, 2,2,4-trimethylpentane; hep, *n*-heptane.  [s] Bracketed figures indicate that only one compound was available with the relevant constellation. Therefore, the calculated and experimental resultant migration moments are necessarily equal. All calculations are based on "linear law."

TABLE III

THE SUBSTITUTED ANISOLES. MOLAR ABSORPTIVITY MAXIMUM OF THE $^1A_{1g} \rightarrow {}^1B_{2u}$ BAND (SMOOTHED CURVE) IN CYCLOHEXANE

| Substituents | Obsd. | Calcd.[b] |
|---|---|---|
| None | 1700[a] | 1700 |
| 2-CH₃O | 1700[a] | 1700 |
| 3-CH₃O | 1700[a] | 1700 |
| 4-CH₃O | 2350[a] | 3650 |
| 2-CH₃ | 1550[a] | 1550 |
| 3-CH₃ | 1500[a] | 1550 |
| 4-CH₃ | 1750[a] | 2058 |
| 2-F | 1480 | 1434 |
| 4-F | 2700 | 2638 |
| 2-Br | 2500 | (2500) |
| 4-Br | 1570 | 1806 |
| 3,5-(CH₃)₂ | 1150[a] | 1338 |
| 2,4-(CH₃)₂ | 1550[a] | 1898 |
| 2,5-(CH₃)₂ | 1500[a] | 1454 |
| 2,6-(CH₃)₂ | 260[a] | 1338 |
| 2,3-(CH₃)₂ | 1100[a] | 1226 |
| 3,4-(CH₃)₂ | 1400[a] | 1946 |

[a] B. T. Commins and A. J. Lindsey, *Anal. Chim. Acta*, **15**, 446 (1956).  [b] Bracketed figures indicate that only one compound was available with the relevant constellation. Therefore, the calculated and the experimental resultant migration moments are necessarily equal. All calculations are based on "linear law."

In Tables II and III are presented data on 87 substituted benzenes.

Previous workers who have investigated the present subject have avoided—partly because of scarcity of reliable data—the presumably present *ortho* effects on the *intensity* of absorption.[17] As will be seen later, these effects do exist, are very important, and can be studied.

**Halogens.**—As far as the secondary band is concerned, the fluorobenzenes present three unique features which make them particularly suitable for a study of the migration moment: (a) there is no observed or predicted *ortho* effect between two *o*-fluorine atoms; (b) the vibrational absorptivity of the fluorobenzenes is very small, being second only to benzene itself; and (c) fluorine is a moderately interacting substituent with a relatively large migration moment.

From the data of Table II and expression III the migration moment of fluorine can be calculated (see Table IV).

It may be observed in Table II that the experimental absorptivities of fluorobenzene, *m*-difluorobenzene,

(17) An *ortho* effect upon the *frequency shifts* of the secondary band for Cl and CH₃, traced to steric causes, has been described.[9]

TABLE IV

ADOPTED SUBSTITUENT AND CONSTELLATION MIGRATION MOMENTS

| Substituent or constellation | $m^{a,b}$ |
|---|---|
| $CH_3O$ | +48.7 (8) |
| F | +23.5 (13) |
| $CH_3$ | +9.0 (8) |
| Cl | +7.2 (9) |
| Br | +2.7 (1) |
| $CF_3$ | −14.7 (7) |
| $CCl_3$ | −15.0 (5) |
| 1,2-(CH₃O)Br | 68.7 (1) |
| 1,2-F(CH₃) | 23.2 (1) |
| 1,2-FCl | 29.5 (1) |
| 1,2-F(CF₃) | 37.5 (1) |
| 1,2-F(CHCl₂) | 40.0 (1) |
| 1,2-(CH₃)₂ | −10.8 (2) |
| 1,2-Cl₂ | −14.0 (6) |
| 1,2-Cl(CF₃) | 25.7 (1) |
| 1,2-Cl(CCl₃) | 26.2 (3) |
| 1,2-Cl(C₂Cl₅) | 31.2 (1) |
| 1,2-Cl(CCl=CCl₂) | 26.9 (1) |
| 1,2-Cl(CCl=CClC₆HCl₄) | 26.2 (1) |
| 1,2,3-F₃ | 0.0 (1) |
| 1,2,3-(CH₃)₃ | 0.0 (2) |
| 1,2,3-Cl₃ | 0.0 (17) |
| 1,3,2-(CH₃)₂(CH₃O) | <15 (1) |
| 1,3,2-(CH₃)₂(CCl₃) | −41.2 (1) |
| 1,3,2-Cl₂(CH₂Cl) | −21.2 (2) |
| 1,3,2-Cl₂(CHCl₂) | −31.2 (5) |
| 1,3,2-Cl₂(CCl₃) | −42.0 (3) |
| 1,3,2-Cl₂(C₂Cl₅) | −53.7 (1) |
| 1,3,2-Cl₂(CCl=CCl₂) | −31.2 (1) |
| 1,3,2-Cl₂(cis-CCl=CClCCl₃) | −25.0 (4) |
| 1,3,2-Cl₂(trans-CCl=CClCCl₃) | −25.0 (3) |
| 1,3,2-Cl₂(cis-CCl=CClC₆Cl₅) | −32.5 (1) |
| 1,3,2-Cl₂(trans-CCl=CClC₆Cl₅) | ∼−29 (1) |
| 1,3,2-Cl₂(COCl) | −24.5 (2) |

[a] The figures in parentheses indicate the number of spectral examples used to compute the moment values listed.  [b] The sign of a constellation moment which is perpendicular to the bond axis of a substituent is that of a hypothetical substituent placed where the substituent is, with its moment equal to that of the constellation. For angular constellation moments the angle would replace the sign. Only their intensities can be given here.

*o*-difluorobenzene, and pentafluorobenzene are about equal, establishing clearly the already-mentioned absence of appreciable *ortho* effect.

Chlorine has a low ($m < 15$) migration moment. Therefore, this cannot be computed from the mono-, di-, or trichlorobenzenes, since the absorptivities fall within the region of appreciable vibrational perturba-

tion. However, its moment can be calculated from the highly absorbing p-chlorofluorobenzene ($\epsilon_{max}$ 980).

The migration moment of bromine is even smaller. A reliable value (+2.7) is calculated from the highly absorbing p-bromofluorobenzene ($\epsilon_{max}$ 800).

The accepted order of mesomeric or resonance interaction for the halogens is F > Cl > Br > I.[18] This should also be the order for the migration moments, but the observed absorptivity of iodobenzene is by far too high ($\epsilon_{max}$ 650). The evaluated migration (or spectroscopic) moment for iodine, therefore, appears to be close to that of fluorine.[8] However, it has been found that in the spectral region where the secondary band of iodobenzene is expected, there also occurs a moderately strong band due to a localized N → Q transition of the iodine.[19]

From comparison of the absorptivities of iodobenzene,[20] m- and p-chloroiodobenzene, and p-fluoroiodobenzene[21] it is concluded that the migration moment of iodine is very small. Therefore, there is no evidence against the halogens standing in the order of their resonance effects.[22]

The small moment of $CH_3$[15] has also been calculated here from the highly absorbing p-fluorotoluene ($\epsilon_{max}$ 1050).

The moment of the $CHCl_2$ group cannot be calculated from the data here available. The p-fluorobenzal chloride has a very low absorptivity ($\epsilon_{max}$ ~275) which shows that that groups have a *negative* migration moment. The moment cannot be calculated from o-fluorobenzal chloride ($\epsilon_{max}$ 1350) either because of the presence of a significant *ortho* effect.

As expected from their low resultant migration moment, the absorptivities of p-fluorobenzal trifluoride, p-chlorobenzal trifluoride, and p-chlorobenzal trichloride fall within the region of appreciable vibrational perturbation.

**Methoxybenzenes.**—The methoxy group is the most strongly interacting substituent here studied. Its moment, as calculated from anisole, is about twice as great as that for fluorine. From this value, very good calculated absorptivities for o- and p-fluoroanisole, o- and m-dimethoxybenzene, and other derivatives are obtained (Table III).

However, a striking anomaly was observed in the case of p-dimethoxybenzene. Its absorptivity is well below the calculated value. This exceptional behavior for the methoxy group is interesting in that it sheds light on the details of the phenomena involved. Further comment on this point is deferred to the discussion of the "saturation effect" later in this paper.

It should be pointed out that o-fluoroanisole and o-dimethoxybenzene do not show any significant *ortho* effect.

**The "Positive" *ortho* Effect.**—Consideration of the data here collected leads to an important generalization: *for ortho-disubstituted benzenes the observed absorptivity is equal to or greater than the calculated value, regardless of the sign of the migration moment of the substituents.*

(18) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 75, 104, 679, 740.

(19) T. M. Dunn and T. Iredale, *J. Chem. Soc.*, 1592 (1952).

(20) American Petroleum Institute Project 44, Duke University, 1949, p. 308.

(21) J. Ferguson and T. Iredale, *J. Chem. Soc.*, 2959 (1953).

(22) Petruska[9] has failed to recognize the existence of such N → Q transitions.

The only exception to this observation is 2,6-dimethylanisole. This rule is interpreted as indicating that the *ortho* effect is predominantly due to steric repulsion between the substituents.

In Table V the exaltation of the resultant migration moment for a number of pairs of *ortho* substituents is given. It is measured by the ratio of the difference between the observed and the calculated resultant moments to the latter. The ratio is taken as a measure of the moment exaltations, instead of the difference, because the latter is observed to decrease when the resultant moment decreases. For example, the sterically strained o-methyl-t-butylbenzene, o-di-t-butylbenzene, o-dibromobenzene, and 1,2,3-trichlorobenzene have a very low absorptivity, even smaller than that of their nonstrained *meta* and 1,3,5- isomers which should have the same (low) migration moments.[7h,23]

| Type of interaction | $m_{calcd}$ | $m_{obsd}$ | Exaltation ratio[a] |
|---|---|---|---|
| $CH_3O \times CH_3O$ | 48.7 | 48.7 | 0.0 |
| $CH_3O \times F$ | 42.6 | 43.2 | 0.0 |
| $F \times F$ | 23.5 | 23.5 | 0.0 |
| $CH_3O \times CH_3$ | 45.0 | 45.0 | 0.0 |
| $F \times CH_3$ | 21.9[b] | 23.2 | 0.05 |
| $F \times Cl$ | 23.8[b] | 27.5 | 0.15 |
| $CH_3 \times CH_3$ | 9.0 | 10.8 | 0.2 |
| $CH_3O \times Br$ | 47.5 | 68.7 | 0.45 |
| $Cl \times Cl$ | 7.2 | 14 | 0.95 |
| $F \times CF_3$ | 33.4[b] | 37.5 | 0.1 |
| $Cl \times CF_3$ | 19.3 | 25.7 | 0.35 |
| $Cl \times CCl_3$ | 19.6 | 26.2 | 0.35 |
| $F \times F \times F$ | 0.0 | 0.0 | 0.0 |
| $Cl \times Cl \times Cl$ | 0.0 | 0.0 | 0.0 |
| $CH_3 \times CCl_3 \times CH_3$ | 24.0 | 41.2 | 0.7 |
| $Cl \times CCl_3 \times Cl$ | 22.2 | 42.0 | 0.9 |

[a] Exaltation ratio = $(m_{obsd} - m_{calcd})/m_{calcd}$. [b] From the *meta* isomer.

In this connection it may be pointed out that the moment for fluorine has been calculated under the implicit assumption that the vibrational perturbation for fluorobenzenes is moderately high. Consequently, it is not surprising that the calculated absorptivities of o- and m-fluorotoluene and chlorofluorobenzene are significantly lower than the observed values (Table II). Because of this, for the calculation of the relevant moment exaltations, the observed values for the *meta* isomers, instead of the calculated moments, have been taken.

If the pairs involving trihalomethyl groups are excluded, the order of increasing moment exaltation is $CH_3O \times CH_3O = CH_3O \times F = F \times F = CH_3O \times CH_3 < F \times CH_3 < F \times Cl < \; < CH_3 \times CH_3 < Cl \times Cl$, where $\times$ symbolizes interaction between the substituents. This is also in the order of increasing steric repulsion. For the pairs involving trihalomethyl groups the series is $F \times CF_3 < Cl \times CF_3 \sim Cl \times CCl_3$ which is also consistent with the steric picture.

The exaltations in the latter series are smaller than that expected in terms of the total bulk of the trihalomethyl groups. Ballester, *et al.*,[16,24] have, however,

(23) A.P.I. Project 44, California Research Corporation, 1953, pp. 520, 521; L. R. C. Barclay, C. E. Milligan, and N. D. Hall, *Can. J. Chem.*, **40**, 1664 (1962).

(24) M. Ballester, C. Molinet, and J. Castañer, *J. Am. Chem. Soc.*, **82**, 4254 (1960).

presented spectral evidence showing that there can be meshing of the substituents and, consequently, a much smaller steric interaction. It can be assumed that the positive end of the trihalomethyl groups will exert some electrostatic attraction for an *ortho* halogen substituent. This may lead to further decrease in the effective volume of the group.

Introduction of a second chlorine atom also *ortho* with respect to the trichloromethyl group is known to give a stronger steric effect as ascertained by the accompanying large wave length shift of the secondary bond observed.[16] Appropriately, the additional moment exaltation is found to be about twice as large as that due to the first *o*-chlorine atom (Table IV).

In general, it appears that the "effective" sizes of the substituents are greater than those found with Stuart–Briegleb scale models.

Steric strain causes ring distortion.[16,24] This could mean an additional disturbance of symmetry in both the ground and excited state which would further increase the "allowedness" of the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition.[15] However, as has been seen in the preceding examples, distortion by itself does not appear to increase significantly the transition moment. It seems *as if* the resonance between the substituents and the benzene nucleus was increased by distortion. This hypothesis is not unreasonable since distortion of the benzene nucleus diminishes its aromaticity and increases, therefore, availability for overlap of ring carbon orbitals with those of the substituents. In the following discussion the authors shall adopt this concept.

**The Constellation Migration Moment.**—The modulus (or intensity) of the resultant molecular moment of a distorted benzene is calculated as usual. However, its angle (or direction) is uncertain since distortion might not increase the moments of the substituents in proportion to their normal values. Because of this uncertainty it has been found convenient to introduce the concept of *constellation migration moment*. This is the resultant migration moment of a constellation or grouping of substituents on the benzene nucleus.

The observed migration moment of durene is 21.5. The moment of the constellation 1,2-$(CH_3)_2$ is one-half of this, or 10.7. This leads to a calculated moment value of 10.7 for the $CH_3$ group also.[15] Similarly, from the observed moment of the 1,2,4,5-tetrachlorobenzene the 1,2-$Cl_2$ constellation moment and, consequently, the Cl moment are found to be 14.0. It is possible that the migration moments so calculated include a vibrational component since the 1,2,4,5-tetra-substituted benzenes are related by symmetry to the $E_g^{+s}$ benzene normal vibrations.[15] If this were so, the moment exaltations for the 1,2-$(CH_3)_2$ and 1,3-$Cl_2$ constellations listed in Table V would be too high. (These moments cannot be calculated from the absorptivities of *o*-xylene and *o*-dichlorobenzene because they are too low.) Because of the symmetry, the ternary constellation moments listed in Table IV should be perpendicular to the bond axis of the central substituent.

The substituted benzenes with a center of symmetry can be constructed from two identical ternary constellations of substituents. The resultant moments are estimated, therefore, to be twice as great as those of

just one such constellation. On the other hand, the latter can be calculated from the absorptivity of a simple substituted benzene possessing such a constellation. Accordingly, the absorptivities of α-H,α-H,α'-H,α'-H-hexachloro-*p*-xylene, 2H,5H-octachloro-*p*-xylene, α-H,α'-H-octachloro-*p*-xylene, and perchloro-*p*-xylene can be calculated from the 1,3,2-$Cl_2(CH_2Cl)$, 1,2-$Cl(CCl_3)$, 1,3,2-$Cl(CHCl_2)$, and 1,3,2-$Cl_2(CCl_3)$ constellation moments, respectively. These moments are in turn obtained from the absorptivities of α-H,α-H-hexachlorotoluene, *o*-H-heptachlorotoluene, α-H-heptachlorotoluene, and perchlorotoluene, assuming the 1,2,3-$Cl_3$ constellation moment to be zero. Further support for this concept includes the following: (a) the absorptivities of 2,6-dichlorobenzylidene chloride and 2-chlorobenzal trichloride are, within the experimental error, equal to those of α-H- and *o*-H-heptachlorotoluene, respectively; and (b) the absorptivity of 1,2,3-trichlorobenzene is very small, even smaller than that of its symmetrical isomer.

Analogous reasoning leads to the conclusion that the 1,3,2-$(CHCl_2)_2Cl$ should have approximately the same constellation moment as 1,3,2-$Cl_2(CHCl_2)$. Indeed, the calculated absorptivity of α-H,α'-H-octachloro-*m*-xylene is in excellent agreement with the experimental. By means of the constellation moments, the absorptivities of 1,2,4-trimethylbenzene, 1,2,4-trichlorobenzene, pentachlorobenzene, *p*-H-heptachlorotoluene, and α-H,-*p*-H-hexachlorotoluene are also calculated.

In these calculations it has been assumed that buttressing effects are negligible.

In the case of "angular" constellations such as 1,2-$Cl(CF_3)$ and 1,2-$Cl(CCl_3)$, the direction of their moments is uncertain. For these cases, limits for the absorptivity of derivatives having such constellations can still be evaluated. The migration moment of the nonflanked chlorines in 2,5-dichlorobenzal trifluoride and 2,4-dichlorobenzal trichloride are found to be greater than 7.5 and 9.6, respectively. The moment of the $CCl_3$ group in 3,4-dichlorobenzal trichloride is 23.1, higher also than its "normal" value (Table IV). These results suggest that *molecular distortion increases also the moment of the "lone" substituents*.

**The "Negative" *ortho* Effect.**—It is well known that the extent of resonance is sensitive to the relative orientation of the conjugating systems. The orientation can in some cases be controlled sterically with *ortho* substituents. In anisole the maximum resonance is achieved when the methyl group lies in the plane of the benzene ring. Because of the angular character of the methoxy group the introduction of a methyl group into the *ortho* position does not alter the conformational situation. However, the introduction of two *ortho* substituents forces the methyl group into a plane almost perpendicular to that of the benzene ring, according to models. The result is that resonance is then strongly inhibited and, consequently, the migration moment drops from 48.7 down to less than 15 units (Table IV).[25]

Ballester, *et al.*,[26] have studied the steric inhibition

(25) A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 2310 (1952).

(26) M. Ballester, C. Molinet, and J. Rosa, *Tetrahedron*, **6**, 109 (1959); M. Ballester, C. Molinet, and J. Rosa, *Anales real soc. españ. fis. quim.* (Madrid), **55B**, 437 (1959); M. Ballester, J. Castañer, J. M. Codina, and F. Lluch, *ibid.*, **56B**, 197 (1960).

of resonance in chlorinated styrenes and stilbenes. They found that resonance interaction can be reduced so much that the vinyl and the styryl groups behave spectroscopically almost like "saturated" substituents. Accordingly, from the absorptivity of *trans*-perchloropropenylbenzene, that of *trans,trans*-perchloro-1,4-bispropenylbenzene can be calculated. It is seen that the configuration of the perchloropropenyl group has practically no influence upon the spectroscopic moment value of the constellations 1,3,2-Cl$_2$(CCl=CClCl$_3$).

The following sequence of constellation migration moments is observed: 1,3,2-Cl$_2$(*cis*-CCl:CClCCl$_3$) (25.0) = 1,3,2-Cl$_2$(*trans*-CCl:CClCCl$_3$) < 1,3,2-Cl$_2$-(*trans*-CCl:CClC$_6$Cl$_5$) (29) < 1,3,2-Cl$_2$(CCl:CCl$_2$) (31.2) < 1,3,2-Cl$_2$(*cis*-CCl:CClC$_6$Cl$_5$) (32.5).

This order agrees with that of increasing conjugation as ascertained by analysis of the conjugation band of the corresponding perchlorocarbons.[27]

Another substituent subject to steric inhibition of resonance is the COCl group.[27]

**The Saturation Effect.**—Deviations from the linear law occur in some methoxy derivatives (Table III). In those abnormal cases it has been found, beyond experimental error, that *the calculated absorptivities are invariably greater than the observed values.*[14]

A clear-cut example is *p*-dimethoxybenzene. Its predicted absorptivity is 1.6 times as great as that observed. However, the agreement is excellent in the cases of the less absorbing *ortho* and *meta* isomers. Such abnormal behavior for the *para* isomer probably is related to the high resultant migration moment. It is postulated that the methoxy group interacts so strongly with the benzene nucleus that a "saturation effect" appears. Substituents which because of their nature and/or relative position to the methoxy group should enhance further the absorptivity of anisole appear to interact less with the benzene nucleus than they normally do.

This "saturation effect" occurs when the resonance effect and/or the polarizability of the second substituent is high. *p*-Fluoroanisole behaves normally since fluorine has a very low polarizability and a migration moment half as great as that of the methoxy group. On the other hand, although the migration moments of the methyl group and bromine are low their polarizabilities are high. Accordingly, in *p*-methylanisole the migration moment of the methyl group is close to zero, while in *p*-bromoanisole that of the bromine is negative. In the latter substance, the bromine appears to behave as a weak electron-accepting substituent.

As expected from the additive behavior of the moments, the saturation effect is greater when the elec-

(27) M. Ballester, J. Castañer, and J. Riera, to be published.

tron-donating substituent is in the *para* position and also when the number of polarizable substituents is greater.[14]

The "saturation effect" may also be responsible for the failure of the "square law." *The linear law could result from a balance between the square law and the saturation effect in the region between that where vibrational perturbation is predominant* ($\epsilon_{max}$ 350) *and the usual upper limit of absorptivities for the secondary band* (3 × 10$^3$).

**Applications.**—The present study has been of decisive help in making band assignment for two important groups of benzene derivatives.[27] It has also facilitated the characterization of benzenoid compounds and helped rule out several structural possibilities and choose the correct one. It has been used to detect contamination in new benzene derivatives.

In a particular case an apparent erroneous literature citation was corrected.[27]

It may be employed in the study of the extent of resonance in resonance-inhibited benzene derivatives. Moreover, it is probably one of the most sensitive and simplest techniques known for the detection of distortion of the benzene nucleus and steric effects of substituents.

The preceding considerations show that the concept of migration moments as presented here is not only a correlation of fundamental significance but also a useful tool.

## Experimental

Two instruments were used: a Hilger "Uvispek" Model H-700 spectrophotometer and a Cary Model 11 MS spectrophotometer. Their calibrations were checked with benzene of spectroscopic quality and with *m*-bis(trichloromethyl)benzene. Matched pairs of stoppered quartz cells were employed. Benzene-free cyclohexane was used. Most of the chlorinated substances were prepared in the Barcelona laboratory in a high state of purity. The rest of the substances were high-quality chemicals purchased from Matheson Coleman and Bell, Eastman Kodak, or K and K laboratories. The purity of most of liquid substances was checked by vapor phase chromatography on a Barber–Coleman Model 61C gas chromatograph.