Interaction Polarizabilities of Electron Releasing and Electron Withdrawing Groups in Aromatic Compounds[1]

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Molar refractions for the sodium D line in benzene solution have been determined for several substituted benzenes containing both electron releasing and electron withdrawing groups. The exaltations in refractions, termed the interaction polarizabilities, P_i, increase with increasing ease of π electron migration along the molecules and with increasing length of the conjugated chains, and are sharply reduced by steric inhibition of resonance. The ortho disubstituted benzenes investigated show negligible exaltations in refraction with the exception of those compounds having intramolecular hydrogen bonds. The order of P_i values for various groups is the same as the order of Doub and Vandenbelt's $\delta\lambda_0$ values.

There is a good agreement for many disubstituted benzenes between the observed molar refractions and the values calculated from the relation $R_d = R_{m_1} + R_{m_2} - R_b$, where R is the molar refraction and the subscripts d, m and b refer to the disubstituted and monosubstituted benzenes and to benzene. The refraction calculated for p-anisidine, for example, is 37.31, compared to an observed value[2] (for sodium light) of 37.30. The above relation does not hold for compounds having electron releasing groups para to electron withdrawing groups. The exaltations observed for these compounds appear to be associated with increased electron mobility resulting from resonance interaction between the groups through the conjugated chain.

In this investigation the molar refractions of a number of these compounds have been determined to compare the exaltations for various combinations of groups. This exaltation, the difference between the observed refraction and that calculated from the above relation, is termed the *interaction polarizability*, and given the symbol P_i. As the majority of compounds of interest are solids, the refractions of all compounds investigated were determined in benzene solution.

Experimental

Preparation and Purification of Compounds.—Most of the compounds listed in Table I were obtained from the Eastman Kodak Company or prepared and purified by standard methods. In all cases the physical properties checked those previously reported. The ethyl p-dimethylaminobenzoate, m.p. 63.5–64.0°, ethyl 3-methyl-4-dimethylaminobenzoate, d^{25}_4 1.0395, $n^{25}D$ 1.5417, and ethyl 3-dimethylaminobenzoate, d^{25}_4 1.0584, $n^{25}D$ 1.5457, were prepared by Dr. Dwight Lincoln and made available for this research through the courtesy of Professor Charles C. Price.

Measurements and Calculations.—Densities were measured with a 5-ml. Lipkin pycnometer. Indices of refraction for the sodium D line were determined with a Pulfrich refractometer. In the absence of solute association, density and the square of refractive index are linear functions of the solute weight fractions. The average values for the $\Delta d/wf_2$ and $\Delta n^2/wf_2$ ratios for each set of solutions are listed in Table I along with the range of concentration of the solutions. The $\Delta n^2/wf_2$ ratio listed for ethyl p-aminobenzoate is an extrapolated value. Measurements were made on from two to four solutions for each compound. The $\Delta d/wf_2$ ratio for p-nitrodimethylaniline was calculated from the data of Marsden and Sutton.[3] The specific refraction of each solute, γ_2, was calculated from the relation $\gamma_2 = \dfrac{\gamma_{12} - \gamma_1 wf_1}{wf_2}$

where $\gamma = \dfrac{n^2 - 1}{n^2 + 2} \cdot \dfrac{1}{d}$ and the subscript 12 refers to the solution. The average value of γ_2 was used in obtaining

the molar refraction, except for ethyl p-aminobenzoate for which the extrapolated value was used. A value of 50.3 was obtained for the refraction of methyl cinnamate in benzene. Values for other monosubstituted benzenes used in obtaining the calculated molar refractions were those for pure liquids taken from the literature. The calculated refraction for nitrodimethylaminodurene was obtained by adding to the calculated refraction of p-nitrodimethylaniline four times the difference, 4.88, between the refractions of toluene and benzene. The observed value for this compound is that reported by Ingham and Hampson.[4]

Discussion of Results

A comparison of the P_i values listed in Table I for p-nitrodimethylaniline and the corresponding durene derivative, in which overlapping of the p_z orbitals is reduced by steric factors, clearly reveals that the exaltation in molar refraction observed for the former compound is associated with resonance interaction between the electron releasing and electron withdrawing groups. Steric inhibition of resonance is likewise indicated in ethyl 3-methyl-4-dimethylaminobenzoate by comparison of its P_i value, 1.0, with the value 3.3 obtained for ethyl p-dimethylaminobenzoate.

The absence of exaltation in the refraction of o-nitroanisole, and the very small value of P_i for o-methoxybenzaldehyde, may well be due to the fact that the shortest conjugated chain in the highly polar structure of o-nitroanisole, $RO^+{=}C{-}C{=}N{-}O^-$, is no longer than in the para quinoid structure of nitrobenzene $C^+{-}C{=}C{-}C{=}N{-}O^-$. The greater length of the conjugated chain $RO^+{=}C{-}C{=}C{-}C{=}N{-}O^-$ in the highly polar structure of p-nitroanisole causes more electrons to be "mobilized" by resonance, resulting in an appreciable exaltation of refraction. Lowry and Allsopp[5] have pointed out that the polarizability of a conjugated system is greater for an extended than for a bent chain and Mulliken has come to the same conclusion from theoretical considerations.[6] The lack of exaltation in the ortho compounds may be due in part to the configuration of their conjugated chains.[7]

The relatively large P_i values obtained for the p-substituted alkyl cinnamates illustrate the increasing interaction polarizability with increasing chain length. The exaltations observed for o-hydroxybenzaldehyde and o-hydroxyacetophenone have been previously attributed[8] to resonance stabilization of highly polar structures by hydrogen bond-

(1) Presented at the 116th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1949.

(2) K. Brand and K. W. Kranz, *J. prakt. Chem.*, **115**, 156 (1927).

(3) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 599 (1936).

(4) C. E. Ingham and G. C. Hampson, *ibid.*, 981 (1939).

(5) T. M. Lowry and C. B. Allsopp, *Proc. Roy. Soc. (London)*, **163A**, 356 (1937).

(6) R. S. Mulliken, *J. Chem. Phys.*, **7**, 356 (1939).

(7) We are indebted to the referee for this latter explanation.

(8) C. Curran, THIS JOURNAL, **67**, 1835 (1945).

	Compound	100 wf_2	$\Delta d/wf_2$	$\Delta n^2/wf_2$	R_D Obsd.	Calcd.	P_i
1	p-Nitrodimethylaniline	1-1.5	0.233	0.48	56.3	47.3	9.0
2	Nitrodimethylaminodurene				63.8	66.8	-3.0
3	p-Nitrothioanisole	4-5	.296	.356	49.0	46.0	3.0
4	p-Nitroanisole	10-11	.280	.194	40.7	39.5	1.2
5	o-Nitroanisole	11-12	.283	.153	39.5	39.5	0.0
6	p-Dimethylaminobenzaldehyde	10-12	.183	.433	51.4	46.7	4.7
7	p-Methoxybenzaldehyde	11-14	.205	.189	40.7	39.5	1.2
8	o-Methoxybenzaldehyde	10-12	.201	.148	39.0	38.8	0.2
9	o-Hydroxybenzaldehyde	11-12	.221	.167	34.6	33.8	0.8
10	p-Methoxyacetophenone	10-12	.182	.150	44.2	43.1	1.1
11	o-Hydroxyacetophenone	10-11	.200	.145	39.1	38.1	1.0
12	p-Methoxybenzonitrile	5-6	.184	.137	38.9	38.4	0.4
13	Ethyl p-dimethylaminobenzoate	5-6	.173	.227	60.5	57.2	3.3
14	Ethyl 3-methyl-4-dimethylaminobenzoate	7-9	.146	.406	63.0	62.0	1.0
15	Ethyl m-dimethylaminobenzoate	5-7	.158	.112	58.1	57.2	0.9
16	Ethyl p-aminobenzoate	5-11	.215	(.222)	48.7	47.0	1.7
17	Methyl anthranilate	10-12	.227	.205	43.6	42.2	1.4
18	Ethyl anisate	7-8	.186	.073	50.2	49.4	0.8
19	Methyl anisate	5-7	.210	.099	45.6	44.7	0.9
20	Methyl salicylate	7-10	.226	.080	40.4	39.7	0.7
21	Ethyl p-methoxycinnamate	5-7	.178	.213	63.5	60.7	2.8
22	Methyl p-dimethylaminocinnamate	4-6	.178	.459	72.6	64.9	7.7

ing. Methyl anthranilate is another example of this effect.

The P_i value, 0.9, for ethyl m-dimethylaminobenzoate suggests an *indirect* interaction between the dimethylamino and carbonyl groups meta to each other: the meta R_2N group promotes a high negative charge on the ring carbon atoms ortho and para to the carbonyl group and thus facilitates electron withdrawal from the ring by the latter group. The reality of this interaction is substantiated by an increase in refraction of 0.7 ml. for this compound from benzene to alcohol solution, evidence of resonance stabilization of highly polar structures by the hydrogen bonding solvent.[9]

A comparison of the P_i values for the various para disubstituted benzenes listed in Table I reveals that the order of polarizability by electron release is $(CH_3)_2N > CH_3S > CH_3O$ and $(CH_3)_2N > H_2N$. A comparison of the P_i values obtained in dioxane for p-aminoacetophenone, 5.8, and for p-hydroxybenzaldehyde, 2.1, reveals $H_2N > HO$. The order of polarizability by electron withdrawal is seen to be $NO_2 > CHO > COCH_3 > COOR > CN$. These orders are in line with those postulated by Ingold[10] for electromeric polarizabilities. Ingold pointed out the necessity of obtaining polarizabilities along the axis of electron oscillation (*i.e.*, of studying the Kerr effect) for a precise evaluation of these orders.

The above orders are in perfect qualitative agreement with the order of $\delta\lambda_0$ values for electron releasing and electron withdrawing groups determined by Doub and Vandenbelt[11] from ultraviolet absorption measurements. These authors pointed out the agreement of this order with that of the

(9) F. M. Palermiti and C. Curran, *ibid.*, 70, 3527 (1948).

(10) C. K. Ingold, *Chem. Revs.*, 15, 225 (1934).

(11) L. Doub and J. M. Vandenbelt, THIS JOURNAL, 69, 2714 (1947).

$\Delta\sigma$ values calculated by Price from Hammett's σ_p and σ_m constants.

Polarizability and light absorption are related by the Drude equation

$$R_v = k \sum_i \frac{f_i}{v_i^2 - v^2}$$

where R_v is the molar refraction for frequency v, k is a constant, f_i is the oscillator strength and v_i the frequency of light absorbed for the ith transition. If the spectrum is a series of symmetrical peaks, f_i is associated with the area under the ith peak and v_i is equal to v_{max}. A second paper by Doub and Vandenbelt[12] reveals that the shifts to longer wave lengths of the three benzene absorption peaks at 183.5, 203.5 and 254 mμ on disubstitution (ortho, meta or para) increase with an increase in the sum of the $\delta\lambda_0$ values of the two complementary groups. The shifts in the 183.5 and 254 mμ peaks are similar for ortho, meta and para disubstitution, but the 203.5 mμ peak is shifted much more by para than by ortho and meta disubstitution. It appears therefore that the shift in this 203.5 mμ peak, termed by Doub and Vandenbelt the first primary peak, is associated with the exaltations in refraction observed for the para derivatives.

It is evident that a comparison of the values of P_i for various groups will be facilitated when the refractions are extrapolated to infinite wave length. We hope to make dispersion measurements on solutions of some of these compounds in this Laboratory in the near future and to compare the R_∞ values with absorption measurements.

(12) Doub and Vandenbelt, *ibid.*, 71, 2424 (1939).