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Halogen Substituents. III. *p*-Halogen and Solvent Effects on the Principal Electronic Transition of Phenol, Anisole and Aniline

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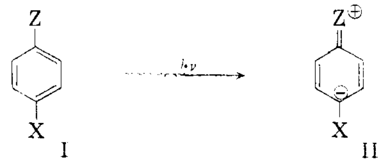
In the gas phase, the energy order for the principal ultraviolet band of *p*-halophenols and *p*-haloanilines corresponds to that previously found for *p*-haloanisoles: I < Br, Cl < H < F. The excitation energies of the anisoles, phenols and anilines are lowered in proceeding from the gas phase to heptane, are lowered further in non-polar solvents of increasing polarizability, and then are sharply raised in acidic polar solvents. The solvent shifts are rationalized in terms of two general factors: (1) the solvent polarizability effect, acting to decrease the excitation energy; and (2) specific solvent orientation effects, acting to give a net increase in excitation energy due to the fact that the electron migration in the transition is away from the functional group. The effect of changing functional group and changing *p*-substituent on the solvent spectral shifts is discussed. Transition moment lengths, determined by the area of the principal band, were measured in some instances. Increases in transition moment length brought about by substituent, functional group or solvent change parallel decreases in excitation energy.

The paper immediately preceding this one deals with solvent effects on the principal electronic transition of *p*-halonitrobenzenes and *p*-haloacetophenones, in which the electron migration on excitation is away from the substituent.[2] The present paper deals in part with solvent effects on the principal electronic transition of *p*-haloanisoles, *p*-halophenols and *p*-haloanilines, in which the electron migration appears to be toward the substituent (represented by equation 1). In addition, gas phase spectral studies, previously reported for the anisoles,[3] have been extended to the phenols and anilines. Transition moment lengths have been determined in a limited number of instances.



(1)

I II

$Z = OCH_3, OH, NH_2$

Experimental

Compounds not commercially available were prepared by standard methods. Final purifications were achieved by several recrystallizations, followed by distillation or sublimation. The compounds were considered sufficiently pure when further purification gave no change in both the ultraviolet spectrum and either the index of refraction or the melting point. Solvent purification has been described.[4] The ultraviolet spectra (slit widths 0.1–0.2) and transition moment lengths were measured as before.[2]

Results

The principal band of the compounds studied was in general structureless, symmetrical about the peak, and free from overlap by other bands, except for anisole, *p*-fluoroanisole, phenol and *p*-fluorophenol. The principal band of the latter compounds was rendered unsymmetrical by the presence of a band just below 200 mμ. In general, the band shape did not change appreciably as the solvent was changed. Exceptions to this were phenol and *p*-fluorophenol, in which the principal band appeared to merge somewhat with a band at lower wave length in the solvents acetonitrile, dioxane, ether, ethanol and methanol. This made measurement of ν_{max} unreliable in these instances, and hence the values are not recorded. Values of ν_{max} are listed in Table I for the anisoles, Table II for the phenols and Table III for the anilines. Values of ϵ_{max} and transition moment lengths, *q*, are listed in Table IV.

TABLE I

VALUES OF $\nu_{max} \times 10^{-1}$ (CM.$^{-1}$) FOR p-$XC_6H_4OCH_3$[a]

Solvent	H	F	Cl	Br	I
Gas phase[b]	4651	4671	4488	4470	4355
Heptane[b]	4553	4610	4397	4415	4273
Cyclohexane	4545	4601	4389	4405	4266
CH_3CN	4553	4606	4389	4407	4282
Dioxane	4535	4593	4384	4401	4273
EtOEt	4551	4599	4393	4413	4282
EtOH	4557	4608	4397	4413	4280
CH_3OH	4564	4614	4401	4416	4288
H_2O	4618	4650[c]	4430	4434	4301
52.5% $HClO_4$	4631	4650[c]	4446	4448	4312
λ_{max}, heptane, mμ	219.6	216.9	227.4	226.5	234.0

[a] All values are averages of two or more determinations, duplicable to ±2–3 × 10^{-1} cm.$^{-1}$ except where noted. [b] Taken from reference 3. [c] In H_2O and 52.5% $HClO_4$, the principal band of *p*-fluoroanisole merged somewhat with the intense band at lower wave length. However, the peak position probably is accurate to ±100 cm.$^{-1}$.

TABLE II

VALUES OF $\nu_{max} \times 10^{-1}$ (CM.$^{-1}$) FOR p-XC_6H_4OH[a]

Solvent	H	F	Cl	Br	I
Gas phase[b]	4847	4875	4539	4545	4407
Heptane	4743	4807	4468	4476	4327
Cyclohexane	4732	4784	4460	4468	4315
CH_3CN[c]	..	..	4416	4432	4308
Dioxane[c]	..	..	4407	4422	4297
EtOEt[c]	..	..	4399	4413	4302
EtOH[c]	..	..	4397	4413	4290
CH_3OH[c]	..	..	4405	4418	4295
H_2O	4755	4826	4456	4458	4321
52.5% $HClO_4$	4808	4852	4492	4496	4352
λ_{max}, heptane, mμ	210.8	208.0	223.8	223.4	231.1

[a] All values are averages of at least two determinations; ν_{max} duplicable to ±2–3 × 10^{-1} cm.$^{-1}$. [b] Gas phase spectra measured at 150°. [c] Absorption of light by the solvent and the presence of a near-lying band prevented accurate measurement of ν_{max} for phenol and *p*-fluorophenol in these solvents.

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(1) National Science Foundation predoctoral fellow, 1956–1959.

(2) W. M. Schubert, J. M. Craven and H. Steadly, THIS JOURNAL, **81**, 1353 (1960).

(3) W. M. Schubert, J. M. Craven and H. Steadly, *ibid.*, **81**, 2695 (1959).

(4) W. M. Schubert, J. Robins and J. L. Haun, *ibid.*, **79**, 910 (1957).

TABLE III

VALUES OF $\nu_{max} \times 10^{-1}$ (CM.$^{-1}$) FOR p-$XC_6H_4NH_2$[a]

Solvent	H	F	Cl	Br	I
Gas phase[b]	4359	4378	4221	4218	4158
Heptane	4274	4340	4139	4136	4045
Cyclohexane	4266	4331	4125	4120	4019
CH_3CN	4188	4250	4044	4044	3976
Dioxane	4161	4234	4036	4040	3968
EtOEt	4181	4241	4042	4039	3968
EtOH	4257	4325	4083	4068	3998
CH_3OH	4283	4348	4112	4092	4018
H_2O	4355	4421	4193	4175	4093
λ_{max}, heptane, mμ	234.0	230.4	241.6	241.8	247.2

[a] All values averages of at least two determinations, duplicable to $\pm 2\text{–}3 \times 10^{-1}$ cm.$^{-1}$. [b] Gas phase spectra measured at 150°.

TABLE IV

VALUES OF TRANSITION MOMENT LENGTHS, q, AND $\epsilon_{max} \times 10^{-3}$ IN HEPTANE[a,b]

	H	F	Cl	Br	I
	p-Haloanilines				
q, Å.	0.69	0.62	0.81	0.87	0.94[c]
$\epsilon_{max} \times 10^{-3}$	9.2	7.4	12.7	13.7	18.6[d]
	p-Haloanisoles				
$\epsilon_{max} \times 10^{-3}$	8.0	5.6	11.9	13.0	19.3[e]
	p-Halophenols				
$\epsilon_{max} \times 10^{-3}$	5.7	4.6	8.6	9.8	14.7[f]

[a] Values of q are averages of two determinations, duplicable to ± 0.01. [b] Values of ϵ_{max} duplicable to $\pm 2\%$. [c] In water as the solvent, the value of q for this compound is 0.89 Å. [d] The value of ϵ_{max} in water for this compound is 16,000. [e] The value of q in heptane for this compound is 0.85 Å. [f] The value of q in heptane for this compound is 0.77 Å.

Gas Phase Results.—The gas phase principal electronic transition energies of the p-haloanisoles previously were reported to be in the order I < Br < Cl < H < F, with the values for the bromo and chloro compounds lying quite close to each other (Table I).[3] The same order now has been found for the p-halophenols (Table II) and p-haloanilines (Table III) except that the values for the chloro and bromo compounds are within experimental error of each other. Thus, stabilization of the excited state relative to the ground state in the polarizability order by halogens appears to be general for transitions of the type in which the electron migration apparently is toward the substituent.[4a]

A comparison of the excitation energies of the three series of compounds (Tables I, II, III) reveals that with any particular p-substituent the excitation energy order is $ArNH_2 < ArOCH_3 < ArOH$. By contrast, the over-all sensitivity of the excitation energy to substituent change is greatest for phenol and least for aniline. Thus, the decrease in excitation frequency from the p-hydrogen to the p-iodo compound is 4400 cm.$^{-1}$ (12.6 kcal.) for phenol, 2960 cm.$^{-1}$ (8.5 kcal.) for anisole and 2010 cm.$^{-1}$ (5.8 kcal.) for aniline.

Solvent Effects.—In the principal electronic transition of nitrobenzenes and acetophenones, the electron migration in proceeding from ground to excited state is *toward* the functional group. In other words, the sites of increased polarity in the excited state not only have the same charge but also approximately the same position, at least as regards the functional group and the ring. Consequently, the solvent molecules, even though oriented by the ground state, are in a generally favorable position to solvate the more polar excited state. This leads to a general lowering of the excitation energy as solvent polarity is increased.[2,5]

By way of contrast, there is a general *increase* in the excitation energies of the anisoles, phenols and anilines as the polarity and, more specifically, the acidity of the solvent is increased (compare alcohol, water and 52.5% perchloric acid in Tables I and II, and dioxane, alcohol and water in Table III). These results probably constitute the best evidence for the conclusion that the electron migration on excitation is *away* from the functional group[5]; for if the migration of electrons is away from the functional group, solvent molecules specifically oriented to the ground state would be in a generally unfavorable position to solvate the excited state, since polarization of the solvent in a sense opposite to its own permanent dipole would be resisted.[5] For example, hydrogen-bond solvation of the basic hetero atom would be a factor operating strongly to decrease the quantity solvent stabilization of excited state *minus* solvent stabilization of ground state, since the hetero atom would be more electron deficient in the excited state. This could account in main part for the fact that excitation energies of all the compounds studied are increased in acidic solvents (Tables I, II, III). Ring solvation by basic portions of the solvent also would act to raise the excitation energy, although specific solvation of the ring is presumably generally less important than specific solvation of the hetero atom. Specific "basic" solvation of the other electron deficient groups attached to the hetero atom is a factor that would act to lower the excitation energy relative to the gas phase, since these groups would become more electron deficient in the excited state. This would act in the direction of increasing the excitation energy as solvent basicity is decreased, presumably in the order phenols > anilines >> anisoles. Specific "acidic" solvation of the p-halogen substituent is probably of relatively little importance.[6]

Whereas the excitation energies of the anisoles, phenols and anilines are increased as solvent polarity is increased, they are decreased in proceeding from the gas phase to non-polar solvents, and are decreased further in non-polar solvents as solvent polarizability is increased (compare heptane, cyclohexane and dioxane). This is probably due to the fact that solvent polarizability is of

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(4a) The gas phase results do not necessarily imply a net electron *acceptance* in the polarizability order; *i.e.*, it may be that the substituent is polarized without any actual exchange of electrons (internal dispersion force).[3] For a quantum mechanical treatment of dispersion force interactions in polyenes see W. T. Simpson, THIS JOURNAL, **73**, 5363 (1951); **77**, 6164 (1955); **78**, 3585 (1956).

(5) For a classification of solvent spectral shifts according to solute type, see N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

(6) Gordy found that the O–D stretching band of CH_3OD has the same position and shape in bromobenzene as in benzene and concluded that there is no hydrogen bonding to the bromine; W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939); see also *C. A.*, **34**, 1913 (1940).

greater importance than solvent orientation in non-polar solvents.[5,7] In the first place, orientation of non-polar solvent to the ground state is probably not very pronounced. In the second place, a non-polar solvent molecule that is polarized in a certain direction by a polar solute site presumably can be polarized readily in the opposite sense should the polarity of the solute site change sign in the excited state. Therefore, regardless of the direction of electron migration, it would be expected that the excitation energy would be lowered in proceeding from gas to non-polar solvent and to non-polar solvents of increasing polarizability.[5,7] Solvent orientation effects probably are not entirely absent, however, since a non-polar solvent that is partially oriented through dipole–polarization interaction to a polar solute site in the ground state probably will not be quite as favorably oriented to this site in the excited state. This should be especially true if the polarity of the solute site changes sign in the excited state.[8] Perhaps this accounts for the fact that the red shift in going from the gas phase to, say, heptane solvent is less for anisole (980 cm.$^{-1}$), phenol (1040 cm.$^{-1}$) and aniline (850 cm.$^{-1}$) than for nitrobenzene (2120 cm.$^{-1}$)[2] and acetophenone (1480 cm.$^{-1}$).[2]

Even in the most polar acidic solvents used, the total forces tending to lower the excitation energy (of which solvent polarization is probably the most important) are strong enough to counterbalance those specific dipole–dipole solvation forces which are tending to raise the excitation energy. For example, except for phenol in 52.5% $HClO_4$ and *p*-fluoroaniline in water, the excitation energies of all the compounds are still slightly less in the most acidic solvents than in the gas phase. An opposition between the red solvent polarization effects and net blue solvent orientation effects would account for the observation that the spectral shifts with changing solvent are generally much smaller for the anisoles, phenols and anilines than for the nitrobenzenes and actophenones, for which these two effects act in the same direction (*i.e.*, both net red).[2,5]

Comparison of Solvent Shifts for Anisoles, Anilines and Phenols.—Separation of the solvent polarization red effect and specific solvent orientation effects is probably best made in terms of equation 2, derived by Bayliss.[7] This is a relationship between the gas to solvent spectral shift and the index of refraction of the solvent. It has been found to hold fairly well for non-polar solvents but not for polar solvents, *i.e.*. the relationship fails when strong specific dipole–dipole interactions are operative between solvent and solute.[7] In this equation ν_{gas} and ν_{sol} are the frequency maxima in gas phase and particular solvent, C

$$\nu_{\text{gas}} - \nu_{\text{sol}} = C \frac{f}{\nu_{\text{gas}} a^3} \frac{n^2 - 1}{2n^2 + 1} \qquad (2)$$

is a constant, f is the oscillator strength of the transition, a is the radius of the solvent cavity occupied by the solute, and n is the index of refraction of the solvent. For a given solute in a series of solvents, $Cf/\nu_{\text{gas}}a^3$ is approximately constant.

A plot of equation 2 for anisole is given in Fig. 1. It is seen that equation 2 is qualitatively obeyed in the less polar solvents. However, in the acidic solvents, water and especially 52.5% $HClO_4$, the excitation energy of anisole is considerably higher than predicted by equation 2. This is a clear indication that hydrogen bonding to the basic ether-oxygen of the ground state acts strongly to reduce solvent stabilization of the excited state relative to the ground state. The fact that the points for methanol and ethanol lie significantly above those for the non-hydroxylic solvents, dioxane, ether and acetonitrile, probably is also a reflection of this factor.

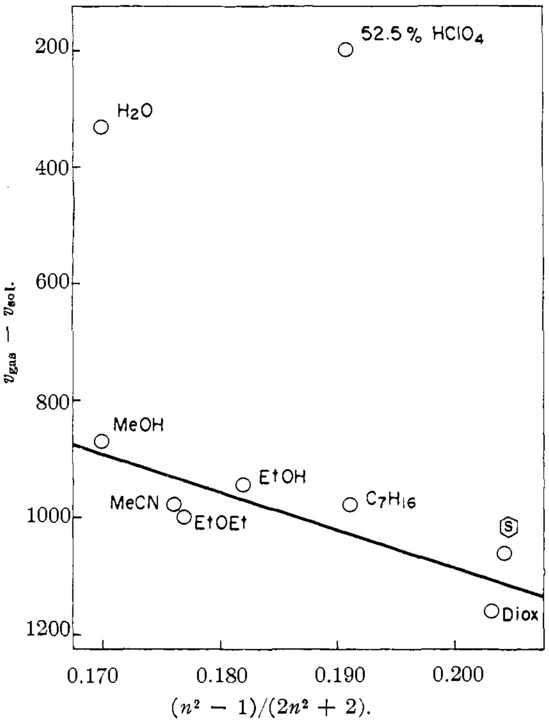

Fig. 1.—Plot of equation 2 for anisole.

The plot of equation 2 for aniline, Fig. 2, shows a complete lack of correlation, indicating strong specific solvent orientation effects with this solute. In the most acidic solvent, water, the excitation energy is very much greater than expected on the basis of the solvent polarization effect alone. Furthermore, the excitation energies in methanol and ethanol are considerably above those in the non-acidic slightly polar solvents, acetonitrile, dioxane and ether. Here, as with anisole, hydrogen bonding to the basic functional group apparently acts strongly to reduce solvent stabilization of the excited state relative to the ground state. Another factor that could play a role here is hydrogen bonding of the amino hydrogens by solvent basic functions which would act specifically to increase solvent stabilization of the excited state relative to the ground state. This could account for the relatively large degree to which the excitation energy is lowered in dioxane, ether and aceto-

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[7] N. S. Bayliss and L. Hulme, *Australian J. Chem.*, **6**, 257 (1953); N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

[8] Presumably, in equilibrium solvation of an electron-rich site the atomic nuclei of the solvent would tend to be more exposed and closer to the site being solvated than in equilibrium solvation of an electron-deficient site.

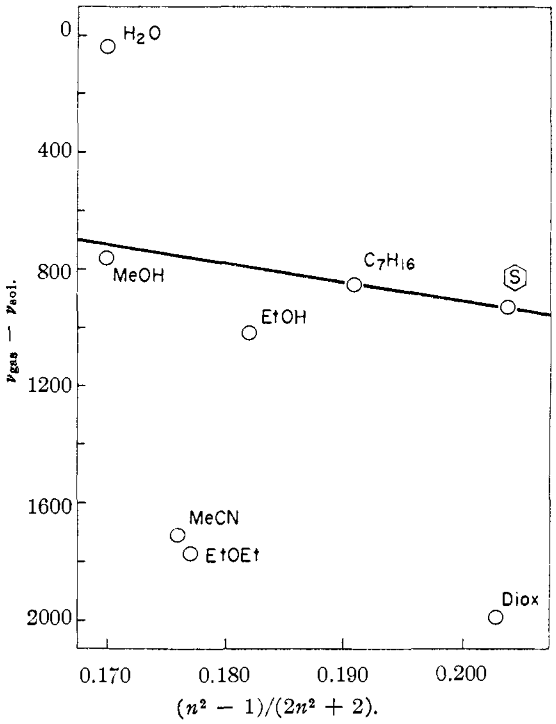

Fig. 2.—Plot of equation 2 for aniline. The line shown has been drawn arbitrarily through the points for heptane and cyclohexane.

nitrile. This factor should be operative in the other oxygen solvents as well, and may account for the relatively low position of the points for methanol and ethanol.

Both the acidic and basic properties of the solvent also appear to be of importance in determining the solvent shifts for the phenols. Figure 3 for *p*-chlorophenol (phenol itself could not be plotted because of a lack of reliable data) also shows a complete lack of correlation with equation 2. The excitation energy rises sharply as one proceeds from alcohols to water to 52.5% $HClO_4$. This is probably largely a reflection of two specific solvation effects: (1) an increase in hydrogen bonding to the phenolic oxygen, and (2) a decrease in hydrogen bonding to the phenolic hydrogen. Hydrogen bonding to the phenolic hydrogen also accounts for the abnormally low excitation energy in basic solvents.

Transition Moment Lengths.—The transition moment length of an electronic transition, *q*, as determined by the area under the spectral band, is a measure of the oscillation of the solute dipole during the interaction with the electric vector of the light.[9] In Table IV it is seen that the transition moment lengths for the principal electronic transition of the anilines in heptane take the order I > Br > Cl > H > F, which is the inverse of the excitation energy order. This is also the order of the values of ϵ_{max}, a less reliable measure of transition probability,[2] for the anilines, anisoles and phenols in heptane (Table IV). In general, it appears that increases in transition moment length brought about

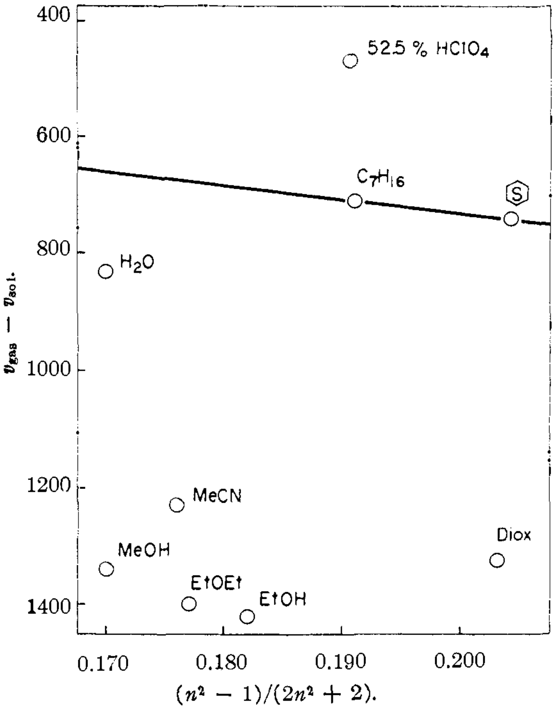

Fig. 3.—Plot of equation 2 for *p*-chlorophenol. The line has been drawn arbitrarily through the points for heptane and cyclohexane.

by substituent, functional group or solvent change parallel decreases in excitation energy.[10] Thus, the *q* order in heptane, *p*-iodoaniline > *p*-iodoanisole > *p*-iodophenol (footnote, Table IV), is the inverse of the excitation energy order. Also, *q* for *p*-iodoaniline is decreased in proceeding from heptane to water (footnote, Table IV), whereas the excitation energy is increased.

Spectral Shifts as a Function of the *p*-Substituent.—The order of gas phase excitation energies for the anisoles, phenols and anilines, and the transition moment lengths for the anilines in heptane have led to the conclusion that the total polarity increase on excitation takes the order I > Br > Cl > H > F. The gas to non-polar solvents red shifts should take the same order, *provided* the spectral shifts were entirely a reflection of the total solute polarity increase on excitation, *i.e.*, provided solvent orientation effects were completely absent. Actually, these red shifts are in the order H > Cl > I > F, Br for the anisoles (Table I), H > I > Cl, Br, F for the phenols (Table II) and I > H, Cl, Br > F for the anilines (Table III). These results indicate the superposition of a solvent orientation effect acting in opposition to the order of the total solute polarity increase on excitation.

Consider next the over-all sensitivity of the excitation energy of the members of a series to solvent *change*, graphically illustrated in Fig. 4 for the anisoles and Fig. 5 for the anilines. The phenols are not plotted, because of incomplete data for phenol itself. These figures are plots of the frequency maxima of the substituted compounds, ν_x, against those of the unsubstituted compound,

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(9) A more complete discussion and leading references are given in the paper immediately preceding this one.

(10) The same general observation was made for *p*-halonitrobenzenes and *p*-haloacetophenones.[2]

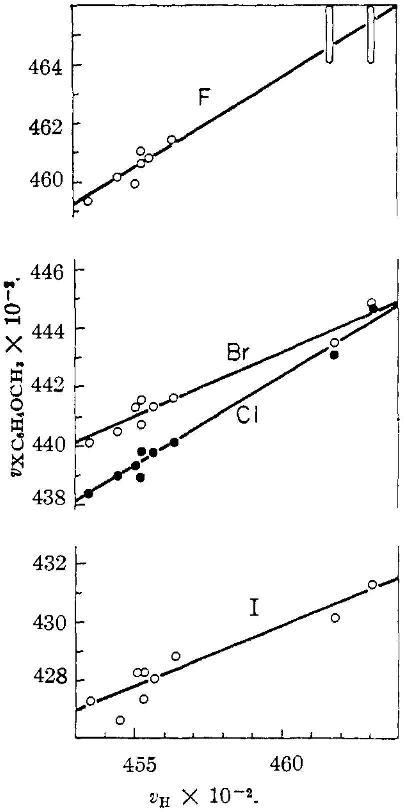

Fig. 4.—Plot of ν_X against ν_H for p-$XC_6H_4OCH_3$ in various solvents.

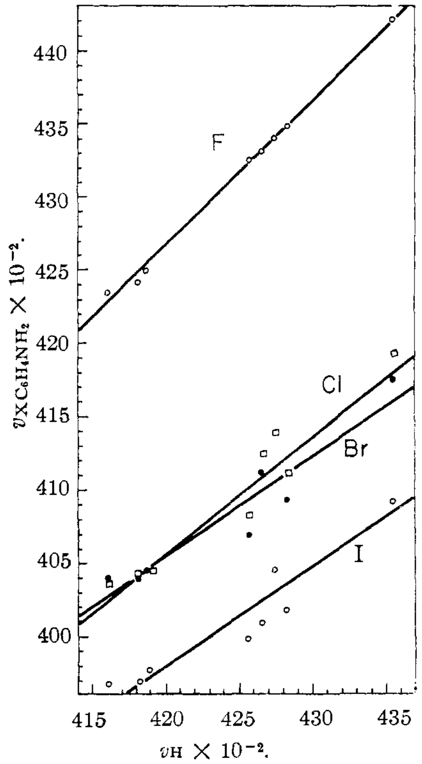

Fig. 5.—Plot of ν_X against ν_N in various solvents for p-$XC_6H_4NH_2$; closed circles for p-Br and squares for p-Cl.

ν_H, in various solvents. Values of the slope, Q_x, together with the standard deviation, s, and the correlation coefficient, r, are given in Table V. The plots show considerable scatter, much more than the corresponding plots for nitrobenzenes and acetophenones.[2] This may be because with the anisoles and anilines the over-all solvent orientation effects are acting to raise the excitation energy relative to the gas phase, in opposition to solvent polarization effects which are acting to lower the excitation energy; with the nitrobenzenes these two factors are acting in the same direction, *i.e.*, to lower the excitation energy. Despite the scatter in the plots, the Q_x values can be taken as qualitative energies of the substituted compounds relative to the parent compound. For the anisoles the Q_x values are in the order H > F, Cl > Br, I and for the anilines, H, F > Cl, Br > I. Less complete data for the phenols have the same general trend. The Q_x orders thus do not reflect the order of *total* solute polarity increase on excitation. Instead, there appear to be specific solvent orientation effects acting to change the excitation energies as solvent is changed in the order F > I, in opposition to the total solute polarity increase on excitation in the order I > F. The results are similar to those found for the p-halonitrobenzenes and p-haloacetophenones and can be given the same tentative explanation.[2] If it is assumed that in the excitation, polarization of the substituent takes place through the bonding electrons,[4] the degree to which negative charge is absorbed by the substituent would be in the order I > F. As a result, the change in polarity, on excitation, could take the order F > I for the p-ZC_6H_4– moiety even though it is in the order I > F for the total molecule. The Q_x orders therefore could possibly be a reflection of the polarity change in the p-ZC_6H_4– moiety, *i.e.*, that part of the molecule which is presumably most strongly solvated.[6]

TABLE V

VALUES OF Q_x FOR p-HALOANISOLES AND p-HALOANILINES; $pK_{BH^\oplus}$ VALUES FOR ANILINES

	H	F	Cl	Br	I
		p-$XC_6H_4OCH_3$			
Q_x	1.00	0.63	0.62	0.44	0.41
S^a	..	.04	.03	.04	.06
r^b	..	.953	.975	.985	.971
		p-$XC_6H_4NH_2$			
Q_x	1.00	1.0	0.8	0.7	0.6
S^a	..	0.02	.1	.1	.1
r^b	..	0.998	.967	.924	.951
$pK_{BH^\oplus}{}^c$	4.62	4.52	3.81	3.91	...

[a] Standard deviation of the slope Q_x. [b] Correlation coefficient of the slope Q_x. [c] Taken from a table in a chapter by H. C. Brown, D. H. McDaniel and O. H. Häfliger in E. A. Braude and F. C. Nachod, "Determination of Organic Structure by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 567.

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