Anal. Calcd. for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 69.80; H, 8.26.

Hydrolysis and isomerization of XIV under similar conditions was used for the more direct preparation of XVII.

4b-Methyl-7-ethylenedioxy-1,2,3,4,4aβ,4b,5,6,7,8,10,10aα-dodecahydrophenanthrene-1,4-dione (XVIII).—To the chromium trioxide–pyridine complex from 300 mg. of chromium trioxide and 3 cc. of pyridine was added a solution of 270 mg. of XVII in 3 cc. of pyridine. The mixture was left at room temperature for two hours and then was diluted with water and extracted with benzene. After removal of the solvent and vacuum-drying of the residue, crystallization from ether gave 190 mg. of product melting at 160–170° along with a small amount of unchanged starting material. The analytical sample was recrystallized three times from ether, m.p. 171–172°.

Anal. Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.51; H, 7.53.

4b-Methyl-1,2,3,4,4aα,4b,5,6,7,9,10,10aα-dodecahydrophenanthrene-1β-ol-4,7-dione.—To a solution of 227 mg. of XV in 5 cc. of acetone was added one drop of 10% hydrochloric acid. The solution was boiled for 15 minutes and then diluted with water and the acetone distilled *in vacuo*. The aqueous suspension was extracted with chloroform and the chloroform solution was dried and evaporated to give 190 mg. (99%) of crystals, m.p. 118–123°. Recrystallization from ether gave a sample melting at 126–127°; λ_{max} 240 mμ, E_{mol} 14,300.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.28. Found: C, 72.67; H, 8.33.

4b-Methyl-1,2,3,4,4aα,4b,5,6,7,9,10,10aα-dodecahydrophenanthrene-1,4,7-trione.—A solution of 140 mg. of 4b-methyl-1,2,3,4,4aα,4b,5,6,7,9,10,10aα-dodecahydrophenanthrene-1β-ol-4,7-dione in 5 cc. of 90% acetic acid was cooled and treated portionwise with 1.4 cc. of 10% chromic acid in 90% acetic acid. After standing at room temperature for 1.5 hours, the product was recovered by the usual procedure; yield 121 mg., m.p. 160–164°. Crystallization from benzene–ether afforded a sample melting at 164–166°; λ_{max} 238 mμ, E_{mol}·15,100.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.27; H. 7.37.

Isomerization of 4b-Methyl-1,2,3,4,4aα,4b,5,6,7,9,10,10aα-dodecahydrophenanthrene-1,4,7-trione to the *anti-trans*-Triketone.—Twenty-three milligrams of the *anti-cis*-triketone, m.p. 164–166° (preceding section), in benzene solution was adsorbed on 2 g. of alkaline alumina. After one hour (less time gave incomplete isomerization) the material was eluted with ether–chloroform (1:1) giving 20 mg. of crystals melting at 98–110°. Recrystallization from ether gave 4b-methyl-1,2,3,4,4aα,4b,5,6,7,9,10,10aβ-dodecahydrophenanthrene-1,4,7-trione, m.p. 117–117.5° alone or on admixture with the triketone obtained from XI by acid hydrolysis.

RAHWAY, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

The Effect of Structure of the Alkyl Group on the Rates of Decomposition of Alkyl Substituted Benzenediazonium Salts[1]

BY EDWARD S. LEWIS AND EMERY B. MILLER

RECEIVED MAY 24, 1952

The rates of decomposition of *m*- and *p*-alkylbenzenediazonium ions in water solution were measured. For the reaction of *p*-alkylbenzenediazonium fluoborates, the substituents, in order of increasing rate constants, are methyl, isopropyl, *s*-butyl and *t*-butyl, although these rate constants vary at most by a factor of only 1.8. With *m*-substituents the order of increasing rate constants is methyl, ethyl and *t*-butyl, with about a fourfold extreme variation. When compared to the unsubstituted compound, all *m*-alkyl substituents accelerate the decomposition and all *p*-alkyl groups retard it. The rate differences are not ascribable entirely to differences in heat of activation, and therefore cannot be explained by inductive and hyperconjugative effects alone.

The effect of alkyl substituents on the rates of various reactions of aromatic systems has been the subject of considerable interest. The concept of hyperconjugation is useful in predicting general effects of alkyl groups, and many more refined ideas have been proposed to explain the differences between the various alkyl groups.[2,3,4] A reaction which lends itself to facile kinetic measurements and has not been investigated from this point of view is the decomposition of dilute solutions of alkyl-substituted benzenediazonium salts in water. The product of this reaction is principally the phenol,[5] which is believed to result from a two-step process[5,6,7]; first, a rate-determining loss of nitrogen to give the aryl cation (eq. 1)

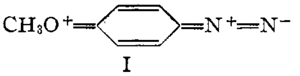
$$ArN_2^+ \longrightarrow Ar^+ + N_2 \qquad (1)$$

followed by the rapid reaction to give the phenol (eq. 2).

$$Ar^+ + H_2O \longrightarrow ArOH + H^+ \qquad (2)$$

The effect of substituents on the rate of diazonium salt decompositions is complicated. Two effects may be considered, an inductive effect and a resonance effect. In reaction (1), the center of positive charge moves from the nitrogen to the aromatic ring. It would therefore be expected from electrostatic considerations alone (the inductive effect) that electron-withdrawing substituents, which also make the ring positive, would retard the reaction. Correspondingly, from the same considerations, electron supplying substituents, like alkyl groups, should facilitate the reaction.

The resonance effect is important with *o*- and *p*-substituents capable of supplying electrons; for instance, the *p*-methoxyl group can interact with the diazonium group, because of the contribution of the structure I.



I

Similarly, *p*-alkyldiazonium ions must have contributions from the analogous no-bond structures. Stabilization resulting from this resonance and the concurrent strengthening of the carbon–nitrogen

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[1] From the Ph.D. Thesis of E. B. Miller, May, 1951.

[2] J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

[3] E. Berliner and F. Bondhus, THIS JOURNAL, **70**, 854 (1948).

[4] E. Berliner and F. Berliner, *ibid.*, **71**, 1195 (1949).

[5] M. L. Crossley, R. H. Kienle and C. H. Benbrook, *ibid.*, **62**, 1400 (1940).

[6] W. A. Waters, *J. Chem. Soc.*, 266 (1942).

[7] E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948 (1940).

bond by the increased double-bond character will make reaction (1) slower with such substituents. This resonance effect thus retards the reaction in just those cases for which the inductive effect would be expected to accelerate it. These competing effects have also been proposed by Hughes.[8]

In the *m*-position only the inductive effect is possible, and the order of increasing rates of *m*-substituents is $NO_2 < Cl < H < CH_3$, but *p*-substituents can exert both effects and the resultant confusing order of rate constants is $OCH_3 < Cl < NO_2 < CH_3 < H$. This result, presumably brought about by the opposing resonance and inductive effects, distinguishes this reaction from others in which the effect of alkyl groups has been observed.

Experimental

Preparation of Materials. Amines.—Both *m*- and *p*-toluidine were commercially available while *p*-*s*-butylaniline, *p*-isopropylaniline and *p*-*t*-butylaniline were prepared by the reduction of the *p*-nitro compounds with tin and hydrochloric acid. These nitro compounds were in turn prepared by the nitration of the commercially available hydrocarbons and were purified by fractional distillation. The amines were purified by repeated crystallization of the acetyl derivatives and kept in this form. The synthesis of *m*-*t*-butylaniline followed standard methods, but because of low yields it is unsatisfactory for any but small scale preparations, and will not be given in detail. It involved the nitration of *p*-*t*-butylacetanilide, hydrolysis to 2-nitro-4-*t*-butylaniline, followed by diazotization, deamination with hypophosphorous acid, and reduction to *m*-*t*-butylaniline. This path to *m*-*t*-butylaniline has been recently improved giving yields better than ours at most steps.[9]

A similar attempt to prepare *m*-isopropylaniline failed when no 2-nitro-4-isopropylacetanilide was obtained. Under slightly different conditions this nitration has recently been accomplished.[10] We also failed in one attempt to prepare *p*-ethylbenzenediazonium fluoborate, because hydrolysis of N-benzoyl-*p*-ethylaniline did not occur under our conditions developed for the acetylamines. It was necessary to use the benzoyl derivative in this case because *o*- and *p*-ethylacetanilide are not readily separated by recrystallization, owing to the lower solubility of the former. Reduction of *m*-nitroacetophenone with tin and hydrochloric acid gave *m*-acetylaniline; a further reduction with hydrazine by the Huang-Minlon modification of the Wolff-Kishner reaction gave *m*-ethylaniline. The identity and purity of the amines were indicated by the melting points of the acetyl derivatives compared to the values in the literature. These are given in Table I.

TABLE I

PROPERTIES OF ALKYLACETANILIDES

Substituent	M.p., °C. found (uncor.)	Lit. m.p., °C.
m-Methyl	66.2–67.3	65[a]
m-Ethyl	B.p. 130 (1 mm.)	Liq.
m-*t*-Butyl	98.8–99.5	99[b]
p-Methyl	148.0–148.8	153[a]
p-Isopropyl	104.9–105.9	102[a]
p-*s*-Butyl[d]	123.8–124.5	125–126[c]
p-*t*-Butyl	170.0–171.5	169[b]

[a] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N.Y., 1948. [b] J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2334 (1928). [c] J. Reilly and W. J. Hickinbottom, *ibid.*, **117**, 103 (1920). [d] Since the *m*- and *o*-isomers of this compound have not been described, the structure was proved by conversion to the *s*-butylchlorobenzene, followed by oxidation to *p*-chlorobenzoic acid, m.p. 239–240°.

The diazonium fluoborates were prepared by hydrolysis of the acetyl derivatives of the amines with hydrochloric acid in an atmosphere of nitrogen, diazotization of the resulting solution and precipitation of the fluoborate from a cold filtered solution of the diazonium salt with 40% fluoboric acid. The crystallization of these salts was immediate in the case of the *m*-compounds, but for the *p*-compounds was quite slow, and several of the latter precipitated first as oils. The white, crystalline solids were then washed with cold 5% fluoboric acid, methanol and lastly ether, and were stored in the dark in a desiccator. The second wash was omitted for all the *p*-substituted compounds except the *p*-methyl, because they are too soluble in methanol. The *m*-alkylbenzenediazonium fluoborates are unstable even in the solid state and can be kept only a short time in the refrigerator.

Kinetic Runs.—The rates of decomposition of the diazonium salts were determined by measuring the volume of nitrogen evolved in an apparatus described elsewhere.[11] A weight of diazonium salt necessary to yield 50–100 ml. of nitrogen at the temperature of the thermostat was decomposed in about 100 ml. of 0.1 *N* hydrochloric acid in this apparatus for these runs. The accuracy of the apparatus was much improved by correcting all volume readings for barometric pressure changes. The runs on *m*-*t*-butylbenzenediazonium fluoborate were made in a smaller apparatus in which pressures were read in a thermostated water manometer at constant volume, instead of volumes at constant pressure. Only about 25 mg. of diazonium salt in about 50 ml. of 0.1 *N* hydrochloric acid was required. In this apparatus supersaturation was avoided by the use of a sealed reciprocating stirrer, instead of the shaking used in the constant pressure apparatus. Rate constants were determined from the slope of the straight lines drawn either for conventional logarithmic plots or plots using the Guggenheim method,[12] both of which gave the same result within the error given in connection with Table II. The water used in the experiments was virtually free from copper (less than 10^{-6} *M* Cu^{++}) but experiments on the *m*-methyl compound showed that the rate was unaltered in the presence of 1×10^{-3} *M* cupric ion. In this case cupric copper has no detectable effect on the rate, in contrast to the situation with the *p*-nitro substituent.[11] Temperatures were measured in the thermostat with a thermometer calibrated at the ice point, the sodium sulfate decahydrate transition point, the sodium bromide dihydrate transition point and the steam point. Because of cooling in the circulating system the temperature in the reaction flask was perceptibly lower, and one measurement at 50° showed that this drop was 0.15°. The uncertainty of temperature differences is much less than this since all temperatures are in error in the same direction. This error is not sufficient to account for the discrepancies between these results and those of Moelwyn-Hughes and Johnson[7] and those of Pray[13] on the unsubstituted compound. Interpolating in their data shows that our reaction was 0.5–0.9° low according to the first reference, or 0.5–0.6° low according to the second. However, our data are in good agreement with those of Crossley, Kienle and Benbrook[6] for several compounds, and therefore the differences in rate constants should probably be ascribed to other sources.

Results

The observed rate constants are given in Table II at various temperatures for which the reaction was conveniently rapid.

Using these values the activation energies $\Delta H^{\ddagger}$ and the logarithms of the pre-exponential factors, *PZ*, in the Arrhenius equation, $k = PZe^{-\Delta H^{\ddagger}/RT}$ were calculated. They are shown in Table III, and also the differences in the entropies of activation of the substituted compounds $\Delta S^{\ddagger}_{S}$ and the unsubstituted compound, $\Delta S^{\ddagger}_{H}$, calculated from the equation $\Delta S^{\ddagger}_{H} - \Delta S^{\ddagger}_{S} = R \log_e (PZ)_H/(PZ)_S$.[14]

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(8) E. D. Hughes, quoted by J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 294 (1951).

(9) H. J. B. Biekart, H. B. Dessens, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **71**, 321 (1952).

(10) H. J. B. Biekart, P. E. Verkade and B. M. Wepster, *ibid.*, **71**, 340 (1952).

(11) E. S. Lewis and W. H. Hinds, THIS JOURNAL, **74**, 304 (1952).

(12) E. A. Guggenheim, *Phil. Mag.*, Ser. 7, 1, 538 (1926).

(13) H. A. H. Pray, *J. Phys. Chem.*, **30**, 1478 (1926).

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TABLE II

RATE CONSTANTS FOR THE DECOMPOSITION OF ALKYLBENZENEDIAZONIUM IONS

Substituent	Temp., °C.	k, sec.$^{-1}$ × 10^4
m-*t*-Butyl	20.30	3.80
m-*t*-Butyl	29.96	14.1 ± 0.3
m-Ethyl	29.96	6.93
m-Ethyl	40.31	27.0
m-Methyl	29.96	3.92
m-Methyl	40.31	15.30
None	46.76	9.39
None	55.44	29.15
p-*t*-Butyl	46.76	1.822
p-*t*-Butyl	62.23	13.25
p-*s*-Butyl	46.76	1.500
p-*s*-Butyl	62.23	11.25
p-Isopropyl	46.76	1.459
p-Isopropyl	52.98	3.27
p-Isopropyl	62.23	10.73
p-Methyl	40.31	0.44 ± 0.03
p-Methyl	52.98	2.39
p-Methyl	62.23	7.79

TABLE III

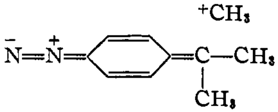
ARRHENIUS EQUATION CONSTANTS FOR THE DECOMPOSITION OF ALKYLBENZENEDIAZONIUM IONS

Substituent	$\Delta H^{\ddagger}$ kcal.	log PZ	$\Delta S^{\ddagger}_{\mathrm{H}} - \Delta S^{\ddagger}_{\mathrm{S}}$, e.u.
m-*t*-Butyl	24.0 ± 0.5	14.5 ± 0.3	5.3 ± 1.3
m-Ethyl	24.8 ± .3	14.7 ± .2	3.9 ± 0.9
m-Methyl	24.8 ± .3	14.7 ± .2	3.9 ± 0.8
None	27.3 ± .3	15.6 ± .2	0.0 ± 1.1
p-*t*-Butyl	27.3 ± .2	15.0 ± .1	3.0 ± 0.6
p-Isopropyl	27.5 ± .2	15.0 ± .1	2.9 ± .6
p-*s*-Butyl	27.8 ± .2	15.2 ± .1	2.0 ± .6
p-Methyl	27.5 ± .4	14.8 ± .2	3.7 ± 1.0

The probable errors are calculated by estimating a probable error of ±1% in the rate constant values, and an uncertainty of temperature of ±0.04°, except where otherwise noted in Table I. This assumption for the probable error of k is very likely an overestimate, as different methods of plotting gave results usually within 0.5%, and the calculated values of $\Delta H^{\ddagger}$ and log PZ using different temperature intervals for those compounds which were run at three temperatures were within the limits given above. The uncertainty of absolute temperature may have been greater than 0.04°, but the uncertainty of the temperature differences, to which both of the functions are most sensitive, was probably much less than this. The errors in entropy of activation differences are calculated from the error in log PZ for a particular substituent alone, and do not include the error in log PZ for the unsubstituted compound. This accounts for the presence of an estimated error in the value for $\Delta S^{\ddagger}_{\mathrm{H}} - \Delta S^{\ddagger}_{\mathrm{S}}$ for no substituent.

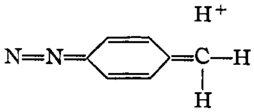
Discussion

The rate constants given in Table II show that in the series of *p*-substituted compounds the order *t*-butyl faster than methyl is observed, and the same order is observed in the *m*-series. Within each of these series the greater accelerating inductive effect of the *t*-butyl group can be invoked for an explanation. The slightly greater inductive effect of the *t*-butyl group is shown, for example, by the dipole moment of *t*-butylbenzene, which is greater than that of toluene.[15] If one accepts the view that hyperconjugation involving structures with no-bond to carbon is less important than hyperconjugation involving no-bond to hydrogen, one would expect that structures such as II



II

would contribute less to *p*-*t*-butylbenzenediazonium ion than structures as III



III

should contribute to *p*-toluenediazonium ion. Thus the rate-decreasing resonance of the diazonium ions becomes less important as the α-carbon atom becomes more highly substituted. The electron-supplying inductive effect would increase going from methyl to *t*-butyl. Thus the combined inductive and resonance effects would be expected to change the rates more than either one alone. It is not possible to observe the isolated resonance effect, but the *m*-alkyl groups presumably do not exert the resonance effect, and therefore show only the inductive effect. A *lower* sensitivity to structure of the alkyl group might then be expected in the *m*-position. The experimental observation that the rate is *more* sensitive to the nature of the alkyl group in the *m*-position than in the *p*-position is therefore in disagreement with this expectation. Several explanations for this failure of the above prediction can be offered. First, all the differences in the rates may not be ascribable entirely to inductive and resonance effects. Second, because of greater proximity a much larger inductive effect could be expected from the *m*- than from the *p*-substituent. Third, the assumption about relative importances of the two types of hyperconjugation may be incorrect.

The first of these explanations can be experimentally tested. Hammett[14] has shown that in order to hold potential energy effects solely responsible for rate differences in a series of related reactions, it is necessary that the entropies of activation be constant. It is seen that within experimental error $\Delta S^{\ddagger}_{\mathrm{H}} - \Delta S^{\ddagger}_{\mathrm{S}}$ is the same for all the *m*-alkyl compounds, but is noticeably higher than that for all the *p*-alkyl compounds, and the unsubstituted compound has still another value. Thus a comparison of the above rates of decomposition of the group of meta with the group of *p*-alkyl benzenediazonium salts must not be made on the basis of potential energy effects alone. The inductive and resonance effects mentioned above are just such potential energy terms, and are therefore insufficient to explain the results. Furthermore, it is seen that among the *p*-substituted compounds there is no evidence that the energy of activation has any

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(15) J. W. Baker and L. G. Groves, *J. Chem. Soc.*, 1144 (1939).

more effect on the rate than does the term containing the entropy of activation. The *m*-substituents however produce a real effect on activation energy, although even here the changes in log *PZ* may be significant. Since it can thus be shown that entropy of activation terms are not all the same and can in fact account for an important part of the rate changes, it is not fruitful to discuss the other two alternative explanations which are based on modifications of the potential energy effects alone. Assignment of effects to potential energy terms alone is especially unjustified in cases of this sort where the variations in rate are small.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NEW MEXICO HIGHLANDS UNIVERSITY]

The Effect of Solvents on the Absorption Spectra of Aromatic Compounds

BY HERBERT E. UNGNADE[1]

RECEIVED MAY 19, 1952

Solvent shifts have been determined for benzene derivatives with electron-donor and electron-acceptor substituents. It is proposed that the direction of the shifts of the high-intensity bands depends on the solvent-solute interaction.

Solvents can affect the fine structure of absorption curves as well as the intensities and wave lengths of the maxima. From the standpoint of fine structure solution spectra of aromatic compounds in paraffin solvents most nearly resemble those in the vapor state. With increasing solvent polarity the spectra suffer a loss in vibrational fine structure which may perhaps serve as a measure of the extent of the solvent interaction.

The absorption spectrum of benzene is only very slightly affected by solvents.[2] Aromatic hydrocarbons more complex than benzene undergo definite shifts of their absorption curves when the polarity of the solvent is changed. Still larger solvent shifts are observed in substituted benzenes with polar substituents.

The direction of the solvent shifts is not always the same for all absorption bands of the same compound and it is therefore necessary to classify the bands. Above 200 mμ most benzene derivatives possess two types of bands which are distinguishable by their relative absorbancies.[3] The high intensity bands, also called K-bands,[3] primary bands[4] or E-bands,[5] are usually displaced to longer wave lengths with increasing polarity of the solvent. The low intensity bands are known as secondary bands[4] or B-bands[3] and are shifted toward higher frequencies when the dielectric constant of the solvent is increased.

In mono-substituted benzene derivatives with electron-acceptor substituents such as COOH, $COCH_3$, CHO and NO_2 the high intensity bands become identical with the red-shift bands of McConnell.[6] When measurements are omitted in solvents where association occurs (*e.g.*, benzoic acid dimer in hydrocarbons, chloroform, etc.),[7] the shifts are progressive from hydrocarbon solvents to water and, for a given solvent pair, roughly proportional to the shift of the corresponding benzene band due to the particular substituent (Table I).

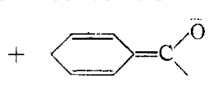
TABLE I

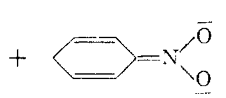
PRIMARY BANDS OF BENZENE DERIVATIVES WITH ELECTRON ACCEPTOR SUBSTITUENTS

Compound	λ_{max} (H_2O)	λ_{max} (EtOH)	$\Delta\lambda$[a]	$\Delta\lambda$[b]
Benzoic acid	230[c]	228[g]	26.5	+2
Acetophenone[d]	245.5[c]	241[e]	42.0	+4.5
Benzaldehyde	249.5[c]	243[h]	46.0	+6.5
Nitrobenzene[f]	268.5[c]	260[i]	65.0	+8.5

[a] Wave length shift of the benzene band at 203.5 mμ due to the substituent.[c] [b] λ_{max} (H_2O) − λ_{max} (EtOH). [c] Reference (4). [d] In hexane λ_{max} 235 mμ[e] and $\lambda_{H_2O} - \lambda_{HC}$ + 10.5 mμ. [e] G. Scheibe, F. Backenköhler and A. Rosenberg, *Ber.*, 59, 2617 (1926). [f] In isoöctane λ_{max} 252 mμ and $\lambda_{H_2O} - \lambda_{HC}$ + 16.5 mμ (W. G. Brown and H. Reagan, THIS JOURNAL, 69, 1032 (1947)). [g] Reference (7). [h] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1349 (1940). [i] H. E. Ungnade, V. Kerr and E. Youse, *Science*, 113, 601 (1951).

These findings are in accord with the conclusions reached by Doub and Vandenbelt,[4] that the absorption bands in mono-substituted benzene derivatives are displaced benzene bands and that the displacements are due to electronic interaction of the group with the nucleus. Polar solvents, such as water, would tend to stabilize polar quinoid resonance forms of the types





The stabilization of the arrangement of the solvent molecules in the excited states would be greater in molecules with strong interaction between substituent and nucleus.

Literature data for monosubstituted benzene derivatives with electron donor groups (OH,[8] OMe,[4,9] SH,[10,11] SR,[11-13] NH_2,[4,9-11,14] NMe_2[14c,15,5]

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[1] Chemistry Department, Purdue University.

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[3] A. Burawoy, *Disc. Faraday Soc.*, **9**, 70 (1950); *J. Chem. Soc.*, 1180 (1939); 2310 (1952).

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