Tetrahedron. Vol. 24, pp. 913 to 943. Pergamon Press 1968. Printed in Great Britain

ELECTRONIC SPECTRA OF MONO-SUBSTITUTED ANTHRAQUINONES AND SOLVENT EFFECTS

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(*Received in Japan* 4 *November* 1966; *accepted for publication* 2 *June* 1967)

Abstract—A systematic investigation of the near UV and visible spectra of mono-substituted anthraquinones and the solvent effects on the longest wavelength $\pi \rightarrow \pi^*$ absorption band of these compounds reveals that the longest wavelength $\pi \rightarrow \pi^*$ band of 1- and 2-substituted anthraquinones with electron donating groups can be assigned to the intramolecular electron transfer transition from the substituents to the anthraquinone nucleus. The effect of the intramolecular hydrogen-bonding between the carbonyl group of the quinone and the adjacent substituents on the $\pi \rightarrow \pi^*$ absorption band has also been investigated.

The absorption frequency-shifts in various solvents indicate that the value of the frequency-shift mainly depends on the strength of the hydrogen bond between the substituents and the solvent molecules. The largest shifts are caused by the interaction between active hydrogen of the substituents and the proton accepting solvents. In the case of 1-substituted anthraquinones, however, the intramolecular hydrogen-bonding is favoured and the solvent shifts are small. In the absence of the intermolecular hydrogen bonds, the solvent shifts are well interpreted by McRae's equation.

INTRODUCTION

DURING the course of basic investigations on anthraquinone dyes, our attention was drawn to the relation between the colour and the constitution of anthraquinone derivatives and to the effect of solvents on their absorption spectra.

Many investigators[1–8] have previously reported the electronic spectra of these compounds and carried out the empirical band assignments, while Kuboyama has assigned theoretically the spectra of anthraquinone by the simple molecular orbital calculation.[9]

Since the electronic structures of anthraquinone derivatives are very complicated, a systematic study of their spectra has not been undertaken. The effect of solvents on the visible band in mono-, di- and poly-amino substituted anthraquinones has been investigated by Egerton and Roach,[10] and in mono-amino substituted anthraquinones by Hida[11] but a systematic study of the solvent effects on the electronic spectra of anthraquinone derivatives in detail has not been reported.

In the present paper we have attempted to elucidate the electronic effect of the substituents and the effect of the intramolecular hydrogen-bonding on the longest wavelength $\pi \rightarrow \pi^*$ absorption band of monosubstituted anthraquinones in non-polar solvents. The interactions between these molecules and the various polar solvents have been investigated from the effect of the latter on these spectra.

RESULTS AND DISCUSSION

The absorption spectrum of anthraquinone consists of at least three $\pi \rightarrow \pi^*$

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bands in the 240 ~ 350 mμ wavelength region, the peaks being located at 252 mμ, 272 mμ and 326 mμ.

The 252 mμ and 272 mμ bands have shoulders on both sides of the principal bands, which can be explained as vibrational structure. The bands at 252 mμ and 326 mμ are empirically assigned to the benzenoid chromophore and the 272 mμ band to the quinoid chromophore.[1]

The bands of substituted anthraquinones, when compared with the corresponding bands of the parent molecule, distinctly shift to shorter or longer wavelengths according to the substituents.

The relationship between these bands shifts and the substituents are in agreement with the observations of Peters and Sumner.[5]

Electron donating groups, introduced into 1- or 2-position of anthraquinone, showed a marked effect in the region longer than 350 mμ. The peak wavelength and molar extinction coefficients of this band in carbon tetrachloride are given in Table 1.

TABLE 1. MAXIMUM WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENTS OF LONGEST WAVELENGTH $\pi \rightarrow \pi^*$ BAND OF MONO-SUBSTITUTED ANTHRAQUINONES IN CARBON TETRACHLORIDE

Substituent R	1-Substituted anthraquinone			2-Substituted anthraquinone		
	m.p.	mμ	ε	m.p.	mμ	ε
NH_2	255°	457	6300	309°	405	4400
$NHCH_3$	170°	497	7200	235°	431	5050
$N(CH_3)_2$	138°	500	5100	186°	452	6000
NHC_6H_5	146°	505	7800	—	—	—
$NHCOCH_3$	224°	420	5930	286°	366	[a]
OH	201°	406	5900	305°	354	[a]
OCH_3	172°	374	5020	201°	362	3200
OC_6H_5	145°	364	3800	158°	359	3600

[a] Since these compounds are practically insoluble in CCl_4, the extinction coefficients could not be obtained exactly.

Concerning this band, as the electron donating character of the substituent increases, the absorption maximum shifts to longer wavelength. As shown in Fig. 1, the absorption frequencies of 2-substituted anthraquinones are parallel with the ionization potentials of the substituents, which are approximated by those of compounds obtained by replacing the anthraquinonyl group by a Me group,[12, *] i.e. the absorption frequencies of this band are affected mainly by the energy of the highest occupied orbital of the substituent. Secondly, this band compared with the other bands shows a remarkably large red shift with the increase of the polarity of solvent (Table 2). This indicates that the excited state formed by the $\pi \rightarrow \pi^*$ transition, compared with the ground state, is an extremely polar state. Finally, 1-dimethylaminoanthraquinone has the smallest extinction coefficient of the N-substituted 1-aminoanthraquinones, although in the 2-substituted series, the dimethylamino derivative has the largest extinction coefficient. Therefore, the extinction coefficient of this band is affected by the steric interaction between the carbonyl group of the quinone and the adjacent substituent. In accordance with these facts, this longest

* A similar relation was obtained by using the ionization potentials of the molecules replaced the anthraquinonyl group with hydrogen.

$\pi \rightarrow \pi^*$ absorption band must be due to intramolecular electron transfer transition from the substituent to the anthraquinone nucleus.

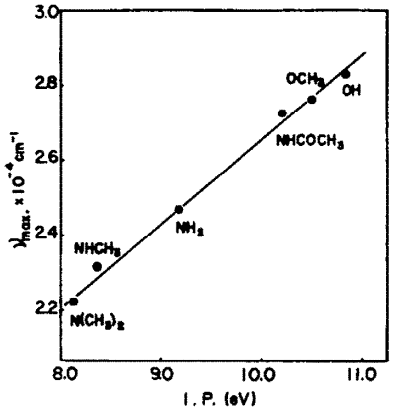

FIG. 1 ν_{max} of 2-R-anthraquinone in carbon tetrachloride *versus* ionization potential of CH_3—R.

TABLE 2. PEAK WAVELENGTHS OF $\pi \rightarrow \pi^*$ BANDS OF 1-AMINO- AND 1-METHYLAMINO-ANTHRAQUINONE MEASURED IN CYCLOHEXANE, METHYL ALCOHOL AND t-BUTYL ALCOHOL

	Peak wavelengths (mμ)					
1-Aminoanthraquinone						
Cyclohexane	241	263	268	278	303	457
Methyl alcohol	244		270		309	480
t-Butyl alcohol	245		273		312	493
1-Methylaminoanthraquinone						
Cyclohexane	244	262	271	279	312	495
Methylalcohol	245		272		314	510
t-Butyl alcohol	245		275		315	513

The following discussion refers to the intramolecular electron transfer band. Figure 2 illustrates that the absorption frequencies of 2-substituted anthraquinones are basically related to σ_s^+, which has been determined[13] from the electronic effect of the substituents on the intramolecular electron transfer band* of *p*-substituted nitrobenzenes in heptane.

This result indicates that there is a close analogy between the electronic transitions in nitrobenzene and anthraquinone substituted with electron donating groups.

The spectra of 1-substituted anthraquinones are modified by the presence of intramolecular hydrogen-bonding between the substituent and the adjacent carbonyl group of the quinone. In order to evaluate the effect of this interaction, the absorption frequencies of 1-substituted anthraquinones in carbon tetrachloride have been

* Nagakura *et al.*[14] theoretically assigned the 240 mμ band of nitrobenzene to the intramolecular electron transfer transition.

plotted against those of 2-substituted derivatives on the assumption that the electronic effect of substituents at 1-position is proportional to that of 2-position.* The results are shown in Fig. 3.

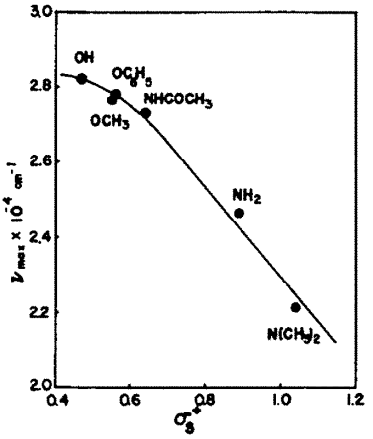

FIG. 2 ν_{max} of 2-R-anthraquinone in carbon tetrachloride *versus* Bloor's constant.

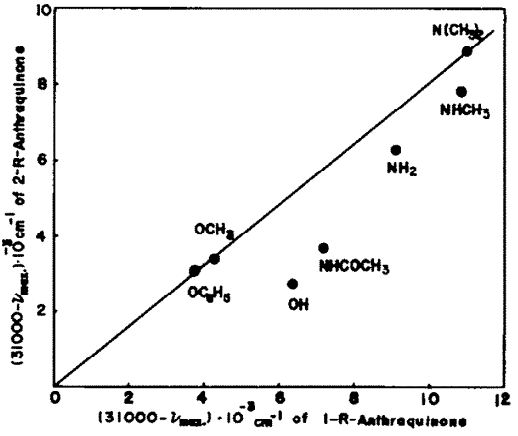

FIG. 3 Plots of ν_{max} of 1-R-anthraquinone against that of 2-R-anthraquinone in carbon tetrachloride.

In the case of phenoxy, methoxy and dimethylamino groups which cannot form chelate structures, the points are almost on a straight line, while the points for hydroxy, acetylamino, amino and methylamino groups are well below the line. It is considered that the deviation from the line is largely caused by the stabilization of the polar excited state due to the intramolecular hydrogen-bonding in 1-substituted anthraquinones. The deviation increases in the order of methylamino, amino, acetylamino and hydroxy groups, which is also the order of increasing proton donating ability of substituents. The slope of the straight line is smaller than unity, indicating that the substituent effect on the absorption peak position is greater in 1-position than in 2-position.

* A similar plot for the same band of anthraquinone derivatives in methyl alcohol has been shown by Peters and Sumner;[5] however, in this case the deviation from the liniarity is affected by the solvent effects. Therefore the effect of intramolecular hydrogen-bonding cannot be discussed in detail.

TABLE 3. DIFFERENCES OF ABSORPTION FREQUENCY ($\Delta\nu$) OF INTRAMOLECULAR ELECTRON TRANSFER BAND IN VARIOUS SOLVENTS AND IN CARBON TETRACHLORIDE, REFRACTIVE INDEXES (n_D) AT Na–D LINE AND STATIC DIELECTRIC CONSTANTS (D) OF SOLVENTS USED[b,d]

$\Delta\nu\ cm^{-1} = \nu$ (in CCl_4) $- \nu$ (in solvents)

Solvent	n_D[a]	D[a]	$\Delta\nu$ of 1-Substituted anthraquinone							$\Delta\nu$ of 2-Substituted anthraquinone					
			NH_2	$NHCH_3$	$N(CH_3)_2$	NHC_6H_5	$NHCOCH_3$	OH	OCH_3	NH_2	$NHCH_3$	$N(CH_3)_2$	$NHCOCH_3$	OH	OCH_3
1 Isooctane	1·392	1·94	−190	−200	−400	−280	[c]	−120	−440	[c]	−600	−500	[c]	[c]	−460
2 Cyclohexane	1·426	2·02	0	−80	−120	−120	50	0	−150	[c]	−440	−150	[c]	[c]	−150
3 Tetrachloro-ethylene	1·506	2·30	100	80	−40	80	110	40	0	[c]	0	0	[c]	[c]	80
4 Carbon disulfide	1·628	2·64	380	320	320	350	220	360	420	540	630	620	[c]	[c]	[c]
5 Benzene	1·501	2·28	520	480	400	390	160	240	560	600	880	850	370	770	520
6 Ethyl ether	1·353	4·34	700	200	120	−80	−470	−60	140	1600	880	290	440	1070	0
7 Ethyl acetate	1·372	6·02	880	440	320	120	−410	−60	350	1710	1470	800	660	1140	300
8 Ethyl benzoate	1·505	6·02	960	710	510	390	50	240	560	1810	1560	1160	870	1360	520
9 Acetone	1·359	20·7	830	440	360	40	−700	−180	350	1860	1370	940	520	1220	320
10 Pyridine	1·510	12·3	1310	710	590	390	−290	190	760	2470	2110	1290	800	1580	450
11 Dimethyl formamide	1·427	36·7	1390	750	660	430	−410	130	690	2810	1930	1290	1080	1930	600
12 Methyl alcohol	1·329	32·6	1050	520	400	80	−1130	−180	490	2370	1810	1200	300	1510	380
13 Isopropyl alcohol	1·375	18·3	1350	590	550	200	−950	0	630	2860	2150	1160	590	1930	450
14 t-Butyl alcohol	1·385	10·9	1600	630	630	310	−830	130	830	3280	2370	1120	730	2200	600

[a] The values of n_D and D for carbon tetrachloride are 1·460 and 2·24.

[b] The $\Delta\nu$ values of 1- and 2-phenoxyanthraquinone are respectively $-140\ cm^{-1}$ and $230\ cm^{-1}$ in acetone, $80\ cm^{-1}$ and $380\ cm^{-1}$ in isopropyl alcohol.

[c] Since these compounds are scarcely dissolved in the solvents or the peak wavelengths are out of the transparency ranges of the solvents, the frequency shifts are impossible to obtain.

[d] The experimental error in determination of $\Delta\nu$ values is less than $\pm 150\ cm^{-1}$.

The plot for 1-dimethylaminoanthraquinone lies on the line in spite of the steric hindrance between the dimethylamino group and the rest of the molecule which is indicated by the decrease of the extinction coefficient (Table 1). As Murrel has pointed out,[15] the intensity of an intramolecular electron transfer band is in general more sensitive to steric factor than to the absorption frequency.

The effect of solvents on intramolecular electron transfer band of mono-substituted anthraquinones. In the investigation of the solvent effects, consideration has been given to hydrogen-bonding, electrostatic interaction and the dispersion force between the solute and the solvent.

Shifts of the absorption frequencies ($\Delta\nu$) in various solvents are summarized in Table 3.

The effect of hydrogen-bonding. The plot of $\Delta\nu$ for 2-substituted anthraquinones against the absorption frequencies in carbon tetrachloride (Fig. 4) shows that the

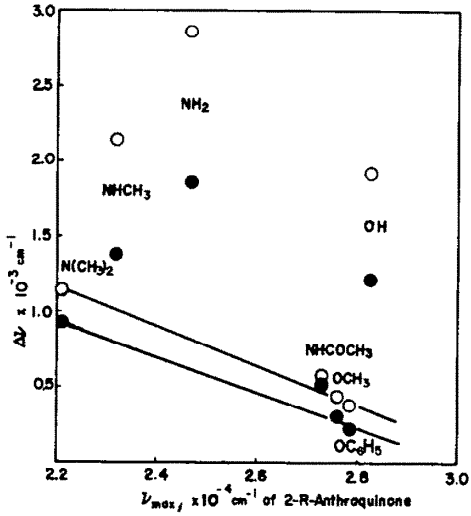

FIG. 4 The maximum absorption frequency(ν_{max}) of 2-R-anthraquinone in carbon tetrachloride *versus* its frequency shift ($\Delta\nu$) in acetone and isopropyl alcohol.

●: in acetone;○: in isopropyl alcohol.

substituents may be classified into: (a) those possessing a hydrogen atom to form hydrogen-bonding, and (b) those not able to form hydrogen-bonds.* The line through the shifts for the dimethylamino; methoxy- and phenoxy-anthraquinones is explicable in terms of the electrostatic and dispersive interactions evaluated by McRae's equation.[16]

The shift for anthraquinones with substituents forming a hydrogen-bond with the solvent molecule deviates upward from the straight line.

These deviations no doubt are mainly caused by the hydrogen-bonding between the substituents and the solvent molecules (X—H $\cdots$ S, X; nitrogen or oxygem atom of substituents, S; solvent molecules) since (a) In the case of dimethylamino, methoxy and phenoxy groups, the difference of $\Delta\nu$ values in acetone and in isopropyl alcohol, the dielectric constants of which are similar to each other, is considerably small.

* Similar results have been reported[17] for the intramolecular electron transfer band of substituted nitrobenzenes.

(b) The methylamino group shows a smaller deviation from the line than the amino group. This is accounted for by the presence of a Me group which must weaken intermolecular hydrogen-bonding. (c) Finally, for proton donating substituents the $\Delta\nu$ values increase in the order of methyl alcohol, isopropyl alcohol and t-butyl alcohol, which corresponds to the order of increasing proton accepting ability of solvent molecules.

These results indicate that the X—H $\cdots$ S type of intermolecular hydrogen bond predominantly contributes to the $\Delta\nu$ shifts while other types of hydrogen bond have a lesser affect on the shifts. When substituents are capable of hydrogen-bonding with solvent molecules, as Mataga[18] has pointed out in the system of β-naphthol and trimethylamine, the excited state is considerably stabilized by the charge transfer in the hydrogen-bonding system, since the hydrogen-bonding at the excited Franck–Condon state would be remarkably strong.

On the other hand, in the case of 1-substituted anthraquinones with proton donating groups other than the amino group, $\Delta\nu$ values in various polar solvents are much smaller than the corresponding values for 2-substituted anthraquinones. This shows that the hydrogen-bonding cannot contribute to $\Delta\nu$ values of 1-substituted anthraquinones because of the formation of intramolecular hydrogen-bonding. Therefore, the effect of polar solvents on such compounds must be due mainly to electrostatic and dispersive interactions. Since $\Delta\nu$ values in 1-aminoanthraquinone are relatively large, the amino group acts as a proton donor to form intra- and intermolecular hydrogen-bonding.

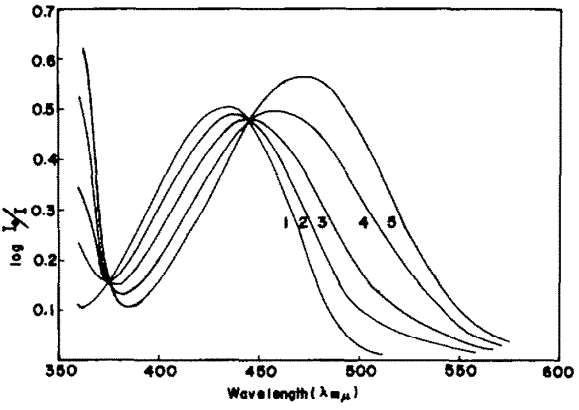

FIG. 5 Spectra of 2-methylaminoanthraquinone in the mixed solvents of carbon tetrachloride and methyl alcohol at 20°.
Concentration of 2-methylanthraquinone: $1{\cdot}09 \times 10^{-4}$ M.
Concentration of methylalcohol: (1) 0, (2) 0·124 M, (3) 0·247 M, (4) 1·24 M, (5) 14·8 M.

More direct evidence for the formation of intermolecular hydrogen-bonding can be obtained by measuring the spectra in mixed solvents containing carbon tetrachloride and a proton acceptor. When the concentration of the proton acceptor is varied at a constant solute concentration, the spectra show isosbestic points (Fig. 5)

which indicate the existence of an equilibrium given by Eq. 1.* The equilibrium constant K was calculated by Eq. 2. The plots of $(1 - d_0^\lambda/d^\lambda)/(A)$ against d_0^λ/d^λ are shown in Fig. 6.

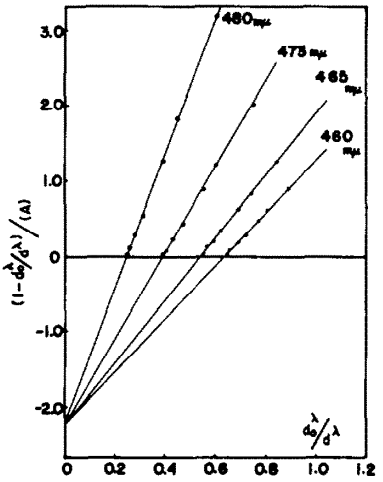

FIG. 6 $(1 - d_0^\lambda/d^\lambda)/(A)$ *versus* (d_0^λ/d^λ) for 2-methylaminoanthraquinone in the mixed solvents of carbon tetrachloride and methyl alcohol at 20°.
Concentration of 2-methylaminoanthraquinone: $1{\cdot}09 \times 10^{-4}$ M.
Concentration of methyl alcohol: 0·124 M ~ 14·8 M.

These plots are linear in all cases indicating 1:1 complex formation in these systems.

$$D + A \overset{K}{\rightleftharpoons} D \cdots\cdots A \tag{1}$$

$$\frac{1 - d_0^\lambda/d^\lambda}{(A)} = -K + (K_c^\lambda/K_D^\lambda) \cdot K \cdot (d_0^\lambda/d^\lambda) \tag{2}$$

TABLE 4. EQUILIBRIUM CONSTANTS FOR HYDROGEN BOND FORMATION BETWEEN 2-METHYLAMINO- AND 1-AMINO-ANTHRAQUINONE AND POLAR SOLVENTS IN CARBON TETRACHLORIDE AT 20°

Solute	Conc. of solute (10^{-4} M)	Polar solvent	Conc. of polar solvent (M)	K(l/mole)
2-Methylaminoanthraquinone	1·088	Acetone	0·136–8·169	2·4
		Acetonitril	0·095–7·628	2·4
		t-Butyl alcohol	0·053–4·241	2·5
		Methyl alcohol	0·124–14·840	2·2
		Ethyl acetate	0·204–6·143	1·5
		Ethyl ether	0·096–3·849	0·6
1-Aminoanthraquinone	1·110	Acetonitril	0·095–7·628	1·0
		Ethyl acetate	0·102–6·144	1·0
		Acetone	0·136–5·444	0·9
		Ethyl ether	0·385–3·849	0·6

* Under similar conditions, the spectral shifts of 1-methylamino-, 1-dimethylamino- and 2-dimethylamino-anthraquinones in the presence of the proton accepting solvents are smaller and the isosbestic points cannot be found distinctly. This indicates that the isosbestic points are caused by the intermolecular hydrogen-bonding.

Where K_c and K_D denote molar extinction coefficients of $D \cdots\cdots A$ and D at wavelength λ mμ respectively, and d_0^λ and d^λ are the apparent absorbances in pure carbon tetrachloride and in mixed solvents, respectively. (A) represents concentration of the proton acceptor. The results are shown in Table 4.

The effect of electrostatic and dispersive interactions. Theoretical investigations of solute–solvent interactions on electronic spectra applying the perturbation theory have resulted in an equation[18] with three terms arranged for solute–solvent interaction. The first term is due to the dispersion force and to the interactions between the solute permanent dipoles and the solvent dipoles thereby induced. The second term is due to the interactions between the permanent dipoles of the solute and solvent molecules, and the third term is due to the interactions between the permanent dipoles of the solvent molecules and the solute dipoles thereby induced (the quadratic Stark effect). Furthermore, it has been shown that the solvent effects on the electronic spectra of phenol blue may be analyzed by Eq. 3 obtained by a simplification based on the assumptions that (1) the weak quadrastic stark effect is neglected, (2) the refractive index of solvent at all frequencies involving the zero frequency is approximated with the values obtained by Na–D line and (3) the weighted mean wavelength (L_0) is a constant for all the solvents. Therefore, Eq. 3 proposed by McRae was adopted in this investigation.

$$\nu_s - \nu_g = (AL_0 + B)\frac{n_D^2 - 1}{2n_D^2 + 1} + C\left(\frac{D-1}{D+2} - \frac{n_D^2 - 1}{n_D^2 + 2}\right) \tag{3}$$

where ν_g and ν_s are the absorption frequencies at vapour phase and solution and $AL_0 + B$, and C are constants which are independent of the properties of the solvents. The values of $AL_0 + B$ and C are determined by applying the least square method to the data of Table 3. The results are given in Table 5 and the comparison of calculated and observed frequency shifts of 1-amino, 1-phenylamino and 2-dimethylamino-anthraquinones are shown in Fig. 7. In Fig. 7, all points are distributed around a theoretical straight line with a root mean square deviation of 90 cm^{-1}

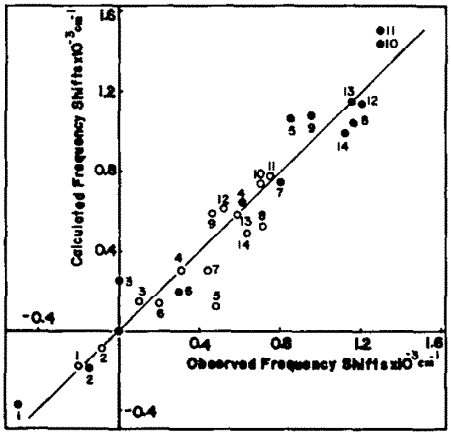

FIG. 7 Calculated *versus* observed frequency shifts in various solvents. Solvent numbers correspond to those listed in Table 3.

○: 1-Methylaminoanthraquinone; ●: 2-Dimethylaminoanthraquinone.

for 1-amino and 2-phenylaminoanthraquinone, and 120 cm^{-1} for 2-dimethylamino-anthraquinone, which is less than the experimental error in determination of the absorption frequency of the solvents. These results indicate that the solvent effects are well analyzed by Eq. 3. From these values in Table 5, it has been found that the

TABLE 5. VALUES OF $(AL_0 + B)$ AND C IN EQUATION 3 BY APPLYING THE LEAST SQUARE METHOD

Mono-substituted anthraquinone		
Substituent R	$-(AL_0 + B)$	$-C$
1-NH_2	8100	[a]
1-NHMe	7000	1300
1-NMe_2	9000	1400
1-NHPh	8400	710
1-OH	7200	370
1-OMe	11900	1300
2-NHMe	17300	[a]
2-NMe_2	15400	2660
2-OMe	14000	1400

[a] Because these compounds are forming the hydrogen bond with the polar solvents used, the values of C are impossible to calculate with Eq. 3.

dispersion force and the electrostatic interaction cause a red shift for all mono-substituted anthraquinones, which is reasonable because the solute polarity increases in the excited state.

The data in Table 5 lead to the following conclusions. Firstly, both $(AL_0 + B)$ and C values increase more for 2-substituted anthraquinones than for 1-substituted isomers. It may be considered that the increment will mainly depend on the differences of the magnitude of the change in dipole moments during the transition, of the geometrical constitution of the molecule and of the charge distributions in the ground and excited states between 1- and 2-substituted anthraquinones. Secondly, the C values decrease in the order of methoxy, dimethylamino, methylamino, phenylamino and hydroxy groups in the case of 1-substituted anthraquinones. This indicates that the dimunition in the C value is caused by the intramolecular hydrogen-bonding, since the solute polarities at the excited state are decreased by the delocalization of charge through such a chelated system.

EXPERIMENTAL

Materials. Anthraquinones substituted with methylamino, dimethylamino, phenylamino, acetylamino, hydroxy, methoxy and phenoxy groups at 1- or 2-position were prepared by the usual procedure and other compounds were obtained commercially. All materials were purified by repeated recrystallizations followed by chromatography on alumina.

The m.ps of these purified compounds were in good agreement with those in literature, and the results of elementary analysis were also consistent with the theoretical values.

Measurements of absorption spectra. The absorption spectra in soln were recorded on a Simazu Automatic Recording Spectrophotometer, model SV 50, in the near UV and visible regions using quartz cells of various pass-length (10 to 100 mm) at room temp (20 ± 1°).

Most solvents used were spectrograde reagents of E. Merck & Co. In case of CCl_4, tetrachloroethylene, AcOEt, ethyl benzoate, and t-butyl alcohol, analytical grade reagents were used after purification by usual procedures.

REFERENCES

[1] R. A. Morton and W. T. Earlam; *J. Chem. Soc.* 159 (1941).
[2] C. J. P. Spruit; *Rec. Trav. Chim.* **68**, 325 (1949).
[3] C. F. H. Allen, C. V. Wilson and G. F. Frame, *J. Org. Chem.* **7**, 169 (1942).
[4] S. E. Sheppard and P. T. Newsome, *J. Am. Chem. Soc.* **64**, 2937 (1942).
[5] R. H. Peters and H. H. Sumner, *J. Chem. Soc.* 2101 (1953).
[6] J. H. Moran and H. I. Stonehill, *Ibid.* 765 (1957).
[7] T. Hayashi and M. Matsuo; *Bull. Chem. Soc. Japan* **35**, 1500 (1962); T. Hayashi and R. Shibata, *Ibid.* **34**, 116 (1961); T. Hayashi, T. Tokumitu, *Ibid.* **38**, 916 (1965).
[8] H. Labhart, *Advances in Molecular Spectroscopy* (Edited by A. Mangini) Vol. 1; p. 255. Macmillan, N.Y. (1962).
[9] A. Kuboyama, *Bull. Chem. Soc. Japan* **31**, 752 (1958); A. Kuboyama, K. Wada, *Ibid.* **39**, 1874 (1966).
[10] G. S. Egerton and A. G. Roach, *J. Soc. Dyers Colourists* **74**, 401 (1958).
[11] M. Hida, *J. Chem. Soc. Japan, Ind. Chem. Soc., Kogyo Kagaku Zasshi* **69**, 874 (1966).
[12] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.* 4434 (1964).
[13] J. E. Bloor, *Chem. & Ind.* 526 (1960).
[14] S. Nagakura, M. Kojima and Y. Maruyama, *J. Mol. Spectroscopy* **13**, 174 (1964).
[15] J. N. Murrell, *J. Chem. Soc.* 3779 (1956).
[16] E. G. McRae, *J. Phys. Chem.* **61**, 562 (1957).
[17] E. W. Crandall and J. Olguin, *J. Org. Chem.* **29**, 2088 (1964).
[18] N. Mataga and Y. Kaifu, *Mol. Phys.* **7**, 138 (1963).