Spectroscopic Studies of Bis(arylamino)anthraquinones

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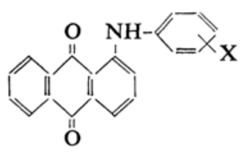
In a previous paper,[1] 1-arylaminoanthraquinones (I) with NO_2, Cl, Me, OMe, and NH_2 as substituents in the aryl group were prepared, and their visible absorption spectra in solution and infrared spectra in the solid state were measured and discussed. On the basis of these results, the effects of the substituent groups were discussed in view of various properties, such as visible absorption maxima or infrared C=O and N–H frequencies. In this paper, the preparation and spectral characteristics of 1,4-, 1,5- and 1,8-bis(arylamino)anthraquinones (II, III, IV) with the above-mentioned groups as substituents (X) in the aryl group will be reported. These are parent compounds of anthraquinone acid or polyester dyes. As was the case with 1-arylaminoanthraquinones, on the basis of the results of the visible and infrared absorption spectra for bis(arylamino)-anthraquinones, the relations between the shifts of the visible absorption peaks, the C=O or N–H frequencies and their structures will be discussed.



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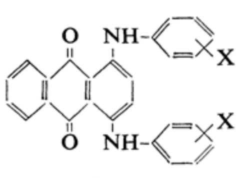

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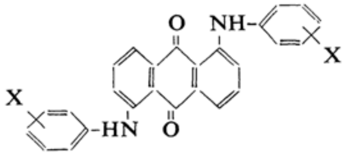

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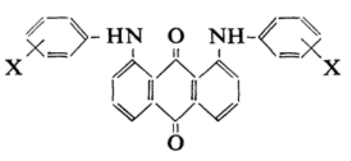

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Results and Discussion

Visible Absorption Spectra.—The visible absorption peaks of bis(arylamino)anthraquinones in *o*-dichlorobenzene are shown in Table I. On the basis of these results, relations between the wavelengths or intensities of the absorption maxima and the positions of the arylamino groups have been discussed. Furthermore, for each series of 1,4-, 1,5- and 1,8-bis(arylamino)-anthraquinones, the effects of the substituent (X) upon the wavelength and the intensity of the absorption maximum have been discussed. Compounds I and III give one visible absorption peak, as in the cases of the corresponding amino- and acylamino-anthraquinones.[1-4] The wavelength of the absorption maximum of III (X=H) is somewhat longer than that of I (X=H), but the intensity of the former is approximately twice that of the latter. Such a relation is also seen with other III's. As was shown by Hartmann's results,[5] the absorption maximum of 1,8-diaminoanthraquinone appeared in the same wavelength region as that of the 1,5-isomer, and the absorption spectrum was characterized by twin peaks of a lower definition with a shoulder at a lower wavelength, peaks which were similar to those observed for the 1,4-isomer. The absorption spectral character of 1,8-diaminoanthraquinone, therefore, appears to be intermediate between those of 1,4- and 1,5-isomers. On the contrary, IV (X=H) showed only one absorption band, located at a somewhat longer wavelength than that of the 1,5-isomer; the intensity of the former absorption is slightly lower than that of the latter, but approximately twice that of I (X=H). II (X=H) gives twin peaks of a similar intensity, unlike those of I (X=H), III (X=H) and IV (X=H). Such a relation is seen with other II's. I, III and IV, each with a strongly electron-attracting $-NMe_3^+$ group as a substituent, gave only one absorption peak in dioxane, but the corresponding II gave a peak at 593 mμ (12400)* with a shoulder in the region

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[1] T. Hayashi and M. Matsuo, This Bulletin, **35**, 1500 (1962).

[2] R. H. Peters and H. H. Sumner, *J. Chem. Soc.*, **1953**, 2101.

[3] G. S. Egerton and A. G. Roach, *J. Soc. Dyers Colorists*, **74**, 401 (1958).

[4] T. Hayashi and R. Shibata, This Bulletin, **34**, 1116 (1961); T. Hayashi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1985 (1960).

[5] H. Hartmann and E. Lorenz, *Z. Naturforsch.*, **72**, 360 (1952).

* Wavelength, mμ (molar extinction coefficient).

TABLE I. VISIBLE ABSORPTION PFAKS OF 1-ARYLAMINO-, 1,4-, 1,5- AND 1,8-BIS-(ARYLAMINO)ANTHRAQUINONES

Substituent of the aryl group (X)		1,4-Derivative 1st Band λ_{max}, mμ (ε_{max})		2nd Band λ_{max}, mμ (ε_{max})
H[a]		607(13000)		647(14300)
p-NO_2[b]	$\underline{547}$*	589	615	630
p-Cl	$\underline{550}$ (5770)	605(12900)		644(13600)
p-Me[c]	$\underline{551}$ (6230)	617(14500)		650(15900)
p-OMe		621(13800)		651(14700)
p-NH_2[b]	$\underline{615}$	$\underline{629}$		656

Substituent of the aryl group (X)	1-Derivative[1] λ_{max}, mμ (ε_{max})	1,5-Derivative λ_{max}, mμ (ε_{max})	1,8-Derivative λ_{max}, mμ (ε_{max})
H	508(5920)	538(13700)[d]	558(13500)[d]
m-NO_2	489(6460)	517(14900)	
p-NO_2	487(10700)		535[b]
m-Cl	501(7220)	531(13900)	
p-Me	514(6190)	544(14400)[e]	561(14100)[f]
p-OMe	516(6000)	546(13500)	
p-NH_2	525(5990)	555[b]	

* An underlined numerical value denotes a shoulder.

a) 1,4-Bis(phenylamino)anthraquinone gave two peaks at 595 and 632 mμ with a shoulder at 550 mμ in ethanol,[6] two peaks at 602.5 and 640 mμ in chlorobenzene[7] and at about 605 and 645 mμ in 1,2,4-trichlorobenzene.[8]

b) In the saturated solution.

c) 1,4-Bis(p-tolylamino)anthraquinone gave two peaks at 600 and 638 mμ with a shoulder at 550 mμ in ethanol,[6] two peaks at 610 and 645 mμ in chlorobenzene,[7] two peaks at 600 and 640 mμ in dioxane,[9] and two peaks at 610 and 645 mμ.[10]

d) Both 1,5- and 1,8-bis(phenylamino)anthraquinones gave a peak at 530 mμ in chlorobenzene.[7]

e) 1,5-Bis(p-tolylamino)anthraquinone gave a peak at 540 mμ in chlorobenzene,[7] and a peak at about 530 mμ in dioxane.[9]

f) 1,8-Bis(p-tolylamino)anthraquinone gave a peak at 550 mμ in chlorobenzene.[7]

of 610—630 mμ (11600).[11] Hence, this broad shoulder seems to correspond to the two absorption peaks of II (X=p-NO_2). I, III and IV, with strongly electron-donating $-NMe_2$ substituents, gave a single absorption peak in dioxane.[12] On the other hand, the corresponding II gave a peak at 638 mμ (15300) with a shoulder at 590 mμ (11000) in dioxane, and a peak at 600 mμ (15500) with a shoulder at 590 mμ and a broad peak in the region of 640—655 mμ in ethanol.[11,12] Here, too, these results are similar to the results for II (X=p-NH_2). Consequently, the relations between the wavelengths or intensities of the absorption maxima and the positions of the arylamino groups agree with those for amino- and acylaminoanthraquinones.[2-4]

In the case of the compound I previously reported,[1] a plot of the wave numbers of the absorption maxima versus the Hammett σ values[13] of the substituents in the aryl group gave a linear relationship, but the plot of the wave numbers varsus the Brown σ^+ values[14,15] was concave; this was different from the case of acylaminoanthraquinones.[4] Here, too, for the peaks of each series, a plot of the wave numbers versus the former substituent constants gave a linear relationship, as is indicated in Figs. 1 and 2. These results can be explained in the same way as in the case of compound I.[1] It is interesting that the linear

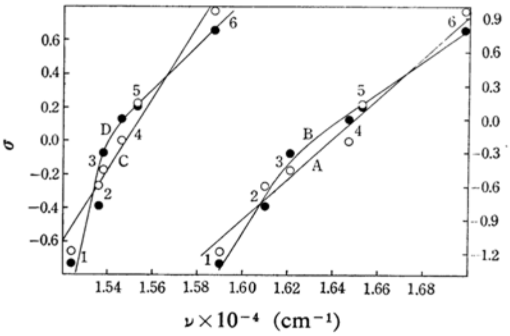

Fig. 1. Plots of wave numbers of the visible absorption maxima versus Hammett σ values and Brown σ^+ values of the substituents of 1,4-bis(arylamino)anthraquinones.

A : Wave numbers of the first bands versus Hammett σ values
B : Wave numbers of the first bands versus Brown σ^+ values
C : Wave numbers of the second bands versus Hammett σ values
D : Wave numbers of the second bands versus Brown σ^+ values

1 p-NH_2, 2 p-OMe, 3 p-Me, 4 H, 5 p-Cl
6 p-NO_2

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[6] K. Naiki, E. Chō and S. Tsuruoka, *J. Soc. Org. Synthet. Chem. Japan* (*Yūki Gōsei Kagaku Kyōkaishi*), **17**, 705 (1959).

[7] S. Nakazawa, ibid., **20**, 584 (1962).

[8] J. Weinstein and C. Merritt, Jr., *J. Am. Chem. Soc.*, **81**, 3759 (1959).

[9] C. F. H. Allen, C. V. Wilson and G. F. Frame, *J. Org. Chem.*, **7**, 169 (1942).

[10] N. S. Dokunikhin and T. N. Kurdyumova, *Zhur. Obshchei Khim.*, **25**, 617 (1955); *Chem. Abstr.*, **50**, 3369 (1956).

[11] M. Ichikawa and M. Okazaki, *J Chem. Soc. Japan, Ind. Chem. Sec.* (*Koguyo Kagaku Zasshi*), **67**, 138 (1964).

[12] M. Ichikawa and M. Okazaki, ibid., **67**, 142 (1964).

[13] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[14] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

[15] H. C. Brown, "Steric Effects in Conjugated Systems," Ed. by G. W. Gray, Butterworths Scientific Publications, London (1958), p. 100.

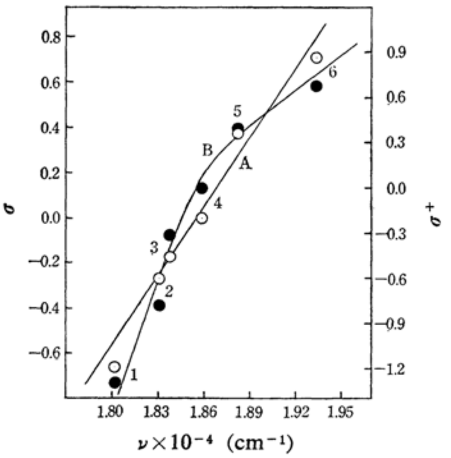

Fig. 2. Plots of wave numbers of the visible absorption maxima versus Hammett σ values and Brown σ^+ values of the substituents of 1,5-bis(arylamino)anthraquinones.

A : Wave numbers versus Hammett σ values

B : Wave numbers versus Brown σ^+ values

1 p-NH_2, 2 p-OMe, 3 p-Me, 4 H, 5 m-Cl, 6 m-NO_2

relationship is established for the plots for both the first and the second peaks of II.

Infrared Absorption Spectra.—Three μ bands of the infrared absorption spectra of a few 1,4-bis(arylamino)anthraquinones as Nujol mull have been observed.[16] In this work, the infrared absorption spectra of 1,4-, 1,5- and 1,8-bis(phenylamino)anthraquinones and their related derivatives as Nujol mull were observed, and information about molecular structures in the solid was obtained.

It has been known that 1,4-, 1,5- and 1,8-disubstituted anthraquinones as Nujol mull show characteristic absorption bands at 820—840 and 720—730, 800—820 and 690—710, and 830—850 and 730—750 cm^{-1} respectively, and that these bands have intensities ranging from medium to very strong.[17] Absorption bands in the region of 800—850 and of 690—750 cm^{-1} for II (X=H), III (X=H) and IV (X=H) are shown in Table II. The respective characteristic absorption bands of II (X=H), 829.9 and 728.3 cm^{-1}, appeared in the corresponding regions of 1,4-disubstituted anthraquinones, and the same results were obtained for III (X=H) and IV (X=H). The intensities of these absorption bands, except the one of the 829.9 cm^{-1} band, were medium or very strong.

TABLE II. ABSORPTION BANDS IN THE REGION OF 800—850 AND OF 690—750 cm^{-1} FOR 1,4-, 1,5- AND 1,8-BIS(PHENYLAMINO)-ANTHRAQUINONES

1,4-Derivative	841.8(w),	829.9(w),	815.0(w),
	744.6(m),	728.3(vs),	695.9(s)
1,5-Derivative	842.5(s),	806.5(vs),	714.3(vs),
	695.9(vs)		
1,8-Derivative	844.6(w),	838.9(m),	819.7(m),
	809.7(m),	744.6(vs),	729.9(w),
	719.4(w),	700.8(s),	694.0(vs)

The absorption bands in the 3 and 6 μ regions of bis(phenylamino)anthraquinones are shown in Table III, and also in Figs. 3, 4 and 5. Compound III (X=H) gave only one C=O band, this being due to the fact that the strengths of the two C=O bands are equal. For IV (X=H), two C=O bands appeared, and,

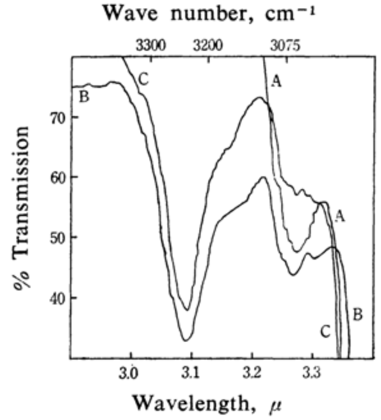

Fig. 3. 3 μ Bands of 1,4-, 1,5- and 1,8-bis-(phenylamino)anthraquinones by Nujol mull technique.

A : 1,4-Derivative, B : 1,5-Derivative,

C : 1,8-Derivative

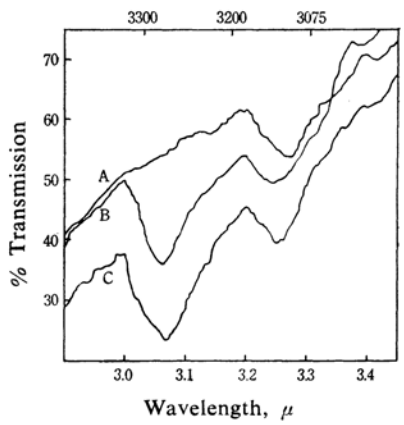

Fig. 4. 3 μ Bands of 1,4-, 1,5- and 1,8-bis-(phenylamino)anthraquinones by potassium bromide disk technique.

A : 1,4-Derivative, B : 1,5-Derivative,

C : 1,8-Derivative

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[16] D. N. Shigorin, "Hydrogen Bonding," Ed. by D. Hadzi, Pergamon Press, London (1959), p. 191.

[17] N. Ōi, *Pharm. Bull. (Tokyo)*, **5**, 153 (1957).

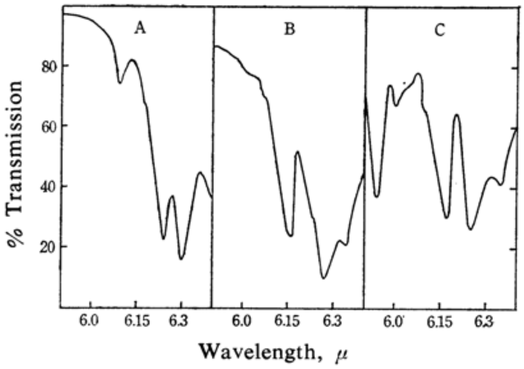


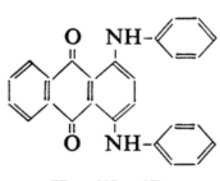
Fig. 5. 6 μ Bands of 1,4-, 1,5- and 1,8-bis-(phenylamino)anthraquinones by Nujol mull technique.
A: 1,4-Derivative, B: 1,5-Derivative,
C: 1,8-Derivative

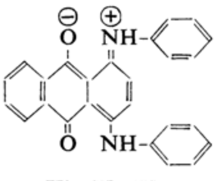
as was the case with 1-substituted anthraquinones with electron-donating groups as substituents, this splitting of the C=O absorption would appear to be the result of electronic dissymmetry.[18,19] The first C=O band at a higher frequency is assigned to the C=O(a)* vibration, since the frequency is closer to the C=O frequency of anthraquinone, and the second C=O band at a lower frequency is assigned to the C=O(b) vibration in the peri-position of the phenylamino group.

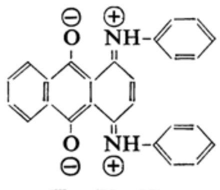
TABLE III. N-H AND C=O FREQUENCIES OF SOLID PHENYLAMINOANTHRAQUINONES

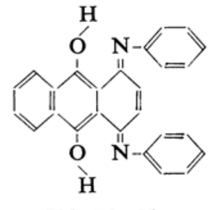
	N-H Frequencies cm^{-1}	C=O Frequencies cm^{-1}	
		(a)	(b)
Anthraquinone[18]		1676	
1-Phenylaminoanthraquinone[1]	3236	1672	1634
1,4-Bis(phenylamino)-anthraquinone	3058		1603
1,5-Bis(phenylamino)-anthraquinone	3236		1623
1,8-Bis(phenylamino)-anthraquinone	3236	1684	1621

In this connection, it is interesting that the N-H and C-H stretching bands of III (X=H) and IV (X=H) appear at about 3.1 and 3.25 μ respectively, while II (X=H) has only one discrete band at the lower wavelength in this region. If the 3058 cm^{-1} band of II (X=H) is assigned to the C-H vibration, its structure must be indicated by IId (X=H) instead of IIa (X=H).


IIa (X=H)


IIb (X=H)


IIc (X=H)


IId (X=H)

Frequencies for the C=N groups[20] are most probably found between 1690 and 1640 cm^{-1}, and the influence of conjugation is usually small. For the IId (X=H) structure, therefore, the observed frequency in II (X=H) at 1603 cm^{-1} should be attributed to the C=N vibration. However, this may be too low a frequency to be normally attributed to the C=N vibration. Furthermore, the absorption of 1,4-diamino- and 1,4-bis(methylamino)-anthraquinones,[18] 1,1′-dianthrimide,[21] indanthrone,[8] and 3,4-phthaloylacridone[22] did not show the C=N band. Thus, there is no precedent for assigning the 1603 cm^{-1} band to the C=N vibration; it should probably be assigned to the C=O vibration. Consequently, this band can not be used to support the IId (X=H) structure containing the C=N bond.

Frequencies of the O-H groups are usually found in the frequency range between 3650 and 3450 cm^{-1}, and the influence of conjugation is quite large.[23] Many of the frequencies for O-H groups of oxanthrone, anthraquinol and their substituted derivatives in a solid[18] were found in the frequency range from 3500 to 3300 cm^{-1}, but the shifts of the frequencies of these O-H groups were not due to conjugation, but mainly to hydrogen bonding. Moreover, the absorptions of 1-arylamino-[1] and 1-benzoylaminoanthraquinones[4], 1,1′-dianthrimide,[21] indanthrone,[8] 1,2- and 3,4-phthaloylacridones,[22] and indigo[24] did not show the O-H band. The 3058 cm^{-1} band

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[18] M. S. C. Flett, *J. Chem. Soc.*, **1948**, 1441.

[19] T. C. Bruice and A. B. Sayigh, *J. Am. Chem. Soc.*, **81**, 3416 (1959).

* The C=O(a) absorptions correspond to the free C=O bands, while the C=O(b) absorptions are assigned to the chelated C=O groups.

[20] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, New York (1958), p. 267.

[21] R. A. Durie and J. S. Shannon, *Australian J. Chem.*, **11**, 189 (1958).

[22] T. Hayashi and J. Maehara, This Bulletin, **35**, 1690 (1962).

[23] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, New York (1958), p. 96.

[24] G. M. Wyman, *J. Am. Chem. Soc.*, **78**, 4599 (1956); W. R. Brode, E. G. Pearson and G. M. Wyman, ibid., **76**, 1034 (1954).

of II (X=H) seems, therefore, to be too low a frequency to be normally assigned to the O–H vibration; thus, this band can not be used to support the structure IId (X=H). Consequently, the 3058 cm^{-1} band should be assigned to the N–H vibration of the arylamino-type structure IIa (X=H). This molecular structure, assigned to its solid state, agrees with that concluded in solution on the basis of the results of visible absorption; moreover, the chemical evidence favors the arylamino-type structure IIa (X=H).

The C=O(b) frequency in the peri-position of the phenylamino group in Table III increases in the order of II (X=H), IV (X=H), III (X=H) and I (X=H); the C=O(b) bond is also strengthened in this order. This result for phenylaminoanthraquinones can be satisfactorily explained by means of the same electronic interpretation as for the shifts of the visible absorption peaks for these derivatives in solutions.

As is indicated in Table IV with 1-(*m*- and *p*-substituted phenyl)aminoanthraquinones, the C=O(b) frequency shifted lower when an arylamino group with electron-donating substituents is placed in the peri-position to the C=O group, while the reverse was found to be true when one with electron-attracting substituents is placed in the same position. A similar result was also obtained for 1-arylamino-5-chloro- and 1,5-bis(arylamino)-anthraquinones. Furthermore, the C=O frequencies of 1-arylamino-5-chloroanthraquinones were much the same as for corresponding 1-arylaminoanthraquinones, this being deduced from the fact that the effects of a chlorine atom on the C=O frequency for 1- and 2-chloroanthraquinones were quite small.[8]

TABLE IV. N–H AND C=O FREQUENCIES OF SOLID 1-ARYLAMINO-, 1-ARYLAMINO-5-CHLORO- AND 1,5-BIS(ARYLAMINO)-ANTHRAQUINONES

Substituent of the aryl group (X)	1-Arylamino-[1]		1-Arylamino 5-chloro-		1,5-Bis-(arylamino)-	
	$\nu_{C=O(a)}$ cm^{-1}	$\nu_{C=O(b)}$ cm^{-1}	$\nu_{C=O(a)}$ cm^{-1}	$\nu_{C=O(b)}$ cm^{-1}	ν_{N-H} cm^{-1}	$\nu_{C=O}$ cm^{-1}
H	1672	1634	1675	1631	3236	1623
p-NH$_2$	1672	1639	1675	1639		
m-NO$_2$	1675	1637			3279	1634
p-Cl	1678	1637	1678	1634		
m-Cl	1681	1637	1681	1637	3247	1629
p-Me	1684	1629	1678	1626	3236	1621
p-OMe	1678	1626			3226	1616

For 1-substituted anthraquinones (V, substituents: Y), the wavelengths of the visible absorption maxima in solution and the C=O stretching frequencies increased in the following order:[1]

maximum wavelengths of the visible spectra:

$$\mathrm{V\ (Y=NHCOC_6H_5) < V\ (Y=NH_2) < V\ (Y=NHCH_3) \lesssim V\ (Y=NHC_6H_5)}$$

frequencies of the C=O stretching bands:

$$\mathrm{V\ (Y=NH_2) < V\ (Y=NHC_6H_5) \lesssim V\ (Y=NHCH_3) < V\ (Y=NHCOC_6H_5)}$$

The fact that the C=O frequencies of V (Y=NHCH$_3$) and V (Y=NHC$_6$H$_5$) were higher than those of V (Y=NH$_2$) should not be attributable to steric hindrance, but to the reduction by the methyl or the phenyl group of resonance within the chromophoric system of V (Y=NHCH$_3$) and V (Y=NHC$_6$H$_5$).[1]

TABLE V. N–H AND C=O FREQUENCIES OF SOLID 1,4- AND 1,5-DISUBSTITUTED ANTHRAQUINONES

Disubstituted anthraquinone	N–H Fre quencies cm^{-1}	C=O Fre-quencies cm^{-1}
1,4-Diamino-[18]	3370, 3250	1610
1,4-Bis(methyl-amino)-[18]	3240	1610
1,4-Bis(phenyl-amino)-	3058	1603
1,4-Bis(benzoyl-amino)-[a]	3125	1686
1,5-Diamino-	3425, 3311[b]	1610
1,5-Bis(methyl-amino)-	3333	1623
1,5-Bis(phenyl-amino)-	3236	1623
1,5-Bis(benzoyl-amino)-[a]	3226	1689

[a] The C=O frequencies of 1-benzoylaminoanthraquinone[4] were observed at 1681, 1669 and 1637 cm^{-1}; the highest frequency was assigned to the free C=O group; the middle, to the chelated C=O group, and the lowest, to the benzoyl C=O group.[4,18] On the other hand, the C=O frequencies of 1,4- and 1,5-bis(benzoylamino)anthraquinones[4] were observed at 1686 and 1639, and 1689 and 1639 cm^{-1}, respectively. As the free C=O group was absent in them, the respective higher frequencies were assigned to the chelated C=O groups and the respective lower frequencies to the benzoyl C=O groups,[4] as in the case of 1-benzoylaminoanthraquinone.

[b] Shigorin[16] gives 3430 and 3310 cm^{-1}.

Here, too, for 1,5-disubstituted anthraquinones (VII, substituents: Y), the wavelengths of the visible absorption maxima in solution increased in the following order:

$$\mathrm{VII\ (Y=NHCOC_6H_5) < VII\ (Y=NH_2) < VII\ (Y=NHCH_3) \lesssim VII\ (Y=NHC_6H_5)}$$

while, as is indicated in Table V, the C=O stretching frequencies increased in the following order:

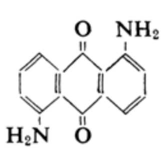
$$\text{VII }(Y=NH_2)<\text{VII }(Y=NHCH_3)=\text{VII }(Y=NHC_6H_5)<\text{VII }(Y=NHCOC_6H_5)$$

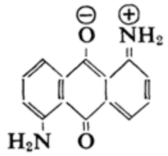
As will be clear from the establishment of simple additivity between the two chromophoric systems within VII, the fact that the C=O frequencies of VII ($Y=NHCH_3$) and VII ($Y=NHC_6H_5$) are higher than that of VII ($Y=NH_2$) can be interpreted in the same way as in the case of V.[1]

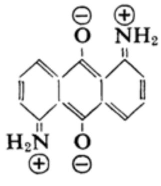
As is indicated in Table V, the N–H frequencies of VII increased in the following order:

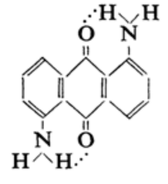
$$\text{VII }(Y=NHCOC_6H_5)<\text{VII }(Y=NHC_6H_5)<\text{VII }(Y=NHCH_3)<\text{VII }(Y=NH_2)$$

and the reverse was found to be true for their C=O frequencies. This fact can be interpreted in the same way as in the case of V;[1] namely, for VIIa ($Y=NH_2$) it seems that it is impossible to form a powerful hydrogen bonding, as in VIId ($Y=NH_2$), between the amino and C=O groups, and that, therefore, a contribution of the ionic structure VIIb ($Y=NH_2$) and VIIc ($Y=NH_2$) to the resonance, rather than the weak hydrogen bonding, is responsible for the considerable lowering of the C=O frequency, the hydrogen bondiag serving only to stabilize the ionic structures. On the other hand, for VII ($Y=NHCH_3$) and VII ($Y=NHC_6H_5$), such resonance within chromophoric systems was reduced by the methyl and phenyl groups respectively. The above-mentioned order of the increase in N–H frequencies, therefore, suggests that the smaller the contribution of the ionic structure to the resonance becomes, the greater the contribution of the hydrogen bonding, as in the case of V.[1]


VIIa ($Y=NH_2$)


VIIb ($Y=NH_2$)


VIIc ($Y=NH_2$)


VIId ($Y=NH_2$)

For monosubstituted anthraquinones, with electron-donating groups as substituents, Peters and Sumner,[2] using a correlation of the Hixon-Johns type,[25] showed the following: An arbitrary straight line was drawn the ordinate scale of which represented the wavelength of the absorption maximum, the abscissa being undefined. The points corresponding to the wavelengths of the visible absorption maxima of 2-substituted anthraquinones were marked on this line, and an arbitrary scale of abscissa was then constructed labelled with the names of the substituents. A plot of the wavelengths of the visible absorption maxima for V versus the scale of the substituents so defined gave a straight line, but a considerable deviation from the linear relation was observed with V with substituents (Y) having internal hydrogen-bonding possibilities. This fact suggests that the latter 1-substituted anthraquinones have wavelengths with absorption maxima greater than would be expected from the electron-donating abilities of their substituents, the excess being attributable to the resonance of the chelate structure.[25] For the latter 1-substituted anthraquinones, the extents of deviation from the straight line were calculated by Hida[26] as follows:

	kcal./mol.
1-Acetylaminoanthraquinone	3.3
1-Methylaminoanthraquinone	1.5
1-Phenylaminoanthraquinone*	1.5
1-Aminoanthraquinone	1.3

Consequently, it is probable that the magnitude of these values is closely related with the hydrogen-bonding energy between their substituent groups and the C=O groups of the latter 1-substituted anthraquinones.[26] Here, for VII, therefore, it seems that this fact has given other evidence for the above-mentioned interpretation of the extent of the contribution of the ionic structure and of the hydrogen bonding to the increase in N–H frequencies.

For 1,4-disubstituted anthraquinones (VI, substituents: Y), the wavelengths of the visible absorption maxima in solution increased in the following order:

$$\text{VI }(Y=NHCOC_6H_5)<\text{VI }(Y=NH_2)<\text{VI }(Y=NHCH_3)\lesssim\text{VI }(Y=NHC_6H_5)$$

The visible absorption maxima of VI ($Y=NH_2$) and VI ($Y=NHCOC_6H_5$) in solution were, moreover, located at far longer wavelengths than those of the corresponding VII ($Y=NH_2$) and VII ($Y=NHCOC_6H_5$). As is indicated in

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[25] R. M. Hixon and I. B. Johns, *J. Am. Chem. Soc.*, **49**, 1786 (1927).

[26] M. Hida, *Dyestuffs and Chemicals* (*Senryo to Yakuhin*), **8**, 493 (1963).

* Peaks of 1- and 2-phenylaminoanthraquinones appeared at 507 and 465 mμ respectively in methanol. From these results, the extent of the deviation for the former was calculated by the present authors.

Table V, however, the C=O stretching frequencies of VI ($Y=NH_2$) and VII ($Y=NH_2$) are the same, and those of VI ($Y=NHCOC_6H_5$) and VII ($Y=NHCOC_6H_5$) are alike. The C=O stretching frequencies for VI, moreover, increased in the following order:

$$\text{VI } (Y=NHC_6H_5) < \text{VI } (Y=NHCH_3) = \text{VI } (Y=NH_2) < \text{VI } (Y=NHCOC_6H_5)$$

This order was, then, the reverse of the increase in the wavelengths of their visible absorption maxima, these being different from the cases of those for V and VII. Furthermore, the order of the increase of the N-H frequencies for VI is not in the decreasing order of their C=O frequencies, this being different from the case of those for VII. It is interesting, moreover, that both the N-H and C=O frequencies of 1, 4-bis(phenylamino)anthraquinone are the lowest among VI's investigated. Because of interaction between their two chromophoric systems, these VI's do not obey the simple additivity rule observed with VII; this interaction is supposed to produce a new chromophore. The above-mentioned results may, therefore, be attributable to the contribution of the ionic structures IIb ($X=H$) and IIc ($X=H$), and to the fact that the decreasing effect of the resonance by the phenyl group in the chromophoric system of 1, 4-bis(phenylamino)anthraquinone is smaller than in that of 1, 5-bis(phenylamino)anthraquinone. By X-ray study, no steric hindrance was estimated in II ($X=H$), and the coplanarity of the phenyl groups was concluded;[27] it seems that these facts have given support to the above-mentioned interpretation.

Experimental

Materials and Apparatus.—The compounds used in this investigation were purified by repeated crystallization and then by chromatography or hot chromatography on alumina in suitable solvents.

The visible absorption spectra were recorded with a Shimadzu spectrophotometer, type QB-50. The infrared absorption spectra of the solid samples were obtained using a Perkin-Elmer Model 21 double-beam spectrophotometer fitted with a rock-salt prism. *o*-Dichlorobenzene was purified by the method recommended for the purification of chlorobenzene.[28]

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[27] N. S. Dokunikhin, G. A. Gol'der and G. S. Zhdanov, *Doklady Akad. Nauk S. S. S. R.*, **119**, 87 (1958); *Chem. Abstr.*, 52, 11512 (1958).

[28] A. Weissberger and E. S. Proskauer, "Organic Solvents," Interscience Publishers, New York (1955), p. 407.