Studies on the Effects of the Substituents for 1-Arylaminoanthraquinones

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In recent years, much effort has been expended in devising a series of anthraquinone acid dyes that are resistant to decomposition by light and to severe washing. The method which has been adopted most widely is to introduce large non-sulfonated groups into established simpler dyes, thereby increasing the molecular size and the affinity for fiber and decreasing the solubility in water[1]. Prior to a discussion of the anthraquinone acid dyes, 1-arylaminoanthraquinones, the parent compounds, will be considered in this paper. Substituent groups (X) include nitro, chloro, methyl, methoxy and amino groups. Their visible and infrared absorption spectra have been measured in solution and in solid respectively. On the basis of these results, the effects of the substituent groups (X) will be discussed in view of various properties, such as wavelengths of absorption maxima and C=O and NH frequencies, similar to the previous discussion of the properties of acylaminoanthraquinones[2].

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[1] W. Bradley, "Recent Progress in the Chemistry of Dyes and Pigments", Royal Institute of Chemistry, London (1958), p. 61.

[2] T. Hayashi and R. Shibata, This Bulletin, 34, 1116 (1961).

Results and Discussion

Visible Absorption Spectra.—The visible absorption spectra of some 1-arylaminoanthraquinones were observed by Hida[3] in a trichlorobenzene solution. For this paper, their spectra have been measured in an *o*-dichlorobenzene solution, and the effects of the substituents on the wavelength of the absorption maximum have been considered.

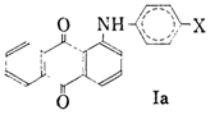
For 1-phenylaminoanthraquinone (I), the contribution of structure Ib to the resonance would be larger and, owing to the $-T$ effect of the phenyl group, the wavelength of the absorption maximum would become longer than that of 1-aminoanthraquinone[*2]. For 1-benzoylaminoanthraquinone (II), the contribution of structure IIb to the resonance would be the largest, but, since this is repressed by the contribution of structure IIc, the wavelength of the absorption maximum becomes shorter than that of 1-aminoanthraquinone. From the results indicated in Table I, one can see that the general pattern of effects on the absorption maxima agrees with the well-known effects[2,4-5] of substituents on the amino group.

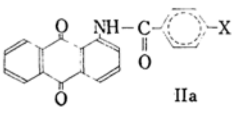
TABLE I. VISIBLE ABSORPTION PEAKS OF 1-ARYLAMINOANTHRAQUINONES

X	Peak
H[a)]	508 (5920)[*3]
p-NO_2[b)]	487 (10700)
m-NO_2	489 (6460)
o-NO_2	483 (9370)
p-Cl	505 (7130)
m-Cl	501 (7220)
o-Cl	499 (6610)
p-NHCOMe	513 (6200)
o-NHCOMe	482 (6220)
p-Me	514 (6190)
o-Me	506 (6390)
p-OMe	516 (6000)
o-OMe	517 (5970)
p-NH_2[c)]	525 (5990)
m-NH_2	515 (6910)
o-NH_2	492 (5980)

The peaks of a), b) and c) appeared at 511 (7590), 488±3 (10000) and 520 mμ (6920)[*3] respectively in trichlorobenzene[3].

In the previous case of 1-acylaminoanthraquinones[2] (II), a plot of the wave numbers of the absorption maximum against the corresponding Hammett σ values[6] concaved upwards, but against the corresponding Brown σ^+ values[7,8] gave a linear relationship. For 1-arylaminoanthraquinones, on the contrary while, the plot of the wave numbers against the former does give a linear relationship, against the latter it does not do so, as is indicated in Figs. 1 and 2. In general, the electron-releasing para substituent, such as amino, methoxy and methyl groups, show the electron-release described by Hammett σ values in a nucleophilic reaction, but they show a greater electron-release than that described by them in an electrophilic reaction. In the latter, the deviations of the plots for these groups may reasonably be attributed to the differing capacities of the substituents for the resonance stabilization of a positively-charged transition state;


Ia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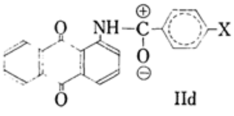
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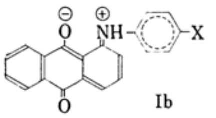
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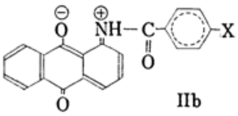
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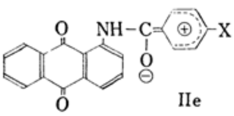
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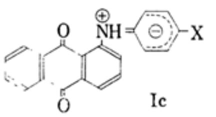
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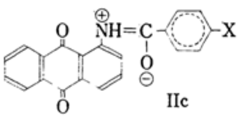
IIc

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[3] Presented at the Meeting of the Society of Organic Synthetic Chemistry of Japan, Tokyo, October, 1960.

[*2] A peak of 1-aminoanthraquinone appeared at 464 mμ (5980)[*3] in *o*-dichlorobenzene.

[*3] Wavelength, mμ, (molar extinction coefficient).

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

[5] W. Bradley and H. Kaiwar, ibid., **1960**, 2859.

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

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

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

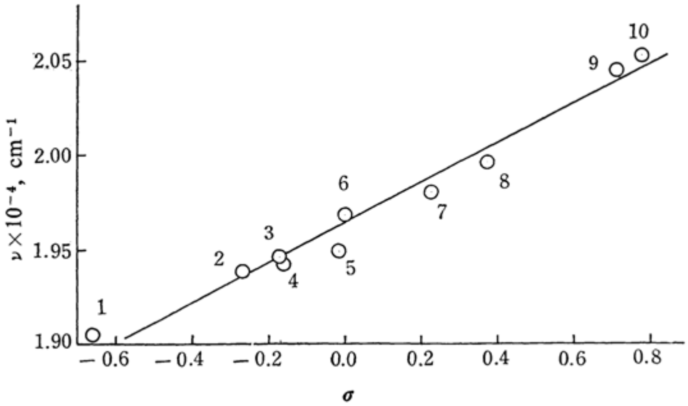

Fig. 1. Plot of wave numbers of the visible absorption maximum against Hammett σ values for 1-arylaminoanthraquinones.

1. p-NH_2, 2. p-OMe, 3. p-Me, 4. m-NH_2, 5. p-NHCOMe, 6. H, 7. p-Cl, 8. m-Cl, 9. m-NO_2, 10. p-NO_2

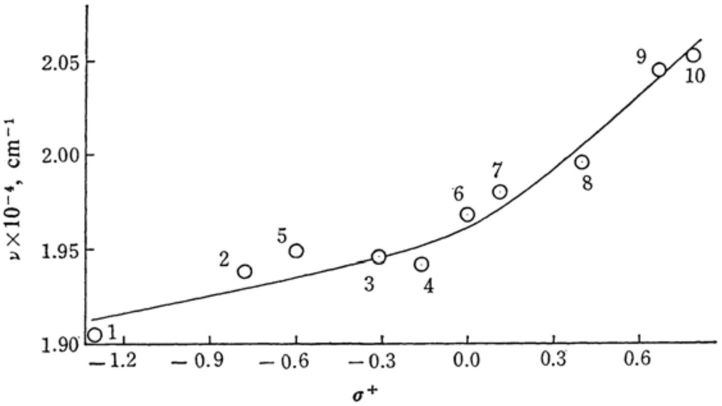

Fig. 2. Plot of wave numbers of the visible absorption maximum against Brown σ^+ values for 1-arylaminoanthraquinones.

the positive charge must be delocalized through resonance interaction, while it is the negative charge which must so be delocalized on the former. Therefore, although some attempts to correlate electrophilic reactions with an alternative set of substituent constants have been proposed by various authors, Brown's set$^{7,8)}$ is apparently the one with the most general applicability. Here, too, the same considerations as noted above are employed in the case of the shifts of absorption maxima. For 1-acylaminoanthraquinones (II), the positive charge indicated in structure IId would be delocalized through resonance with electron-releasing groups, as indicated in structure IIe, but for 1-arylaminoanthraquinones(I), unshared electrons of nitrogen in structure Ia would be delocalized through the resonance with electron-attracting groups, as indicated in structure Ic. The former is consistent with the previous data for 1-acylaminoanthraquinones$^{2)}$, and the latter, with the present data for 1-arylaminoanthraquinones.

For the visible absorption spectra of 7-substituted derivatives of 3,4- and of N-methyl-3,4-phthaloylacridones reported by Bradley$^{5)}$, a plot of the wave numbers of the absorption maximum against the corresponding Hammett σ values gives a linear relationship, as is indicated in Fig. 3. This fact shows that the type of electron displacement for 3,4-phthaloylacridone is similar to that of 1-phenylaminoanthraquinone, as was deduced from the similarity in their chemical structures. It has been suggest by Bradley$^{5)}$ that 3,4-phthaloylacridone's similarity to 1-phenylaminoanthraquinone in its red-violet color, indicates that it is a true acridone, not a hydroxyacridone. The establishment of this linear relationship may also support Bradley's suggestion.

Here, too, as in the previous case of 1-acylaminoanthraquinones$^{2)}$, the wavelength of the

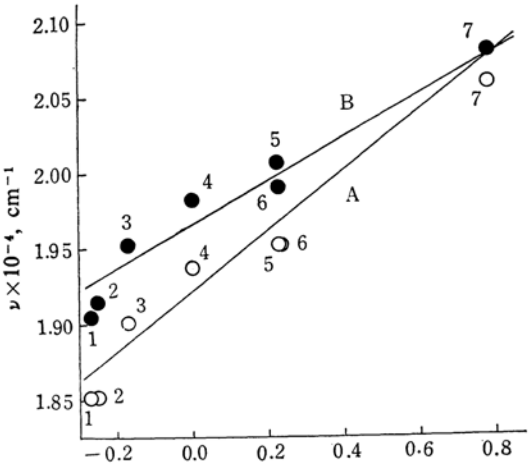

Fig. 3. Plot of wave numbers of the visible absorption maximum against Hammett σ values for 7-substituted derivatives of 3, 4- and of *N*-methyl-3, 4-phthaloylacridones.
A : 3, 4-Derivatives
B : *N*-Methyl-3, 4-derivatives
1. OMe, 2. OEt, 3. Me, 4. H, 5. Cl,
6. Br, 7. NO_2

absorption maximum is shorter for the *o*-nitroderivative than for the *m*- and *p*-isomers; such a relation is also seen in the other *o*-derivatives, except for the *o*-methoxy derivative, as Table I indicates. The wavelength and intensity of the absorption maximum for the *o*-methyl derivative differ little from those of 1-methylaminoanthraquinone[*4]. The effect of the *o*-tolyl group for the former should, therefore, be much the same as that of the methyl group for the latter; this fact shows that the aryl ring is twisted around the C–N linkage between the aryl ring and the imino group in the arylamino group. The twisting may be attributed to the steric hindrance or to the repulsion between the *o*-methyl and CH groups in the 2 position of the anthraquinone nucleus. For the *o*-nitro derivative, too, the hypsochromic shift is probably due to such a twisting of the aryl ring. If it were due to the twisting of the nitro group around the C–N linkage between the benzene ring and the nitro group, the wavelengths of the absorption maxima of the *o*- and *m*-isomers would be much the same, but the wavelengths increase in the order of the *o*-, *p*- and *m*-isomers. For the *o*-amino derivative, since the wavelengths increase in the order of the *o*-, *m*- and *p*-isomers and since, moreover, the wavelength is for the first shorter than for 1-phenylaminoanthraquinone, the twisting may also arise. For the *o*-methoxy derivative, the wavelength of the absorption maximum differs little from that of the *p*-isomer; this fact shows that such twisting may not arise because of the reduced extent of the steric hindrance or because of the repulsion due to the free rotation of the methyl group in the methoxy group.

Infrared Absorption Spectra. — Three micron infrared absorption spectra bands for a few 1, 4-diarylaminoanthraquinones have been observed as Nujol mull[9)], but the spectra of 1-arylaminoanthraquinones have not yet been observed. In this work, the latter were observed as Nujol mull on account of their limited solubility; then information was gained about their structure in the solid.

TABLE II. 3 AND 6 μ-BANDS OF SOLID 1-ARYLAMINOANTHRAQUINONES

X	3 μ-Bands, cm⁻¹ (NH frequencies)	6 μ-Bands, cm⁻¹ (C=O frequencies)	
		(a)	(b)
H[a)]	3236	1672	1634
p-NO_2	3311	1672	1639
m-NO_2	3268	1675	1637
o-NO_2	3257	1675	1650
p-Cl	3236	1678	1637
m-Cl	3257	1681	1637
o-Cl	3279	1672	1645
p-Me	3247	1684	1629
o-Me	3247	1678	1637
p-OMe	3215	1678	1626
o-OMe	3289	1672	1634
p-NH_2	3236, 3378, 3460[b)]	1664	1623
m-NH_2	3236, 3390, 3484[b)]	1681	1631
o-NH_2	3236, 3390, 3472[b)]	1681	1629

a) NH, C=O (a) and (b) frequencies were observed at 3247, 1678 and 1639 cm⁻¹ respectively by the potassium bromide disk technique.
b) The two higher frequencies are assigned to the respective NH vibration of the amino group.

Table II lists the observed NH and C=O frequencies of 1-arylaminoanthraquinones, while those of 1-phenylaminoanthrquinone are indicated in Figs. 4 and 5. For every item in this table, as in the previous case of 1-acylaminoanthraquinones[2,10)], the first carbonyl bands at a higher frequency are assigned to the respective C=O (a) vibrations, since these frequencies (1660~1680 cm⁻¹) are closer than the others to the C=O frequency (1676 cm⁻¹)[11)] of anthraquinone; the second carbonyl bands at a lower

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[*4] A peak of 1-methylaminoanthraquinone appeared at 504 mμ (6480)[*3] in *o*-dichlorobenzene.

9) D. N. Shigorin, "Hydrogen Bonding", Ed. by D. Hadzi, Pergamon Press, London (1959), p. 191.
10) T. Hayashi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1985 (1960).
11) M. S. C. Flett, *J. Chem. Soc.*, **1948**, 1441.

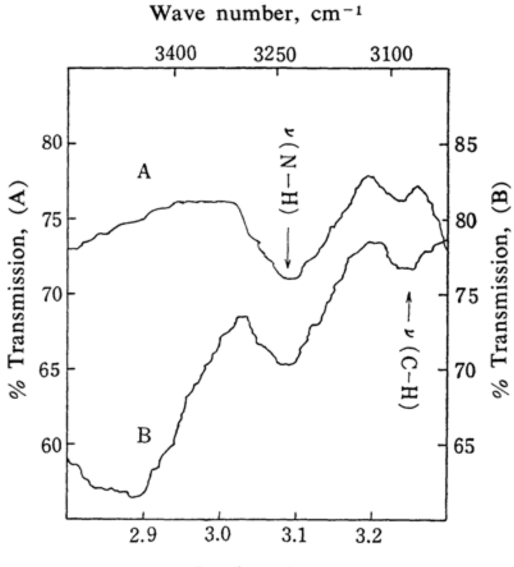

Fig. 4. 3 μ-Bands of 1-phenylaminoanthraquinone.

A : Nujol mull technique
B : KBr disk technique

frequency are assigned to the respective C=O (b) vibrations in the peri-position of the arylamino group.

For visible absorption spectra in solution, the wavelengths of the absorption maximum for 1-methylamino- and 1-dimethylamino-anthraquinones were longer than for 1-aminoanthraquinone; the wavelengths of the first and the second were alike, but their intensity decreased in the order of the first, last, and second[4]. The fact that 1-methylaminoanthraquinone had a longer wavelength than would be expected was attributed to the resonance possibility developed by the formation of the chelate structure, while the considerably reduced intensity of 1-dimethylaminoanthraquinone was thought to be due to the steric hindrance between the methyl and the C=O (b) group[4,12]. Similar phenomena have been seen in some other cases[4-5,13-14]. On the other hand, as is indicated in Table III, the fact that a C=O (b) frequency was higher for 1-methylamino- than for 1-aminoanthraquinones was attributed to the reduction of resonance by the methyl group within the former chromophoric system, and the unusually high frequency of 1-dimethylaminoanthraquinone was partly attributed to the similar reduction by methyl groups and partly to the steric hindrance between the methyl and the C=O (b) groups[11]. Similar results have been reported in some other cases[13-14]. Here, too, for visible absorption spectra in solution, the wavelength of the absorption maximum was longer for 1-phenylamino- than for 1-amino- and 1-methylamino-anthraquinones, although the C=O (b) frequency for the first was higher than for the second and was the same as that of the last. This fact may not be attributable to steric hindrance, but to the reduction by the phenyl group of resonance within the chromophoric system of the first, this being similar to the above-mentioned reduction by the methyl group for the last.

TABLE III. NH AND C=O (b) FREQUENCIES OF SOLID 1-SUBSTITUTED ANTHRAQUINONES

	NH frequency cm⁻¹	C=O (b) frequency cm⁻¹
1-Aminoanthraquinone[11]	3420, 3300	1612
1-Methylaminoanthraquinone[11]	3300	1635
1-Phenylaminoanthraquinone	3236	1634
1-Benzoylaminoanthraquinone[2]	3175	1669
1-Dimethylaminoanthraquinone[11]		1645

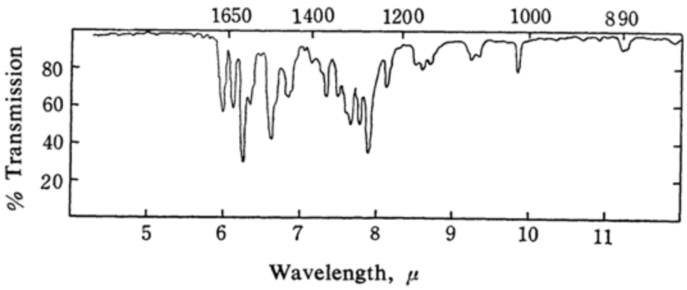

Fig. 5. The infrared spectrum of 1-phenylaminoanthraquinone by Nujol mull technique.

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[12] W. R. Brode, "The Roger Adams Symposium", John Wiley & Sons, Inc., New York (1955), p. 16.

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

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

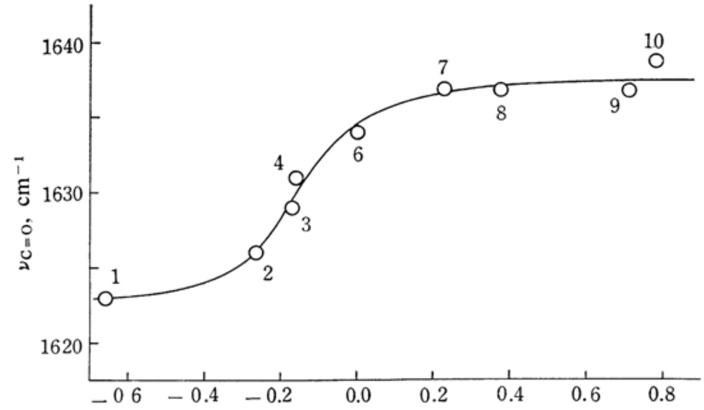
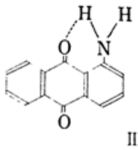
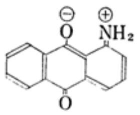


Fig. 6. Plot of C=O frequencies against Hammett σ values for 1-arylaminoanthraquinones.

As is indicated in Table III, the NH frequency lowers in the order of 1-amino-, 1-methylamino-, 1-phenylamino- and 1-benzoylamino-anthraquinones, and the reverse is found to be true for a C=O (b) frequency. For 1-aminoanthraquinone III, it seems that it is impossible to form a powerful hydrogen bonding, as in IIIa, between the amino and C=O (b) groups, and that, therefore, a contribution of the ionic structure IIIb to the resonance, rather than the weak hydrogen bonding, was responsible for the considerable lowering of the C=O (b) frequency, the hydrogen bonding serving only to stabilize the ionic structure[11,15]. On the other hand, for 1-methylamino- and 1-phenylamino-anthraquinones, such resonance within chromophoric systems was reduced by the methyl and phenyl groups respectively. The above-mentioned order of the lowering of NH frequencies, therefore, suggests that the smaller the contribution of the ionic structure to the resonance becomes, the greater the contribution of the hydrogen bonding.



IIIa



IIIb

As is indicated in Table II, for *m*- and *p*-substituted 1-arylaminoanthraquinones, the C=O (b) frequency lowers for the ones with electron-releasing substituents, while the reverse is found to be true for the derivatives with electron-attracting groups, as in the case of those for 1-acylaminoanthraquinones[10]. These results are similar to the general pattern of substituent effects on the shift of the visible absorption maximum in solution. The effects of these substituents on the shift of the C=O (a) frequency were small, similar to those for 1-acylaminoanthraquinones[10].

A plot of the C=O (b) frequencies obtained from solids of 1-acylamino-anthraquinones against the corresponding Hammett σ values gave an S-shaped relationship; this result served to explain the shades of dyed cotton[10]. Here, too, a similar plot for 1-arylaminoanthraquinones gives the same result, as is indicated in Fig. 6. The C=O (b) bond was, therefore, strengthened to much the same degree for the derivatives with any of the electron-attracting substituents. This fact may also serve to elucidate the shades of anthraquinone acid dyes on fiber.

Here, as indicated in Table II, the C=O (b) frequency of the *o*-nitro derivative is considerably higher than those of the *m*-, *p*-isomers and 1-methylaminoanthraquinone; it is a little higher than that of 1-dimethylaminoanthraquinone, in which the unusually high C=O (b) frequency was partly attributed to steric hindrance, as has been noted above. These facts show that the aryl ring of the *o*-nitro derivative is twisted around the C–N linkage between the aryl ring and the imino group, and that the twisting may be attributed to the above-mentioned steric hindrance or to repulsion, as in the case of the molecule in solution. On the contrary, the C=O (b) frequencies of the other *o*-derivatives are 6～8 cm^{-1} higher than those of the corresponding *p*-isomers. It seems probable, therefore, that the above-mentioned twisting of the aryl rings for *o*-chloro and *o*-methyl derivatives does not arise in a solid, as in the cases of *o*-methoxy and *o*-amino derivatives, this being different from the molecule in solution. For former

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[15] H. Bloom, L. H. Briggs and B. Cleverley, *J. Chem. Soc.*, **1959**, 178.

o-derivatives, such twisting may be suppressed in a solid where the molecules are packed closely.

Experimental

Materials and Apparatus. — 1-Arylaminoanthraquinones with methyl or methoxy group as a substituent were prepared by condensing 1-chloroanthraquinone with substituted aniline in nitrobenzene, but nitro derivatives were prepared by condensing 1-aminoanthraquinone with the appropriate chloronitrobenzene in nitrobenzene, as has been described by Ullmann[16] and Takegawa[17]. They were obtained in good yields. Chloro derivatives were prepared in only a poor yield by either above-mentioned method. Acetylamino derivatives were prepared by acetylation of the corresponding amino derivatives with acetic anhydride, these having been prepared by reduction of the corresponding nitro derivatives with sodium dithionite at 65°C, as has been described by Ullmann[16]. All materials were purified by recrystallization and then by chromatography or hot chromatography on alumina in benzene, monochloro- or dichloro-benzene. The results are given in Table V.

TABLE V. 1-ARYLAMINOANTHRAQUINONES

X	M. p.[a] °C	N, %	
		Found	Calc.
H	146[b]	4.64	4.68
p-NO_2	314[c]	8.09	8.14
m-NO_2	246	8.11	8.14
o-NO_2	295[d]	8.13	8.14
p-Cl	212	4.15	4.20
m-Cl	202[e]	4.12	4.20
o-Cl	227	4.17	4.20
p-NHCOMe	176[f]	7.81	7.86
o-NHCOMe	266[g]	7.80	7.86
p-Me	163[h]	4.46	4.47
o-Me	192[i]	4.44	4.47
p-OMe	155[j]	4.24	4.25
o-OMe	177[k]	4.21	4.25
p-NH_2	204[l]	8.85	8.91
m-NH_2	212	8.88	8.91
o-NH_2	204[m]	8.86	8.91

a) All melting points are uncorrected.
b), d), f), g) and m) Ullmann[16] gives m. p. 147.5, 293, 176, 257 and 204°C (corr.) respectively.
c) and l) Takegawa[17] gives m. p. 311 and 206~206.5°C (corr.) respectively.
e) and i) D. R. Pat. 251103; Frdl., 11, 251 (1912), gives m. p. about 190°C.
h) Zahn[18] gives m. p. 156~157°C.
j) and k) Cook[19] gives m. p. 153~154 and 177°C respectively.

The visible absorption spectra were obtained by a Shimadzu spectrophotometer, type QB-50. The infrared absorption spectra were obtained using the Nujol mull technique; a Perkin-Elmer Model 21 double beam spectrophotometer fitted with a rocksalt prism was also used. Purification of *o*-dichlorobenzene was done by the method recommended for monochlorobenzene[20].

The authors wish to express their deep thanks to Professor Yoshio Nagai and Professor Shimpachiro Kato of the University of Tokyo for their helpful suggestions and encouragement in the course of this work, and also to Mr. Akira Hara of the Tokuyama Research Laboratory of the Idemitsu Kōsan Co. for their infrared measurements.

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[18] K. Zahn and H. Koch, *Ber.*, **71**, 172 (1938).
[19] A. H. Cook and W. Waddington, *J. Chem. Soc.*, **1945**, 402.
[20] A. Weissberger and E. S. Proskauer, "Organic Solvents", Interscience Publishers, New York (1955), p. 407.