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## INFRARED ABSORPTION SPECTRA AND HYDROGEN BONDING OF SOME SOLID AMINOANTHRAQUINONES

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Various aminoanthraquinone (A.A.Q.) dyes were prepared and recrystallised from the appropriate solvents. Chemical analysis, NMR and m.p.' determination were followed. The infrared absorption spectra of the dyes were investigated assigned and discussed in detail at a wide range of  $3800-650\text{ cm}^{-1}$ . Evidences for the existence of intramolecular hydrogen bonding in others were established.

According to the energy of hydrogen bond, the various dyes were arranged in a descending order of magnitude and a correlation with the presence of  $-\text{NH}_2^+$  group was put forward.

**Keywords :** Infrared Absorption Spectra; Hydrogen Bonding; Aminoanthraquinones

### INTRODUCTION

A clear understanding and a detailed account of the infrared absorption spectral properties of aminoanthraquinone dyes is required for the explanation of their dyeing value and photochemical properties.

Lee and Wilmshure (1966) investigated the infrared absorption intensity of the carbonyl band in some hydroxy substituted quinones. The C—O, C—C and aromatic ring vibrational modes were assigned. Anthraquinone and its symmetrical substituted derivatives give a single carbonyl band near  $1600\text{ cm}^{-1}$  (Flett, 1948). The infrared absorption spectra in  $1600-1680\text{ cm}^{-1}$  region for a number of hydroxyanthraquinone acetate had already been investigated (Lee & Wilmshure, 1950). The acetate carbonyl absorbance was found to consist of two overlapping bands arising as a result of Fermi resonance between a combination tone and the acetate carbonyl fundamentals. On studying the IR spectrum of the  $\alpha$ -hydroxyanthraquinone, Brochman and Frouch (1975) found that the  $-\text{CH}$  stretching frequency of  $\alpha$ -OH group is missing and the carbonyl frequency is lowered by  $40\text{ cm}^{-1}$  as a result of hydrogen bond formation.

The spectrophotometric studies on some hydroxyanthraquinones in the visible UV and IR regions (Issa *et al.*, 1970, 1972) revealed that, the overlap of molecular orbitals of C = O and C = C systems is influenced by both the positions and numbers of  $-\text{OH}$  groups.

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Shigorin and Dokanikhin (1955) studied the presence of H-bond in the vibration and electronic spectra of amino substituted anthraquinones and showed that the  $\beta$ -aminoanthraquinone was bound in the crystalline state by intermolecular H-bonds but was monomeric in  $\text{CCl}_4$ . The hydrogen bond becomes more stable (Zaitsev *et al.*, 1971) with increasing size of alkyl group in  $\beta$ -position of aminoanthraquinones; also, the transition from gas to solution or crystalline state does not weaken the H-bonding.

The association of aminoanthraquinones with organic solvents ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_6$ , Ph—OMe, Ph—NO<sub>2</sub> and dioxane) was shown by the IR-spectra (Zaitsev & Trankvillitskaya, 1975) as it takes place *via* H-bonding.

The major goal of the present work is to study in detail the IR absorption spectra of quinone, various substituted aminoanthraquinones, assign their characteristic bands, and study the effect of substitution on the frequency of the carbonyl group and the aminogroup.

On the other hand, IR spectroscopic studies afford a convenient method for detecting the presence of hydrogen bonding which lowers the O—H or N—H stretching frequencies in the aminoanthraquinone dyes.

#### EXPERIMENTAL

##### (A) Preparation of Aminoanthraquinone (A. A. Q.) Dyes

Dyes I—VI were supplied as pure chemicals from Merk and purified by recrystallization from the appropriate solvents. But, the other dyes were prepared by methods as previously recommended with some detailed modifications (Schumacher, 1975; Bredereck *et al.*, 1972; and Metwally, 1976).

The dyes were purified by recrystallization and the degree of purity was tested by NMR and chemical analysis.

##### (B) IR Absorption Measurements

The KBr pellet technique was used. The dyes were mixed with reagent grade KBr in the ratio (1 : 350) and pressed into pellets (220 kgm/cm<sup>2</sup>). The spectra were recorded on a Unicam SP 1000 spectrophotometer (L. T. D., Cambridge, England in the range 3800–625 cm<sup>-1</sup>).

#### RESULTS AND DISCUSSION

The room temperature infrared absorption spectra and the assignment of their important and characteristic bands are reported in Table I. These are interpreted in the light of the molecular structure of the few investigations, already reported. It seems, however, that no detailed IR spectral studies have been carried out on the compounds under investigation. The band assignment given is achieved by the comparison method and considering the effect of substitution on the different band positions. The method is more or less similar to that applied in the case of some aromatic compounds (Mecke & Greinocher, 1957) and azobenzene (Maier & Englert, 1958).

TABLE I

*Infrared absorption bands and their assignments*

I	II	III	IV	V	VI	VII	VIII	IX	Band assignment
3440	3460	3460	3450	—	3430	3425	3460	3440	$\nu_{\text{asym}}$ .NH <sub>2</sub>
3320	3350	3360	3340	—	3320	3300	3380	3340	$\nu_{\text{sym}}$ . NH <sub>2</sub>
—	—	—	—	—	320	3200	3145	—	$\lambda_{\text{CH}^{\text{OH}}}$ of (COOH)
3140	3100	3080	3125	3140	3110	3120	3100	3110	$\nu_{\text{asym}}$ .aromatic C—H
3070	3050	3020	3040	3090	3020	3080	3020	3020	$\nu_{\text{sym}}$ .aromatic C—H
—	—	—	—	3040	—	—	—	—	$\nu_{\text{NH}_3^+}$
—	—	—	—	2640	—	—	—	—	$\nu_{\text{NH}_3^+}$
—	—	—	—	—	—	—	—	1700	$\nu_{\text{C=O}}$ (carboxylic)
—	—	—	—	—	—	—	1685	—	$\nu_{\text{C=O}}$ free
1675	1685	—	1663	1682	—	—	1675	1685	$\nu_{\text{C=O}}$ free
1650	1635*	1630	1640	1640	1630	1650	1650	1645	} $\nu_{\text{C=O}}$ bonded
—	—	—	—	—	1620	1610	—	—	
1610	1595	1610	1610	—	1590	1595	1600	1610	$\delta_{\text{NH}_2}$
1585	1580	1600	1600	1589	1580	1580	1575	1570	$\nu_{\text{C=C}}$ quin.
1550	1565	—	1545	1550	1545	1530	1545	1560	$\nu_{\text{C=C}}$ sketal vib.
—	—	—	—	—	1420	1420	—	—	$\nu_{\text{C-O}}$
1405	1405	1400	1405	1400	1408	1400	1410	1408	$\delta$ aromatic C—H
1325	1330	1330	1325	1328	1331	1330	1330	1330	$\nu_{\text{C-N}}$
1285	1310	1285	1280	1295	1303	1320	1290	1300	$\nu_{\text{C-C}}$ quinone
—	—	—	—	1190	—	—	—	—	$\nu_{\text{asym}}$ . SO <sub>3</sub> H
1100	1120	1095	1057	1090	1103	1100	1100	1122	$\delta$ aromatic C—H
—	—	—	—	1049	—	—	—	—	$\nu_{\text{sym}}$ . SO <sub>3</sub> H
—	—	—	—	—	905	900	—	—	$\nu$ OH
800	800	810	800	—	798	795	802	810	$\gamma$ NH
—	848	—	—	840	—	—	830	845	$\gamma$ C—H, 2-adjacent H. atoms
740	723	—	—	753	725	737	742	750	$\gamma$ C—H, 4-adjac. H. atoms.
709	—	710	715	—	—	—	—	—	$\gamma'$ C—H, 3-adj. H. atoms.
—	—	—	—	680	—	—	—	—	$\nu$ C—S of SO <sub>3</sub> H
—	—	—	—	—	—	730	—	—	$\nu$ C—Br.

\*Intermolecular hydrogen bond.

 $\nu$ -Stretch. vib.  $\delta$  bend.,  $\gamma$  0.0 plane bend.,  $\gamma'$  0.0 plane deform.

The band assignment for aminoanthraquinone dyes can be readily obtained by comparing with that of anthraquinone. The latter compound may be considered as 9,10 diketoanthracene or  $\alpha, \beta - \alpha', \beta'$ -dibenzoquinone. The IR spectrum of anthraquinone would exhibit bands corresponding to 0-disubstituted benzene and the benzoquinone nucleus. Since anthracene and anthraquinone belong to the same

symmetry group  $D_{2h}$  (Clar, 1950; and Coulsen, 1948), the IR active bands for both compounds would be of the same type, though might differ somewhat in position and/or in intensity, Thus, the assignment given for the IR spectrum of anthracene (Bruhn & Mecke, 1961) should be considered in obtaining that for the spectrum of anthraquinone. The bands at 1680, 1600, 1315 and 1290  $\text{cm}^{-1}$  are not apparent in the spectrum of anthracene as being due to the quinone nucleus (Bellamy, 1958), while those of 1342 and 825  $\text{cm}^{-1}$  may correspond to the weak anthracene bands at 1347 and 812  $\text{cm}^{-1}$ . The increase in intensity of the latter bands in anthraquinone can be ascribed to the polarizing influence of the carbonyl groups on charge distribution and hence on the vibrating dipoles.

A satisfactory assignment for bands of aminoanthraquinones can be attained by comparison with anthraquinone if the symmetry group of the two compounds are either identical or not very different. Thus, the spectrum of 1,5-diaminoanthraquinone (III) should be first compared with that of the parent anthraquinone. The new bands observed in the spectrum of the dye III are due to the vibrations of  $\text{NH}_2$  group, the slight change of the symmetry of the molecule and to the change in type of substituent, For the purpose of detailed account the IR spectrum is divided into four regions : 3800–2000  $\text{cm}^{-1}$ , 2000–1500  $\text{cm}^{-1}$ ; 1500–1000  $\text{cm}^{-1}$ . and 1000–650  $\text{cm}^{-1}$ .

#### (A) Absorption in 3800–2000 $\text{cm}^{-1}$ region

In this region, the O—H, N—H,—and C—H stretching vibration bands may appear. The IR spectrum of the dye III shows two sharp bands at 3360 and 3460  $\text{cm}^{-1}$ , also the dyes I, II, III, IV, VIII and IX show two bands around 3340 and 3450  $\text{cm}^{-1}$  which can be assigned to  $\nu_{\text{sym}}(\text{NH}_2)$  and  $\nu_{\text{asym}}(\text{NH}_2)$  respectively. The  $\nu_{\text{sym}}(\text{NH}_2)$ , for the dye III is in accordance with that calculated by the empirical relation : (Vogel, 1961).

$$\nu_{\text{sym}}(\text{NH}_2) = 345.5 + 0.876 \nu_{\text{asym}}(\text{NH}_2)$$

Thus,  $\nu_{\text{sym}}(\text{NH}_2)$  equals to 3376  $\text{cm}^{-1}$  which is close to the observed  $\nu_{\text{sym}}(\text{NH}_2)$ . The similarity between the calculated value of  $\nu_{\text{sym}}(\text{NH}_2)$  and that assigned in the IR spectrum of the dye III can be attributed to the intramolecular hydrogen bonds formed between the  $\text{NH}_2$  groups and the carbonyl groups. This opinion is further supported by the lower frequency of the carbonyl group, this behaviour is also observed for I, II, IV, VI, VII, VIII and IX. But in case of the dye II, the type of hydrogen bonding is essentially intramolecular hydrogen bond which is further supported by the appearance of two carbonyl bands as 1658 $\text{cm}^{-1}$  and 1635 $\text{cm}^{-1}$ . The presence of only two  $\text{NH}_2$  stretching vibration bands in the IR spectrum of the dye III is an evidence for the equal participation of both  $\text{NH}_2$  groups in the hydrogen bonding. On the other hand, the IR spectra of the hydroxylic containing dyes VI and VII exhibit broad bands at 3200 $\text{cm}^{-1}$  and two carbonyl bands at 1620 and 1610  $\text{cm}^{-1}$  respectively which indicate that the hydroxy groups in the dyes VI and VII are involved in hydrogen bonding. Also a broad band located at 3145 $\text{cm}^{-1}$  is observed in the IR spectrum of the dye VIII. The band can be assigned to  $\nu_{\text{O-H}}$  of the carboxylic group.

The IR spectra of the dyes under investigation reveal two weak absorption bands around 3100 and 3020 $\text{cm}^{-1}$  which can be attributed to asymmetric stretching vibrations of aromatic C—H respectively. The IR spectrum of the dye V shows strong bands at 2640 $\text{cm}^{-1}$  which is ascribed to  $\text{NH}_3^+$  (Nakanishi, 1965) indicating the existence of this type of dye as Zwütter ion.

(B) *Absorption in 2000–1500  $\text{cm}^{-1}$  Region*

The IR spectrum of the dye III reveals a single carbonyl band at 1630  $\text{cm}^{-1}$ , while the IR spectra of the dyes I, II, IV, V, VIII and IX reveal two absorption carbonyl bands (*see* Table I). This is due to the fact that in the dye III, the two carbonyl groups of the quinonoid system are involved in hydrogen bonding while in the dyes I, II, IV, V, VIII and IX only one carbonyl group participates in hydrogen bonding. Moreover, the IR spectra of the dyes VIII and IX show bands at 1685 and 1700  $\text{cm}^{-1}$  which can be assigned to  $\nu_{\text{C}=\text{O}}$  of the carboxylic group and  $\nu_{\text{C}=\text{O}}$  of the aldehyde group respectively. On the other hand, the carbonyl bands appear in the IR spectra of the dye VI at 1630 and 1620  $\text{cm}^{-1}$  and of the dye VII at 1650 and 1610  $\text{cm}^{-1}$ . The low frequency values observed for the two carbonyl bands indicate that the carbonyl groups are involved in hydrogen bonding. The presence of the two carbonyl bands, inspite of the two carbonyl groups (involved in hydrogen bonding) is due to unequal participation of the amino and hydroxy groups in hydrogen bonding. Moreover, the appearance of  $\nu_{\text{O}-\text{H}}$  at 3200 $\text{cm}^{-1}$  in the IR spectra of the dyes VI and VII indicates that the  $\nu_{\text{C}=\text{O}}$  of the dye VI at 1620 $\text{cm}^{-1}$  and of the dye VII at 1610  $\text{cm}^{-1}$  can be assigned as  $\nu_{\text{C}=\text{O}}$  associated with the chelated hydroxyl groups.

Since the IR spectra of the aminoanthraquinone dyes which have no intramolecular hydrogen bonding between the amino group and the carbonyl of the quinonoid system reveal single carbonyl band (Zaitsev *et al.*, 1971), the energy of intermolecular hydrogen bond between the carbonyl group of the quinonoid system and the amino group can be estimated qualitatively from the shift of the  $\nu_{\text{C}=\text{O}}$  frequency (bonded) in the aminoanthraquinone dyes with respect to  $\nu_{\text{C}=\text{O}}$  frequency (free) of the same dye.

Thus, one can arrange the dyes (which contain free and bonded carbonyl frequency) according to the energy of the hydrogen bond between the carbonyl and amino groups as follows :

$$\text{IV} < \text{I} < \text{VIII} < \text{IX} < \text{V}$$

from which one can conclude that the dye V has the highest intramolecular hydrogen bond energy. This is due to the presence of  $-\text{NH}_3^+$  which strengthens the hydrogen bond. The existence of the hydrogen bond causes a high orbital overlap between the molecular orbitals of the carbonyl group and C = C of the quinonoid system, hence decreases the stretching vibration of C = C bond to 1560–1590  $\text{cm}^{-1}$ .

Thus, the strong to medium IR bands observed in the region 1500–1590 $\text{cm}^{-1}$ , (Table I) can be assigned to the stretching vibrations of C = C of quinonoid system.

Also, the IR spectra of all dyes under investigation reveal two strong to medium bands near  $1560$  and  $1470\text{cm}^{-1}$ , which are attributed to skeletal vibration of aromatic ring.

On the other hand, the in-plane bending vibrations of the amino group appears around  $1600\text{cm}^{-1}$  in the spectra of all dyes.

(C) *Absorption in the 1500–1000  $\text{cm}^{-1}$  region*

The IR spectra of the dyes VI and VII show broad band at  $1420\text{cm}^{-1}$  which is attributed to  $\delta_{\text{OH}}$ . The high frequency of  $\delta_{\text{OH}}$  and its broadening confirm the existence of hydrogen bond. Also these two dyes reveal strong bands at  $1256$  and  $1270\text{cm}^{-1}$  for dyes VI, VII respectively which can be assigned to  $\nu_{\text{C-OH}}$ . On the other hand, the IR spectra of the dyes under investigation show a strong to medium band in the IR range :  $1280\text{--}1310\text{cm}^{-1}$ , which can be attributed to stretching vibrations of quinonoid C—C bonds. Also a band around  $1330\text{cm}^{-1}$  is observed corresponding to stretching vibrations of C—N bond.

The IR spectra reveal two bands around  $1100$  and  $1405\text{cm}^{-1}$  which can be attributed to inplane bending modes of aromatic C—H. The IR spectrum of dye V shows two  $\nu_{\text{sym}} \text{SO}_3$  and  $\nu_{\text{asym}} \text{SO}_3^-$ . The third band corresponding to  $\nu_{\text{SO}_3^-}$  appears at  $680\text{cm}^{-1}$ .

(D) *Absorption in the 1000–650 $\text{cm}^{-1}$  region*

The IR spectra of all dyes except the dyes III and IV show a strong band in the  $718\text{--}753\text{cm}^{-1}$  region corresponding to the out of plane deformation of the four adjacent hydrogen atoms. On the other hand, the dyes I, III and IV reveal a strong band at  $709$ ,  $710$  and  $715\text{cm}^{-1}$  respectively corresponding to the out of plane deformation of the three adjacent hydrogen atoms. The IR spectra of dyes II, VI, VIII and IX show a strong band in the region  $830\text{--}848\text{cm}^{-1}$  corresponding to out of plane deformation of two adjacent hydrogen atoms. On the other hand, the IR spectra of the dyes V and VII reveal two strong bands at  $680$  and  $730\text{cm}^{-1}$  respectively which can be attributed to stretching vibrations of the C—S bond of the sulphonate group and stretching vibrations of the C—Br bond respectively.

### CONCLUSION

Evidences are given for the existence of intramolecular hydrogen bonds formed between the  $\text{NH}_2$  groups and the carbonyl group, for the dyes I, III, IV, VII, VIII and IX. But in the case of the dye II, the type of hydrogen bonding is essentially intermolecular hydrogen bond.

Accordingly, one can arrange the dyes (which contain free and bonded carbonyl frequency) according to the energy of the hydrogen bond between the carbonyl and amino groups in a descending order as follows :

$$\text{V} > \text{IX} > \text{VIII} > \text{I} > \text{IV}$$

from which one can conclude that the dye V has the highest intramolecular hydrogen bond energy. This is correlated with the presence of  $-\text{NH}_3^+$  which strengthens the hydrogen bond.

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