

FIG. 3

that there is very little to choose between the three strengths.

Figure 3 shows the rate of discharge of static electricity using 64 millicuries in the air duct both after sieving and after scooping. In both cases the static charge falls down rapidly to less than 1 kV.

Although it will be seen from the graph that 32 millicuries would be sufficient we have decided to instal two pieces of 25 millicuries each to provide a total strength of 50 millicuries. This has been based on the consideration of the half-life of the isotope.

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INFRARED SPECTRA OF 1, 4-DIHYDROXY, 2-METHYL AND 1, 8-DIHYDROXY, 3-METHYL ANTHRAQUINONE

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ABSTRACT

The infrared spectra of 1, 4-dihydroxy, 2-methyl and 1, 8-dihydroxy, 3-methyl anthraquinones have been recorded in the region $600\text{--}4,000\text{ cm}^{-1}$ and the fundamental frequencies assigned. The effect of intramolecular hydrogen bonding on the various vibrational modes have been discussed. Aliphatic and aromatic nature of methyl group is discussed in detail.

INTRODUCTION

THE infrared spectra of 1, 4-naphthoquinone and 9, 10-anthraquinone and the chelated hydroxyquinones have been recorded by Hadzi and Sheppard¹ with a view to study the effect of intramolecular hydrogen bonding. The carbonyl stretching frequencies of various *p*-quinones have been studied by several workers²⁻⁵. Shigorin *et al.*⁶ have recorded the infrared spectra of a series of hydroxy and amino derivatives of anthraquinone in the range of C=O , OH and NH group vibrations in solid and vapour state and found strong intramolecular hydrogen bonding in such molecules even at a temperature of $280\text{--}300^\circ\text{C}$. The present investigation deals with the infrared study of 1, 4-dihydroxy, 2-methyl and 1, 8-dihydroxy, 3-methyl anthraquinone in the region $600\text{--}4000\text{ cm}^{-1}$ with a view to study the effect of hydrogen bonding on various vibrational modes and to discuss the methyl group vibrations in detail.

EXPERIMENTAL PROCEDURE

The infrared spectra of the compounds have been recorded with the help of a Perkin-Elmer 621 Grating Spectrophotometer in the region $600\text{--}4000\text{ cm}^{-1}$, using paste of the compounds in nujol mull pressed between two NaCl windows. The accuracy of the measurement has been estimated to be $\pm 2\text{ cm}^{-1}$ and is uniform throughout the region. The chemicals used were supplied by the National Chemical Laboratory, Poona, and were further purified by the process of sublimation.

RESULTS AND DISCUSSION

The molecular structures of the compounds 1, 4-dihydroxy, 2-methyl and 1, 8-dihydroxy, 3-methyl anthraquinones are as shown in Fig. 1. Both the molecules belong to the point group symmetry C_2 . The 81 normal modes of vibrations are divided into symmetry species $55 a' + 26 a''$. The infrared spectra of the molecules are shown in Fig. 2. The vibrational assignments of the observed bands are given in Table I.

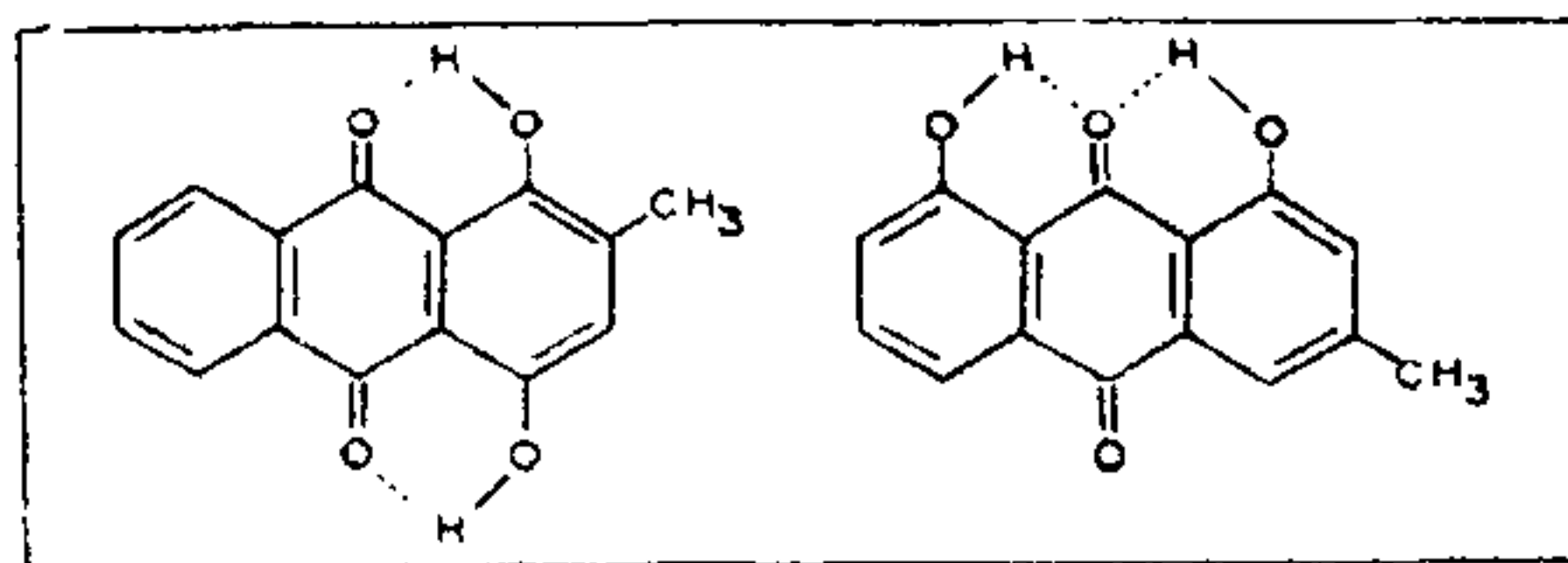


FIG. 1. Structural diagrams of 1, 4-dihydroxy, 2-methyl and 1, 8-dihydroxy, 3-methyl anthraquinones.

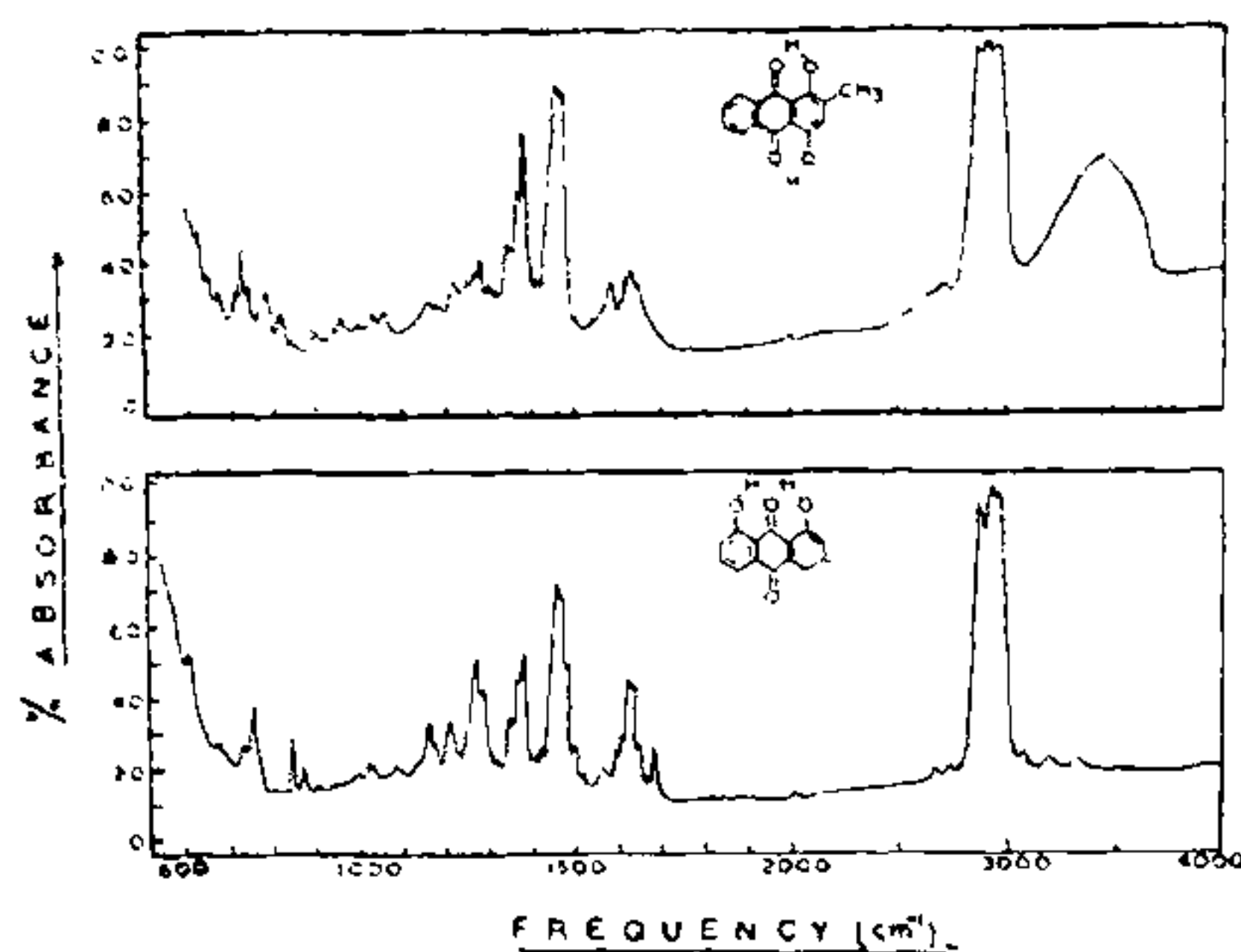


FIG. 2. Infrared spectra of 1, 4-dihydroxy, 2-methyl and 1, 8-dihydroxy, 3-methyl anthraquinones.

The C=O stretching bands are observed with strong intensity in the region 1590–1680 cm^{-1} for anthraquinone and all of its hydroxy derivatives^{7,8}. The bands with frequencies 1632 cm^{-1} in 1, 4-dihydroxy, 2-methyl and 1680 and 1630 cm^{-1} in 1, 8-dihydroxy, 3-methyl anthraquinone are identified as the C=O stretching frequencies. It is observed that there are two bands corresponding to C=O stretching mode in the second molecule while there is only one band in case of the first molecule. This has been attributed to the symmetrical and unsymmetrical hydrogen bonding in the two molecules.

The band with frequency 3440 cm^{-1} in 1, 4-dihydroxy, 2-methyl anthraquinone has been assigned as due to O-H...O, stretching mode of vibration, which gains support from Stuart and Sutherland⁹. However, there are two bands at 3345 and 3200 cm^{-1} in case of 1, 8-dihydroxy, 3-methyl anthraquinone, which have been assigned to the same mode. The obvious reason for this splitting seems to lie in the structural peculiarity of the molecule 1, 8-dihydroxy, 3-methyl anthraquinone. The two OH bonds on either side of C=O bond give rise to hydrogen bonds being formed on each side resulting in diminution and then Fermi resonance. It is in this way that the two frequencies 3345 and 3200 cm^{-1} may be understood in place of one frequency 3440 cm^{-1} .

TABLE I

Vibrational assignment of 1, 4-dihydroxy, 2-methyl and 1, 8-dihydroxy 3-methyl anthraquinones

1, 4-dihydroxy, 2-methyl anthraquinone	1, 8-dihydroxy, 3-methyl anthraquinone	Assignment
3440 (s)		O-H stretching
	3345 (vw)	do.
	3200 (vw)	do.
	3068 (vw)	C-H do.
2975 (vs)	2980 (vs)	C-H stretching in CH ₃ group (asymmetric)
2860 (vs)	2864 (vs)	C-H stretching in CH ₃ group (symmetric)
2730 (vw)	2730 (vw)	Combination tone
	2670 (vw)	
	1680 (vs)	C=O stretching
1645 (sh)	1644 (sh)	
	1634 (sh)	
1632 (s)	1630 (vs)	C=O stretching
1622 (sh)	1610 (sh)	C-C stretching
1586 (s)	1598 (vw)	do.
1542 (vw)	1565 (w)	
	1516 (vw)	
1497 (sh)	1496 (sh)	
	1480 (sh)	C-C stretching
1472 (sh)	1470 (sh)	do.
1450 (sh)	1450 (sh)	C-CH ₃ asymmetric deform.
1423 (sh)	1425 (vw)	
	1408 (vw)	C-C stretching
1370 (s)	1370 (sh)	C-CH ₃ symmetric deform.
1350 (vw)	1350 (vw)	
1322 (sh)		
1304 (vs)	1314 (vw)	C-C stretching
1277 (s)	1277 (sh)	
	1275 (vs)	
1263 (sh)		
1250 (w)		C-C stretching
1220 (w)		O-H angle deform. i.p.
1188 (vw)	1213 (s)	C-H bending i.p.
	1175 (w)	do.
	1116 (s)	do.
1518 (vw)		O-H angle deform. i.p.
	1090 (w)	C-H bending i.p.
1058 (vw)		
1032 (w)	1027 (w)	C-H bending i.p.
998 (vw)	996 (vw)	C-CH ₃ rocking
956 (w)		C-H bending o.p.
936 (vw)		Skeletal deform. i.p.
895 (vw)	905 (w)	C-H bending o.p.
	872 (s)	
850 (vw)	842 (vs)	O-H bending o.p.
813 (s)	818 (w)	C-H bending o.p.
	805 (w)	Skeletal deform. o.p.
784 (s)		O-H bending i.p.
743 (s)	755 (vs)	C-H bending o.p.
725 (vs)		Skeletal deform. i.p.
715 (sh)	736 (w)	C-CH ₃ stretching
	690 (vw)	C-H bending o.p.
677 (vw)	676 (vw)	Ring breathing
647 (vw)	668 (vw)	C-CH ₃ wagging
630 (vw)		

The C-C stretching vibrations are observed in the region 1250–1622 cm^{-1} . The bands with frequencies 1250, 1304, 1472, 1586 and 1622 cm^{-1} in 1, 4-dihydroxy, 2-methyl anthraquinone and with

frequencies 1314, 1408, 1470, 1480 1598, and 1610 cm^{-1} in 1, 8-dihydroxy, 3-methyl anthraquinone are identified as due to C—C stretching vibrations. The bands at 936 and 725 cm^{-1} in 1, 4-dihydroxy, 2-methyl anthraquinone are identified as due to in-plane skeletal mode of vibration. The bands at 677 and 676 cm^{-1} in 1, 4-dihydroxy, 2-methyl and 1, 8-dihydroxy, 3-methyl anthraquinone respectively have been assigned to the ring breathing mode vibration.

The C—H in-plane-bending mode of vibrations and out-of-plane-bending mode of vibrations are observed in the regions 1027–1213 cm^{-1} and 690–956 cm^{-1} respectively. The bands at 1032, 1188 cm^{-1} and at 743, 813, 895 and 956 cm^{-1} in 1, 4-dihydroxy, 2-methyl anthraquinone have been identified as due to C—H in-plane and out-of-plane-bending modes of vibration respectively. The corresponding frequencies in case of 1, 8-dihydroxy, 3-methyl anthraquinone are observed at 1027, 1090, 1166, 1175 and 1213 cm^{-1} and 690, 755, 818 and 905 cm^{-1} .

METHYL GROUP VIBRATIONS

The methyl group in these two molecules is directly attached to the ring which will be perturbed by its substitution in contrast to the case of 1-methylamino anthraquinone,* where the methyl group is not attached to the ring directly, but is attached to the nitrogen atom of the amino group. Thus we expect difference between the methyl group vibrations for N—CH₃ and C—CH₃, the former contributing towards aliphatic and the latter towards aromatic properties of the molecule. Table II, gives the assignment of the methyl group vibration in these three molecules.

TABLE II

Methyl group vibrations in 1, 4-dihydroxy, 2-methyl 1, 8-dihydroxy, 3-methyl and 1-methylamino anthraquinones

1-Methyl- amino anthra- quinone	1, 4-Di- hydroxy 2-methyl A.Q.	1, 8-di- hydroxy 3-methyl A.Q.	Assignment
2951	2975	2980	C—H asymmetric stretch.
2872	2860	2864	C—H symmetric stretch.
1461	1450	1470	C—H ₃ asymmetric deform.
1425	1370	1370	C—H ₃ symmetric deform.
N—CH ₃	C—CH ₃	C—CH ₃	

The CH₃ deformation modes show sensitivity to the electronegativity of the attached atoms^{10,12}, the symmetric deformation being particularly sensitive and the symmetric CH₃ deformation modes are reported at 1440–1410 cm^{-1} for N—CH₃ and 1385–1370 cm^{-1} for C—CH₃¹⁰⁻¹².

* Our recent work, communicated to *Current Science*, Bangalore-6.

The CH₃ symmetric deformation modes in the present case are identified at 1370 cm^{-1} and at 1425 cm^{-1} in case of 1-methylamino anthraquinone, agreeing well with the results reported earlier.

The most conspicuous feature brought forth due to hydrogen bonding is the removal of degeneracy of the C=O stretching mode of vibration in case of 1, 8-dihydroxy, 3-methyl anthraquinone. In case of 1, 4-dihydroxy, 2-methyl anthraquinone, only one band at 1632 cm^{-1} is observed, corresponding to the C=O stretching mode. The corresponding band in the parent molecule anthraquinone is at 1675 cm^{-1} . As it is evident from Fig. 1, both the C=O groups of 1, 4-dihydroxy, 2-methyl and one C=O groups of 1, 8-dihydroxy, 3-methyl anthraquinone are associated with hydrogen bonds. As a result, both the C=O modes of vibration in the first case and one C=O mode of vibration in the second case are suppressed, giving rise to single band in the first case and two bands in the second case. Thus as a result of the present study, we can conclude that :

(a) The degeneracy of the C=O stretching mode frequency is removed when the hydrogen bonding makes the two C=O groups unsymmetrical (Fig. 1 b), and

(b) The degeneracy is not removed when hydrogen bonding is symmetrical with respect to two C=O bonds. However, there is also a shift of the frequencies in this case (Fig. 1 a).

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