

respectively. This can be shown by expanding the repulsive term of potential (2) in power series as

$$P \log \left( 1 + \frac{\phi}{r^4} \right) = \frac{P\phi}{r^4} - \frac{P\phi^2}{2r^8} + \frac{P\phi^3}{3r^{12}} - \frac{P\phi^4}{4r^{16}} + \dots$$

The right hand side is equivalent to

$$\frac{C_1}{r^4} - \frac{C_2}{r^8} + \frac{C_3}{r^{12}} - \frac{C_4}{r^{16}} + \dots$$

where  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are constants. The physical meanings of these terms are the van der Waals dipole-dipole, dipole-quadrupole, etc., interaction terms. This potential (2) probably includes some of these interaction terms giving better agreement in comparison to (3) and (4). The potentials (3 and 4) do not include such interaction terms which are important in considering the energies of alkali hydride molecule (XH) which dissociates to yield  $X^+$  and  $H^-$ .

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### Wide Line NMR Investigation of Anthraquinone, *m*-Nitrobenzaldehyde & 3-Hydroxypyridine at Room Temperature

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The proton magnetic resonance studies of solid anthraquinone, *m*-nitrobenzaldehyde and 3-hydroxypyridine have been made to confirm the rigidity of the crystal lattice and molecular motions (if present) at room temperature. The lattices of anthraquinone and 3-hydroxypyridine are rigid at room temperature (22-2°) while some molecular deformation is observed in *m*-nitrobenzaldehyde.

THE PMR study of the title compounds has been made to gain information concerning the structure and motion of these molecules in the solid state.

The structure of anthraquinone was refined by Murty<sup>1</sup> by three-dimensional Fourier methods, using form factors obtained by an empirical method<sup>2</sup>. The crystal which belongs to the space group  $P2_1/a(3=2)$ , is monoclinic, short needle shaped, the needle length being parallel to the *b*-axis:  $a = 15.810 \pm 0.015 \text{ \AA}$ ;  $b = 3.942 \pm 0.005 \text{ \AA}$ ;  $c = 7.885 \pm 0.10 \text{ \AA}$  and  $\beta = 102^\circ 43' \pm 2'$ .

In the absence of any precise data regarding the molecular structure of *m*-nitrobenzaldehyde and 3-hydroxypyridine, the models of the compounds were made assuming the standard values of the bond distances and angles.

In *m*-nitrobenzaldehyde, the ring was assumed to be unsymmetrical with the bond distances C—C = 1.36 Å and 1.44 Å alternately. The C—C bond connecting the aldehyde group was assumed

TABLE 1 — THEORETICAL AND EXPERIMENTAL PROTON SECOND MOMENTS OF THE COMPOUNDS

Compound	Theoretical proton second moment			Expt proton second moment (G <sup>2</sup> )
	Intra-molecular (G <sup>2</sup> )	Inter-molecule (G <sup>2</sup> )	Total (G <sup>2</sup> )	
Anthraquinone	4.005	5.83	9.83	11.91 ±1.0
<i>m</i> -Nitrobenzaldehyde	25.90	6.41	32.31	26.5 ±1.0
3-Hydroxypyridine	2.44	6.91	9.35	10.72 ±1.0

to be 1.50 Å with C—O = 1.201 Å, C—H = 1.07 Å  $\widehat{CCH} = 124^\circ 6'$  and  $\widehat{CCO} = 123^\circ 2'$ .

In 3-hydroxypyridine, the ring was assumed to be unsymmetrical with bond distances C—C = 1.36 Å and 1.44 Å alternately and C—N = 1.355 Å. The C—O bond connecting the hydroxy group was assumed to be 1.379 Å with O—H = 0.944 Å,  $\widehat{COH} = 105.04^\circ$  and  $\widehat{CCO} = 123^\circ 2'$ .

The theoretical rigid lattice value of proton second moment was calculated from the expression based on Van-Vleck's theory<sup>3</sup> for polycrystalline samples. The proton second moment consists of two parts—the intramolecular contribution  $S_1$  and intermolecular contribution  $S_2$ .

Using Bearden and Watts<sup>4</sup> values, the simplified equation to compute  $S_1$  (gauss<sup>2</sup>) can be written as:

$$S_1 = \frac{715.9}{N} \sum_{j < k} \gamma_j \gamma_k \text{ gauss}^2$$

The calculations of  $S_2$  were made applying the method adopted by Andrew and Eades<sup>5</sup>.

The experimental proton second moment at room temperature (22.2°) were determined from the derivative traces using trapezium rule.

The theoretical and experimental results for the title compounds are given in Table 1.

The experimental value of second moment for anthraquinone (11.91 ± 1.0 G<sup>2</sup>) agrees well with the theoretical value (9.83 G<sup>2</sup>). Hence it can be inferred that the lattice of anthraquinone is effectively rigid at room temperature.

Lonsdale *et al.*<sup>7</sup> have measured thermal coefficients for anthraquinone at five different temperatures. It was shown that the oxygen atom possess a large independent out-of-plane liberation. There is no sign of any accompanying out-of-plane liberation of the outer carbon atoms.

The large discrepancy in the experimental and theoretical result in the case of *m*-nitrobenzaldehyde may be attributed to the molecular motion or crystal deformation in the solid *m*-nitrobenzaldehyde. The good agreement between the theoretically estimated (9.35 G<sup>2</sup>) and experimentally observed (10.72 ± 1.0 G<sup>2</sup>) proton second moment values for 3-hydroxypyridine indicates that the lattice of this compound is essentially rigid and no molecular motion exists at room temperature.

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### Adsorption Isotherms of Carbon Dioxide at 273°K on Adsorbent Carbons & Evaluation of Microporosity using Dubinin Equation

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Adsorption isotherms of carbon dioxide (273°K) at low pressures up to about 200 torr on a variety of adsorbent carbons are reported. The slope of the linear Dubinin plot gives a measure of the adsorbate-adsorbent interaction while the intercept gives a measure of microporosity or effective surface area of the adsorbent. The values are in fair agreement with those obtained from BET technique based on low temperature (78°K) adsorption of nitrogen. The degassing of charcoal at 600° causes a considerable rise while that of carbon blacks causes a slight fall in microporosity. The degassing of each at 1000° causes a fall in microporosity, more so in charcoal than in carbon blacks.

SEVERAL investigations on the adsorption of carbon dioxide by microcrystalline carbons<sup>1-7</sup> at temperatures around 273°K and comparatively low pressures up to 200 torr have been reported and data have been used for estimating microporosity or conventional surface area by applying Dubinin equation<sup>8</sup>. The widely used BET method has been criticized and has been shown to provide a measure of total internal volume in micro- and transitional pores and not of microporosity<sup>9</sup>. It was thought of interest to study adsorption of carbon dioxide at 273°K and pressures approaching 200 torr on a series of adsorbent carbons in order to check the applicability of Dubinin equation and to compare specific surface area values obtained by this technique with those obtained by the conventional BET technique. It may also be of interest to know the effect of degassing on surface areas of these materials.

Charcoal, prepared by the carbonization of cane sugar<sup>10</sup>, a few samples of carbon blacks including Graphon (a highly graphitized material received as gift from Cabot Corporation, USA) and five commercially available activated carbons were used. Adsorption of carbon dioxide was studied volumetri-

cally using a self-fabricated equipment after the well known BET apparatus. Carbon (0.2 g oven-dried at 120°) was taken for each experiment. The pressure range studied varied from ~2 to ~200 torr. Equilibrium was attained within 1 hr at each pressure. The saturation pressure ( $p_s$ ) of carbon dioxide (purity 99.8%) at 273°K was taken as 34.4 atmospheres.

In accordance with Dubinin equation (1)

$$\log V = \log V_0 - D (\log p_s/p)^2 \quad \dots(1)$$

(where  $V$  is volume of carbon dioxide adsorbed at equilibrium pressure  $p$ ,  $V_0$  is micropore capacity,  $p_s$  = saturation pressure of the gas and  $D = 2.303 kR^2T^2/\beta^2$  where  $\beta$  is the affinity coefficient of the adsorbate and  $k$  is a constant). The plots of  $(\log p_s/p)^2$  against  $\log V$  for a number of carbon blacks and sugar charcoals were linear. The slope of the linear plot gives the value of  $D$  while the intercept at  $(\log p_s/p)^2 = 0$  provides the value of  $V_0$ , taken as a measure of microporosity, or as a measure of effective surface area<sup>5</sup>. Taking  $17 \text{ \AA}^2$  as molecular area of carbon dioxide at 273°K (ref. 7), microporosity can be converted into conventional surface area which is accessible to  $\text{CO}_2$  molecules through pore entrances of width  $>4.2 \text{ \AA}$  which is molecular thickness of  $\text{CO}_2$ . Since  $D$  is inversely proportional to  $\beta^2$ , a higher value of  $D$ , evidently, indicates smaller adsorbate-adsorbent affinity. It appears, therefore, that the adsorbate has a greater attractive interaction with the first 9 carbon blacks than with the activated carbons. This is in conformity with the observations of Lamond and Marsh<sup>6</sup> who found the value of  $D$  to rise, and therefore, the affinity to fall, on activating polyfurfuryl alcohol carbon to increasing burn offs. Walker *et al.*<sup>7,11</sup> also found the value of  $D$  to be higher in activated carbons than in carbon molecular sieve materials. In activated carbons, the pores are relatively wider and hence the number of pore walls per g is smaller. The adsorbate interaction is, therefore, relatively smaller. The values of  $D$  in the case of Graphon, Kosmos 40 and Philblack A, which are essentially non-porous, are appreciably higher. The adsorbate interaction is very low due to virtual absence of pore walls.

The specific surface area values as obtained by the conventional BET technique based on low temperature (78°K) adsorption of nitrogen are also included in Table 1 for the sake of comparison. Considering the differences of approach in the two methods the agreement in the values obtained may be taken as fairly satisfactory. In any case, the objection to the use of conventional BET technique on the ground of condensation of nitrogen in pores<sup>9</sup> does not appear to be valid as the value of surface area obtained by this technique then would have been much higher. However, there are distinct advantages in using carbon dioxide since it is a readily available and 273°K is the temperature which can easily be maintained.

The effect of degassing sugar charcoal and some of the carbon blacks on their surface area, about which very little information is available in the literature, is shown in Table 2. It is seen, in the first instance, that degassing of sugar charcoal at

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