LETTERS TO THE EDITOR

VIBRATIONAL SPECTRA OF DEUTERATED ANILINE

THE introduction of deuterium atoms leaves essentially unchanged all properties of aniline molecule associated with the electronic structure and force field but affects those properties dependent on the mass notably the vibrational frequencies. Therefore, the introduction of isotope provides a very powerful tool for sorting out different kinds of molecular vibrations. The aniline molecule, as evidenced by many indirect evidences,[1-3] belongs to C_s symmetry. So the 36 fundamental vibrations of deuterated aniline are divided into two parts, 25 to symmetric vibrations a' and 11 to non-symmetric vibrations a''. Table I shows the assignments

TABLE I

Comparison of fundamental ground state vibrations of aniline and aniline-d_7

Aniline	Aniline-d_7	Assignment
3440	2532	a', ND_2 stretch
3360	2465	a', ND_2 stretch
3088	2280	a', C—D stretch
3063	2260	a', C—D stretch
1602	1575	a', ring stretch
1586	1464	a', ring stretch
1468	1426	a', ring stretch
1501	1403	a', ring stretch
1279	1290	a', C—N D_2 stretch
1309	1252	a', ring stretch
1618	1194	a', N—D_2 bend i.p.
1326	1067	a', C—D bend i.p.
984	975	a', ring deform i.p.
998	952	a', ring breath
1175	923	a', C—D bend i.p.
1155	867	a', C—D bend i.p.
1120	835	a', C—D bend i.p.
812	817	a', C—N D_2 bend i.p.
1029	807	a', C—D bend i p
1054	752	a'', ND_2 twist
959	740	a'', C—D bend o.p.
618	520*	a', ring deform. i.p.
415	424*	a'', ring deform o.p.
233	209*	a'', ring deform o.p.

* These values are obtained from ultraviolet absorption studies.[5]

of the vibrational frequencies of deuterated aniline and comparison to the respective aniline frequencies.[4]

The samples of aniline and aniline-d_7 were obtained by B.A.R.C., Tromaby, and they were used without further purification. The infrared absorption spectra were recorded on H-800 Spectrophotometer fitted with sodium chloride optics.

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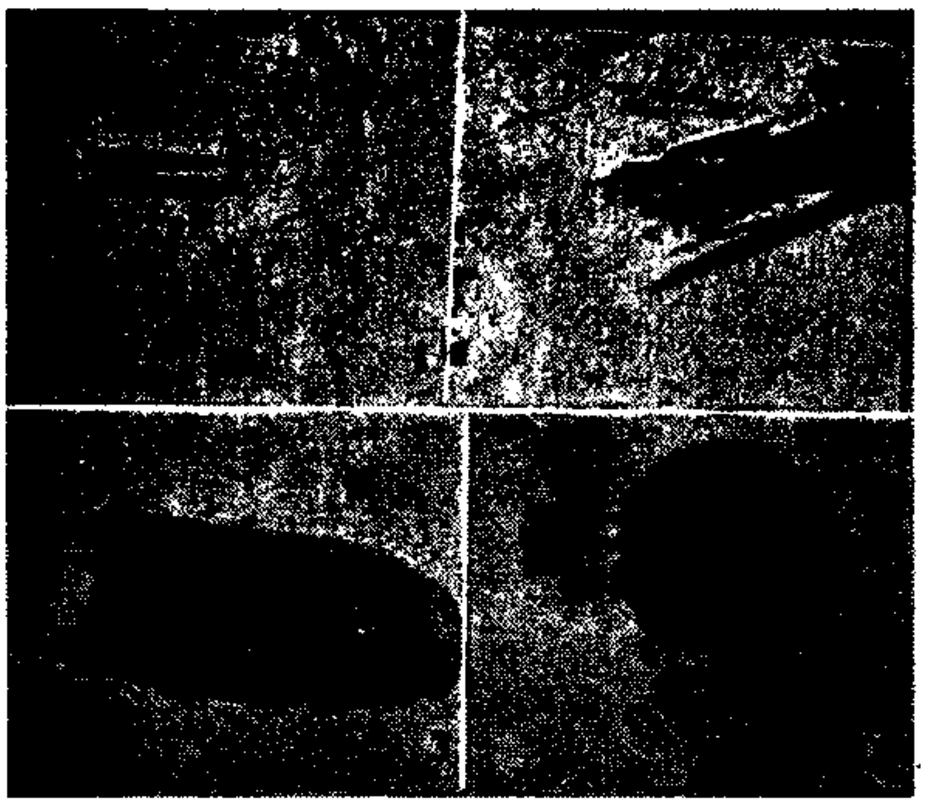
ON THE DEPOSITION OF CRYSTALLINE MATTER IN URINARY CALCULI

URINARY calculi are known to consist of both crystalline as well as colloidal matter.[1,2] The interrelationship between the colloidal and the crystalline components of bladder stones is none-too-well understood. The mechanism of formation and pathogenesis of urinary calculi are, also, still obscure. An electron-optical study of the nature and mode of crystallisation in bladder stones is in progress in this laboratory and the present report deals with some preliminary results of electron micrographic studies.

The calculi studied were from Delhi area where the disease is endemic amongst children belonging to poor families.[2] The stones were chocolate-brown in colour with a nodular surface.[2] Some of the stones were as much as an inch long in cross-section. The calculi were cut into two halves and small sections of the stones were scooped out from different regions and carefully powdered in an agate mortar. The powdered samples were first examined by X-ray powder diffraction employing Cu K_α radiation from a Philips 1010 X-ray diffraction unit. X-ray diffraction data indicated the presence of whewellite (calcium oxalate monohydrate) and acid ammonium urate as the main components.

The powdered samples were then examined in a Philips EM-100 electron microscope. For this purpose, specimens were prepared by allowing a drop of dilute aqueous suspension of the powdered sample to evaporate on a cellulose acetate substrate which was supported on a 200 mesh copper grid.

Three distinct kinds of crystallisation on amorphous substrates were observed in the electron-micrographic scannings. The first kind was in the form of rods (Fig. 1) with one



FIGS. 1–4. Different kinds of crystallization in urinary calculi. Fig. 1. Crystalline rods (× 4,000) Fig. 2. Amorphous hollow fibrils in which precipitation occurs (× 4,200). Fig. 3. Discrete crystallites on the surface of amorphous cylindrical substrate, white patches indicate places from which crystallites were dislodged (× 9,000). Fig. 4. Globular matrix containing crystallites (× 12,000).

pointed end. The density of crystalline material within these rods was not necessarily uniform; at high magnification, the opacity to electrons varied along the length of many rods scanned. Apparently, this type of precipitation occurred in fibrils, lacking any fine structure, shown in Fig. 2. The fibrils, which are not crystalline, in the sense that they do not give any electron diffraction pattern, are most probably organic in nature.

Figure 3 illustrates a second kind of crystallisation. In this case, small discrete crystallites were found lodged on the surface of hollow cylinders; the precipitation was not continuous within the amorphous cylindrical substrates. Some of the crystallites were dislodged from their positions most probably when the calculi were powdered.

Another kind of crystallisation was found to occur in globular substrates (Fig. 4). The globules have the appearance of coacervates in which crystallisation has occurred. The outer portion of the globules were amorphous to electrons.

It is clear from the above that more than one mode of precipitation of crystalline matter on amorphous organic matrices is operative in the formation of urinary calculi.

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Dept of Chemistry, M. V. R. Rao.
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AGE OF THE TIPAM SANDSTONES

Ever since the discovery[1] of vertebrate fossils in the upper beds of the Boka Bil stage of the Surma Series in Assam, the age of the overlying Tipam Sandstones has been in doubt. On the evidence of marine invertebrate fossils[2] palæontologists assigned a Pliocene age to the Tipam Sandstones but because of absence of any break in sedimentation and partly because the Tipam Sandstones laterally merge into the Boka Bil beds, field geologists urged a Miocene age for the beds, which prevailed. The mammalian fossils recently discovered in the underlying Boka Bil beds include *Dorcatherium* sp. which first appears in the Nagri stage of the Siwaliks and the Nagri stage has been dated by Lewis[3] as belonging to the Pontian. The Tipam Sandstones must therefore be younger than the Boka Bil beds or at most of Pontian age, if they laterally merge with the latter.

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EXTROVERT CORPUS LUTEUM IN TWO SPECIES OF INDIAN BATS

The occurrence of the extrovert corpus luteum is a rare phenomenon among the mammals and has been noticed in two species of British horse-shoe bats (Matthews, 1937), in the African insectivore, *Elephantulus myurus* (Van der Horst and Gillman, 1940, 1942), and in the mouse-tailed bat, *Rhinopoma kinneari* (Anand Kumar, 1965). While investigating the development of the corpus luteum in several species of Indian bats in this laboratory it was noticed that the corpus luteum becomes completely extroverted in *Hipposideros fulvus*