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STRUCTURAL MODEL FOR BENZIDINE-VERMICULITE

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Abstract—A combination of X-ray diffraction, infrared, and chemical data has established that the ion exchange of vermiculite with singly charged benzidine cations in an aqueous solution at pH 1.6 results in a black, highly ordered benzidine-vermiculite intercalate. The intercalate has a basal spacing of 19.25 Å and a primitive unit cell with "a" and "b" edges parallel and equal to those of vermiculite. The number of benzidine molecules per cell is equal to its electric charge. In this structure the benzidine molecules are steeply inclined to the silicate surfaces and close-packed within domains. The domains contain alternating rows of benzidine cations; from row to row the planes are either approximately parallel or perpendicular to the (120) plane, but along any one row the planes of the aromatic rings are parallel to each other. Hydrogen bonding operates between amine nitrogens and surface oxygens.

Key Words—Benzidine, Hydrogen bonding, Intercalation, Vermiculite, X-ray diffraction.

INTRODUCTION

The interaction of benzidine (4,4′-diaminobiphenyl) with clays has been extensively studied since 1940 when Hendricks and Alexander described a method to identify members of the montmorillonite group by the formation of a blue complex when benzidine is adsorbed and oxidized by the clay. Subsequently, Solomon *et al.* (1968) reported that benzidine oxidized to benzidine-blue at exposed aluminum atoms on crystal edges and at transition metal atoms in the higher valency state within the silicate structure. Tennakoon *et al.* (1974) presented direct Mössbauer spectroscopic evidence for the involvement of structural iron(III) in the oxidation-reduction process leading to the formation of colored benzidine radical cations in montmorillonite. Recent work by McBride (1979) has shown that clay-edge aluminum sites are relatively unimportant in the oxidation of benzidine.

By quantitatively studying the adsorption of benzidine from aqueous hydrochloride solutions in contact with various montmorillonites, Furukawa and Brindley (1973) concluded that at pH <3.2, divalent and monovalent species were taken up by displacement of the exchangeable cations, but at higher pH, the monovalent species was preferentially adsorbed. They further considered that the total amount of benzidine adsorbed was equal to the amount of unoxidized cation taken up by exchange plus an amount of semiquinone produced by oxidation-reduction processes.

In a study of the color reactions of benzidine and chrysoidine (2,4-diamino-azobenzene) with montmorillonite and other clays, Vedeneeva (1950) emphasized the importance of steric parameters in establishing the linkages between the organic molecules and the silicate sheets. This worker concluded that in benzidine-montmorillonite, the C–N bonds of the organic cations are parallel to the surfaces of the silicate sheets and that the NH_2 groups are located over oxygen ions. Others, including Hendricks (1941) and Greene-Kelly (1955), also concluded that benzidine has its principal axis parallel to the basal plane in montmorillonite.

Knowledge of the benzidine-clay linkage plays a key role in designing methods to combat pollution resulting from the industrial use of biphenyls. Benzidine has been identified as a carcinogen and, because it is produced in some industrial processes, its sorption by soil clays is of considerable interest (Zierath *et al.*, 1980).

Previous workers have chiefly been concerned with the various charged species and radicals formed by benzidine when it is intercalated between clay layers, however, the structures of such intercalates are generally not known. As part of a program concerned with the structures of clay-organic intercalates (Slade *et al.*, 1978; Raupach *et al.*, 1979), we report here the partial structure of a black intercalate formed by vermiculite with benzidine hydrochloride in an aqueous solution at pH 1.6.

EXPERIMENTAL

Material

The vermiculite used for the present work came from Young River in Western Australia; this vermiculite was saturated with sodium and the structural formula was determined by X-ray fluorescence analysis to be:

$$(Mg_{2.499}Fe^{3+}{}_{0.397}Ti_{0.005}Mn_{0.012}Al_{0.088})$$
$$(Al_{1.221}Si_{2.779})O_{10}(OH)_2(Na_{0.682}Ca_{0.018}K_{0.007})$$

The benzidine dihydrochloride salt was obtained from Tokyo Kasei Kogyo Limited, Japan, and an almost saturated stock solution was made by stirring the salt in distilled water at about 40°C.

Sample preparation

The benzidine-vermiculite was prepared by refluxing flakes (about 1.5 × 0.8 × 0.1 mm) of the Na-saturated

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vermiculite in the benzidine dihydrochloride solution. Refluxing at 90°C was continued for 3 weeks, but at intervals the supernatant solution was changed and a few flakes were removed for examination by X-ray powder diffraction. The exchange reaction was monitored by observing the development of a rational set of 00ℓ reflections based upon a fundamental spacing of 19.246 Å. To remove excess salt, the flakes were finally carefully washed with hot distilled water.

Infrared methods

The infrared (IR) spectra were obtained using attenuated total reflectance (ATR) as described by Raupach *et al.* (1979). Briefly, spectra of single clay flakes or groups of flakes were recorded by using single reflection hemicylinders, of germanium or TlBr/TlI (KRS 5), fitted to ATR assemblies manufactured by Research and Industrial Instruments Co. Matched ATR units were positioned in both beams of a Perkin-Elmer 521 spectrophotometer operating with 4× slits and purged with dry nitrogen.

X-ray diffraction methods

A value of 19.25 ± 0.02 Å for d(001) was calculated from the 2θ values of the first 19 orders in the 00ℓ spectra. Measurements were obtained directly from an X-ray diffractometer chart produced by a Norelco diffractometer fitted with the following slits and using Fe-filtered CoKα radiation: divergence 0.25°, receiving 0.146 mm before a 1° slit. The scan speed was 1°/min.

For Fourier analysis a flake was mounted about its "b" axis on a Supper two-circle single crystal diffractometer (equi-inclination Weissenberg geometry). Intensity data for filtered MoKα radiation were collected automatically for 45 00ℓ reflections; the algorithm for the data-collection program is essentially that of Freeman *et al.* (1970). A standard reflection was measured periodically throughout the data-collection cycle, and the errors associated with each experimentally observed structure factor were derived from the counting statistics by the data-collection algorithm. Experimental intensities were corrected for Lp factors and for absorption using a linear absorption coefficient of μ = 12.86 cm^{-1} and the algorithm of Burnham (1963). Phases for the observed structure factors were computed initially from the z coordinates for the silicate atoms only. The parameters used were those of Mathieson (1958) but modified for the larger c-dimension of benzidine-vermiculite. Structure factors were calculated with the ORFLS program of Busing *et al.* (1962). Subsequently, as the positions of the organic atoms became known they were also included in the trial structure.

Upon completion of the exchange reaction, a number of carefully selected flakes of benzidine-vermiculite were oriented upon either their "a" or "b" axes and their a*b* planes photographed. Initially this was done by setting flakes perpendicular to the incident X-ray beam; they remained stationary during exposures. Subsequently, areas of the a*b* plane well away from the direct beam, as well as regions above and below the a*b* plane (sections cutting c*), were examined either by tilting the flakes with respect to the incident beam (again no movement imparted to flakes or films) or by using a precession camera. For precession photography with MoKα radiation long exposures (two weeks or more) were needed.

RESULTS

Chemical

Analysis of the Young River vermiculite-benzidine intercalate, carried out by the Australian Microanalytical Service, shows the material to contain 19.55% C, 2.48% H, and 4.28% N on a vacuum-dry basis. In relation to the structural formula of the Young River vermiculite these analyses show 1.59 molecules of benzidine per single layer unit cell (from the nitrogen value) or 1.35 molecules per cell as calculated from the carbon value; the value for hydrogen was not used because of the possible loss or gain of H. The mean of these two numbers (1.47) agrees with the vermiculite interlayer charge (1.45 charge units per single layer cell) and leads to the conclusion that each organic cation carries but a single charge. The totality of the charges on the benzidine completely satisfies the exchange capacity of the vermiculite. This result was unexpected because the exchange reactions were carried out at a pH near 1.6 with slightly undersaturated solutions of benzidine *di*hydrochloride. At 20°C the solutions were saturated and gave a pH of 1.6; this value dropped less than 0.1 units on warming the solutions from 20° to 90°C. From Furukawa and Brindley's work (1973) on montmorillonite the exchange reaction at pH <3.2 was expected to involve mainly divalent species.

Powder and single crystal X-ray diffraction photographs of the benzidine salt crystals, removed from their mother liquor at 20°C, showed them to be of a single homogeneous phase having unit-cell dimensions quite different from those of either benzidine or benzidine dihydrochloride. The benzidine salt crystals had the following composition: C = 67.68%, H = 4.82%, N = 13.02%, and Cl = 15.1% compared with benzidine monohydrochloride (theoretical composition: C = 65.31%, H = 5.94%, N = 12.69% and Cl = 16.07%) and benzidine dihydrochloride (C = 56.05%, H = 5.49%, N = 10.89% and Cl = 27.57%). Although the experimental values for H and Cl are low in comparison with their theoretical equivalents, and bearing in mind that the single crystal diffraction patterns were sharp and different from those of benzidine or its dihydrochloride, the existence of benzidine monohydrochloride as a distinct species is certain.

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Therefore, because the exchange reactions were actually carried out with benzidine cations, the one-to-one relationship between the number of charges and the number of saturating organic cations per single layer cell is appropriate if the benzidine cations are singly charged. It should be mentioned that benzidine dihydrochloride will crystallize from a saturated solution provided the pH is lowered to 0.6 by the addition of HCl. However, attempts to carry out the exchange reactions with divalent benzidine cations (at pH 0.6) merely caused a disintegration of the vermiculite flakes.

Infrared

Figure 1 shows the IR spectra in the range 3750–2300 cm^{-1} of benzidine, its mono- and dihydrochlorides, and the benzidine-vermiculite intercalate. Further details and assignments for the spectra will be discussed in a subsequent paper on these and associated compounds. Figure 1 shows that the spectrum of benzidine-vermiculite is closer to that of the monovalent salt than it is to that of the divalent salt.

The spectrum of benzidine dihydrochloride contains well-developed broad bands from the amine salt groups at about 2830 and 2560 cm^{-1}. In contrast, the spectrum of benzidine shows only a series of sharp absorption bands above 3000 cm^{-1} associated with NH_2 groups. Both NH_2 and amine salt groups are present in the monovalent salt and also in the benzidine-vermiculite intercalate. In the spectrum of the latter, the intensities of the NH_3^+ bands are relatively weaker than those of the corresponding bands in the spectrum of the monovalent salt. The benzidine-clay intercalate thus contains mainly NH_2 groups, and most of its benzidine is probably in the radical cationic form.

Two hydrogen bond distances for O . . . H–N may be estimated from the bands for the intercalate at 3228 and 2580 cm^{-1}. These distances represent the extremes of a range of four or five hydrogen bond maxima in the spectrum; from the relationships of Schuster *et al.* (1976) the range of hydrogen bond lengths is therefore 2.93–2.62 Å. A further useful feature of the complete benzidine-vermiculite spectrum, obtained with polarized radiation, relates to the fact that the strong out-of-plane C–H bending vibration at 800 cm^{-1} is very highly polarized, indicating that the aromatic rings are steeply inclined to the silicate surface.

X-ray diffraction

Electron density distribution projected onto the "c" axis of the unit cell. A one-dimensional Fourier projection was computed from 45 orders of 00ℓ structure factors initially phased from the model with the silicate portion only (Figure 2). To explain this curve, Fourier images were calculated for models in which the angle of rise of the C–N bonds of the intercalated benzidine

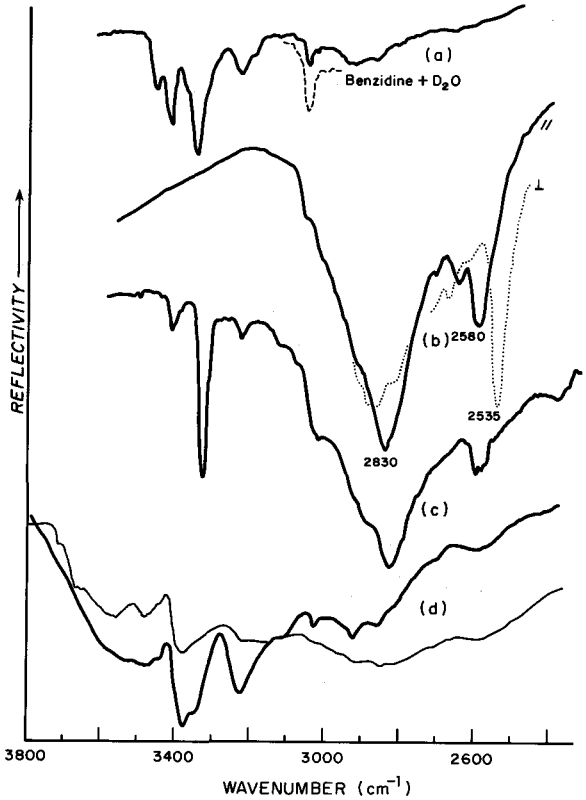


Figure 1. Infrared attenuated total reflectance spectra over the range 3750–2300 cm^{-1} for (a) benzidine crystals with parallel radiation using a Ge hemicylinder at 28° incidence and 5× expansion, (b) benzidine dihydrochloride single crystal using a Ge hemicylinder at 40° incidence and 3× expansion, (c) benzidine monohydrochloride single crystal with parallel radiation using a Ge hemicylinder at 45° incidence and 4.3× expansion, (d) benzidine vermiculite intercalate with parallel radiation using a KRS-5 hemicylinder at 50° incidence and 4× expansion (thick line), and using a Ge hemicylinder at 26° incidence and 5× expansion (thin line).

molecules ranged from 45° to 90°. A satisfactory fit was only found when the benzidine molecules were very steeply inclined to the vermiculite layers. This result agreed with the IR data. With this finding established, work upon the one-dimensional Fourier projection was set aside until the diffraction pattern in the a*b* plane had been considered.

*The diffraction pattern in the a*b* plane.* Stationary-crystal, stationary-film photographs of benzidine-vermiculite flakes set perpendicular to the direct beam show not only the reflections expected for vermiculite, but an additional group of strong, sharp reflections close to the direct beam. By tilting the flake, other, much weaker reflections further from the direct beam were revealed. Although such photographs were easily and quickly made, they suffer from geometrical distor-

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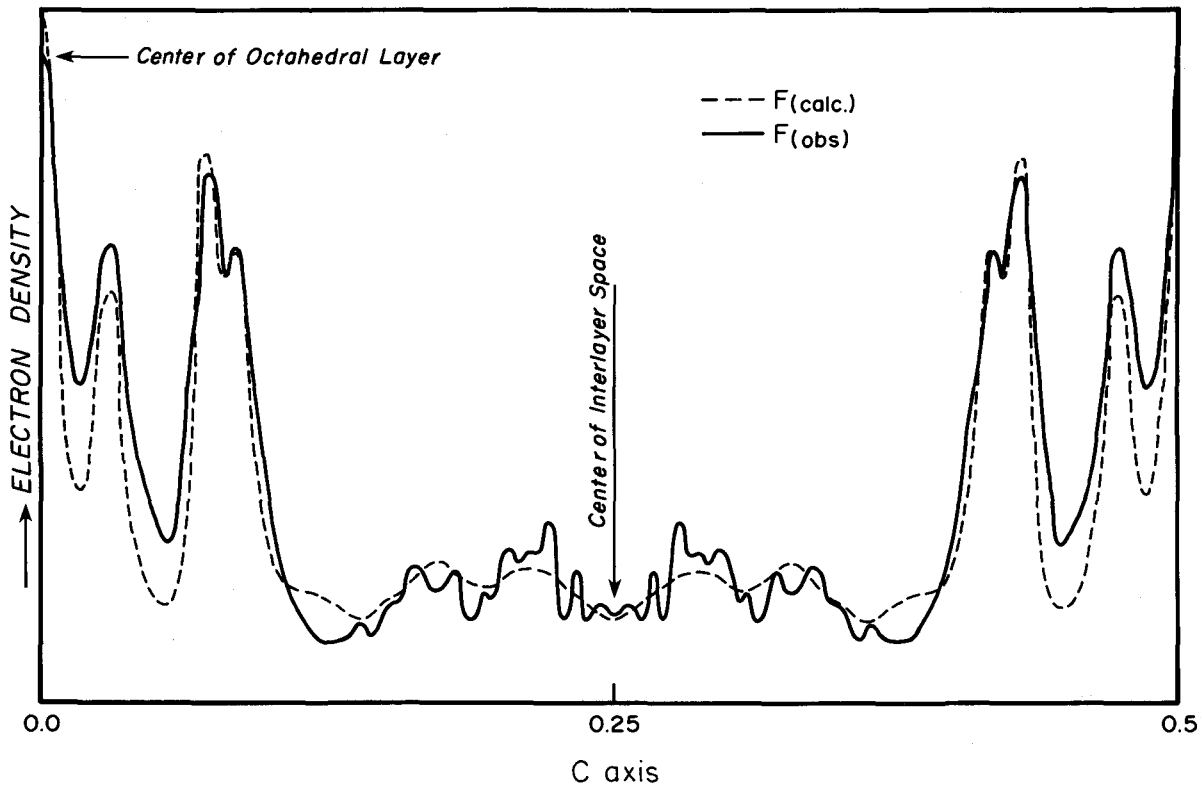


Figure 2. One dimensional Fourier projection onto the "c" axis, of the electron density in benzidine-vermiculite.

tions caused by the projection of planar reciprocal lattice sections onto the photographic plate. In the present experiment this plate was curved. A second disadvantage arose from the structural disorder between the silicate layers, which causes hk reflections to become rods parallel to c*. If a knowledge of the exact ℓ indices of points along these rods is required the stationary geometrical system is inconvenient. To overcome these disadvantages a photograph of the a*b* plane of benzidine-vermiculite was taken with a Huber precession camera (Figure 3).

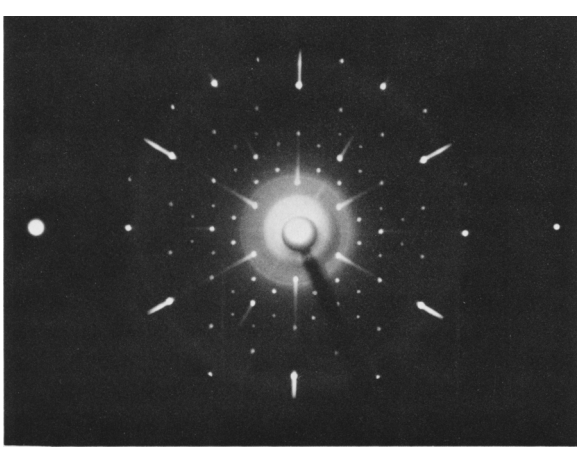


Figure 3. Precession photograph of benzidine-vermiculite (Young River), c axis zero level, $\bar{\mu}$ = 15°, MoKα; 45 kV, 26 mA, 6 days.

The interpretation of this pattern was based upon the realization that it is a composite pattern (Figure 4a) obtained by superimposing the three resultants given by rotating a simpler fundamental pattern (Figure 4b) successively through 60°. From the fundamental reciprocal lattice illustrated in Figure 4b, the vermiculite and the intercalated vermiculite unit cells appear to be the same size, although the c-face centering of the former is destroyed and therefore the cell changes to primitive during the benzidine exchange reaction.

A primitive benzidine-vermiculite cell can be produced by considering the surface of a single silicate sheet as a hexagonal array (of ditrigonal rings of oxygen atoms) with alternate rows of rings populated by entities whose scattering differs from those in adjacent rows. Because the superlattice points in the a*b* net are arranged along lines parallel to b*, the rows (between which there is contrasting scattering power) on the silicate surface must be perpendicular to the "b" axis.

A primitive cell could be produced by siting benzidine molecules, with their long axes nearly vertical, over the centers of those rings of surface oxygen atoms

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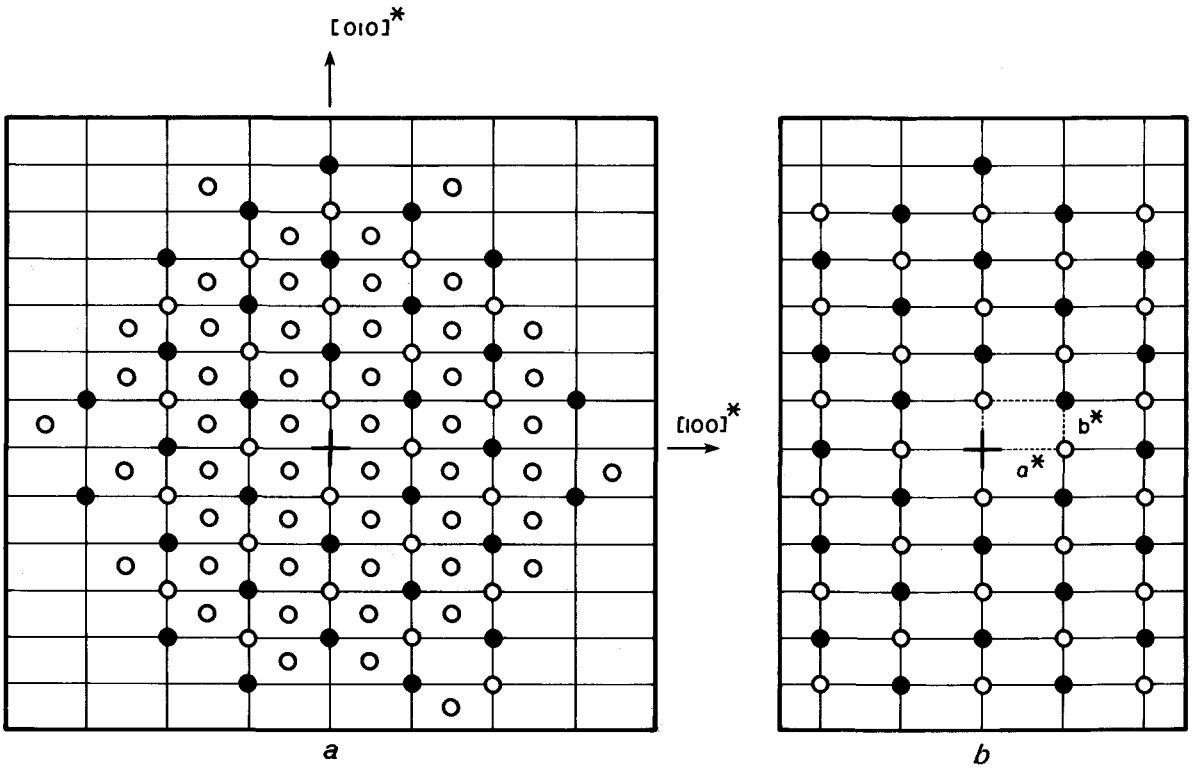


Figure 4. Schematic representation of reflections for benzidine-vermiculite. Reflections due to unreacted vermiculite are shown as dots; the extra reflections caused by intercalation are shown as circles. (a) Representation of the composite a*b* plane. (b) Representation of a fundamental component of Figure 4a.

along alternate rows perpendicular to "b." Such a model only incorporates one molecule of benzidine per unit cell and thus does not explain the chemistry of the Young River vermiculite-benzidine intercalate. This problem can be overcome if benzidine molecules are sited over the centers of oxygen rings along every row. However, to maintain a primitive unit cell, the orientation of the organic molecules in alternate rows must be different. By taking into account packing requirements, and the argument developed in the previous section, the model shown in Figure 5a was arrived at.

The 120, $1\bar{2}0$, $\bar{1}20$ and $\bar{1}\bar{2}0$ reflections are considerably more intense than any of the other reflections produced by the benzidine intercalation. To ensure that the model illustrated in Figure 5a is compatible with this observation, hk0 structure factors were computed by using a specially modified version of ORFLS. The modification allowed all of the symmetry operators for a given space group to be applied to a specified set of atoms (here space group 15 operators were applied to the silicate atoms only), whereas for a second set (the interlayer atoms) only the identity and the centrosymmetric transformations were applied. The positional parameters for the silicate atoms were taken from Mathieson (1958) and adjusted to a unit cell with $a = 5.33$, $b = 9.18$, $c = 38.79$ Å, and $\beta = 97°$. The coordinates of the atoms in the benzidine molecules were obtained from the three-dimensional scale model prepared from Figure 5a and illustrated in Figure 5b. This latter figure shows that for each unit cell no more than a pair of benzidine molecules can exist in the interlayer, their nitrogen atoms being directed towards the center points of the ditrigonal rings of oxygen atoms which form the opposed surfaces of adjacent silicate layers. To observe the effects upon the structure factors for the extra hk0 reflections due to intercalation, the model was varied by altering the angles between the principal axes of the benzidine molecules and the crystallographic axes. The resulting changes of the structure factors were plotted on an a*b* net. The essential correctness of the model represented by Figures 5a and 5b was confirmed, as it was the only configuration which produced the observed pattern of structure factors, i.e., 120, $\bar{1}\bar{2}0$ very strong; $2\bar{1}0$, $\bar{2}10$ strong; the rest medium to weak. It should be noted that the experimental pattern has a mirror plane of symmetry perpendicular to the a*b* plane and through b*. The presence of such a mirror is compatible with the equal probability that, within ordered domains, the planes containing the benzidine molecules nearest the cell corners can be inclined either to the left or the right of the "b" axis. The molecules at the cell center positions are arranged as appropriate.

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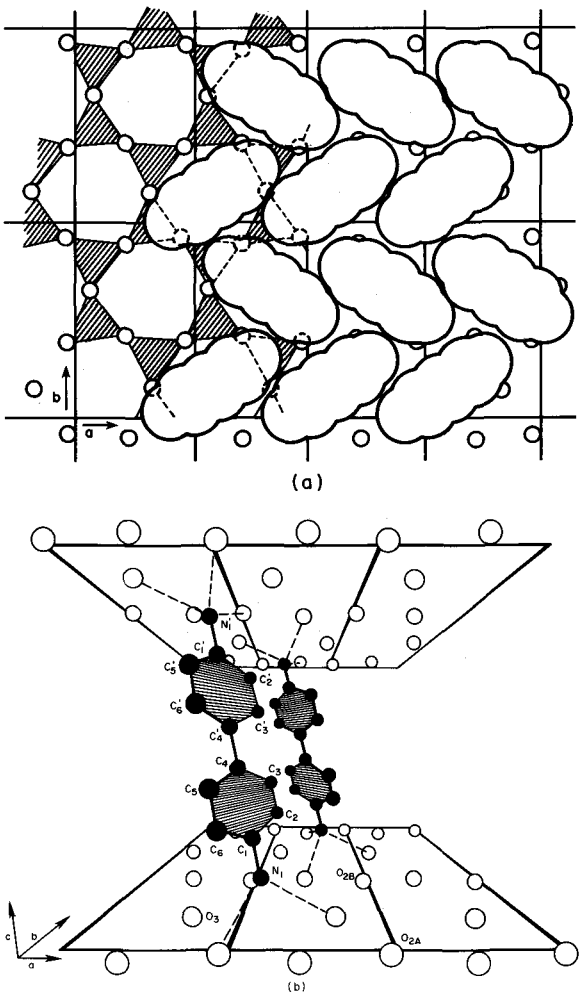


Figure 5. Schematic presentation of the interlayer cation arrangement in a fully ordered domain of benzidine-vermiculite. The benzidine cations are drawn from their van der Waals radii reduced to the same scale as that used for the vermiculite cell. The centers of the oxygens in the silicate surface are shown as small circles, and an indication of the hexagonal array of ditrigonal rings formed by them is given. (b) The model for the structure of benzidine vermiculite as viewed along the b axis. Possible hydrogen bonds to surface oxygens are shown thus by dashed lines.

Initially, the calculations were made with the amino nitrogen atoms equidistant from the symmetry related oxygen atoms of the two opposed layers. Subsequently, small changes were made to this arrangement, and their effects were monitored by comparing calculated and experimentally derived electron densities as projected onto the "c" axis. The best fit resulted when the amino groups were at slightly different distances from the silicate surfaces.

Table 1 lists the 00ℓ structure factors, and Table 2 gives the coordinates for the atoms in the final model. The dashed curve in Figure 2 represents the Fourier projection of the atoms of the full model onto the "c" axis of the unit cell.

Table 1. Comparison of mutually scaled observed and calculated structure amplitudes for benzidine-vermiculite.

00ℓ	$F_{obs.}$	$F_{calc.}$	00ℓ	$F_{obs.}$	$F_{calc.}$
002	742	421	00,52	40	−22
004	322	143	00,54	10	6
006	96	−59	00,56	very weak	29
008	162	−70	00,58	very weak	34
00,10	222	187	00,60	very weak	11
00,12	337	283	00,62	very weak	−11
00,14	266	202	00,64	very weak	−16
00,16	90	−11	00,66	8	2
00,18	130	−116	00,68	41	30
00,20	167	−165	00,70	22	41
00,22	51	−27	00,72	30	32
00,24	96	111	00,74	7	10
00,26	111	149	00,76	34	−5
00,28	125	136	00,78	very weak	−4
00,30	110	94	00,80	very weak	8
00,32	80	66	00,82	30	14
00,34	65	72	00,84	very weak	11
00,36	54	66	00,86	13	2
00,38	56	75	00,88	27	−7
00,40	62	86	00,90	very weak	−8
00,42	74	82	00,92	37	−3
00,44	75	71	00,94	40	2
00,46	55	40	00,96	very weak	4
00,48	27	−2	00,98	26	23
00,50	very weak	−29			

Overall R factor = 0.21.

DISCUSSION

On the basis of the experimental data available for the Young River vermiculite-benzidine intercalate it is not possible at present to provide a full description of its structure in the classical sense. Such a description would require the determination of many more variables than can be computed from the poor diffraction patterns given by the Young River intercalate. Reflections with more general indices than those mentioned here are extremely diffuse and, as the modulation of intensities by the organic component is weak, little use can be made of them.

The development of extra reflections in the a*b* plane is therefore quite important because, although they are only observable near the direct beam, their presence and the broad distribution of their intensities enable a probable structure to be arrived at.

Although most of the present work was carried out on the intercalate formed by benzidine with the medium charged Young River vermiculite, similar intercalates were also prepared with the higher charged vermiculites from Llano County, Texas (for compositions, see samples 1 and 7 of Norrish, 1973). The products formed with these materials have the same basal spacing and similar extra reflections to those given by the Young

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River vermiculite. Therefore, in spite of the charge variations, the structure of each of these materials is similar.

The model proposed for the structure of benzidine-vermiculite represents a close-packed, ordered domain. With increasing charge, the size of the fully ordered domains can be expected to increase and so the packing of molecules within the interlayer regions as a whole will more closely approach the limiting situation represented by the model. In materials carrying less than two charges per unit cell, the packing of the organic molecules will be less dense than the limit shown in Figure 5a. However, a single domain will necessarily contain equal numbers of benzidines with their ring planes inclined both to the left and to the right of the "b" axis. Support for this concept of the effect of charge, comes from a comparison of the extra reflections: in the diffraction patterns given by the Young River vermiculite-benzidine intercalate, these reflections are more diffuse than in the Llano equivalent.

Although considerable evidence exists to show that benzidine molecules become involved in such chemical reactions as rearrangement, charge transfer, and polymerization, the structure of benzidine as determined in its dihydrochloride by Chung *et al.* (1972) satisfies our experimental data. Nevertheless, the benzidine rings are packed in close proximity both to the silicate surfaces and to one another; this packing, coupled with the electric field imposed by the vermiculite sheets, could cause small distortions of the benzidine structure which this study would not have detected.

The fact that the intensities of the NH_3^+ bands in the IR spectrum of the intercalate are weaker than the corresponding bands in the monovalent salt is evidence for a hydrogen transfer process occurring when the monovalent benzidine cations become incorporated into the intercalate structure. Chemical analysis of the Young River vermiculite-benzidine intercalate shows the ratios of H/C and H/N to be less than for benzidine monohydrochloride, confirming that hydrogen is displaced into the silicate structure, or otherwise lost from the system.

Table 2. Atomic coordinates and temperature factors for benzidine-vermiculite.

Atom	x	y	z
(Mg, Fe, Al) oct.	0.0000	0.0000	0.000
(Mg, Fe, Al) oct.	0.0000	0.3333	0.000
(Mg, Fe, Al) oct.	0.0000	0.6667	0.000
(Si, Al) tet	0.3970	0.0000	0.0715
(Si, Al) tet	0.3970	0.3333	0.0715
O_1	0.3580	0.0000	0.0276
O_1	0.3580	0.3333	0.0276
O_1	0.3580	0.6667	0.0276
O_{2B}	0.1470	0.4040	0.0850
O_{2A}	0.1470	0.9290	0.0850
O_3	0.4340	0.1670	0.0850
N_1 molecule 1	0.9662	0.1634	0.1246
C_1 molecule 1	0.9906	0.1634	0.1749
C_2 molecule 1	0.8255	0.0436	0.1847
C_3 molecule 1	0.8443	0.0490	0.2200
C_4 molecule 1	0.0375	0.1634	0.2329
C_5 molecule 1	0.1876	0.2832	0.2097
C_6 molecule 1	0.1689	0.2525	0.1762
C_4' molecule 1	0.0844	0.1961	0.2742
C_3' molecule 1	0.9287	0.0218	0.2974
C_2' molecule 1	0.9531	0.0436	0.3335
C_1' molecule 1	0.0844	0.1416	0.3464
C_6' molecule 1	0.2533	0.2451	0.2883
C_5' molecule 1	0.2814	0.2614	0.3252
N_1' molecule 1	0.1313	0.1307	0.3850
N_1 molecule 2	0.4662	0.6634	0.1126
C_1 molecule 2	0.4906	0.6634	0.1513
C_2 molecule 2	0.6876	0.5763	0.1629
C_3 molecule 2	0.7064	0.5871	0.2003
C_4 molecule 2	0.5375	0.6634	0.2209
C_5 molecule 2	0.3499	0.7778	0.2067
C_6 molecule 2	0.3311	0.7832	0.1719
C_4' molecule 2	0.5844	0.6961	0.2622
C_3' molecule 2	0.7814	0.5763	0.2751
C_2' molecule 2	0.8002	0.5871	0.3112
C_1' molecule 2	0.5844	0.6416	0.3344
C_5' molecule 2	0.4250	0.8050	0.3241
C_6' molecule 2	0.3874	0.8000	0.2880
N_1' molecule 2	0.6313	0.6307	0.3730
	Temperature factors (B)		

Atoms of the silicate structure 1.5×10^{-15} cm^2.
Atoms of the organic structure 2.5×10^{-15} cm^2.

Although the amount of benzidine in the intercalate equals the exchange capacity of the vermiculite and adsorption appears to occur largely by an exchange process involving monovalent benzidine cations, our chemical results do not rule out the possibility that some divalent and some oxidized species may also be present in small amounts. The black color of the vermiculite-intercalates contrasts strongly with the colorless nature in their salt crystals. This color difference suggests that a charge disturbance, possibly associated with an oxidation process, occurs in the aromatic rings upon intercalation.

Work in progress shows that benzidine montmorillonite has a basal spacing of 15.5 Å under the conditions of our experiments. Therefore its structure is quite different from that proposed here for benzidine-vermiculite. The surface charge densities in montmorillonite and in vermiculite can cause different packing arrangements in their benzidine intercalates. There is room for both divalent (Furukawa and Brindley, 1973) and monovalent benzidine cations to lie flat and to satisfy the exchange capacity of montmorillonite. In vermiculite, only divalent cations would have sufficient room to lie flat; monovalent species would have to stand at an angle to the surface and so give rise to spacings above 15.5 Å, in agreement with our findings.

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REFERENCES

Burnham, C. W. (1963) GNABS, program for computing transmission factors for crystals of essentially arbitrary shape: Geophysical Laboratory, Carnegie Institution, Washington, D.C. (personal communication).

Busing, W. R., Martin, K. O., and Levy, H. A. (1962) ORFLS, A fortran crystallographic least-squares program: *Oak Ridge Natl. Lab. Tech. Mem.* **305,** Oak Ridge National Laboratory, Tennessee, 75 pp.

Chung, H. K., Hoon, S. K., and Hyun, S. S. (1972) The crystal structure of benzidine dihydrochloride: *J. Korean Chem. Soc.* **16,** 18–24.

Freeman, H. C., Guss, J. M., Nockolds, C. E., Page, R., and Webster, A. (1970) Operation of a computer-controlled equi-inclination x-ray diffractometer. *Acta Crystallogr.* **A26,** 149–152.

Furukawa, T. and Brindley, G. W. (1973) Adsorption and oxidation of benzidine and aniline by montmorillonite and hectorite: *Clays & Clay Minerals* **21,** 179–288.

Greene-Kelly, R. (1955) Sorption of aromatic organic compounds by montmorillonite Pt. 1—orientation studies: *Trans. Faraday Soc.* **51,** 412–424.

Hendricks, S. B. (1941) Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to van der Waals forces: *J. Phys. Chem.* **45,** 65–81.

Hendricks, S. B. and Alexander, L. T. (1940) A qualitative color test for the montmorillonite type of clay minerals: *Amer. Soc. Agron. J.* **32,** 455–458.

Mathieson, A. Mc. L. (1958) Mg-vermiculite: A refinement and reexamination of the crystal structure of the 14.36 Å phase: *Amer. Mineral.* **43,** 216–227.

McBride, M. B. (1979) Reactivity of adsorbed and structural iron in hectorite as indicated by oxidation of benzidine: *Clays & Clay Minerals* **27,** 224–230.

Norrish, K. (1973) Factors in the weathering of mica to vermiculite: in *Proc. Int. Clay Conf., Madrid, 1972,* J. M. Serratosa, ed., Div. Ciencias C.S.I.C., Madrid, 417–432.

Raupach, M., Emerson, W. W., and Slade, P. G. (1979) The arrangement of paraquat bound by vermiculite and montmorillonite: *J. Colloid Interface Sci.* **69,** 398–408.

Schuster, P., Zundel, G., and Sandorfy, C. (1976) *The Hydrogen Bond, Recent Developments in Theory and Experiments, II. Structure and Spectroscopy:* Elsevier North-Holland, Amsterdam, 653–682.

Slade, P. G., Raupach, M., and Emerson, W. W. (1978) The ordering of cetylpyridinium bromide on vermiculite: *Clays & Clay Minerals* **26,** 125–134.

Solomon, D. H., Loft, B. C., and Swift, Jean D. (1968) Reactions catalysed by minerals IV. The mechanism of the benzidine blue reaction on silicate minerals: *Clay Miner.* **7,** 389–397.

Tennakoon, D. T. B., Thomas, J. M., and Tricker, M. S. (1974) Surface and intercalate chemistry of layered silicates. Part II. An iron-57 Mössbauerbauer study of the role of lattice-substituted iron in the benzidine blue reaction of montmorillonite: *J. Chem. Soc. Dalton Trans.* **20,** 2211–2215.

Vedeneeva, N. E. (1950) The mechanism of the colored reaction of benzidine with montmorillonite: *Kolloid. Zhur.* **12,** 17–24.

Zierath, D. L., Hassett, J. J., and Bauwart, W. L. (1980) Sorption of benzidine by sediments and soils: *Soil Science* **129,** 277–281.

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Резюме—Комбинация данных по рентгеновской порошковой дифракции, инфракрасном и химическом анализах показала, что результатом обмена ионов вермикулита с однозаряженными бензидиновыми катионами в водных растворах при pH = 1,6 является черный, сильно упорядоченный, прослоеннчй бензидино-вермикулит. Этот продукт миеет промежуток 19,25 Å и примитивную элементарную ячейку с краями "a" и "b," параллельными и равными по величине краям в вермикулите. Число молекул бензидина в ячейке равно его электрическому заряду. В этой структуре модекулы бензидина круто наклонены к силикатовым поверхностям и плотно упакованы внутои областей. Области содержат переменные ряды бензидиновых катионов; от ряда до ряда плоскости или приблизительно параллельны или перпендикулярны к плоскости (120), но вдоль любого ряда плоскости ароматических колец параллельны между собой. Водородная связь действует между аминовыми атомами азота и поверхностными атомами кислорода. [E.C.]

Resümee—Eine Kombination von Röntgendiffraktion-, Infrarot-, und chemischen Daten hat gezeigt, daß der Ionenaustausch von Vermiculit mit einfach geladenen Benzidinkationen in einer wässrigen Lösung bei pH 1,6 zu einer schwarzen, gut geordneten Benzidin-Vermiculit Wechsellagerung führt. Die Wechsellagerung hat einen Basisabstand von 19,25 Å und eine primitive Elementarzelle mit "a" und "b" Kanten parallel und gleich denen von Vermiculit. Die Zahl der Benzidinmoleküle pro Elementarzelle entspricht der elektrischen Ladung. In dieser Struktur sind die Benzidinmoleküle steil zu den Silikatoberflächen und in dichtbesetzten Domänen angeordnet. Diese Domänen enthalten abwechselnde Reihen von Benzidinkationen; von Reihe zu Reihe sind die Benzidinebenen entweder nahezu parallel oder senkrecht zur (120)-Fläche angeordnet, aber innerhalb einer Reihe sind die Ebenen der aromatischen Ringe zueinander parallel. Wasserstoffbrückenbindung besteht zwischen Aminstickstoffen und den Oberflächensauerstoffen. [U.W.]

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Résumé—La combinaison de données de diffraction aux rayons-X et d'analyse infrarouge et chimique a établi que l'échange des ions de vermiculite avec les cations de benzidine simplement chargés dans une solution aqueuse à un pH de 1,6 resulte en un intercalate noir benzidine-vermiculite très ordonné. L'intercalate a un espacement de base de 19,25 Å et une maille primitive ayant les côtés "a" et "b" parallèles et ègaux à ceux de la vermiculite. Le nombre de molécules de benzidine par maille est égal à sa charge électrique. Dans cette structure, les molécules de benzidine sont fortement inclinées vers les surfaces silicates et sont arrangées de manière très compacte endéans les domaines. Les domaines contiennent des rangées alternantes de cations benzidine; d'une rangée à l'autre, les surfaces planes sont soit approximativement parallèles, soit perpendiculaires à la surface plane (120), mais le long d'une seule rangée, les surfaces planes contenant les anneaux aromatiques sont parallèles l'une à l'autre. La liaison d'hydrogène se passe entre les nitrogènes aminés et les surfaces oxygènes. [D.J.]

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