The final purification was achieved by fractional adsorption of the methyl ether with Nuchar 00. The chloride was converted to the methyl ether by neutralizing a solution of the dye chloride in methyl alcohol with sodium methylate. This solution was boiled with a small amount of Nuchar and filtered hot. The methyl ether was then adsorbed from the filtrate with a large amount of Nuchar, and extracted from the adsorbent with chloroform. After evaporation of the chloroform the residue was dissolved in methyl alcohol, and the final product precipitated with water and dried *in vacuo;* m. p. 58–60°.

Anal. Calcd. for $C_{28}H_{30}N_2O$: C, 82.4; H, 6.92. Found: C, 81.6, 81.8; H, 6.90, 6.99.

Preparation of N,N'-Tetraphenyl-*p,p'*-diaminotriphenylmethyl Methyl Ether.—The preparation of the chloride of this dye was similar to that of the chloride of IV, except that the reactants were heated on the steam-bath for twelve hours instead of three hours, and the washings were with 4 *N* hydrochloric acid solution instead of 1 *N* hydrochloric acid. The crude product was then washed with hexane and toluene several times. The dye was dissolved in methyl alcohol, neutralized with sodium hydroxide, and extracted with carbon tetrachloride and water. The carbon tetrachloride solution was washed, dried, filtered, and the dye precipitated by adding dry hydrogen chloride. The dye was converted into the methyl ether, which was extracted in benzene, dried, filtered, precipitated with hexane, and dried *in vacuo;* m. p. 138–140°.

Anal. Calcd. for $C_{44}H_{36}N_2O$: C, 87.0; H, 5.96. Found: C, 86.4, 86.1; H, 6.27, 6.29.

Preparation of N-Dimethyl-N'-diphenyl-*p,p'*-diaminotriphenylmethyl Methyl Ether.—One mole of dimethylaminobenzophenone, one mole of triphenylamine, and two moles of $POCl_3$ were heated for two hours at 130°. The reaction mixture was treated with water, and the product dissolved in methyl alcohol containing sodium hydroxide, and this solution extracted with water and carbon tetrachloride. After washing, drying, and filtering the solution, the dye was precipitated with dry hydrogen chloride. The dye was dissolved in methyl alcohol, neutralized with alcoholic sodium hydroxide solution, and treated with benzene and water. The benzene solution of the methyl ether was washed, dried, filtered, and the benzene evaporated. The amorphous dye was chilled in contact with methyl alcohol until firm, ground in a mortar while cold, and allowed to stand overnight with methyl alcohol. It was washed several times with methyl alcohol, filtered and dried *in vacuo;* m. p. indefinite.

Anal. Calcd. for $C_{34}H_{32}N_2O$: C, 84.3; H, 6.66; N, 5.78. Found: C, 84.8, 84.3; H, 6.56, 6.49; N, 5.93, 5.93.

Preparation of N-Dimethyl-N'-phenylmethyl-*p,p'*-diaminotriphenylmethyl Chloride.—The preparation and purification scheme for this dye is similar to that for III. The reaction mixture, however, was heated for forty-eight hours on a steam-bath. The yield was very poor.

Preparation of the Methyl Ether of Malachite Green.—A sample of malachite green from the National Aniline Co. was dissolved in methyl alcohol, neutralized with alcoholic sodium hydroxide, extracted with benzene, washed, dried, filtered, evaporated to dryness, dissolved in methyl alcohol, and precipitated with water; m. p. 138–140°.

Viridine Green.—Two samples were used, one a chloride, and the other a mixture of the carbinol and the anhydro base. Both were prepared by Dr. T. L. Hill.

Acknowledgment.—We wish to thank Mr. Charles W. Koch for the microanalyses reported in this article.

Summary

Six phenyl diaminotriphenylmethane dyes were prepared and their absorption spectra compared with the spectra of malachite green and Döbner's violet.

The phenyl group was found to increase the wave length of both *x*- and *y*-bands.

In the phenylated dyes the substitution of a hydrogen atom for a N-methyl group increased instead of decreased the wave lengths of both *x*- and *y*-bands.

The asymmetry produced by a double phenylation of one nitrogen atom decreased the wave length of both *x*- and *y*-bands.

These effects were shown to be independent of the solvent.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

Raman Spectrum of the Deuterohydroxylammonium Ion

BY O. REDLICH AND I. I. FRIEDMAN

The Raman spectra of deuterium compounds are known to be a useful aid in checking and completing the interpretation of vibration spectra.

Deuterohydroxylamine deuterochloride was prepared by exchange of 4.8 g. of recrystallized hydroxylamine hydrochloride with eleven portions of heavy water (99.5%). Finally the salt was dissolved in 5 g. of D_2O. The deuterium content was checked after the fourth exchange by a determination of the density of the water distilled off the substance. A mole fraction of 0.65 was found, while 0.60 was calculated from the amounts of heavy water. The mole fraction in the final solution was calculated to be 0.985. This corresponds to the mole fractions 0.94 for D_3NOD^+, 0.042 for D_2HNOD^+ in the solute, and 0.03 for HOD in the solvent.

The spectra of H_3NOH^+ and D_3NOD^+ contain several bands, very broad lines and only one sharp line 1005 and 987 cm.$^{-1}$, respectively. The centers are given in Table I. The last column shows the isotopic quotient *q*, *i.e.*, the ratio of the corresponding frequencies of the light and heavy compounds.

The results for the light compound agree well with the figures of Edsall[1] and the less complete spectra of Ananthakrishnan[2] and of Bernstein and Martin.[3]

The data for both compounds are in essential agreement with the discussions of Edsall and of

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[1] J. T. Edsall, *J. Chem. Phys.*, **5**, 225 (1937).

[2] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, **A5**, 87 (1937).

[3] H. J. Bernstein and W. H. Martin, *Trans. Roy. Soc. Canada*, [III] **31**, 95 (1937).

TABLE I

VIBRATION FREQUENCIES IN CM.$^{-1}$

	H_3NOH^+			D_3NOD^+			
	freq.	int.	width	freq.	int.	width	q
a	..	..	...	2980	1	50	...
b	3630	3	60	2620	3	100	1.385
c	3470	7	270	2520	7	110	1.377
d	3240	4	70	2360	5	70	1.373
e	..	..	...	2230	4	40	...
f	2960	5	100	2150	4	60	1.377
g	2700	2	80	2035	2	50	1.327
h	2000?	0	120	1430	0	60	...
i	1618	3	50	1195	2	30	1.354
k	1519	3	40	1138	3	40	1.335
l	1197	2	50	880	2	30	1.360
m	1005	10	...	987	8	...	1.018

The bands *b* and *c* overlap. Error of frequency *m*: ±1 cm.$^{-1}$.

Ananthakrishnan. The bands *b*, *c*, *d*, and *i* are to be attributed to the solvent. One has to assume, however, that the stretching and bending vibrations of the hydroxyl group are covered by *c* and *i*.

If the hydroxyl vibrations are disregarded and the hydroxyl group considered a mechanical unit, a simplified model of the symmetry C_{3v} is obtained. The bands *f* and *g* represent the totally symmetric and degenerate NH stretching vibrations, *k* and *l* the corresponding bending vibrations. Line *m* is known to represent the vibration of the NH_3 group against the OH group.

The correlations of the lines of the light and heavy compounds are based on the fact that $1 < q < \sqrt{2}$, and on the intensities. No arbitrary choice is left in the correlations.

Band *h* of the light compound, 2000 cm.$^{-1}$, appeared only on one spectrum and is uncertain. No correlation with 1430 cm.$^{-1}$ of the heavy substance is suggested. The latter frequency also appeared only on one heavily exposed spectrum; it might be due to the small amount of HOD present in the solution. The weak band *a* probably corresponds to a vibration of D_2HNOD^+. The low intensity of this band and the absence of any water band of higher frequency indicate that only little hydrogen was present.

In the case of bromoform,[4] the appearance of an entirely new line in the spectrum of the deuterium compound could be explained without any doubt by accidental degeneracy. A similar explanation will be expected for band *e*. The last column of Table I indicates that this band must be due to the combination of a hydrogen frequency with the frequency $m = 987$ cm.$^{-1}$ since otherwise the accidental degeneracy would occur also in the light compound. The combination $i + m = 2182$, and a fundamental of approximately the same frequency can be made responsible for the bands *e* and *f* of the heavy compound. No other combination furnishes a satisfactory representation of the data. This interpretation supports the assumption that band *i* is produced not only by water but also by the hydroxyl group of the hydroxylammonium ion.

Summary

The Raman spectra of the light and heavy hydroxylammonium ions have been measured and interpreted.

(4) O. Redlich and W. Stricks, *Sitz. Ber. Akad. Wiss. Wien.*, IIb, **145**, 77 (1936), or *Monatsh.*, **67**, 213 (1936).

PULLMAN, WASHINGTON RECEIVED MARCH 6, 1945

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Habit Modification of Ammonium Dihydrogen Phosphate Crystals during Growth from Solution

BY HARRY J. KOLB AND JOSEPH J. COMER

Introduction

Adsorption at the crystal–solution interface is far from the stage in development which adsorption at the gas–solid interface has reached. It appeared desirable to make further investigations which might lead to more information on this type of adsorption. Previous investigations of adsorption at the crystal–solution interface with subsequent modification in crystal habit have been excellently reviewed by W. G. France,[1] who has made most of the contributions to the field in this country. But because of the lack of knowledge as to the mechanism of the crystal modifications, due in a large part to the relative complexity of concentrated ionic solution chemistry in general, a survey was made for crystals whose structures are well-known and might yield interesting data in adsorption studies. Ammonium dihydrogen phosphate was selected with others, primarily because of its relatively simple crystal habit under normal conditions. Experiments have now been completed on the growth of this crystal in the presence of foreign metal ions.

Experimental

Ammonium dihydrogen phosphate crystals were grown in a large water-bath, the temperature of which could be maintained constant to ±0.1°. Eight stainless steel tanks were placed on two aluminum trays in the bath. Each tank was filled with ammonium dihydrogen phosphate solution and the thermostat then set at the saturation

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(1) Alexander, "Colloid Chemistry," Reinhold Publishing Corp., New York, N. Y., 1944, Vol. 5, p. 443.