group. Two singlet-singlet n → π* transitions ($^1U \leftarrow {}^1A$) were resolved in *p*-benzoquinone,[7] in which the near-degeneracy was removed to give transitions differing in energy by approximately 800 cm.$^{-1}$. It is possible that the prominent bands at 23656 and 23729 cm.$^{-1}$ in 9,10-anthraquinone may correspond to the origins of the vibrational analyses of the two $^1U \leftarrow {}^1A$ transitions. The lowest $^1U \leftarrow {}^1A$ transitions cannot both be allowed by symmetry in a centro-symmetric molecule or in a crystal in which the site symmetry is C_i, as is the case here. The very weak band at 23559 cm.$^{-1}$ is the lowest frequency band in the region. It may correspond to the 0–0 band of a $^1U \leftarrow {}^1A$ transition which is forbidden by symmetry, and either of the more prominent bands which have been selected as origins of the analyses may correspond to the addition of a non-symmetric lattice mode to the forbidden 0–0 band. The spectra are too complex to enable any definite conclusions to be drawn about this point. Furthermore, the high-frequency end of the spectrum is overlapped by an apparent continuum which obscures the bands above 26000 cm.$^{-1}$. The continuum is probably due to the $^1L_b \leftarrow {}^1A$ transition, which is diffuse in *p*-benzoquinone and in the other quinones.[26] Additional absorption at lower frequencies corresponding to a $^3U \leftarrow {}^1A$ transition could not be detected in 9,10-anthraquinone in crystals which were several hundred microns thick. The $^3U \leftarrow {}^1A$ transition in this molecule therefore appears to be considerably weaker than the corresponding transition in *p*-benzoquinone.

(b) **1,4-Naphthoquinone.**—The $^1U \leftarrow {}^1A$ absorption transition in crystalline 1,4-naphthoquinone is shown in Fig. 3, and the bands are listed in Table II with a partial analysis. This transition shows no detectable intensity or energy dichroism in the cleavage plane. The crystal structure has not been reported. The lowest frequency band at 21789 cm.$^{-1}$ is very prominent and may be the 0–0 band of a transition which is allowed by symmetry. Considerably more progress can be made with the vibrational analysis of the $^1U \leftarrow {}^1A$ transition of this molecule, since there appears to be only one prominent origin. Although it is not much more intense than the neighboring bands, the band at 21932 cm.$^{-1}$ stands out quite noticeably, since it is much sharper. It may be the 0–0 band of the other $^1U' \leftarrow {}^1A$ transition. The $^3U \leftarrow {}^1A$ transition has not been located in this molecule in crystals which were sufficiently thick to give complete absorption in the region of the $^1U \leftarrow {}^1A$ transition, and it is therefore concluded that this transition in 1,4-naphthoquinone is not as intense as it is in *p*-benzoquinone. The $^1U \leftarrow {}^1A$ absorption is overlapped at the high-frequency end by an apparent continuum from the π → π* transition.

Acknowledgment.—I am grateful to Professor A. B. F. Duncan for his continued interest and encouragement in this work.

ROCHESTER, NEW YORK

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[26] P. K. Seshan, *Proc. Indian Acad. Sci.*, **3A**, 172 (1936).

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Concerning the Structure and Composition of Pyrocatechol–Boric Acid–Pyridine Complexes

BY DONALD F. KUEMMEL AND M. G. MELLON

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Reports in the literature describe two complexes, melting around 123 and 179°, which can be isolated from the pyrocatechol–boric acid–pyridine system, but they do not agree on the ratio of the constituents in the complexes. By comparison of the ultraviolet absorption spectra of the complexes with the spectra given by mixtures of the constituents, this difficulty has been resolved, and the ratio of the constituents in the two complexes definitely established. These spectra also indicate that the complexes are completely dissociated into their constituents (pyrocatechol, boric acid and pyridine) in absolute ethanol solutions.

Introduction

During the course of an investigation of the ultraviolet absorption spectra of complexes of boric acid with polyhydroxy organic compounds, it was desired to prepare the pyridine salt of the complex acid formed between pyrocatechol and boric acid. A survey of the literature revealed that two complexes have been isolated from the pyrocatechol–boric acid–pyridine system. Conflicting reports were found on the composition and melting points of one of these complexes.

Meulenhoff,[1] working with a hot, concentrated mixture of pyrocatechol, boric acid and pyridine in the molecular ratio 2:1:1, respectively, isolated a product melting from 122 to 123°. His analyses (Table I) for carbon and boron indicated that the product was pyridinium dipyrocatecholborate, having the expected 2:1:1 ratio of pyrocatechol:boric acid:pyridine. Boric acid complexes of this type are usually assigned structure I.

Subsequently, Schäfer[2] isolated a product of similar melting point, 125 to 126°, from a 3:1:1 mixture of pyrocatechol, boric acid and pyridine, respectively. His elemental analyses (Table I) definitely indicated that the material was pyridinium tripyrocatecholborate, a hitherto unknown type, having a 3:1:1 ratio of the constituents. Structure II was assigned by Schäfer to this complex. He stated that pyridinium tripyrocatecholborate (II) always separated from mixtures of the constituents, whether the starting ratio of pyrocatechol:boric acid:pyridine be 1:1:1, 2:1:1, 3:1:1, or 2:1:2. Also he suggested that Meulenhoff's product, because of its melting point and mode of

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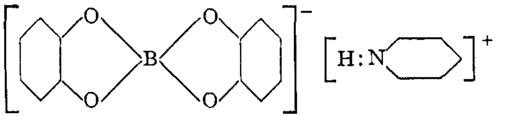
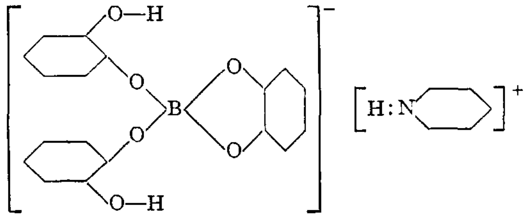
[1] J. Meulenhoff, *Rec. trav. chim.*, **44**, 150 (1925).

[2] H. Schäfer, *Z. anorg. allgem. Chem.*, **259**, 255 (1949).

preparation, was probably the same pyridinium tripyrocatecholborate (II).



I, pyridinium dipyrocatecholborate (mol. wt. 307.1)



II, pyridinium tripyrocatecholborate (mol. wt. 417.2)

By treating this pyridinium tripyrocatecholborate with pyridine, Schäfer[2] isolated a product melting from 179 to 180°, the analyses (Table I) of which conformed to that of the pyridinium dipyrocatecholborate (I).

In view of the fact that the widely accepted structure for salts of pyrocatecholboric acid corresponds to I rather than II, and inasmuch as Schäfer is the only one who has reported on complexes having structures like II, it seemed desirable to reinvestigate the ratio of the constituents in the two complexes described above.

In the present study, the ultraviolet absorption spectra of the complexes were obtained; these spectra proved highly satisfactory for distinguishing between the complexes and determining the ratio of the constituents.

Experimental

Preparation of Complex Melting Around 123°.—This complex was prepared according to Meulenhoff[1] from a 2:1:1 mixture of pyrocatechol, boric acid and pyridine, respectively. Three and one-tenth grams of boric acid was dissolved in 20 ml. of hot water and added to a second solution containing 11 g. of pyrocatechol in 15 ml. of hot water. To this hot mixture 4 ml. of pyridine was added dropwise with stirring. The mixture became turbid after most of the pyridine was added. Upon cooling this mixture in a water-bath, a white, lumpy product separated rapidly. This was washed sparingly with water on a Büchner funnel and air dried. About 8 g. of crude product was obtained, melting from 122 to 125°. The solid changed in appearance during the melting point determination, possibly because of sublimation of the pyridine. After recrystallization from chloroform, as suggested by Schäfer,[2] white needles were obtained, melting from 122 to 124°, with the same change in appearance of the solid again being noted during the heating. Analyses for these products are given in Table I. Carbon, hydrogen and nitrogen were determined by conventional microanalytical techniques. Boron was determined by fusion with sodium carbonate, dissolution of the melt in hydrochloric acid, neutralization to methyl orange with sodium hydroxide after elimination of the carbon dioxide, and titration with standard alkali to a phenolphthalein end-point in the presence of mannitol.

Preparation of Complex Melting Around 179°.—This complex was prepared from the pyridinium tripyrocatecholborate according to the method of Schäfer.[2] Ten grams of the pyridinium tripyrocatecholborate was dissolved in 8 ml. of pyridine, giving a brownish-yellow solution. After 2 to 3 hours standing, crystals began to separate. Ninety ml. of benzene was then added in small portions over a 6-hour period. After standing overnight, the crystals were filtered off, washed with 100 ml. of benzene, and air dried. About 6.7 g. of product was obtained. This product had a melting point range of 176 to 178°, but changed in appearance around 170°. All melting points mentioned herein are uncorrected. The analyses of this product are given in Table I.

TABLE I

ANALYSIS OF PYRIDINIUM PYROCATECHOLBORATES

Theoretical	C, %	H, %	N, %	B, %
Pyridinium dipyrocatecholborate $C_{17}H_{14}O_4NB$	66.48	4.60	4.56	3.52
Pyridinium tripyrocatecholborate $C_{23}H_{20}O_6NB$	66.21	4.83	3.36	2.59
Literature				
Meulenhoff[1] m.p. 122 to 123°	66.57	...	...	3.5
Schäfer[2] m.p. 125 to 126°	66.3	4.72	3.45	2.59
Schäfer[2] m.p. 179 to 180°	65.85	4.65	4.36	3.49
Present work				
Crude product m.p. 122 to 125°	65.11	5.15	3.70	2.40
Recrystallized product m.p. 122 to 124°	64.98	5.25	3.45	2.40
Crude product m.p. 176 to 178°	66.29	4.80	4.50	3.65

Absorption Spectra.—All absorption spectra were obtained on a Cary Model 10-11M recording spectrophotometer, using matched 1-cm. quartz cells, and a spectral band width of approximately 1 ångström.

Figure 1 shows the absorption spectra of 0.0002 *M* solutions of the products melting from 122 to 125° and from 176 to 178°, assuming a 2:1:1 ratio in both cases, and the spectrum given by a corresponding mixture of the individual constituents in the same ratio. Figure 2 shows the absorption spectra of the complex melting from 122 to 125°, and a corresponding mixture, assuming a 3:1:1 ratio of the constituents. Fig. 3 gives the spectra of pyridinium ion–pyrocatechol mixtures compared to that given by a corresponding mixture of pyridine and pyrocatechol. All spectra shown were obtained on absolute ethanol solutions with the same solvent in the reference cell.

Discussion

Although the analyses (Table I) of both the crude and recrystallized products melting around 123° indicate this complex is pyridinium tripyrocatecholborate (II), a more convincing demonstration of the ratio of the constituents is given by the ultraviolet absorption spectrum of the complex, shown in Figs. 1 and 2. The excellent agreement between spectra in Fig. 2, where the 3:1:1 ratio was assumed, coupled with the obvious differences in Fig. 1 between the spectrum of this complex, assuming a 2:1:1 ratio, and that given by a corresponding mixture of the constituents, definitely indicates that the complex melting around 123° is pyridinium tripyrocatecholborate (II), having the 3:1:1 composition.

The ratio of the constituents in the complex melting around 179° is apparent from Fig. 1. The spectrum given by this complex, assuming a 2:1:1 ratio, follows closely the spectrum given by a corresponding mixture in the same ratio, thus indicating the complex melting around 179° is pyridinium dipyrocatecholborate (II).

The absorption spectrum in absolute ethanol of the recrystallized complex melting from 122 to 124°, again assuming the 3:1:1 ratio, is also almost identical with that given by the corresponding mixture of the constituents. Recrystallization affected

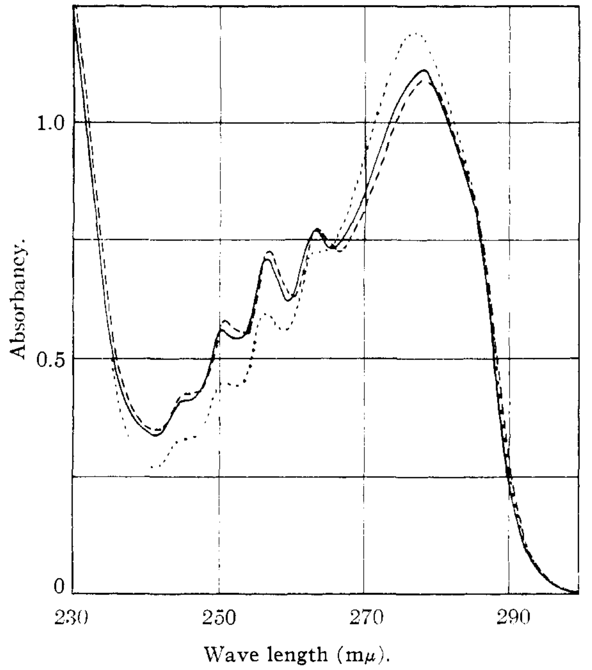


Fig. 1.—Absorption spectra of complexes melting from 122 to 125° and from 176 to 178° and corresponding mixture of the constituents, assuming 2:1:1 ratio: ------, 0.0002 *M* solution of complex melting from 176 to 178°, assuming 2:1:1 ratio; ...., 0.0002 *M* solution of complex melting from 122 to 125°, assuming 2:1:1 ratio; ——, solution 0.0004 *M* in pyrocatechol, and 0.0002 *M* in both boric acid and pyridine.

significantly neither the analysis nor absorption spectrum of the complex.

Absorption spectra of aqueous solutions of the complex melting around 123° and corresponding mixtures of the constituents have the same general appearance as those of Figs. 1 and 2, and show the same agreement or disagreement. The spectrum of the complex in chloroform solution shows three absorption maxima of almost equal height at 257, 263 and 275 mμ. A corresponding mixture of pyrocatechol and pyridine (3:1) in chloroform shows small but significant differences in absorption compared to that shown by the complex in the 270 to 290 mμ region.

It was found that the curves given by the mixtures in Figs. 1 and 2 are identical with those obtained by adding up the absorbancies of individual solutions of pyrocatechol and pyridine in corresponding concentrations. Boric acid does not absorb in the ultraviolet, does not affect the absorption of pyridine or pyrocatechol at the concentration level of the present studies, and hence was not a necessary constituent of the mixtures used to duplicate the spectra of the complexes. In view of these facts, the close agreement of the spectra in Figs. 1 and 2 is a demonstration of the complete dissociation of the complexes into their constituents (pyrocatechol, pyridine and boric acid) in alcoholic solution. Further evidence that only the constituents are present in solutions of the complexes is given in Fig. 3, where the spectra of pyridinium ion–pyrocatechol mixtures are compared to the spectrum given by a corresponding mixture of pyridine and pyrocatechol. It can be seen that, if the pyridinium ion was present in solutions of the complexes to any great extent, spectra much different from that shown by solutions of the complexes would be expected. The comparison shown in Fig. 3 involved concentrations related to pyridinium dipyrocatecholborate (I), having the 2:1:1 composition. Similar conclusions apply to solutions of pyridinium tripyrocatecholborate (II).

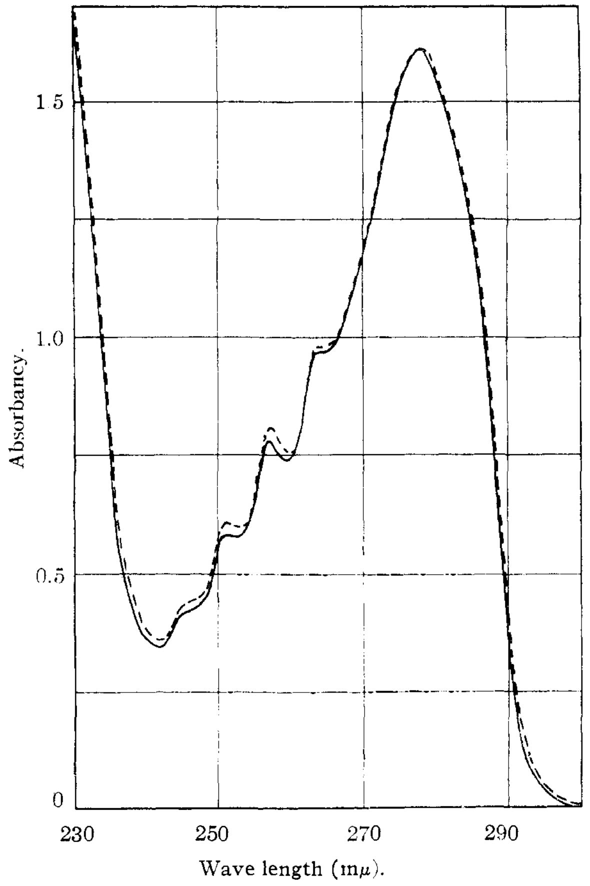


Fig. 2.—Absorption spectra of complex melting from 122 to 125° and corresponding mixture of the constituents, assuming 3:1:1 ratio: ——, 0.0002 *M* solution of complex, assuming 3:1:1 ratio; ------, solution 0.0006 *M* in pyrocatechol, and 0.0002 *M* in both boric acid and pyridine.

Nothing could be concluded from the significant differences noted in the spectrum of the chloroform solution of the 3:1:1 complex compared to that given by a 3:1 pyrocatechol–pyridine mixture. Difficulties were encountered in preparing solutions suitable for the comparison because of the low solubility of the complex, and the relative insolubility of boric acid in chloroform. Also, decomposition of chloroform solutions of pyrocatechol and the complex is evident after about one hour standing, with yellowish-brown colors developing in the solutions.

The complete dissociation of these complexes into their constituents in absolute ethanol is somewhat surprising, particularly in the case of the pyridinium dipyrocatecholborate (I). Non-aqueous solvents, such as ethanol and ether, are frequently used in the isolation of boric acid complexes, and it is generally thought that the stability of the complexes is greater in non-aqueous solvents than in water. This dissociation is also surprising in view of the fact that the complexes are thought to exist as ion pairs, rather than some type of molecular complex.

A literature survey revealed that Andress and Topf[3] have studied the ultraviolet absorption spectra of two complexes which can be isolated from the salicylic acid–boric acid–sodium hydroxide system. They found that sodium disalicylborate in absolute ethanol gives a spectrum which differs from that given by a corresponding mixture of the individual constituents, showing the stability of this complex in absolute ethanol. On the other hand, disodium disalicyltriborate in the same solvent gives the same spectrum as a corresponding mixture, indicating the dissociation of this complex into its constituents. Through the use of ultraviolet spectra, Andress and Topf also found evidence that boric acid complexes are present in dilute aqueous mixtures of boric and chromotropic acids. Their work on chromotropic acid (4,5-dihydroxy-2,7-naphthalenedisulfonic acid) has been confirmed and applied to the spectrophotometric determination of boron by the present authors.[4]

The work reported herein, and the reference cited above, indicate that no general conclusions can be made concerning the stability of boric acid complexes with polyhydroxy organic compounds. The stability appears to vary with the solvent, the polyhydroxy compound, and perhaps even the base used to stabilize the complex.

Summary

The ultraviolet absorption spectra of complexes isolated from the pyrocatechol–boric acid–pyridine system show that the complex melting around 123° has a 3:1:1 ratio of pyrocatechol:boric acid:pyridine, respectively, and the complex melting around 176° has a 2:1:1 ratio of the constituents. These ratios are in accordance with the previous reports of Schäfer.[2]

Comparison of the spectra of the complexes with corresponding mixtures of the individual constituents indicated complete dissociation of these complexes into their constituents in absolute ethanol solution. No evidence of pyridinium ion was found in ethanol solutions of the complexes, despite the fact that the complexes are thought to consist of ion pairs.

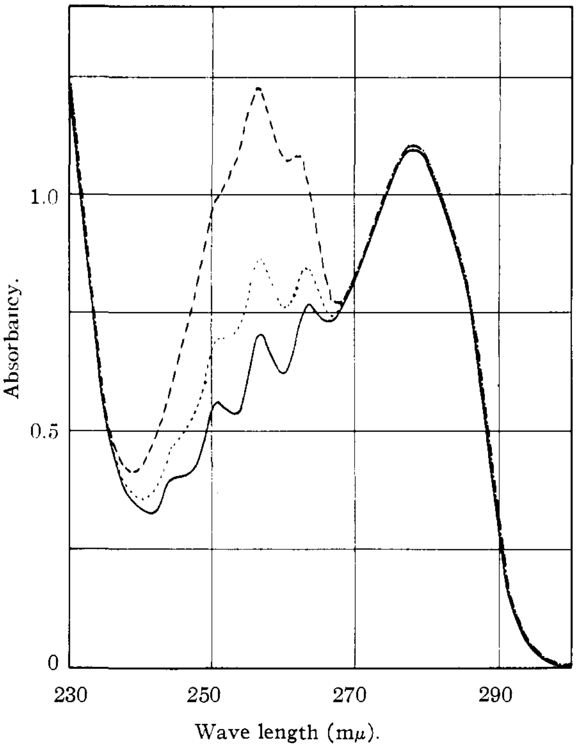


Fig. 3.—Comparison of spectra of pyridinium ion-pyrocatechol mixtures with corresponding mixture of pyrocatechol and pyridine. All solutions 0.0004 *M* in pyrocatechol and 0.0002 *M* in pyridine: ——, no acid added; ...., approximately 0.0001 *N* in sulfuric acid; – – – –, approximately 0.007 *N* in sulfuric acid.

LAFAYETTE, INDIANA

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[3] K. Andress and W. Topf, *Z. anorg. allgem. Chem.*, **254**, 52 (1947).

[4] D. F. Kuemmel and M. G. Mellon, *Anal. Chem.*, in press.