[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

The Electronic Spectra and Structure of the Quinones[1]

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The lowest n → π* transitions of 9,10-anthraquinone and 1,4-naphthoquinone have been studied in absorption, using single crystals, polarized light and low temperatures. Partial vibrational analyses are given for the very complex vibrational structure which is observed in these transitions. Evidence is presented that two singlet-singlet n → π* transitions may appear in the spectra of naphthoquinone and anthraquinone. The spectra are compared with the spectra of 1,4-benzoquinone, and regularities in the spectra of the quinones are discussed. Tentative assignments for the electronic transitions are suggested, based on a consideration of the Platt free-electron classification and the intensity dichroism of the crystal absorption spectra.

Introduction

There has been considerable interest in recent years in the weak, long wave length absorption transitions in molecules containing the carbonyl group. These transitions, in which an electron is excited from a non-bonding p-orbital localized on the oxygen atom to a π-antibonding molecular orbital extending over the molecular framework (n → π* transitions), have been studied and analyzed in H_2CO,[3] $(HCO)_2$,[4] $(CH_3CO)_2$,[5] $(ClCO)_2$[6] and *p*-benzoquinone.[7] In previous papers[5,6] it has been pointed out that many of the spectral features of the conjugated ketones are successfully accounted for by the predictions of the simple LCAO-MO molecular orbital theory which was applied by McMurry[8] to these molecules.

Since a study of the electronic spectra of *p*-benzoquinone already has been performed,[7] it was felt that corresponding measurements for the higher quinones might reveal additional information about this class of molecules. In the present paper, the results of such a study are reported. Earlier literature data are also examined and correlated, and spectral regularities are used to provide a basis for a classification of the electronic spectra of the quinones.

Experimental

The apparatus used to study the electronic absorption spectra of single crystals at low temperature has been described previously.[9] The spectra in this work were recorded at 77°K. (liquid nitrogen) and at 4°K. (liquid helium), using single crystals and polarized light.[9] The spectra were photographed on Kodak 103-F plates, using a tungsten ribbon filament lamp as a light source for the absorption spectra. The absorption spectra for the n → π* transitions are very sharp at 4°K., and the accuracy of the measurements is approximately 3 cm.$^{-1}$.[10] The compounds were from Eastman Kodak Company and were purified by sublimation under reduced pressure.

Fluorescence or phosphorescence of the quinones was either absent or too weak to be photographed with the available equipment.

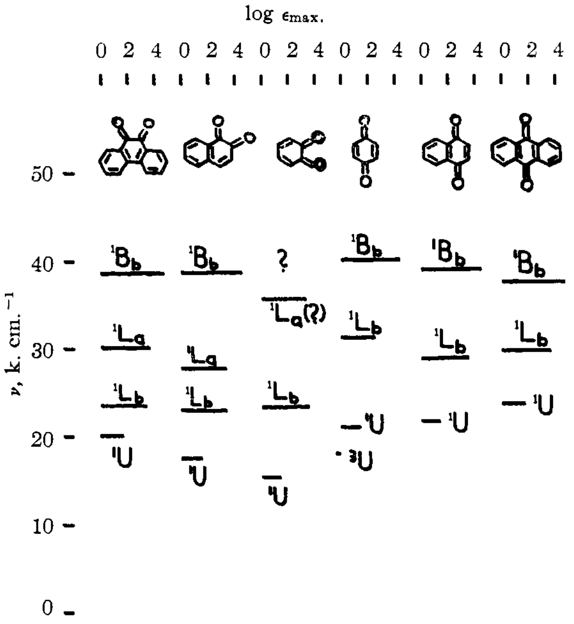

Fig. 1.—Spectral resemblances and assignments for the electronic transitions of the quinones. The band origins are estimated from the solution spectral data and may be uncertain by 1 k.cm.$^{-1}$ for the π → π* transitions.

Results

The absorption bands which are observed at 4°K. in crystals which are 5 to 30 μ thick are listed in Tables I and II for 9,10-anthraquinone and 1,4-naphthoquinone, respectively. Microphotometer tracings of these transitions are shown in Figs. 2 and 3.

Discussion and Interpretation

1. Assignment of the Electronic Transitions in the Quinones.—Before considering the details of the analyses of the very sharp but very complex spectra which are observed for the n → π* transitions of these molecules, it is worthwhile to examine the previous literature in an effort to understand some of the features common to all of the quinones. Hartmann and Lorenz[11] have reported the absorption spectra of a large number of quinones in solution in dioxane. An examination of the spectra which they have recorded reveals that the similarities between the spectra of the various quinones are far more marked than are the differences. It is apparent that there are three regions

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[3] See A. D. Cohen and C. Reid, *J. Chem. Phys.*, **24**, 85 (1956) for earlier references.

[4] J. C. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954).

[5] J. W. Sidman and D. S. McClure, THIS JOURNAL, **77**, 6461, 6471 (1955).

[6] J. W. Sidman, *ibid.*, **78**, 1527 (1956).

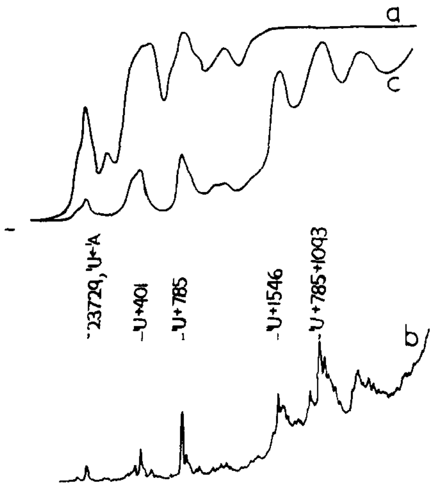
[7] J. W. Sidman, *ibid.*, **78**, 2363 (1956).

[8] H. M. McMurry, *J. Chem. Phys.*, **9**, 231, 241 (1941).

[9] J. W. Sidman, *J. Chem. Phys.*, **25**, 115, 122 (1956).

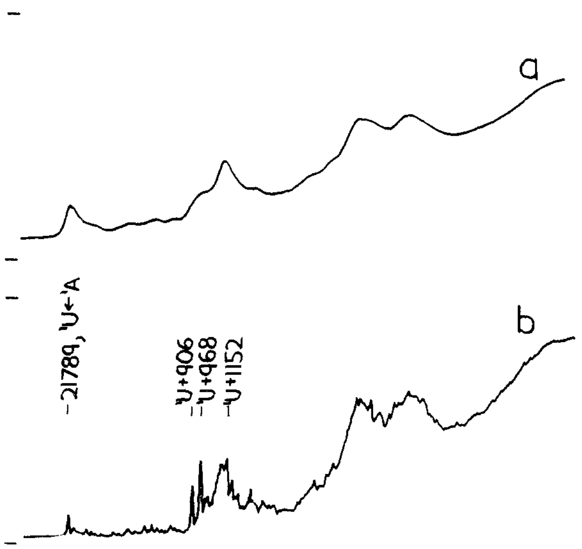
[10] 1 kayser = 1 cm.$^{-1}$; 1 kilokayser = 1000 cm.$^{-1}$ = 1 kcm.$^{-1}$.

[11] H. Hartmann and E. Lorenz, *Z. Naturforsch.*, **7a**, 360 (1952).



ν, cm.⁻¹.

Fig. 2.—Microphotometer tracing of the ¹U ← ¹A transition in crystalline 9,10-anthraquinone: a, for light polarized along the *a*-axis and the *ac* plane; b, same as above, 4°K.; c, same as above, but for light polarized along the *c*-axis, 77°K.



ν, cm.⁻¹.

Fig. 3.—Microphotometer tracing of the ¹U ← ¹A transition in crystalline 1,4-naphthoquinone: a, for light polarized along either extinction direction in the cleavage plane, 77°K.; b, same as above, 4°K.

TABLE I

ABSORPTION SPECTRUM OF 9,10-ANTHRAQUINONE CRYSTAL, 4°K.

Intensity	ν, cm.⁻¹	Assignment
vw	23559	¹U′ ← ¹A, 0–0 (?)
w	23602	
w	23628	
vs	23656	¹U′ ← ¹A, origin of analysis
w	23687	
vvs	23729	¹U ← ¹A, origin of analysis, 0–0 (?)
ms	23740	¹U + 14, lattice
w	23768	
w	23815	
ms	23883	¹U′ + 227, a_g
ms	23925	¹U + 196, a_g
w	23961	
w	24000	
w	24024	
s	24065	¹U′ + 409, a_g
ms	24093	¹U′ + 437, a_g
ms	24111	¹U + 2(196)
vs	24130	¹U + 401, a_g
vs	24173	¹U + 444, a_g
s	24190	¹U + 444 + 14
m	24207	
s	24269	¹U + 540, a_g
w	24326	
w	24361	
s	24428	¹U′ + 772, a_g
w	24458	
vvs	24514	¹U + 785, a_g
s	24541	¹U + 2(401)
m	24577	¹U + 401 + 444
m	24595	
ms	24626	¹U′ + 970, a_g; ¹U + 2(444)
ms	24655	¹U + 926, a_g
w	24685	
w	24740	
m	24763	
w	24793	
ms	24822	¹U′ + 1166, a_g(?); ¹U + 1093, a_g
m	24859	
ms	24875	¹U + 1146, a_g
w	24906	¹U + 785 + 401
w	24947	¹U + 444 + 785
w	24980	
w	24999	
ms	25064	¹U + 785 + 540
m	25095	
m	25121	
w	25151	
m	25188	
ms	25239	¹U′ + 1583, a_g } C=O
vs	25275	¹U′ + 1546, a_g } stretch(?)
ms	25297	¹U + 2(785)
s	25318	¹U + 1146 + 444
m	25353	
m	25385	
w	25420	
w	25448	
s	25524	
vs	25606	¹U + 785 + 1093
s	25648	¹U′ + 1583 + 409
s	25678	¹U + 1546 + 401
s	25722	¹U + 1546 + 444
m	25759	
ms	25834	
ms	25871	
ms	25899	
m	25932	
m	25971	
m	26010	
continuum	26189	
	26230	
	26252	
	26319	
	26357	
	26466	
	26768	

TABLE II

ABSORPTION SPECTRUM OF 1,4-NAPHTHOQUINONE CRYSTAL, 4°K.

Intensity	ν, cm.$^{-1}$	Assignment
vvs	21789	$^{1}\mathrm{U} \leftarrow {}^{1}\mathrm{A}$, origin of analysis, 0–0 (?)
ms	21823	24, lattice
ms	21838	2(24)
w	21869	3(24)
m	21896	107, lattice
m	21913	124; 107 + 24
ms, very sharp	21932	$^{1}\mathrm{U}' \leftarrow {}^{1}\mathrm{A}$, 0–0 (?)
w	21948	
m	21964	
w	21982	
m	21998	
m	22039	
s	22125	336,a$_1$
w	22160	
m	22172	
m	22223	
m	22234	
s	22245	456,a$_1$
w	22290	
s	22360	571,a$_1$
w	22380	
w	22400	
s	22410	621,a$_1$
w	22435	
w	22449	
w	22460	2(336)
m	22483	
w	22512	
s	22542	753,a$_1$
m	22559	
w	22568	
w	22598	
w	22611	
w	22651	
s	22680	
vvs	22695	906,a$_1$; 2(456); 336 + 571
w	22730	336 + 621
vvs	22757	968,a$_1$
ms	22786	968 + 24
ms	22804	2(571)
s	22865	621 + 456
s	22885	753 + 336
s	22900	
s	22921	2(571)
vs	22941	1152,a$_1$
m	22969	
s	22987	571 + 621
m	23009	753 + 456
ms	23025	906 + 336; 2(621)
m	23057	
m	23094	336 + 968
s	23107	968 + 336; 571 + 753
m	23136	906 + 456
s, broad	23198	968 + 456(?)
s, broad	23237	
s, broad	23274	906 + 571; 1152 + 336
m	23319	571 + 968
m	23352	
m	23385	
m	23415	1152 + 456(?)
m	23450	
m	23479	
m	23507	1152 + 571
m	23534	
s, broad	23559	1152 + 621
m	23602	2(906)
s	23649	906 + 968(?)
s	23695	
s	23726	2(968)
s	23762	
s	23797	
vs	23822	
vs	23840	1152 + 906
vs	23861	
vs	23884	
vs	23905	1152 + 968
vvs	23929	
vvs	23953	
s	23984	
s	24004	
s	24039	
vs	24070	
vs	24099	2(1152)
s	24137	
s	24182	
s	24199	
s	24233	
s	24257	
continuum	24297	
	24343	
	24392	
	24628	
	24778	
	24963	
	25105	

of absorption which are common to nearly all of the *p*-quinones.

(a) The lowest transition lies between 20 and 25 k.cm.$^{-1}$, with log $\epsilon_{\max}$ of approximately 1.5 to 2.0.

(b) The next transition is in the vicinity of 29 k.cm.$^{-1}$, with log $\epsilon_{\max}$ of approximately 3.0 to 3.5. It is higher in energy (32 k.cm.$^{-1}$) and less intense in *p*-benzoquinone (log $\epsilon_{\max}$ 2.5).

(c) The highest transition lies between 38 and 41 k.cm.$^{-1}$ with log $\epsilon_{\max}$ of 4.3 to 5.0.

The spectral resemblances and assignments are shown in Fig. 1. The absorption spectra of the parent aromatic hydrocarbons show among themselves differences which are far greater than the differences shown among the spectra of the quinones. Consequently, it appears that the quinone ring in the higher quinones is partially isolated from the rest of the molecule and that the higher quinones may be treated simply as vinyl substituted *p*-benzoquinones. This conclusion is not unexpected, since no unexcited resonance structures can be drawn in which the C–C bonds of the carbonyl carbon atoms have any double bond character. This is further supported by the X-ray crystallographic analyses of the structures of *p*-benzoquinone[12] and 9,10-anthraquinone,[13] which show that the C–C bonds of the carbonyl carbon possess little double bond character, since they are 1.50 Å. in length. The lack of much double bond character in these bonds therefore prevents the π-electronic delocalization from extending over the

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(12) J. M. Robertson, *Proc. Roy. Soc.* (*London*), **A150**, 106 (1935).

(13) S. N. Sen, *Ind. J. Phys.*, **31**, 347 (1948).

entire skeleton, so that the quinone ring itself may be taken as the chromophoric group in discussing the spectra of the higher quinones.

Hartmann and Lorenz[11] consider the 21 to 23 k.cm.$^{-1}$ and the 29 to 32 k.cm.$^{-1}$ absorption systems of *p*-benzoquinone to be due to $n \rightarrow \pi^*$ transitions and the 38 to 41 k.cm.$^{-1}$ system to be due to a $\pi \rightarrow \pi^*$ transition. Nagakura and Kuboyama[14] have applied the solvent-shift technique of McConnell[15] to the spectra of several quinones. From their results, the $n \rightarrow \pi^*$ assignment for the weak 21 k.cm.$^{-1}$ band is confirmed, but the stronger 30 k.cm.$^{-1}$ band is clearly seen to be $\pi \rightarrow \pi^*$, since it shifts to lower energies in solvents of high dielectric constant. Consequently, the 30 and 40 k.cm.$^{-1}$ transitions in the *p*-quinones will be considered as $\pi \rightarrow \pi^*$ transitions.

The $\pi \rightarrow \pi^*$ transitions of aromatic molecules have been classified by Platt on the basis of a simple free-electron model.[16] Recent experimental work has verified the validity of this semi-empirical classification scheme in many aromatic molecules.[9] Platt has further discussed the continuous change from the round-field type of molecule, in which the lowest transitions are forbidden by angular-momentum type selection rules, to the long-field type of molecule, in which the angular momentum is no longer a good quantum property.[17] The quinones are a type of molecule which is intermediate between the round-field molecule (polyacene) and the long-field molecule (polyene). In the round-field molecule, angular-momentum coupling rules analogous to the Hund rules place the excited states with many angular nodes in the free-electron π-wave function (high angular momentum) at a lower energy than the excited states with fewer angular nodes (lower angular momentum). The large number of angular nodes in the wave function for the low excited states leads to a near-cancellation of the transition moment for transitions between the ground state and the lower excited states (L states), whereas the transitions between the grounds state and the higher excited states (B states) are more intense. In the long-field molecule, linear-momentum, rather than angular momentum, is (approximately) a good quantum property. The lowest transition in the polyenes and polymethine dyes is often the most intense transition in the spectrum, showing that there is no near cancellation of the transition moment as there is in the polyacenes.

An examination of the spectra of the *p*-quinones reveals that they probably belong more to the round-field than to the long-field type of molecule, since the lowest $\pi \rightarrow \pi^*$ transition is less intense than the higher $\pi \rightarrow \pi^*$ transition by a factor of eight to ten. The lowest $\pi \rightarrow \pi^*$ transition in *p*-benzoquinone is approximately 2 k.cm.$^{-1}$ higher in energy and is weaker than the corresponding transition in 1,4-naphthoquinone and 9,10-anthraquinone by a factor of ten. The lowest $\pi \rightarrow \pi^*$ transition in *p*-benzoquinone may be forbidden by the $g \leftarrow\!\!/\!\!\rightarrow g$ symmetry selection rule, as the simple LCAO–MO calculations by Nagakura and Kuboyama would predict.[18] However, in 9,10-anthraquinone, which also possesses a center of symmetry, the corresponding transition is approximately ten times as intense. Since symmetrical substitution has increased the intensity of this transition by such a large factor, the spectroscopic moment theory of Platt leads to the conclusion that the transition is g — u and not g — g.[19] It is also possible to account for this intensity difference on the basis of an increase in the long-field character of the quinone ring in 9,10-anthraquinone and in the higher quinones relative to 1,4-benzoquinone. This is supported by the observed increase of the 2,3-carbon–carbon bond in 1,4-benzoquinone from 1.32 Å.[12] to a value of 1.40 Å. for the corresponding inter-ring bond in 9,10-anthraquinone.[13]

The weaker and lower $\pi \rightarrow \pi^*$ transition of these molecules is therefore classified as $^1L \leftarrow {}^1A$, and the more intense and higher $\pi \rightarrow \pi^*$ transition is classified as $^1B \leftarrow {}^1A$, using the notation developed by Platt for the round-field molecules.[16] In the L_b state, the free-electron π-wave function possesses a nodal surface at each atom in the π-skeleton, whereas in the L_a state, there are nodal surfaces through each bond. Using the polarization diagram,[16] it is seen that the $^1B_b \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ transitions in the *p*-quinones would possess transition moments lying in the molecular plane and perpendicular to the axis through the oxygen atoms, whereas the $^1B_a \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$ transition moments would lie along the axis joining the oxygen atoms. From a study of the polarized absorption spectra of single crystals of *p*-benzoquinone at low temperatures,[7] it was concluded that the transition moment for the strong $\pi \rightarrow \pi^*$ transition, and possibly also for the weaker $\pi \rightarrow \pi^*$ transition, is perpendicular to the axis joining the oxygen atoms.[20] In the next section, it will be shown that the study of the polarized absorption spectra of single crystals of 9,10-anthraquinone leads to the same conclusion. Consequently the strong $\pi \rightarrow \pi^*$ transition near 38 k.cm.$^{-1}$ in the *p*-quinones is assigned as $^1B_b \leftarrow {}^1A$, and the moderately intense $\pi \rightarrow \pi^*$ transition near 30 k.cm.$^{-1}$ is assigned as $^1L_b \leftarrow {}^1A$. The $^1B_b \leftarrow {}^1A$ transition is also the most intense transition in the polyacenes.[16] The weaker $n \rightarrow \pi^*$ transition near 22 k.cm.$^{-1}$ is assigned as $^1U \leftarrow {}^1A$. The spectral resemblances and assignments for the quinones are shown in Fig. 1. The $^1B_a \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$ transitions do not appear in the spectra of the *p*-quinones below 45 k.cm.$^{-1}$, but it is possible that the additional transition in the *o*-quinones may be the $^1L_a \leftarrow {}^1A$ transition. The correspondences between the *o*- and the *p*-quinones are also shown in Fig. 1, although these are less certain.

By considering the higher quinones as vinyl-substituted benzoquinones, it is possible to give a

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(14) S. Nagakura and A. Kuboyama, THIS JOURNAL, **76**, 1003 (1954).

(15) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(16) J. R. Platt, *ibid.*, **17**, 484 (1949).

(17) J. R. Platt, *ibid.*, **18**, 1168 (1950).

(18) S. Nagakura and A. Kuboyama, *J. Chem. Soc. Japan*, **74**, 499 (1953).

(19) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

(20) The transition moment for an allowed $\pi \rightarrow \pi^*$ transition must lie in the molecular symmetry plane, since each π-orbital is antisymmetric with respect to reflection in this plane.

good account of the variation in the transition energies. Thus, the n $\rightarrow$ π^* transitions are shifted to higher energies when a hydrogen atom is replaced by the electron-donating vinyl groups. The blue shift of the n $\rightarrow$ π^* transition in the higher quinones parallels the blue shift of the n $\rightarrow$ π^* transition of oxalyl chloride[6] relative to biacetyl[5] or glyoxal[4] and the blue shift of the n $\rightarrow$ π^* transitions of the xyloquinones relative to benzoquinone.[7] It is due to an increase in the energy of the excited state relative to the ground state, since the n $\rightarrow$ π^* transition leads to a transfer of electronic charge from the oxygen to the carbon atoms.[21] Presumably, substitution of hydrogen by an electron-withdrawing group should lead to a red shift of an n $\rightarrow$ π^* transition, although this has not yet been tested experimentally.

2. The n $\rightarrow$ π^* Transitions in the Crystalline Quinones.—Having discussed the general features of the spectra of the quinones, an attempt will now be made to interpret some of the finer details of the n $\rightarrow$ π^* transitions. The single crystals were prepared by allowing a melt to crystallize between quartz plates, and pressure was applied to produce crystals thin enough to show vibrational structure in the n $\rightarrow$ π^* transitions. This limited the plane of observation to the cleavage plane. The molecules will be discussed individually.

(a) **9,10-Anthraquinone.**—The absorption spectrum of 9,10-anthraquinone shows a strong intensity dichroism in the cleavage plane, with the absorption being considerably weaker for light polarized along the direction of the growth lines than for light polarized perpendicular to the direction of the growth lines. As was also found for the crystal absorption spectrum of *p*-benzoquinone, there is no detectable dichroic (Davydov) splitting of the bands in this weak transition.[7] The crystal structure has been accurately determined by Sen,[13] who found the crystal to be monoclinic, with space group C^5_{2h},$P2_{1/a}$ and two molecules per unit cell. Sen has conclusively shown that earlier analyses in which the space group was assigned as orthorhombic are not correct. The optical data for this crystal are based on the orthorhombic space group,[22] and Sen has continued to label the crystallographic axes according to the orthorhombic space group. The unique symmetry axis in the monoclinic system is designated as the *b*-axis. For this crystal, the unique symmetry axis corresponds to the axis which was labeled as the *c*-axis by earlier workers who used the orthorhombic space group assignment. The crystallographic face which was normal to the light beam in these experiments was identified as the (010) or *ac*-face, by observing the optical indicatrix pattern which is seen through a polarizing microscope when converging monochromatic light is focused on the crystal face.[23] The absorption for *a*-polarized light is therefore more intense than for *c*-polarized light (Fig. 2). An examination of the electron density projections given by Sen shows that this dichroism is qualitatively consistent with a molecular transition moment lying in the molecular plane and perpendicular to the molecular oxygen–oxygen axis, as was found for the n $\rightarrow$ π^* transitions and the lowest π $\rightarrow$ π^* transition of *p*-benzoquinone.[7] The transition moment direction for this weak n $\rightarrow$ π^* transition in crystalline anthraquinone is considered to be due to crystal-induced mixing with a more intense π $\rightarrow$ π^* transition which is polarized transversely to the oxygen–oxygen molecular axis. By analogy with *p*-benzoquinone, the upper state of the very intense transition at 38 k.cm.$^{-1}$ which has been assigned as $^1B_b \leftarrow {}^1A$, is considered to be the state which is perturbing the ^1U state by crystal-induced mixing. The upper state of the 30 k.cm.$^{-1}$ transition, which has been assigned as $^1L_b \leftarrow {}^1A$, may also contribute to this effect.

Nakamoto has examined the polarized absorption spectra of single 9,10-anthraquinone crystals at room temperature.[24] He reports that *b*-polarized light is more strongly absorbed than *c*-polarized light, but he does not indicate which space group is used to label the axes, nor does he indicate the method used to identify the plane and axes under observation. It is surprising that no vibrational structure is resolved in his work, since some vibrational structure can be resolved even at room temperature for this transition. In any case, Nakamoto's conclusion that the absorption polarized in the plane of the rings is "bathochromic" to light polarized perpendicular to the rings is clearly incorrect, since the low-temperature spectra show no detectable dichroic splitting (less than 3 cm.$^{-1}$).

The bands of this absorption transition are very sharp at 4°K., and the spectrum is very complex (Fig. 2, Table I). There are many bands with similar intensity which are very close together, and there are no obvious progressions or repeating patterns which would simplify the analysis. The high-resolution n $\rightarrow$ π^* transitions of *p*-benzoquinone were found to be quite complex in the crystal[7] and in the vapor,[25] and the n $\rightarrow$ π^* transitions in the higher quinones are even more complex. It appears that single quanta of many vibrational frequencies are excited and that numerous lattice modes are also excited in the electronic transition. A tentative and partial analysis of this transition is given in Table I. Part of the complexity may be due to the presence of two electronic transitions in this region, since there are two n-orbitals which would be predicted to be nearly degenerate. The degeneracy is accidental in the sense that the n-orbitals belong to different irreducible representations of the molecular point

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(21) L. E. Orgel, *J. Chem. Soc.*, 121 (1955).

(22) A. N. Winchell, "Optical Properties of Organic Compounds," Academic Press, New York, N. Y., p. 80.

(23) The optic plane is the (100), or *bc*-plane, according to reference 22. An acute bisectrix pattern is seen in the cleavage plane, with the growth lines in the cleavage plane lying parallel to the line joining the "eyes." Since one extinction direction in the cleavage plane is parallel to the growth lines, the growth lines must then correspond either to the *b*- or to the *c*-direction. The acute bisectrix pattern is displaced to one side of the center of the field, showing that the optic plane is not strictly perpendicular to the cleavage plane which is under observation. Since extinction occurs exactly parallel and perpendicular to the growth lines, the cleavage plane must contain the unique symmetry axis of the monoclinic system. The growth lines must therefore correspond to the *c*-axis of the orthorhombic system, and the face under observation must be the (010), or *ac*-plane.

(24) K. Nakamoto, THIS JOURNAL, **74**, 392 (1952).

(25) L. Light, *Z. physik. Chem.*, **122**, 414 (1926).

group. Two singlet-singlet $n \rightarrow \pi^*$ 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 $\pi \rightarrow \pi^*$ transition.

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

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

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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).