cross-linking contaminants as follows: 200 g. of vinyl pelargonate and 800 g. of urea were dissolved in 4000 ml. of methanol. The solution was allowed to stand overnight at room temperature (27°) and then filtered, yielding 320 g. of complex. Addition of water to the precipitate dissolved the urea and yielded 80 g. (40% of the original ester) of vinyl pelargonate, $n^{30}\text{D}$ 1.4284, as a water-insoluble colorless oil.

The methanol filtrate from the separation of the first crop of complex was cooled to 2° and an additional 316 g. of complex was obtained. The vinyl pelargonate isolated from it weighed 78 g. (39% yield), $n^{30}\text{D}$ 1.4280.

The second methanol filtrate was concentrated to about one-fourth its volume and cooled to room temperature. The yield of urea complex obtained at this stage was 187 g. from which 41 g. (20% yield) of vinyl pelargonate was isolated.

The total yield of vinyl pelargonate recovered was 99%. A portion of each fraction was polymerized[6] and soluble polymers were obtained from each.

Recovery of Vinyl Palmitate from Mixtures.—Twenty-six grams of crude vinyl palmitate, also containing polyvinyl palmitate, inhibitors and unknown (colored) components, was added to 500 ml. of methanol. Some polyvinyl palmitate precipitated and was separated by filtration. Seventy-five grams of urea was dissolved in the filtrate and the solution was allowed to stand overnight at room temperature. The quantity of complex which precipitated was 44 g. and it contained about 40% of the vinyl palmitate originally present in the crude mixture. Vinyl palmitate recoveries of as high as 83% have been obtained by increasing the ratio of urea to crude vinyl palmitate to about 5:1.

The recovered vinyl palmitate formed thermoplastic soluble polymers when heated with benzoyl peroxide.[6]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OSAKA UNIVERSITY]

Peculiarity of Dichroism of Aromatic Molecular Compounds. I. The Dichroisms of Quinhydrone, *s*-Trinitrobenzene–*p*-Bromoaniline and Related Compounds

BY KAZUO NAKAMOTO

From the measurements of dichroisms of quinhydrone, chloranil–hexamethylbenzene, *s*-trinitrobenzene–*p*-bromoaniline and picryl chloride–hexamethylbenzene, the crystal structures of which had been determined by X-ray analysis, the following general rule has been derived: "for the first bands which are supposed to consist of absorptions principally due to π-electrons and the substituents of the benzene rings, the absorptions with the electric vectors vibrating perpendicular to the ring plane are always bathochromic and hyperchromic to the absorptions with those vibrating parallel to it." This result is quite reverse to the case of common aromatic compounds, and gives interesting suggestions to the nature of the intermolecular forces in molecular compounds.

Introduction

In order to explain the intense color of molecular compounds, a number of researches have been carried out from various physical and chemical points of view. Recently Michaelis and Granick[1] measured the absorption spectra of molecular compounds of the quinhydrone type in solutions. But in the solution all of them dissociate into their components, although not completely. So it is necessary for us to measure their absorptions in crystalline state. These studies, however, have never been attempted, because of the difficulty in getting large but thin crystals suitable for ordinary measurements of absorption spectra. By making use of the microscopic method,[2] this difficulty can be easily avoided. In the previous works,[2,3] the dichroisms of the π-bands in common aromatic compounds have been observed and the following general rule established; "the $\|$-absorption is always bathochromic and hyperchromic to the $\perp$-absorption." Here, $\|$- or $\perp$-absorption means the spectrum by the light with the electric vector abundant with the parallel or perpendicular component to the benzene ring. So it seems very interesting to investigate whether the above rule holds also for the molecular compounds. A few compounds whose crystal structures had been determined by X-ray analysis were selected and their dichroisms in the visible and ultraviolet region were quantitatively measured.

Experimental

Materials (1) Quinhydrone.—Microcrystals by Merck and Co., Inc., were used, monoclinic system, m.p. 169°. Thick crystals are violet-black and have metallic luster due to their surface reflections; straight extinction, when observed from the *c*-axis. Thin crystals are dichroic; violet red, with polarized light parallel to the needle axis (*a*-axis) and red, with polarized light perpendicular to it.

(2) Chloranil–Hexamethylbenzene—Blood red solution is obtained at once, when the dilute alcoholic solutions of both the components are mixed in the molar ratio of 1:1. By natural evaporation of the solvent red acicular crystals are produced, m.p. 198°; rhombic system; straight extinction; strongly dichroic; deep violet, parallel to the needle axis (*a*-axis) and reddish-yellow, perpendicular to it.

(3) *s*-Trinitrobenzene–*p*-Bromoaniline—Orange acicular crystals are produced when the dilute alcoholic solutions of both the components are mixed in the molar ratio of 1:1 and the mixed solution is evaporated, m.p. 109°; monoclinic system; straight extinction; orange, parallel to the needle axis (*a*-axis) and bright yellow, perpendicular to it (*b*-axis).

(4) Picryl Chloride–Hexamethylbenzene—Deep yellow acicular crystals are prepared by mixing the chloroform solutions of both the components at the molar ratio of 1:1, and allowing the solution to evaporate at room temperature, m.p. 148°; rhombic system; straight extinction; deep yellow, parallel to the needle axis (*a*-axis), and light yellow, perpendicular to it.

Results and Discussion

Part I. Molecular Compounds of the Quinhydrone Type. (1) Quinhydrone.—In 1935, Palacios and Foz[4] studied the crystal structure of quinhydrone, but their result was not perfect. Recently Osaki and Matsuda[5] succeeded in its

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[1] L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944).

[2] K. Nakamoto, *ibid.*, **74**, 390 (1952).

[3] K. Nakamoto, *ibid.*, **74**, 392 (1952).

[4] J. Palacios and O. R. Foz, *Anales soc. españ. fís. quím.*, **33**, 627 (1935).

[5] K. Osaki and H. Matsuda, *Acta. Cryst.*, in press.

complete analysis. According to their result, benzene rings of both the components are almost parallel to the *c*-axis, inclining by about 34° to the (100) plane. They are piled up alternately along the *a*-axis, making their molecular planes almost parallel to each other as shown graphically in Fig. 1. Moreover, the normal distance between two layers is 3.16 Å., a value which is very short in comparison with the distance 3.5 ~ 3.7 Å. in common aromatic compounds.

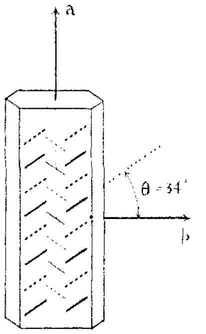

Fig. 1.—The orientations of hydroquinone and quinone in quinhydrone crystal: —, hydroquinone, ----, quinone. Fine lines show the molecules of the next inner layer. (*c*-axis is normal to the paper plane).

Absorption curves for linearly polarized lights with the electric vectors parallel to the *a*- and *b*-axes, respectively, are shown in Fig. 2, and their numerical data characterizing these spectra are summarized in Table I.

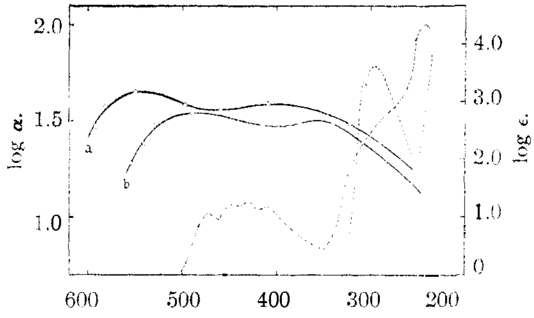

Fig. 2.—Absorption spectra of quinhydrone and its components: — - — -, quinone; - - - -, hydroquinone.

TABLE I

	1st band		2nd band	
	λ_{max}, mμ	log α_{max}	λ_{max}, mμ	log α_{max}
a-abs.	550	1.65	410	1.58
b-abs.	490	1.55	360	1.50

$\Delta\lambda_{max}$ 60, Δlog α_{max} 0.1, $\Delta\lambda_{max}$ 50, Δlog α_{max} 0.08

From the comparison of these two curves with the absorption spectra of hydroquinone and quinone in solutions, we may conclude that the first bands at 550 and 490 mμ consist of π-absorption band of the benzene ring and those characteristic of quinone. But as is shown in the spectrum of quinone, the absorption band principally due to the π-electrons (λ_{max} *ca.* 280 mμ; log ϵ_{max} *ca.* 2.8) is much stronger than that of the carbonyl groups (λ_{max} 430 mμ; log ϵ_{max} 1.26). So we may assume these superposed bands consist mainly of the π-band under the influence of the carbonyl band. These bands correspond to the charge-transfer spectra, which is discussed in detail by Mulliken.[6] That is, they are responsible for the transfer of π-electrons between two aromatic molecules.

Now let us consider the relation between the direction of the electric vector of the polarized light and the plane of the benzene ring in the crystal. As mentioned above, in quinhydrone crystal, all the benzene rings are inclined by 34° to the (100) plane. Accordingly, if the same discussion in the previous report[3] is applied to the present case, we can easily derive that *a*- and *b*-absorptions are abundant with the perpendicular and parallel components to the ring plane, respectively. Thus, in quinhydrone crystal, the ⊥-absorption is bathochromic and hyperchromic to the ‖-absorption.

(2) **Chloranil–Hexamethylbenzene.**—According to Anderson,[7] the crystal of chloranil–hexamethylbenzene has a similar structure to quinhydrone. The absorption curves with polarized lights whose electric vectors parallel to the *a*- and *b*-axes, respectively, are shown in Fig. 3, and their numerical data are given in Table II.

TABLE II

	1st band		2nd band	
	λ_{max}, mμ	log α_{max}	λ_{max}, mμ	log α_{max}
a-abs.	620	1.9	380	1.82
b-abs.	460	1.63		

$\Delta\lambda_{max}$ 160, Δlog α_{max} 0.27

Dotted lines in Fig. 3 show the absorption spectra of chloranil and hexamethylbenzene in alcoholic solutions. The former spectrum has no distinct maxima, gradually reducing its intensity as the wave length increases. This broad band is ascribed to the superposed absorption of the strong π-band and the weak band of the substituents. In hexamethylbenzene, its π-band is at 275 mμ as reported before.[2]

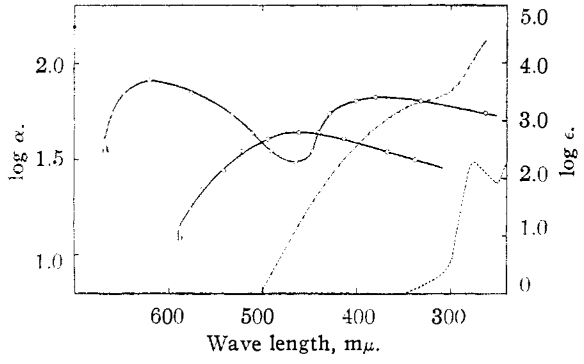

Fig. 3.—Absorption spectra of chloranil–hexamethylbenzene: ·········—·—, chloranil; - - - - -, hexamethylbenzene.

From the similar discussion as in quinhydrone, we can deduce that the first bands at 620 and 460 mμ in crystalline state consist principally of the π-absorptions under the influence of the substituents.

Thus, the same conclusion as before is deduced.

Part II. Molecular Compounds of the Nitrobenzene Type. (3) ***s*-Trinitrobenzene–*p*-Bromoaniline.**—According to Powell, Huse and Cooks,[8] in the crystal of the molecular compound of *s*-

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[6] R. S. Mulliken, THIS JOURNAL, **72**, 605 (1950).

[7] J. S. Anderson, *Nature*, **140**, 584 (1937).

[8] H. M. Powell, G. H. Huse and P. W. Cooks, *J. Chem. Soc.*, 153 (1943).

trinitrobenzene–*p*-iodoaniline, benzene rings of both the components are almost parallel to the *c*-axis and piled up alternately along the *a*-axis, making an angle of 30° with the (100) plane (see Fig. 1). The normal distance between the benzene planes is as close as 3.26 Å. The crystal of *s*-trinitrobenzene–*p*-bromoaniline may have a similar structure to the above mentioned iodine homolog.

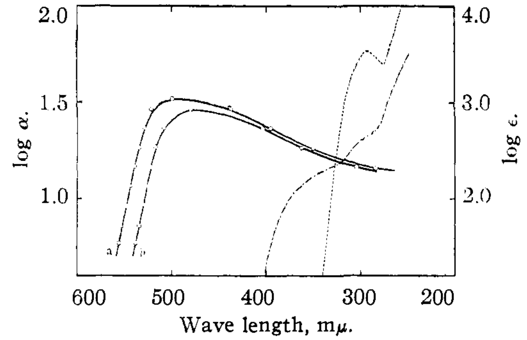

Fig. 4.—Absorption spectra of *s*-trinitrobenzene–*p*-bromoaniline: — — — —, *s*-trinitrobenzene; - - - - -, *p*-bromoaniline.

Figure 4 shows the absorption curves for polarized lights whose electric vectors vibrating parallel to the *a*- and *b*-axes, respectively, and their numerical data are summarized in Table III.

TABLE III

	λ_{max}, mμ	log α_{max}
a-abs.	500	1.52
b-abs.	480	1.47
	$\Delta\lambda_{max}$ 20,	$\Delta\log\alpha_{max}$ 0.05

Dotted lines in the same figure show the absorption spectra of *s*-trinitrobenzene and *p*-bromoaniline in alcoholic solutions. From the comparison of these two curves with that of crystalline state, we may conclude that the broad bands seen in the crystalline state are the superposed absorptions of the substituted groups (–Br, $-NH_2$ and $-NO_2$) and π-electrons of the benzene rings. But as seen in the spectrum of *s*-trinitrobenzene, the π-absorption is generally much stronger than the absorption of the substituted groups. So, broad bands in the crystalline state are originated in the π-absorptions under the influence of the substituted groups. As the angle θ between the direction of the benzene rings and the (100) plane is 30° and smaller than 45°, we may conclude that the ⊥-absorption is bathochromic and hyperchromic to the || -absorption.

(4) **Picryl Chloride–Hexamethylbenzene.**—According to the X-ray analysis of Powell and Huse,[9] in the crystal of this molecular compound, all the benzene rings of both the components are almost parallel to the (100) plane and piled up alternately along the *a*-axis (needle axis), though there are observed local disorder structures. The absorption curves with polarized lights whose electric vectors vibrating parallel and perpendicular, respectively, to the *a*-axis are given in Fig. 5, and their numerical data are summarized in Table IV.

TABLE IV

	λ_{max}, mμ	log α_{max}
⊥-abs.	400	1.83
||-abs.	370	1.73
	$\Delta\lambda_{max}$ 30,	$\Delta\log\alpha_{max}$ 0.1

Dotted lines in Fig. 5 show the absorption spectra of both the components in alcoholic solutions. Similar interpretations of these spectra as before lead us the conclusion that broad bands in crystalline state consist mainly of the π-absorptions. Conforming the result of the X-ray analysis with these spectroscopic data, we can reach the same conclusion as before.

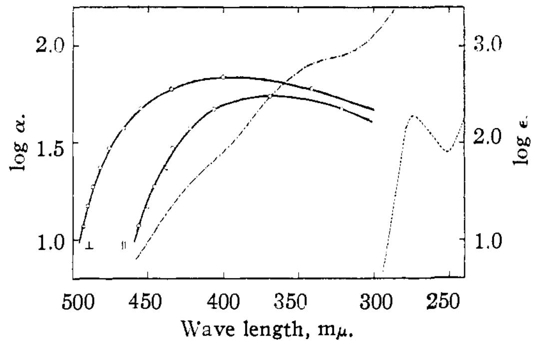

Fig. 5.—Absorption spectra of picryl chloride–hexamethylbenzene: — — — —, picryl chloride; - - - -, hexamethylbenzene.

General Discussion of the Results

From the measurements of dichroisms of the four molecular compounds, the following general rule has been found: "*For the first bands which are supposed to consist of absorptions principally due to π-electrons, the absorption with the electric vector vibrating perpendicular to the benzene ring is always bathochromic and hyperchromic to the absorption with those vibrating parallel to it.*"

In conclusion, the above rule must be discussed from the viewpoint of electronic theory.

In the common aromatic crystals, van der Waals attraction between benzene layers are weak, and the overlap of the π-electron clouds in the direction perpendicular to the benzene ring is small. In fact, the normal distance between benzene layers, which is not less than 3.5 Å., is considerably large in comparison with those of the molecular compounds. Accordingly, the density distribution of π-electrons is larger in the || -direction than in the ⊥-direction, as already mentioned in the former work.[3] This means π-electrons are more mobile in the || -direction than in the ⊥-direction.

In the molecular compounds, however, there occur some kinds of interactions between benzene layers. This fact is verified by the results of X-ray analysis, which show that two components of the compound are piled up alternately along the needle axis, making their benzene planes almost parallel to each other. More striking is that the normal distance between benzene layers is generally shorter than that of common aromatic compounds. The nature of this intermolecular forced neither ionic nor covalent, as already shown by Powell, *et al.*[8,9] Above results of dichroism measurements have led us the following conclusion.

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(9) H. M. Powell and G. H. Huse, *Nature*, **144**, 77 (1939); *J. Chem Soc.*, 435 (1943).

When two components are mixed and two kinds of molecules approach each other, there occur induced dipole moments in both molecules by the mutual polarizing forces. They come nearer by the attraction between these dipoles. When they enter in the effective fields of π-electrons of the paired molecules to each other, there occurs overlapping of the π-electron clouds in the ⊥-direction.

In other words, π–π attraction between benzene layers is induced by the close approach of the two components. As a result, the density distribution of π-electrons becomes larger in the ⊥-direction than in the ‖-direction. That is, π-electrons become more mobile in the ⊥-direction rather than in the ‖-direction. This result is in good accordance with the view of the charge-transfer spectrum,[6] which leads to the conclusion that the electric moment vibrates along the ⊥-direction. Thus, the reversity of the dichroic property in molecular compounds is explained by the π–π attraction in the ⊥-direction. The strength of this π–π attraction can be discussed semiquantitatively by the comparisons of $\Delta\lambda_{\max}$ and $\Delta \log \alpha_{\max}$. As shown above, these values are larger in quinhydrone than in *s*-trinitrobenzene–*p*-bromoaniline, which means the former is more stable than the latter. Similar results are obtained by the comparisons of the normal distance between benzene layers and the heat of sublimation[10] in both compounds.

If this π–π attraction becomes too strong, the molecule is highly polymerized even in the solution. Thus, Scheibe, *et al.*,[11] have found the "Z-band" in the solution of the cyanine type dyes.

From the measurements of dichroisms in the molecular compounds, the following conclusion has been reached: "The nature of the intermolecular force is the π–π attraction in the ⊥-direction by the approach of both components due to mutual polarizing forces.

The author expresses sincere thanks to Prof. R. Tsuchida, Mr. S. Yamada, K. Osaki and H. Matsuda for their kind advices and encouragements throughout this work.

(10) I. Nitta, S. Seki, H. Chihara and K. Suzuki, Scientific Papers from the Osaka University, No. 29 (1951).

(11) G. Scheibe, *Kolloid Z.*, **82**, 2 (1938).

NAKANOSHIMA, KITA, OSAKA, JAPAN

RECEIVED SEPTEMBER 24, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of B-Trichloroborazole[1,2]

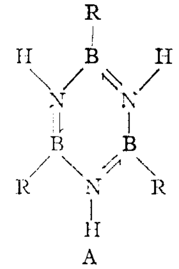
BY D. L. COURSEN[3] AND J. L. HOARD

Analysis of the X-ray diffraction data obtained from single crystals of B-trichloroborazole has led to a complete determination of structure. Three-dimensional Fourier methods including corrections for finite termination of series were used to give accurate values of the atomic coördinates. The molecular configuration of B-trichloroborazole closely resembles that of *sym*-trichlorobenzene. Bond distances and interbond angles with estimated probable errors for the B-trichloroborazole molecule of symmetry D_{3h} are: B–N = 1.413 ± 0.010 A.; B–Cl = 1.760 ± 0.015 Å.; ∠NBN = 119 ± 1°; ∠BNB = 121 ± 1°. Some considerations which illuminate the nature of the reliability coefficient also are presented.

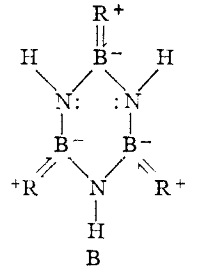
Introduction

The remarkable similarity in the physical properties of benzene and borazole ($B_3N_3H_6$) was pointed out by the discoverers[4] of the latter compound. Their assignment of an aromatic ring structure closely resembling that of benzene to the borazole molecule has received strong support from electron diffraction studies[5] and also from comparisons of spectra.[6]

There has seemed to be some uncertainty concerning the effect which is produced in the boron-nitrogen ring by replacing hydrogen atoms of borazole by other substituents. Wiberg[7] has suggested that B-substitution of groups with strong negative induction effects favors the aromatic structure A. The following substituents on boron are listed by Wiberg in the order of decreasing effectiveness in producing double bond character in the borazole ring: Cl > H > CH_3 > $N(CH_3)_2$.



A



B

However, a study of the spectra of B-trichloroborazole, borazole and B-trimethylborazole has been interpreted[6] as indicating that both the methyl and the chlorine substituted compounds have less aromatic character than has borazole. It was suggested,[6] moreover, that this result for B-trichloroborazole would be expected if the contribution from structures of the type B were to become sufficiently important.

The results obtained in our study of B-trichloroborazole, while compatible with contributions to the structure of the molecule from both limiting formulations A and B, indicate that double bond

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[1] Supported in part by the Office of Naval Research, Contract No. N6ori-91, Task Order 4, Project No. NR052020, in part by the Atomic Energy Commission, Contract No. AT(30-1)-878.

[2] Preliminary account presented at the Spring (1950) Meeting of the American Crystallographic Association held at the Pennsylvania State College.

[3] Eastern Laboratory, E. I. du Pont de Nemours & Co., Gibbstown, New Jersey.

[4] A. Stock and E. Pohland, *Ber.*, **59B**, 2215 (1926).

[5] (a) A. Stock and R. Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931); (b) S. H. Bauer, THIS JOURNAL, **60**, 524 (1938).

[6] C. W. Rector, G. W. Schaeffer and J. R. Platt, *J. Chem. Phys.*, **17**, 460 (1949).

[7] E. Wiberg, unpublished report obtained by the Office of Naval Research, EXOS:ONR:N425:RR:1h, Serial No. 12987, June 10, 1947.