with chilled 10% aqueous ammonia, and followed by immediate washing and distillation of solvent; yield 33.4 g. of a greasy solid, m.p. 70–75° with previous softening (*Anal.* Found: OH, 9.16). Recrystallization from 35–60° petroleum ether afforded 21.9 g. of a dry crystalline mixture, m.p. 79–84° (found: OH, 10.94), which was fractionally crystallized with the use of petroleum ether and of hexamethyldisiloxane containing small amounts of acetone or ethanol. There was obtained 7.8 g. of the first compound "A," as long needles with m.p. 110–111°; and 3 g. of poorly defined crystals of an isomeric compound "B," m.p. 82–84°. X-Ray powder diffraction patterns show a dissimilarity of structure between these two materials. However, compound "A" is isomorphous with and apparently structurally similar to a crystalline 1,3-diethyl-1,3-diphenyldisiloxanediol, m.p. 86–86.5°,[25] prepared in a similar manner.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OSAKA UNIVERSITY]

Dichroisms of Benzene Rings. I. The Dichroisms of Hexamethylbenzene and Hexabromomethylbenzene

BY KAZUO NAKAMOTO

The dichroisms of hexamethylbenzene and hexabromomethylbenzene, the crystal structures of which had been perfectly determined by X-ray analysis, were measured by the microscopic method. In both the cases, remarkable dichroisms were observed; the absorption for the polarized light whose electric vector vibrates parallel to the benzene ring was always more bathochromic and hyperchromic than the absorption for the light polarized perpendicularly to the benzene plane.

Introduction

A number of studies have been carried out regarding the absorption spectra of organic compounds in solutions, and their results are applied widely to various regions of organic chemistry. But absorption spectra in crystalline states have scarcely been observed, notwithstanding their theoretical and experimental importances.

This fact is due to technical difficulties. In order to measure the absorption of the crystal, it is necessary to get a large single crystal and polish its planes optically parallel, with thickness of $10^{-2}\sim 10^{-3}$ cm., which allows us to measure the absorption. Moreover, if the measurement of the pleochroism is required, we must polish the crystal taking its axial relations in consideration.

By this method, Krishnan and his co-workers[1,2] and Scheibe[3] have measured the dichroisms of aromatic crystals of the condensed ring system. But its application is possible only when large single crystals are obtainable.

In order to measure the absorption of ordinary compounds whose crystals are obtainable only in microcrystalline states, some special device is required. Scheibe and his collaborators[4] have measured the dichroisms of benzene and hexamethylbenzene crystals, by making use of the assemblage of its microcrystals which orientate practically parallel to each other. But to get the correct results, it is desirable to measure the pleochroism with only one single crystal. Fortunately, Tsuchida[5] has invented a new method, which enables us to make measurements of pleochroism in the visible and ultraviolet region with a single microscopic crystal easily obtainable in ordinary procedures of preparation. Many studies[6] on absorption spectra of crystals using this method have been carried out.

The present paper deals with the measurement of the dichroism in the π-electron band of the benzene ring. To make the discussions clearer and simpler, two aromatic compounds whose crystal structures had been perfectly determined by X-ray analysis were selected and their dichroisms in the ultraviolet region were quantitatively measured.

Experimental

Materials.—Hexamethylbenzene $C_6(CH_3)_6$ was recrystallized from the alcoholic solution, m.p. 164°, colorless planar crystal, triclinic system (α = 44°27′), oblique extinction, extinction angle being 44°. Hexabromomethylbenzene $C_6(CH_2Br)_6$ was prepared by the method of Beintema, Terpstra and von Weerden.[7] They were recrystallized from the ethylene bromide solution, m.p. 297°, colorless hexagonal prism, rhobohedral system, straight extinction.

Measurements.—The method of measuring the dichroism of the microcrystals has already been stated in the former reports.[5] In each case, the finest single crystal was selected under the microscope, by which the image of the crystal was enlarged and projected on the slit of a spectrograph in the eventual dichroism measurements. The extinction coefficient per mm., α, is given by the following expression

$$\alpha = \frac{0.9}{d} \log \frac{a_0}{a}$$

where d is thickness in mm. of the crystal, and a_0 and a are angles of the rotating sector for light through the crystal and the light for comparison.

Results and Discussion

(1) **Hexamethylbenzene.**—In 1934, Orelkin and Lonsdale[8] studied the crystal structure of hexamethylbenzene. In 1939, Brockway and Robertson[4] carried out its Fourier analysis again. According to their results, all the benzene rings in this crystal are parallel to the (001) plane and along this plane occurs the perfect cleavage. Microcrystals obtained from the alcoholic solution

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(1) K. S. Krishnan and P. K. Seshan, *Z. Krist.*, **89**, 538 (1934).

(2) K. S. Krishnan and S. Banerjee, *ibid.*, **91**, 173 (1935).

(3) G. Scheibe, *Z. angew. Chem.*, **52**, 631 (1939).

(4) G. Scheibe, St. Hartwig and H. Müller, *Z. Elektrochem.*, **49**, 372 (1943).

(5) R. Tsuchida and M. Kobayashi, *Bull. Chem. Soc. Japan*, **13**, 619 (1938); *J. Chem. Soc. Japan*, **60**, 769 (1939); "Colour and Structure of Metallic Compounds," Zoshindo, Osaka, 1944, p. 180.

(6) S. Yamada, THIS JOURNAL, **73**, 1182, 1579 (1951).

(7) J. Beintema, P. Terpstra and W. T. von Weerden, *Rec. trav. chim.*, **54**, 962 (1935).

(8) B. Orelkin and K. Lonsdale, *Proc. Roy. Soc.* (*London*), **A144**, 630 (1934).

(9) L. O. Brockway and T. M. Robertson, *J. Chem. Soc.*, 1324 (1939).

have generally such shapes as shown in Fig. 1. (Dotted lines drawn in the crystal show the direction of benzene rings.) The direction of the (001) plane is easily known from the cleavage on the crystal surfaces and the measurements of the extinction angle.

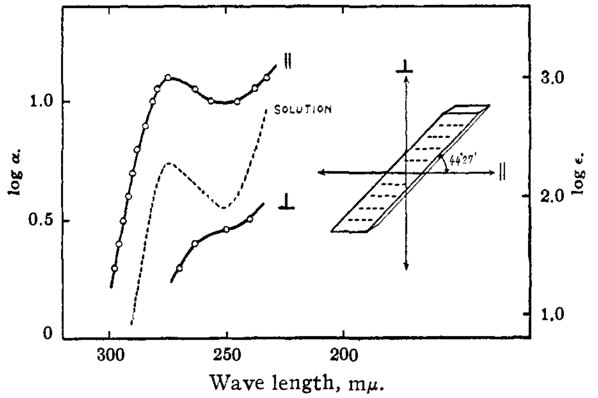

Fig. 1.—Absorption spectra of hexamethylbenzene.

The absorption curves by linearly polarized light with the electric vectors parallel and perpendicular to the (001) plane are shown in Fig. 1, and their numerical data are shown in Table I. As the benzene rings are orientated parallel to the (001) plane, the light vibrating parallel to the crystal plane is the light with the electric vector parallel to the benzene rings.

Hereafter the direction of the light vector referred to the benzene ring is expressed with symbols $\parallel$ or $\perp$.

TABLE I

	$\lambda_{\max}$ mμ	log $\alpha_{\max}$	$\alpha_{\max}$
$\parallel$-abs.	275	1.10	12.6
$\perp$-abs.	250	0.46	2.8

$\Delta\lambda_{\max} = 25$, $\Delta \log \alpha_{\max} = 0.46$, $\alpha_{\max\parallel} : \alpha_{\max\perp} = 4.5:1$.

Dotted line in the same figure shows the absorption spectrum of hexamethylbenzene in an alcoholic solution. ($\lambda_{\max}$ 275 mμ; log $\epsilon_{\max}$ 2.26.) Hexamethylbenzene has at least two absorption bands, the band of the longest wave length at 275 mμ is due to the π-electrons of the benzene ring, the next band of strong intensity is originated by its σ-electrons.

Remarkable dichroism was found in the π-band of hexamethylbenzene as is shown above; the $\parallel$-absorption is remarkably more bathochromic and hyperchromic than the $\perp$-absorption. The result of Scheibe, *et al.*,[4] is different from the above, especially in its wave length shift. The reason of this discrepancy seems to be due to the difference in measuring methods. That is, they observed the dichroism of the assemblage of many single crystals, which were obtained by cooling a melt between the quartz plates. In their method, however, we cannot expect that the mutual orientations of the benzene rings in every single crystal are not perfectly parallel to each other. On the other hand, it is the characteristic of our method to use only one single crystal. So we may conclude that the above result is more reliable than theirs.

(2) **Hexabromomethylbenzene.**—According to the X-ray analysis of Beintema, Terpstra and von Weerden,[7] all the benzene rings in the crystal lie parallel to each other and perpendicular to the *c*-axis, as is shown in Fig. 2.

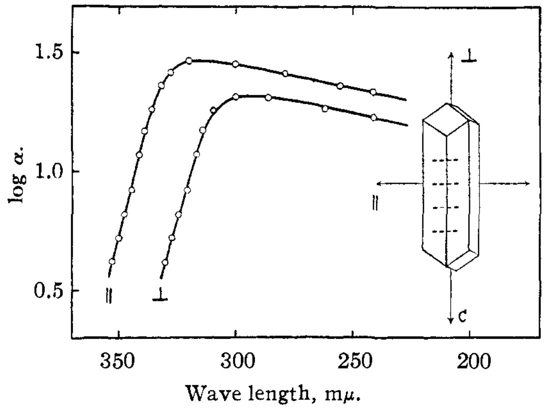

Fig. 2.—Absorption spectra of hexabromomethylbenzene.

The absorption curves by linearly polarized light with the electric vectors parallel and perpendicular to the *c*-axis are shown in Fig. 2, and their numerical data are given in Table II.

TABLE II

	$\lambda_{\max}$, mμ	log $\alpha_{\max}$	$\alpha_{\max}$
$\parallel$-abs.	320	1.46	28.8
$\perp$-abs,	300	1.31	20.4

$\Delta\lambda_{\max} = 20$, $\Delta \log \alpha_{\max} = 0.15$, $\alpha_{\max\parallel} : \alpha_{\max\perp} = 1.4:1$.

Also in the present case, $\parallel$-absorption is more bathochromic and hyperchromic than the $\perp$-absorption. Instead of the two distinct bands in hexamethylbenzene, a single broad band was observed. The latter is the superposed absorption of π-electrons and bromine atoms.

So far, it is impossible for us to analyze these superposed bands into the component π- and bromine-bands. But we could get the extinction coefficients of the same order, by subtracting $\alpha_{\max}\parallel$ and $\alpha_{\max}\perp$ in hexamethylbenzene from the corresponding values in hexabromomethylbenzene.

$\parallel$-abs. $28.8 - 12.6 = 16.2$
$\perp$-abs, $20.4 - 2.8 = 17.6$

The residual coefficients are almost equal in both directions, which means they could be ascribed to the bromine absorption.

In other words, this fact means the following result: a remarkable dichroism similar to the case of hexamethylbenzene exists also in the bromine derivative. But the isotropic absorption of six bromine atoms may participate in both the absorptions and make less remarkable the dichroism due to π-electrons of the benzene ring.

It has been found that the π-band of the benzene ring in hexamethylbenzene is strongly dichroic, the $\parallel$-absorption being more bathochromic and hyperchromic than the $\perp$-absorption.

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