Dichroisms of Benzene Rings. IV.
The Dichroisms of Diphenyldiacetylene and Naphthazarine

By Kazuo NAKAMOTO

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Introduction

In the former papers of this series,⁽¹⁾ remarkable dichroism of the benzene ring has been found in common aromatic crystals and molecular compounds. From the viewpoint of quantum mechanics, however, the triple bond is expected to show more remarkable dichroism than the double bond because the former has two π-electrons in each carbon atom. So it is of interest to measure the dichroism of the triple bond and to compare it with that of the benzene ring.

In the present study, the dichroism of diphenyldiacetylene whose crystal structure had been perfectly determined by X-ray analysis has been measured quantitatively in the ultraviolet region. The result seems noteworthy, indicating remarkable dichroism of the triple bond independent of the dichroism of the benzene ring.

Of particular interest in the field of molecular structure is the problem of determining whether naphthazarine, 5, 8-dihydroxy-1, 4-naphthoquinone, exists as a molecular compound similar to quinhydrone or as the monomer in crystalline state. The result of the dichroism measurement has led us to the conclusion that a formation of molecular compound is not probable so far as the assumed orientation of molecules is correct.

Experimental

Materials.—(1) Diphenyldiacetylene—Colourless acicular crystals were obtained by recrystallization from an alcoholic solution. M. p. 87°. Monoclinic system. Straight extinction. Dichroism can not be observed with the naked eye. (2) Naphthazarine—The Friedel-Crafts synthesis between hydroquinone and maleic anhydride⁽²⁾ was employed for the preparation of this substance. Recrystallization from a ligroin solution produced violet needle crystals similar to quinhydrone. Since naphthazarine slowly decomposes on heating in the air, its melting point was identified as the diacetate (m. p. 192°). Monoclinic system. Straight extinction. Thin crystals show slight dichroism; rose, when viewed with linearly polarized light whose electric vector vibrates parallel to the c-axis (needle axis), and rose red, with the light vibrating parallel to the b-axis.

Measurements.—Dichroisms of the crystals were measured quantitatively by the microscopic method with microcrystals as described before⁽¹⁾. Spectra of the alcoholic solutions were measured by photographic method using the rotatory sector. In each graph, the ordinates, α and ε denote absorption coefficient per mm. of the crystal, and molar extinction coefficient of the solution, respectively.

Results and Discussion

(1) **Diphenyldiacetylene.**—In 1940, Wiebenga⁽³⁾ studied the crystal structure of diphenyldiacetylene and succeeded in its Fourier analysis. According to his result, planar molecules of diphenyldiacetylene are piled up along the c-axis, making their molecular planes almost parallel to the a-axis and inclined by an angle of 25° referred to the b-axis.

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(1) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 390, 392 and 1739 (1952).

(2) K. Zahn and P. Ochwat, *Ann.*, **462**, 81 (1928).

(3) E. H. Wiebenga, *Z. Krist.*, **102**, 193 (1940).

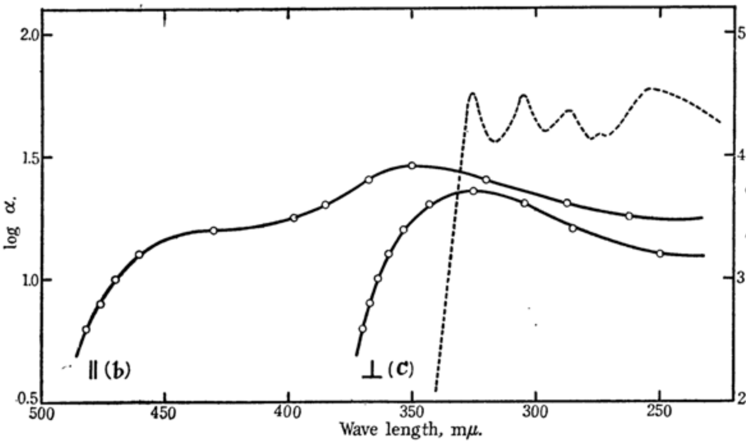

Fig. 1.—Absorption spectra of diphenyldiacetylene.

Absorption spectra by linearly polarized light with the electric vectors vibrating parallel to the *b*- and *c*-axes, respectively, are recorded in Fig. 1. Numerical data characterizing these spectra are given in Table 1.

Table 1

	1st band (acetylene band)		2nd band (benzene band)	
	λmax.	log αmax.	λmax.	log αmax.
b-abs.	430	1.20	350	1.45
c-abs.			325	1.30

The absorption spectrum of diphenyldiacetylene in an alcoholic solution is also given in Fig. 1 (dotted line). As is clearly shown in the spectra of diphenylpolyin series,(4) the four distinct bands at 326, 305.3, 287.4 and 275.5 mμ are the absorptions due to the acetylene group in the molecule. The next broad band appeared at 255 mμ is attributed to the absorption resulting from the π-electrons of the benzene rings.

As is seen above, the acetylene band is bathochromic in respect to the benzene band. This relation may hold also for the spectra in crystalline state. In the *b*-absorption of crystalline state, therefore, the first band at 430 mμ and the second band at 350 mμ are concluded to be due to the acetylene group and the benzene ring, respectively. In the *c*-absorption, however, only one maximum which may be ascribed to the benzene band appears at 325 mμ, because the acetylene band is too weak in this polarized light. Nevertheless, we can expect that the *b*-absorption of the acetylene band is bathochromic and hyperchromic to the *c*-absorption from experimental analogy between the dichroism of the benzene ring and that of the acetylene group.

Comparing the result of X-ray analysis with the above spectroscopic discussion, we may conclude that the absorption parallel to the acetylene bond and the benzene rings is bathochromic and hyperchromic to the absorption perpendicular to them. Thus the acetylene group shows the same dichroic property as the benzene ring, except the former indicates more remarkable dichroism than the latter.

(2) **Naphthazarine.**—It has been a subject of much discussion both experimental and theoretical to decide whether naphthazarine exists as a molecular compound similar to quinhydrone or as the monomer in crystalline state. In an attempt to solve this problem, measurements of the dichroism of naphthazarine crystals have been made in the visible and ultraviolet region. As to the X-ray study on this crystal, Palacios and Salvia(5) have measured only the dimension of its unit cell and no further detailed study has been undertaken.

According to their result, the unit cell of naphthazarine crystal(6) is as follows:

$$a=3.85,\ b=8.02,\ c=14.5\,\text{Å}.\ \beta=97°6'$$

Considering that *a* is nearly equal to ordinary

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(4) M. Nakagawa et al., *J. Chem. Soc. Japan*, **72**, 561 (1950); 73, 141 (1951).

For another example, see W. D. Celmer and I. A. Solomons, *J. Am. Chem. Soc.*, **74**, 3840 (1952).

(5) J. Palacios and R. Salvia, *Anales. soc. españ. fis. quim.*, **32**, 49 (1934).

(6) Naphthazarine has at least two modifications. The one was recently used by Rogers for the measurement of magnetic anisotropy (*J. Am. Chem. Soc.*, **69**, 1506 (1947)). The other was studied by Palacios and Salvia as stated above, and used here for the dichroism measurement.

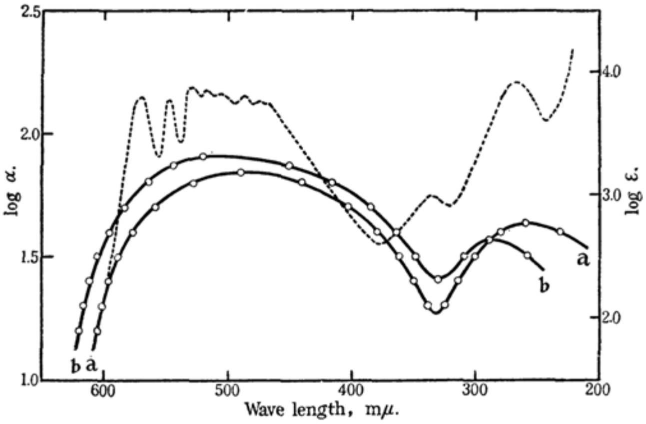

Fig. 2.—Absorption spectra of naphthazarine.

distance which separates aromatic layers, it seems probable that the molecules are piled up along the a-axis. Thus, the absorption spectra by linearly polarized lights with the electric vector vibrating parallel to the a- and the b-axes have been measured. Their curves and numerical data are given in Fig. 2 and Table 2, respectively.

Table 2

	λmax.	log αmax.	λmax.	log αmax.
a-abs.	490	1.84	250	1.64
b-abs.	510	1.92	290	1.57

The absorption spectrum of naphthazarine in an alcoholic solution is also shown in Fig. 2 (dotted line). It has a broad intense band with vibrational structure between 570~470 mμ, which may be ascribed to the absorption principally due to the π-electron system in the molecule. The first bands at 510 and 490 mμ in crystalline state coincide with the above π-band in liquid state. Therefore we conclude that the π-band is bathochromic and hyperchromic in the b-absorption rather than in the a-absorption.

Conforming the probable orientation of molecules with the above result, we can reach the conclusion that the absorption parallel to the molecular plane is bathochromic and hyperchromic to the absorption perpendicular to it. In other words, the general rule about the dichroism of molecular compounds does not hold here and naphthazarine indicates similar dichroic property to common aromatic crystals. This conclusion suggests to us that a possibility of forming a molecular compound like quinhydrone is not probable in the present case.

If there exists any overlap of the π-orbitals that are thrust out perpendicularly from each molecular plane, the feature of the spectra would be expected to produce a marked change.(1)

Summary

Absorption spectra of diphenyldiacetylene and naphthazarine in crystalline state as well as in solution have been measured quantitatively in the visible and ultraviolet region. In the former compound, it has been found that the acetylene group indicates similar dichroic property to the benzene ring except for the fact that the dichroism of the former is more remarkable than that of the latter. From the dichroic property of naphthazarine, it has been concluded that the substance exists as the monomer and does not form the molecular compound like quinhydrone even in crystalline state.

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Department of Chemistry, Faculty of Science,
Osaka University, Osaka