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Dichroisms of Benzene Rings. II. The Dichroisms of *m*-Dinitrobenzene and Anthraquinone

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The dichroisms of *m*-dinitrobenzene and anthraquinone, the crystal structures of which had been perfectly determined by X-ray analysis, were measured by the microscopic method. The regularity in the previous report was found to hold also for the present cases; the ‖-absorptions were always more bathochromic and hyperchromic than the ⊥-absorptions. In conclusion, the above general rule about the π-band of the benzene ring was criticized from the viewpoint of electronic theory.

Introduction

In the previous study,[1] the dichroisms of hexamethylbenzene and hexabromomethylbenzene crystals, in which all the benzene rings are parallel to each other, were measured and remarkable dichroisms were observed. But such a simple structure is rarely found in crystals of most of the common aromatic compounds; that is, their benzene rings are apt to incline to each other.

Accordingly, in the present work, *m*-dinitrobenzene and anthraquinone whose benzene rings are not parallel to each other have been selected and their dichroisms in the visible and the ultraviolet region have been measured by the microscopic method. The angle between neighboring molecular planes is known from the data of their X-ray analysis.

Experimental

Materials. ***m*-Dinitrobenzene.**—Colorless acicular crystals were obtained by the recrystallization from the alcoholic solution, m.p. 91°, rhombic system, straight extinction. Remarkable cleavages are found along the (100) plane, as shown in Fig. 1. The X-ray vibration photographs along the three axes were taken with the crystal used for the dichroism measurement, and the axial relation was confirmed referring to the data of the X-ray analysis.

Anthraquinone.—Light yellow acicular crystals were produced from the amyl acetate solution, m.p. 273°, rhombic system, straight extinction, hexagonal prism. Cleavages are observed along the (110) and (010) planes, as shown in Fig. 2.

Apparatus.—The method of measuring the dichroism of the microcrystals has already been stated in the former report.[1]

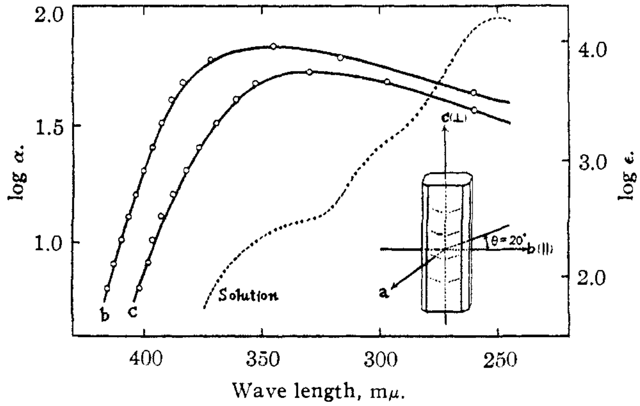

Fig. 1.—Absorption spectra of *m*-dinitrobenzene.

Discussion of the Results

(1) ***m*-Dinitrobenzene.**—According to the X-ray analysis of Archer,[2] all the benzene rings are parallel to the *a*-axis, inclining at an angle of 20° to the *b*-axis and piled up along the *c*-axis, as shown in Fig. 1. (Dotted lines drawn in the crystal show graphically the orientation of the molecule.) The absorption curves by linearly polarized light with the electric vectors parallel to the *b*- and *c*-axes are shown in Fig. 1, and their numerical data are summarized in Table I.

TABLE I

	$\lambda_{\max}$, mμ	log $\alpha_{\max}$
b-abs.	345	1.83
c-abs.	330	1.73
$\Delta\lambda_{\max}$ = 15		Δ log$\alpha_{\max}$ = 0.1

The dotted line in the same figure shows the absorption spectrum of *m*-dinitrobenzene[3] in an aqueous solution. From the shape of this curve, we can easily discriminate between the first band at about 340 mμ (log $\epsilon_{\max}$ 2.45) and the second band at about 300 mμ (log $\epsilon_{\max}$ 3.10). They are due to the nitro groups and the π-electrons in the molecule, respectively.

But in the crystalline state, they are superposed into one broad band, being more bathochromic than the absorption in solution. In other words, the mutual Stark effects of neighboring molecules produced a single complicated level. Consequently, it is impossible for us to take out the π-band only. But as seen in the spectrum of the solution, the π-absorption is about five times stronger than that of the nitro groups. So the following assumption may be permitted that the dichroism observed in the crystalline state is principally due to the anisotropic character of π-electrons under the influence of the nitro groups.

As seen in Fig. 1, the absorption parallel to the *b*-axis is more bathochromic and hyperchromic than the one parallel to the *c*-axis.

But the dichroism of the π-band observed here is less remarkable than in the case of hexamethylbenzene crystal.

This difference is due to the following reason. In hexamethylbenzene, the dichroism could be measured in the direction perfectly parallel or perpendicular to all the benzene planes, because every ring therein was parallel to each other. But in *m*-dinitrobenzene, there exists no direction parallel or perpendicular to every molecular plane, because they are inclined to each other. So we used linearly polarized lights parallel to the *b*- and *c*-axes, as stated above. The angle θ which the *b*-axis makes with the benzene plane is about 20°, and smaller than 45°. Consequently if the light

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[1] K. Nakamoto, THIS JOURNAL, **73**, 390 (1951).

[2] E. M. Archer, *Proc. Roy. Soc.* (*London*), **A188**, 51 (1946).

[3] G. Kortüm, *Z. physik. Chem.*, **B42**, 50 (1939).

vector is decomposed into two components, parallel and perpendicular to the benzene plane, the former component is larger than the latter of the light parallel to the *b*-axis. Namely, the light parallel to the *b*- (or *c*-)axis is abundant with the component parallel (or perpendicular) to the ring plane.

Thus, the regularity found in the previous report,[1] holds also for the present case; the ||-absorption is more bathochromic and hyperchromic than the ⊥-absorption. But the value of $\Delta \log\alpha_{max}$ is greatly decreased compared with the dichroism of hexamethylbenzene, because the angle θ is not zero.

(2) **Anthraquinone.**—According to the X-ray analysis of Hertel and Römer,[4] all the planar molecules of anthraquinone are parallel to the (001) plane. But recently Sen[5] has found that they make an angle of 27° with the *b*-axis, as seen in Fig. 2. The absorptions by linearly polarized light with the electric vectors parallel to the *b*-and *c*-axes were measured. Their curves and numerical data are given in Fig. 2 and Table II.

The dotted line in the same figure shows the absorption spectrum of an alcoholic solution.[6] The bands at 400 mμ ($\log\epsilon_{max}$ 2.0), 328 mμ (3.78) and 252 mμ (4.64) are the absorptions due to the carbonyl groups, π-electrons and σ-electrons of the molecule, respectively. Broad bands seen in the crystalline state are the superposition of the absorptions due to the carbonyl groups and the π-electrons. As the angle θ is 27°, and smaller than 45°, the same regularity as before holds also for the present case.

TABLE II

	λ_{max}, mμ	$\log\alpha_{max}$
b-abs.	380	1.84
c-abs.	355	1.74
$\Delta\lambda_{max}$ = 25		$\Delta \log\alpha_{max}$ = 0.1

General Discussion of the Results

From the measurements of dichroisms of the π-band in hexamethylbenzene, hexabromomethylbenzene, *m*-dinitrobenzene and anthraquinone, the following general rule has been derived: *the absorption with the electric vector vibrating parallel to the benzene ring is always more bathochromic and hyperchromic than the absorption with the electric vector vibrating perpendicularly to it.*

So if the above rule is applied to the crystal whose structure has not yet been perfectly determined by X-ray analysis, the orientation of benzene rings in the crystal will be found from the dichroism measurement. Thus the study of pleochroism plays an important role in the determination of the crystal structure, along with the X-ray analysis.

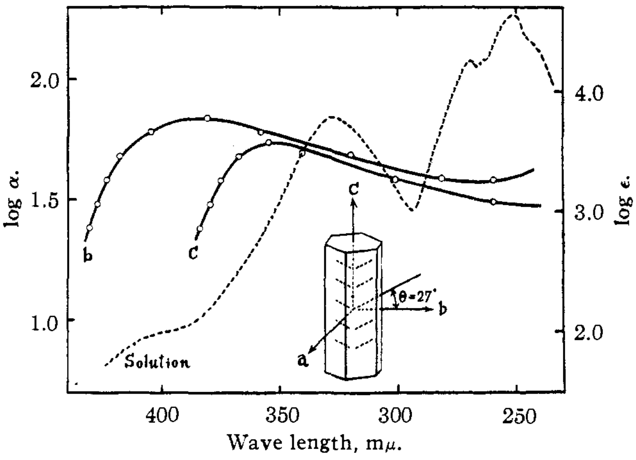

Fig. 2.—Absorption spectra of anthraquinone.

In conclusion, the above general rule is supported by electronic theory.[7,8] According to quantum mechanics, the π-electrons are more mobile in the ||-direction than in the ⊥-direction. In the direction along the benzene plane, *i.e.*, in the ||-direction, therefore, the electronic transition requires less energy and is more probable than in the ⊥-direction.[9] Thus, the ||-absorption becomes more bathochromic and hyperchromic than the ⊥-absorption.

The author wishes to express sincere thanks to Prof. R. Tsuchida for his kind guidance and Mr. Matsuda for his help in the X-ray experiment.

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RECEIVED JUNE 8, 1951

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(4) E. Hertel and G. H. Römer, *Z. physik. Chem.*, **B11**, 91 (1931).

(5) S. N. Sen, *Indian J. Phys.*, **22**, 347 (1948).

(6) R. A. Morton and W. T. Earlam, *J. Chem. Soc.*, 161 (1941).

(7) E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," 1940, p. 53.

(8) For example, see, M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," 1949, p. 10.

(9) For quantum mechanical treatments, see M. G. Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938); R. S. Mulliken, *ibid.*, **7**, 353 (1939).