Peculiarity of Dichroism of Aromatic Molecular Compounds. II. The Dichroisms of *s*-Trinitrobenzene—Anthracene and 4, 4′-Dinitrodiphenyl—Diphenyl

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Introduction

An earlier paper of this series⁽¹⁾ is concerned with dichroism of typical molecular compounds and the general rule regarding the dichroism of the first band principally due to the π-electrons of the benzene rings. That is, the absorption by the light with the electric vectors vibrating perpendicular to the molecular planes of both the components is always bathochromic and hyperchromic to the absorption by the light with those vibrating parallel to those planes. So, in the present investigation, measurements of dichroisms of molecular compounds, *s*-trinitrobenzene—anthracene and 4, 4′-dinitrodiphenyl — diphenyl have been made in visible and ultraviolet regions, and their results have been discussed applying the general rule stated above.

Experimental

Materials.—(1) *s*-Trinitrobenzene—Anthracene —Fine orange acicular crystals are produced by mixing the methanol solutions of both the components in the molar ratio of 1:1, and allowing the solution to evaporate at room temperature. M. p. 164°. Monoclinic system. Straight extinction. This substance shows dichroism; orange, when viewed with linearly polarized light whose electric vector vibrates parallel to the *c*-axis (needle axis) and light yellow, when observed with those vibrating parallel to the *b*-axis.

(2) (4, 4′ - Dinitrodiphenyl)$_3$ — Diphenyl — Pale yellow acicular crystals are prepared by mixing the hot acetone solutions of both the components in the molar ratio of about 3:1 and allowing the solution to cool gradually. Monoclinic system. A striking characteristic of this crystal is that it has no clear melting point, owing to continuous decomposition with the elevation of temperature.⁽²⁾ Straight extinction. Dichroism can not be observed with the naked eye.

Measurements.—Dichroisms of the crystals have been quantitatively measured by the microscopic method with microcrystals, as described in the former paper.⁽³⁾

Results and Discussion

(1) ***s*-Trinitrobenzene—Anthracene.**—In 1932, Briegleb and Schachowskoy⁽⁴⁾ studied the absorption spectrum of this molecular compound in chloroform solution and calculated the heat of dissociation from their spectroscopic data. As to the crystal structure, Hertel and Römer⁽⁵⁾ have inferred the orientation of both the molecules from the observed values of the lattice constants alone, and no further report has been presented.

Fig. 1 records the absorption spectra by linearly polarized lights with the electric vectors vibrating parallel to the *c*- and *b*-axes, respectively. The absorption curve of pure anthracene crystal by ordinary light is also shown for comparison (Curve 4). Absorption curves of both the components (Curve 1 and 2) and the molecular compound (Curve 3)⁽⁴⁾ in liquid state are given in Fig. 1. From the comparison of the absorption curves in crystalline state with that of the components in solution, it is evident that the bands at 500∼400 mμ in crystalline state consist mainly of the

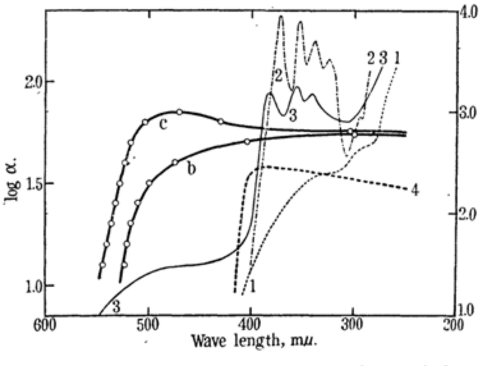

Fig. 1.—Absorption spectra of *s*-trinitrobenzene-anthracene and its components: 1, *s*-trinitrobenzene; 2, anthracene; 3, *s*-trinitrobenzene-anthracene; 4, anthracene in crystalline state (by ordinary light).

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

(2) K. Suzuki, Presented before the Division of Structural Chemistry at the 4th Meeting of the Japan Chemical Society, Tokyo, April, 1951.

(3) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 390 (1952).

(4) G. Briegleb and T. Schachowskoy, *Z. physik. Chem.*, **B 19**, 255 (1932).

(5) E. Hertel and G. H. Römer, ibid., **B 11**, 77 (1931).

absorption due to the π-electron system of aromatic rings of both the molecules. It should be noted that these bands absorb the same region with the characteristic band of the molecular compound in Curve 3. As already discussed in the former work,(1) all of these absorptions at 500∼400 mμ are essentially attributed to the intermolecular charge-transfer spectra resulting from an inter-benzoid overlap of the π-orbitals. Curve 3, however, does not indicate any distinct maximum since the anisotropic absorption in crystalline state is reduced by random orientation of molecules in liquid state.

As is shown in Fig. 1, the c-absorption is bathochromic and hyperchromic to the b-absorption. This result offers a further evidence to support the validity of the general rule for the dichroism of molecular compounds, if we accept the crystal structure predicted by Hertel and Römer for this compound. In other words, the c-absorption is bathochromic and hyperchromic to the b-absorption, because both the component molecules are piled up alternately along the c-axis making their molecular planes parallel to each other and the overlap of the π-orbitals that are thrust out perpendicularly from each molecular plane occur along the c-axis. We have, therefore, shown conclusively that the dichroism of this molecular compound can be interpreted by the general rule described before.

(2) **(4, 4′-Dinitrodiphenyl)$_3$—Diphenyl.** — Since 1946, Saunder and his co-workers(6) have studied the crystal structure of molecular compounds of 4, 4′-dinitrodiphenyl with various substituted diphenyls. According to their results, all of these compounds have a definite type of structure in which dinitrodiphenyl molecules form layers in face-centred array and lie one above another with a spacing of about 3.7 A. In a continuous arrangement of these layers, long tubular cavities are left running through the structure, and the other component molecules occupy these cavities and lie nearly normal to the planes containing dinitrodiphenyl molecules. The orientations of both the molecules in the crystal are shown graphically in Fig. 2. That is, these compounds have a peculiar structure which is quite different from that of typical molecular compounds. Moreover, based on the measurements of the closest intermolecular distance of approach, Saunder and his co-workers concluded that there is no localized bonding between the component molecules. So it is expected that the dichroism of such a compound will be considerably modified as compared with that of typical molecular compounds.

In the present paper, one of these molecular compounds, *(4, 4′-dinitrodiphenyl)$_3$—diphenyl*, is selected and its dichroism has been measured in the ultraviolet region. Absorption spectra by linearly polarized lights with the electric vectors vibrating parallel to the b- and c-axes, respectively, are shown in Fig. 2, and their numerical data are given in the following table.

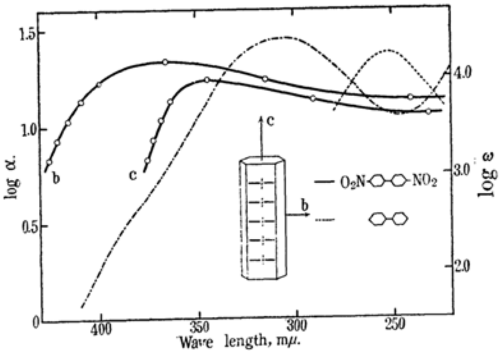

Fig. 2.—Absorption spectra of 4, 4′dinitrodiphenyl-diphenyl: —-—-, 4, 4′-dinitrodiphenyl; ----, diphenyl.

Table

	λmax. (mμ)	log αmax.
b-abs.	365	1.34
c-abs.	345	1.24

The spectra of both the components in alcoholic solutions are also marked in the same figure.

According to Niekerk and Saunder,(7) in the crystal of this compound, dinitrodiphenyl molecules are nearly parallel to the (001) plane, whereas diphenyl molecules are nearly normal to it and lie on the (010) plane. Comparing these results with our spectroscopic data, we may conclude that the b-absorption is the spectrum by the light whose electric vector vibrates parallel to the molecular plane of dinitrodiphenyl and perpendicularly to that of diphenyl. On the other hand, the c-absorption is the spectrum by the light whose electric vector vibrates perpendicularly to the molecular planes of dinitrodiphenyl and parallel to that of diphenyl.

So far, it is impossible to analyze these bands into the two absorptions due to dinitrodiphenyl and diphenyl, respectively. As is shown in the spectra of both the components in solution, however, dinitrodiphenyl (λmax, 308 mμ; log εmax, 4.39) is far more bathochromic to diphenyl (251 mμ; 4.26). It is reasonable to assume that this relation holds also for the spectra of both the components in crystalline state. Moreover, according to the stoichiometrical consideration of the mixing ratio in this compound, dinitrodiphenyl is expected to play a main rôle in the dichroism of the crystal. Thus, in the longer wave length region of these spectra, both the b- and c-absorptions can be assumed to consist principally of the absorption due to dinitrodiphenyl.

The fact that the b-absorption is bathochromic

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(6) D. H. Saunder, *Proc. Roy. Soc. London*, **A 188**, 31 (1946).

(7) J. N. van Niekerk and D. H. Saunder, *Acta Cryst.*, **1**, 44 (1948).

and hyperchromic to the *c*-absorption suggests that the general rule about the dichroism of common aromatic crystals(8) holds also for the longer wave length region in these spectra. Namely, the absorption which is parallel to the molecular plane of dinitrodiphenyl is bathochromic and hyperchromic to the absorption which is perpendicular to it. Thus, the results obtained from the dichroism measurement have led us to the conclusion that there does not exist $\pi-\pi$ attraction in the direction normal to the molecular plane of dinitrodiphenyl. In other words, the foregoing consideration suggests that the dichroism of this molecular compound is explicable on the assumption that it is only a kind of mixed crystals except that it has a definite combining ratio determined solely by the geometrical consideration in crystal structure.

Summary

Measurements of the dichroisms of molecular compounds, *s*-trinitrobenzene—anthracene and 4,4′-dinitrodiphenyl—diphenyl have been made quantitatively made in the visible and ultraviolet region. It can be concluded that the crystal of the former compound has the same dichroic property as the typical molecular compound already given in the previous report. The dichroism of the latter compound suggests that there exists no special attraction in the direction normal to the molecular plane of dinitrodiphenyl.

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(8) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 392 (1952).