Dichroisms of Benzene Rings. III. The Dichroism of *m*-Nitronitrosobenzene Monomer

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Introduction

In the previous works, the dichroisms of aromatic compounds(1), (2) and molecular compounds(3) have been measured, and the general rules about the π-band have been found in respective cases. Throughout these works, however, the band at the longest wave length side

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

was always superposition of the strong π-band and the weak band due to the substituents of the benzene ring. Accordingly, it was impossible to observe the dichroism characteristic of the substituents.

To measure the dichroism of the substituent band independently of the intense π-band, it is necessary to select a substance whose spectrum in crystalline state shows the band of the former, far apart from the latter in the ultraviolet region. As was shown in the spectrum of anthraquinone crystal,(2) the carbonyl band is superposed on the intense π-band, although they show definite peaks in solution. So the substance, which has both the bands far apart in the spectrum of the solution, is suitable for our purpose.

Nitrosobenzene derivatives have, generally, their characteristic bands due to the nitroso group at 700~800 mμ, and the π-bands due to the benzene ring at 300~400 mμ. They are therefore expected to appear separately even in the crystalline state.

In the present study, the spectra of *m*-nitronitrosobenzene monomer in crystalline state as well as in solution have been measured, and the results have been discussed in comparison with that of *m*-dinitrobenzene which had been reported before.(2)

Experimental

Material.—*m*-Nitronitrosobenzene was prepared by reduction of *m*-dinitroboenzene according to the method of Alway and Gortner.(4) Colourless powder (dimer). It melts at 91° to become a green liquid (monomer). For the purpose of getting fine crystals suitable for the measurement of dichroism, the ordinary method of recrystallization from the solution is not available, because the substance is unstable and apt to polymerize. By mixing the alcoholic solutions of *m*-nitronitrosobenzene and *m*-dinitrobenzene in the molar ratio of 1:1, light green acicular crystals were obtained. They are isomorphous to pure *m*-dinitrobenzene crystal, and have similar properties to it. Spectroscopic measurement, described later, revealed that they are composed of 25 per cent nitroso compound and 75 per cent dinitro compound. They show straight extinction, and dichroic property; light green by linearly polarized light with the electric vector vibrating parallel to the c-axis (needle axis), and light yellow, by the light with those vibrating perpendicular to it (b-axis).

Measurements.—Absorption spectra in solution were measured by the rotating sector method. Dichroism of the crystal was measured by the microscopic method mentioned in the former work.(1) Throughout these experiments, infrared sensitive photo-plates were used to measure the green region.

Results and Discussion

(1) The Spectrum of the Solution

Absorption spectra of *m*-dinitrobenzene and pure *m*-nitronitrosobenzene in alcoholic solutions are shown in Fig. 1. Numerical data characterizing these spectra are given in the following table.

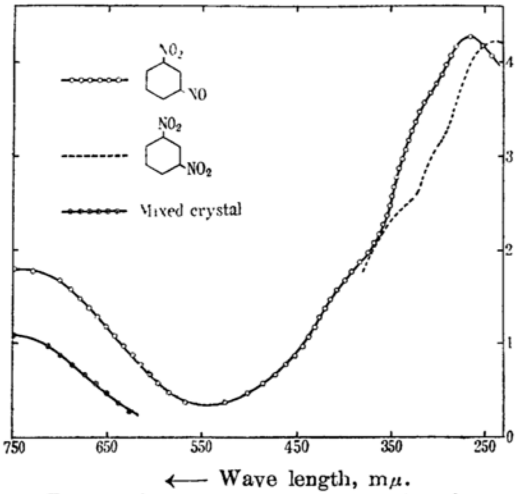

Fig. 1.—Absorption spectra of *m*-nitronitrosobenzene, *m*-dinitrobenzene and their mixed crystal in alcoholic solutions.

	Nitroso band	Nitro band	π-band	σ-band
m-Dinitrobenzene		330(2.5)	300(3.1)	250(4.2)
m-Nitronitrosobenzene	750(1.8)	390(1.8)	320(3.4)	265 (4.25)

Here the $\lambda_{max.}$ is expressed in mμ, and the log $\varepsilon_{max.}$ is given in brackets, respectively.

As is shown above, the substitution of one of the nitro groups by the nitroso group causes the occurrence of the nitroso band at about 750 mμ, and gives bathochromic and hypochromic effects to the nitro band. But the same substitution gives only small bathochromic and hyperchromic effects to the π- and σ-bands in the ultraviolet region. These changes in the spectrum can be easily explained by the facts that the nitroso group is more unstable than the nitro group, and a substitution of an unstable group for a stable group gives, generally, bathochromic and hyperchromic effects to all the bands in a molecule.

The absorption spectrum of an alcoholic solution of the mixed crystal is also shown in Fig. 1. From the comparison of log ε at 750 mμ in these two curves, the crystal was estimated to contain as much *m*-nitronitrosobenzene as 25 per cents.

(2) The Dichroism of the Crystal

The crystal used for the measurement contains

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(4) F. J. Alway and R. A. Gortner, *Ber.*, **38**, 1900 (1905).

25 per cent nitroso compound, as spectroscopically shown before. Practically, two components can mix at any ratio in crystal, and, moreover, no colour change can be seen at the mixing of their solutions. These chemical facts suggest that in the crystal used, the two components exist merely in a mixed state and not as a molecular compound.

So far, its crystal structure is unknown, although that of pure *m*-dinitrobenzene has been thoroughly studied.⁽²⁾ So the Debye-Scherrer photographs of both the crystals have been taken, as shown in Fig. 2. The resemblance of the two photographs means that the two crystals have similar structure and so, its crystal structure can be presumed as follows: the planar molecules* of *m*-nitronitrosobenzene in *m*-dinitrobenzene crystals are piled up along the needle axis (c-axis), making their molecular planes almost parallel to the a-axis and inclined by about 20° to the b-axis, as graphically shown in Fig. 3.

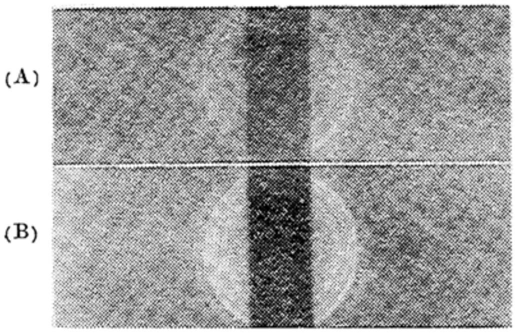

Fig. 2.—Debye-Scherrer photographs of pure *m*-dinitrobenzene (A) and the mixed crystal (B)

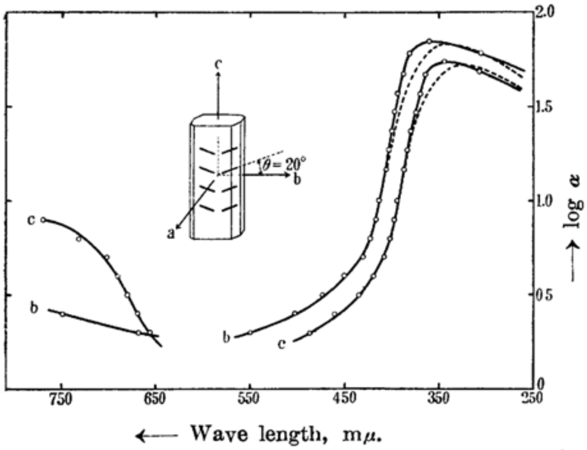

Fig. 3.—Absorption spectra of the mixed crystal (solid lines) and *m*-dinitrobenzene (broken lines) in crystalline states.

Absorption curves by linearly polarized lights with the electric vectors vibrating parallel to the b- and c-axes are shown in Fig. 3. As the angle θ between the molecular plane and the b-axis is only 20° and smaller than 45°, the light with the electric vector parallel to the b- (or c-) axis is abundant with the parallel (or perpendicular) component to the molecular plane. Conforming to these discussions with the experimental result, we can reach the conclusion that the ∥-absorption in the ultraviolet region is bathochromic and hyp~~so~~erchromic to the ⊥-absorption, whereas the former in the visible region is remarkably hyp~~s~~ochromic to the latter.

(3) The Dichroisms of pure *m*-Nitronitrosobenzene Monomer

If the absorption due to pure *m*-dinitrobenzene is reduced from the above results, the dichroism of pure *m*-nitronitrosobenzene is obtained.

(i) Visible Region

As is clearly shown in the former work, *m*-dinitrobenzene has no absorptions in the visible region. So the above result in this region is exclusively due to pure nitroso compound. Thus, it is concluded that the ⊥-absorption is hyp~~so~~erchromic to the ∥-absorption. The origin of this band is the nitroso group in the molecule, as is definitely shown in the spectrum of the solution. As a result, the absorption responsible for the green colour of *m*-nitronitrosobenzene is concluded to be due to the electronic transition polarized perpendicularly to the C—N—O bond. Recently Fenimore⁽⁵⁾ obtained the same result as above. He, however, used the assemblage of many microcrystals which orientated practically parallel to each other, and measured the dichroism in the narrow range between 700∼800 mμ. Whereas, we used only one single crystal, and measured in a wider range between 750∼250 mμ.

(ii) Ultraviolet Region

Broad bands seen in the ultraviolet region consist mainly of the π-absorption, as already discussed in the former paper.⁽²⁾ In Fig. 3 is shown the present result (solid lines) along with the dichroism of *m*-dinitrobenzene (broken lines). Both spectra are very similar to each other, except that the former is slightly bathochromic in comparison with the latter. This result suggests that both substances have similar dichroic property, and the dichroism of the π-band does not suffer any considerable change, even if *m*-dinitrobenzene in the crystal is replaced by *m*-nitronitrosobenzene.

Thus, we conclude that the ∥-absorption in pure *m*-nitronitrosobenzene is bathochromic and hyp~~so~~erchromic to the ⊥-absorption. If both molecules formed a molecular compound, the feature of the spectrum would be quite different.⁽³⁾ This result, along with the above mentioned chemical facts, confirms the theory that the crystal observed here is only a mixed crystal, and not a molecular compound.

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* The steric configuration of nitrosobenzene derivatives is a subject of much discussion. None of these crystals, however, have ever been studied by X-ray analysis. So, in the present paper, the C-N-O bond is assumed to be nearly linear and coplanar with the benzene plane.

(5) C. P. Fenimore, *J. Am. Chem. Soc.*, **70**, 3114 (1948).

Summary

Absorption spectra of *m*-nitronitrosobenzene monomer in crystalline state as well as in solution have been measured quantitatively in the visible and the ultraviolet regions. In its π-band of the ultraviolet region, the general rule about the π-band of the benzene ring was found to hold also for the present case. In regard to the nitroso band of the visible region, the absorption by linearly polarized light with the electric vector vibrating perpendicular to the C—N—O bond was hyperchromic to the absorption by the light with those vibrating parallel to it. This result suggests that the green colour of *m*-nitronitrosobenzene is due to the electronic transition polarized perpendicularly to the C—N—O bond.

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