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# Mechanism of the Color Reaction between *m*-Dinitrobenzene and Alkali Cyanide. II. Color Reaction Products of 2,4-Dinitroaniline with Potassium Cyanide (Organic Analysis. LXXII[1])

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Four main coloring matters (I, II, III and IV) were isolated in crystalline forms in the color reaction of 2,4-dinitroaniline with potassium cyanide and their chemical structures were investigated.

I was determined as 2,3-diamino-6-nitrobenzamide. II and III were characterized as 2,3-dihydro-3-oxo-1H-indazole derivatives as shown in Chart 1. IV was 2,6-dinitro-3-aminophenol. The schema of reaction to form those coloring matters was also presented.

In a previous paper of this series,[3] the mechanism of color reaction between *m*-dinitrobenzene and potassium cyanide was discussed by isolating cyano- and nitro-substituted 2,3-dihydro-3-oxo-1H-indazoles as the main coloring matters of the reaction. This paper extends the study to the color reaction of 2,4-dinitroaniline with potassium cyanide.

## Isolation of the Reaction Products

An aqueous ethanol solution of 2,4-dinitroaniline gives a deep violet color when heated with a large excess of potassium cyanide. The reaction conditions to give the maximum intensity of the developed color were almost identical with those of *m*-dinitrobenzene.[3] Therefore, the procedure adopted to isolating reaction products was almost similar to that described in the previous paper, except that the molar ratio of potassium cyanide to 2,4-dinitroaniline, 3:1, was chosen to minimize the formation of brown resinous matter, which increased with the increasing molar ratio of potassium cyanide.

The reaction mixture was neutralized with phosphoric acid and extracted with ethyl acetate. The dried extract on evaporating the solvent was dissolved in ethyl acetate and separated chromatographically on alumina to give four main fractions, which were divided by their colors on alumina.

The largest and first fraction, which showed a brown band on alumina, gave red brown needles of mp 209—211° (decomp.) (I).

The second and third fractions formed a red violet and a violet band on alumina, and gave dark red violet needles with metallic luster of mp 218—220° (decomp.) (II) and dark violet needles with metallic luster of mp higher than 300° (decomp.) (III), respectively.

The fourth fraction, an yellow band on alumina, gave red brown prisms of mp 216° (IV). This substance was yielded in an enough amount to characterize when the color reaction was continued for a longer time. The fourth fraction also left a small amount of orange prisms of mp 204—206°, but they could not be obtained in enough quantity for a further study.

Many other small fractions were observed on the chromatogram, but they were difficult to treat successfully.

1) Part LXXI: K. Kohashi, Y. Ohkura and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **18**, 2151 (1970).
2) Location: *Katakasu, Fukuoka.*
3) T. Momose, Y. Ohkura and J. Shiota, *Chem. Pharm. Bull.* (Tokyo), **16**, 2370 (1968).

The absorption spectra of I, II, III and IV (Fig. 1) showed their maxima at 487, 510, 527 and 415 m$\mu$, respectively, when dissolved in a sodium dihydrogen phosphate–sodium hydroxide buffer solution of pH 13.4. This pH value corresponded to that of the reaction medium. On the other hand, the reaction mixture had two absorption bands around 500 and 410 m$\mu$ (Fig. 1). The former might mainly be caused by I, II and III and the latter partly by IV, indicating that the separated products were the main coloring matters of the reaction.

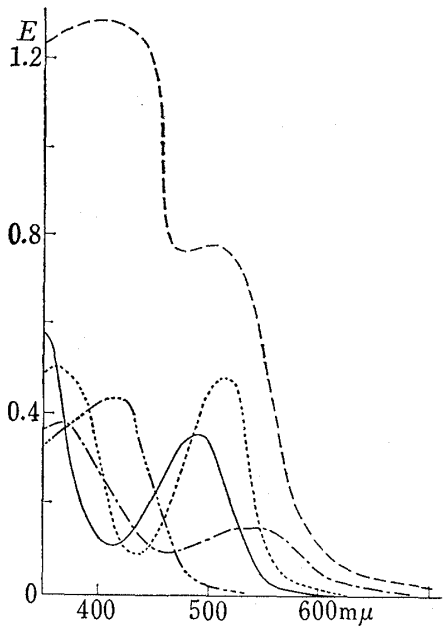



Fig. 1. Absorption Spectra of I, II, III, IV and the Reaction Mixture, dissolved in Buffer Solution of pH 13.4

———: 9.4 $\mu$g/ml solution of I
----------: 13.2 $\mu$g/ml solution of II
—·—·—: 5.2 $\mu$g/ml solution of III
— ··· —: 10.0 $\mu$g/ml solution of IV
— — —: 200 times diluted mixture with the buffer solution.

**Structures of the Reaction Products and Reaction Mechanism**

The molecular formula of I was established from the molecular ion ($M^+$) in a high resolution mass spectrum (MS) as $C_7H_8O_3N_4$. The infrared (IR) spectrum of I showed the presence of amino, nitro, acid amide and adjacent two aromatic hydrogens by their absorption bands at 3490 and 3325 ($\nu_{NH_2}$), 1545 and 1340 ($\nu_{NO_2}$), 1655 and 3190 ($\nu_{C=O}$ and $\nu_{NH_2}$), and 820 $cm^{-1}$ ($\delta_{CH}$, out of plane), respectively. The MS supported the presence of those functional groups in the molecule by the fragment ions of $M^+$-$NH_3$, $M^+$-$NH_3$–NO, $M^+$-$2NH_3$–NO, $M^+$-$NO_2$–CO and $C_6H_5N_2$. The presence of adjacent two aromatic hydrogens was confirmed in the nuclear magnetic resonance (NMR) spectrum of the compound by the signals of two doublets at 6.32 and 7.80 $\delta$ (Table I). Furthermore, these chemical shifts suggested that the amino and nitro groups were located at *p*,*p*′-positions. Two broad signals shown in Table I were assumed to be caused by the protons of two amino groups, because they disappeared immediately after adding a small amount of heavy water to the sample solution even in the absence of a trace amount of an acid. A signal ascribable to amide was not observed in the NMR spectrum, though its existence was suggested in the IR spectrum. The same phenomenon was also observed in the NMR spectrum of authentic benzamide dissolved in the same solvent.

Acetylation of I gave a diacetate as orange needles, mp 241°, which had ester carbonyl bands at 1700 and 1735 $cm^{-1}$ in the IR spectrum and a practical singlet due to acetyl protons in the NMR spectrum (Table I).

These evidences clearly indicated that I was 2,3-diamino-6-nitrobenzamide. It is significant to note that such an *o*-aminobenzamide as I was isolated from the reaction mixture, because it was already postulated as one of the possible intermediate of the main coloring matters, 2,3-dihydro-3-oxo-1H-indazoles in the previous paper.[3]

The measured value of $M^+$ of II in the MS agreed well with the formula of $C_7H_6O_3N_4$, and main fragment ions observed were $M^+$-$NO_2$, $M^+$-$NO_2$–$NH_3$ and $C_6H_5N_2$. The IR spectrum of II had characteristic bands caused by aromatic amino, acid amide, nitro and adjacent two aromatic hydrogens at 3415 ($\nu_{NH}$), 3265 and 1660 ($\nu_{NH}$ and $\nu_{C=O}$), 1520 and 1370 ($\nu_{NO_2}$) and 825 $cm^{-1}$ ($\delta_{CH}$, out of plane), respectively. Two broad signals at 6.80 and 8.45 $\delta$ in the NMR spectrum (Table I) were assigned to aromatic amino and imino protons, respectively, from their integral intensities and the result of deuterium exchange. A signal ascribed to amide

Table I. NMR Spectral Data[a,b] of I, I-Diacetate, II and III

| Product | Solvent | Ar H | Amino H or imino H | Acetyl H |
|---|---|---|---|---|
| I | $(CD_3)_2CO$ | 6.32 d<br>1H, $J$=8.4<br>7.80 d<br>1H, $J$=8.4 | 6.60 b<br>2H<br>7.37 b<br>2H | |
| I-Diacetate | $CF_3COOH$ | 8.38 d<br>1H, $J$=9.0<br>8.65 d<br>1H, $J$=9.0 | | 2.60 s<br>6H |
| II | $(CD_3)_2CO$ | 7.08 d<br>1H, $J$=9.6<br>7.37 d<br>1H, $J$=9.6 | about 6.80 b<br>2H<br>about 8.45 b<br>1H | |
| III | $(CD_3)_2CO$ | 6.28 s<br>1H | 6.65 b<br>1H<br>7.60 b<br>2H | |

a) Chemical shifts and $J$ are expressed in $\delta$ (ppm) and cps, respectively.
b) Following abbreviations are used. s: singlet, d: doublet, b: broad

proton was not observed in the NMR spectrum[4] as in the case of I. On the other hand, II showed the similar chemical behaviors to those of 2,3-dihydro-3-oxo-1H-indazole described in the previous paper.[3]

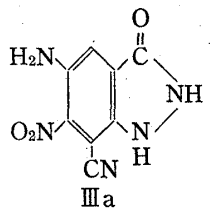
Above data directly indicated that the compound might have a structure of 2,3-dihydro-4-nitro-3-oxo-1H-indazole which had an amino group in 5 or 7 position of the molecule. The chemical shifts of adjacent two aromatic protons (7.08 and 7.37 $\delta$) in the NMR spectrum (Table I) suggested that the amino group might be present at 5 position, otherwise the distance between two shifts might become greater than the present value mainly by the deshielding effect of 4-nitro group and the shielding effect of 7-amino group on 5- and 6-protons, respectively. Therefore, II should be 2,3-dihydro-4-nitro-5-amino-3-oxo-1H-indazole.

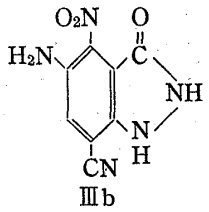
From the value of $M^+$ of III in the MS, III was determined to have the formula of $C_8H_5O_3N_5$, and the main fragment ions were $M^+$-NH, $M^+$-NO, $M^+$-$NO_2$–$NH_3$ and $C_6H_5N_2$. The IR spectrum of III suggested that the presence of amino, acid amide, nitrile, nitro and isolated aromatic hydrogen in the molecule by absorption bands at 3505 and 3325 ($\nu_{NH_2}$), 3175 and 1690 ($\nu_{NH}$ and $\nu_{C=O}$), 1560 and 1310 ($\nu_{NO_2}$) and 895 $cm^{-1}$ ($\delta_{CH}$, out of plane), respectively. The NMR spectrum of the compound (Table I) showed a singlet at 6.28 $\delta$ which confirmed the existence of an isolated aromatic hydrogen. Two broad signals were ascribed to aromatic amino and imino protons as shown in Table I from the result of deuterium exchange. The existence of acid amide, which was suggested by the IR spectrum, was not confirmed from the NMR spectrum similarly as in the case of II. Furthermore, III showed the same chemical behaviors as those of II.

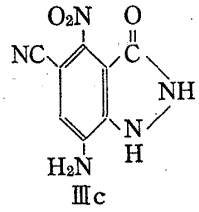
Those spectral evidences and the chemical behaviors indicated that III should be a 2,3-dihydro-3-oxo-1H-indazole derivative which had a nitro, a nitrile and an amino group in the benzene ring of the molecule, and three possible structures of IIIa, IIIb and IIIc might be considered.

The difference of the substituent contribution to the chemical shift of aromatic proton in the NMR spectrum among the three structures might be occured by the substituted positions of nitrile and acid imino groups. An intense shielding effect of *o*-amino group on the

4) This fact seemed to be the same phenomenon that authentic 2,3-dihydro-3-oxo-1H-indazole dissolved in acetone-$d_6$ or dimethylsulfoxide-$d_6$ gave no signal due to imide proton in the NMR spectrum.


IIIa


IIIb


IIIc

aromatic proton might be reduced by the deshielding effect of *o'*-nitrile in the structures of IIIb and IIIc.[5] On the other hand, the deshielding effect of *o*-acid imino group on the aromatic proton was already shown to be negligible in 2,3-dihydro-6-nitro-3-oxo-1H-indazole-5-carbonitrile dissolved in dimethylsulfoxide-$d_6$ (the chemical shift of aromatic protons=7.41 $\delta$), as reported in the previous paper.[3] Consequently in the stucture of IIIa, the chemical shift of aromatic proton might be mainly controlled by the shielding effect of *o*-amino group, but not by the weak effect of *p*-nitrile, *m*-nitro and *m'*-imino groups. Therefore, the structure of IIIa might most satisfactorily explain the present value of chemical shift, and so III might be 2,3-dihydro-5-amino-6-nitro-3-oxo-1H-indazole-7-carbonitrile.

It is of much interest to yield 2,3-dihydro-3-oxo-1H-indazoles in the present reaction as well as in the color reaction of *m*-dinitrobenzene and potassium cyanide, and now it may be said that such indazole derivatives are in general the main coloring matters of the reactions between *m*-dinitrobenzene derivatives and alkali cyanides.

IV was identified as 2,6-dinitro-3-aminophenol[6] by the direct comparison of its physical properties with an authentic sample. It is note worthy that the phenol partly concerned with the color development in the reaction.

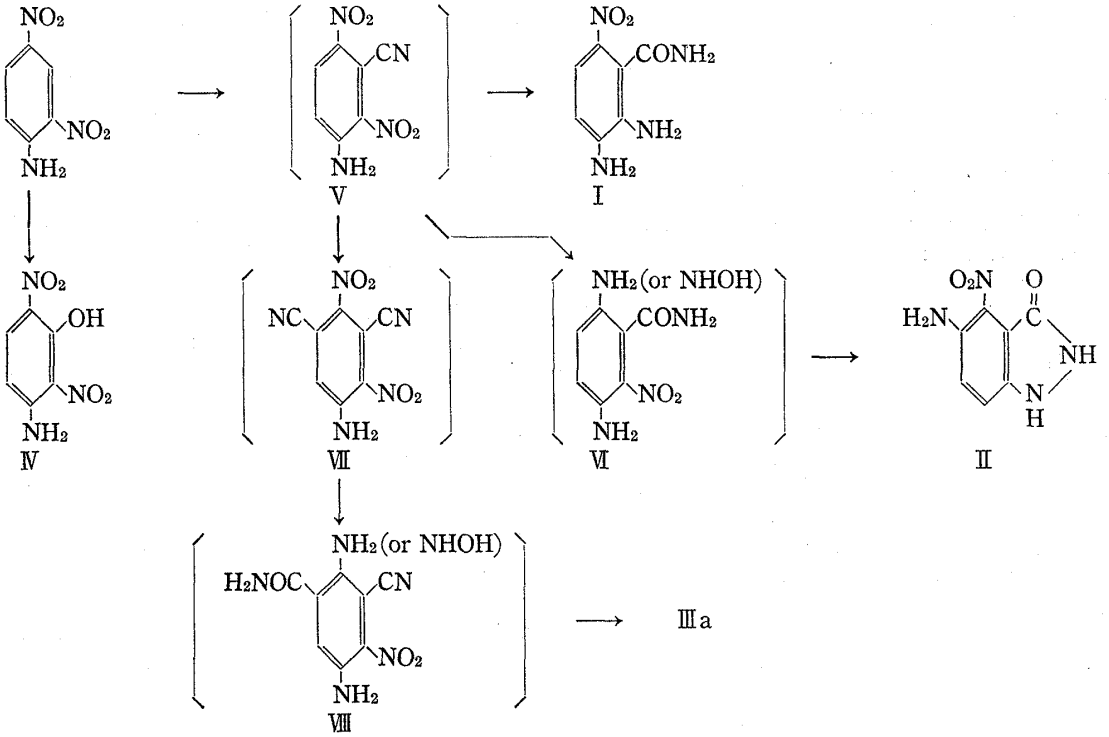


Chart 1. Schema of the Reaction to Form I, II, III and IV

5) J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," II, Pergamon Press, London and New York, 1966, p. 749.

6) This phenol had already been obtained in the reaction of 2,4-dinitroaniline with potassium cyanide, but the structure had remained unknown; E. Lippmann and F. Fleissner, *Monots. Chem.*, 7, 95 (1886). Later, it was determined as 2,?-dinitro-3-amino-phenol; W. Borsche and E. Feske, *Chem. Ber.*, **61**, 690 (1928). The questioned position of the nitro group was decided to be located at 6 from the NMR spectral data described in Experimental.

Now, the schema of reaction to form I, II, III and IV might be expressed as shown in Chart 1. A nitrile was first introduced in 3 position of 2,4-dinitroaniline to form V, then hydrolized to an acid amide, and the nitro group in 2 position was reduced to form I. On the other hand, when the 4-nitro group of V was firstly reduced, the resulting amino or hydroxylamino group of VI might combine with the amide group by oxidation or dehydration to afford II.

If one more nitrile was introduced in 5 position of V to form VII, IIIa might be formed by the ring closure of the reduction and hydrolysis product (VIII) of VII in the same way as described above.

IV might be formed by introducing a hydroxyl group in 3 position of 2,4-dinitroaniline by the prolonged heating under the alkaline condition of the reaction.

## Experimental[7]

**Isolation of the Reaction Products**——To a solution of 10 g of 2,4-dinitroaniline in 100 ml of EtOH, 10.5 g of KCN dissolved in 100 ml of $H_2O$ was added and heated at 70° for 15 min with occasional shaking. After cooling by adding ice–water, the mixture was carefully neutralized with diluted $H_3PO_4$, and $N_2$ gas was passed through the mixture for 30 min to remove HCN.

The resulting mixture was extracted with about 300 ml of AcOEt 3 times and the combined AcOEt layer was washed with $H_2O$, dried over $Na_2SO_4$, and evaporated to almost dryness *in vacuo*. The residue was dissolved in 100 ml of AcOEt by warming and poured onto a column packed with 500 g of HCl–treated and strongly activated alumina,[8] and eluted with AcOEt to afford four large fractions, from which the crystals (I, II, III and IV) were separated when the each eluate was concentrated.

**I**——Red brown needles, mp 209—211° (decomp.) (from AcOEt), Yield 40 mg. Soluble in acetone and AcOEt, insoluble in benzene and $H_2O$. Mass Spectrum *m/e*: 196.060 ($M^+$), 179.033 ($M^+$-$NH_3$), 149.035 ($M^+$-$NH_3$–NO), 132.008 ($M^+$-2$NH_3$–NO), 122.072 ($M^+$-$NO_2$–CO), 105.044 ($C_6H_5N_2$). UV $\lambda_{max}^{H_2O\ (pH\ 13.4)}$ m$\mu$ (log $\varepsilon$): 487 (3.88).

**I-Diacetate**——65 mg of I was treated with $Ac_2O$ and $H_2SO_4$ in the usual manner. After adding $H_2O$, the mixture was neutralized with $NaHCO_3$ and separated crystals were recrystallized from MeOH to orange needles, mp 241°. Yield 30 mg. *Anal.* Calcd. for $C_{11}H_{12}O_5N_4$: C, 47.14; H, 4.32; N, 19.99. Found: C, 47.21; H, 4.31; N, 20.05.

**II**——Dark red violet needles with metallic luster, mp 218—220° (decomp.) (from acetone and benzene (1:3)). Yield 50 mg. Soluble in acetone, sparingly soluble in AcOEt, ether and benzene, insoluble in $H_2O$. Mass Spectrum *m/e*: 194.044 ($M^+$), 148.049 ($M^+$-$NO_2$), 131.025 ($M^+$-$NO_2$–$NH_3$), 105.044 ($C_6H_5N_2$). UV $\lambda_{max}^{H_2O\ (pH\ 13.4)}$ m$\mu$ (log $\varepsilon$): 510 (3.85), 355 (3.88).

**III**——Dark violet needles with metallic luster, mp 300°< (from acetone, yield 20 mg. Soluble in acetone, sparingly soluble in AcOEt, ether, benzene and $H_2O$. Mass Spectrum *m/e*: 219.039 ($M^+$), 204.027 ($M^+$-NH), 189.040 ($M^+$-NO), 156.018 ($M^+$-$NO_2$–$NH_3$), 105.047 ($C_6H_5N_2$). UV $\lambda_{max}^{H_2O\ (pH\ 13.4)}$ m$\mu$ (log $\varepsilon$): 527 (3.80), 360 (4.19).

**IV**——2,6-Dinitro-3-aminophenol, red brown prisms, mp 216° (from AcOEt), yield 10 mg when the reaction was continued for 40 min. This substance was more easily eluted with acetone than with AcOEt in the chromatographic separation. No depression was observed on admixture with an authentic sample. Its IR spectrum was identical with that of an authentic sample. NMR ($(CD_3)_2SO$) $\delta$: 6.48 (1H, doublet, $J$=10.2 cps, ArH), 7.95 (1H, doublet, $J$=10.2 cps, ArH), 7.76 (3H, broad singlet, OH and $NH_2$). The broad singlet disappeared by treating with $D_2O$. UV $\lambda_{max}^{H_2O\ (pH\ 13.4)}$ m$\mu$ (log $\varepsilon$): 415 (3.93).

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7) UV spectra were measured by a Shimadzu SV-50A Spectrometer in a cell of 10 mm optical length, IR spectra by a Koken DS-301 Spectrometer in KBr pellets, NMR spectra by a JNM C-60H Spectrometer at 60 Mc with tetramethylsilane as internal standard, and MS by a Hitachi JM-7E Mass Spectrometer.

8) Commercial activated alumina (Ishizu, 300 meshes) was dispersed in 20% HCl, allowed to stand for 2 days and filtered. After washing with $H_2O$, it was air–dried and activated at about 150° for about 6 hr.