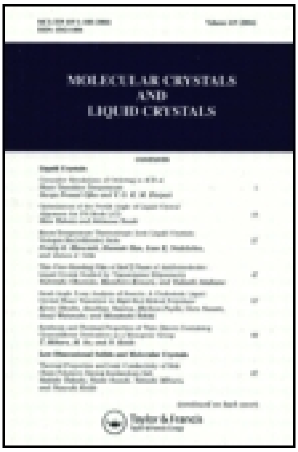

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Reaction Product of Tcnq with P-Phenylenedimalononitrile and the Chromic Phenomena

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REACTION PRODUCT OF TCNQ WITH P-PHENYLENEDIMALONONITRILE AND THE CHROMIC PHENOMENA

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Abstract Complex formation of 7,7,8,8-Tetracyanoquinodimethane (TCNQ) with p-phenylenedimalononitrile (molr ratio 1:2) was assumed by DSC and IR spectral measurements. The complex shows very sensitive chromic phenomena when it contacts with moist air or with metal carbonates due to formation of TCNQ anion radical or formation of the anion radical salts.

INTRODUCTION

7,7,8,8-Tetracyanoquinodimethane (TCNQ) and two types of the salts represented by $M^+(TCNQ^{\cdot-})$ and $M^{n+}(TCNQ^{\cdot-})_n(TCNQ)$ have been investigated extensively to obtain high electrical conductivity materials. The TCNQ anion-radical salts were synthesized by treatment of TCNQ with metal iodide or with certain metals in acetonitrile at room temperature.[1] Recently we obtained a product that shows very sensitive chromic phenomena by treatment the TCNQ anion radical salts with HCl. This report describes structure and chromic phenomena of the product.

PREPARATION AND PROPERTIES OF THE PRODUCT

We obtained $M^+(TCNQ^{\cdot-})$ and $M^+(TCNQ^{\cdot-})(TCNQ)$ by grind of a mixture of TCNQ and metal hydroxide. For example, a mixture of TCNQ and potassium hydroxide (molar ratio, 2:3) was ground in a mortar for 2 h under sun light irradiation. Navy blue powdered solid was washed with ethanol to remove unreacted potassium hydroxide and then with acetonitrile and ether on the filter to obtain $K^+(TCNQ^{\cdot-})$ in 80% yield. Similar treatment was carried out to the mixture of molar ratio; NaOH : TCNQ = 2 : 3, CsOH : TCNQ = 3 : 2 to obtain $Na^+(TCNQ^{\cdot-})$ and $(Cs^+)_2(TCNQ^{\cdot-})_2(TCNQ)$ respectively in high yield. IR spectra of these products were identical with that of authentic samples. Navy blue of the anion-radical salts changed to greenish-yellow when it was treated with hydrochloric acid. We found that the greenish-yellow precipitate, named A, shows very sensitive chromic phenomena when it contacts with metal carbonate or with many organic materials like phenol derivatives, triaryl methane, triaryl carbinol, fluorene derivatives, and 2,4,5-triaryl imidazole derivatives.

Example 1. At first we pushed a palm on clean white filter paper. No image is observed of course on the filter paper. Then, we painted with a light yellow dioxane solution of A on the filter paper. Image of the palm appeared at once with blue showing clear finger prints.

Example 2. We painted some pictures on the white clean filter paper with aqueous solution of K_2CO_3, Cs_2CO_3, or $SrCO_3$. After drying, dioxane solution of A was applied to the filter paper randomly. The picture written on the filter paper took color clearly with blue, purple, or green respectively. FIGURE 1 and TABLE I show absorption spectra of the colored papers.

TABLE I Absorption Maxima of Colored Paper

SALT	λ_{max}(nm)						
Li_2CO_3	361				642	735(sh)	846
Na_2CO_3	336	383	497(sh)	584	655(sh)		917
K_2CO_3	336	380		585	653(sh)		868
Rb_2CO_3	368		505	618			946
Cs_2CO_3	343		524	578		773	855

IR, ESR, and NMR spectra of A suggested that A consists of TCNQ, p-phenylenedimalononitrile (H_2TCNQ) and another unidentified substance. The group of L.R.Melby reported that treatment of salt of $TCNQ^{\cdot-}$ with strong mineral acid affords a mixture of TCNQ and H_2TCNQ.[1b]

On the other hand, we found that products which were obtained by milling of mixtures of TCNQ and H_2TCNQ in various molar ratios show the same chromic phenomena as that of A. The milled solid in the molar ratio of TCNQ:H_2TCNQ=1:2, named B, showed the strongest coloration. To clarify the mechanism of the chromic phenomena we carried out IR, UV, DSC measurements of the milled solid.

DSC diagrams

TABLE II shows thermal analytical data of milled products of TCNQ with H_2TCNQ.

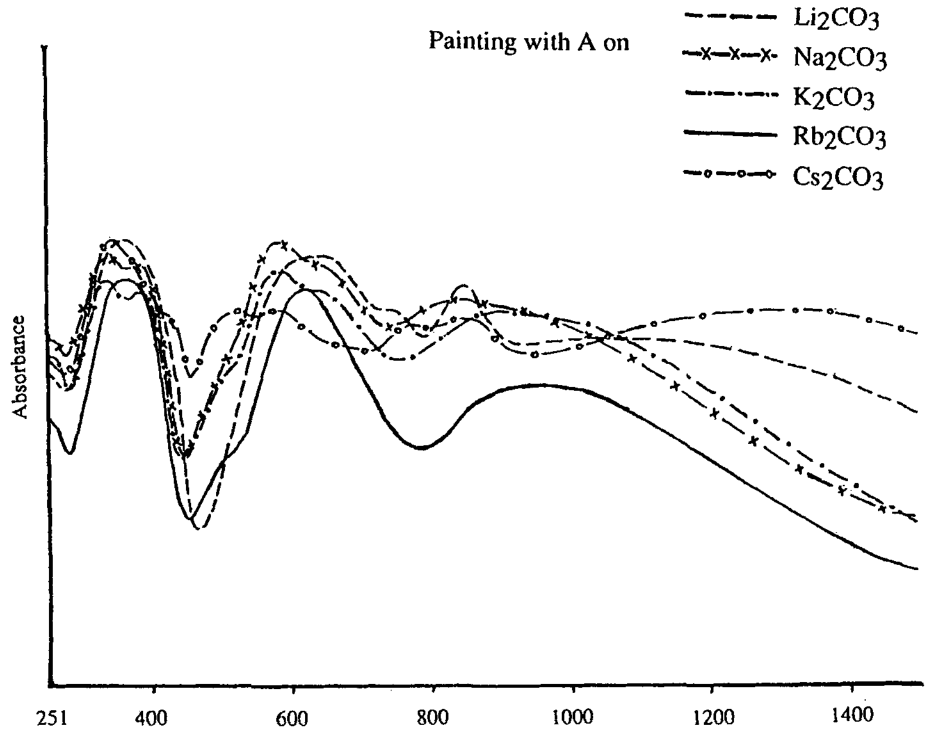


FIGURE 1 Absorption spectra of colored paper

TABLE II Thermal Analyses of the Milled Products (DSC) (Molar Ratio, TCNQ:H_2TCNQ), ° C

molar ratio	endothermic change(Δ H,J/g)	exothermic change (Δ H, J/g)
1: 10	229(38)	242(274)
1: 7	229(130)	244(322)
1: 3	229(184)	243(371)
1: 2	229(192)	245(362)
2: 3	229(178) 292(5)	245(323)
1: 1	229(158) 293(29)	244(276) 347(109)
3: 2	229(134) 292(37)	245(248) 340(180)
2: 1	229(91) 293(65)	244(240) 347(194)
3: 1	229(70) 293(211)	245(151)
7: 1	229(33) 293(363)	242(55)
10: 1	228(16) 293(418)	238(22)

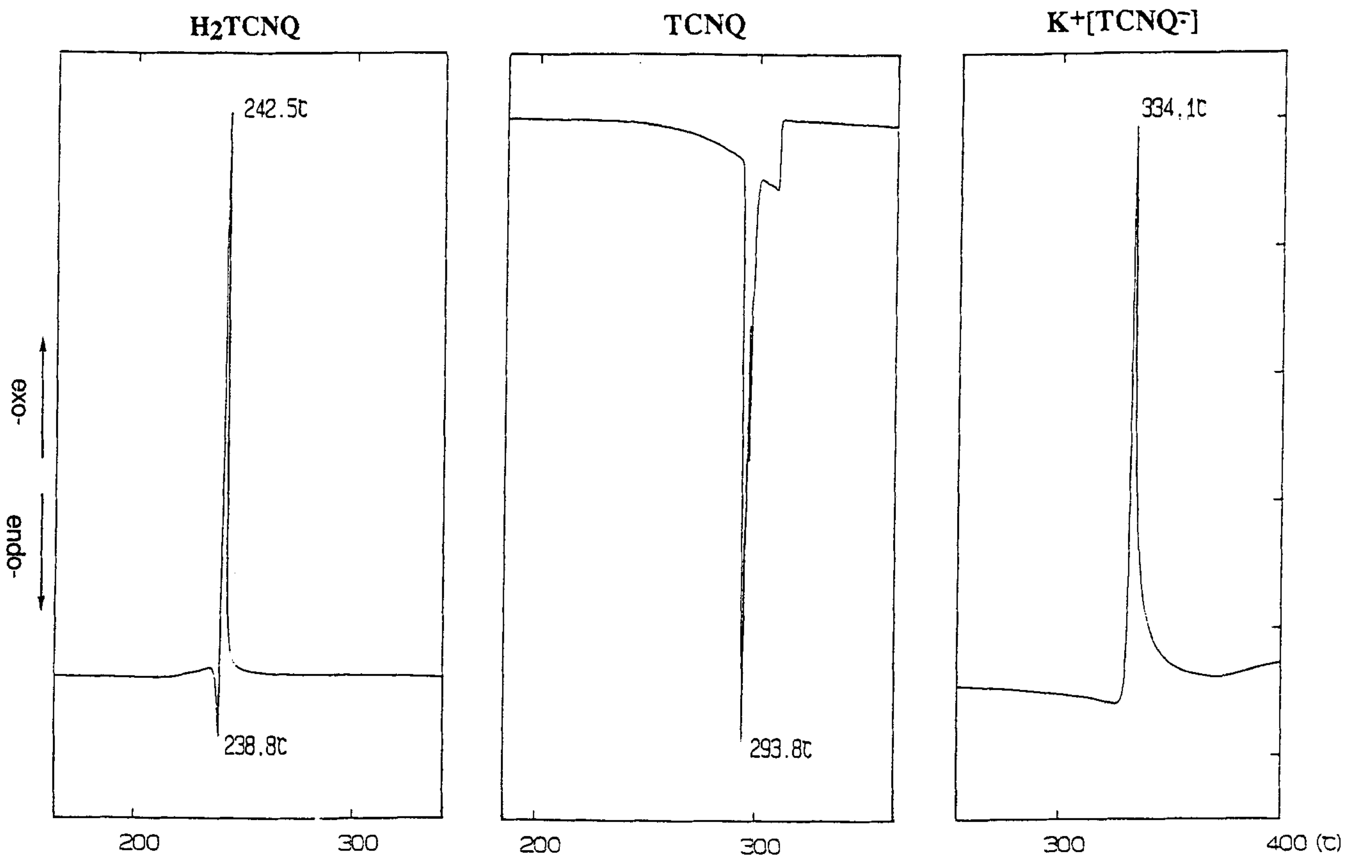


FIGURE 2 DSC diagrams of H_2TCNQ, TCNQ, and $K^+(TCNQ^-)$

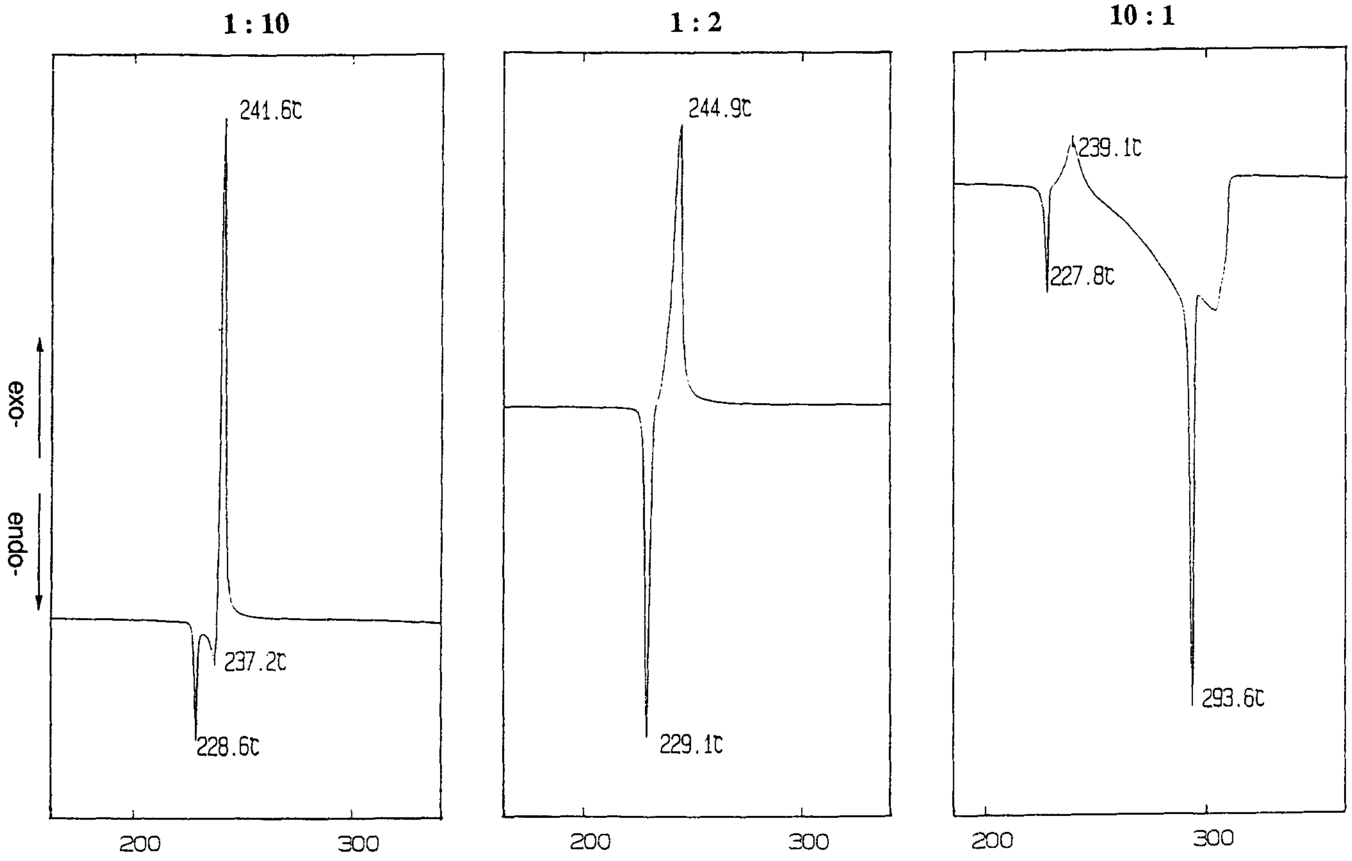


FIGURE 3 DSC diaframs of milled solids in molar ratio (TCNQ:H_2TCNQ), 1:10, 1:2, 10:1.

FIGURE 2 shows thermal analyses (DSC) of TCNQ, H_2TCNQ, and $K^+(TCNQ^{\cdot-})$ and FIGURE 3 shows thermal analyses of milled products in molar ratios, TCNQ: H_2-TCNQ= 1:10, 1:2, and 10:1. All the samples that showed the chromic phenomena exhibited endothermic change around 229°C. FIGURE 4 shows enthalpy change at about 229 °C of the milled solids. The solid B that displayed strongest coloration showed largest enthalpy change.

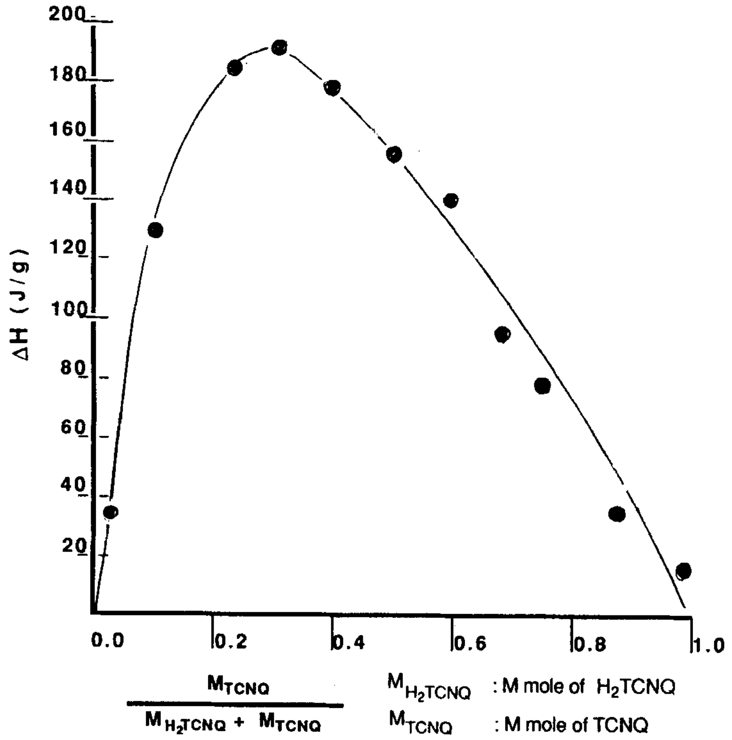


FIGURE 4 Enthalpy Changes (ΔH) around 229° C of the Milled Products

IR Spectra

FIGURE 5 shows IR spectrum of B measured in hexachlorobutadiene(C_4Cl_6) (4000-2000cm^{-1}), and in Nujol (1800-650 cm^{-1}).

TABLE III shows characteristic IR bands of B,TCNQ,H_2TCNQ, and $K^+(TCNQ^{\cdot-})$.
IR spectra of B showed both absorptions of TCNQ and H_2TCNQ. A slight difference was observed in increase of ν_{CN} absorption at 2265, decrease of ν_{CN} absorption at 2258 cm^{-1} compare to that of H_2TCNQ, and a little higher wavenumber shift from 2222 to 2226 compared to that of TCNQ. A new absorption appeared at 842 cm^{-1}that was

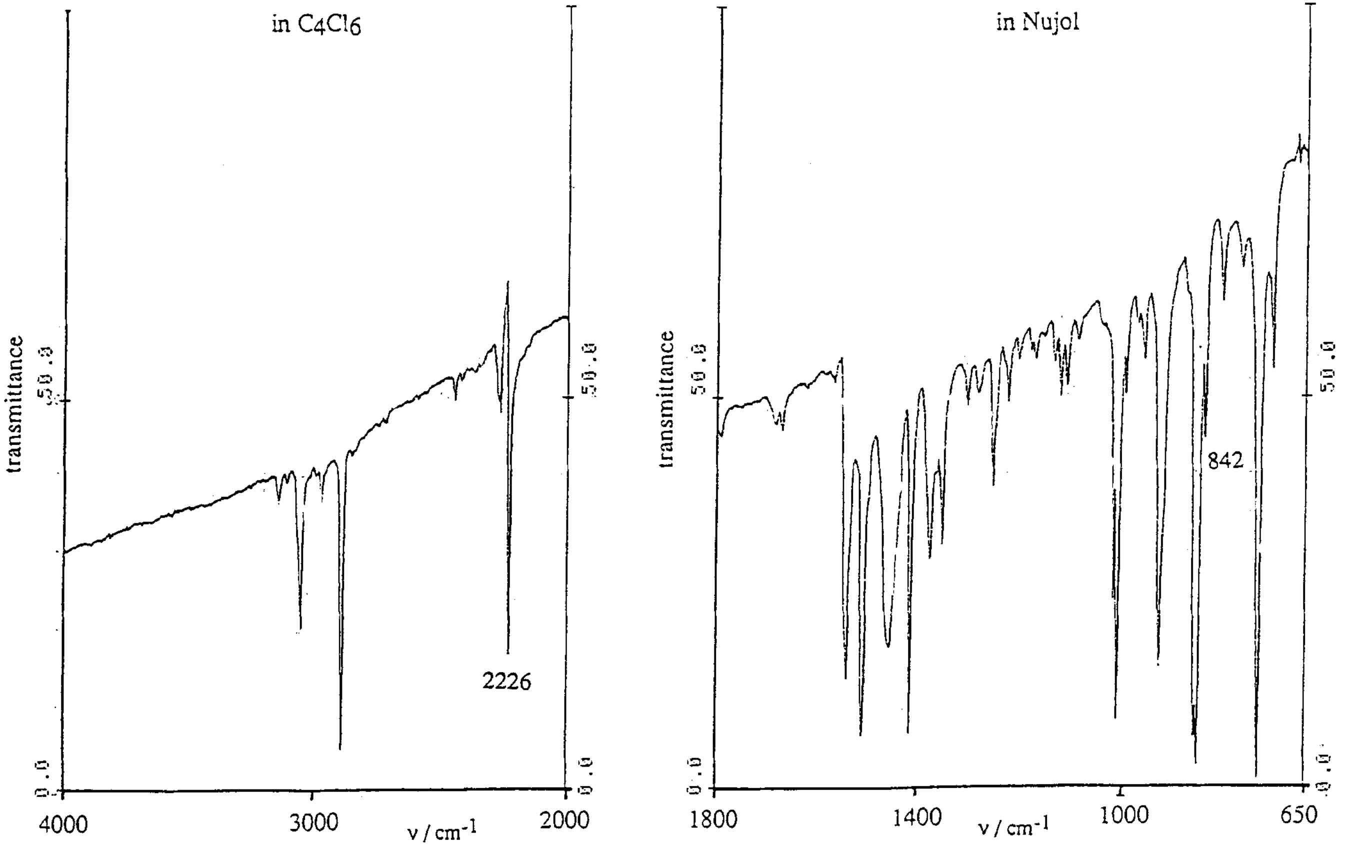


FIGURE 5 IR spectrum of B

assigned as δCH(out of plane). Appearance of the band at lower wavenumber than those of TCNQ and H_2TCNQ may indicate an increased electron density on the aromatic ring of the milled products. All milled products that exhibit the chromic phenomena showed the absorption at 842 cm^{-1}. Increase in the amount of H_2TCNQ displayed an increasese of the absorption at 842 cm^{-1}. The absorption in B (TCNQ:H_2TCNQ=1:2) was strongest in the various milled solids.

TABLE III Characteristic IR absorptions of B, TCNQ, H_2TCNQ and K^+(TCNQ$^{\cdot-}$)

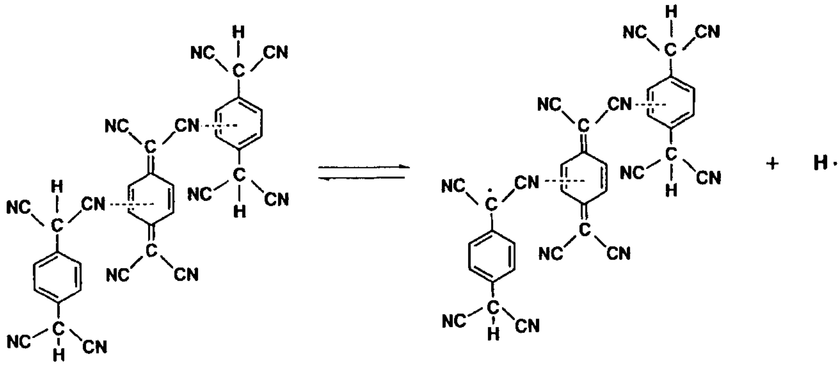
	ν_{CN}, (cm^{-1})	$\delta_{CH(out\ of\ plane)}$, ($cm^{-1}$)
B	2265(w),2258(w),2226(s)	862(s),856(s),842(m)
TCNQ	2222(m)	861(s)
H_2TCNQ	2268(sh),2258(m-w)	854(s)
K^+[TCNQ$^{\cdot-}$]	2196(s),2180(s),2168(s)	824(m)

Electronic Absorption Spectra

Absorption spectra of B showed absorptions at 378(sh) and λ_{max} 404 nm in dioxane. Characteristic absorption bands due to TCNQ anion radical at 675, 780, and 870 nm were not observed, however weak ESR signal due to free radical, g=2.00350 was detected. Crystallization of both A and B in organic solvents such as CH_3CN, THF, and MeOH gave pure TCNQ, and H_2TCNQ that is containing free radical. However individual TCNQ and H_2TCNQ did not show the rapid and remarkable chromic phenomena, although H_2TCNQ shows very slow color change from colorless to brown by the treatment that mentioned above in moist air.

Structure

Existence of largest enthalpy change at 229 °C in the 1:2 mixture, appearance of new δCH(out of plane) at 842 cm^{-1}, appearance of ESR signal corresponding to free radical reveals formation of weak complex between TCNQ and H_2TCNQ in the solid state. From these spectral results we assumed the structure of B as scheme 1.



Scheme 1 structure of B

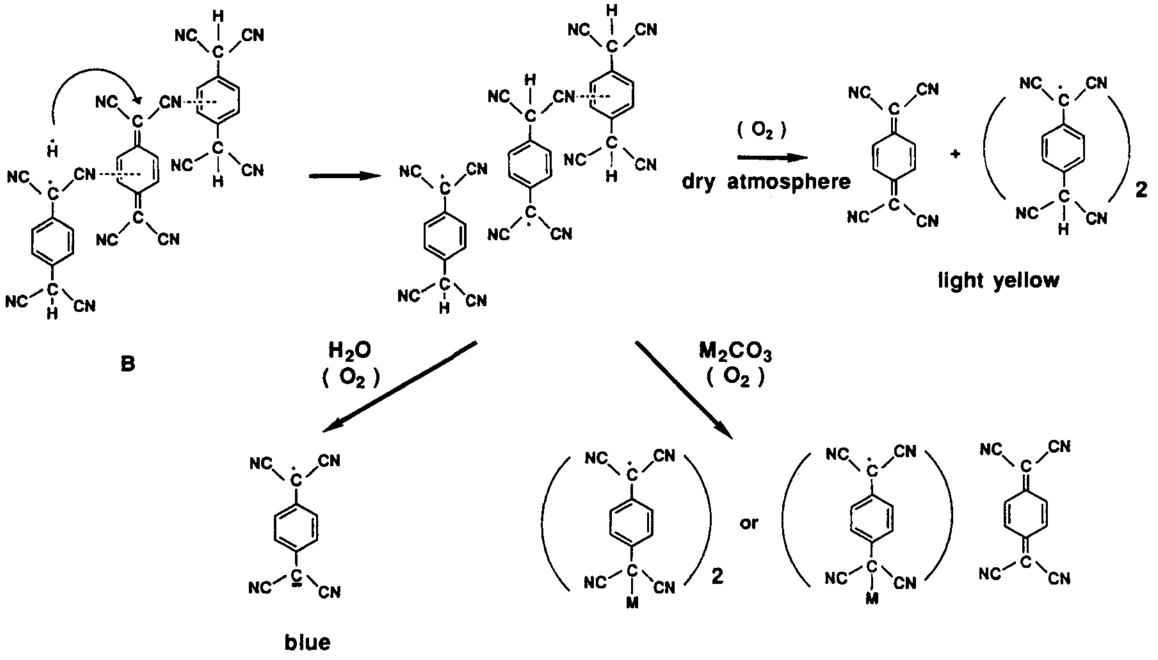
Chromic phenomena

A white filter paper was painted with dioxane solution of B under nitrogen atmosphere then dried. The resulting filter paper changed to light yellow. When the light yellow filter paper was put in a vessel containing neither oxygen nor water vapor, the paper did not show color change(condition 1). On the other hand, if the vessel had no water vapor but contained oxygen, the filter paper colored to light green(condition 2). The light yellow filter paper gradually colored to green when it was put in a vessel containing water vapor but no oxygen(condition 3). When the filter paper left in a moist air, containing oxygen, the paper turns blue immediately(condition 4). TABLE IV shows the coloration mentioned above. The colorations is described in scheme 2. We used dioxane as solvent because the solvent prevents chemical change of the free radical to TCNQ anion radical.

TABLE IV Chromic Phenomena under Various Conditions

condition	water vapor	oxygen	color
1	none	none	light yellow
2	none	containing	light green
3	containing	none	green (gradually)
4	containing	containing	blue(immediately)

Scheme 2 Mechanism of Chromic Phenomena



When dioxane solution of B was applied to a picture that was drawn by solutions of organic compounds such as oxalic acid, resorcinol, (4-hydroxyphenyl)-phenanthro[9,10-d]-imidazole, 3,6-dimethyl-9-(4-methyl benzoyl)fluorene or 2,4',4"-trimethoxyphenylmethane on clean filter paper then dried, beautiful color appeared for example, yellow, red, purple, green, or blue.

Details of the coloration on the organic compounds are now in progress.

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