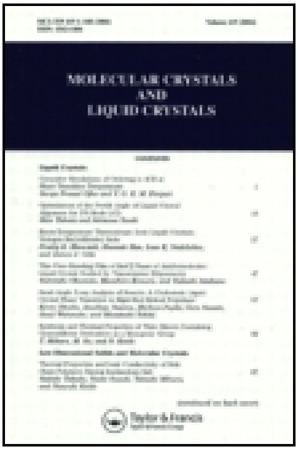


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Polymorphisms and Colourations of 4,5,-Bis(4-Methoxyphenyl)-2-(3-Nitrophenyl0-1H-Imidazole

Y. Sakaino [a] , Y. Inouye [b] [a] , H. Kakisawa [b] [a] & T. Takizawa [c] [a]

[a] Department of Chemistry, Faculty of Education Gunma University, Maebashi, Gunma, 371, JAPAN

[b] Department of Chemistry, University of Tsukuba, Sakuramu Niiharigun, Ibaraki, 305, JAPAN

[c] Department of Physics, General Science, Gunma University, Maebashi, Gunma, 371, JAPAN

Version of record first published: 13 Dec 2006.

To cite this article: Y. Sakaino , Y. Inouye , H. Kakisawa & T. Takizawa (1988): Polymorphisms and Colourations of 4,5,-Bis(4-Methoxyphenyl)-2-(3-Nitrophenyl0-1H-Imidazole, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 161:1, 255-281

To link to this article: http://dx.doi.org/10.1080/00268948808070252

Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 1988, Vol. 161, pp. 255–281
Reprints available directly from the publisher.
Photocopying permitted by license only.

Printed in the United States of America

POLYMORPHISMS AND COLOURATIONS OF 4,5-BIS(4-METHOXYPHENYL)-2-(3-NITROPHENYL)-1H-IMIDAZOLE

Y.SAKAINO
Department of Chemistry, Faculty of Education
Gunma University, Maebashi, Gunma, 371, JAPAN.

Y.INOUYE AND H.KAKISAWA
Department of Chemistry University of Tsukuba,
Sakuramu Niiharigun, Ibaraki, 305, JAPAN.

T.TAKIZAWA
Department of Physics, General Science, Gunma
University, Maebashi, Gunma, 371, JAPAN.

Abstract 4,5-Bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1H-imidazole [I] crystallized in several coloured states such as red, orange, yellow, by changing solvents. From X-ray powder diffraction, d.s.c. thermograms and I.R. spectra, the red and the two yellow crystals were found to be polymorphic forms of [I]. The polymorphisms are based on differencies in the hydrogen bonds. The red crystals have a hydrogen bond of the type -NH---O=. The NH hydrogen of one molecule bonds to the nitro oxygen of another. One of the two yellow crystals has hydrogen bonds of the type -NH---N=. The NH of one molecule bonds to the nitrogen on the other's imidazole ring. Another yellow crystal has two kinds of hydrogen bonds, -NH----N= and -NH---OMe-, the NH of one molecule with the methoxy oxygen of another molecule. On the other hand, the orange crystals have solvent of crystallization. The solvent was connected with the imidazole ring and hinders direct hydrogen bonding between two imidazole rings. Colouration of the red crystals is due to an intermolecular charge transfer effect and a hydrogen bond of the type -NH---O= contributes to form a more planar structure of the molecule and to form the intermolecular CT complex.

INTRODUCTION

We have found recently that 4,5-bis(4-methoxyphenyl)-2-(4-nitrophenyl)-1H-imidazole crystallizes in several coloured states, yellow, orange, dark red and black, by changing the crystallization solvents. One of the crystals showed chromotropic properties by heating, trituration, or drying[1,2]. Solvent of crystallization and intermolecular hydrogen bonds have been shown to play an essential role in the chromotropic behaviour. Moreover, the coexistence of p-methoxyphenyl and p-nitrophenyl groups capable of conjugation with the imidazole ring was believed to be the origin of the large bathochromic colour shifts due to their push and pull substituent effects[2]. Thus it is interesting to study the chromotropic behaviour of a m-nitro analogue, 4,5-bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1H-imidazole [I] in which the nitro group can not conjugate with the imidazole ring. Recrystallization of [I] from various solvents gave red, orange, yellow or light yellow crystals. Among seven kinds of crystals obtained, three were found to be polymorphic forms of [I]. The remaining four contained solvents of crystallization. By removal of the solvents, the latter crystals changed into two of the former and a new polymorphic form of [I]. This report describes the polymorphic behaviours and the origin of the colouration of those crystals.

CRYSTALLIZATION SOLVENTS AND CRYSTALS OF [I]

Relation between the crystallization solvents and crystals is shown in TABLE I. Crystallization of [I] from an alcohol like methanol, ethanol or sec-propanol gave red crystals (1). From chloro-

TABLE I. Recrystallization Solvents and Crystal Colours

Cryst. No.	Solvent	Colour	Shape	Hue λd(nm)	Chroma Pe(%)	Lightness Y(%)
(1)	MeOH	red	plates	609	33	10
(2)	$CHCl_3$	light-yellow	cottony needles	574	72	61
(3)	t-BuOH	orange	needles	586	87	42
(4)	C_6H_6	golden-yellow	leaflets	578	78	78
(5)	dioxane	light-yellow	silky needles	572	65	70
(6)	"	orange	silky needles	596	81	24
(7)	"	yellow	prisms	574	74	53
(8)	EtOH	orange	needles	584	84	37

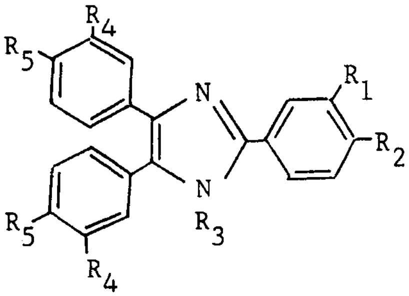
form it gave light yellow cottony needles (2). Crystallization from t-BuOH or t-BuOH-acetone (8:1) gave orange needles,(3). The crystals, (3), contained one mole of t-BuOH as solvent of crystallization and the solvent could be removed by heating at 106°C with a change of colour to yellow to give (3'). Crystallization from benzene gave golden-yellow leaflets (4). On the other hand, crystallization from dioxane-water gave four crystals, (1),(5),(6) and (7). Orange needles, (6), were formed by the usual crystallization procedure. Yellow needles, (5), were obtained by further addition of water to the filtrate after removal of (6) at room temperature. If the solution was moderately warmed, (1) was precipitated instead of (5). Yellow prisms, (7), were formed slowly in dioxane-water (3:1) solution.

Crystals (4),(6), and (7) also contained solvent of crystallization. If the solvents were removed by heating, these crystals changed to (3'),(5), and (1), respectively. TABLE II shows the change in the crystals upon the removal of the solvents. Elemental analyses of (1),(2),(3'), and (5) gave the same analytical data corresponding to the formula $C_{23}H_{19}N_3O_4$ of [I]. Rf values on t.l.c. chromatograms,(chloroform-acetone 10:1) of these crystals were also identical.

X-RAY POWDER DIFFRACTION

X-ray powder diffraction patterns of (1),(2),(3') and (5) are shown in Figure 1 with the 2θ-values of the five strong peaks. From the results we concluded that the crystals (1),(2),(3') and (5) are polymorphs of [I].

D.S.C. THERMOGRAMS



	R_1	R_2	R_3	R_4	R_5
[I]	NO_2	H	H	H	OMe
(8)	NO_2	H	Me	H	OMe
(9)	NO_2	H	H	NO_2	H
(10)	H	OMe	H	H	OMe
(11)	NO_2	H	H	H	H
(12)	NO_2	H	Me	H	H
(13)	H	H	H	H	OMe
(14)	H	OMe	H	H	H
(15)	H	CN	H	H	OMe
(16)	H	OMe	H	NO_2	H

TABLE II. Removal of Solvent of Crystallization and Change of the Crystals.

Cryst. No.	Temp. (C)	Removed Solv.	New Cryst.	Colour
(3)	106	1M t-BuOH	(3')	Yellow
(4)	94	1/2 M C_6H_6	(3')	Yellow
(6)	90	3/2 M Dioxane	(5)	Yellow
(7)	106	1/2 M Dioxane	(1)	Red

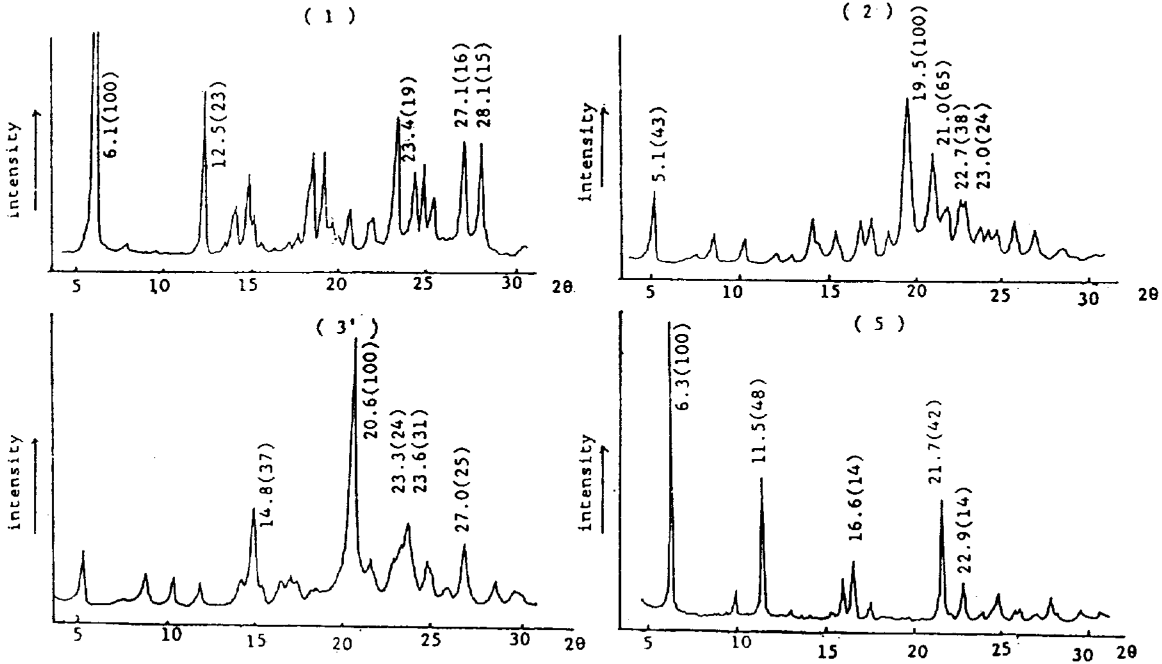


Figure 1. X-ray Powder Diffraction Patterns of (1),(2),(3') and (5). The 2θ values of the strong peaks are shown with their relative intensities in parentheses

D.s.c. thermograms of crystals (1),(2),(3') and (5) are shown in Figure 2. Enthalpy changes of the crystals are tabulated in TABLE III. Crystals of (1) showed two endothermic changes . One appeared as a broad absorption with a maximum at 233°C and another at 245°C. The former absorption is attributable to transformation of (1) to (2). The latter is the melting enthalpy since (1) showed a colour change from red to yellow at about 233°C and i.r. spectrum of the yellow substance was the same as that of (2). (2) melted at 245°C with the colour turning to red. The red liquid solidified with the colour as it was when cooled rapidly but resulted in a mixture of red and yellow substances when cooled slowly. I.R. spectra of the red solid resembles that of (1) but showed absence of hydrogen bonds of the type -NH---O= (vide infra). The solidified substance could be converted to (2) by reheating above 135° C. Crystals of (2) were not transformed into any other crystalline form during heating up to the melting point.

Crystals, (3), showed an endothermic change at 106°C due to removal of t-BuOH. This was confirmed by disappearance of ^{1}H n.m.r. signals at δ1.1(s,9H,Me) and 4.1(s,1H,OH) in DMSO-d_6 and by elemental analyses before and after heating the crystals (TABLE VII). (3') shows two thermal changes . One is a small broad endothermic change of 3.38 KJ mol^{-1}. The other is the melting enthalpy of (3'). The former is reversible by temperature variation and the energy is too small to consider the destruction of intermolecular hydrogen bonds by heating. Since (3') has a hole caused by loss of t-BuOH, the molecule sitting near the hole may move slightly by the heating.

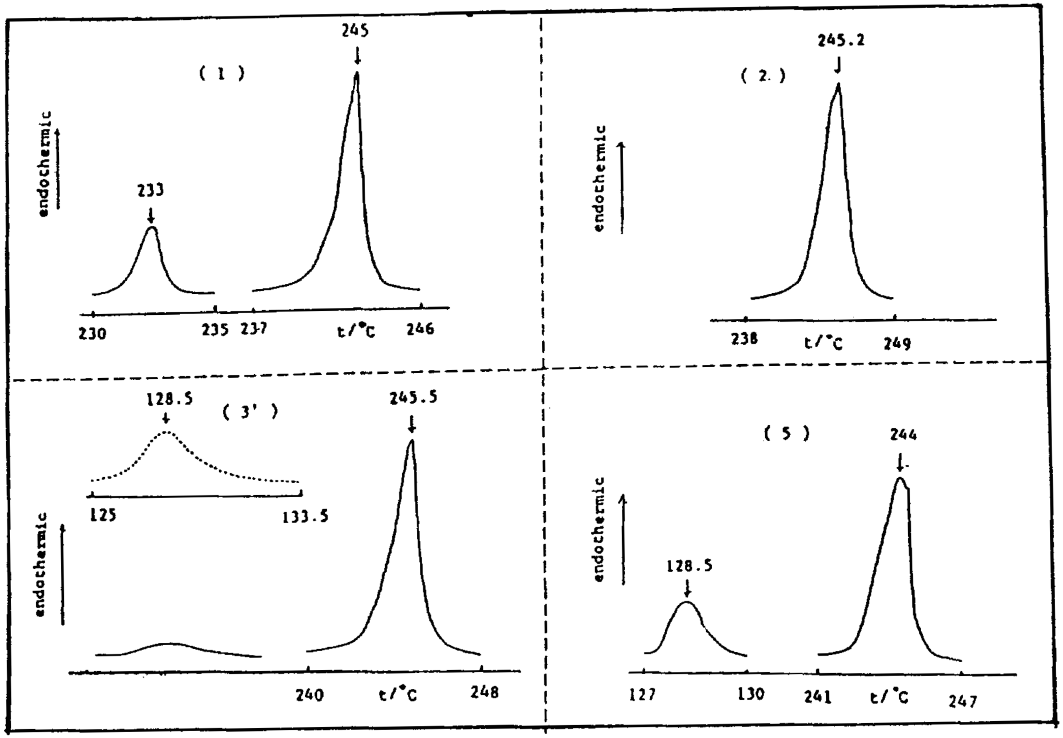


Figure 2. D.S.C. Thermograms of Crystals (1),(2),(3') and (5). The dotted line is the absorption around 130°C, shown with the scale expanded.

(4) and (5) also showed small reversible endothermic changes.

I.R. SPECTRA.

I.R. spectra of crystals (1),(2),(3'), and (5) measured in hexachlorobutadiene(C_4Cl_6), 4000-2000 cm^{-1}, and in Nujol, 1800-600 cm^{-1} are shown in Figure 3 and 4. The characteristic I.R. bands of these crystals and related imidazole derivatives are shown in TABLES IV and V.

Crystal (1).

The I.R. spectra of (1) are quite different from that of the others in the ν_{NH}, $\nu_s NO_2$ and ν_{as}=C-O-C regions. (1) showed ν_{NH} at 3424(m) and 3384(m) cm^{-1} in hexachlorobutadiene whereas the absorption appeared at 3452 cm^{-1} in dilute CCl_4 solution. Other crystals show ν_{NH} absorptions as broad bands between 3250 and 2500 cm^{-1} due to a hydrogen bond of the type -NH---N=[4,5]. The shift to lower wavenumber of 3452 to 3424 and 3384 cm^{-1} and the sharp and medium shape in (1) clearly indicate existence of a hydrogen bond of another type such as -NH---O=[2]. The split into two absorptions is due to difference in the hydrogen-bond distance (see Figure 10,A). Red crystals, (1), showed absorptions at 1576(m-w), 1562(w) and 1516(s) cm^{-1}. These bands are assignable to the ring stretching vibration of aryl groups and imidazole groups[5], and $\nu_{as}NO_2$ respectively. (1) showed two $\nu_s NO_2$ absorptions at 1352(s) and 1344(s) cm^{-1}. The lower frequency band suggests the existence of an intermolecular hydrogen bond between nitro oxygen and NH hydrogen .

(1) showed two ν_{as}=C-O-C absorptions at 1262(s) and 1246(s) cm^{-1} while the other crystals,

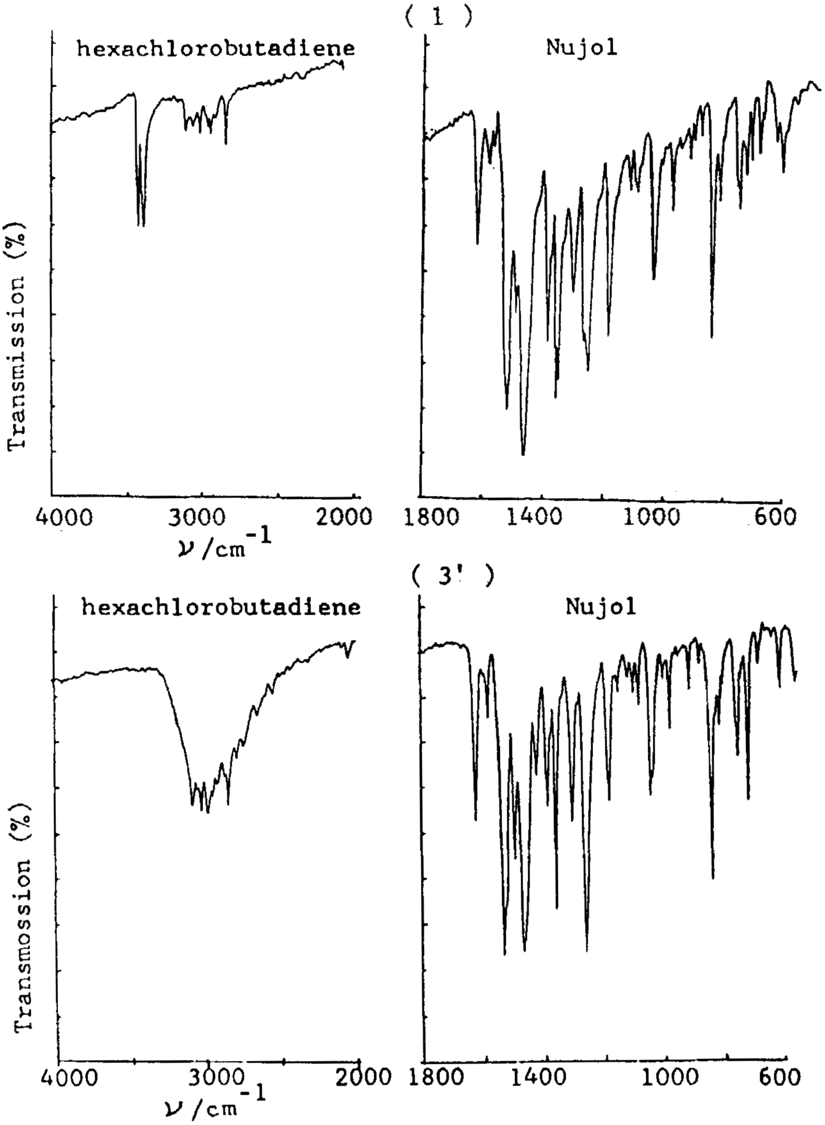


Figure 3. I.R. Spectra of Crystals (1) and (3').

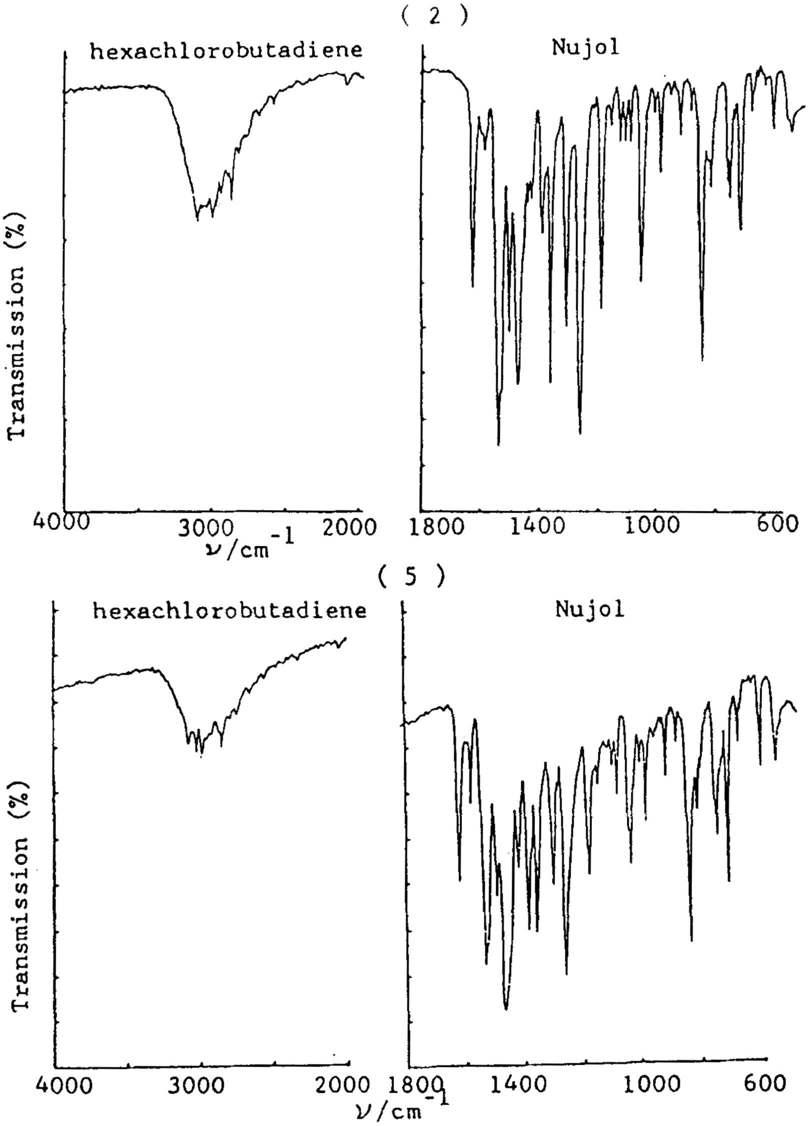


Figure 4. I.R. Spectra of Crystals(2) and (5)

TABLE III. Enthalpy Change of Crystals (1),(2) (3') and (5).

Cryst. No.	Peak (°C)	ΔH $KJ \cdot mol^{-1}$	Peak (°C)	ΔH $KJ \cdot mol^{-1}$
(1)	233	6.88	245	25.7
(2)			245	26.9
(3')	128.5	3.38	245	26.1
(5)	128.5	6.60	244	24.8

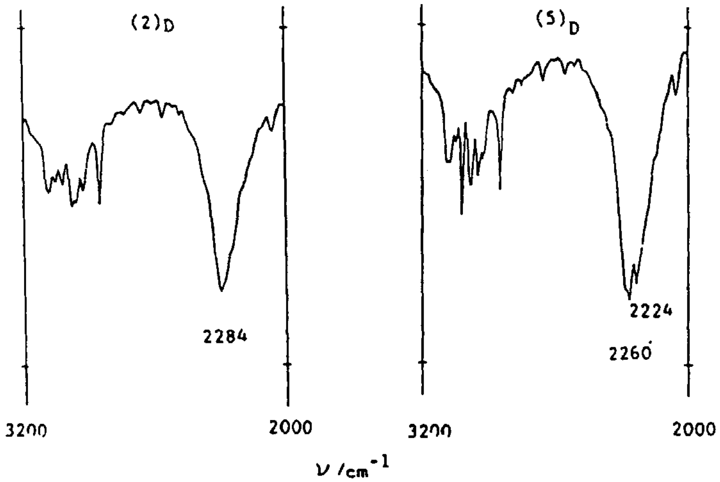


Figure 5. I.R. Spectra between 3200-2000 cm^{-1} of deuterated Analogues of (2) and (5) in C_4Cl_6.

TABLE IV. Characteristic I.R. Absorptions of Crystals (1) - (13) in C_4Cl_6.

Cryst.No.	ν_{NH}	ν_{ND}	$\nu_{CH}(OMe)$
(1)	3424,3384 m m	2600,2524 m m	2896,2836 w w-m
(2)	3250-2500 br,m	2284 br,m	2836 w-m
(3)	3264 m		2840 w-m
(3')	3300-2600 br,w	2268,2228 br,m br,m	2836 w-m
(5)	3300-2600 br,m	2260,2224 m m	2840 w-m
(6)	3264 m-s		2852,2840 w-m, w-m,sh
(7)	3236 m-s		2856,2836 w m
(8)			2840 w-m
(9)	3320 m		
(10)	3250-2700 br,m		2836 w-m
(11)	3200-2600 br,m		
(13)	3300-2600 br,m		2836 m-w

s=strong, m=medium, w=weak, sh=shoulder, br=broad

TABLE V. Characteristic I.R. Absorptions of Crystals (1) - (13) in Nujol.

Cryst.No.	$_{as}NO_2$	$_{s}NO_2$	CH (p-OMe-C_6H_4)	CH (m-NO_2-C_6H_4)
(1)	1516 s	1352, 1344 s s	832 s	908, 894, 808, 750 w w m m
(2)	1532 s	1352 s	832 s	906 804, 752 m m m
(3)	1528 s	1348 s	836 s	914 802, 746 m m m
(3')	1532 s	1352 s	832 s	906 804, 742 m m m
(5)	1532 s	1350 s	832 s	906 804, 742 m m m
(6)	1524 s	1346 s	832 s	906 810, 744 m m m
(7)	1532 s, sh	1350 s	838 s	918, 902, 810, 744 w m m m
(8)	1538 s	1354 s	840 s	906, 802, 768 m m w-m
(9)	1532 s	1352 s		910 808, 762 m m m
(10)			832 m	
(11)	1544 m-s	1354 s		908, 804, 758 m m m
(12)	1536 s	1350 s		908, 804, 758 m m m
(13)			834 s	

s=strong, m=medium, w=weak, sh=shoulder, br=broad

(2),(3),(5) and (13), showed the band only at 1252(s) cm^{-1}. The splitting into two bands in this crystal denotes non-equivalence of the two p-methoxyphenyl groups. Existence of the intermolecular hydrogen bond (-NH---O=) hinders both the exchange of NH proton in the imidazole ring from 1 to 3, and the rotation of m-nitrophenyl groups about the imidazole ring. One of the two p-methoxyphenyl groups in (1) is assumed to be coplanar but the other is considerably rotated compared to the imidazole ring. On the other hand, ν_s=C-O-C absorption showed no splitting and, observed at 1030(m) cm^{-1}, exhibits non participation in hydrogen bonding.

Other differences were observed in δ CH(out of plane) regions of the m-nitrophenyl group (TABLE V). (1) showed δ CH bands of H isolated from m-nitrophenyl group at 908(w) and 894(w) cm^{-1}. Other crystals (2),(3') and (5) showed the band at 906(m) cm^{-1} and (9) at 910(m) cm^{-1}. As it is well known that increase of charge density on the ring shifts the δ CH to lower wavenumber and vice versa[6], the splitting into two bands of the δCH in (1) may arise from the different charge density on the ring. On the other hand δ CH(out of plane) of p-methoxyphenyl group in (1) was observed at 832(s) cm^{-1} and shows neither shifting nor splitting.

Crystals (2) and (5)

I.R. spectrum of (2) was very similar to that of (5) but differed in the ν_{NH}, ν_{CH}(OMe), δ_{as}(OMe, rocking), and ν_s=C-O-C regions. Figures 5 and 6 show these differences.

ν_{NH} and ν_{CH}(OMe) of these crystals were examined in the deuterated analogues $(2)_D$ and $(5)_D$, in which the NH of the imidazoles was substituted

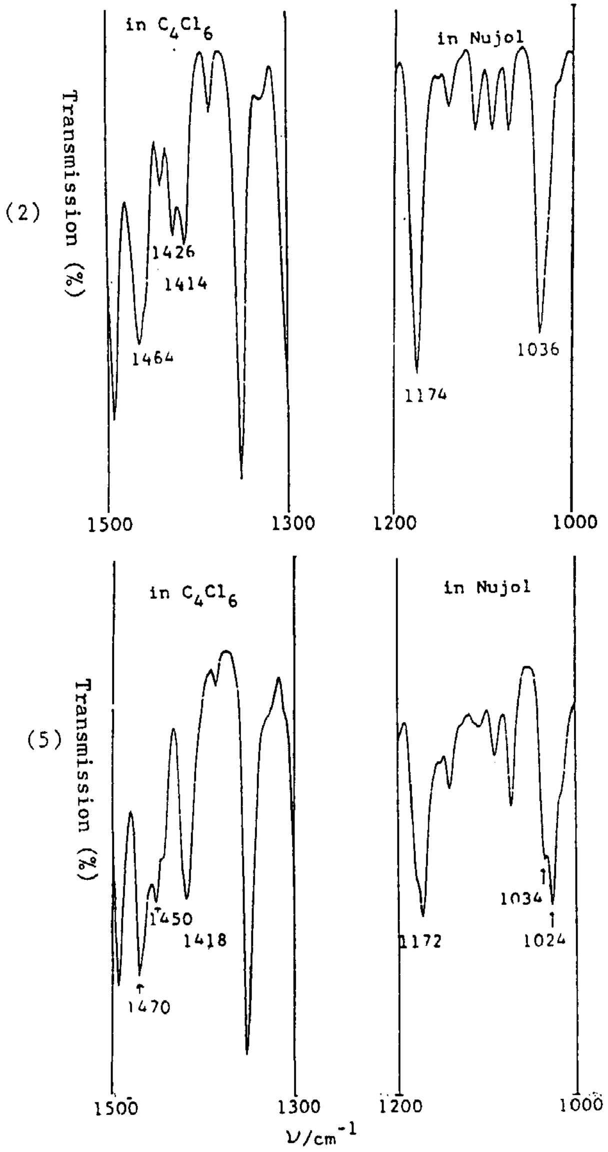


Figure 6. Expanded I.R. Absorptions between 1500-1300 and 1200-1000 cm^{-1} of (2) and (5).

with deuterium. As shown in Figure 5, the ν_{ND} band in (2) is located between 2450 and 2100 cm^{-1}, maximum at 2284 cm^{-1}, at medium intensity. Broadness of the band shows the intermolecular hydrogen bond to be of the type -NH---N=[4,5]. On the other hand, the absorption in $(5)_D$ lay between 2500 and 2100 cm^{-1} having two maxima at 2260 and 2224 cm^{-1}. The splitting shows existence of another type of hydrogen bonding, for example MeO---NH-, in addition to the -NH---N=.

In the 1600-1500 cm^{-1} region, (2) absorbs at 1590(w), 1578(m-w), 1532(s) and 1520(m-s) cm^{-1}, and (5) at 1588(vw), 1578(m), 1532(s) and 1516(m) cm^{-1}, (10) at 1590(w), 1580(m-w), 1552(w), 1520(m-s) and 1502(s) cm^{-1}. The absorption at 1532 cm^{-1} in (2) and (5) was assigned as ν_{as} NO_2. The ν_{as} NO_2 lay in the normal region for that of aromatic nitro compounds.

ν_s NO_2 in (2) and (5) appeared at the same position (1352 cm^{-1}) as that of the other compounds. It shows the absence of a hydrogen bond including the nitro oxygen.

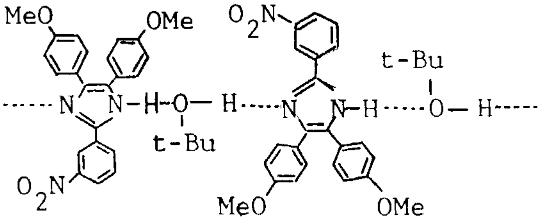
ν_{as}=C-O-C absorption at 1252(s) cm^{-1} in (2) and (5) corresponds to a mean value of the absorptions in (1) at 1262 and 1246 cm^{-1}. The two p-methoxyphenyl groups in (2) and (5) seem to twist to a similar extent to the imidazole ring plane.

As shown in Figure 6, (5) showed several split pairs, at 1470 and 1450 cm^{-1}(δ_{as}Me), at 1179 (sh) and 1172 cm^{-1}(δCH of OMe,rocking), at 1034 and 1024 cm^{-1}(ν_s=C-O-C). The splitting of the δ_{as}Me band may arise by the formation of a hydrogen bond, -MeO---NH-, one methoxy oxygen bonding with the NH hydrogen in another molecule. The separated bands collapsed to one band on elevation of temperature. At 150 °C, these absorptions appeared at 1463, 1174, 1034 cm^{-1} respectively. The absorptions reverted to the original on cooling. Subtraction of two I.R. spectra of (5), measured at 150° and 26°C, showed broad ν_{NH} absorption at around 3350-3000 cm^{-1}, having a maximum at 3200 cm^{-1}. Subtraction of the two I.R. spectra, initial and re-cooled samples, showed no absorption in that region. Moreover, the ν_{ND} of $(5)_D$ observed at 2260 cm^{-1} at room temperature, shifted to 2273 cm^{-1} with decrease of the absorption at 2224 cm^{-1} by heating up to 150°C. The absorption reverted to original on cooling. The result shows that one of the methoxyl groups contributes to the hydrogen-bonding of the type -MeO---HN- which is reversed by heating. Reversible endothermic change observed in d.s.c. measurement is attributable to the change in the hydrogen bond.

I.R. spectra measured above 230°C of (2) and (5) were identical to each other.

Crystals (3)

The orange needles,(3), showed ν_{NH} absorption between 3350 and 3250 cm^{-1} with a maximum at 3264 cm^{-1} at medium intensity. No absorption was observed at higher wavenumber than the ν_{NH} absorption. Accordingly, t-BuOH in (3) appears to link by hydrogen bonds as below.



(3) showed absorptions in the 1600-1480 cm^{-1}

region at 1588(w), 1578(w), 1566(w), 1528(s), 1524(sh,s) and 1492(m) cm^{-1} in Nujol. The absorption at 1528(s) and 1524(sh,s) are assigned to $\nu_{as}NO_2$ and ring vibration of the imidazole respectively. ν_sNO_2 absorption appeared at 1348(s) cm^{-1} as a sharp band. Neither splitting nor broadening of the band was observed showing no hydrogen bonding between nitro oxygen and NH-proton.

Crystals (3')

When crystals of (3') were kept in a refrigerator for a month, the crystals changed to (5). Although the X-ray powder diffraction pattern of (3') was different from the other crystals (1),(2) and (5), I.R. spectra and D.S.C. diagrams resembled closely those of (5). So we assumed no substantial difference in the geometrical conformation of the molecules in (3') and (5) except for the crystal packing.

Crystal (7)

Crystals of (7) have half a mole of dioxane as solvent of crystallization. ν_{NH} absorption of (7) appeared between 3300-3150 cm^{-1} with a maximum at 3236 cm^{-1} at medium intensity. (7) showed absorptions in the 1600-1480 cm^{-1} region at 1576(w), 1562(m), 1535(sh,s), 1520(s) and 1490(m-s) cm^{-1} in Nujol.

The strong band at 1535 and 1520 cm^{-1} is assigned to ν_{as} NO_2 and ring vibration of the imidazole respectively. ν_sNO_2 was observed at 1354 cm^{-1} as a strong and sharp band. The results show no hydrogen bond between the nitro oxygen and NH-proton. $\delta_{as}Me$ at 1462(m), $\delta CH(OMe$,rocking) at 1174 cm^{-1} showed no splitting.

Other Crystals (4) and (6)

Crystals of (4) showed ν_{NH} absorption between 3250 and 2700 (m-w) cm^{-1}. Other characteristic absorptions were identical with that of (2) which is shown in TABLE V. Although (4) has solvent of crystallization but the solvent neither affects the characteristic I.R. absorptions of νNH,νNO_2 , δCH, nor the colouration of the crystals (TABLE I). After removal of the solvent by the heating, the I.R. spectra was same as that of (3'). Crystals of (6) showed ν_{NH} absorption at 3264(m-s) cm^{-1} due to the hydrogen bond between the NH proton of imidazole with the oxygen of dioxane. $\nu_{as}NO_2$ absorption of (6) at 1524 lay at a lower wavenumber than that of (2),(3') and (7). Since (6) and (3) have orange colour, the shift to lower wavenumber of the absorption seemed to correlate with the colouration.

NMR SPECTRA

Non equivalence of the methoxy group of (5) was also observed in ^{1}H N.M.R. spectra. The ^{1}H N.M.R. spectrum of (5) in dioxane-d_8 (Figure 7) initially showed signals at δ8.62(1H),8.48(1H),8.15(1H), 7.65(1H)(m-nitrophenyl group) and 11.32(NH), 7.50 and 6.84(A_2B_2,$MeOC_6H_4$), 7.40 and 6.76 (A_2B_2, $MeOC_6H_4$), 3.80(OMe) and 3.75(OMe). But the signals of p-methoxyphenyl groups gradually changed with time or heating. The aromatic proton signal turned to a broad multiplet at δ7.45 and 6.85 and the two OMe signals collapsed to a broad singlet at 3.75, Figure 7(b).

ABSORPTION SPECTRA

Crystals of (1),(2),(3') and (5) gave the same

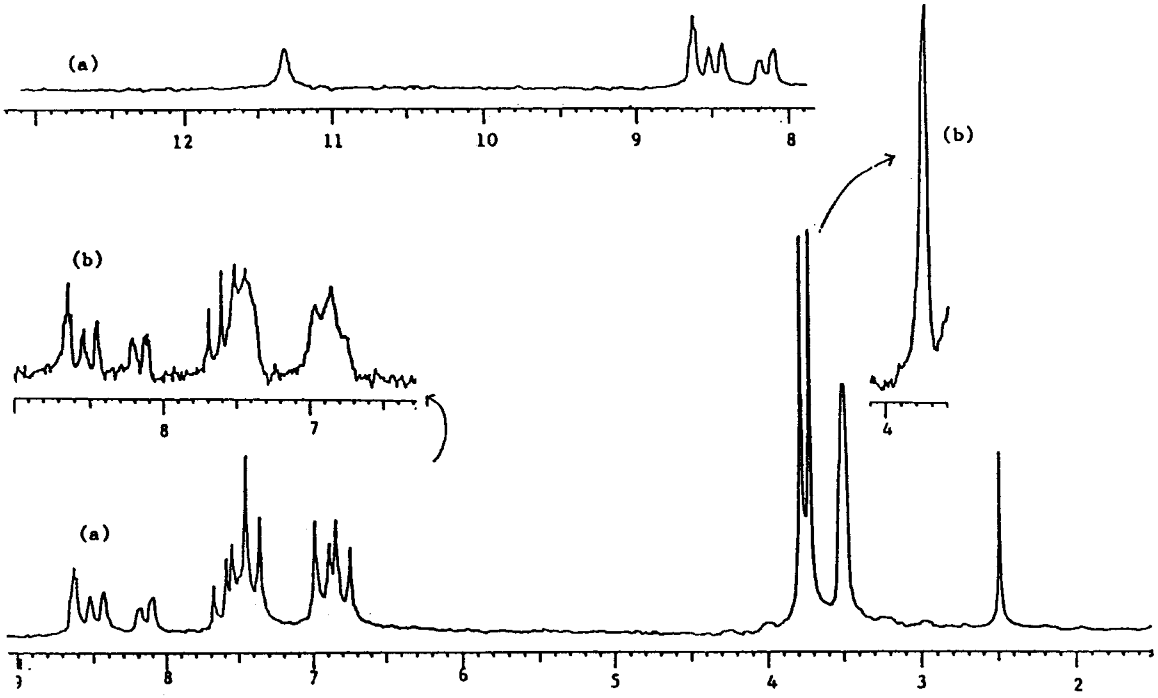


Figure 7. ^{1}H NMR Spectra of (5) in Dioxane-d_8(a) and the spectral change by heating (b).

absorption spectra in solution. Solvent effects of the spectra (TABLE VI) suggested that the longest wavelength band of the spectra is not the intramolecular CT band, since no red shift with decreased absorbance in polar solvents was observed[7]. The absorption obeyed Beer's law at a concentration of 10^{-5} mol dm^{-3} at constant temperature. The results show no association of [I] under the concentration used.

The spectra measured for crystalline states were different. As shown in Figure 8 , these crystals show differing spectra in the visible region. To clarify the difference between the spectra , subtractions between two spectra were attempted,(Figure 9). Since the absorption of (5) lay in the shortest wavelength region, (5) was chosen for subtraction. Obtained difference spectra, (3)-(5) and (8)-(5), showed symmetrical absorption around maxima at 497.8 and 495.2 nm respectively. On the other hand, the difference spectrum (1)-(5), showed unsymmetrical absorption along the axis of wavelength at 511.2 nm. The result suggests the inclusion of another absorption at the longer wavelength. To clarify the point, (3), which showed the closest absorption to (1), was chosen as for subtraction. The difference spectrum, (1)-(3), gave symmetrical absorption with a maximum at 564 nm. This may be due to a hidden absorption in the spectrum of (1)-(5).

COLOURATION AND PROPERTIES OF THE CRYSTALS

X-ray crystal analysis* of (1) showed that an imidazole ring of one molecule faces a m-nitrophenyl ring of another molecule at a distance of about 3.3 Å as shown in Figure 10,B. The

TABLE VI, UV Spectra of [I] in Various Solvents at 20°C.
* in saturated solution

Solvent	λ_{max}:nm, (10^{-4} ε)			
AcOH		282(3.2)		310(2.4)
EtOH	237(2.1)	286(2.0)	298(sh,1.8)	325(1.7)
DMF			291(2.5)	330(2.1)
$CHCl_3$			290(1.5)	330(1.3)
Dioxane		289(2.4)		328(2.0)
Benzene			290(3.3)	330(2.5)
CCl_4*		286		334

TABLE VII, The Result of Elemental Analyses
* (6)$\xrightarrow{\Delta}$(6')=(5), (7)$\xrightarrow{\Delta}$(7')=(1)

Cryst.	Mol.Formula	Found(%)			Calcd.(%)		
		C	H	N	C	H	N
(1)	$C_{23}H_{19}N_3O_4$	68.87	4.77	10.56	68.81	4.77	10.46
(2)	"	68.77	4.77	10.39		"	
(3')	"	68.73	4.72	10.42		"	
(4')	"	68.71	4.71	10.48		"	
(5)	"	68.64	4.74	10.36		"	
(6')*	"	68.66	4.74	10.38		"	
(7')*	"	68.82	4.73	10.51		"	
(3)	$C_{23}H_{19}N_3O_4$ $C_4H_{10}O$	68.15	6.12	8.79	68.18	6.16	8.84
(4)	$C_{23}H_{19}N_3O_4$ 1/2 C_6H_6	71.23	5.05	9.21	70.89	5.04	9.54
(6)	$C_{23}H_{19}N_3O_4$ 3/2 $C_4H_8O_2$	65.29	5.84	7.85	65.26	5.87	7.87
(7)	$C_{23}H_{19}N_3O_4$ 1/2 $C_4H_8O_2$	67.33	5.16	9.45	67.39	5.21	9.43
(8)	$C_{24}H_{21}N_3O_4$	69.18	5.13	10.15	69.38	5.09	10.11
(9)	$C_{21}H_{13}N_5O_6$	58.49	2.98	15.85	58.47	3.03	16.23
(10)	$C_{24}H_{22}N_2O_3$	74.51	5.70	7.22	74.59	5.73	7.24
(11)	$C_{21}H_{15}N_3O_2$	73.64	4.51	12.24	73.88	4.42	12.30
(12)	$C_{22}H_{17}N_3O_2$	74.13	4.84	11.75	74.35	4.82	11.82
(16)	$C_{22}H_{16}N_4O_5$ 1/3 H_2O	62.57	3.73	13.40	62.54	3.98	13.27

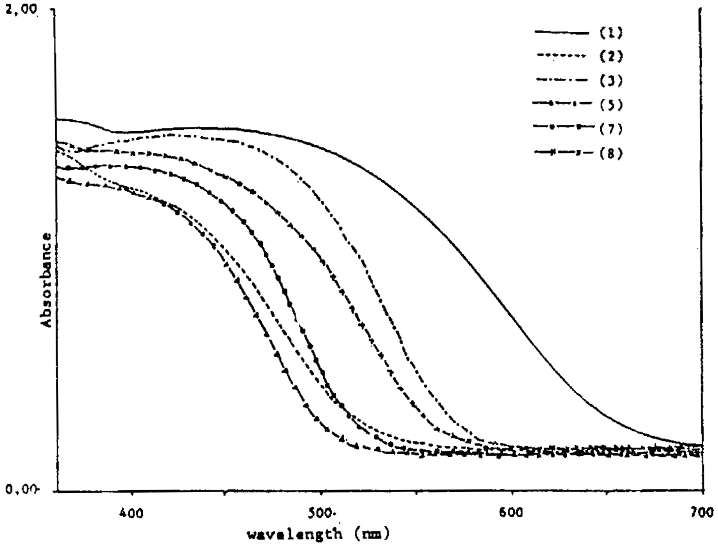


Figure 8. Absorption Spectra of Crystals (1),(2), (3),(5),(7) and (8).

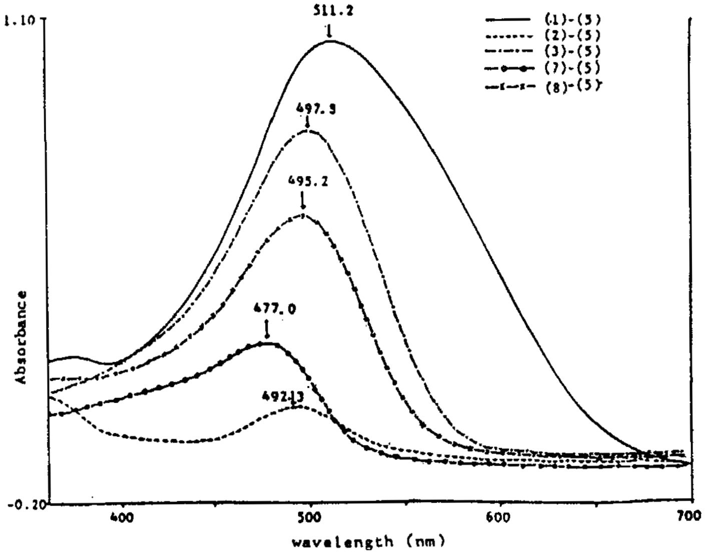


Figure 9. Difference Spectra between Crystals.

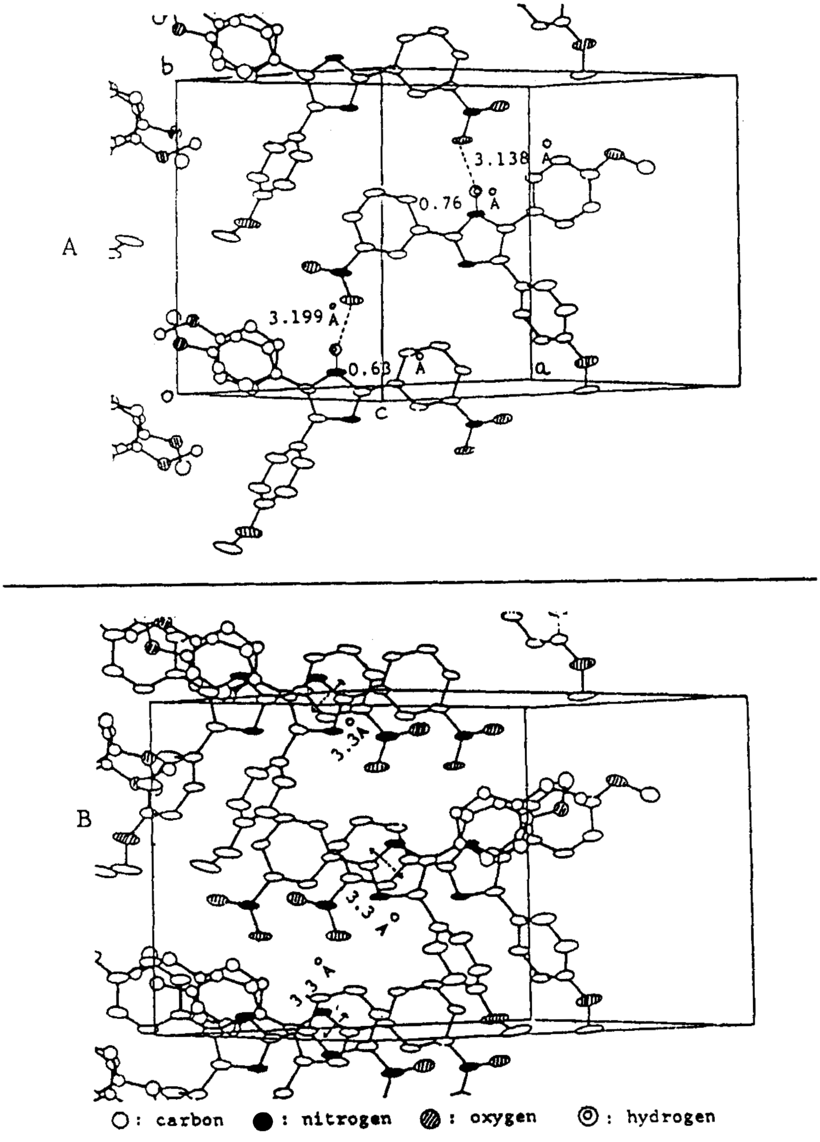


Figure 10. A: Hydrogen Bond in (1)
B: The Approach Distance of the Complex in (1)

approach distance 3.3 Å is smaller than that usually associated with van der Waals forces. Accordingly the absorption maximum observed at 564 nm in the difference spectra (1)-(3) may be due to formation of a intermolecular π-π CT complex. The complex formation shows a shift of the $\nu_{as}NO_2$ to lower wavenumber. The lower shift of the band observed in (1) at 1516 cm^{-1}, may be due to the formation of the complex. The hydrogen bond of the type -NH---O= in (1) is helpful in forming a more planar structure than in the crystals (2) and (5), which have -NH---N= type H-bonding. The planar structure may make possible formation of the intermolecular complex, formed by electro-negative imidazole ring with the electron positive m-nitrophenyl group. Crystal analysis of (7)** showed the m-nitrophenyl ring neither faces the imidazole ring nor the other aromatic ring. Accordingly, (7) does not form a π-π complex. The crystal colour of N-methyl derivative (8) is orange yellow. If the colouration of (8) is due to intermolecular CT complex formation between the imidazole ring and m-nitrophenyl ring, I.R. absorptions due to the N-Me group show the shift to higher wavenumber. (8) showed $\nu_{as}CH$ at 2952, ν_sCH 2840, $\delta_{as}Me$ 1462, and δ_sMe at 1380 cm^{-1}. These absorptions lay in the normal region and no shifts to higher wavenumbers are observed. Crystal colours of (3) and (6) are orange. Resemblance of the difference spectra, (3)-(5):497.8 nm(0.80 abs) and (6)-(5):505.4 nm(0.84 abs), suggests the colouration of these crystals have the same cause as that of (8),(8)-(5):495.2 nm(0.57 abs). $\nu_{as}NO_2$ absorptions of (3) and (6) observed at 1528 and 1524 cm^{-1} lay at lower wavenumber than that of the yellow crystals (5) or (2) at 1532 cm^{-1}. The result denotes increased planarity of their structure. Therefore the colourations of (3) and (6) are not due to complex formation but are due to increased resonance effects in those molecules. Solvents in (3),(6) and the methyl group in (8) restrict the approach of the two rings to form the complex. Low absorption observed in (2)-(5) may be due to the twisted structure of (2) . The crystals (5) and (7) also do not form the complex.

---

* As shown in figure 10, one of the methoxyphenyl ring is disordered having two orientations in the ratio of 6:4 . Details will be reported in the near future.

** Details will be reported in the near future.

REFERENCES

1. Y.Inouye and Y.Sakaino, Acta Crystallogr., Sect. C. 41, 1106 (1985).
2 Y.Sakaino, T.Takizawa, Y.Inouye and H.Kakisawa, J. Chem. Soc. Perkin Trans. 2, 1623 (1986).
3 Y.Inouye and Y.Sakaino, Bull. Chem. Soc. Jpn., 59, 3295 (1986).
4. M.R.Grimmet, Advances in Heterocyclic Chemistry, edited by A.R.KATRITZKY and A.J.BOULTON, (Academic Press, New York, 1970),12, p.144.
5. D.M.White and J.Sonnenberg, J. Org. Chem., 29, 1928 (1964).
6. a. R.D.Kross and V.A.Fassel, J. Amer. Chem. Soc., 79, 38 (1957).
   b. A.M.Hindaway, A.M.C.Nassar and R.M.Issa, Indian J. Chem., 19A, 615 (1980).
7. a. M.Oki, K.Mutai, Tetrahedron, 26, 1181(1970).
   b. Y.Sakaino and H.Kakisawa, Nippon Kagaku Kaishi, 1449 (1978).
8. H.Tanino, T.Okada and T.Goto, Bull. Chem. Soc. Jpn., 45, 1480 (1972).
9. E.H.White and M.J.C.Harding, Photochem. Photobiol., 4, 1132 (1965).