Chromotropism of Imidazole Derivatives. Part 1. 4,5-Bis-(4-methoxyphenyl)-2-(4-nitrophenyl)imidazolium Acetate Dihydrate

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4,5-Bis-(4-methoxyphenyl)-2-(4-nitrophenyl)imidazolium acetate dihydrate (**1**) in the crystalline state exhibits a sensitive colour change from orange-yellow to red on treatment by various methods (drying, trituration, or heating). The colour change was reversible below 70 °C but above 70 °C the change was irreversible and the colour deepened. Compound (**1**) was deprotonated with the loss of one mole of water of crystallization under treatment and can revert to the original by absorption of one mole of water. On heating to 100 °C, (**1**) lost all solvent of crystallization to give a deep red material (**2**). (**2**) Was considered to be 4,5-bis-(4-methoxyphenyl)-2-(4-nitrophenyl)imidazole which was linked by hydrogen bond from the imino group in one molecule to the nitro oxygen in another. Compound (**2**) reverted to (**1**) in saturated AcOH–H_2O vapour.

It is well known[1] that dimers of 2,4,5-triarylimidazolyl radicals, obtained by the oxidation of 2,4,5-triarylimidazoles, have chromotropic properties. The dimers reversibly dissociate to the imidazolyl radicals upon photo-irradiation, heating, and trituration. Such properties however, have not yet been found in 2,4,5-triarylimidazoles themselves.

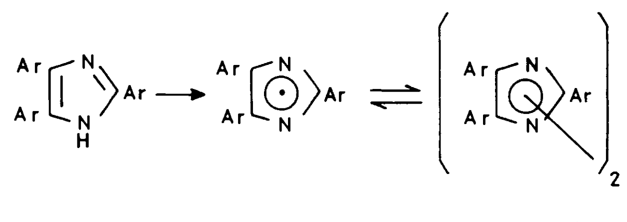
We have recently found that the crystals of 4,5-bis-(4-methoxyphenyl)-2-(4-nitrophenyl)imidazolium acetate dihydrate (**1**) show a rapid colour change (orange-yellow to red) upon drying, trituration, or heating. The colour change is reversible below 70 °C, but above 70 °C is irreversible and the colour is deeper. This report describes the chromotropic behaviour of the crystals of (**1**) and the structural interpretation of these phenomena.

Results and Discussion

Crystal Structure and Spectroscopic Properties of (**1**).—Pure 4,5-bis-(4-methoxyphenyl)-2-(4-nitrophenyl)imidazole was recrystallized from acetic acid–water. Orange-yellow crystals of (**1**) were obtained as flat plates. From elemental analysis and i.r. and ^1H n.m.r. spectra, the crystals of (**1**) were found to be an acetate of the imidazole containing two moles of water of crystallization, $C_{23}H_{20}N_3O_4{}^+\cdot OAc^-\cdot 2H_2O$. *X*-Ray analysis of a single crystal of (**1**)[2] showed that the imidazole ring is protonated and is in nearly the same plane as the *p*-nitrophenyl group. The other two *p*-methoxyphenyl groups are at angles of 39.9 and 139.4° to the imidazole ring. As shown in Figure 1, the imidazole ring is linked by hydrogen bonds to the acetoxy group and the water molecule through two nitrogen atoms. The hydrogen-bonding network through the solvents of crystallization plays an important role in the crystal packing of the molecules.

I.r. and ^1H n.m.r. spectra of (**1**) and the related compounds (**2**)—(**7**) are shown in Tables 1 and 2, and Figure 2.

The characteristic bands in the i.r. spectrum of (**1**) (Figure 2), measured as Nujol mulls and in hexachlorobutadiene, are shown in Table 1. The assignments are based on comparisons with the related compounds (**2**)—(**7**). The ^1H n.m.r. spectrum of (**1**) in $CDCl_3$ (Table 2) shows a composite signal for water and carboxy protons at δ 5.52 (s, 5 H), 2.03 (OAc), 8.18 and 7.92 (A_2B_2 $J = 9$ Hz, $NO_2C_6H_4$), 7.38 and 6.82 (A_2B_2, $2 \times MeOC_6H_4$), and 3.80 (OMe).



The colour of the crystals of (**1**) (Table 3) was measured on a colourmeter and was found to be very sensitive to temperature.

Chromotropic Behaviour of (**1**).—*Drying*. Crystals of (**1**) turned from orange-yellow to red [Table 3; (**1a**)] when dried over P_2O_5 under reduced pressure but the colour reverted to the original upon moisture absorption. The n.m.r. spectrum of the dried red sample (**1a**) showed a downfield shift of the composite proton signal of water and the carboxy group to δ 8.54 with an accompanying decrease in the signal intensity, from 5 H to 3 H; this signal reverted to the original intensity and chemical shift upon moisture absorption. When the dried red sample was exposed to D_2O vapour, the signal showed an intensity of only three protons. The results show that (**1**) loses only one molecule of water of crystallization on drying. This is also shown in the i.r. spectrum [Figure 2, (**1a**)]. In Nujol and in hexachlorobutadiene, 3 260 (νOH) and 1 648 cm^{-1} (δOH) of (**1**) decreased in intensity upon drying. When the dried red sample (**1a**) was placed for 20 min in a vessel saturated with water vapour, the colour reverted to the original and the i.r. spectrum of the sample completely agreed with that of the starting compound (**1**). In D_2O, a new broad absorption at 2 448 cm^{-1} (due to νOD) instead of 1 648 cm^{-1} was recognized, with disappearance of the signal at 1 686 cm^{-1} and reversion of the signals at 1 614 and 1 422 cm^{-1}. A change was also noted in the i.r. absorption due to the acetoxy group: an increase in a new absorption at 1 686 cm^{-1} was accompanied by decreases in the signals at 1 614 ($\nu_{as}CO_2{}^-$) and 1 422 cm^{-1} ($\nu_sCO_2{}^-$). The signal at 1 686 cm^{-1} is too low to assign to νC=O of free acetic acid and thus the liberated acetic acid may be bonded with both the imidazole group and the water molecule by the hydrogen bonds. The deprotonation of the imidazole nitrogen by drying is also proved by the appearance of the characteristic absorptions of aryl-1*H*-imidazole[3] at 1 614m sh, 1 602ms, 1 585wm, and 1 494ms cm^{-1}.

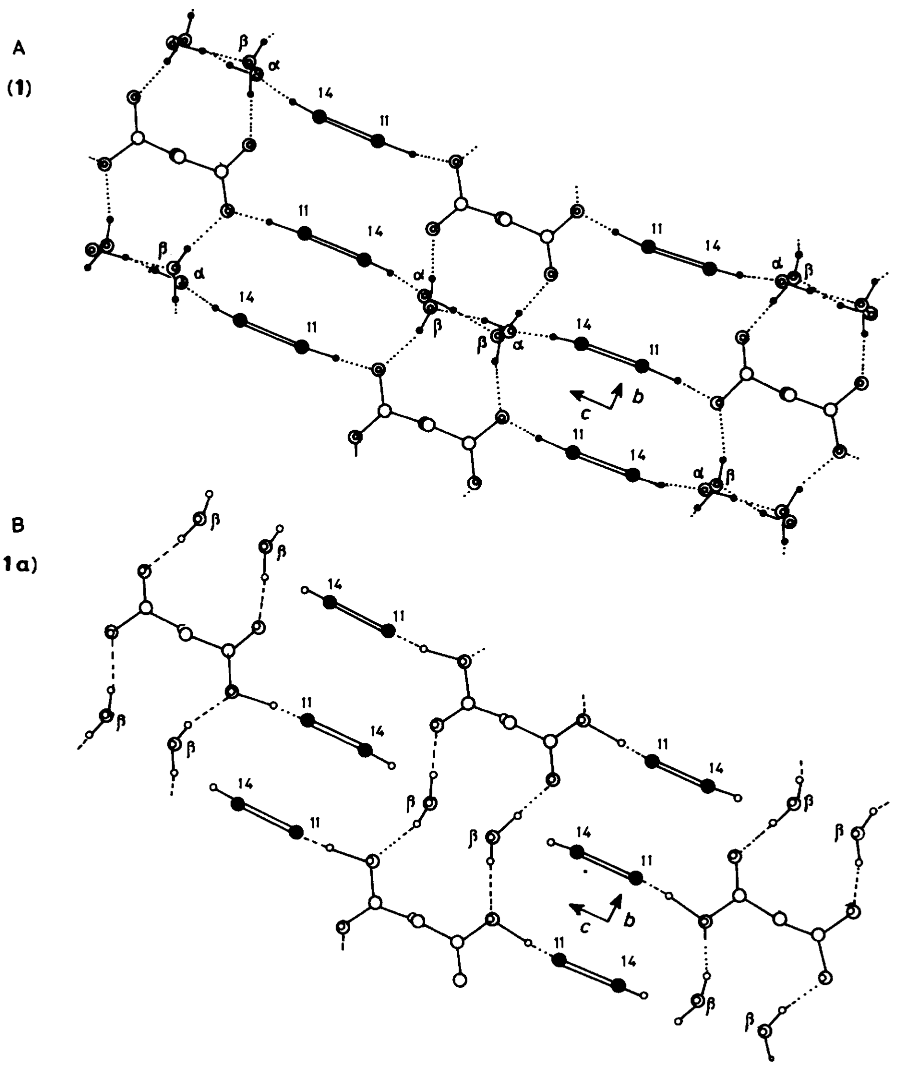
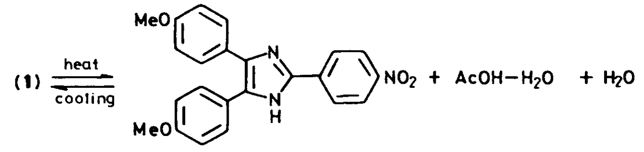


Figure 1. Aspects of hydrogen bonds in (**1**) and (**1a**). A, Three-dimensional crystal packing projected on the *bc* plane: ○, carbon; ⊚, oxygen; ●, nitrogen; small circle, hydrogen; dotted line, hydrogen bond; double lines show the imidazole. B, Removal of water molecule from (**1**) by drying

We can explain these phenomena as follows. If one water molecule α in [Figure 1 (**1**)] is removed by drying, the other water molecule β and the acetoxy group are able to move in, converting the imidazolium acetate into 1*H*-imidazole and acetic acid, as shown in [Figure 1, (**1a**)]. The imidazole ring is still linked by hydrogen bonds to acetic acid. If the alteration of the crystal structure is small, the water molecule can return to its original place by absorption of moisture and the initial crystal structure re-forms.

Trituration. When (**1**) was triturated in a mortar, the orange-yellow colour turned to red. The i.r. spectrum of the red sample showed a similar absorption to that of the dried sample of (**1**); a new weak and broad absorption appeared at 1 700 cm^{-1}, while the absorptions at 1 648, 1 614, and 1 422 cm^{-1} decreased. Hydrated crystals are often dehydrated by trituration, and the mechanism of colouration of (**1**) by trituration seems similar to that by drying.

Heating. When (**1**) was heated to 70 °C, the colour changed rapidly from orange-yellow to red and then reverted to the original on cooling. The i.r. spectrum, measured at 60 °C, displayed a new absorption at 1 718 cm^{-1} with an accompanying decrease in the absorptions at 1 614 and 1 422 cm^{-1}. The new band disappeared again on cooling, with increased absorptions at 1 614 and 1 422 cm^{-1}. It may be due to changes in the imidazolium acetate dihydrate (**1**) to give imidazole, as in the Scheme.



Scheme.

The absorption at 1 718 cm^{-1}, higher than that of the dried red sample (1 686 cm^{-1}), may be due to differences in the hydrogen bonds of the acetic acid. On heating from 70—80 °C the red colour deepened further and traces of it remained on cooling. The colour of a sample heated at 84 °C (**1b**) became red (Table 3) and the colour did not change on cooling.

The i.r. spectrum of (**1b**) displayed a marked absorption at 1 718 cm^{-1} (br m) with disappearance of the absorptions at 1 614 and 1 422 cm^{-1}. The ^{1}H n.m.r. sepctrum of the sample, which was heated at *ca.* 84 °C under atmospheric pressure before drying at 2 Torr at room temperature, was identical to that of (**1**) except for the downfield shift of a composite proton signal of the carboxy group and water, with an accompanying

Table 1. I.r. spectra (cm^{-1}) of (**1**)—(**7**)*

	In hexachlorobutadiene								In Nujol								In Nujol or in hexachlorobutadiene							
	ν_{NH}				ν_{CH}(OMe,Me)				δOH	$\nu CO_2{}^-$		νNO_2			δ_{CH}(Aryl)		Other absorptions between 1 620 and 1 460 cm^{-1}							
										ν_{as}	ν_s	ν_{as}		ν_s										
(**1**)				3 196 br,m	2 964 w	2 932 w		2 840 w	1 648 m	1 614 s	1 422 m	1 530 s		1 342 s	858 sh	842 s	1 614 s			1 574 m-s		1 504 s		1 462 s
(**2**)	3 420 w	3 332 m				2 936 w	2 908 w	2 832 w				1 510 s	1 340 s	1 320 sh	852 s	832 s	1 614 sh	1 604 s	1 582 m	1 574 m	1 540 w		1 492 s	1 464 m-s
(**3**)			3 240 br,m-w		2 964 w			2 836 w				1 512 s	1 342 s		850 s	830 s	1 614 m	1 598 s	1 582 m		1 536 w		1 492 s	1 462 m
(**4**)			3 220 m		2 964 w			2 836 w				1 520 s	1 340 s		854 s-m	834 s	1 616 m	1 598 s		1 576 m	1 538 w	1 506 s	1 494 s	1 464 m
(**5**)					2 964 w	2 930 w	2 900 w	2 840 w				1 524 s	1 344 s		854 s	834 s	1 614 m	1 598 s				1 506 s	1 494 s	1 464 m
(**6**)				3 044 br-w	2 952 w			2 836 w								834 s	1 614 m			1 574 m-w	1 540 w	1 520 s	1 498 s	1 462 m
(**7**)				3 168 br,m-w		2 932 w		2 836 w							846 s	830 s	1 614 sh	1 606 s				1 520 s	1 498 s	1 464 m-s

* br, broad; s, strong; m, medium; w, weak; sh, shoulder.

Table 2. ^{1}H N.m.r. data of (**1**)—(**7**)

	2-Aryl-H	4,5-Aryl-H	OMe	Solvent of crystallization	NH
(**1**) ($CDCl_3$)	8.18, 7.92 (A_2B_2, 4 H, *J* 9 Hz)	7.38, 6.82 (A_2B_2, 8 H, *J* 9 Hz)	3,80 (s, 6H)	2.03 (OAc) 5.53 (CO_2H-H_2O) (s, 3 H) (s, 5 H)	
(**2**) ($CDCl_3$)	8.20, 7.93 (A_2B_2, 4 H, *J* 9 Hz)	7.43, 6.83 (A_2B_2, 8 H, *J* 9 Hz)	3.81 (s, 6 H)		
(**3**) ($CDCl_3$)	8.18, 7.88 (A_2B_2, 4 H, *J* 9 Hz)	7.40, 6.82 (A_2B_2, 8 H, *J* 9 Hz)	3.78 (s, 6 H)		10.21 (br, 1 H)
(**4**) ($CDCl_3$)	8.21, 7.94 (A_2B_2, 4 H, *J* 9 Hz)	7.45, 6.85 (br-A_2B_2, 4 H, *J* 9 Hz)	3.80 (s, 6 H)	3.70 (dioxane) (s, 8 H)	10.0 (br, 1 H)
(**5**) ($CDCl_3$)	8.33, 7.93 (A_2B_2, 4 H, *J* 9 Hz)	7.46, 6.98 (A_2B_2, 4 H, *J* 9 Hz) 7.30, 6.77 (A_2B_2, 4 H, *J* 9 Hz)	3.88 (s, 3 H) 3.78 (s, 3 H)		3.54 (Me) (s, 3 H)
(**6**) ($CDCl_3$)	7.85, 7.35 (m, 2 H) (m, 3 H)	7.45, 6.83 (A_2B_2, 8 H, *J* 9 Hz)			
(**7**) (CD_3COCD_3)	8.30, 7.72 (A_2B_2, 4 H, *J* 9 Hz)	7.45, 6.82 (A_2B_2, 8 H, *J* 9 Hz)	3.80 (s, 6 H)		

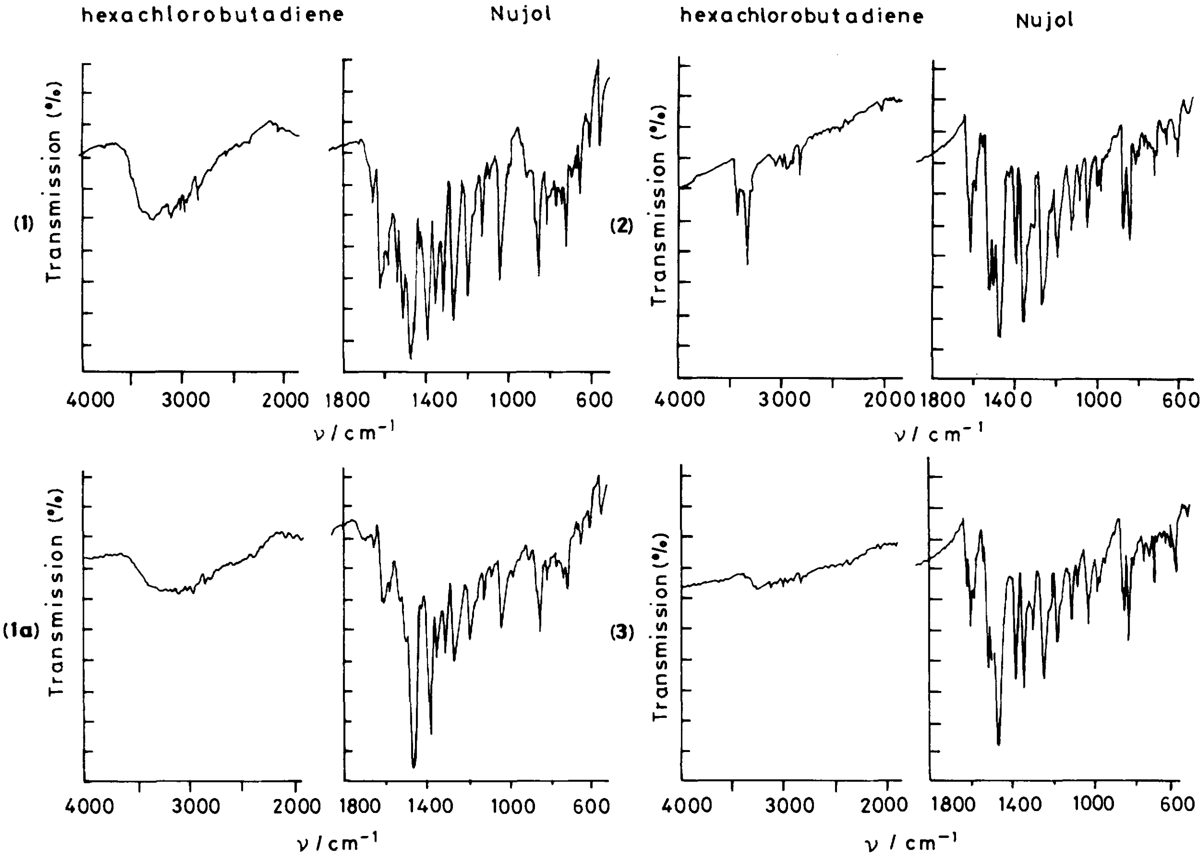
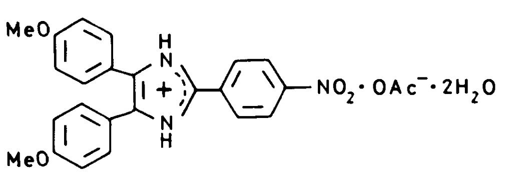


Figure 2. I.r. spectra of (**1**)—(**3**)

decrease of signal intensity. This shows that one mol each of water and acetic acid still remain in the sample. When the sample was continuously heated at *ca.* 84 °C under reduced pressure, the composite proton signal of the carboxy group and water, and the OAc signal, both decreased in intensity. The results suggest that one of the two moles of water of crystallization in (**1**) participates in a strong hydrogen bond with acetic acid.

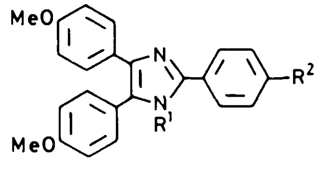
On elevation of temperature, (**1**) melts at *ca.* 98 °C but recrystallizes again upon removal of the solvent of crystal-



(1)

(1a) dried sample of (1)

(1b) 84°C heated sample of (1)



(2) R^1=H,R^2= NO_2 ; 100°C heated sample of (1)

(3) R^1=H,R^2= NO_2 ; crystallized in benzene

(4) R^1=H--dioxane,R^2= NO_2;crystallized in dioxane

(5) R^1= Me, R^2= NO_2

(6) R^1= H, R^2= H

(7) R^1= H, R^2= CN

lization. When (1) was heated at *ca.* 100 °C under reduced pressure, the colour became dark red, and was not reversible on cooling. This dark red material was (2).

Differential scanning calorimetry (d.s.c.) of (1) showed several endothermic changes at *ca.* 84, 94, and 100 °C as shown in Figure 3.

Endothermic changes from 81—86 °C and 90—110 °C were observed as 2.7 × 10^3 and 4.6 × 10^4 J mol^{-1}, respectively. Although the i.r. spectrum of (1) measured at 84 °C showed a marked νC=O absorption, due to acetic acid from imidazolyl acetate, the endothermic change at *ca.* 84 °C was small. It may be due to the coexistence of exothermic changes with the large endothermic change of the deprotonation reaction. Formation of a new hydrogen bond between acetic acid and water or reversion of the twist of the *p*-methoxyphenyl groups to form a more planar molecule would have made a considerable contribution to the exothermic changes.

The *X*-ray powder diffraction pattern of the sample heated to *ca.* 84 °C showed a weaker and broader peak than that of (1). Thus, acetic acid and water, once moved by heating to 84 °C, seem unable to return to their original position on cooling, and thus the colour change becomes irreversible. The i.r. spectrum of (1) in KBr at *ca.* 100 °C showed a remarkable νC=O absorption at 1 718 cm^{-1} while the i.r. spectrum of (2) showed no such absorption. The large endothermic energy changes at *ca.* 100 °C in d.s.c. is attributable to the melting of crystals of (1) and to the removal of the solvent of crystallization.

Elemental analysis of (2) showed the same molecular formula, $C_{23}H_{19}N_3O_4$, as the parent imidazole (3). Compound (3) was obtained by recrystallization of 4,5-bis-(4-methoxyphenyl)-2-(4-nitrophenyl)imidazole from benzene as orange prisms containing no solvent of crystallization. Polymorphism is consider-recrystallizes again upon removal of the solvent of crystallization. When (1) was heated at *ca.* 100 °C under reduced able in the crystals of (2) and (3). Although no crystals of (2) suitable for *X*-ray analysis could be obtained, the structure of (2) is briefly mentioned.

Table 3. Colour of crystals (1)—(5)

	Colour	Hue λ_D/nm	Chroma Pe(%)	Lightness Y	
(1)	Orange-yellow	588	81.4	44.8	21 °C
(1a)	Red	603	57.1	13.0	20 °C, humidity 5%
(1b)	Red	618	40.6	8.5	
(2)	Dark red	700	31.7	6.7	
(3)	Orange-yellow	589	82.5	31.4	
(4)	Red	605	70.3	21.8	
(5)	Orange	597	80.3	32.1	

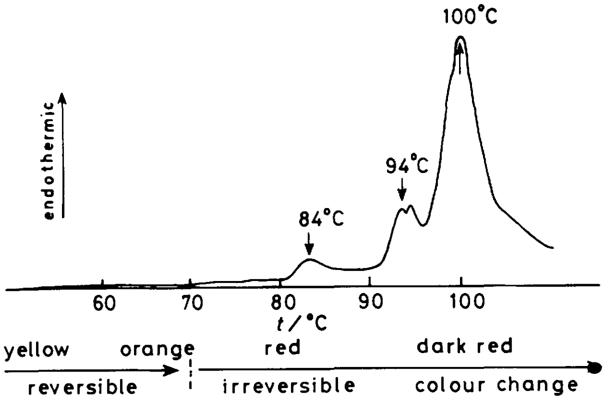


Figure 3. D.s.c. and colour change of (1)

The ^{1}H n.m.r. spectrum of (2) was slightly different from that of (3). Compound (3) showed an A_2B_2 signals at δ 7.40 and 6.82 (*J* 9 Hz) for eight protons of two *p*-methoxyphenyl groups, the lowfield part at 7.40 being a little broad at first. The signal changed to a typical A_2B_2 pattern after about two days. The result shows rotation of the *p*-methoxyphenyl group about the imidazole ring in the solid state. The NH proton signal was observed at δ 10.2 (br, 1 H).

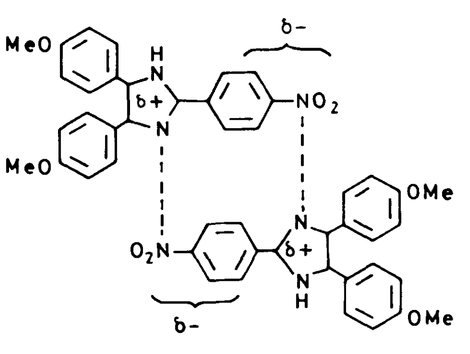
On the other hand, (2) showed a typical A_2B_2 pattern at δ 7.43 and 6.83 (*J* 9 Hz) for the eight protons of the *p*-methoxyphenyl groups and the signal showed no change on standing. No NH proton signal could be detected. The other signals of (2) were almost the same as those of (1). These results suggest that (2) is a more planar molecule than is (3) in the solid state.

The u.v. spectrum of (2) in solution was the same as that of (3). The longest absorption maxima in some solvents are shown in Table 4. The absorptions obeyed Beer's law at a concentration of 10^{-5} mol dm^{-3} at constant temperature. Thus, compound (2) exists as a 1*H*-imidazole structure, neither in an association nor as a tautomeric structure in solution under the concentrations measured. In the solid state however the colour and i.r. spectrum of (2) differed from those of (3). While (3) was orange-yellow, (2) was dark red. Because of this large difference in colour, (2) is considered to have a different structure from (3) in the solid state. A possible structure is an intermolecular CT complex, formed by the electropositive imidazole ring with the electro-negative *p*-nitrophenyl group (I), or an association of planar molecules (II).

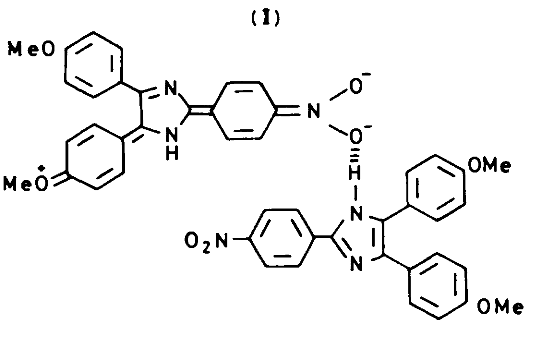
Kross *et al.*[4] and Hindaway *et al.*[5] have examined the i.r. spectra of the CT complex of *N*-substituted aniline with an aromatic nitro compound and reported that $\nu_{as}NO_2$ and δCH

Table 4. Longest wavelength absorption maxima of (**2**) in various solvents at 20 °C

Solvent	AcOH	EtOH	Dioxane	C_6H_6	$CHCl_3$	DMF
$\lambda_{max.}$/nm	372	406	410	412	415	422
$\delta 10^{-4}\ \varepsilon$	1.27	1.75	1.97	1.75	1.71	1.81



(**I**)



(**II**)

of the acceptor are sensitive to the complex formation. As shown in Table 1 and Figure 2, $\nu_{as}NO_2$ and δCH of *p*-substituted aryl groups[3] in (**3**) were observed at 1 512(s), 850(s), and 830(s), while (**2**) showed at 1 510(s), 852(s), and 832(s) cm^{-1} in Nujol. The shift to higher wavenumber or splitting into two bands for $\nu_{as}NO_2$ which has been reported by Hindaway's group[5] was not observed in (**2**). The lower wavenumber shift of δCH of the acceptor[4] was also not observed in (**2**). From these facts, the charge-transfer complex (**I**) was not formed.

On the other hand, a new absorption at 1 320 cm^{-1} for ν_sNO_2 appeared as a shoulder. It may be due to an intermolecular hydrogen bond from the imino hydrogen of one molecule to the nitro oxygen of another. The existence of the hydrogen bond is demonstrated by a shift of ν_{NH} to lower wavenumber. Compound (**2**) showed ν_{NH} at 3 456 cm^{-1} in dilute CCl_4 solution whereas it appeared at 3 420(w) and 3 332(m) cm^{-1} in Nujol. ν_{NH} Of (**3**) appeared as a broad band at 3 240 cm^{-1} due to a hydrogen bond of the type –NH···N=,* while the absorption at 3 332 cm^{-1} was medium and sharp. The shift to lower wavenumber (3 456 to 3 332 cm $^{-1}$) clearly indicates existence of a hydrogen bond and the sharp and medium band (Figure 3) showed a hydrogen bond of another type, –NH···O–. The weak absorption of 3 420 cm^{-1} may be due to the ν_{NH} of a non-hydrogen bonded NH group. The –NH···O– was examined by the ν_{NH} absorption of (**4**) obtained by recrystallization of (**3**) from dioxane. Crystals of (**4**) thus formed had one mole of dioxane whose oxygen might be linked to the NH group by a hydrogen bond. ν_{NH} Of (**4**) was observed at 3 220 cm^{-1} as a sharp and medium band in Nujol and was similar to the absorption at 3 332 cm^{-1} of (**2**). I.r. absorptions of (**2**) observed at 1 614(sh), 1 604(s), 1 585(m), 1 540(w), and 1 492(s) cm^{-1}, in Nujol, were assigned to characteristic absorptions of aryl 1*H*-imidazole.[3] From these results we concluded that (**2**) has structure (**II**).

The colour of (**2**) may be due to intermolecular hydrogen bond and intramolecular charge-transfer effects. Because (**2**) is more planar than (**3**) there are push and pull substituent effects in addition to electron donation from the imidazole to the 2-aryl group.[7]

When (**2**) was left in contact with saturated AcOH–H_2O vapour overnight, it turned orange-yellow. The i.r. spectrum agreed with that of (**1**). Crystals of (**3**) also turned into (**1**) over AcOH–H_2O vapour after three days. These results show the high stability of the structure (**1**).

Experimental

M.p.s were determined on a Büchi 510 apparatus and were uncorrected. I.r. spectra were recorded at room temperature on a Hitachi 270—50 spectrometer and, for variable temperatures, a Hitachi IRH-2 heating cell and its electric cell were used. ^{1}H N.m.r. spectra were measured for the indicated solvent with tetramethylsilane as internal standard on a Hitachi R-24B spectrometer. D.s.c. was carried out using SEIKO SSC-573 and SSC-540 heat leakage scanning calorimeters. The apparatus was calibrated by reference to the melting enthalpy of benzil. U.v. spectra were recorded on a Hitachi EPS-3T spectrometer with Komatsu CTE and CTR cooling circulators. The crystals were measured on a Tokyo Denshoku TC-360 U colourmeter and I.C.I. chromaticity diagrams were used. *X*-Ray powder diffraction patterns were recorded on a Rigaku D-3F diffractometer.

Preparation of 4,5-*Bis*-(4-*methoxyphenyl*)-2-(4-*nitrophenyl*)-*imidazole: Crystals of* (**3**).—This compound was prepared according to a slightly modified procedure of Davidson *et al.*[8] by reluxing anisil (10 g, 0.037 mol), *p*-nitrobenzaldehyde (5.8 g, 0.038 mol), and ammonium acetate (55 g) in glacial acetic acid for 2 h. The mixture was poured into ice–water and neutralized with aqueous ammonia to give a precipitate. The precipitate was warmed in 6M-HCl and the hydrochloride salt was collected on a filter paper. After washing with water, the product was recrystallized from ethanol to obtain a hydrochloride, yellow leaflets, m.p. 282 °C (decomp). The hydrochloride was suspended in water (100 cm^3) containing potassium hydroxide (3 g), and extracted with ethyl acetate. After washing with water, drying (Na_2SO_4), and evaporation, the residue was again purified by preparative t.l.c. ($CHCl_3$–CH_3COCH_3 15:1). Extraction of the main band by ethyl acetate gave a deep red oil (10 g) which crystallized in benzene. At first, needles separated by the crystals gradually turned to orange prisms over several days. Compound (**3**) turned red at *ca.* 192 °C and melted at 220—221 °C by slow elevation of temperature (Found: C, 68.6; H, 4.7; N, 10.4. Calc. for $C_{23}H_{19}N_3O_4$: C, 68.8; H, 4.8; N, 10.5%).

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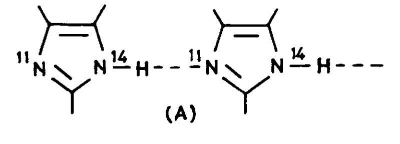
* A single-crystal *X*-ray analysis of (**3**)[6] showed the existence of a weak hydrogen bond between N(11)···(14) (x, $\frac{1}{2} - y$, $\frac{1}{2} + z$)—H(14) 3.190(5) Å, where N(11)···(14) = 2.46(3) Å, H(14)—N(14) = 0.87(3) Å, and ø[N(11)–H(14)–N(14)] = 141.8° as in (A).



(A)

Preparation of (**1**)—To a boiling acetic acid solution of (**3**), water was added until the solution became turbid. After cooling (**1**) was precipitated as orange-yellow leaflets, m.p. 98, and then 217—218 °C (Found: C, 60.4; H, 5.3; N, 8.6. Calc. for $C_{23}H_{19}N_3O_4 \cdot AcOH \cdot 2H_2O$: C, 60.4; H, 5.5; N, 8.45%).

Preparation of (**2**).—Crystals of (**1**) were heated at *ca.* 100 °C for 2 h under 2 Torr to obtain deep red material (**2**), m.p. 220—221 °C, by slow heating (Found: C, 68.8; H, 4.6; N, 10.5. Calc. for $C_{23}H_{19}N_3O_4$: C, 68.8; H, 4.8; N, 10.5%).

Preparation of (**4**).—Crystals (**4**) were obtained by recrystallization of (**3**) from dioxane, red columns, m.p. 148, and then 197 °C (Found: C, 66.3; H, 5.5; N, 8.6. Calc. for $C_{23}H_{19}N_3O_4 \cdot C_4H_8O_2$: C, 66.2; H, 5.7; N, 8.6%).

Preparation of (**5**).—Crystals of (**3**) (2 g, 0.005 mol) were dissolved in acetone (100 cm^3) and then dimethyl sulphate (1.5 cm^3) and powdered anhydrous potassium carbonate (2.1 g) were added. The mixture was refluxed under stirring for 3 h. After cooling, the mixture was poured into water and the precipitated orange crystals were collected by filtration. Recrystallization from ethanol gave (**5**) as orange needles (0.3 g), $\lambda_{max.}$(EtOH) 239 (ε 25 200 $dm^3 mol^{-1} cm^{-1}$), 267 (25 000), and 386 nm (13 200).

Preparation of (**6**) *and* (**7**).—These compounds were prepared by the same procedure as that of (**3**), using the appropriate aldehyde, anisil, and ammonium acetate. Compound (**6**) was recrystallized from ethanol, prisms, m.p. 198—199 °C (lit.,[9] 197 °C); $\lambda_{max.}$(EtOH) 235 (ε 23 400) and 304 nm (28 400). Compound (**7**) was recrystallized from ethanol, light yellow needles, m.p. 242—243 °C (Found: C, 75.5; H, 5.0; N, 11.0; Calc. for $C_{24}H_{19}N_3O_2$: C, 75.6; H, 5.0; N, 11.0%); ν_{CN} 2 228 cm^{-1}; $\lambda_{max.}$ (EtOH) 240 (ε 19 500 $dm^3 mol^{-1} cm^{-1}$), 253(sh), 280 (11 900), and 359 nm (20 600); yield 61.5%.

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