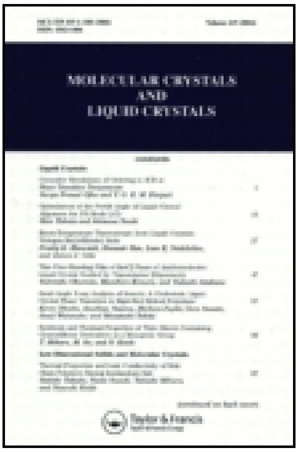


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Complex Formation of Imidazole Derivatives and Properties of the Products

Yoshiko Sakaino [a], Norikatsu Shimizu [a], Nobutaka Takahashi [a] & Katsushi Matsushima [a]

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

Version of record first published: 22 Sep 2006.

To cite this article: Yoshiko Sakaino, Norikatsu Shimizu, Nobutaka Takahashi & Katsushi Matsushima (1990): Complex Formation of Imidazole Derivatives and Properties of the Products, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 187:1, 145-153

To link to this article: http://dx.doi.org/10.1080/00268949008036037

Mol. Cryst. Liq. Cryst., 1990, vol. 187, pp. 145–153
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

COMPLEX FORMATION OF IMIDAZOLE DERIVATIVES AND PROPERTIES OF THE PRODUCTS

Yoshiko SAKAINO, Norikatsu SHIMIZU, Nobutaka TAKAHASHI
AND Katsushi MATSUSHIMA.
Department of Chemistry, Faculty of Education, Gunma
University, Maebashi, Gunma, 371, JAPAN.

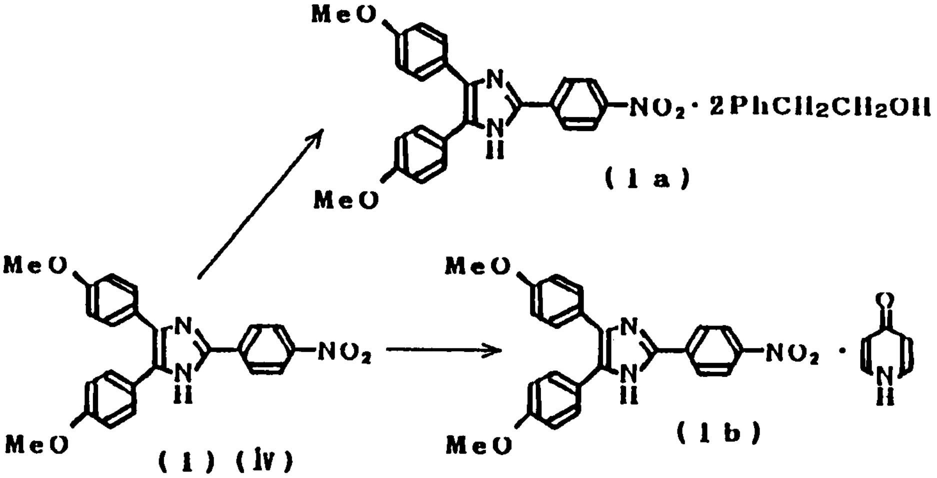
Abstract A thermochromic complex which gives out rose fragrance with the color change, and inclusion complexes which emit intense solid state fluorescence, were obtained by grinding of imidazole derivatives with 2-phenylethanol and carboxylic acid. Preparation and properties of these complexes are described.

INTRODUCTION

We have found recently that imidazole derivatives form inclusion complexes with many organic reagents. Some of the products show remarkable thermochromism and some of the products show intense fluorescence. Fluorescent properties of 2,4,5-triarylimidazole are well known but solid state fluorescence of inclusion of the imidazole derivatives with carboxylic acids has not yet been shown. This report describes formation of these complexes and properties of the products.

THERMOCHROMIC COMPLEX FORMATION

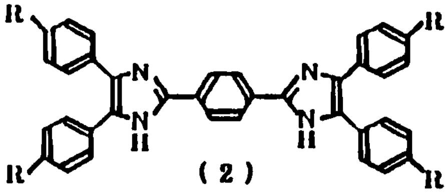
(1) forms four polymorphic crystals; (i) yellow prisms, (ii) red needles, (iii) vermillion fine needles, and (iv) dark red fine needles. The polymorph (iv) is formed at 100°C by heating an acetate dihydrate of (1) or at 140° C by heating an inclusion complex of (1) with dioxane[1]. Polymorph (iv) easily reacts with many organic reagents in the solid state to give the complexes. For example, (iV) forms thermochromic complexes with 2-phenyl



(1a)

(1) (iv)

(1b)



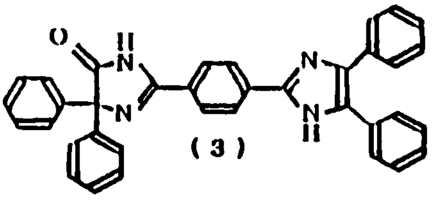
(2)

$(2) + 2CCl_3CO_2H \longrightarrow (2')$

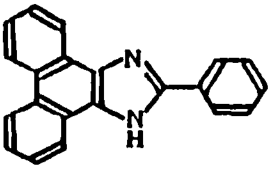
$(2) + 4CCl_3CO_2H \longrightarrow (2'')$

$(2) + 4CF_3CO_2H \longrightarrow (2''')$

	R
(2a)	H
(2b)	Cl
(2c)	OMe



(3)



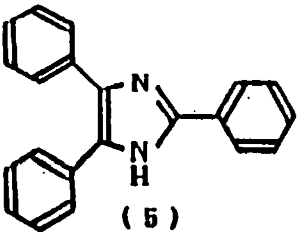
(4)

$(3) + CCl_3CO_2H \longrightarrow (3)$

$(3) + 5CCl_3CO_2H \longrightarrow (3'')$

$(4) + 2CCl_3CO_2H \longrightarrow (4'')$

$(4) + 2CF_3CO_2H \longrightarrow (4''')$



(5)

ethanol, and r-pyridone.

WITH 2-phenyethanol A 1:2 molar mixture of polymorph (iv) and 2-phenyl ethanol, ground in a mortar gave complex (1a). (1a) is also formed by crystallization of (1) in 2-phenylethanol and precipitated as yellow needles. Elemental analysis of (1a) gave the analytical data corresponding to the formula $C_{23}H_{19}N_3O_4 \cdot 2C_6H_4CH_2CH_2OH$. NMR in $CDCl_3$ showed δ8.20,7.95(A_2B_2, 4H, p-NO_2-Ph), 7.30,6.85(A_2B_2,8H,p-MeO-Ph), 7.25(m,10H,Ph-), 3.85(t,4H,-CH_2),3.8(s,6H,OMe), 2.9(t,4H,-CH_2-) and 1.85(m,2H,OH). IR absorption of (1a) measured in Nujol showed $\nu_{NH---OH---}$, a strong broad absorption maximum at 3191 cm^{-1}. The absorption shows a lower wavenumber shift compared to that of (iv) which appears at 3420(w),3332(m) cm^{-1}, and νOH of 2-phenylethanol which appears at 3337(s,br) cm^{-1}. A D.S.C. diagram of (1a) showed weak and gradual endothermic change from 50°C and strong endothermic change from 89°C up to 97°C with two peaks at 93°C and 94°C. (1a) turns orange yellow above 50°C and the colour deepens with elevation of temperature. At 93°C, (1a) shows deep red and melts at 94°C. The endothermic change, maximum at 93°C, is attributable to removal of 2-phenylethanol from (1). The maximum at 94°C can be assigned as melting enthalpy change. Product (1a'), which is obtained by the heating at 93°C under 2 Torr, showed red. The IR spectrum of the red product was same as that of the polymorph (iv). Table I shows data of colour analysis of (1a) and (1a'). If the heating is done in glass tubes, the red colour reverts to original colour on the cooling. Interestingly (1a) shows rose fragrance together with the colour change. Differences in absorption spectra, (1a')-(1a), showed an absorption maximum at 570 nm. One mole of the two moles of 2-phenylethanol bonds with the imidazole ring weakly and leaves above 50°C. The other 2-phenylethanol molecule bonds tightly to the imidazole ring by a hydrogen bond and leaves at 93°C. The mechanism of the

TABLE I. Crystal colours before and after heating of (1a)

	Hue λd (nm)	Chroma Pc (%)	Lightness Y (%)
(1a)yellow	570	82.1	54
(1a')red	618	44.1	4.4

TABLE II. Molar ratios, and $\nu_{c=o}$ absorptions of complexes (2a-c),(3)-(5) with CCl_3COOH

Cryst. No.	Host No.	Molor ratio Host:Gurst	$\nu_{c=o}$ cm^{-1}
2a'	2a	1 : 2	1646 (s)
2b'	2b	1 : 2	1650 (s)
2c'	2c	1 : 2	1646 (s)
3'	3	1 : 1	1648 (s)
4'	4	1 : 1	1662 (s)
5'	5	1 : 1	1652 (s)

thermochromism of (1a) can written as follows.

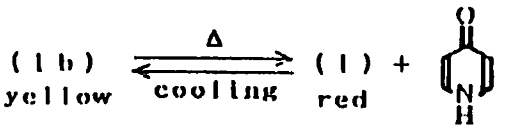
$$\begin{tikzcd}
(1a) \arrow[r, shift left, "\text{below } 89^\circ C"] & (1)\cdot PhCH_2CH_2OH \arrow[l, shift left, "\text{cooling}"] \arrow[d, shift left, "\Delta"] \\
 & \underset{\text{red}}{(1)} + \underset{\text{rose fragrance}}{PhCH_2CH_2OH} \arrow[u, shift left]
\end{tikzcd}$$

With γ-pyridone

When an equimolar mixture of polymorph (iv) and γ-pyridone was ground in a mortar or recrystallized in $CHCl_3$ which contains γ-pyridone, a yellow 1:1 host-guest complex (1b) was formed. Complex formation of the product is confirmed by elemental analysis, solution NMR, UV-VIS, IR spectra and D.S.C. thermogram measurement. (1b) also shows thermochromism between 120° and 210°C. That is, (1b) shows colour change from yellow to orange at about 120°C and the colour deepens on further heating. At 210° C, (1b) shows red colour and melts at 220°C. When the crystal of (1a) melts in sealed glass tube by heating, the red colour reverts to the original on cooling. However (1b) could not revert to original after melting . Figure 1 shows change of ν_{ND} of (1b) on variation of temperature; Absorption maxima at 2238 and 2268 cm^{-1}, decreased with the rise of temperature but absorbance maxima at 2358 cm^{-1} increased. The absorption at 2358 cm^{-1} is near that of polymorph (iv) . Accordingly, the red colour may be due to formation of free imidazole (1) by the heating. The mechanism of the thermochromism can be written as shown below.

Fluorescence

Imidazole derivatives (2)~(5) form complexes with trichloro



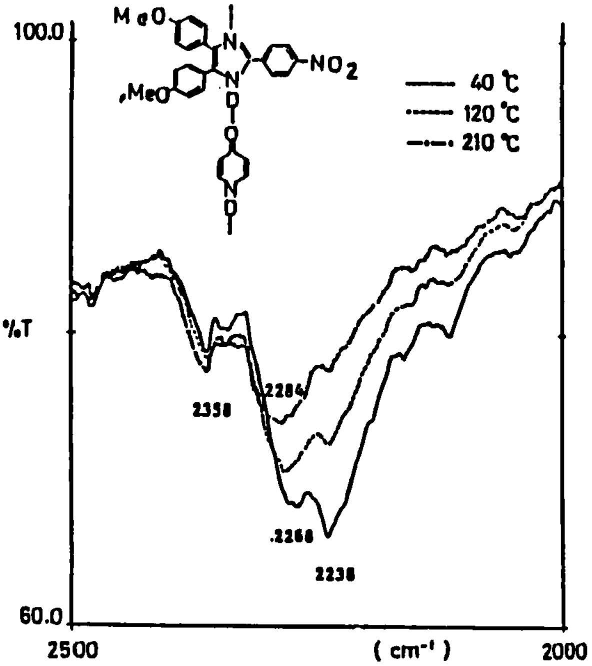


FIGURE 1. ν_{ND} change of (1b) on variation of temperature

acetic acid. For example (2a) (307 mg, 0.6 mmol) and trichloro acetic acid (201 mg, 1.2 mmol) was ground in a mortar for 30 min. then crystallized from dioxane containing 0.2 % trichloro acetic acid to give yellow needles (2'). Analytical data of the product corresponded to the formula $C_{36}H_{26}N_4 \cdot 2CCl_3COOH$(Found:C,57.04;H,3.7;N,6.42, Calcd:C,57.10;H ,3.35;N,6.66%).

Similar treatment of imidazole derivatives (3)~(5) gave the 1:1 complex with trichloro acetic acid. Table II shows molar ratio, melting points, and $\nu_{C=O}$ absorption of the complexes formed of imidazole derivatives (2)~(5) with trichloro acetic acid.

Fluorescence of (2) in solution has been reported[2,3] but the fluorescent property in the solid state has not been known. Imidazoles (2)~(5) fluoresce only weakly as solid states. Complexes (2')~(5') exhibit stronger fluorescence but the intensities are less satisfactory. Further addition of trichloro acetic acid to the imidazole complex resulted in intense fluorescence. For example, a mixture of imidazole derivative (3) (298 mg,0.56 mmol) and trichloro acetic acid (458 mg, 2.8 mmol), ground in a mortar for 30 min, gave light yellow powder with greenish fluolescence. The product(molar ratio 1:5) shows increased fluorescence and the intensity was about 13 times of that of (3) itself and 3.6 times of fluorescence of terphenyl. Table III shows Host-Guest molar.ratios of the inclusion complexes, excitation wavelength, absorption maxima of the fluorescences and relative intensities of these compared to that of imidazole itself. These imidazole derivatives also form inclusion complexes with CF_3COOH and show stronger fluorescence (Table IV). Hydrochlorides of these derivatives exhibit stronger fluorescence than that of complexes with CF_3COOH. However complexes with p-toluene sulfonic acid, acetic acid, formic acid, and benzoic acid shows weaker fluorescence than that of (1) with trichloro acetic acid. Inclusion complex (2'') show two $\nu_{C=O}$ absorptions at 1754(m-s) and 1650 (s) cm^{-1}. Trichloro acetic acid exhibits a band

TABLE III. Fluorescence of imidazole derivatives (2)~(5) with CCl_3COOH

No	Molar ratio host:guest	λ_{excit} (nm)	λ^{fl}_{max} (nm)	Relative Intensity
2a	1 : 0	382	466	1
2a''	1 : 4	405	450	23.1
2b	1 : 0	387	478	1
2b''	1 : 4	399	444	39.5
2c	1 : 0	358	461	1
2c''	1 : 4	437	503	25.7
3	1 : 0	360	461	1
3''	1 : 5	456	492	1,2.9
4	1 : 0	365	398	1
4''	1 : 2	374	440	3.3
5	1 : 0	347	383	1
5''	1 : 2	359	396	9.9

TABLE IV. Fluorescence of imidazole derivatives (2)~(4) with CF_3CO_2H

No	Molar ratio host:guest	λ_{excit} (nm)	λ^{fl}_{max} (nm)	Relative Intensity
2a	1 : 0	382	466	1
2a'''	1 : 4	398	446	42.4
2b	1 : 0	387	478	1
2b'''	1 : 4	377	432	29.5
2c	1 : 0	358	461	1
2c'''	1 : 4	442	543	43.7
3	1 : 0	360	461	1
3'''	1 : 5	416	469	29.1
4	1 : 0	365	398	1
4'''	1 : 2	384	442	3.0

at 1754 cm^{-1}. The complex (2''') also shows two $\nu_{C=O}$ bands at 1780(m) and 1650(s) cm^{-1} and trifluoro acetic acid shows the band at 1780 cm^{-1}. On the other hand, DTA of (2''') shows four endothermic changes at 126.5°, 140°, 190° and 203°C with weight-loss at every peak. Accordingly, 2 moles of the 4 moles of carboxylic acids may bond tightly by hydrogen bonds, but the others bond weakly to the imidazole.

REFERENCES

1. Y.Sakaino, T.Takizawa, Y.Inouye and H.Kakisawa, J. Chem. Soc. Perkin Trans. 2, 1623 (1986).
2. V.S.Marevtsev, A.I.Shienok, V.G.Luchina, Yu.D.Khamchuov, and M.I.Cherkashin., Izv. Akad, Navk SSSR, Ser. Khim., 1505(1985).
3. V.S.Marevtsev, A.I.Shienok, and M.I.Cherkashin, Izv.Akad.Nauk SSSR,Ser.Khim.,2469(1987).