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Piezochromism of Acridinols

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Synopsis. Piezochromic properties of acridinols and phenazinols have been examined. Only 3-acridinols showed piezochromism. This phenomenon was found to correspond to the formation of lactam isomers of the hydroxy compounds in 20 % aqueous solution of ethanol.

Recently, functional dyes which show chromotropic properties have attracted great interests. To our knowledge, a few reviews and some papers have been reported on the piezochromic compounds.[1–10] The mechanism of piezochromism can be classified into 3 cases: 1) twisting of C=C bond as observed in the cases of 10,10′-bianthrone,[3] diphenylmethyleneanthrone,[4] diphenylmethylenexanthene,[4] and diflavylene,[5] 2) C–C bond cleavage to form stable radicals as reported in the cases of bicumaranyl,[6] dimers of triarylimidazolyl,[7] and dimers of tetraphenylpyrryl,[8] and 3) isomerization as reported in the case of 9-phenyl-3-acridinol.[9] In the last case, yellow crystals of 9-phenyl-3-acridinol were converted into red one by pressing or rubbing.[9] In 1961, Cairns-Smith et al. have reported that the yellow solid mainly existed in the lactim form and red one might contain both the lactim and the lactam form.[10] This report examines the piezochromism of acridinols and phenazinols.

Results and Discussion

Figure 1 shows the reflection spectra of 9-cyclohexyl-3-acridinol (**1e**). Compound **1e** turned from yellow to orange by pressing (ca. 100 kg cm^{-2}) or grinding in a mortar. After pressing the solid, the reflectance at around 500 nm decreased, suggesting that the yellow solid changed to orange one. The orange solid did not revert to the original yellow solid on standing for 2 years in a desiccator at room temperature. However, by the addition of a drop of organic solvents such as ethanol, benzene, carbon tetrachloride, and acetone, etc. to the solid, the color immediately recovered from orange to yellow. When this yellow solid was pressed or grinded, the color changed to orange again.

Figure 2 shows the absorption spectra of **1e**. The absorption maximum was observed at 350 nm in hexane. While new absorption, which is attributed to the lactam isomer of **1e**, was observed at 460 nm in 20% aqueous solution of ethanol. This new absorption was not observed in acetonitrile, suggesting that a polar protic solvent is suitable to observe the lactim-lactam isomerization of acridinols and phenazinols.

Table 1 summarizes the results of piezochromism and the formation of the lactam isomer of acridinols and phenazinols in 20% aqueous solution of ethanol. As has been reported, 9-phenyl-3-acridinol (**1a**), which can exist in a lactam isomer in 20% aqueous solution

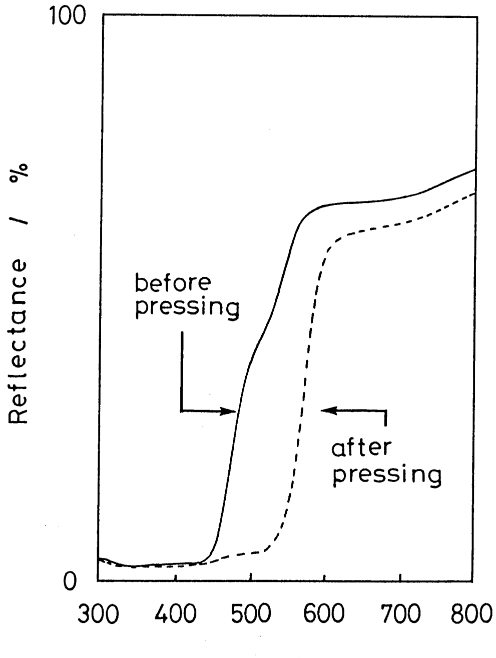


Fig. 1. Reflection spectra of 9-cyclohexyl-3-acridinol (**1e**).

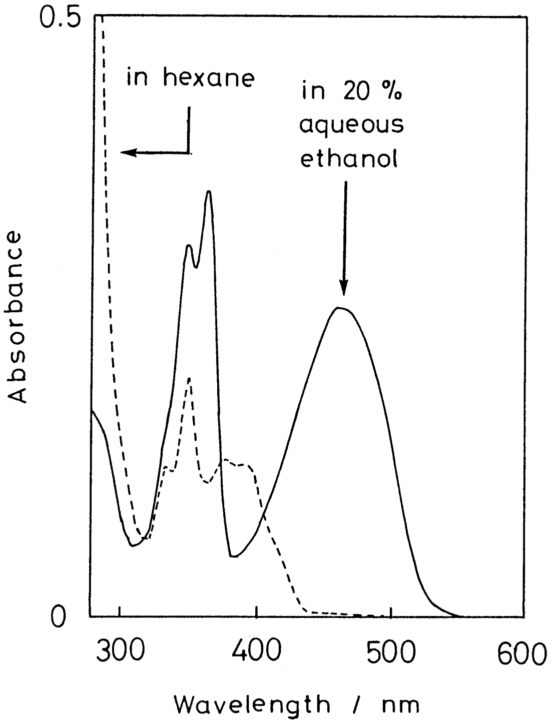
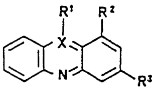


Fig. 2. Absorption spectra of 9-cyclohexyl-3-acridinol (**1e**). Concentration of **1e** was 3.30×10^{-2} mmol dm^{-3}.

Table 1. Piezochromism and Formation of Lactam Isomers of Acridinols and Phenazinols in 20 % Aqueous Ethanol



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Run	Compound	X	R¹	R²	R³	Piezo-chromism	Formation of lactam isomer[a)]
1	**1a**	C	C_6H_5	H	OH	yes	yes
2	**1b**	C	C_6H_5	H	OCH_3	no	no
3	**1c**	C	H	H	OH	yes	yes
4	**1d**	C	CH_3	H	OH	yes	yes
5	**1e**	C	C_6H_{11}	H	OH	yes	yes
6	**1f**	C	*m*-$CH_3C_6H_4$	H	OH	yes	yes
7	**1g**	C	*p*-$CH_3C_5H_4$	H	OH	yes	yes
8	**1h**	C	*m*-ClC_6H_4	H	OH	yes	yes
9	**1i**	C	*p*-ClC_6H_4	H	OH	yes	yes
10	**1j**	C	*p*-$CH_3OC_6H_4$	H	OH	yes	yes
11	**1k**	C	1-$C_{10}H_7$	H	OH	yes	yes
12	**1l**	C	2-$C_{10}H_7$	H	OH	yes	yes
13	**1m**	C	*o*-HOC_6H_4	H	H	no	no
14	**1n**	C	*p*-HOC_6H_4	H	H	no	no
15	**1o**	C	C_6H_5	OH	H	no	no
16	**1p**	N	—	OH	H	no	no
17	**1q**	N	—	H	OH	no	no

a) In 20% aqueous ethanol.

of ethanol, showed piezochromism (run 1). 3-Methoxy-9-phenylacridine (**1b**) did not show piezochromism, suggesting that lactam form is necessary to show piezochromism (run 2). 9-Unsubstituted, 9-alkyl, and 9-aryl-3-acridinols (**1c**)—(**1l**) showed both piezochromism and the formation of the lactam isomer in the solvent (runs 3—12). Their absorption maxima in hexane were observed at around 350 nm. While the absorption spectra in 20% aqueous solution of ethanol showed new absorption at around 460 nm. They also showed piezochromism from yellow to orange in color. In the cases of 9-(2-hydroxyphenyl)acridine (**1m**), 9-(4-hydroxyphenyl)acridine (**1n**), 9-phenyl-1-acridinol (**1o**), and phenazinols (**1p**) and (**1q**), neither piezochromism (even at a pressure of ca. 300 kg cm^{-2}) nor the formation of the lactam isomer was observed (runs 13—17).

It was concluded that only 3-acridinols, that can form the lactam isomers in 20% aqueous solution of ethanol, showed piezochromism.

Experimental

Instruments. NMR spectra were recorded on a JEOL JNM GX-270 spectrometer. Mass spectra were taken on a Shimadzu 9020 DF spectrometer at 70 eV. Melting points were measured with a Yanagimoto micro melting point apparatus and uncorrected. UV and reflection spectra were recorded on Hitachi 330 and U-3400 spectrophotometers, respectively.

Materials. Acridinols (**1a**), (**1c**)—(**1o**) were prepared by the reaction of diphenylamines with carboxylic acids (the Bernthsen reaction). They were purified by column chromatography (SiO_2, $CHCl_2$-EtOH) and recrystallized from ethanol. 3-Methoxy-9-phenylacridine (**1b**) was synthesized by the methylation of 9-phenyl-3-acridinol (**1a**) using diazomethane. 1-Phenazinol (**1p**) was purchased from Tokyo Kasei Kogyo Co., Ltd. 2-Phenazinol (**1q**) was synthesized as described in the literature.[11)] The purity of all materials was checked by TLC. The physical and spectral data are shown below:

9-Phenyl-3-acridinol (**1a**): mp: 258—260 °C (decomp) (lit[10)] 264 °C); MS *m/z* (rel intensity) 271 (M$^+$, 100).

3-Methoxy-9-phenylacridine (**1b**): mp: 135 °C (lit[10)] 137—138 °C); MS *m/z* (rel intensity) 285 (M$^+$, 100).

3-Acridinol (**1c**): mp: 255—256 °C (decomp) (lit[12)] >250 °C); MS *m/z* (rel intensity) 195 (M$^+$, 100).

9-Methyl-3-acridinol (**1d**): mp: 251—252 °C (decomp) (lit[12)] >250 °C); MS *m/z* (rel intensity) 209 (M$^+$, 100).

9-Cyclohexyl-3-acridinol (**1e**): mp: 257—258 °C (decomp); MS *m/z* (rel intensity) 277 (M$^+$, 100); Found: *m/z* 277.1473. Calcd for $C_{19}H_{19}NO$: M, 277.1466.

9-(*m*-Tolyl)-3-acridinol (**1f**): mp: 242—244 °C (decomp); MS *m/z* (rel intensity) 285 (M$^+$, 100); Found: *m/z* 285.1162. Calcd for $C_{20}H_{15}NO$: M, 285.1153.

9-(*p*-Tolyl)-3-acridinol (**1g**): mp: 262—263 °C (decomp); MS *m/z* (rel intensity) 285 (M$^+$, 100); Found: *m/z* 285.1176. Calcd for $C_{20}H_{15}NO$: M, 285.1153.

9-(3-Chlorophenyl)-3-acridinol (**1h**): mp: 200—202 °C (decomp) MS *m/z* (rel intensity) 305 (M$^+$, 100); Found: *m/z* 305.0624. Calcd for $C_{19}H_{12}NOCl$: M, 305.0607.

9-(4-Chlorophenyl)-3-acridinol (**1i**): mp: 270—272 °C (decomp); MS *m/z* (rel intensity) 305 (M$^+$, 100); Found: *m/z* 305.0621: Calcd for $C_{19}H_{12}NOCl$: M, 305.0607.

9-(4-Methoxyphenyl)-3-acridinol (**1j**): mp: 251—252 °C (decomp); MS *m/z* (rel intensity) 301 (M$^+$, 100); Found: *m/z* 301.1095. Calcd for $C_{20}H_{15}NO_2$: M, 301.1102.

9-(1-Naphthyl)-3-acridinol (**1k**): mp: 227—229 °C (decomp); MS *m/z* (rel intensity) 321 (M$^+$, 100); Found: *m/z* 321.1143. Calcd for $C_{23}H_{15}NO$: M, 321.1153.

9-(2-Naphthyl)-3-acridinol (**1l**): mp: 234—235 °C (decomp); MS *m/z* (rel intensity) 321 (M$^+$, 100); Found: *m/z* 321.1132. Calcd for $C_{23}H_{15}NO$: M, 321.1153.

9-(2-Hydroxyphenyl)acridine (**1m**): mp: 275—277 °C (decomp) (lit[13)] 289—290 °C); MS *m/z* (rel intensity) 271 (M$^+$, 100).

9-(4-Hydroxyphenyl)acridine (**1n**): mp: >300 °C (lit[13] 355—356 °C); MS m/z (rel intensity) 271 (M^+, 100).

9-Phenyl-1-acridinol (**1o**): mp: 164—165 °C (decomp); MS m/z (rel intensity) 271 (M^+, 100); Found: m/z 271.0980. Calcd for $C_{19}H_{13}NO$: M, 271.0997.

2-Phenazinol (**1q**): mp 251—252 °C (lit[11] 253—254 °C); MS m/z (rel intensity) 196 (M^+, 100).

Piezochromism of Acridinols and Phenazinols. Press test was carried out using an oil press (Riken Power model P-16). After pressing the sample, the color change was observed.

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