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X-Ray Structures of Electrochromic Compounds. Colorless 3,3-Dimethyl-2-(p-dimethylaminostyryl)indolino-[1,2-b]oxazoline and Colored 2-(p-Dimethylaminostyryl)-1-hydroxyethyl-3,3-dimethyl-indolinium Bromide

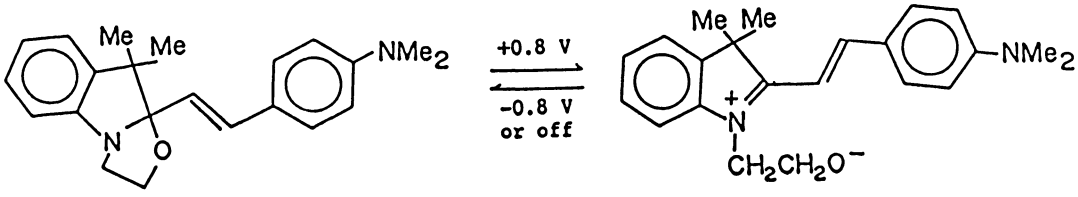
Satoshi KAWAMI, Hiroshi YOSHIOKA, Kazumi NAKATSU,* Tsuneki OKAZAKI,† and Masaaki HAYAMI†

Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662

†Japanese Research Institute for Photosensitizing Dyes, Fujita, Okayama 700

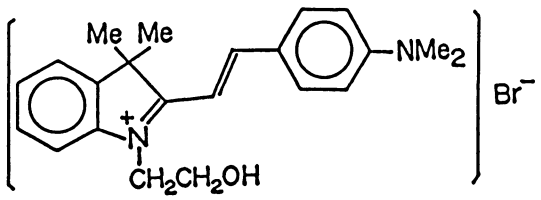
The X-ray structure analyses of the title compounds have revealed that in the former intramolecular steric overcrowding of atoms around the spiro-carbon atom and a distortion of the oxazoline ring are present, while in the latter the hydroxyethyl group takes an adequate orientation for the reverse change.

Some compounds containing both indoline ring and styryl group in a molecule exhibit electrochromism that shows remarkable color change on applying electric field. Scheme 1 shows tentatively the relevant electrochromic reaction: 3,3-dimethyl-2-(p-dimethylaminostyryl)indolino[1,2-b]oxazoline (1) undergoes cleavage of the C(spiro)-O bond of oxazoline ring by applying +0.8 V field to transform into colored 2-(p-dimethylaminostyryl)-3,3-dimethyl-indolinio-1-ethanolate (2), which returns reversibly to 1 by applying momentarily inverse field or by turning the



Colorless form, 1
λ_{max} = 295 nm in hexane

Colored form, 2
λ_{max} = 547 nm in methanol



Hydrobromide of colored form, 2

Scheme 1. Electrochromic reaction of the title compounds.

circuit off.[1,2] A colored salt, 2-(p-dimethylaminostyryl)-1-hydroxyethyl-3,3-dimethylindolinium bromide (3), was synthesized to stabilize 2, though no hydrogen bromide is contained in practical devices. To obtain better understanding on the correlation between molecular substitution, conformation and electrochromic reactivity, the molecular and crystal structures of a pair of colorless, 1, and colored species, 3, have been determined by X-ray structure analyses.

Single crystals of 1 were grown from an acetone solution and those of 3 were obtained by diffusion of petroleum-ether vapor into an acetone solution. Intensities were measured by a four-circle automatic diffractometer with graphite-monochromated Mo Kα radiation up to $2\theta = 55°$, and were corrected for Lorentz and polarization factors. Altogether 2473 and 2137 reflections with $|Fo| > 3\sigma(Fo)$ for 1 and 3, respectively, were used for the structure determination. Structures were solved by the direct method with MULTAN 78.[3] Block-diagonal least-squares refinements including all the hydrogen atoms converged R to 0.080 for 1 and 0.075 for 3.

Table 1. Crystal Data

	1	3
Formula	$C_{22}H_{26}N_2O$	$(C_{22}H_{27}N_2O)^+Br^-$
Crystal System	Monoclinic	Orthorhombic
Space Group	$P2_1/a$	$P2_12_12_1$
Cell Dimensions		
a/Å	24.777(5)	12.398(3)
b/Å	8.233(2)	17.382(5)
c/Å	9.209(2)	9.689(8)
β/°	97.20(1)	-
Z	4	4
D_x/g cm^{-3}	1.1920(4)	1.3214(5)

Table 1 gives the crystal data. Figures 1a and 1b show the molecular structures with atomic labelling and interatomic distances in Å.

In the colorless form, 1, the most outstanding property is the steric crowding of atoms around the spiro-C2 atom. The C2 atom is located slightly out of the plane of N1-C8-C9-C3 by 0.41 Å. The oxazoline ring is nearly in an envelope form: the C2 atom deviates by 0.51 Å from the mean plane of N1-C20-C21-O. Thus the conformation about the C20-C21 bond is almost cis, the torsion angle being only 9.4°. Moreover the N1-C2-O angle of 103.6° is much less than the normal tetrahedral angle. The geometry around N1 is markedly pyramidal, the sum of the valence angles being 328.6°. Several close intramolecular contacts between non-bonded atoms, shown in Fig. 1a, are worth noting: some of which are apparently shorter than the sum of the corresponding van der Waals radii. These findings imply that the oxazoline ring contains a considerable strain, which would cause the bond cleavage in the electric field.

The O-C2 bond, which is expected to be cleaved under electric field, is normal in length and slightly but not significantly longer than the O-C21 bond. In the photochromic substances, the bonds to be cleaved on UV irradiation are significantly elongated from the usual bond lengths.[5,6] Thus, in the electrochromic reactions, the change of the relevant bond length would appear only when the substances are placed in the electric field.

The molecule assumes trans configuration about the C10=C11 bond, which is shorter by about 0.05 Å than the normal double bond: reasons for this unusual length are not evident. The plane through C2, C10, C11 and C12 makes the dihedral

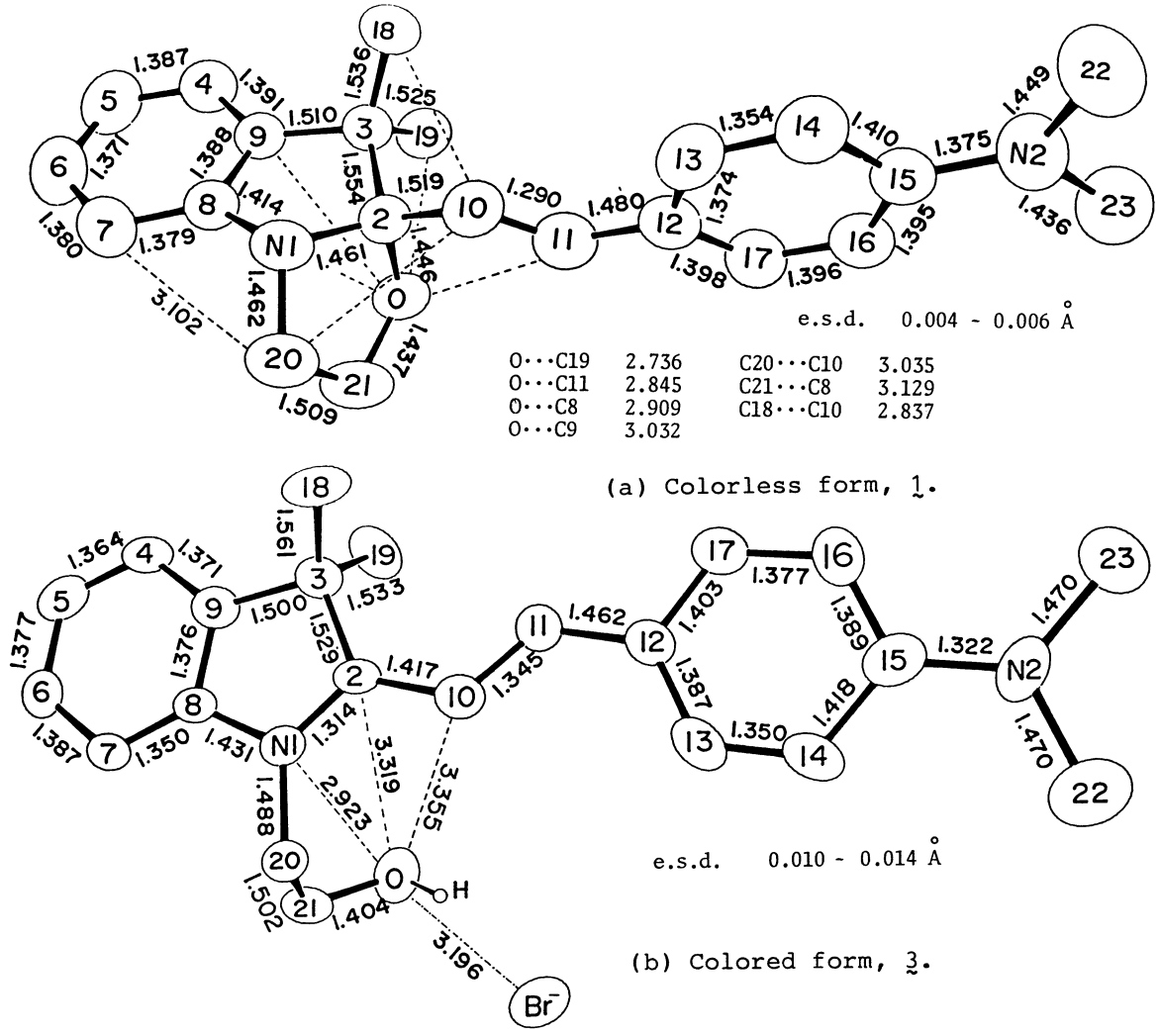


Fig. 1. ORTEP diagrams[4] of the molecular structures with 30% probability envelopes.

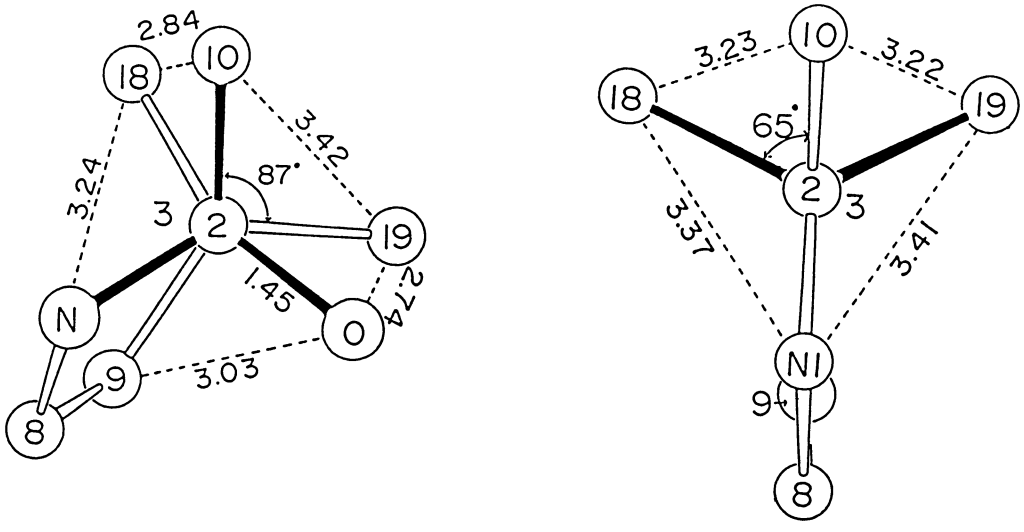


Fig. 2. Newmann projections along the C2-C3 bond.

angle of 77.4° with the indoline ring. In the styryl group, the N2-C15 length shows partial double-bond character, but no apparent indication for usual quinoid form contribution[7] is observed.

In the crystal structure of 1, the molecules are held together by van der Waals forces and no unusual intermolecular contacts were found.

The cleavage of the C2-O bond causes the change of hybridization of the C2 atom from sp^3 to sp^2, and subsequently changes in molecular conformation and geometry. The C10-C11 and C2-N1 lengths correspond to those of the localized double bond. In the dimethylaminobenzyl group a tendency of π-electron localization is also remarkable.

The N1-C20-C21-OH fragment takes one of the two possible gauche conformations: the O atom is located so as to take advantage to form the C2-O bond in the colorless state. A CNDO-MO calculation[8] of 3 showed that the net charge on C2 is +0.2e and that on O is -0.3e. Thus the electrostatic interaction between the C2 and O atom would be a driving factor for the reverse reaction.

Figure 2 compares Newmann projections along the C2-C3 bond in both structures. Notably in 1, the conformation is far from the ideal gauche form: e.g. the torsion angle C10-C2-C3-C19 being 87°. On the other hand, in 3 the pyroline ring is planar, and the two methyl groups, C18 and C19, are symmetrically located with respect to the pyroline ring plane. The non-equivalent and equivalent environment of the methyl groups in 1 and 3, respectively, are also concluded from a ^{1}H-NMR study of a solution.

In the crystal structure of 3, the hydrogen bond of OH...Br^- type was found, as shown in Fig. 1b. No other unusual intermolecular contacts were found.

Present study has shown that steric overcrowding of atoms is an important factor that affects the electrochromic transformation. Further studies will be needed to elucidate detailed structural dependence on the electrochromic reactions.

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