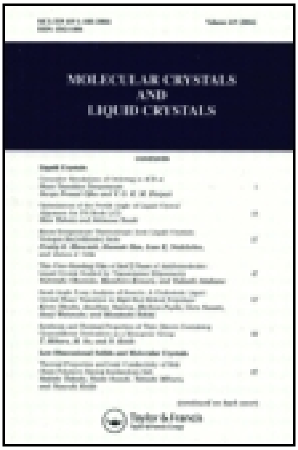

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PROTON TRANSFER IN *N*-SALICYLIDENEANILINES –EFFECT OF CHARGE-TRANSFER INTERACTION

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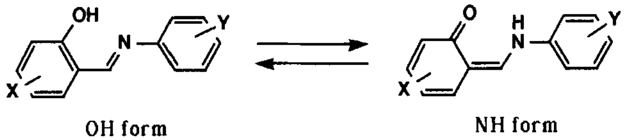
ABSTRACT The structural and optical studies on the proton transfer in various charge transfer complexes of *N*-salicylideneaniline derivatives are presented. The OH···N hydrogen-bond structure has been found to be variable by adjustment of the intermolecular interactions.

INTRODUCTION

The proton transfer accompanied by a configurational change of the π-electron structure may be one of the useful functionality for constructing a novel type of molecular systems. For example, if we could construct a molecular conductor based on this type of molecules, the charge transport might strongly be modulated by the proton motion.[1,2] As an approach to such a system, we have been studying the proton transfer in *N*-salicylideneanilines.[3,4,5]



N-Salicylideneanilines were known to crystallize into two types; one showed photochromism and the other showed thermochromism.[6] Both chromic behaviors arise from a proton transfer from the hydroxyl oxygen to the imine nitrogen as shown above. Particularly interested are the thermochromic crystals, in which planar molecules are stacked to form a one-dimensional column. A series of our structural and optical studies of the thermochromic crystals have indicated that the hydrogen-bond structure and the proton transfer behavior have some dependence on the molecular shape and on the

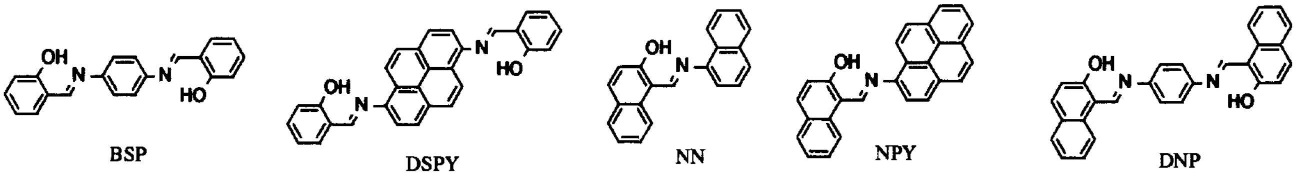


FIGURE 1. N-Salicylideneaniline derivatives studied.

TABLE I. Crystal data of charge-transfer complexes of *N*-salicylideneanilines.

	BSP·TCNQ	DSPY·TCNQ	NN(TCNQ)$_2$	NPY·TCNQ	DNP·TCNQ	(NPY)$_2$F$_4$TCNQ	DNP·F$_4$TCNQ
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.424(3)	9.085(2)	8.360(1)	11.131(2)	10.221(3)	10.836(2)	10.079(2)
b/Å	11.128(3)	25.694(4)	14.969(2)	17.804(3)	10.342(2)	14.294(3)	10.377(2)
c/Å	8.203(1)	7.252(1)	7.595(1)	8.151(1)	7.829(2)	8.076(2)	8.013(2)
α/deg	90.87(2)	90.96(1)	91.26(1)	100.68(1)	102.96(1)	106.86(2)	104.38(1)
β/deg	100.95(2)	106.27(1)	92.05(1)	90.14(1)	103.25(1)	101.52(2)	100.74(2)
γ/deg	130.48(1)	104.46(1)	113.36(1)	115.23(1)	95.87(1)	91.75(2)	93.57(2)
V/Å^3	631.3(3)	1566.8(5)	871.4(2)	1429.8(4)	774.7(4)	1167.8(5)	792.4(3)
Z	1	2	1	2	1	1	1

intermolecular charge-transfer interaction. Presently, we are extending the system to charge-transfer complexes, in which *N*-salicylideneanilines are employed as a donor component.

In this report, we show the hydrogen-bond structures in various charge-transfer complexes of *N*-salicylideneanilines, and indicate the correlation between the proton transfer and the charge-transfer interaction.

RESULTS AND DISCUSSION

N-Salicylideneaniline derivatives studied are shown in Fig. 1, and the crystal data are listed in Table I. In the crystals of these charge transfer complexes so far studied, the donor and acceptor components are mixed along the direction in which the maximum overlap between the molecules is achieved. As expected from their structures, these complexes are not very good conductors; 10^4-$10^{12}\Omega$ cm at room temperature.

Figure 2 shows the hydrogen-bond structure in these complexes. Each map consists of the framework and contours. The contours were obtained from the difference Fourier syntheses calculated by taking the parameters of the hydroxyl hydrogen out of the refined structures. Therefore, these electron density maps are supposed to reflect the distribution of the hydrogen in the hydrogen bond. It can be seen that there are three types of the hydrogen distribution; the OH type for BSP·TCNQ and DSPY·TCNQ, the NH type for NN(TCNQ)$_2$, NPY·TCNQ, and DNP·TCNQ, and the intermediate type for DNP·F$_4$TCNQ and (NPY)$_2$F$_4$TCNQ. The CO distance also charges with reflecting the hydrogen distribution.

In Fig. 3, the energy of the charge transfer bands are plotted vs. the CO distance which is a reliable index whether the hydrogen-bond structure corresponds to the OH or NH form. From this plot, it can be seen that the intermediate structure appears when the energy of the charge transfer band is smaller. It should be noted that these differences in the CO distance, namely the hydrogen position, do not arise from the differences in the crystal structure or in the composition, since the difference clearly appears in the pair of the DNP complexes, DNP·TCNQ and DNP·F$_4$TCNQ, which are completely isomorphous.

The energy of the charge transfer bands are then plotted vs. the difference of the redox potential between the donor and acceptor molecules in Fig. 4. As expected from the model proposed by Torrance,[7] a linear correlation is observed. From this figure, it can be seen that the intermediate hydrogen-bond structure appears when the ground state is close to the boundary between the neutral and ionic ones. Therefore, the intermediate

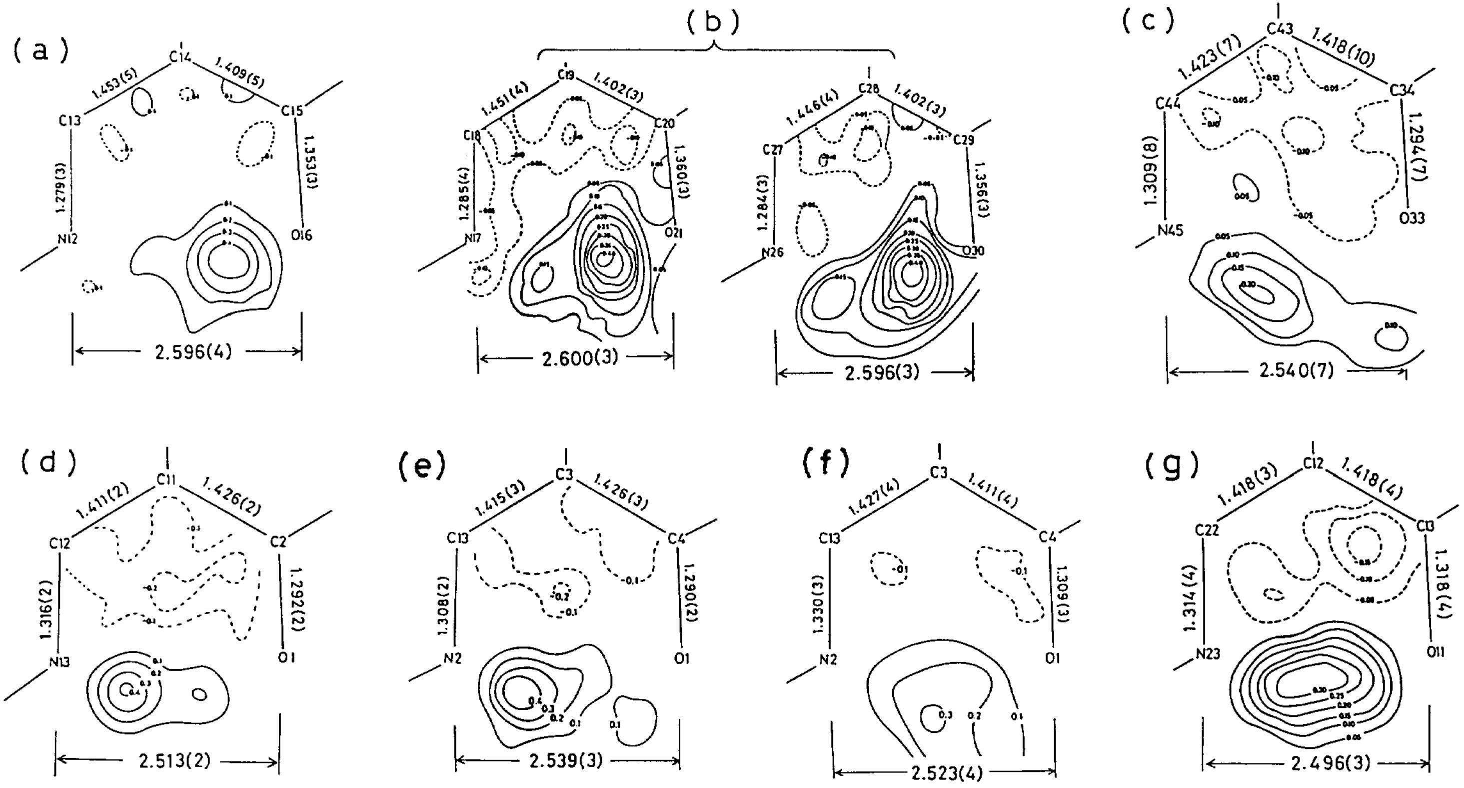


FIGURE 2. Difference synthesis maps (e/Å^3) and the interatomic distances (Å) of the hydrogen-bonded chelate rings of BSP·TCNQ (a), DSPY·TCNQ (b), NN(TCNQ)$_2$ (c), NPY·TCNQ (d), DNP·TCNQ (e), DNP·F$_4$TCNQ (f), and (NPY)$_2$F$_4$TCNQ (g).

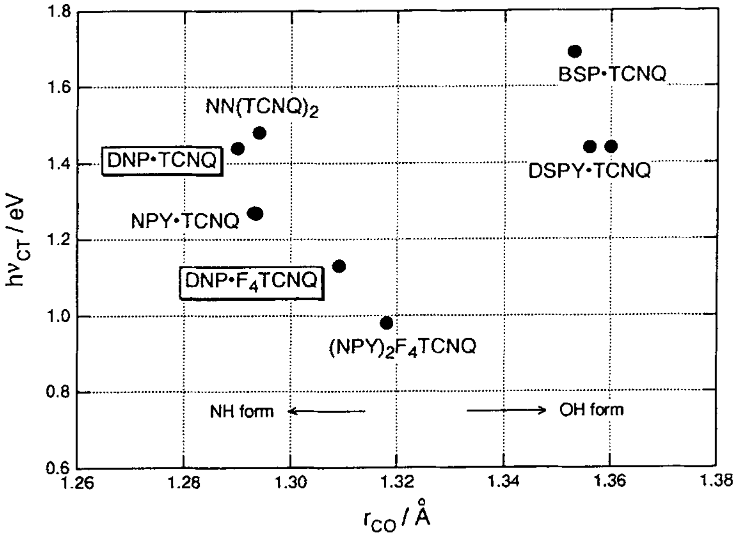


FIGURE 3. Energy of the charge-transfer band vs. the CO distance.

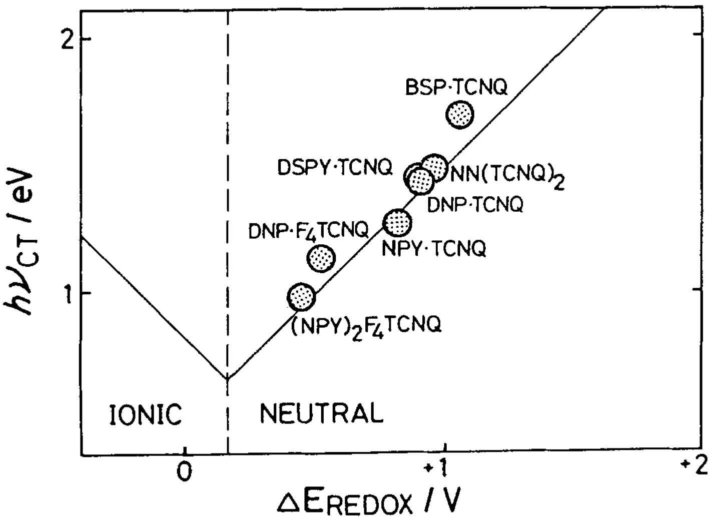


FIGURE 4. Energy of the charge-transfer band vs. the difference of the redox potential between donor and acceptor.

structure is supposed to result from the mixing of an ionic character in the neutral ground state. This situation has some similarity with the charge transport in molecular crystals, and the proton motion in the intermediate structure is expected to be effective to modulate the potential which is felt by conduction electrons. Such a coupling between proton and electron will provide a clue to constructing molecular systems possessing novel functionality.

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