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Studies on Photochromic Salicylideneanilines. II.[1] The π-Electronic States and Reactivities of Salicylideneaniline Tautomers as studied by the Pariser–Parr–Pople Method

MAMORU KAMIYA and YUKIO AKAHORI

Shizuoka College of Pharmacy[2]

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The π-electronic structures of the photochromic salicylideneaniline tautomers were investigated on the basis of the Pariser–Parr–Pople method. The calculated results were used for interpretation of the experimental ultraviolet spectra and the effects of the π–π^* excitation upon the intramolecular hydrogen–transfer.

Introduction

A series of recent studies by Cohen, *et al.*[3–6] have revealed that the photochromism of salicylideneaniline and its derivatives (anil) is caused by photo–reversible isomerization between the enol and keto tautomers resulting from an intramolecular hydrogen–transfer. Subsequently, investigations on the detailed reaction mechanisms, and the absorption and emission spectra of anil have been performed by many workers. But it seems at present that clear–cut explanations have not been given about the following points, the structure of the photocolored product, the mechanism of photofading, the origin of a characteristic emission spectrum in low–temperature rigid solution and the effect of hydrogen–bonding solvents on the ultraviolet (UV) absorption spectrum.

Here, as an attempt for getting some theoretical insight into such unsettled matters we report a semiempirical SCF-MO study on the electronic structures and reactivities of the salicylideneaniline tautomers.

Result and Discussion

Calculation Procedure

The present calculation was performed according to the standard Pariser–Parr–Pople SCF method[7,8] with the configuration–interaction procedure including all singly excited configurations from occupied to vacant orbitals. The valence–state ionization potential (I) and electron affinity (A) were taken as follows (eV) by reffering to the paper of Hinze and Jaffe:[9]

$$I(=\!C-)=11.16,\ I(=\!O)=17.28,\ I(-O-)=34.75,\ I(=\!N-)=14.12,\ I(-\overset{|}{N}-)=28.53$$

$$A(=\!C-)=0.03,\ A(=\!O)=2.01,\ A(-O-)=13.75,\ A(=\!N-)=1.78,\ A(-\overset{|}{N}-)=11.96$$

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[2] Location: *Oshika 2-2-1 Shizuoka-shi, Shizuoka.*

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TABLE I. Pertinent Data for the Absorption Spectra of Salicylideneaniline Tautomers

a) Enol Tautomer

Theoretical

Method	ΔE_s(eV)[a]	f[b]	mx[c]	my[d]	ΔE_T(eV)[e]
[1][f] ΔI_P(O,N)[g]$=0$ eV	4.18	0.61	−1.29	0.04	2.86
	4.80	0.07	−0.29	0.28	3.60
	5.05	0.01	−0.004	−0.15	3.79
	5.36	0.10	0.41	−0.24	4.05
	5.89	0.37	−0.82	0.21	4.46
	6.24	0.07	−0.12	−0.31	
	6.66	0.49	−0.44	0.81	
ΔI_P(O,N)$=1$ eV	4.24	0.59	−1.26	0.01	2.93
	4.82	0.07	−0.31	0.27	3.62
	5.06	0.01	−0.002	−0.16	3.81
	5.36	0.11	0.41	−0.25	4.09
	5.92	0.40	−0.85	0.21	4.45
	6.30	0.07	−0.19	−0.31	
	6.68	0.50	−0.42	0.83	

	ΔE_s(eV)	f	ΔE_T(eV)		ΔE_s(eV)	f	ΔE_E(eV)
[2][h] ΔI_P(O,N)$=0$ eV	4.01	0.61	2.72	ΔI_P(O,N)$=1$eV	4.04	0.58	2.76
	4.54	0.13	3.28		4.55	0.13	3.29
	4.69	0.002	3.42		4.69	0.003	3.42
	5.07	0.03	3.87		5.07	0.03	3.90
	5.73	0.78	4.17		5.75	0.81	4.16
	6.18	0.04			6.22	0.05	
	6.41	0.37			6.42	0.39	

Experimental

In t-Butanol[i]		In methanol[j]		In methylcyclohexane[j]	
ΔE_s(eV)	$\varepsilon\times10^{-3}$	ΔE_s(eV)	$\varepsilon\times10^{-3}$	ΔE_s(ev)	$\varepsilon\times10^{-3}$
3.67	11.5	3.69	11.97	3.63	10.5
3.90	1.08	4.00	sh	4.00	sh
4.10	9.9	4.61	13.6	4.10	8.45
4.63	12.9	5.56	21.56	4.63	12.42
5.44	19.8			5.46	19.70
5.61	19.9				
~6.2	~20.0				

b) Keto Tautomers

Theoretical

cis			*trans*		
ΔE_s(eV)	f	ΔE_T(eV)	ΔE_s(eV)	f	ΔE_T(eV)
3.28	0.83	1.29	3.27	0.90	1.22
4.77	0.14	2.88	4.80	0.15	2.86
4.82	0.29	3.46	4.81	0.16	3.46
5.08	0.005	4.13	5.08	0.006	4.14
5.63	0.24	4.24	5.57	0.14	4.19

a) singlet excitation energy
b) oscillator strength
c) x component of transition moment
d) y component of transition moment
e) triplet excitation energy
f) inclusion of core resonance integrals (β_{rs}) over all atomic pairs
g) The decrement of the I(-O-) or the increment of the I(=N-) derived from $O^{-\delta}\cdots H\text{-}N^{+\delta}$ charge transfer model.
h) Inclusion of β_{rs} over adjacent atomic pairs except the β_{NO}, where $\beta_{C\text{-}C}$ in benzene ring is taken as −2.39 eV.
i) Taken from quoted ref. 11.
j) Taken from qouted ref. 5.

Some corrections were made for the I(–O–) and I(=N–) on the basis of a charge–transfer model associated with the internal OH··N hydrogen bond. The one–center repulsion integral was evaluated by the I–A approximation, the two–center repulsion integral being calculated by the Pariser–Parr method. The core resonance integral $\beta_{\mu\nu}$ (eV) was estimated according to the equation, $\beta_{\mu\nu}=-\frac{1}{2}S_{\mu\nu}\,(I(\mu)+I(\nu))$ where $S_{\mu\nu}$ is the theoretically calculated overlap integral between the μth and νth 2pπ-slater-type orbitals,[10] or according to the equation $\beta_{\mu\nu}=-2.39\ S_{\mu\nu}/S$ where S is the overlap integral between two carbon 2pπ-orbitals separated by 1.39 Å. In reference to a result of X-ray analysis by Bregman, *et al.*[11] the enol tautomer was regarded as a planar molecule with r_{C-C} in benzene ring=1.39 Å, $r_{C(7)-C(8)}=1.44$ Å, $r_{C(8)-N(9)}=1.27$ Å, $r_{N(9)-C(10)}=1.42$ Å, $r_{C(5)-O(6)}=1.35$ Å and all bond angles=120°. The keto tautomer was also approximated with a planar molecule with $r_{C-C}=1.39$ Å, $r_{C-N}=1.42$ Å, $r_{C-O}=1.20$ Å and all bond angles=120°. The numberings of the molecules are given in Figure 1.

Actual numerical calculations were carried out with the HITAC 5020-E computer at the University of Tokyo.

Interpretation of Calculated Results

Ottolenghi and McClure[12] reported that the UV absorption spectra of salicylideneanilines and their analogs without the *ortho*-hydroxy group exhibit remarkable difference chiefly in relative maximum intensities, and that this may be attributed to the formation of the intramolecular hydrogen–bond in salicylideneanilines because hydrogen–bonding polar solvents, such as water, tend to eliminate such difference and at the same time lower the photochromic activity of salicylideneanilines. Therefore, the valence–state ionization potentials of the oxygen and nitrogen atoms in the enol tautomer were tentatively parametrized in a proper range around the standard values by taking into account a charge–transfer structure of $\overset{-\delta}{O}\cdots H\text{–}\overset{+\delta}{N}$ type derived from the delocalization model of hydrogen bond. Such a treatment has been often applied to SCF calculations on the molecules forming intra- or intermolecular hydrogen–bonds. The results of the calculated excitation energy and oscillator strength are summarized in Table I, together with the experimental values.

This indicates that in any case of the two different calculation methods a counteracting change of the I(–O–) and I(=N–), *i.e.*, decrease of the I(–O–) and increase of the I(=N–), resulting from inclusion of the effect of the OH···N intramolecular hydrogen–bond tend to raise the lowest singlet π–π^* excitation energy and this calculated value is 0.3∼0.5 eV higher than the experimental value of ∼3.6 eV. The next high value of the calculated excitation energy (∼4.8 eV in method [1] and ∼4.5 eV in method [2]) is rather close to the experimental value of 4.63 eV. But in this case it becomes to be difficult to assign the two weak bands at 4.10 and 3.90 eV observed in *t*-butanol which were correlated, by Ottolenghi and McClure[11] who studied the UV spectrum of salicylideneaniline in comparison with those of a series of analogous molecules, with the appearance of forbidden bands due to a change of the molecular symmetry caused by the hydrogen–bond formation. As for the benzylideneaniline spectrum also, a theoretical analysis by Jaffe, *et al.*[13] has led to inadequate intensity of the bands in this region and the cause of this disagreement was attributed to the reduced symmetry of benzylideneaniline molecule relative to the azobenzene and stilben molecules. At any rate, a straightforward assignment of the bands has not been made by SCF calculations hitherto reported. We presume, as one of the other possibilities, that these bands may be related to formation of the *cis*-keto tautomer with a low concentration of which presence has been suggested by a N^{15}–H spin coupling in nuclear magnetic resonance

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(NMR) by Dudek and Dudek[14] and by the experimental fact by Ledbetter[15a] and by Becker and Richey[15b] that salicylideneaniline in a hydrogen-bonding solvent at room temperature and/or in a nonpolar solvent added with a small amount of organic acid at 77°K shows an absorption band at 440 mμ has usually been associated with the *cis*-keto formation. It is of much interest to note that these bands disapper by adding a solvent breaking down the intramolecular hydrogen-bond, such as water.

On the other hand, the two theoretical bands ($\sim$5.3 eV and $\sim$5.9 eV in method [1]) seem to correspond to the experimental bands at $\sim$5.4 eV and $\sim$5.6 eV, respectively, though method [2] gives a rather different result in this region.

It is also of interest to note that the effect of the hydroxy-group upon the predicted polarization direction of the π–π^* transitions of the enol tautomer. The calculated polarization direction of the first π–π^* band is found to be almost along the long axis, in agreement with that of the first π–π^* band of benzylideneaniline calculated by Smith.[16] However, the transition moment of the second π–π^* band is predicted to make an angle of 41$\sim$42° to that of the first π–π^* band, which is in contrast to the corresponding angle of 73° for benzylideneaniline calculated by Smith.[15] This may be possibly due to the effect of the hydroxy-group on the second transition arising from ring excitation. As for the other transitions with higher excitation energy, the angle which these make to the x-axis are found as follows; 88$\sim$90° (5.0 eV), $-30\sim-31$° (5.3 eV), ~-14° (5.9 eV), 58$\sim$68° (6.2$\sim$6.3 eV), 61$\sim$63° (6.6 eV).

The presently obtained value of the lowest $^3(\pi,\pi^*)$ state energy, 2.7$\sim$2.9 eV, is considerably higher than the value of $\sim$2.0 eV estimated by Ottolenghi and McClure[12] on the basis of the corresponding experimental values of the analogous molecules, and rather close to the $\sim$2.5 eV emission observed by the preceding two authors[12] and by Richey and Becker[17] in low-temperature rigid solution, although Ottolenghi and McClure assigned this emission to the lowest $^3(n,\pi^*)$ state on the basis of a characteristic solvent-dependent shift.

The calculated results for the absorption spectra of the keto tautomers are in poor agreement with the excitation energies for a few bands assigned by several workers to the π–π^* transition of the keto tautomers; The 435 mμ, *i.e.* 2.85 eV absorption maximum which was observed in alcoholic and/or acidic solution and assigned by Ledbetter[15a] to the spectrum of *cis*-keto tautomer is different from the calculated first π–π^* excitation energy, 3.28 eV, and the 480 mμ, *i.e.* 2.58 eV band of the photocolored product is far from the calculated first π–π^* excitation energy, 3.27 eV of the *trans*-keto tautomer which is regarded, in most papers, as responsible for the photocolored product.

As for the photochromic mechanism, most of the studies reported hitherto seem to suggest that the intramolecular hydrogen-transfer is started with a photoexcited singlet state ($^1(\pi,\pi^*)$ or $^1(n,\pi^*)$) and the moderately stable colored *trans*-keto tautomer is produced *via* an intermediate of the *cis*-keto tautomer. On the other hand, Becker and Richey[14b,17] have proposed recently that the photocolored product is not the *trans*-keto tautomer but a non-equibrium form of the *cis*-keto tautomer twisted about the C(7)–C(8) bond, and that this species is yielded from the photoexcited singlet of the enol tautomer *via* a short-lived intermediate which has undergone proton-transfer but retains the planarity of the enol tautomer. The molecular diagrams of the enol tautomer have been calculated for the ground and lowest excited singlet and triplet states by the method [1] with the I(–O–) and I(–N=) corrected by 0.1 eV, and the results are shown in Figure 1. These results indicate that the π–π^* excitations tend to cause a decrease of$^{\pi}_{\mathrm{O}}$ $p_{(6)-\mathrm{N}(9)}$, an increase of $p^{\pi}_{\mathrm{C}(5)-\mathrm{O}(6)}$ and slightly

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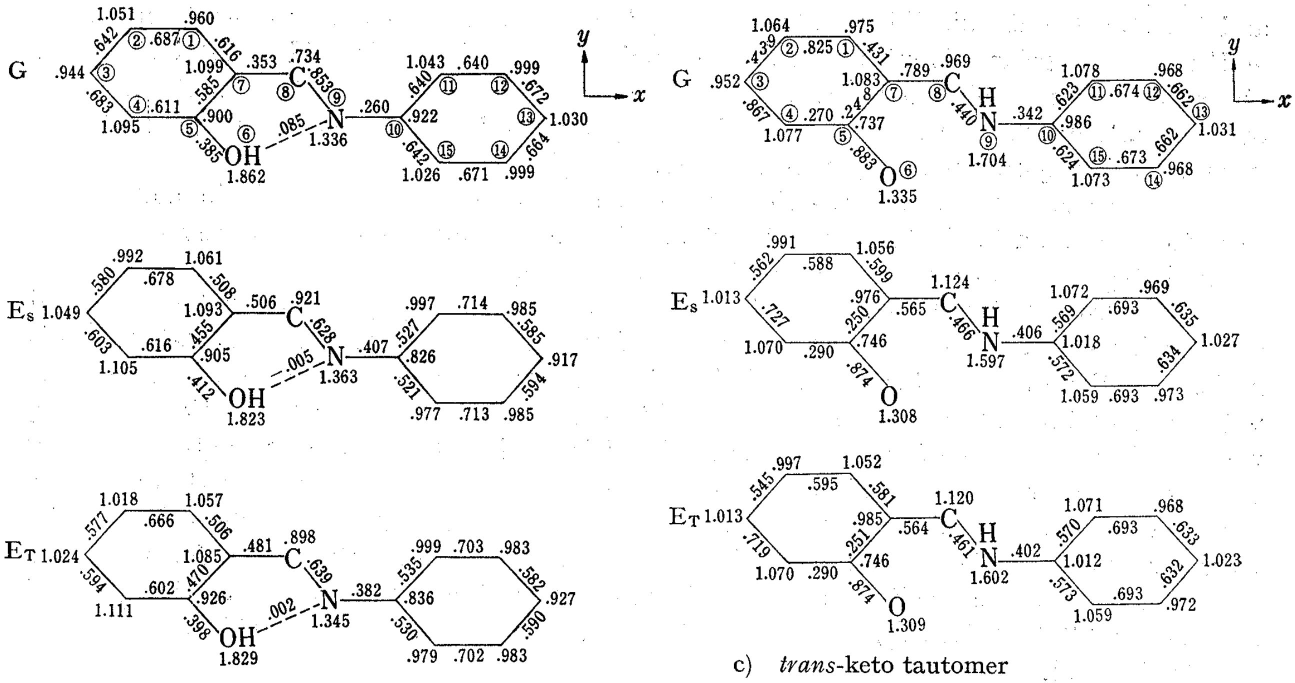
a) enol tautomer

b) *cis*-keto tautomer



c) *trans*-keto tautomer

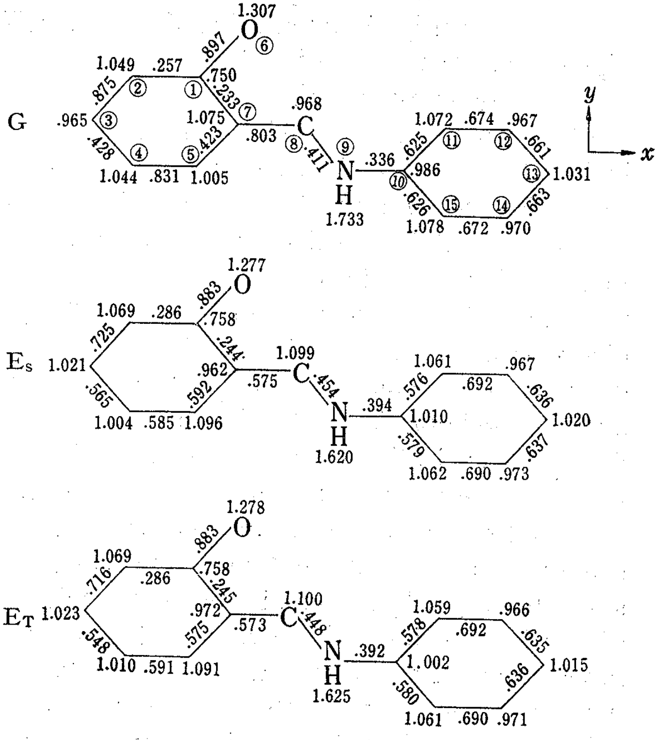


Fig. 1. Photoexcitation Effects on the π-Electronic Distribution

G: ground state E_S: lowest excited singlet state

E_T: lowest excited triplet state

but clearly counteracting changes of $q^{\pi}_{O(6)}$ and $q^{\pi}_{N(9)}$. These appear to predict that the π–π^* photoexcitations give rise to such a π-electronic state as facilitate proton-transfer. Also, the usually accepted reaction course *via* an intermediate of the *cis*-keto tautomer seems to be substantiated by predicting more stability of the *cis*-keto tautomer relative to the *trans*-keto tautomer (E^{π}(*cis*-keto) $= -763.54$ eV $<E^{\pi}$(*trans*-keto) $= -756.19$ eV) and a remarkable decrease of $p^{\pi}_{C(7)-C(8)}$ of the *cis*-keto tautomer on the photoexcitations. It is of interest to note that in the enol tautomer of salicylideneaniline a photo-induced decrease of the π-bond order of the bridging C–N bond which favours rotation about this bond but acts so as to prevent the internal hydrogen-transfer occurs moderately in comparison with the extreme trend for benzylideneaniline (0.778 (G)→0.344 (E_S), 0.371 (E_T)) which is known to undergo *cis-trans* photoisomerization.

It is an interesting object of study to examine whether or not the photofading caused by irradiation into the 480 mμ band of the colored product takes place once again *via* the *cis*-keto tautomer. In this respect the present calculation indicates that the *trans*-keto tautomer undergoes remarkable decrease of $p^{\pi}_{C(7)-C(8)}$ on excitation and at the same time the *cis*-keto tautomer exhibits decrease of both $q^{\pi}_{O(6)}$ and $q^{\pi}_{N(9)}$ which seems as unfavourable at least for the proton-transfer. Thus, a simple photofading process of *trans*-keto $\xrightarrow{h\nu}$ *cis*-keto → enol can not be predicted by the present calculation.