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The *cis-trans* Isomerization of Schiff Bases

GUNNAR WETTERMARK and EVERT WALLSTRÖM

Institute of Physical Chemistry, University of Uppsala, Uppsala, Sweden

Aromatic Schiff bases have been photoisomerized and the kinetics for the thermal relaxation process has been investigated. The rate constant for this process was related to two quantities obtained from MO–LCAO calculations, namely L.E.I. (localization energy for *cis-trans* isomerization) and bond order for the azomethine link.

INTRODUCTION AND THEORY

A *cis-trans* isomerization about a double bond can be pictured as a rotation through a configuration in which the π-electron clouds are oriented perpendicular to each other, *i.e.* are uncoupled. On the basis of this model, the energy required to decouple the π-electrons represents the barrier to the isomerization. The barrier height can be approximated as the difference between the π-energy of the entire conjugated system and the sum of the π-energies of the two radical fragments which are formed when the π-electrons are uncoupled at the bond in question. This energy difference is denoted L.E.I. (localization energy for a *cis-trans* isomerization).[1] For a series of homologues, it is expected that the height of the barrier is the dominating variable. At a given temperature the thermal isomerization will then satisfy the equation:

$$\log k = c_1 \times \text{L.E.I.} + c_2 \tag{1}$$

where k is the rate constant and c_1 and c_2 constants ($c_1 < 0$).

The determination of L.E.I. requires calculations on the parent molecule and the two radical fragments. It is advantageous to consider the relationship between L.E.I. and bond order of "the isomerizing bond". Pullman and Pullman[1] derived the following expression for an alternating hydrocarbon.

$$\text{L.E.I.} = 2\ \beta\ \{p_{\mu\nu} + \sum_{\substack{r<s \\ rs \neq \mu\nu}} (p_{rs} - p_{rs}')\} \tag{2}$$

In eqn. (2) $p_{\mu\nu}$ is the bond order for the bond which is isomerized, p refers to the parent molecule and p' to the radical fragments. Since usually $\sum_{\substack{r<s \\ rs \neq \mu\nu}} (p_{rs} - p_{rs}') \ll p_{\mu\nu}$ the dominating term in eqn. (2) is $p_{\mu\nu}$ and one expects

a proportionality between the rate of the isomerization and the bond order, $p_{\mu\nu}$, of the parent molecule.

$$\log k = c_3\, p_{\mu\nu} + c_4 \tag{3}$$

In eqn. (3) c_3 and c_4 are constants ($c_3 < 0$).

Unfortunately the experimental conditions such as solvent, pH, and temperature are significantly different in various investigations. Therefore it has been difficult to test the relationship between L.E.I. and the isomerization rates from the literature data.[2] Recently, the *cis-trans* isomerization about the C=N bond has been studied in detail.[3] *Meta-* or *para*-substituted benzylideneanilines yielded rate constants which correlated well to the Hammett σ-constants of the substituents.[4,5] The positive proportionality constant implies that low electronic density at the C=N bond facilitates the reaction. It is therefore reasonable that Schiff bases should obey eqn. (1).

RESULTS AND DISCUSSION

Experimentally determined rate constants. A series of Schiff bases having the structure

$$\Phi'\text{—CH=N—}\Phi'' \tag{4}$$

were synthesized. The symbols Φ' and Φ'' represent phenyl, naphthyl, or anthranyl groups. Buffered ethanol solutions of these compounds were studied by the flash photolysis method. All solutions developed transient species having the same general characteristics as the transient observed with the benzylideneaniline derivatives.[4] The changes in optical density after exposure to a flash of light were essentially reversible. After repeated flashing, a permanent optical density change was, however, observed. The kinetics for the decay of the transient was first order yielding the rate constants, k_{exptl}, shown in Table 1. There was no noticeable difference in the rate of decay for solutions having different buffer strength.

It is reasonable to assume that the rate constants in Table 1 refer to the thermal *cis-trans* relaxation.[3-5] In general it is not known how the equilibrium (5) is shifted after photoisomerization.

$$\textit{cis}\text{-isomer} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \textit{trans}\text{-isomer} \tag{5}$$

In eqn. (5) k_1 and k_2 are the respective rate constants. For some derivatives of benzylideneaniline it is known that the *trans*-form is thermally favoured, *i.e.* $k_1 > k_2$, and it has accordingly been assumed that the rate constant obtained from flash photolysis experiments approximates k_1. The fact that Schiff bases can be subjected to photocyclization with low quantum yield is in agreement with our experimental observations that an irreversible process is also present.[6-9]

For the Schiff bases in Table 1, the rate constants, k_{exptl}, showed no dependence on buffer strength. When *N*-benzylidene-*p*-dimethylaminoaniline

Table 1. Experimentally determined rate constants together with the values of L.E.I. and p_{CN} calculated from MO—LCAO calculations assuming a planar configuration.

	Compound Φ'	Φ''	k_{exptl} (sec^{-1})	L.E.I.[a] (units of β)	p_{CN}[a] (units of β)
A1	phenyl	phenyl	1.4 ± 0.3	1.441	0.8041
A2	»	1-naphthyl	9.2 ± 0.3	1.362	0.7915
A3	»	2-naphthyl	2.5 ± 0.1	1.415	0.8012
A4	»	1-anthranyl	11.9 ± 0.5	1.322	0.7877
A5	»	2-anthranyl	5.4 ± 0.2	1.380	0.7986
B1	1-naphthyl	phenyl	1.0 ± 0.1	1.379	0.7890
B2	»	1-naphthyl	8.3 ± 0.3	1.302	0.7760
B3	»	2-naphthyl	2.3 ± 0.1	1.354	0.7861
B4	»	1-anthranyl	11 ± 2	1.262	0.7719
C1	2-naphthyl	phenyl	1.7 ± 0.5	1.423	0.8006
C2	»	1-naphthyl	11.1 ± 0.5	1.345	0.7879
C3	»	2-naphthyl	3.7 ± 0.2	1.398	0.7978
C4	»	1-anthranyl	18 ± 3	1.305	0.7840
D1	9-anthranyl	phenyl	0.032 ± 0.003	1.281	0.7659

[a] Using the Hückel parameters: $\alpha_C = \alpha$, $\alpha_N = \alpha + 0.4\beta$, $\beta_{CC} = \beta_{CN} = \beta$.

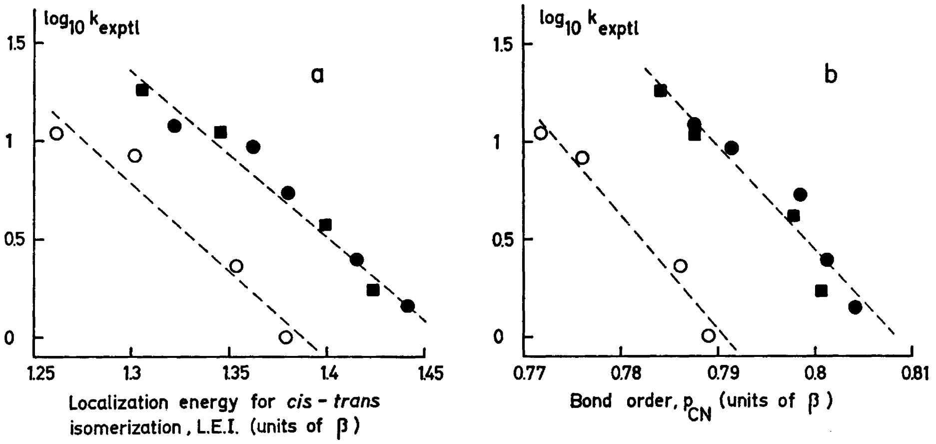
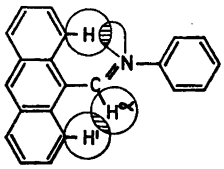


Fig. 1. Plot of the experimental rate constant *versus* theoretically obtained quantities. ● compounds from series A; ○ compounds from series B; ■ compounds from series C. ● and ■, taken together, yield the following results:
Diagram a) regression line: $\log_{10}k_{exptl} = -8.36 \times$ L.E.I. $+ 12.22$;
correlation coefficient = 0.98.
Diagram b) regression line: $\log_{10} k_{exptl} = -53.8 \times p_{CN} + 43.5$;
correlation coefficient = 0.96.
○ yield the following characteristics:
Diagram a) regression line: $\log_{10} k_{exptl} = -9.03 \times$ L.E.I. $+ 12.54$;
correlation coefficient = 0.97.
Diagram b) regression line: $\log_{10}k_{exptl} = -58.9 \times p_{CN} + 46.6$;
correlation coefficient = 0.98.

and *N*-benzylidene-*p*-methoxyaniline were similarly isomerized it was noted that the rate constant increased with higher buffer strength.[4] It was assumed that the high proton affinity of these compounds was connected with the buffer catalysis. Measurements of the base strength of the Schiff bases in Table 1 yielded results in agreement with this hypothesis.[10]

MO—LCAO calculations for a planar configuration. The values of L.E.I. and p_{CN} calculated in the Hückel approximation are also shown in Table 1. The resonance integral was the same, β, for all bonds. The Coulomb integral was equal to α for the carbon atoms and $\alpha + 0.4\ \beta$ for the nitrogen atom. It is seen from Table 1 that within the individual groups of compounds A, B, and C the rate constants decrease as L.E.I. and p_{CN} increase. Furthermore, from Fig. 1 it is seen that the rate constant for the reaction is approximately proportional to both L.E.I. and p_{CN}.

Steric hindrance. Log k_{exptl} correlates well to both L.E.I. and p_{CN}. The obvious question arises "Why do not all compounds follow the same relation?" Only groups A and C join but group B is described by a different equation. One explanation would be that the configuration at the N—Φ'' bond is essentially the same for all groups Φ''; *cf.* structure (4). At Φ'—C, however, when Φ' equals 1-naphthyl or 9-anthranyl, steric hindrance is relieved through rotation around the Φ'—C axis.



(6)

Structure (6)[11] illustrates the sterical interaction for compound D1 in the *trans* configuration. Considering only van der Waals' forces between the two hydrogen atoms H^1 and H^α it is estimated that a rotation of about 70° is required to move the atoms outside the "touching distance". ("The touching distance" is defined as the sum of the two van der Waals' radii.)

In the Hückel calculation a rotation around a double bond is usually accounted for by modifying the resonance integral for the rotating bond according to the function $\beta \cos \theta$, where θ is the rotation angle. Using this relation but keeping all other parameters the same as in the previous calculations, the bond order p_{CN} was calculated for different values of θ and are presented in Fig. 2.

The value of log k_{exptl} for compound D1 is -1.49 and the bond order would have to be of the order of 0.836β to fit the relation given for groups A and C in Fig. 1. This corresponds to an angle of 50° according to the curve in Fig. 2. For the compounds B a rotation around Φ'—C of about 25° is sufficient.

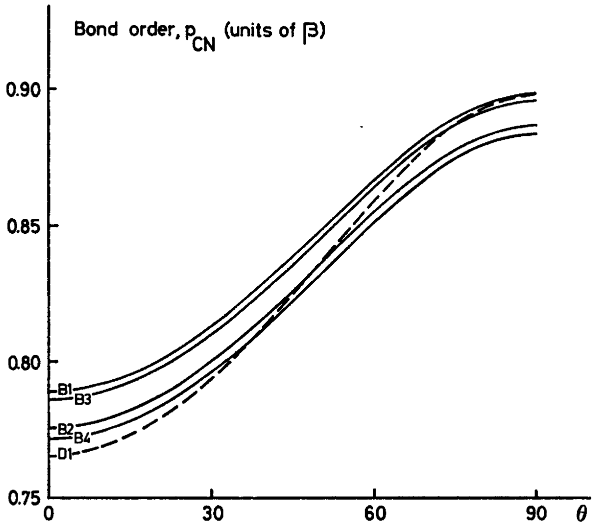


Fig. 2. The bond order for the azomethine bond *versus* the angle of rotation, θ degrees, around the Φ'—C link, using the angular dependence $\beta \cos \theta$ for the resonance integral of this link. For all other links the resonance integral was kept equal to β. The Coulomb integral equalled α for the carbon atoms and $\alpha + 0.4\beta$ for the nitrogen atom.

EXPERIMENTAL

A pulse of ultraviolet light was obtained from a fast flash photolysis unit (Apparatus V of this Institute used at 2000 joules, 25 kV).[13] The relaxation rate was recorded using a kinetic spectrophotometer essentially consisting of a G.E. iodine-tungsten lamp, Zeiss MM 12 monochromator, E.M.I. 9552 A phototube, and Tektronix 533 oscilloscope. The readings were based on spectral changes in the region 350—410 mμ.

The molar concentration of the Schiff bases was 10^{-5}. The solvent was acetate buffered absolute ethanol (A.B. Vin- och Spritcentralen). Two buffer concentrations were used 2.09×10^{-4} and 1.05×10^{-3} M in acetic acid, buffer ratio $[\mathrm{HOAc}]/[\mathrm{OAc}^-] = 1.40$ in both cases. The reaction vessel was thermostated at 30.0 ± 0.3°C with a 10 % acetic acid solution, which also served as a cut-off filter for the exciting light.

The Hückel calculations were carried out on the CDC 3600 computer of the University.

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