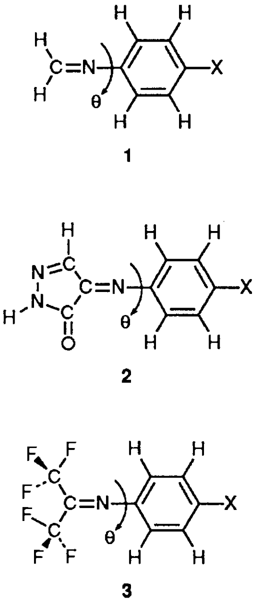
On the Conformation of the Inversion State in the Thermal *E,Z* Isomerization of Aromatic Azomethines

Hans-Jörg Hofmann,[a] Tsutomu Asano[b] and Renzo Cimiraglia[c]

[a] *Sektion Biowissenschaften, University of Leipzig, D-7010 Leipzig, Germany*
[b] *Department of Chemistry, Faculty of Engineering, Oita University, Oita 870-11, Japan*
[c] *Dipartimento di Chimica e Chim. Ind., Universita di Pisa, I-56100 Pisa, Italy*

Ab initio STO-3G calculations with full geometry optimization on substituted formaldehyde-, pyrazolone- and hexafluoroacetone-anils indicate different conformations of the linear inversion state in the thermal *E,Z* isomerization of aromatic azomethines dependent on the extent of push–pull conjugation in the molecular systems; based on this fact, an explanation of Hammett plot deviations from linearity found for special azomethines becomes possible without the assumption of a competition between the inversion and rotation mechanism in the *E,Z* isomerization.

Some aspects of the mechanism of *E,Z* isomerization of aromatic azomethines are still under debate.[1–4] The central point of the discussion is the relation between the inversion mechanism, where the nitrogen atom is rehybridized to sp in the linear inversion state, and the rotation mechanism, where rotation about the carbon–nitrogen double bond takes place. Whereas nowadays the inversion mechanism is believed to be the best explanation in most cases, studies of the substituent influence in a variety of compounds seem to support the rotation mechanism for some derivatives.[5–8] Thus, the finding of non-linear, *e.g.* V-shaped, Hammett plots for the isomerization rate of substituted hexafluoroacetone-[5] and pyrazolone-anils[6] led to the proposal of a change between the inversion and rotation mechanisms dependent on the nature



X = H, OH, NH_2, NMe_2, NO_2

Scheme 1

Table 1 Calculated energy differences between the perpendicular and planar phenyl ring conformation of the linear inversion states and *E*,*Z* inversion barriers of various aromatic azomethines[a]

Substituent X	ΔE^b	$\Delta E_{inv}{}^b$
	1[c]	
NO_2	−34.2	113.5
H	−21.8	121.8
OH	−12.8	127.1
	2[d]	
NO_2	−19.8	104.0
H	−7.7	109.5
NH_2	3.9	110.1
NMe_2	5.8	109.2
	3[e]	
NO_2	−17.6	96.1
H	−6.5	101.8
NH_2	5.0	102.1

[a] Calculations are based on the HONDO7 program package.[10] [b] In kJ mol^{-1}. [c] For total energies, see Ref. 9. [d] Total energies of the *syn* forms in au: NO_2: −776.400; H: −575.692; NH_2: −630.013; NMe_2: −707.162. [e] Total energies of the basic forms in au: NO_2: −1 182.215; H: −981.508; NH_2 −1 035.829.

of the substituents. Similar conclusions were drawn for benzoylacetanilides[7] and iminomalonates,[8] respectively. Deviations from linearity in the Hammett plots seem to occur with increased push–pull conjugation involving the azomethine bond.

Recently, one of us unequivocally demonstrated by the study of solvent, temperature and pressure effects on the rate of isomerization of substituted *N*-benzylideneanilines, pyrazolone- and hexafluoroacetone-anils that the rotation mechanism can be excluded for these compounds.[3,4] An explanation of the experimental data could be possible based on the inversion mechanism when assuming conformation differences for the *N*-phenyl group in the linear inversion state. Thus, a planar orientation (θ = 0°, *cf.* Scheme 1) was postulated for derivatives with electron-donating substituents and a perpendicular one (θ = 90°) for those with electron-attracting substituents.

In this paper, we want to confirm this hypothesis by quantum chemical calculations on the three substituted aromatic azomethines *N*-methyleneaniline, **1**, 2,3-dihydro-3-oxopyrazolylideneaniline **2**, and *N*-hexafluoroisopropylideneaniline **3**. Scheme 1 shows the structure of the linear inversion states. The calculations were based on *ab initio* SCF MO theory employing the STO-3G basis set, which has been proved to be reliable enough for the description of conformational problems of this type.[9] The geometries of the various molecules were completely optimized. In the case of the substituted *N*-methyleneanilines, we refer to our previous results given in ref. 9.

Table 1 summarizes the energetic relations between the two alternative conformations for the molecules examined, and the calculated inversion barriers. For the derivatives **1** without any push-pull conjugation, the perpendicular *N*-phenyl ring orientation is the most stable one on examining its rotation in the linear inversion state. Obviously, conjugation of the nitrogen p_z orbital electrons into the *N*-phenyl ring is favoured and additionally supported by electron-withdrawing substituents, but diminished by donator groups as indicated by the actual energy differences between the corresponding planar and perpendicular conformations. Linear Hammett plots with positive slopes should, therefore, be expected correlating the inversion barriers of these derivatives, which is supported by the theoretical and experimental data.[1,2]

The competition between planar and perpendicular phenyl ring orientations becomes immediately visible in the case of compounds **2** and **3**. In the corresponding linear arrangements, the perpendicular conformations remain the most stable ones for the unsubstituted compounds and the derivatives bearing electron-attracting groups in the *N*-phenyl ring. However, the realization of push-pull systems by introduction of electron-donating substituents favours the extension of conjugation through the azomethine linkage. Thus, the planar conformations become competitive and even correspond to the most stable phenyl ring orientation when examining the rotation potential curve in the inversion state. The inversion barriers for the amino-substituted and unsubstituted derivatives have nearly the same value. The inversion barrier for the dimethylamino-substituted compound **2** is lower than that of the unsubstituted derivative now. Thus, the deviations from linearity in the Hammett plots for these derivatives become understandable. The results of our calculations confirm the justification of the assumption of conformation differences in the inversion states of aromatic azomethines dependent on the nature of the substituents at the carbon–nitrogen double bond. These conclusions may be at least partially transferred to the problem of *E*,*Z* isomerization of aromatic azo compounds.

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