

**Table I. First-Order Rate Constants ( $k/s^{-1}$ ) for Thermal *Z/E* Isomerization of *N*-Benzylideneanilines 12–15 in Benzene at 25 °C**

X	Y			
	4-NMe <sub>2</sub>	4-NO <sub>2</sub>	2,4-(NO <sub>2</sub> ) <sub>2</sub>	2,4,6-(NO <sub>2</sub> ) <sub>3</sub>
4-NMe <sub>2</sub>	0.133	0.258	8.73	9.24
4-MeO	0.214	0.330 (0.36) <sup>a</sup>	0.0369	0.0169
4-PhO	0.994	1.08		
4-Me	0.794	1.07	0.117	
4-F	0.653	0.945	0.101	
4-Cl	2.77	3.24	0.344	0.138
4-Br	3.59	4.13		
4-CF <sub>3</sub>	33.7	42.2	2.94	
4-COOEt	70.3	68.1		
4-NO <sub>2</sub>	704	395 (347) <sup>a</sup>	36.2	19.3
3-MeO	2.50	2.95		
3-Me	2.05	2.52	0.305	
3-F	6.51	7.26		
3-Cl	7.20	8.35	0.767	
3-CF <sub>3</sub>	10.5	12.7	1.15	
3-NO <sub>2</sub>	18.0	18.6	3.14	
H	2.17	2.73 (3.00) <sup>a</sup>	0.284	

<sup>a</sup> Reference 34.

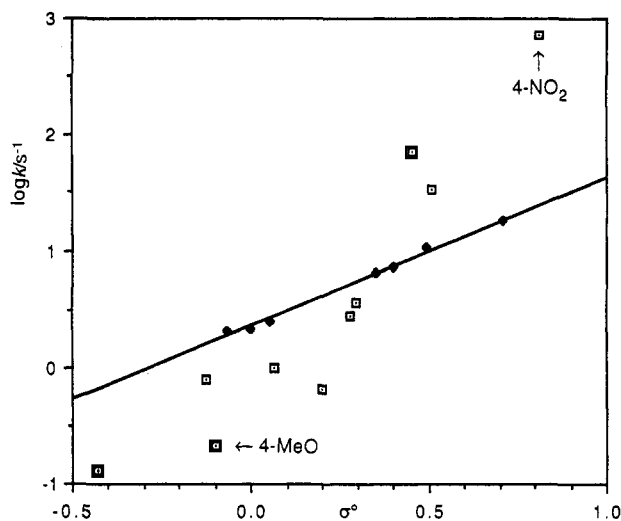
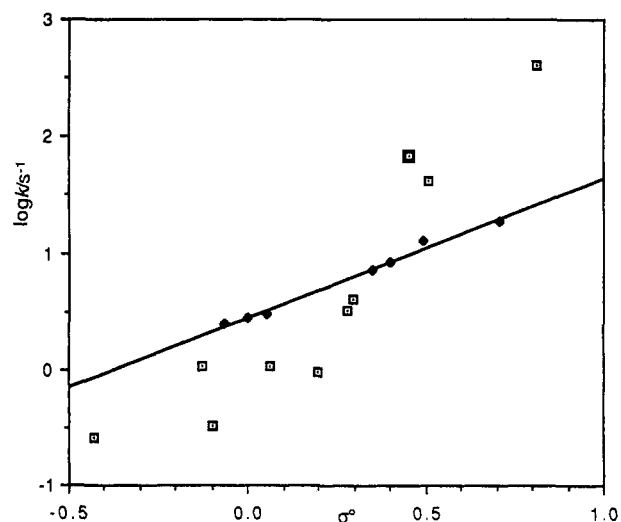
solubility in common solvents. It dissolved in dipolar aprotic solvents but decomposed rapidly at room temperature. However, the IR spectrum (KBr) showed an absorption at 1613 cm<sup>-1</sup>. Spectrograde benzene (Wako Pure Chemical Ind.) was used as received.

**Kinetic Measurements.** All rate constants were measured by flash spectroscopy; details are described elsewhere.<sup>18,17</sup>

**ab Initio Calculations.** The *ab initio* calculations on the substituted *N*-phenylformaldehydes and *N*-benzylideneanilines were performed using GAUSSIAN92<sup>44</sup> and SPARTAN<sup>46</sup> program packages, respectively. The geometries of the *N*-phenylformaldehydes were completely optimized employing the *ab initio* 3-21G and 6-31G\* basis sets.<sup>46</sup> In selected cases, complete geometry optimization was possible at the MP2/6-31G\* basis set level. Otherwise, the calculation of the correlation energy by means of the MP2 formalism is based on the corresponding 3-21G and 6-31G\* optimized geometries. The thermochemical data arise from the calculated vibrational frequencies. In case of the *N*-benzylideneanilines, the geometries were optimized at the 3-21G level. On the basis of these geometries, the *ab initio* 6-31G\* and MP2 calculations were performed.

## Results and Discussion

The first-order rate constants for *Z/E* isomerization of *N*-benzylideneanilines 12–15 in benzene at 25 °C are given in Table I. Direct comparison with the literature values<sup>34</sup> is possible in three cases, and they are in fairly good agreement. Plots of the logarithms of the rate constant against Taft's normal substituent constant  $\sigma^\circ$  of X are shown in Figures 1–3. Some of the (polynitrobenzylidene)-anilines were unstable and decomposed during or after recrystallization, and they are not included in the table. As can be seen clearly from Figure 3, the 4-dimethylamino group on the aniline moiety clearly accelerated the reaction at least in 14 and 15. However, with the exception of this strongly electron-donating substituent, the rate constant increased moderately with an increase in the electron-attracting tendency of X and the points for the para

**Figure 1.** Plot of  $\log(k/s^{-1})$  against  $\sigma^\circ$  for *Z/E* isomerization of 12:  $\blacklozenge$ , meta substituents;  $\square$ , para substituents.**Figure 2.** Plot of  $\log(k/s^{-1})$  against  $\sigma^\circ$  for *Z/E* isomerization of 13:  $\blacklozenge$ , meta substituents;  $\square$ , para substituents.

substituents deviated from the best straight line that could be drawn through the points for the meta substituents both in electron-donating and -attracting ones. Since this reaction is a simple one-step procedure, it is not possible to assume a change in rate-determining step to rationalize the downward deviations for the electron-donating groups. A mechanistic change cannot be invoked either, because a change in mechanism always causes the plot to be concave up. Therefore, the analysis of the general tendency in the substituent effect has to be based on a single-step one-route mechanism. Since the magnitude of the deviation was obviously larger for the electron-attracting substituents,<sup>47</sup> the results were best correlated with the substituent constants by the following Yukawa–Tsuno style equation with two resonance contribution parameters  $r^+$  and  $r^-$ .

$$\log(k/k_0) = \rho[\sigma^\circ + r^+(\sigma^+ - \sigma^\circ) + r^-(\sigma^- - \sigma^\circ)] \quad (1)$$

As can be seen from Figures 4 and 5, the correlations are

(47) For example, in 12b,  $\log(k_{\text{obs}}/k_{\text{calc}}) = -0.90$  and  $\sigma^+ - \sigma^\circ = -0.70$ , while in 12j  $\log(k_{\text{obs}}/k_{\text{calc}}) = 1.45$  and  $\sigma^- - \sigma^\circ = 0.44$ .

(48) The plots for 12 and 13 were almost identical, and the one for 13 is omitted.

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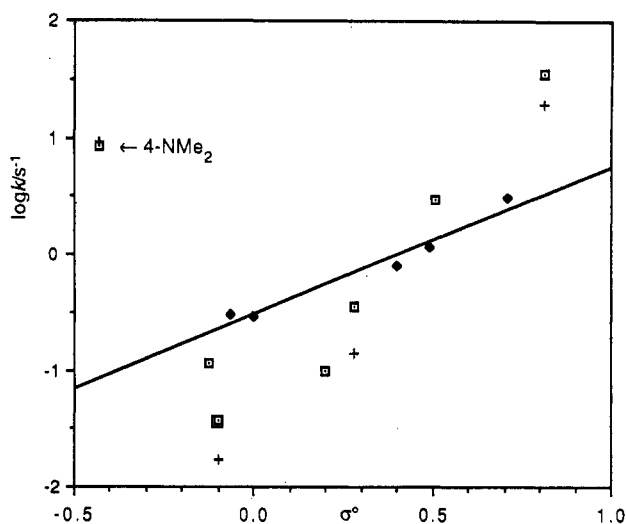


Figure 3. Plot of  $\log(k/s^{-1})$  against  $\sigma^0$  for *Z/E* isomerization of 14 and 15:  $\blacklozenge$ , meta substituents (14);  $\square$ , para substituents (14);  $+$ , para substituents (15).

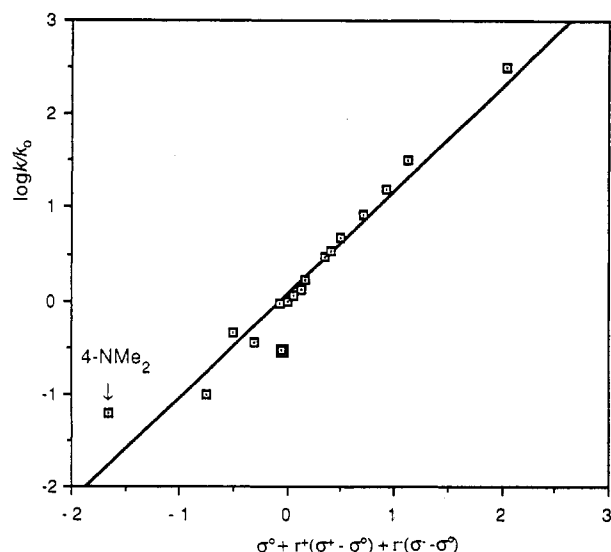


Figure 4. Plot of the substituent effects in 12 according to eq 1.

satisfactory.<sup>48</sup> The values of the parameters are given in Table II. All of the parameters were similar in the three groups of compounds, indicating that the nature of the activated complex is essentially the same despite the large electronic difference of the benzylidene component. It is difficult to rationalize the results without assuming the perpendicular transition state 9. The positive  $\rho$  values in 13 and 14 cannot be reconciled with the planar transition state 11 because inductive electron attraction by X must destabilize this transition state when the benzylidene group has strongly electron-attracting nitro group(s). The observed strong stabilization of the transition state by the electron-attracting resonance interactions is understandable in the perpendicular conformation considering the contribution of a canonical structure 9'. This perpendicular inversion mechanism is in agreement with our previous conclusion based on the *ab initio* calculations.<sup>26,27</sup> Lower activation enthalpies and moderately negative activation entropies observed for 12j, 13j, and 14j (Table III) also support this conclusion. If the nitrogen-phenyl bond has a partial double-bond character by the contribution of 9', it will inevitably restrict the rotation of the

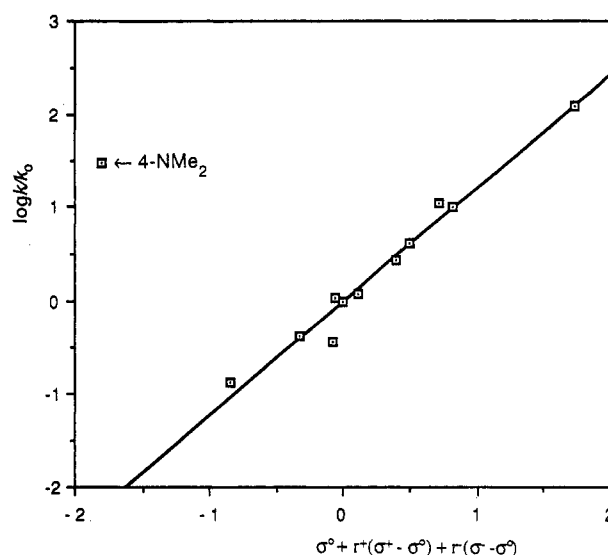


Figure 5. Plot of the substituent effects in 14 according to eq 1.

Table II. Values of the Parameters in Equation 1

	<i>N</i> -benzylideneanilines		
	12	13	14
$\rho$	$1.26 \pm 0.14$	$1.18 \pm 0.13$	$1.22 \pm 0.15$
$r^+$	$0.94 \pm 0.16$	$0.97 \pm 0.15$	$1.06 \pm 0.21$
$r^-$	$2.79 \pm 0.58$	$2.56 \pm 0.54$	$2.08 \pm 0.57$
$r^a$	0.985	0.985	0.986

<sup>a</sup> Correlation coefficient.

phenyl ring and a decrease in the entropy as well as enthalpy will be expected. The fact that the  $r^-$  values were much larger than that for the dissociation of anilinium ions or phenols ( $r^- = 1$ ) indicates the effectiveness of the resonance interactions between the phenyl group and the nitrogen atom when the atom is sp-hybridized. The downward deviation of the points for the electron-donating para substituents is either the result of resonance stabilization of the *Z*-isomer or the indication of destabilization of the activated complex by an increase in electron density on the phenyl carbon connected to the nitrogen (16). To the best of our knowledge, this kind of indirect destabilization has not been reported yet. Even in the ionization of phenols, the substituent effects could be satisfactorily described by eq 2. However, as will be discussed later, the

$$\log(K/K_0) = \rho[\sigma^0 + r^-(\sigma^- - \sigma^0)] \quad (2)$$

most stable conformation of (*Z*)-*N*-benzylidene-4-hydroxyaniline (17, X = OH) has the rotation angle  $\phi$  of 48.6° probably because of steric reasons. Therefore, it would be reasonable to attribute the downward deviations to the destabilization of the transition state.<sup>49</sup> Although the values of  $r^+$  were smaller than  $r^-$ , the parameter was close to 1 in all three cases studied. This may again be taken to indicate the unusually strong interactions between the sp-hybridized nitrogen and the  $\pi$  electron system directly connected to it.

The deviation of the points for 4-(dimethylamino) group must be a result of intervention of the planar inversion

(49) If the substituent stabilizes the *Z*-isomer despite this rotation angle, it will lower the energy of the planar transition state more because of its preferred conformation for the resonance. It will result in upward deviation as observed for the dimethylamino group.

**Table III. First-Order Rate Constants ( $k/s^{-1}$ ), Activation Enthalpies ( $\Delta H^\ddagger/kJ mol^{-1}$ ), and Activation Entropies ( $\Delta S^\ddagger/J K^{-1} mol^{-1}$ ) for the Thermal *Z/E* Isomerization of *N*-Benzylideneanilines in Benzene**

compd	$k/s^{-1}$					$\Delta H^\ddagger$	$\Delta S^\ddagger$
	10 °C	15 °C	25 °C	35 °C	45 °C		
12a		0.0407	0.133	0.389	1.05	80.0	6.6
12q	0.450	0.769	2.17	5.97	17.9	75.7	15.8
12j	210	327	704	1380		52.0	-16.1
13a		0.0845	0.258	0.726	1.88	76.3	-0.2
13q		1.01	2.73	7.44	17.9	70.9	1.4
13j	121	192	395	781	1500	50.8	-24.9
14b		0.0093	0.0369	0.113	0.310	84.8	11.6
14d	0.0227	0.0380	0.117	0.331	0.897	76.6	-5.8
14e	0.0205	0.0344	0.101	0.306	0.785	76.2	-7.9
14q	0.0527	0.0880	0.284	0.761	2.07	76.4	0.6
14f	0.0661	0.114	0.344	0.976	2.51	75.7	0.2
14h	0.609	0.983	2.94	9.05	20.9	74.7	15.1
14j	10.4	15.3	36.2	90.3	174	59.1	-16.5

**Table IV. Solvent Effects on the Isomerization Rate ( $k/s^{-1}$ ) of Selected *N*-Benzylideneanilines at 25 °C**

compd	solvent			
	benzene	acetone	acetonitrile	methanol
14a	8.73	5.74	3.34	4.00
15a	9.24	9.37	7.06	10.2

**Table V. Pressure Effects on the Isomerization Rate ( $k/s^{-1}$ ) of 4-(Dimethylamino)-*N*-(2,4,6-trinitrobenzylidene)aniline 15a in Methanol at 25 °C**

pressure/ MPa	$k$	pressure/ MPa	$k$
0.1	10.2	180	10.4
60	9.4	240	11.9
120	11.4		

mechanism. The possibility of rotation mechanism was clearly denied by the lack of solvent (Table IV) and pressure (Table V) effect on the isomerization.

The actual relation between the two inversion possibilities was examined by means of *ab initio* calculations on selected substituted *N*-phenylformaldimines 18 and *N*-benzylideneanilines 17 employing the 3-21G and 6-31G\* basis sets. The results for the *N*-phenylformaldimines in Table VI demonstrate that the unsubstituted compound and the nitro derivative show the perpendicular inversion state distinctly preferred over the planar one. Force constants calculations indicate the perpendicular conformation to be a saddle point with one negative eigenvalue of the force constants matrix, whereas the planar arrangement exhibits two negative eigenvalues. The opposite is true for the 4-(dimethylamino) group. Here, the planar inversion state is more stable than the perpendicular one and is characterized by one negative eigenvalue of the force constants matrix. An interesting result was found for the 4-hydroxy derivative both at the 3-21G and 6-31G\* basis set level. Although the perpendicular inversion state is still somewhat more stable than the planar one, both states are unequivocally characterized as genuine transition states by the frequency calculations. Thus, a parallel reaction route for the inversion has to be considered in this case. Even if this result may change employing still better basis sets and considering correlation energy, it demonstrates that this possibility has to be taken into consideration for special substituent constellations. Inclusion of correlation energy is in favor of the planar arrangement for the nitro compound without changing the principal stability order but in favor of the perpendicular orientation in all other cases. The same opposite influence of donor and acceptor groups on the energy difference between the planar and the perpendicular

**Table VI. Quantum-Chemical Data for the Energy Difference between the Planar and Perpendicular Inversion States ( $\Delta E/kJ mol^{-1}$ ), the Inversion Barriers ( $\Delta E_{inv}/kJ mol^{-1}$ ), and the Activation Enthalpies ( $\Delta H^\ddagger/kJ mol^{-1}$ ) and Entropies ( $\Delta S^\ddagger/J mol^{-1} K^{-1}$ ) for Substituted *N*-Phenylformaldimines 18**

X/basis set	$\Delta E$	$\Delta E_{inv}$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
NMe <sub>2</sub> <sup>a</sup>	3-21G	-6.9	90.6	79.5
	MP2/3-21G//3-21G	4.3	96.5	
	6-31G*	-2.6	111.5	98.0
MP2/6-31G**/6-31G*	8.8	108.6		
OH <sup>b</sup>	3-21G	1.9	90.1	77.0
	MP2/3-21G//3-21G	12.5	91.7	
	6-31G*	0.5	112.4	97.3
	MP2/6-31G**/6-31G*	11.6	107.2	
		(11.4) <sup>c</sup>	(108.5) <sup>c</sup>	
H <sup>d,e</sup>	3-21G	15.4	80.3	69.3
	MP2/3-21G//3-21G	22.5	85.6	
	6-31G*	15.6	102.8	89.6
	MP2/6-31G**/6-31G*	21.0	101.6	
		(21.6) <sup>c</sup>	(102.0) <sup>c</sup>	
NO <sub>2</sub> <sup>f</sup>	3-21G	38.2	60.9	52.6
	MP2/3-21G//3-21G	33.2	76.5	
	6-31G*	36.4	87.2	76.2
	MP2/6-31G**/6-31G*	35.9	89.5	
		(34.4) <sup>c</sup>	(91.0) <sup>c</sup>	

<sup>a</sup> 3-21G:  $\phi = 7.0^\circ$ . 6-31G\*:  $\phi = 36.6^\circ$ . <sup>b</sup> 3-21G:  $\phi = 24.0^\circ$ . 6-31G\*:  $\phi = 39.8^\circ$ . <sup>c</sup> Full optimization at the MP2/6-31G\* level. <sup>d</sup> 3-21G:  $\phi = 31.8^\circ$ . 6-31G\*:  $\phi = 45.3^\circ$ . <sup>e</sup> Formaldimine inversion barrier: MP2/6-31G\*\*/6-31G\* = 113.5 kJ mol<sup>-1</sup>, for further values, see ref 50. <sup>f</sup> 3-21G:  $\phi = 38.9^\circ$ . 6-31G\*:  $\phi = 50.4^\circ$ .

conformations is also found for the zero-point vibration energies and the vibration enthalpies. The entropy influence is generally small. Thus, in case of the *N*-phenylformaldimines, a conformation change of the inversion transition state should only be expected for substituents of very high electron-donating power. As already shown in a former paper,<sup>50</sup> the inversion barriers of aromatic azomethines are considerably lower than for the reference compound formaldimine (Table VI). The inversion barriers are distinctly higher at the 6-31G\* basis set level in comparison to the 3-21G basis set calculations. This could be explained by the well-known fact that split-valence and double- $\zeta$  basis sets without polarization functions underestimate inversion barriers.<sup>46</sup> Correlation energy influence is relatively small for the 6-31G\* basis set. Complete geometry optimization considering correlation

Table VII. Quantum-Chemical Data for the Energy Difference between the Planar and Perpendicular Inversion States ( $\Delta E/\text{kJ mol}^{-1}$ ) and the Inversion Barriers ( $\Delta E_{\text{inv}}/\text{kJ mol}^{-1}$ ) for Substituted *N*-Benzylideneanilines 17 and the Experimentally Observed Activation Energies<sup>a</sup> ( $\Delta E_{\text{inv}}^{\text{exp}}/\text{kJ mol}^{-1}$ )

X/basis set	$\Delta E$	$\Delta E_{\text{inv}}$	$\Delta E_{\text{inv}}^{\text{exp}}$
NH <sub>2</sub> <sup>b</sup>	3-21G	-8.1	59.1
	MP2/3-21G//3-21G	-0.4	76.4
	6-31G*/3-21G	-5.4	77.7
OH <sup>d</sup>	3-21G	2.8	60.6
	MP2/3-21G//3-21G	9.2	72.5
	6-31G*/3-21G	3.6	79.4
H <sup>e</sup>	3-21G	15.4	53.4
	MP2/3-21G//3-21G	18.9	68.5
	6-31G*/3-21G	17.8	72.3
NO <sub>2</sub> <sup>f</sup>	3-21G	37.6	39.0
	MP2/3-21G//3-21G	30.1	60.8
	6-31G*/3-21G	37.8	59.6

<sup>a</sup> In cyclohexane (ref 5). <sup>b</sup>  $\phi = 40.1^\circ$ ,  $\theta = 39.3^\circ$ . <sup>c</sup> 4-NMe<sub>2</sub> derivative. <sup>d</sup>  $\phi = 48.6^\circ$ ,  $\theta = 33.8^\circ$ . <sup>e</sup>  $\phi = 66.6^\circ$ ,  $\theta = 22.4^\circ$ . <sup>f</sup>  $\phi = 76.6^\circ$ ,  $\theta = 15.6^\circ$ .  
<sup>g</sup> Extrapolated from Hammett plot.

energy at the 6-31G\* level does not change the results obtained by means of MP2 calculations based on the 6-31G\* SCF geometries (Table VI). Correction for zero-point vibration and finite temperature of the experimental determination of the barriers based on the calculated vibrational frequencies decreases the barriers considerably. The principal conclusions from the calculations on the *N*-phenylformaldehydes are confirmed by the theoretical data for the *N*-benzylideneaniline derivatives (Table VII). Most important is the result for 4-amino compound, which indicates that the planar inversion state remains more stable now, although the energy difference is small, than the perpendicular one even if correlation energy is considered. Thus, in molecules with stronger push-pull character of the substituents at the azomethine linkage, the planar inversion state should have a good chance to be realized as indicated by our former results on substituted hexafluoroacetone and pyrazolone azomethines.<sup>26,27</sup> In the case of the *N*-benzylideneanilines, comparison of the theoretical and experimental values for the inversion barriers becomes partially possible. The 6-31G\* inversion barriers are in rather good agreement, whereas the 3-21G inversion barriers seem to be somewhat underestimated as already found and discussed for the *N*-phenylformaldehydes.

It may be interesting to analyze the kinetic data based on the assumption of a parallel route of the inversion mechanism which has got some support from the theoretical data at least for special substituents. By extrapolating eq 1 and inserting the estimated rate constant for perpendicular inversion ( $k_1$ ) to eq 3, the rate constants for planar inversion ( $k_2$ ) were calculated. They are listed in

$$k_{\text{obs}} = k_1 + k_2 \quad (3)$$

Table VIII along with  $k_1$  values. It can be seen clearly that planar inversion is much faster even if the benzylidene group has a dimethylamino group in its 4-position. However, the planar inversion can be realized only when the aniline moiety has a mesomerically strong electron-donating substituent such as a dimethylamino group as predicted by our calculations. It must be pointed out that

Table VIII. Rate Constants for Perpendicular ( $k_1/\text{s}^{-1}$ ) and Planar ( $k_2/\text{s}^{-1}$ ) Inversion in *N*-Benzylidene-4-(dimethylamino)anilines

compd	$k_1$	$k_2$
12a	0.018	0.115
13a	0.028	0.230
14a	0.0018	8.73

little deviation from eq 1 was observed even in the 4-methoxy group. Although the introduction of the second nitro group into the benzylidene component increased the planar inversion rate *ca.* 40 times, the substitution of the 4-(dimethylamino) group with a nitro group (from 12a to 13a) showed only a marginal effect on the rate. Similar insensitivity was also observed in the perpendicular inversion, and it is not possible to provide rationalizations for these observations at this point. The introduction of the third nitro group also did not show noticeable kinetic influence (Table I). This might be the result of the decrease in conjugation of the phenyl group with the central  $\pi$  bond caused by steric interactions between the third nitro group and the rest of the molecule, i.e., the nitrogen lone pair and/or the hydrogen atom(s) on the methine and the ortho carbon of the aniline ring.

By examination of the structure of the (*Z*)-*N*-phenylformaldehydes and (*Z*)-*N*-benzylideneanilines by means of the quantum chemical methods, a regular substituent influence on the rotation of the phenyl rings becomes visible (Tables VI and VII). Rotation of the *N*-phenyl ring is increased by electron-attracting substituents and decreased by electron-donating groups. Thus, the tendency of the nitrogen lone pair conjugation into the phenyl ring occurs already in the basic compounds. The opposite substituent influence exists for the C-phenyl ring rotation of the *N*-benzylideneanilines where electron-donor groups increase and acceptor groups decrease the rotation angle.

## Conclusions

From the results in this and previous reports,<sup>24-27</sup> it can now be safely concluded that perpendicular and planar conformations are possible at the inversion transition state for the *Z/E*-type isomerization of *N*-arylazomethines. The planar inversion where the *N*-aryl group is in conjugation with the carbon-nitrogen double bond is realized when the aryl group has a strong electron-donating substituent on its 4-position. In the perpendicular transition state, the interactions between the nitrogen lone pair and the aryl  $\pi$  electron system is exceptionally strong.

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**Supplementary Material Available:** <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of 12c,k,m-o, 13k,m,o, 14e,h,n,o, and 15j (30 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

## Picoline and Toluene: A Comparison of Structural Properties and Relative Stabilities of Their Monolithiated Derivatives

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Energy differences between five isomeric monolithiated 4-picoline 6a ( $\eta^3$  at C $\alpha$ /C4/C3), 6b ( $\eta^5$  at N1/C2/C3/C6/C5), 6c ( $\eta^2$  at C $\alpha$ /C4), 6da (N1-lithiated), and 6e ( $\eta^3$  at C3/C4/C5) were calculated by *ab initio* (MP2/6-31+G\*\*/6-31G\*) and semiempirical (MNDO) methods. With this basis set and inclusion of the ZPE correction, 6a-c and 6e turn out to be quite close in energy (within 0.13 kcal mol<sup>-1</sup>). 6c and 6e are transition structures. The N-lithiated structure 6da is least stable (about 5.5 kcal mol<sup>-1</sup>, compared with the above compounds). MNDO overemphasizes the instability of 6da by about 11 to 16 kcal mol<sup>-1</sup>. However, the *ab initio* calculated structural parameters of the anionic part of 6da compare quite well with those of a model of a "dimeric" structure 8, in which the 4-picoyl and the NH<sub>2</sub> anion are arranged in the characteristic lithium-bridged bis-amide fashion as found, e.g., for [LDA(TMEDA)]<sub>2</sub> complexes. Furthermore, the heterocyclic moiety of the model compounds 8 and 6da reveal significant similarities to X-ray structural data of closely related [4-(CH<sub>3</sub>CRCH<sub>3</sub>)-C<sub>5</sub>H<sub>4</sub>N]Li(TMEDA or (THF)<sub>2</sub>)<sub>2</sub> complexes (R = H, CH<sub>3</sub>) 3, 4a, and 4b. TMEDA or THF coligands almost do not influence the structural parameters of the anionic part. Therefore, 6da and the C $\alpha$ -substituted models [4-(CH<sub>3</sub>CRC<sub>5</sub>H<sub>4</sub>N)Li (6db: R = H, 6dc: R = CH<sub>3</sub>), which are accessible to reliable *ab initio* calculations, represent the most simplified structures to describe this part of such complexes adequately. Similar aspects for the interpretation of a variety of known benzyllithium X-ray structures (which differ in the nature of the coligands involved) are found by calculating the four analogous " $\pi$ - $\eta$ " isomers 1a,b. In this context, MNDO should be used with caution, as relative stabilities and activation barriers disagree significantly with high level *ab initio* calculations. In contrast to MP2/6-31+G\*\*/6-31G\* calculations, MNDO predicts *ortho*-lithiated toluene 7 to be more stable than 1a,b.

### Introduction

In the past two decades major progress has been made in the elucidation of the molecular and electronic structure of organolithium compounds.<sup>1</sup> Bonding in these "carbanions", as well as in their heteroatom analogues, e.g., amides,<sup>2</sup> is dominated by electrostatic interactions between the lithium cations and the anionic moieties. In general, structures and properties depend to a significant extent on the degree of aggregation and on the coordination of donor (solvent) molecules. In  $\pi$ -delocalized carbanions and in polyolithium compounds, the lithium cations are often found in non-classical positions, that is "bridging" between centers of negative charge. MO calculations of Schleyer *et al.*<sup>3</sup> predicted symmetrical bridging for the unsolvated, monomeric alkali metals salts of the allyl anion, the prototype for a  $\pi$ -delocalized carbanion. Crystal structures of allyllithium<sup>4</sup> and derivatives<sup>5</sup> essentially confirmed this prediction. In benzyllithium, more than

one bridging position for the metal cation is available. The preference for coordination to C $\alpha$  and C<sub>ortho</sub> over coordination to the aromatic ring, seen in various X-ray structures of benzyllithium and derivatives, was rationalized in a recent theoretical study by Sygula and Rabideau,<sup>6</sup> who concluded that the  $\eta^3$  isomer 1a is the most stable structure, followed by the ring-lithiated  $\eta^5$  form 1b, which is found to be 1.7 kcal mol<sup>-1</sup> less stable (MP2/6-311G\*\*/3-21G).

Our experimental investigations deal with a related topic, the reactivity behavior of several lithiated 4-alkylpyridines 2, in which the moieties R<sup>1</sup> and R<sup>2</sup> were varied as summarized in Chart I.<sup>7,8</sup> X-ray investigations indicate that, at least in case of R<sup>1</sup> = H, R<sup>2</sup> = CH<sub>3</sub> (compound 3), and R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub> (compound 4a), these TMEDA complexes and the THF complex 4b (Figure 1) are dimers. In solution, <sup>6</sup>Li,<sup>1</sup>H-HOESY showed lithium contacts only to *ortho*-hydrogen atoms of the heterocyclic moiety.<sup>8,9</sup> MNDO calculations of a representative dimer appear to be in acceptable agreement with the X-ray structure.<sup>9</sup>

*Ab initio* calculations of such dimers 3, 4a, and 4b including their TMEDA or THF moieties would clearly be desirable, but exceed our present computer capacity. Therefore, in this paper we discuss the following aspects: (a) To which extent does the nitrogen atom in 2 influence the relative stabilities of the isomeric monolithiated C( $\alpha$ )-picoyl anion isomers compared with those of the benzyl anion? (b) Are these "observed" X-ray structures of the

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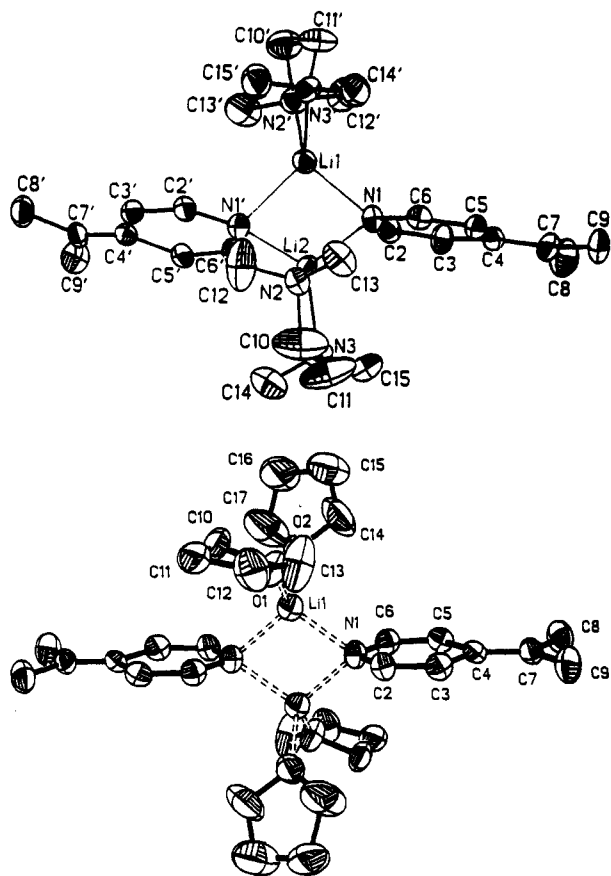
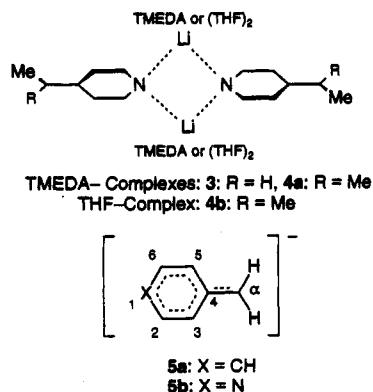
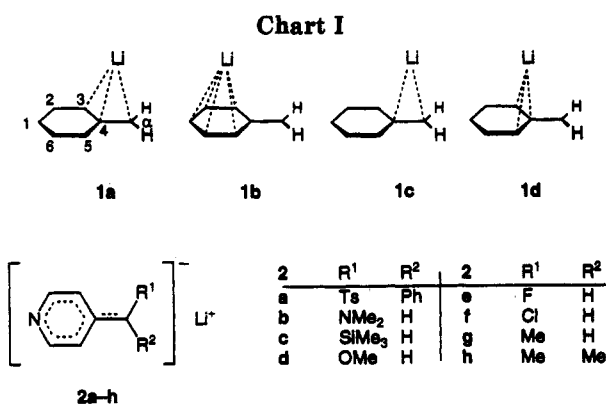


Figure 1. X-ray structures of 4a,<sup>9</sup>  $[\{4-(\text{CH}_3\text{CCH}_3)\text{-C}_5\text{H}_4\text{N}\}\text{Li}(\text{TMEDA})\}_2$  (top) and 4b,  $[\{4-(\text{CH}_3\text{CCH}_3)\text{-C}_5\text{H}_4\text{N}\}\text{Li}(\text{THF})\}_2$  (bottom).



TMEDA complexes 3 and 4a or the THF complex 4b related to any of the unsolvated gas-phase monomers? Which gas phase structure may serve as a more realistic

model to describe structural and electronic properties of those lithiated species in the condensed phase? (c) To which extent do MNDO results agree with best available *ab initio* calculations?

In the theoretical part of this paper we first discuss the structural properties of the parent compound (4-picoline) and the picolyl anion 5b together with its monolithiated derivatives 6a-6dc. These compounds are compared with the structural analogs 1a-c of the benzyl series. For reasons given below, we include the *ortho*-lithiated toluene 7 and the transition states of the benzyllithium (TS- $\alpha$ ) and the *ortho* isomer (TS-*ortho*) formation. Finally, in case of the heterocyclic systems we compare the *ab initio* results for the monomeric structures 6 together with a model of a dimeric structure (compound 8) with the X-ray structures of the dimers 3, 4a and 4b.

## Results and Discussion

**X-Ray Investigations.** The crystal structures of the TMEDA complexes 3 and 4a have been previously reported.<sup>9</sup> Both belong to the  $[\{4-(\text{CH}_3\text{CR})\text{C}_5\text{H}_4\text{N}\}\text{Li}(\text{TMEDA})\}_2$  (with R = H, CH<sub>3</sub>) type of complexes and show significant distortion. Assuming  $D_{2h}$  symmetry for an idealized dimer like 4a, this distortion seems to be the result of the steric demand of the TMEDA ligands<sup>2a</sup> and crystal packing effects.<sup>10</sup>

The THF complex  $[\{4-(\text{CH}_3\text{CCH}_3)\text{C}_5\text{H}_4\text{N}\}\text{Li}(\text{THF})\}_2$ , 4b, shows only a minor deviation from  $D_{2h}$  symmetry (Figure 1, for specific bond lengths see Table II). Both heterocyclic ring systems are exactly coplanar; the dihedral angle C(3)-C(2)-N(1)-Li(1) is 90.4°. Figure 2 summarizes the interatomic distances in the central Li(1)-N(1)-Li(2)-N(1') segments. The averaged values of the four Li-N bond lengths (4a, 2.097 Å; 4b, 2.078 Å) indicate a slight elongation in favor of the TMEDA complex. The anionic moieties reveal the characteristics of N-substituted 4-alkylidene-1,4-dihydropyridines. Their bond lengths are not affected by the nature of the coligands.<sup>22</sup>

**Ab Initio and MNDO Calculations: Procedure.** *Ab initio* calculations were performed using the Gaussian 90<sup>11a</sup> and Cadpac 4.1<sup>11b</sup> program packages. Semiempirical calculations were run using the program VAMP.<sup>11c</sup> All geometries were optimized both at MNDO<sup>11d</sup> and HF/6-31G\*<sup>11e</sup> levels and characterized as minima, saddle points, etc. by calculation of vibrational frequencies. Structures of anionic species were optimized using the 6-31+G\* basis set.<sup>11f</sup> Energy calculations, including electron correlation at the MP2 level,<sup>11g</sup> were performed on the 6-31G\*

(10) For details see Refs 2 and 9.

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