Mechanism of Thermal Z/E Isomerization of Substituted N-Benzylideneanilines. Nature of the Activated Complex with an sp-Hybridized Nitrogen Atom

Tsutomu Asano,*,† Hiroyuki Furuta,† Hans-Jörg Hofmann,*,‡ Renzo Cimiraglia,§ Yuho Tsuno,⊥ and Mizue Fujio⊥

Department of Chemistry, Faculty of Engineering, Oita University, Oita 870-11, Japan, Fachbereich Biowissenschaften, Universität Leipzig, D-7010 Leipzig, Germany, Dipartimento di Chimica, Universita di Ferrara, I-44100 Ferrara, Italy, and Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka 812, Japan

Received February 16, 1993

In order to study the mechanism of thermal geometrical isomerization involving a sp²-hybridized nitrogen atom, kinetic effects of substituent, solvent, and pressure were studied in substituted N-benzylideneanilines. The effect of the substituent on the aniline moiety was almost independent of the electronic nature of the benzylidene group, and the results could be described satisfactorily by $\log (k/k_0) = \rho [\sigma^{\circ} + r^+ (\sigma^+ - \sigma^{\circ}) + r^- (\sigma^- \sigma^{\circ})]$, except for the 4-(dimethylamino) group. The r-values were more than twice as large as r^+ , suggesting strongly that the aniline ring is in conjugation not with the carbon-nitrogen π bond but with the nitrogen lone pair in the transition state. The lower activation enthalpies and fairly large negative activation entropies observed in N-(4-X-benzylidene)-4-nitroanilines also support this view. When a dimethylamino group exists in the 4-position of the aniline ring, the rate constants observed were larger than that expected from the above equation. This deviation suggests the existence of a reaction route where the two phenyl groups become coplanar in the transition state. Ab initio calculations on selected N-phenylformaldimines and N-benzylideneanilines were performed to characterize the actual relation between both reaction possibilities as alternative and parallel routes, respectively. On the basis of the experimental data, the rate constants for the two inversion isomerizations were estimated by assuming parallel reactions for three cases.

Introduction

The mechanism of Z/E-type thermal isomerization involving sp²-hybridized nitrogen(s) continues to impose challenging problems on organic chemists. Such reactions are well-known for a variety of azoarenes and azomethines. For example, (Z)-azobenzene was first isolated by Hartley in 1937,¹ and it was shown to regenerate the E-isomer in several hours at room temperature in solution.² Similarly. a relatively slow spectral change observed after the xenonflash irradiation of solution of substituted azobenzenes³ or N-benzylideneanilines^{4,5} was attributed to thermal Zto E isomerization. Coalescence of ¹⁹F-NMR signal was also observed in N-(hexafluoroisopropylidene)anilines 1.



and the rate of the degenerate isomerization was calculated from the results.⁶ The interest in the mechanism was

- [‡] Universität Leipzig. ¹ Universita di Ferrara.

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aroused by the proposal of nitrogen inversion by Binenboym and his co-workers for difluorodiazene (transition state 2).⁷ Now it is generally agreed that their conclusion is applicable to most of the cases.⁸ One notable exception is the reaction of push-pull-substituted azobenzenes such as 4-(dialkylamino)-4'-nitroazobenzene. Involvement of a highly polar rotational transition state 3 was proposed by Whitten³ on the basis of the kinetic effects of solvent, and it was shown later that the mechanism depends upon the polarity of the reaction medium, i.e., inversion (via 4) in nonpolar solvents and rotation in polar ones.^{13,17-19} The two-route mechanism was unequivocally proved by concave-up Arrhenius plots observed in benzene, 1,4-dioxane,

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0022-3263/93/1958-4418\$04.00/0

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⁽⁸⁾ Rationalizations for this mechanism include (1) lower energy barrier (50–100 kJ mol⁻¹) than that expected from the π bond energy, (2) facile isomerization of an azobenzene unit incorporated into a ring system where the rotation of the phenyl ring around the nitrogen-nitrogen bond is sterically difficult, 9,10 (3) the slight decrease in polarity during activation as evidenced by slower reaction in polar solvents¹¹ and by a smaller energy of solvent transfer (from cyclohexane to cyclohexanone) for the activated complex than that for (Z)-azobenzene,^{12,13} and (4) the retardation of isomerization of imines by complex formation with trimethylaluminum¹⁴ and by protonation^{5,16} or by hydrogen-bond formation on the imino nitrogen atom.16

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and other solvents with medium polarity. A similar tworoute mechanism was proposed for some N-arylazomethines such as 1, 5a, 6, 7, and 8, on the basis of the



kinetic effects of the substituent X on the aniline moiety.^{6,20-23} In all of these compounds, the isomerization was accelerated both by electron donation and attraction by the substituent X. While the acceleration by electronattracting substituents was rationalized by an increase in contribution of a canonical structure 9' in the (perpendicular) inversion transition-state 9, the electron-donating



substituents were believed to accelerate the reaction by inducing the rotation mechanism. Since most of these compounds carry electronegative substituent(s) on the imino carbon, considering a dipolar transition state such as 10 was seemingly justifiable. However, the examination of the kinetic effects of solvent and pressure revealed that in 1 and 5a, the polarity of the reactant decreased slightly even in the case of $X = NMe_2$.^{24,25} The results could not be reconciled with a highly polar rotation transition state, and the acceleration by electron-release from X had to be rationalized in the framework of the inversion mechanism. Therefore, the existence of a conformationally different (planar) inversion transition state 11 where the aryl group is in conjugation with the carbon-nitrogen π bond was assumed for the strongly electron-donating substituents. This conclusion was supported by ab initio calculations on 1 and 5b.^{26,27} In these compounds, the perpendicular inversion was energetically favored for $X = NO_2$ and H, while the planar inversion was preferred for $X = NH_2$ both in the gas phase and in water. However, the

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intervention of the planar inversion mechanism was yet to be proven for a compound that is most closely related to azobenzene, i.e., N-benzylideneaniline. Therefore, the effects of the substituent X were studied experimentally and theoretically for N-arylazomethines 12-15, 17, and 18 to shed light on the electronic and structural features of the species with an sp-hybridized nitrogen atom.





Methods

Materials. N-Benzylideneanilines (12-15) were prepared from the corresponding benzaldehyde and aniline. They were purified by recrystallization from benzene, hexane, or a mixture of the two. Column chromatography (silica gel/benzene) was also used in the case of 4-(dimethylamino)-N-(2,4,6-trinitrobenzylidene) aniline 15a. All of the isolated products gave satisfactory elemental analyses. The melting/decomposition points (in °C) are as follows: 12a, 238-9 (lit.28 239-40); 12b, 142.5-3 (lit.29 143); 12c, 151-2; 12d, 124-5 (lit.²⁹ 123); 12e, 139.5-4 (lit.²⁹ 137); 12f, 154-5 (lit.29 153); 12g, 161-2 (lit.29 162); 12h, 155-5.5 (lit.29 151); 12i, 120-22 (lit.²⁹ 121); 12j, 208.5-9.5 (lit.³⁰ 207); 12k, 92 (lit.³¹ 82); 121, 80 (lit.³¹ 79); 12m, 86-7; 12n, 81-1.5; 12o, 94-5 (lit.³² 81-2); 12p, 112-3 (lit.29 112); 12q, 101.5-2.5 (lit.29 100); 13a, 226 (lit.³⁰ 223-4); 13b, 137 (lit.²⁹ 134); 13c, 146-7 (lit.³³ 143-5); 13d, 127-7.5 (lit.²⁹ 124); 13e, 114-4.5 (lit.²⁹ 112); 13f, 134-5 (lit.²⁹ 132); 13g, 166-7 (lit.29 164); 13h, 126-7 (lit.29 128); 13i, 183.5-4 (lit.29 180); 13j, 205-5.5 (lit.³⁴ 203); 13k, 97-8; 13l, 98-9 (lit.²⁹ 98); 13m, 89.5-90; 13n, 110 (lit.³⁵ 107-9); 13o, 81-2; 13p, 155-6 (lit.²⁹ 152); 13q, 92-2.5 (lit.³⁴ 93); 14a, 216-7 (lit.³⁶ 211); 14b, 133-3.5 (lit.³⁷ 129); 14d, 155 (lit.38 152); 14e, 122; 14f, 164-5 (lit.39 161.5); 14h, 106; 14j, 173 (lit.³⁷ 169.5); 14l, 135-5.5 (lit.⁴⁰ 130); 14n, 144-5.5 (lit.41 137); 140, 138.5-9; 14p, 141 (lit.37 138); 14q, 133-4.5 (lit.42 133); 15a, no clear melting point (lit.³⁶ 268); 15b, 184 (lit.⁴³ 182); 15f, 181-2 (lit.43 180); 15j 179-80. The structures of newly reported compounds and the ones with an inconsistent melting point were confirmed by ¹H- and ¹³C-NMR spectra (supplementary material) except 15a. It was not possible to obtain satisfactory spectra for this compound because of its poor

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

	Y			
х	4-NMe ₂	4-NO ₂	2,4-(NO ₂) ₂	2,4,6-(NO ₂) ₃
4-NMe ₂	0.133	0.258	8.73	9.24
4-MeO	0.214	0.330 (0.36)ª	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		
$4-CF_3$	33.7	42.2	2.94	
4-COOEt	70.3	68.1		
$4-NO_2$	704	395 (347)ª	36.2	19.3
3-MeŌ	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 ₃	10.5	12.7	1.15	
3-NO ₂	18.0	18.6	3.14	
н	2.17	2.73 (3.00)ª	0.284	

^a 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⁻¹. Spectrograde benzene (Wako Pure Chemical Ind.) was used as received.

Kinetic Measurements. All rate constants were measured by flash spectroscopy; details are described elsewhere.^{13,17}

ab Initio Calculations. The ab initio calculations on the substituted N-phenylformaldimines and N-benzylideneanilines were performed using GAUSSIAN92⁴⁴ and SPARTAN⁴⁶ program packages, respectively. The geometries of the N-phenylformaldimines were completely optimized employing the *ab initio* 3-21G and 6-31G* basis sets.⁴⁶ 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 values³⁴ 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 σ° 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 electronattracting tendency of X and the points for the para



Figure 1. Plot of log (k/s^{-1}) against σ° for Z/E isomerization of 12: \blacklozenge , meta substituents; \Box , para substituents.



Figure 2. Plot of log (k/s^{-1}) against σ° 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 electrondonating 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,47 the results were best correlated with the substituent constants by the following Yukawa-Tsuno style equation with two resonance contribution parameters r^+ and r^- .

$$\log \left(k/k_{o} \right) = \rho \left[\sigma^{\circ} + r^{+} (\sigma^{+} - \sigma^{\circ}) + r^{-} (\sigma^{-} - \sigma^{\circ}) \right]$$
(1)

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

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

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



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



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

satisfactory.⁴⁸ 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 ρ 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.^{26,27} Lower activation enthalpies and moderately negative activation entropies observed for 12i, 13i, and 14i (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

N-benzylideneanilines			
12	13	14	
1.26 ± 0.14	1.18 ± 0.13	1.22 ± 0.15	
0.94 ± 0.16	0.97 单 0.15	1.06 0.21	
2.79 ± 0.58	2.56 ± 0.54	2.08 2 0.57	
0.985	0.985	0.986	
		$\begin{tabular}{ c c c c c } \hline N-benzylideneanilin\\\hline 12 & 13\\\hline 1.26 \pm 0.14 & 1.18 \pm 0.13\\ 0.94 \pm 0.16 & 0.97 \textcircled{0} 0.15\\ 2.79 \pm 0.58 & 2.56 \pm 0.54\\ 0.985 & 0.985\\\hline \end{tabular}$	

^a 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

$$\log \left(K/K_{o} \right) = \rho \left[\sigma^{\circ} + r^{-} (\sigma^{-} - \sigma^{\circ}) \right]$$
(2)

most stable conformation of (Z)-N-benzylidene-4-hydroxyaniline (17, X = OH) has the rotation angle ϕ 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.⁴⁹ 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 π 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 $(\Delta H^*/kJ \text{ mol}^{-1})$, and Activation Entropies $(\Delta S^*/J \text{ K}^{-1} \text{ mol}^{-1})$ for the Thermal Z/E Isomerization of N-Benzylideneanilines in Benzene

			k/s ⁻¹				
compd	10 °C	15 °C	25 °C	35 °C	45 °C	ΔH^*	ΔS^{\bullet}
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
1 4e	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
14 f	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
1 4j	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

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

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

pr	essure/ 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 ($\Delta E/kJ \mod^{-1}$), the Inversion Barriers ($\Delta E_{inv}/kJ \mod^{-1}$), and the Activation enthalpies ($\Delta H^*/kJ$ mol⁻¹) and Entropies ($\Delta S^*/J \mod^{-1} K^{-1}$) for Substituted N-Phenylformaldimines 18

X/basis set	ΔE	ΔE_{inv}	ΔH^*	ΔS^*
NMe ₂ ª				
	-6.9	90.6	79.5	-4.8
MP2/3-21G//3-21G	4.3	96.5		
6-31G*	-2.6	111.5	98.0	-0.3
MP2/6-31G*//6-31G*	8.8	108.6		
OH				
3-21G	1.9	90.1	77.0	1.8
MP2/3-21G//3-21G	12.5	91.7		
6-31G*	0.5	112.4	97.3	7.4
MP2/6-31G*//6-31G*	11.6	107.2		
	(11.4)°	(108.5)°		
H ^{d,e}				
3-21G	15.4	80.3	69.3	-4.3
MP2/3-21G//3-21G	22.5	85.6		
6-31G*	15.6	102.8	89.6	-2.2
MP2/6-31G*//6-31G*	21.0	101.6		
	(21.6)¢	(102.0)°		
NO ₂ /				
3-21G	38.2	60.9	52.6	-7.8
MP2/3-21G//3-21G	33.2	76.5		
6-31G*	36.4	87.2	76.2	-6.6
MP2/6-31G*//6-31G*	35.9	89.5		
	(34.4)°	(91.0)°		

^a 3-21G: $\phi = 7.0^{\circ}$. 6-31G*: $\phi = 36.6^{\circ}$. ^b 3-21G: $\phi = 24.0^{\circ}$. 6-31G*: $\phi = 39.8^{\circ}$. ^c Full optimization at the MP2/6-31G* level. ^d 3-21G: $\phi = 31.8^{\circ}$. 6-31G*: $\phi = 45.3^{\circ}$. ^e Formaldimine inversion barrier: MP2/6-31G*//6-31G* = 113.5 kJ mol⁻¹, for further values, see ref 50. ^f 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,⁵⁰ 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- ζ basis sets without polarization functions underestimate inversion barriers.⁴⁶ Correlation energy influence is relatively small for the 6-31G* basis set. Complete geometry optimization considering correlation

⁽⁵⁰⁾ Hofmann, H.-J.; Cimiraglia, R.; Tomasi, J. J. Mol. Struct. THEOCHEM 1987, 152, 19.

Table VII. Quantum-Chemical Data for the Energy Difference between the Planar and Perpendicular Inversion States ($\Delta E/kJ \text{ mol}^{-1}$) and the Inversion Barriers ($\Delta E_{\text{inv}}/kJ \text{ mol}^{-1}$) for Substituted N-Benzylideneanilines 17 and the Experimentally Observed Activation Energies⁴ ($\Delta E_{\text{inv}}e^{xp}/kJ \text{ mol}^{-1}$)

(,		
X/basis set	ΔE	$\Delta E_{ m inv}$	$\Delta E_{\mathrm{inv}}^{\mathrm{exp}}$
NH2 ^b			
3-21G	-8.1	59.1	78.2°
MP2/3-21G//3-21G	-0.4	76.4	
6-31G*//3-21G	-5.4	77.7	
OHd			
3-21G	2.8	60.6	76.1
MP2/3-21G//3-21G	9.2	72.5	
6-31G*//3-21G	3.6	79.4	
He			
3-21G	15.4	53.4	70.1
MP2/3-21G//3-21G	18.9	68.5	
6-31G*//3-21G	17.8	72.3	
NO ₂ /			
3-21G	37.6	39.0	66.1 ^g
MP2/3-21G//3-21G	30.1	60.8	
6-31G*//3-21G	37.8	59.6	

^a In cyclohexane (ref 5). ^b ϕ = 40.1°, θ = 39.3°. ^c 4-NMe₂ derivative. ^d ϕ = 48.6°, θ = 33.8°. ^e ϕ = 66.6°, θ = 22.4°. ^f ϕ = 76.6°, θ = 15.6°. ^f 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 zeropoint 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-phenylformaldimines 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. 26,27 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-phenylformaldimines.

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

$$k_{\rm obs} = k_1 + k_2 \tag{3}$$

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 electrondonating 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/s^{-1}) and Planar (k_2/s^{-1}) Inversion in N-Benzylidene-4-(dimethylamino)anilines

k1	k2		
0.018	0.115		
0.028	0.230		
0.0018	8.73		
	k1 0.018 0.028 0.0018		

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 π 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-phenylformaldimines 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,^{24–27} 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 π electron system is exceptionally strong.

Acknowledgment. One of us, R.C, wishes to express his gratitude to the Italian CNR through its ICQEM laboratory in Pisa for kind availability of its computational facilities; partial financial contribution from the Italian MURST is also acknowledged. We are also grateful to Professor Kawasaki of Shinshu University for providing the unpublished spectra of some of the N-benzylideneanilines and to Professor Honjo of Oita University for his helpful discussions. Part of this work was supported by Fonds der Chemischen Industrie.

Supplementary Material Available: ¹H- and ¹³C-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.