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Short Communication

NMR Spectroscopic Study of the (*Z*)/(*E*)-Isomerism of 1-Aryl-3-arylamino-2-propen-1-ones in Solution and in the Crystalline State

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Summary. ^{1}H, ^{13}C, and CP/MAS ^{13}C NMR spectra of six *p*-substituted 1-aryl-3-arylamino-2-propen-1-ones in solution and in the solid state are reported and discussed. In the proton-accepting solvent dimethylsulfoxide, electronegative substituents shift the isomeric equilibrium to the (*E*)-isomer. Bulky substituents promote crystallization of the (*Z*)-form.

Keywords. ^{1}H, ^{13}C, CP/MAS ^{13}C NMR; Enaminones; (*Z*)/(*E*)-Isomerization.

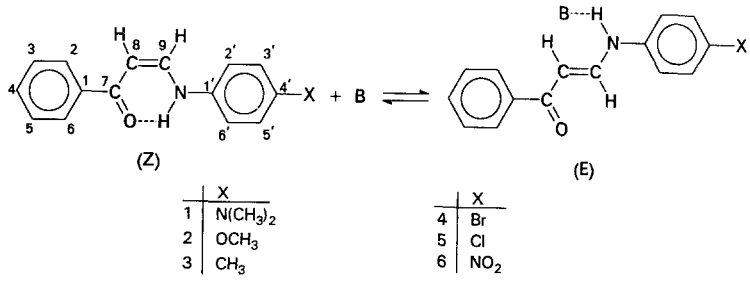
NMR-Spektroskopische Untersuchung der (*Z*)/(*E*)-Isomerie von 1-Aryl-3-arylamino-2-propen-1-onen in Lösung und im Kristallzustand (Kurze Mitt.)

Zusammenfassung. ^{1}H-, ^{13}C- und CP/MAS-^{13}C-NMR Spektren von sechs *p*-substituierten 1-Aryl-3-arylamino-2-propen-1-onen in gelöstem und festem Zustand werden berichtet und diskutiert. In protonenakzeptierendem Dimethylsulfoxid verschieben elektronegative Substituenten das Gleichgewicht zum (*E*)-Isomer. Große Substituenten begünstigen die Kristallisation in der (*Z*)-Form.

Introduction

A great number of structural studies on *Schiff* bases derived from 3-oxoaldehydes and aromatic primary amines have already been reported [1–16]. It is known that these compounds can potentially exist in keto-imine, keto-enamine or enol-imine forms, but only the keto-enamine structure has been detected in all investigated cases. This tautomeric form exists as an equilibrium mixture of (*Z*)- and (*E*)-isomers, its composition being solvent-, concentration- and structure dependent. Although (*Z*)/(*E*)-isomerization of keto-enamines has already been extensively studied, to our

knowledge, there is no systematic spectroscopic investigation on the influence of substituents in the aniline ring on the equilibrium. This paper describes our NMR spectroscopic studies of the (*Z*)/(*E*)-isomerism of *p*-substituted 1-aryl-3-arylamino-2-propen-1-ones **1–6** (Scheme 1) in solution and in the crystalline state.



Scheme 1

Results and Discussion

The quantitative data on the isomerism of **1–6** in solution are obtained from the signal intensities in the ^{1}H NMR spectra (Table 1) and summarized in Table 2. In $CDCl_3$ solution, there are no proton-accepting centers stabilizing the (*E*)-isomer form; therefore, only the (*Z*)-form is present. In the proton-accepting *DMSO*-d_6, the (*Z*)/(*E*)-equilibrium depends on the influence of the substituent on the proton-donating ability of the NH group and consequently on the strength of its hydrogen bonds–intramolecular for the (*Z*)- and intermolecular for the (*E*)-isomer. With the gradual decrease of the electron-donating and increase of the electron-withdrawing character of substituents, the amount of the (*E*)-isomer form gradually increases (Table 2). A good correlation is observed between $\log(Z)/(E)$ and the σ_R^0 constants of the substituents ($r = 0.92$, $s_0 = 0.19$). It is evident that the substituents influence the balance between inter- and intramolecular hydrogen bonding. Electronegative substituents increase the acidity of the NH group and its intermolecular hydrogen

Table 1. ^{1}H NMR chemical shifts (in ppm)[a] and coupling constants (in Hz)[b] of aminoketones $C_6H_5COCH{=}CHNHC_6H_4X$-*p* **1–6** in *DMSO*-d_6 and in $CDCl_3$[c] solutions

	δ_{NH}			δ_{H-8}			$^3J_{H-8,H-9}$		
	(*Z*)		(*E*)	(*Z*)		(*E*)	(*Z*)		(*E*)
1	12.22	(12.28)	9.98	6.00	(5.94)	6.30	7.5	(7.5)	12.5
2	12.15	(12.21)	10.05	6.05	(5.97)	6.40	7.7	(7.8)	12.5
3	12.10	(12.17)	10.10	6.10	(6.00)	6.40	7.7	(7.8)	12.5
4	12.00	(12.13)	10.15	6.15	(6.05)	6.45	7.8	(7.8)	12.6
5	12.00	(12.13)	10.15	6.15	(6.07)	6.45	7.8	(7.8)	12.7
6	12.05	(12.25)	10.65	6.30	(6.15)	6.65	7.7	(8.3)	12.5

[a] $\delta_{H-9} = 7.4–7.5$ for (*Z*)- and 8.0–8.1 for (*E*)-isomers; [b] $^3J_{H-9,NH} = 12.2–12.5$ for (*Z*)- and 12.5–12.7 for (*E*)-isomers; [c] chemical shifts and coupling constants in $CDCl_3$ are given in parentheses

Table 2. ^{13}C NMR chemical shifts (in ppm) of vinyl carbon C-8 of aminoketones **1–6**[a] in solution and in the crystalline state; amounts of (*Z*)- and (*E*)-isomers

	State	(*Z*)	(*E*)	(*Z*)/(*E*)-ratio (%)
1	$CDCl_3$	92.1	–	100/0
	DMSO-d_6	91.7	(96)	72/28
	Cryst.	90		100/0
2	$CDCl_3$	92.8	–	100/0
	DMSO-d_6	92.4	96.4	65/35
	Cryst.	91		100/0
3	$CDCl_3$	93.1	–	100/0
	DMSO-d_6	92.8	96.9	50/50
	Cryst.		97	0/100
4	$CDCl_3$	94.2	–	100/0
	DMSO-d_6	93.8	98.3	57/43
	Cryst.		100	0/100
5	$CDCl_3$	94.1	–	100/0
	DMSO-d_6	93.8	98.2	57/43
	Cryst.		100	0/100
6	$CDCl_3$	96.8	101.6	100/0
	DMSO-d_6	96.4		40/60
	Cryst.	93		100/0

[a] Other chemical shifts in *DMSO*-d_6: C-7, 188.4–190.5 (*Z*) and 186.8–188.0 (*E*); C-9, 144.8–146.7 (*Z*) and 144.0–147.3 (*E*); benzoyl ring, 138.6–140.5 (C-1), 128.4–128.7 (C-2, C-6), 126.9–127.5 (C-3, C-5), 131.4–132.4 (C-4); chemical shifts of the aniline ring carbon atoms strongly depend on the substituents

bond with *DMSO*-d_6 and stabilize the (*E*)-isomer complex form. One can assume that the corresponding effect on the intramolecular hydrogen bond in the (*Z*)-isomer is weakened and complicated due to through-bond interaction between the electron-withdrawing substituent and the carbonyl group, causing a decrease in its proton-accepting ability. As a result, in *DMSO*-d_6 solution electronegative substituents shift the equilibrium to the (*E*)-isomer.

To determine the structure of crystalline aminoketones **1–6**, their solid state high resolution ^{13}C NMR spectra were compared with those of solutions in $CDCl_3$ ((*Z*)-isomer only) and in *DMSO*-d_6 (mixture of (*Z*)- and (*E*)-isomers) (Table 2). The chemical shift of the vinyl carbon C-8 is most sensitive to the isomerization effect ($\Delta\delta$: 4–5 ppm) (Table 2). For carbonyl and azomethine carbons C-7 and C-9, the effects are much weaker ($\Delta\delta$ *ca.* 2 and 1 ppm, respectively). It appears that in contrast to solutions in *DMSO*-d_6, only one isomer exists in the crystalline state, and its structure is more probably controlled by the substituents' size rather than by their electronic properties. It is likely that bulky substituents ($N(CH_3)_2$, OCH_3, NO_2) increase the anisometry of the molecule, thus promoting its crystallization in the (*Z*)-form, while the keto-amines with less bulky substituents (CH_3, Cl, Br) crystallize in the (*E*)-form.

Experimental

^1H and ^{13}C NMR spectra of 5% solutions were recorded on a Bruker AC 200 spectrometer; solid state CP/MAS ^{13}C NMR spectra were measured on a Bruker CXP 100 spectrometer; δ values are reported in ppm with respect to *TMS*. The solvents were used without further purification.

Enaminones **1**–**6** were prepared in a manner similar to that described by *Rateb* [12] and *De Kimpe* [14], using only minor changes in the conditions. All compounds were purified by repeated recrystallization and their purity checked by elemental analyses, IR and NMR spectra.

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