^{1}H-NMR STUDY OF A TRANSFER OF SUBSTITUENT EFFECTS IN *para*-SUBSTITUTED BENZYLIDENEANILINES AND THEIR CONJUGATE ACIDS

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^{1}H-NMR spectra of isomeric 4-substituted-4′-ethyl benzylideneanilines have been measured in CCl_4 and in trifluoroacetic acid. From correlations of chemical shifts with the Hammett σ_p constants and increments a_i of chemical shifts it has been deduced that chemical shifts of signals of sterically hindered protons are considerably affected by van der Waals repulsion of electron clouds and by change of diamagnetic anisotropy of double bond and aromatic ring currents. Chemical shifts of proton signals of the individual derivatives also permit to study conformational changes in the molecules besides transmission of substituent effects. Coalescence temperatures of doublets of CH= protons in the protonated benzylideneanilines only depend on nature of substituents and are the same for the both isomeric derivatives.

Non-planar conformation of benzylideneanilines was proved by spectroscopic methods[1,2] and X-ray analysis[3]. Although crystallographic data indicate deviation of both benzene rings from the plane of CH=N bond, it is generally accepted that in solutions benzaldehyde ring is coplanar with this bond, unless it contains bulky *ortho*-substituents. Deviation of the aniline ring from the plane of the rest of molecule is of such magnitude that the overall stabilizing effect of $\pi-\pi$ and $n-\pi$ conjugation of electrons at nitrogen with the aromatic π-electrons is maximum[4]. If all other effects are neglected, then the deviation angle Φ can be calculated by differentiation of the relation:

$$f(\Phi) = \cos \Phi + 2 \sin \Phi \,, \qquad (1)$$

where $\cos \Phi$ represents conjugation of aniline ring with π-electron at nitrogen, and the expression $2 \sin \Phi$ reflects conjugation with two n-electrons of the free electron pair at nitrogen. The angle Φ is then equal to arctg $2 = 63.5°$. Literature[4] gives a more complicated procedure involving influence of π-bond order of the rotating N—C bond on the magnitude of the angle Φ. Differentiation of that relation gives
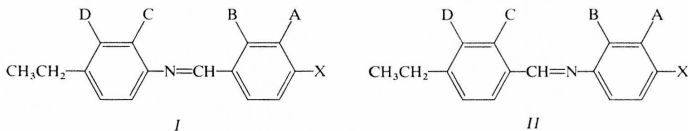
$$\Phi = \mathrm{arctg} \left((1.2 + p_{NC})/2p_{NC} \right) . \qquad (2)$$

Taking π-bond order[5] $p_{NC} = 0.356$, we get $\Phi = 65.5°$. However, the latter procedure leads to contradictory results. It is known[3] that substitution of *para*-hydrogen by nitro group in aniline part of benzylideneaniline results in shortening of the N—C bond round which the ring is rotated. If this shortening were caused by greater participation of π-electron at nitrogen in conjugation and, hence, increase in π-bond order, then, according to Eq. (2), the angle Φ would have to de-

crease. On the contrary, greater participation of n-electrons of nitrogen in conjugation results in increase of the angle Φ, and then the dependence (2) of the angle Φ on π-bond order is not valid. From available experimental data it is impossible to decide which of the alternatives is correct.

^{1}H-NMR spectroscopy was also used for elucidation of conformation of benzylide- neanilines. Substituent effect on chemical shifts of CH= proton signal[6-14] and signal of OH proton forming hydrogen bond with azomethine nitrogen[15] were investigated.

Transmission of effects of *para*-substituents to other places in the molecule has not yet been thoroughly investigated. Therefore, we prepared two series of 4-substi- tuted-4′-ethylbenzylideneanilines *I* and *II* and measured their ^{1}H-NMR spectra. For comparison the spectra of the compounds were measured also in trifluoroacetic acid, since protonation can localize the free electron pair at nitrogen and make the molecule planar[1,6].

$$CH_3CH_2 \underset{D}{\overset{C}{\bigcirc}} N=CH \underset{B}{\overset{A}{\bigcirc}} X \qquad CH_3CH_2 \underset{D}{\overset{C}{\bigcirc}} CH=N \underset{B}{\overset{A}{\bigcirc}} X$$

I   *II*

$$X = N(CH_3)_2, \; OH, \; CH_3, \; C_2H_5, \; H, \; Cl, \; COCH_3, \; NO_2$$

EXPERIMENTAL

Benzylideneanilines *I* and *II* were prepared by one of the following methods. *A*: Equimolar amounts of substituted benzaldehyde and aniline were refluxed in ethanol for 30 min. The product was crystallized from ethanol (charcoal) until constant melting point. *B*: Equimolar mixture of benzaldehyde and aniline was heated at 120°C 1 h. The reaction product was distilled under reduced pressure. *C*: Equimolar amounts of substituted benzaldehyde and aniline were refluxed in CCl₄ 5 h, and the water formed was separated in a separator. The product was crystallized from CCl₄ (alumina) until constant melting point. *D* (ref.[17]): Substituted benzaldehyde (2 mol) and substituted aniline (1 mol) were heated at 130°C for 6 h. The unreacted substituted aniline was removed by fractional crystallization from CCl₄. The product was purified by crystallization from CCl₄ (alumina) until constant melting point.

The prepared benzylideneanilines were characterized by melting points (Table I). Their purity and identity were checked by elemental analyses and ^{1}H-NMR spectra.

The ^{1}H-NMR spectra were measured with a Tesla BS 487C spectrometer (80 MHz) in 0·5M solutions in CCl₄, using tetramethylsilane (TMS) as internal standard. Spectra of the protonated benzylideneanilines were obtained with 0·5M solutions in trifluoroacetic acid, using hexamethyl- disiloxane (HMDSO) as internal standard. Frequences of the individual peaks were read by means of a precise frequency generator[19] with accuracy ±0·001 Hz. Chemical shifts of signals of *para*-

substituted benzenes were calculated as for an AA′BB′ system. For determination of coalescence temperatures t_c (°C) the temperature probe of the spectrometer was calibrated according to the procedure recommended by the manufacturer. The t_c temperature values were read with the accuracy of ± 1°C.

TABLE I

Preparation of Benzylideneanilines I and II

Substituent	I		II	
	method	m.p., °C	method	m.p., °C
$N(CH_3)_2$	A	96	A	102
OH	A	200·5	A	176·5
OCH_3	A	55·5	A	61
C_2H_5	A	42	A	42
H	B	115/0·2^a	B	113·5/0·2^{a,b}
Cl	A	83·5	A	76·5
$COCH_3$	A	92	C	75
NO_2	A	85·5	D	76

^{a} B.p. °C/Torr; ^{b} ref.[18] b.p. 208—210°C/20 Torr; m.p. 2—3°C.

TABLE II

Chemical Shifts^a of Signals of Benzylideneanilines I in δ (ppm) and Correlation^b with σ_p Constants

Substituent	σ_p	$\delta_{CH=}$	δ_{CH_2}	δ_{CH_3}	Δ_{Et}
$N(CH_3)_2$	−0·830	8·177	2·610	1·231	1·380
OCH_3	−0·268	8·244	2·616	1·232	1·385
C_2H_5	−0·151	8·296	2·621	1·232	1·389
H	0	8·332	2·626	1·237	1·388
Cl	0·227	8·279	2·625	1·234	1·391
$COCH_3$	0·502	8·359	2·631	1·237	1·394
NO_2	0·778	8·444	2·660	1·258	1·402
b	—	0·151	—	—	0·013
a	—	8·299	—	—	1·389
r	—	0·9332	—	—	0·9672
P	—	99·5	—	—	99·9

^{a} 0·5M Solution in CCl_4; tetramethylsilane as internal standard; ^{b} $\sigma_p = a + b\delta$; r correlation coefficient; P correlation significance in %.

RESULTS AND DISCUSSION

Internal chemical shift of ethyl group $\Delta_{Et} = \delta_{CH_2} - \delta_{CH_3}$ depends on electronegativity of the atom to which the ethyl group is bonded[20]. Thus it can be estimated from the Δ_{Et} values of the benzylideneanilines *I* and *II* how the change of substituent X at *para*-position influences electron density at *para'*-position. If the substituent effects are transmitted through π bonds, then the transmission is weakened by increasing deviation[5,21] (depending on cos Φ) and drops to a half for $\Phi = 60°$. The slope of the correlation of Δ_{Et} *vs* the Hammett σ_p constants[22] is approximately the same for both sets of compounds *I* and *II* (Tables II and III) being roughly half that of the corresponding correlations for planar conjugated acids (Tables IV and V). Our finding agrees well with the value calculated from Eq. (*1*), *i.e.* 63·5°, and with results of UV spectroscopy[2] (44−64°) and X-ray analysis[3] (41−55°).

Chemical shift of the proton signal of methine group can be correlated very well with the σ_p constants[22] in the case of azomethines *I* and both conjugated acids *I* and *II* (Tables II, IV and V). All the three correlations have positive slopes, which indicates a transmission of substituent effects through conjugated system. In contrast to that, correlation slope of the proton signals of CH= groups of the azomethines *II* is small and negative, and the correlation less reliable ($r = -0.8113$, $P = 97\%$) than the foregoing three ones (Table III). This fact was observed by other authors[8−14], too, and was explained by a smaller substituent effect, by a decrease of conjugation,

TABLE III

Chemical Shifts[a] of Signals of Benzylideneanilines *II* in δ (ppm) and Correlation[b] with σ_p Constants

Substituent	σ_p	$\delta_{CH=}$	δ_{CH_2}	δ_{CH_3}	Δ_{Et}
N(CH$_3$)$_2$	−0·830	8·327	2·646	1·237	1·409
OCH$_3$	−0·268	8·301	2·656	1·242	1·414
C$_2$H$_5$	−0·151	0·296	2·659	1·241	1·417
H	0	8·290	2·666	1·248	1·418
Cl	0·227	8·255	2·672	1·252	1·420
COCH$_3$	0·502	8·263	2·676	1·251	1·425
NO$_2$	0·778	8·281	2·712	1·275	1·437
b	—	−0·037	—	—	0·016
a	—	8·289	—	—	1·419
r	—	−0·8113	—	—	0·9435
P	—	97·0	—	—	99·8

[a,b] See Table II.

TABLE IV

Chemical Shifts[a] of Signals of Protonated Benzylideneanilines *I* in δ (ppm), Coalescence Temperatures, ΔG^+ and Correlation[b] with σ_p Constants

Substituent	σ_p	$\delta_{CH=}$	t_c, °C	ΔG^+ kcal mol^{-1}	δ_{CH_2}	δ_{CH_3}	Δ_{Et}
OH	−0·370	8·448	74·5	17·93	2·323	0·836	1·487
CH₃	−0·268	8·467	70·5	17·71	2·327	0·845	1·482
C₂H₅	−0·151	8·630	64·5	17·39	2·345	0·855	1·490
H	0	8·743	54·0	16·83	2·354	0·862	1·492
Cl	0·227	8·752	41·0	16·14	2·355	0·861	1·494
COCH₃	0·502	8·975	17·5	14·88	2·372	0·869	1·503
NO₂	0·778	9·061	3·5	14·14	2·378	0·871	1·507
b	—	0·543	−64·471	—	—	—	0·020
a	—	8·669	53·113	—	—	—	1·491
r	—	0·9776	−0·9970	—	—	—	0·9633
P	—	99·9	99·9	—	—	—	99·9

[a] 0·5M Solutions in CF_3COOH; hexamethyldisiloxane as internal standard; [b] see Table II.

TABLE V

Chemical Shifts[a] of Signals of Protonated Benzylideneanilines *II* in δ (ppm), Coalescence Temperatures, ΔG^+ and Correlation[b] with σ_p Constants

Substituent	σ_p	$\delta_{CH=}$	t_c, °C	ΔG^+ kcal mol^{-1}	δ_{CH_2}	δ_{CH_3}	Δ_{Et}
OH	−0·370	8·568	57·5[c]	17·02	2·437	0·892	1·545
OCH₃	−0·268	8·572	57·5[c]	17·02	2·439	0·899	1·540
C₂H₅	−0·151	8·630	64·5	17·39	2·442	0·904	1·538
H	0	8·690	54·0	16·83	2·454	0·906	1·547
Cl	0·227	8·689	42·0	16·19	2·456	0·905	1·551
COCH₃	0·502	8·919	18·5	14·94	2·487	0·922	1·565
NO₂	0·778	8·956	5·5	14·25	2·494	0·919	1·575
b	—	0·363	−65·043	—	—	—	0·031
a	—	8·680	54·540	—	—	—	1·548
r	—	0·9683	−0·9960	—	—	—	0·9437
P	—	99·9	99·9	—	—	—	99·8

[a,b] See Table IV; [c] not included into the correlation.

or by a field effect of substituent. Having found almost equal transmission of substituent effects to ethyl group in the sets *I* and *II*, we consider the above explanations to be incorrect or, at least, insufficient. Moreover, the equal transfer of a substituent effect through the azomethine bond in both directions is also obvious from the ^{19}F-NMR spectra of two isomeric series of 4-substituted-4'-fluorobenzylideneanilines[16] analogous to our series *I* and *II*.

If the chemical shift of the CH= proton signal were influenced only by electron density change, then the correlation slope would have to diminish only and not change its sign. However, from the results obtained it can be concluded that the chemical shift of this proton signal is affected in some other way, most probably by proximity of the hydrogens of aniline ring placed in *ortho* position to CH=N bond (hydrogens B). In planar arrangement[5] this distance is only 0·17 nm. Repulsion of about 2 kcal . . mol^{-1} was calculated[2] for the angle of deviation of aniline ring $\Phi \approx 60°$. This means that the smaller is the twist angle[2], the more the electron clouds about these hydrogen atoms deform each other. If this angle is decreased along the series from the NO$_2$ to the N(CH$_3$)$_2$ derivative, increasing deformation of electron clouds results in lowered shielding of the corresponding hydrogen atoms and downfield shift of the signal. This dependence of chemical shift on substituent has negative slope. Both effects, *i.e.* the electron density change and change of van der Waals repulsion almost compensate each other, and the resulting correlation slope is small and negative. In addition to it, changed deviation of aniline ring causes the CH= proton to change its position in the space affected by ring currents of this aromate, which represents a further contribution to chemical shift of signal of azomethine hydrogen[14]. We suppose that combination of these sterically dependent contributions to shielding also causes lowering of the respective correlation coefficient. If there is not equal geometry in a series of compounds, then it is impossible to expect a good correlation of chemical shifts with constants characterizing only the influence on electron density near the considered atom. Of course, influence of mutual deformations of electron clouds and sterical deviation on chemical shifts can be observed also on the signals of the corresponding hydrogens of aniline ring.

Chemical shifts of signals of aromatic hydrogen atoms in *para*-disubstituted benzenes are advantageously correlated with the a_i increment values[23] for one variable substituent X, the other substituent (usually a complex group) being kept constant during correlation. The correlation can be expressed as follows[24].

$$\delta = (7·27 + a_j) + a_i(1 + Ka_j) . \tag{3}$$

Eq. (*3*) expresses the deviation of the effects of both substituents from additivity characterized by increments a_i and a_j. We used this correlation to check the correctness of assignments of chemical shifts to individual hydrogen atoms, to evaluate the influence of 4-ethylphenylazomethine substituent on hydrogen atoms in *meta* and

TABLE VI

Chemical Shifts[a] of Signals of Benzylideneanilines I in δ (ppm) and Correlation[b] with a_i Increments

Substituent	a_{ortho}	δ_A	a_{meta}	δ_B	a_{para}	δ_C	δ_D
$N(CH_3)_2$	-0.66	6.565	-0.18	7.628	-0.67	7.041	7.003
OCH_3	-0.48	6.835	-0.09	7.728	-0.44	7.065	1.010
C_2H_5	-0.14	7.172	-0.06	7.725	-0.17	7.072	7.034
H	0	—	0	—	0	7.085	7.047
Cl	0.03	7.341	-0.02	7.749	-0.09	7.090	7.035
$COCH_3$	0.62	7.866	0.14	7.866	0.21	7.097	7.059
NO_2	0.95	8.189	0.26	7.964	0.38	7.137	7.100
b	—	0.978	—	0.731	—	0.079	0.086
a	—	7.276	—	7.771	—	7.093	7.051
r	—	0.9979	—	0.9946	—	0.9486	0.9548
P	—	99.9	—	99.9	—	99.8	99.9

[a] See Table II; [b] $a_i = a + b\delta$; r correlation coefficient; P correlation significance in %.
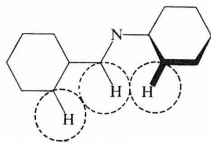
TABLE VII

Chemical Shifts[a] of Signals of Benzylideneanilines II in δ (ppm) and Correlation[b] with a_i Increments

Substituent	a_{ortho}	δ_A	a_{meta}	δ_B	a_{para}	δ_C	δ_D
$N(CH_3)_2$	-0.66	6.589	-0.18	7.093	-0.67	7.705	7.145
OCH_3	-0.48	6.779	-0.09	7.077	-0.44	7.708	7.167
C_2H_5	-0.14	7.034	-0.06	7.072	-0.17	7.725	7.172
H	0	—	0	—	0	7.734	7.181
Cl	0.03	7.245	-0.02	7.030	-0.09	7.714	7.192
$COCH_3$	0.62	7.840	0.14	7.069	0.21	7.734	7.203
NO_2	0.95	8.117	0.26	7.114	0.38	7.746	7.244
b	—	0.959	—	0.053	—	0.039	0.081
a	—	7.216	—	7.075	—	7.728	7.195
r	—	0.9989	—	0.3052	—	0.9290	0.9314
P	—	99.9	—	50	—	99.5	99.5

[a,b] See Table VI.

ortho positions (hydrogens A and B), and to confirm the effects of deformation of electron clouds on chemical shifts of the signals of aniline ring protons (B) which are near the azomethine proton. If a substituent exerts only electron-donor or electron-acceptor effects, then the correlation slope (*b*) is close to unity[24]. This is the case in all the studied compounds for the hydrogen atoms A (Tables VI—IX). In contrast to that, the correlation slope for hydrogen atoms B of the derivatives *II* is almost zero, and the correlation coefficient indicates that the correlation is very bad (Table VII). This findings confirms (*cf.* above analogy of azomethine hydrogen) that further effects on chemical shift are operating which almost compensate the effect of substituent electronegativity. *E.g.* nitro group causes lowering of electron density in aromatic ring and downfield shift of the proton B signal. However, if simultaneous increase in deviation of the ring diminishes the effects of van der Waals repulsion on deformation of electron cloud about these hydrogen atoms, then a reverse shift of signal results. Besides that, change of position of hydrogen B with respect to the double bond CH=N will cause a change in contribution of diamagnetic anisotropy of the double bond to shielding of these hydrogen atoms. This makes the correlation coefficient of this correlation very low.

For hydrogen atoms of 4-ethylphenyl grouping a relatively good correlation of chemical shifts with the increments a_{para} was found (Tables VI—IX). These values characterize transmission of effects of substituent X to carbon atom in *para*-position of the same benzene ring[22,23]. In this case, too, the correlation slopes are roughly the same except for that one which concerns hydrogen atoms C in compounds type *II* (Table VII). The decrease in correlation slope can be explained by a secondary deformation of electron cloud about the hydrogen C by the deformed electron cloud of CH= hydrogen atom. This deformation is smaller than that of B hydrogens (the distance of hydrogen atom C from methine hydrogen is 0·25 nm)[5], and molecular geometry is not affected, since in this part the molecule is planar regardless of nature of the substituent. Therefore, only the slope is diminished, but the correlation coefficient remains high.

From the given changes in chemical shifts of signals of the hydrogen atoms CH=, B and C it follows that the deviation angle of aniline ring increases along the series of benzylideneaniline derivatives *II* from N(CH$_3$)$_2$ to NO$_2$. It means that (as in the case of anilines) shortening of the bond between nitrogen and the adjacent ring in

Table VIII

Chemical Shifts[a] of Signals of Protonated Benzylideneanilines I in δ (ppm) and Correlation[b] with a_i Increments

Substituent	a_{ortho}	δ_A	a_{meta}	δ_B	a_{para}	δ_C	δ_D
OH	−0·56	6·778	−0·12	7·678	−0·45	7·066	7·027
OCH$_3$	−0·48	6·810	−0·09	7·728	−0·44	7·073	7·034
C$_2$H$_5$	−0·14	7·171	−0·06	7·672	−0·17	7·160	7·034
H	0	—	0	—	0	7·206	7·054
Cl	0·03	7·288	−0·02	7·730	−0·09	7·193	7·051
COCH$_3$	0·62	7·956	0·14	7·956	0·21	7·291	7·084
NO$_2$	0·95	8·077	0·26	8·116	0·38	7·316	7·096
b	—	0·917	—	1·188	—	0·311	0·082
a	—	7·282	—	7·792	—	7·211	7·061
r	—	0·9939	—	0·9793	—	0·9951	0·9555
P	—	99·9	—	99·9	—	99·9	99·9

[a] See Table IV; [b] see Table VI.

Table IX

Chemical Shifts[a] of Signals of Protonated Benzylideneanilines II in δ (ppm) and Correlations[b] with a_i Increments

Substituent	a_{ortho}	δ_A	a_{meta}	δ_B	a_{para}	δ_C	δ_D
OH	−0·56	6·733	−0·12	7·195	−0·45	7·652	7·166
OCH$_3$	−0·48	6·752	−0·09	7·238	−0·04	7·649	7·166
C$_2$H$_5$	−0·14	7·034	−0·06	7·160	−0·17	7·672	7·171
H	0	—	0	—	0	7·703	7·188
Cl	0·03	7·177	−0·02	7·216	−0·09	7·700	7·194
COCH$_3$	0·62	7·902	0·14	7·501	0·21	7·797	7·231
NO$_2$	0·95	8·087	0·26	7·591	0·38	7·819	7·240
b	—	0·957	—	1·166	—	0·211	0·093
a	—	7·214	—	7·295	—	7·730	7·201
r	—	0·9941	—	0·9594	—	0·9570	0·9473
P	—	99·9	—	99·9	—	99·9	99·8

[a,b] See Table VIII.

benzylideneanilines is due to a greater participation of n-electrons in conjugation with electrons of the aromate, and, hence, the dependence of the deviation angle on π-bond order (Eq. (2)) is incorrect.

Protonated forms of the both types of azomethines *I* and *II* show very good correlations with the respective increments a_i (Tables VIII and IX). The correlation slope is considerably high for the hydrogen atoms B and C near the positively charged nitrogen atom, which means that in planar arrangement also here some other effects influence the chemical shift (not only mere transmission of electron-donor or -acceptor effects of substituents).

Interaction of hydrogen atom of methine group with that at nitrogen atom in the protonated azomethines *I* and *II* results in splitting of its signal into a doublet ($^3J \approx 17$ Hz). This doublet can be observed with the greater part of the measured substances at room temperature; nitro and acetyl derivatives give the doublet on cooling. Signal of the hydrogen atom $\overset{(+)}{N}H$ cannot be seen in spectrum, since it coincides with that of the solvent proton. Gradual increasing of temperature during measurements causes gradual approaching of peaks, until, at a certain temperature, they coalesce into one peak (Tables IV and V). At this coalescence temperature (t_c, °C) the rate of proton exchange between $\overset{(+)}{N}H$ and solvent is given by Eq. (4) ref.[25]

$$k_c = \pi |v_\infty| \, 2^{-1/2} , \tag{4}$$

where v_∞ is the maximum distance of the both peaks of a doublet. For $v_\infty = 17$ Hz it follows $k_c = 37 \cdot 76 \text{ s}^{-1}$. The free enthalpy of activation for the proton exchange at nitrogen at the temperature T_c (K) can be calculated from Eq. (5)[25].

$$\Delta G^{\ddagger}_{T_c} = 4 \cdot 57 \, T_c \left(10 \cdot 32 + \log \left(T_c / k_c \right) \right) . \tag{5}$$

The energy difference between the ground state and the activated complex for the greater part of the protonated derivatives *I* and *II* depends only on nature of the substituent X and not on its position (*i.e.* whether aniline or benzaldehyde ring is substituted). Chemical shifts of signals of the methine protons as well as the coalescence temperatures t_c correlate well with the Hammett σ_p constants (Tables IV and V). Only the t_c values for the methoxy and hydroxy derivatives of the series *II* deviate from the correlation, the reason of which we cannot reliably explain so far.

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