# MOLECULAR CONFORMATION AND ELECTRONIC STRUCTURE OF AZOMETHINES

# III. ELECTRONIC ABSORPTION SPECTRA OF *para*-SUBSTITUTED N-BENZYLIDENEMETHYLAMINES

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#### ABSTRACT

The absorption spectra in the vapour phase, in cyclohexane and methanol solutions of *para*-substituted benzylidenemethylamines have been measured and discussed in terms of solvatochromic and substituent effects. A comparison with the absorption spectra of benzylideneanilines of the  $p-R \cdot C_6H_4 \cdot CH : N \cdot C_6H_5$  type confirms that these compounds have a non-planar conformation with the aniline ring twisted out of the  $C_6H_5 \cdot CH : N \cdot plane$ .

## INTRODUCTION

The determination of the conformation of benzylideneaniline derivatives on the basis of electron absorption spectra and dipole moments has been dealt with previously<sup>1-3</sup>. To elucidate the problem we selected some molecules with the  $p-R \cdot C_6H_4 \cdot CH : N \cdot$  system because the most intense band observed in the electronic spectrum of benzylideneaniline, at approximately 260 nm, is said to arise from a local excitation within the  $C_6H_5 \cdot CH : N \cdot$  system.

For this study, derivatives with the general formula

$$(1) R = NMe_{2}; (2) R = OH; (3) R = OMe; (4) R = Me; (5) R = H; (6) R = Cl; (7) R = Br; (8) R = CO_{2}H; (9) R = CO_{2}Et; (10) R = NO_{2}$$

were chosen; the aim of the present paper is both to determine the effect of the substituent groups on the p-R-benzylidenemethylamines spectra and to compare the same spectra with those of the analogous benzylideneanilines.

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Some of the selected compounds have just been reported<sup>4-11</sup>, but there are very few<sup>9,10</sup> reports of experimental data concerning the UV spectra and they have not yet been subject to any systematic study; only the unsubstituted compound has been studied experimentally and also from the theoretical point of view<sup>12</sup>.

## EXPERIMENTAL

Infrared spectra were obtained of solids as potassium bromide discs and of liquids as capillary films with a Hitachi–Perkin-Elmer Model 257 spectrophotometer. All the reported benzylidenemethylamines show a strong C : N absorption between 1640 and 1650 cm<sup>-1</sup>.

## Materials

The benzylidenemethylamines (1), (2), (4), (7), (8) and (10) were prepared by mixing five equivalents of a 35 % aqueous solution of monomethylamine for each equivalent of the corresponding aldehyde. The crude products were purified by distillation in vacuo (compounds 4 and 7) or recrystallized several times from anhydrous ethanol<sup>13</sup> (compounds 1, 2, 7 and 8).

The benzylidenemethylamines (3), (5) and (6) were prepared according to the procedure of Winn and coworkers<sup>11</sup>. The first two were purified by distillation in vacuo and the last one by preparative gas chromatography, using a  $2 \text{ m} \times 10 \text{ mm}$  column, packed with SE 30 (20%) on Chromosorb P (30–60 mesh).

Compound (9) was obtained by boiling compound (8) in anhydrous ethanol for 30 h. The solution was then cooled and filtered; the resultant crystals were washed with ether and recrystallized.

All the compounds rapidly changed to aldehydes and amines when exposed to the atmosphere at room temperature. The experimental data were generally collected within a few minutes after distillation; when this was not possible, the freshly obtained product was stored under nitrogen, in the dark and at low temperature. Purity was checked by IR spectra.

Physical data for the p-R-benzylidenemethylamines are listed in Table 1.

## Ultraviolet absorption spectra

The spectra of the compounds dissolved in anhydrous methanol<sup>13</sup> and in cyclohexane Spectrograde reagent were obtained. All the precautions previously mentioned<sup>1,2</sup> were taken before recording the spectra. Absorption in solution was measured by a recording Hitachi–Perkin-Elmer Model 124 spectrophotometer, over the 210–360 nm range for  $10^{-3}$ ,  $10^{-4}$  and  $10^{-5}$  moles  $1^{-1}$  solutions in silica cells with an optical path of 1 cm.

#### TABLE 1

Compound	Physical state	M.P. (°C)	B.P. (°C)	P(mm Hg)	n <sup>D</sup> 25°	Purif. <sup>b</sup>	Ref.	
1	Clear brown	55-57	125	0.25	<u> </u>	D+C	_	
	needles	(54–58)ª	95	0.15			7	
2	Clear yellow needles	175–177			—	С		
3	Colourless liquid		53	0.12	1.5669	D		
	-		(125–126)	(15)			10	
4	Colourless liquid		42	0.16	_	D	_	
5	Colourless liquid	-	65	15	1.5503	D		
	• · ·		(89–90)	(30)			10	
6	Colourless liquid		90	28	1.5693	GC	_	
			(65–66)	(1.5)	_		10	
7	Colourless liquid	_	43	0.03	1.5939	D		
8	Clear yellow needles	150-152	_			С	<del></del>	
9	Clear yellow needles	214-215		_		С		
10	Yellow plates	1056			_	С		
		(106)			—		9	
		(105–107)					11	

PHYSICAL DATA FOR THE para-SUBSTITUTED BENZYLIDENEMETHYLAMINES

<sup>a</sup> Values in parentheses denote literature data.

<sup>b</sup> Purification method: D = distillation in vacuo; C = crystallization; GC = gas chromatography.

Vapour phase spectra were recorded on the same spectrophotometer, as previously reported<sup>3</sup>.

## Data analysis

A linear regression analysis was used to determine statistical relationships between two variables. The correlation coefficient r was first selected as indicator to determine how well the regression line fits the observed data. For testing the regression hypothesis the F statistic test<sup>14</sup> was used and the sample value of F was calculated; on the basis of the degrees of freedom in the numerator and denominator of the F ratio and referring to the F distribution tables, the probability P of exceeding the  $F_{\text{crit}}$  value was determined.

To compare the estimated slope coefficients of the straight lines we used the t test<sup>15</sup>: when the  $t_{crit}$  value to the 0.01 level, for the opportune degrees of freedom, exceeds the sample value of t, we conclude that the slope coefficients compared do not differ.

The data for R = OH were not introduced into the calculation of the correlations.

Calculations were performed on an IBM 1620 (20 K) computer.

## **RESULTS AND DISCUSSION**

The wavelengths of absorption maxima of benzylidenemethylamines in solution and in the vapour phase together with their extinction coefficients in anhydrous methanol and cyclohexane are given in Table 2.

The solution spectra of benzylideneamines show the same general shape: a more intense shorter-wavelength peak\* that appears in the unsubstituted derivative

## TABLE 2

Substituent	Methan	ol	Cyclohe.	Vapour <sup>b</sup>		
	λ(nm)	ε	$\lambda(nm)$	ε	<i>λ(nm</i> )	
NMe <sub>2</sub>	325 (305)° 231	22100 20200 10000	325 318 232	25300 25800 8750	(330) 286*	
ОН			296	2400	(290)	
			(285)	4800	(283.5)	
	267.5	21300	258	20500	248*	
ОМе	(294)	5950	294	2700	290.5	
	(286)	9100	(286.5)	4900	(283)	
	265	17300	261.5	19000	253*	
Ме	(291)	1860	290	880	(285.5)	
	(280)	3370	280	1270	275.5	
	253	18500	251.5	17170	240.5*	
Н	(286)	880	286.3	730	283	
	(277)	1330	276.5	970	273	
	244	15000	243	16300	232.5*	
Cl	290.5	1330	290	1380	287.5	
	280.5	2100	280.5	1950	278	
	250	19450	251	20250	243*	
Br	292 (282) 253.5	1700 3000 20900	290 282 254	1250 1930 23500	-	
CO₂H	 257	 18700	(296) (287.5) 258	800 1600 15700	(295) (284) 247*	
CO₂Et			(298)	1700	(297)	
			(287.5)	2400	(285)	
	257	15200	258	18500	247*	
NO <sub>2</sub>	273	26700	275	25600	255*	

UV SPECTRA OF para-SUBSTITUTED BENZYLIDENEMETHYLAMINES

<sup>a</sup> The solvent in the spectra of compounds (2), (7) and (9) has 2 % by volume of methanol.

<sup>b</sup> The asterisk refers to the most intense maximum.

<sup>e</sup> Wavelengths in parentheses denote inflections.

\* Except for R = p-NMe<sub>2</sub> where the most intense peak is shifted at the longest wavelength (318 nm in cyclohexane).

at 243 nm ( $\epsilon = 16300$ ) in cyclohexane, and a low intensity longer-wavelength band with fine structure at 280–290 nm, sometimes appearing as a shoulder on the most intense peak.

## Solvatochromic effects

It can be deduced from data in Table 2 that there are some regularities in the differences between the wavenumber  $(cm^{-1})$  of the absorption maximum of the most intense peak in the spectrum in cyclohexane  $(v_{CE})$  and the one in methanol  $(v_{MeOH})$ : for the nucleophilic substituents  $v_{MeOH} < v_{CE}$  and for the electrophilic substituents the reverse is true. Recently Finkel'shtein and Krasnoshchekova<sup>16</sup> have deduced and experimentally verified, for benzylideneanilines of the  $C_6H_5 \cdot CH : N \cdot C_6H_4 \cdot R$  type, that the magnitude of the solvatochromic effects  $\Delta v_{1,2} = v_1 - v_2$ , i.e. the shifts in the spectral absorption bands due to a change in solvent from 1 to 2, are correlated with Hammett  $\sigma$  constants by the equation

 $(\Delta v_{1,2})_j = m + n\sigma_j$ 

To test this equation, values of  $\Delta v_{1,2} = v_{CE} - v_{MeOH}$  are plotted against  $\sigma$  values<sup>17</sup> in Fig. 1. The relation obtained is not the result of chance coincidence: the satisfactory observed fit can therefore be regarded as confirmation of the correctness of the general considerations advanced by Finkel'shtein and Krasnosh-chekova<sup>16</sup>. Similar relationships are not found on changing from vapour phase to solutions in cyclohexane or methanol, but this was not unexpected as vapour phase spectra have been recorded at very different temperatures.



Fig. 1. Relation of the solvatochromic effect of benzylidenemethylamines p-R · C<sub>6</sub>H<sub>4</sub> · CH : NMe to Hammett  $\sigma$  constants (r = 0.97; P < 1 %).

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There are some qualitative conclusions<sup>18</sup> that we may draw about the effect of solvent on the absorption spectra of benzylidenemethylamines.

For derivatives with nucleophilic substituents, a red shift was observed when the molecule changed from the gaseous state to solution in cyclohexane and methanol, i.e., with increasing dielectric constant. The red shift should be due to an increase in the dipole moment on electronic excitation<sup>19</sup> and should indicate that the solvent effect on the wave number approximately depends on dielectric constant, i.e. on interaction of polarization forces.

For derivatives with electrophilic substituents, a red shift was observed between the gaseous state and solution in cyclohexane but a blue shift was observed between cyclohexane and methanol solutions. In this negative solvatochromism the shift depending on the refractive index of the solution should be superimposed on to the dielectric constant dependence: in fact, a blue shift can be expected with decreasing refractive index as from cyclohexane to methanol.

## Substituent effects

In order to investigate further the electronic spectra of our compounds, the shortest-wavelength band shifts ( $\Delta v$ , in wave number) of the benzylidenemethylamine relative to the *para*-substituted compounds were plotted, for each environment, against Hammett  $\sigma$  constants<sup>17</sup> and  $\sigma^+$  constants<sup>17</sup>. As the statistical tests for the  $\Delta v - \sigma$  straight lines were in any case the better ( $r \ge 0.99$  and P < 1%), the correlation with the  $\sigma$  constants was chosen. It can be seen from Figs. 2a and 2b, and indirectly from Fig. 2c, that the plots of  $\Delta v$  against  $\sigma$  have the form of two intersecting lines: the application of the *t* test allows us to conclude that, for each solvent,  $\rho_n$  is not equal to  $\rho_e$  whilst the  $\rho_n$  or the  $\rho_e$  values do not differ on changing the environment.

On an a priori basis there is, of course, no guarantee that substituents in electronically excited molecules will exert their effect by the same interaction mechanisms that are also important for the molecules in the electronic ground states. When the significant interaction mechanisms are different, simple extra-thermodynamic relationships cannot be expected to  $exist^{20}$ . Since the frequency shift expresses the differential perturbative effect of the substituent in the ground and first excited states, the existence of the correlations  $\Delta v - \sigma$  is strongly indicative that, for each derivative, the interaction mechanisms are essentially comparable and that the transition is of the same type in the series.

Moreover, the experimental fact that the band shifts correlate better with the  $\sigma$  constants than with the  $\sigma^+$  constants should indicate that the effect of direct polar conjugation between the *para*-substituents in the aryl nucleus of benzylidenemethylamine and the C: NMe group is small and therefore the N-methyl formimidoyl group has extremely weak electron-acceptor properties. This result agrees very well with that of Minkin et al.<sup>21</sup>.

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Fig. 2. Plots of  $\Delta \nu$  for benzylidenemethylamines ( $\bullet$ ) against the  $\sigma$  constants: (a) in methanol  $(r_n = 0.996; r_e = 0.998; P < 1\%)$ ; (b) in the vapour phase  $(r_n = 0.990; r_e = 0.975; P < 1\%)$ . (c) The plot of  $\nu$  for benzylidenemethylamines in cyclohexane  $(r_n = 0.998; r_e = 0.990; P < 1\%)$  and for benzylideneanilines ( $\odot$ ) in isooctane  $(r_n = 0.993; r_e = 0.997; P < 1\%)$  against the  $\sigma$  constants. (d) The plot of calculated  $\Delta E$  against h (see text).

The experimental data on the effect of *para*-substitution and on the values and the sign of the  $\rho$ -constants are accounted for by the following considerations.

According to Burawoy and Critchley<sup>9</sup>, a conjugation band is displaced to longer wavelengths by any structural modification which increases the polarizability of the electrons in the absorbing system, such as an "electron shift" in the ground state coinciding with the direction of the "effective" charge migration of the transition.

The opposite sign in the  $\rho_n$  and  $\rho_e$  can be correlated therefore with the direction of the effective electron migration of the transition: for R = H and for the electron-repelling substituents the migration is towards the C : NMe group, whilst for the electron-attracting substituents it is towards the R group.

The  $|\rho_n| > |\rho_e|$  values can be explained on the basis of the electron-attracting character of the C: NMe group. When the benzylidenemethylamine is substituted with an electron-repelling group in the *para*-position, the effects of the separate groups are enhanced. Owing to this reinforced electron shift, the polarities of the terminal groups will be considerably greater than those in the benzylidenemethylamine and in the benzene derivatives  $R \cdot C_6H_5$ , respectively. These electron shifts become more pronounced as the electron-repelling power of the substituent and the polarity of the absorbing system increase. As it coincides with the direction of the effective charge migration, the increased electron polarizability is responsible for the resulting red shift.

There is also a correlation with the solvatochromic effect: when cyclohexane is replaced by the more "polar" methanol, the electron shift still increases in the same direction, accounting for the red shift  $\Delta v_{1,2}$ , apart from any consideration on hydrogen bonding.

When the substituent is electron-attracting in character there is still an increase of the electron shifts with increasing electron-attracting power of the substituents and the polarity of the substrates in the same direction of the effective charge migration. However, this effect is weakened by the electron shift in the  $C_6H_5 \cdot CH$ : NMe system, which is in the opposite direction to that of the effective charge migration of the transition.

On replacement of cyclohexane by methanol, the electron shift is in the opposite direction and then the observed blue shift is explained. The  $|\rho_n| > |\rho_e|$  values are consequently justified.

As the main effects of the *para*-substituents on the  $\pi$ -electron distribution are determined by the electronic interaction between the substituent and the aromatic nucleus to which they are attached, the energies of the most intense  $\pi-\pi^*$ transition in *para*-substituted derivatives can be qualitatively calculated by application of simple LCAO-MO methods to benzylidenemethylamine describing the perturbative effect of each substituent simply as a variation of the Coulomb integral<sup>22</sup> h of the carbon atom 6 (see scheme in Fig. 3). This integral has positive values for electron-attracting and negative values for electron-repelling substituents.

In Fig. 2d the energy  $\Delta E$  of the  $\psi_4 \rightarrow \psi_5$  transition - in  $\beta$  unity - is plotted against the *h* values. It can be seen, also from Fig. 2c, that there is a qualitative agreement between calculated and experimental data. The direct comparison with the energy of the  $\psi_4 \rightarrow \psi_5$  transition is justified by Kubota and Yamakawa's<sup>12</sup> interpretation of the benzylidenemethylamine spectrum; the most intense shortestwavelength band is related to the  ${}^{1}L_a$  styrene band (in the Platt notation). The excited state can be identified, at a first approximation, with the  $V_4^{5}$  singlet configuration to which a one-electron transition from the highest occupied  $\pi$ -orbital  $(\psi_4)$  to the lowest vacant  $\pi$ -orbital  $(\psi_5)$  is associated.

The low-intensity, longest-wavelength band does not seem to be sensitive to the substituent; this band is related to the  ${}^{1}L_{b}$  styrene band  ${}^{12}$ , in which the major



Fig. 3. Scheme for LCAO-MO calculations.

contributing configurations in the excited state are the iso-energetic singlet configurations  $V_3^{5}$  and  $V_4^{6}$ . The band is considered to arise from a local excitation within the benzene ring and it is therefore justified that, substantially, there is no change in the energy of transition when the substituents in the *para* position are varied.

## Correlation with benzylideneanilines $R \cdot C_6 H_4 \cdot CH : N \cdot C_6 H_5$

The correlation between the electronic spectra of benzylidenemethylamines and benzylideneanilines can be deduced on the basis of cyclohexane and isooctane solution spectra, from all the data available in the literature on non-polar solvents and the environment effects in these solvents.

The literature data<sup>23,24</sup> concerning the frequencies of the most intense band in the spectra of some p-R-benzylideneanilines (A) together with those of the related p-R-benzylidenemethylamines (B) are summarized in Table 3. The  $(v_B - v_A)$  shifts, the intensity ratios  $\varepsilon_A/\varepsilon_B$  and the experimental oscillator strength ratios  $f_A/f_B$  of the parent absorption bands are also listed; f values were estimated according to the Sandorfy approximation<sup>25</sup>. The  $v_A - \sigma$  plot for the substituted benzylideneanilines is given in Fig. 2c: the  $v_A - \sigma$  straight lines have an excellent correlation and the plot has again the form of two intersecting lines with  $|\rho_n| > |\rho_e|$ . In Fig. 2d the plot of LCAO-MO calculations similar to that for the benzylidenemethylamines is also reported: a qualitative agreement between experimental and calculated data is found.

One can see, from Table 3, that on varying the substituents there is some regularity in the spectroscopic behaviour of the two bands. The  $(v_B - v_A)$  shifts fluctuate in a fairly limited range around 2400 cm<sup>-1</sup>,  $\varepsilon$  ratios are nearly unity and f ratios are in the range 1.1–1.5. Moreover, the general behaviour of the  $\Delta v - \sigma$  correlation and the  $\rho_n$  and  $\rho_e$  values for the benzylideneanilines do not differ from those of the benzylidenemethylamines.

Substit- uent	Benzylideneanilines (A) (isooctane)			Benzylidenemethylamines (B) (cyclohexane)			$(v_B - v_A)$	$\varepsilon_A/\varepsilon_B$	f <sub>A</sub>  f <sub>B</sub>	
	r	ε	f	Ref.	v	ε	f	•		
NMe <sub>2</sub>	29410	31100	0.54	23	31445	25800	0.49	2035	1.21	1.10
он	36365ª	20000	0.59	24	38760	20500	0.39	2620	0.98	1.51
ОМе	35715	20900	0.49	23	38240	19000	0.38	2525	1.10	1.29
Me	37455	19600	0.48	23	39760	17170	0.35	2305	1.14	1.37
н	38170	17300	0.59	23	41150	16300	0.39	2980	1.06	1.51
Cl	37175	20700	0.48	23	39760	20250	0.40	2505	1.02	1.20
Br	36900	22000	0.52	23	39370	23500	0.45	2470	0.94	1.16
NO <sub>2</sub>	34720ª	16300	0.68	2	36365	25600	0.72	1645	0.64	0.94

DATA FOR MAXIMA OF THE MOST INTENSE UV BAND ( $\nu$  in cm<sup>-1</sup>)

<sup>a</sup> In cyclohexane.

TABLE 3

In our opinion the existence of these analogies is a clear and good test that the reported benzylideneanilines of the type  $p-R \cdot C_6H_4 \cdot CH : N \cdot C_6H_5$  have a molecular conformation with the aniline ring twisted around the "single" N-Ar bond. This was also previously reported<sup>3</sup> on the basis of vapour phase spectra. The most intense band in the benzylideneaniline spectrum really arises from an electronic transition mainly involving the  $C_6H_5 \cdot CH : N \cdot$  planar fragment of the molecule. The red and hyperchromic effect on the absorption maximum of this band in going from benzylidenemethylamine to benzylideneaniline is due to the introduction of the partially rotated phenyl group.

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