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Theoretical Approach of the Conformations of Benzylidene Aniline Using the PCILO Method

Patrice Jacques and Jean Faure

Laboratoire de Photochimie Générale, Equipe de Recherche Associée au CNRS n° 386,
Ecole Supérieure de Chimie, F-68093 Mulhouse cédex, France

The conformational properties of benzylidene aniline (BA) were investigated using the PCILO method. Evidence has been provided that the optimization of geometry plays a prominent part, in agreement with recent experimental work on photoelectron spectroscopy by Haselbach.

Key words: Benzylidene aniline, conformational analysis of ~

1. Introducing the Problem

Many studies, both theoretical and experimental, have been undertaken on the BA molecule, the main attention being focused upon its UV-spectrum [1–3]. As a matter of fact, this spectrum differs dramatically from those of azobenzene and stilbene (*iso-electronic molecules*). To sum up the present state of this conformational problem, it is noteworthy that El-Bayoumi [4] studied the variation of the spectrum under the influence of:

a) the substituents on the aniline (ϕ_N) and benzyl (ϕ_C) "moieties",
b) the solvents,
c) the protonation.

This author construed the observed effects by assigning a non planar structure to BA: the value of the angle ϕ_1 (Fig. 1) would be of about 90°, thus allowing the conjugation of the lone pair with the π system of the benzene ϕ_N. The spectrum would then result from the superposition of the absorption of both "moieties" ϕ_N, ϕ_C. Kanamaru and Kimura [5] arrive at the same conclusion by studying the photoisomerization of BA. Besides, a crystallographic study by Bürgi [6] yields a value of 55° for ϕ_1. From a theoretical point of view, all studies [7–9] carried

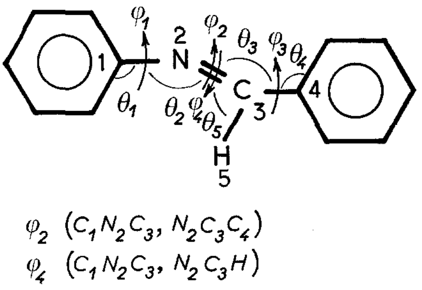

Fig. 1. Conformational parameters of benzylidene aniline (BA)

out within the scope of semi-empirical methods, without any adjustment of the parameters, lead to a value of 90° for ϕ_1.

However, in a very recent investigation performed by means of photoelectron spectroscopy, Haselbach [9] came to the conclusion that ϕ_1 is close to 36°, thus a value lower than that which was obtained using X-ray analysis and *a fortiori* than the value resulting from the theory which nevertheless takes into account a free molecule.

This discrepancy led us to take up once again the problem in the scope of the PCILO method,[1] but by optimizing the geometry, having a feeling that it is essential in this conformational problem, and hence for similar studies concerning azoïc dyes [10], where fuller information concerning the program used is given.

2. Conformational Results

The choice of the geometry seems to be important and in the present case two possibilities are feasible:

1) either to use the geometry deduced from X-ray analysis,
2) or to use the standard geometry provided by a compilation of the results obtained through the method considered or through a method founded on a closely related theoretical basis.

Two series of calculations have been performed, the former one starting from the geometry mentioned by Bürgi [6], the latter one founded on standard geometry as defined by Pople [11] (Tables 1 and 2). In both cases, ϕ_1 has been found equal to 90° for the most stable conformer.

The next step was the optimization of the main valence and dihedral angles which are likely to influence the total energy; they are depicted on Fig. 1. The values of ϕ_1 obtained are 51° and 43° for X-ray geometry and standard geometry respectively.

At this stage of the calculations, it is essential to stress the wide difference between both geometries, especially as far as the bond lengths of the $C_1N_2C_3C_4$ framework are concerned (and particularly, the length of C_3N_2). An optimization of the

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[1] Without optimization this method leads also to $\phi_1 = 90°$ [8].

bond lengths was consistently also to be taken into account. As to this point, it should be kept in mind that the different conformational parameters are not independent of one another. The results obtained for the *trans* and *cis* forms after simultaneously optimizing lengths and angles are recorded in Tables 1 and 2. Besides, Table 2 collects some available experimental data concerning the BA molecule.

Table 1. Initial and final geometries (bond lengths) (Å)

	Bürgi [6]	Standard, Pople [11]	This work	
			trans	*cis*
C—N	1.460	1.400	1.412	1.418
C=N	1.237	1.320	1.307	1.307
C—C	1.496	1.460	1.455	1.460

Table 2. Comparison theory/experience

Geometries	θ_1	θ_2	θ_3	θ_4	θ_5	ϕ_1	ϕ_2	ϕ_3	ϕ_4	E (kcal/mol.)	μ (D)	μ_{exp} (D)
Haselbach [9] *trans*						36°						
Bürgi [6] *trans*	123.7	119.9	122.7	120.1		55°		10.0				
Standard Pople [11]	120.0	120.0	120.0	120.0	120.0	0°		0.0	0.0			
	Theoretical results of the present study											
trans	123.0	120.0	122.7	120.0	120.0	36°	180.0	0.0	0.0	70 648.3	1.80	1.57 [14] 1.60 [15]
cis	122.0	118.0	129.1	121.0	114.5	40°	0.0	36.0	180.0	70 646.8	2.10	2.18 [19b]

Before comparing theory and experimental data, it will be appreciated that:

1) Both initial geometries lead to the same terminal geometry after complete optimization. The value of such an optimization is apparent in so much as the choice of the initial geometry is not compulsory, taking for granted that this is not always beneficial.
2) Choosing the X-ray geometry is not the best way to study a molecule in the gas phase, the theoretical equilibrium geometry being in that case closer to the standard geometry. Moreover it is consistent that interatomic distances may vary when shifting from the gas phase to the crystalline state.

3. Comparison with the Experimental Data

The main result of our study concerns the theoretical value of ϕ_1 found equal to 36°, in close agreement with the data reported by Haselbach [9].[2]

In the present case, the comparison between theory and experimental data is particularly appealing in so far as there are no solvation effects interfering with the experimental determination. It may be enlightening to observe that optimizing the valence angles already led to a result close to the experimental data. This latter point provides means to account for the failure of the calculations using the PCILO, CNDO/2, MINDO/3 methods when the valence angles are kept constant.

As was recently stressed by Nurmukhametov and Vasilenko [12], the problem of the relationship between the conformation and the UV-spectrum of BA is not solved. As to this point it is important to observe that Haselbach [9] also proved that the UV-spectrum is not modified by solvation in heptane (contrarily to an earlier study by Pitea and Grasso [13]). Thus, in solution, BA would keep a conformation close to that one in gas phase ($\phi_1 \simeq 40°$), this conclusion being at variance with the inferences of El-Bayoumi ($\phi_1 \simeq 90°$). However, the theoretical potential well is not pronounced (the energy barrier corresponding to ϕ_1 is of the order of 1 kcal/mole), which could account for the fact that El-Bayoumi's conclusion have been biased by a modification in the conformation following upon the addition of the substituent.

On the other hand, the hypothesis put forward by Haselbach seems to be confirmed – at least qualitatively – by the value of the theoretical dipole moment: the magnitude of this significant physical quantity ranges from $\mu = 1.8$D ($\phi_1 = 36°$) to $\mu = 1.5$D ($\phi_1 = 90°$); the experimental determination yields $\mu = 1.57$D [14], 1.60D [15].

Another relevant result of our study concerns the enthalpy differences between the *cis* and *trans* forms. The theoretical approach of Warren [7] (CNDO/2) led to a *cis* form slightly destabilized ($\simeq 0.3$ kcal/mole), a result conflicting with the generally admitted fact that only the *trans* form occurs in solution. This statement is founded for the most part upon two facts:

a) a single signal has been observed at $\tau = 1.58$ ppm in connection with H_5;
b) the *p* disubstituted derivatives of BA display the same dipole moment value as BA [16].

The UV-spectrum of the *cis* form was recently reported [19b]; the main peak lies at about $\lambda = 245$ nm and the corresponding absorption coefficient is nearly twice as high as that of the *trans* form at the same wavelength. It was expected that the study of the influence of the temperature on the UV-spectrum would allow the

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[2] The excellent agreement might be incidental as the experimental determination is affected by a number of rather serious errors. The relevant fact of our calculations is that ϕ_1 has been found to be a great deal lower than 90°.

determination of the theoretical value of ΔH *cis-trans*. In fact, the shift of the peak and the change of ε as the temperature is varied, make the interpretation of the observed variations questionable. The *cis* form does not seem to occur at room temperature and therefore the theoretical value of ΔH reported here is also too low. Besides, it appears that predicting the ΔH value of BA by comparing it with those measured for stilbene [17] (2.6 kcal/mole, solution) and for azobenzene [18] (9.9 kcal/mole, solid) is not possible.

The last item of comparison concerns the magnitude of the dipole moment of the *cis* form ($\mu = 2.1$D) which fits closely data recently reported ($\mu = 2.2$D) [19a].

4. Conclusion

The present investigation shows that the PCILO method is particularly suitable in so far as conformational research is applied to the case of complete optimization, the benefit in the case of single molecules being to get rid of the initial geometry.

This method provides moreover outstanding results as for dipole moment values and the correct order of stability for the *trans* and *cis* forms, which confirm previous conclusions of these authors [10].

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