The Conformation of *trans* Benzylidene Aniline from the PCILO and CNDO/S Methods: Role of the three Relevant Bond Lengths —N=CH—

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The conformation of *trans* benzylidene aniline (BA) was investigated, using the PCILO and CNDO/S methods. On the basis of a recent gas phase structure determination, the PCILO method proved very efficient when the valence and dihedral angles were optimized. Moreover, the CNDO/S method establishes clearly the non planarity of BA and gives a quite satisfactory interpretation of the UV spectra when appropriate bond lengths are choosen for the —N=CH— skeleton.

1. Introduction

We recently reported a preliminary investigation on the *trans* and *cis* conformations of benzylidene aniline (BA), using the PCILO method [1]. This paper was concerned with an estimate of the dihedral angle φ_1 (Fig. 1), in view of the fact that the only experimental result available at that time (relating to that molecule in the gas phase) was a value of φ_1 ($\cong 36^\circ$) derived by Haselbach [2] from a photoelectron study (see Table 2). However, the conformational study of *trans* BA in the gas phase recently published by Traetteberg [3] prompted us to reinvestigate the matter by means of the PCILO method since all the geometrical parameters (bond lengths, valence and dihedral angles) of interest are now experimentally known: we have soon stressed in Ref. [1] the fact that the geometrical parameters are not independent. Thus, it seemed to us of interest to test the validity of the PCILO method in conformational analysis, by comparing the calculated values with the *whole* set of geometrical parameters available in [3]. Indeed, comparison of very recent results [4, 5] based on the CNDO/S method reveals the striking influence of the choice for the $-\mathrm{N}=\mathrm{CH}-$ bond lengths on the φ_1 value.

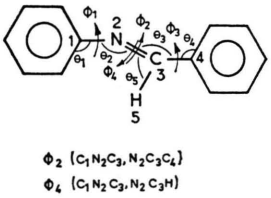

Fig. 1. Conformational parameters of benzylidene aniline.

2. Calculations

The experimental data are shown in Tables 1 and 2, together with the theoretical values obtained after a simultaneous optimization of the angular parameters. The bond lengths were kept constant (when also optimized, the geometry described in [1], referred as PCILO in this paper, is obtained in each case). The method of computation is detailed in [8].

Our results based on the CNDO/S method refer to the full paper [4].

3. Discussion

It is noteworthy that both X-ray and gas phase electron diffraction studies yield values of φ_1 which are nearly equal (and θ_1, θ_3, θ_4), contrasting with

Table 1. Calculated and experimental bond lengths (Å) of *trans* benzylidene aniline.

	Calculation		Experiment	
	Standard Pople [7]	PCILO Optimization [1]	Bürgi [6]	Traetteberg [3]
C—N	1.400	1.412	1.460	1.432
C=N	1.320	1.307	1.237	1.284
C—C	1.460	1.455	1.496	1.440

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Table 2. Comparison theory/experiment for the valence and dihedral angles of *trans* benzylidene aniline. (The calculated values are optimized according to the PCILO method and depend on the bond lengths adopted for —N=CH—).

	θ_1'	θ_2	θ_3	θ_4	θ_5	φ_1	φ_2	φ_3	φ_4
Experiment									
Haselbach [2] (P.E.)						36			
Bürgi [6] (X-ray)	123.7	119.9	122.7	120.1		55		10.0	
Traetteberg [3] (gas phase)	122.7	115.0	125.0	120.0	118.0	52			
Calculation									
Bürgi [6] (X-ray)	121.2	118.3	123.2	120.4	122.4	51.5	178.0	0.0	− 1.5
Traetteberg [3] (gas phase)	121.4	118.4	123.5	120.6	120.2	49.3	180.0		
PCILO [1]	123.0	120.0	122.7	120.0	120.0	36.0	180.0	0.0	0.0
Standard Pople [7]	122.0	117.4	122.9	120.7	120.2	42.8	179.0	0.0	0.0

widely different bond lengths, more especially as regard the C = N double bond. This discrepancy may be explained by the strong interactions involved in the crystal phase. *It thus seems reasonable to take into account in the following discussion the results obtained by* Traetteberg [3], *as fitting most closely the reality.*

3.1. PCILO Method

For the sake of clarity it was deemed advisable to set apart the conclusions concerning the bond lengths from those relating to the angles.

· *Bond lengths*

Optimization of the bond lengths according to the PCILO method [1] results in a close agreement with the experimental data (see Table 1). This is surprising, as the PCILO method is based on the approximation entered into the CNDO/2 method, which leads to poor results when applied to the determination of the bond lengths of conjugated molecules. A survey of Table 2 reveals that the choice of the three bond lengths of the − N = CH − group affects mainly the dihedral angle φ_1, and to a lower extent the valence angles θ_1, θ_2, θ_5.

· *Valence and dihedral angles*

As regards the φ_1 value, the PCILO geometry leads to moderate agreement with experience. Moreover, the calculated θ_2 value is too high by 5°. However, the adoption of the bond lengths obtained by Traetteberg [3] leads to a much better correlation with the experimental values: the φ_1, θ_2 values are in this case 49.3° and 118.3°, which compare quite well with the experimental values 52° and 115°, respectively. However, it should be acknowledged (Table 2) that the role played by the bond lengths of the − N = CH − is somewhat confusing: adoption of the data derived by Bürgi (X-ray) [6], although quite at variance with those of Traetteberg (gas phase) [3], leads to calculated angles in fair agreement with experience [3]. But, adoption of the PCILO method lengths, which fit best experimental ones, result in calculated angles in less good agreement with experience as in the above case. In our opinion, this difficult question arises from the fact that the energy plot is very flat in the vicinity of the energic minimum.

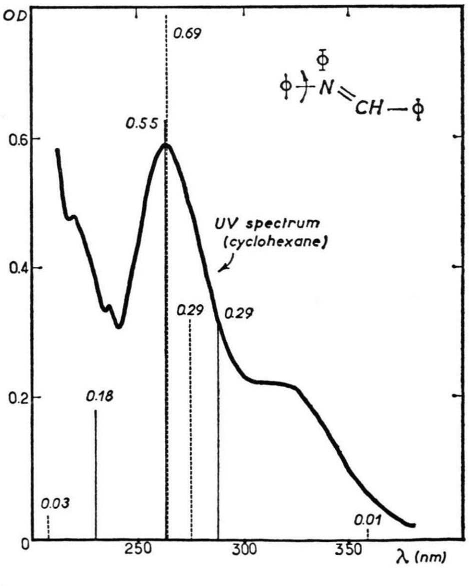

Fig. 2. Calculated transitions with oscillator strengths from the CNDO/S method. —— $\varphi = 50°$ [4] (bond lengths from gas phase [3]); ---- $\varphi = 35°$ [5] (bond lengths from X-ray [6]).

3.2. CNDO/S Method

We performed in Ref. [4] and extensive study of the conformation of *trans* BA using the CNDO/S procedure. Our calculations were based on the geometry from Traetteberg [3] and indicated a value close to 50° for φ_1 as illustrated in Figure 2. However, Akaba et al. [5] concluded to a φ_1 value close to 35° using the same CNDO/S procedure but a geometry based on Bürgi's results. Inspection of Fig. 2 reveals that our calculations fit experimental data significantly better than those by Akaba, thus illustrating the role played by the three abovementioned bond lengths.

4. Conclusion

Benzylidene aniline constitutes a rigorous test for the ability of semi-empirical quantum mechanical methods to determine the conformation of conjugated molecules.

This investigation allows the conclusion of Ref. [1] to be extended: the PCILO method accounts quite satisfactorily for *all* experimental angular parameters when a complete optimization of these parameters has been performed. To our opinion, this method is reliable enough to provide useful information on the conformation of conjugated molecules when not experimentally attainable.

Indeed, CNDO/S works quite satisfactorily as long as appropriate bond lengths are choosen.

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