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Conformations of Some Monosubstituted *N*-Benzylideneanilines

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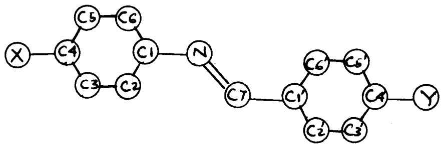
Theoretical computations , using quantum mechanical PCILO method, have been carried out on the conformations of four monosubstituted *N*-benzylideneanilines—*N*-benzylidene-4-nitroaniline (**1a**), *N*-benzylidene-4-dimethylaminoaniline, *N*-(4-nitrobenzylidene)aniline, and *N*-(4-dimethylaminobenzylidene)-aniline. The aniline ring is found to be most twisted (60°) in **1a**, while in all other cases , the twist angle is 30°. The results have been compared with earlier experimental findings and rationalized in terms of two factors contributing to nonplanarity , namely , the overlapping of bridge nitrogen lone pair with the π-system of the aniline ring and a steric interaction between the azomethine hydrogen and one of the ortho hydrogens in the aniline ring.

Experimental and theoretical studies on the molecular conformation of *N*-benzylideneanilines have been reported by a number of workers.[1–5] These studies were initially meant to account for the marked dissimilarity in the electronic absorption spectra of *N*-benzylideneanilines (**BA**) and the isoelectronic molecules stilbene (**S**) and azobenzene (**AB**). It is now generally agreed that the difference arises on account of nonplanar conformation of *N*-benzylideneaniline in contrast to the nearly planar structure of azobenzene and stilbene.

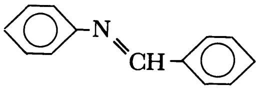
We have reported earlier the results of theoretical (perturbative configuration interaction over localized orbitals, PCILO) computations on the conformation of *N*-(4-dimethylaminobenzylidene)-4-nitroaniline (**1e**), *N*-(4-nitrobenzylidene)-4-dimethylaminoaniline (**1f**), and the corresponding stilbene (**2**) and azobenzene (**3**) derivatives.[6] The computed conformations were rationalized in terms of two factors that facilitate the nonplanar structure: i) An interaction of the nitrogen lone pair and the aromatic system (CT-2)[7] and ii) repulsion between the hydrogen in -CH=N- and one of the ortho hydrogens of the aniling ring, which is released by the twisting of the *N*-phenyl bond. On the other hand there could also be intramolecular charge transfer between the substituents (CT-1). Smaller the twist angle, larger is the contribution of CT-1.[7]

Recently, Akaba et al. have reported the results of their NMR (Proton and ^{13}C) studies on mono- and di-(in the two aromatic rings) substituted *N*-benzylideneanilines.[4,5] The nonadditivity of substituent effect observed for **1** ($X=NMe_2$) and **1** ($Y=NO_2$) is interpreted in terms of substituent–substituent interactions (synonimous with CT-1, described earlier) accompanied by conformational changes with substituents in these *N*-benzylideneanilines. It was found that for *N*-benzylideneanilines carrying the variable substituent X on the anilinobenzene ring, the azomethine protons undergo upfield shifts with increasing electron-withdrawing property of X, whereas those for *N*-benzylideneanilines carrying the variable substituent Y on the benzylidene benzene ring exhibited the expected low field shifts with increasing electron-withdrawing property of Y. This anomalous upfield shift of the azomethine proton has been attributed to the increase in the twist angle of the aniline ring from the molecular plane containing -C=N- bond.

The theoretical and experimental facts accumulated so far indicate that the substitution in the rings is an important factor in determining the twist angles Φ and θ. Most spectroscopists, however, seem to emphasize that the origin of nonplanarity can be attributed to the

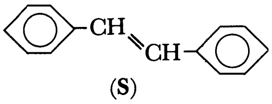


1a: $X=NO_2$; $Y=H$
1b: $X=NMe_2$; $Y=H$
1c: $X=H$; $Y=NO_2$

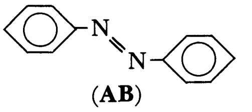


(**BA**)

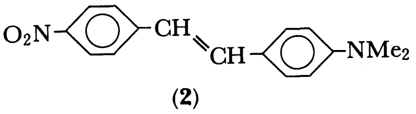
1d: $X=H$; $Y=NMe_2$
1e: $X=NO_2$; $Y=NMe_2$
1f: $X=NMe_2$; $Y=NO_2$



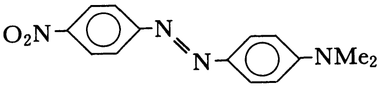
(**S**)



(**AB**)



(**2**)



(**3**)

delocalization of the azomethine lone pair. We report here the theoretical computations of the conformations of four monosubstituted *N*-benzylideneanilines (**1a**—**d**). A preliminary communication of this work was made earlier[6] as corroborating evidence in favour of our contention that *N*-benzylideneaniline conformations depend both, on the delocalization of the bridge nitrogen lone pair and ortho hydrogen interactions. The present paper deals with a detailed report on the conformational energetics of these molecules and a comparison of the computed results with earlier findings that illustrates an interesting interplay between theory and experiment.

Procedure

Among the more recently developed theoretical methods for all-valence electrons, PCILO is extensively used in conformational studies, because of its proven success with quite diverse types of molecules.[8–14] This method was therefore chosen for present work. It may, however, be mentioned that the PCILO method requires the choice of definite pattern of localized chemical bonds. The investigation under report deals with molecules involving delocalized bonds. Difficulties, that may arise in the calculations on such molecules within the PCILO framework have been discussed in some detail in our earlier communications.[6,15]

The torsion angles have been indicated in the structures **1** and are defined as

$$\Phi = C_2\text{-}C_1\text{-}N\text{-}C_7$$
$$\theta = N\text{-}C_7\text{-}C_{1'}\text{-}C_{2'}$$

the clockwise direction being positive. The cis and trans dihedral angles have been taken as 0 and 180°, respectively.

Since it is considered that the theoretical equilibrium geometry in the gas phase is closer to the standard geometry rather than X-ray values, we have adopted the standard geometries from People and Beveridge.[16] All bond angles involving sp^2 and sp^3 hybrid orbitals, have been taken as 120 and 109.47°, respectively.

The PCILO energies have been computed as a function of Φ and θ at 30° intervals with preselected values of the other geometrical parameter.

Results and Discussion

***N*-Benzylidene-4-nitroaniline (1a):** There are four reports on the conformation of **1a**. Skrabal and collaborators[17] from a comparison of its electronic absorption spectra with *N*-benzylideneaniline, have proposed that the twist angle of the aniline ring (Φ) should be of the same order as that in case of *N*-benzylideneaniline, which is 55°. Theoretical calculations (CNDO/s) and UV spectral studies by Akaba et al. indicate Φ=70—85° and that the twist of the aniline ring in soln and gas phase is more than *N*-benzylideneaniline itself.[1] This contention was further confirmed from the photoelectron spectra.[2] From NMR measurements on substituted *N*-benzylideneanilines, it was proposed that the introduction of the electron-withdrawing nitro group at the 4-position of the aniline ring enhances the delocalization of nitrogen (of -N=CH-) lone pair electrons into the ring that leads to an increase in the value of Φ in solution which in turn changes the ring current effect by the aniline ring exerted on HC (7) resulting in an anomalous upfield shift.[5]

Results of the present computations show that the aniline ring in **1a** is twisted by 60° in either directions. The rotational energy barrier with respect to the planar conformation is 1.96 kcal mol^{-1} (1 cal=4.184J). It is seen from the results described in Table 1, Φ=30 to 90° through 60°, represents low energy regions indicating that the molecule has a good deal of conformational flexibility in this region. This situation is sim-

Table 1. Preferred Conformations of Monosubstituted *N*-Benzylideneanilines

Molecule	Energy of the planar conformation kcal mol^{-1}	Global minimum Φ/deg	Global minimum θ/deg	Low-energy regions Φ/deg	Low-energy regions θ/deg	Low-energy regions Energy kcal mol^{-1}
1a	1.96	60	0	30	0	0.28
		−60	0	−30	0	0.28
				90	0	0.53
				−90	0	0.53
1b	1.53	30	0	60	0	0.82
		−30	0	−60	0	0.82
1c	1.51	30	0	60	0	0.06
		−30	0	−60	0	0.06
				90	0	0.78
				−90	0	0.78
1d	1.54	30	0	60	0	0.16
		−30	0	−60	0	0.16

ilar to the value of Φ=70—85°, proposed by Akaba et al.[1] PCILO calculations on *N*-benzylideneaniline itself give value of 36° of Φ.[12] Thus, it is seen that theoretical computations and spectral measurements (UV, PES, and NMR) lead to the same conclusion that the aniline ring in **1a** is more twisted than *N*-benzylideneaniline.

***N*-Benzylidene-4-dimethylaminoaniline (1b):** UV absorption spectra by Skrabal et al.[17] reveal only a small torsion angle for the aniline ring in **1b**. Although the NMR work is not very explicit about the conformational state of this particular molecule, it appears by implication that two opposite factors will operate here (a) in the absence of any electron-attracting substituent at the 4-position on the benzylidene ring, the through-conjugative interaction is obviously impaired leading to less planarity and (b) on the other hand, presence of the electron-donating dimethylamino group would lead to a smaller twist angle, Φ.

The present computational results indicate the aniline ring to be twisted out of plane by ±30°. This conformation is of 1.53 kcal mol^{-1} higher energy than the planar conformation. The low energy region is confined to ±60° with an energy barrier of 0.82 kcal mol^{-1}. These results clearly indicate that there must, at least, be one more factor contributing to nonplanarity, besides the delocalization of the nitrogen lone pair. As described in our earlier work,[6] we identify the factor as the interaction between HC(2) and HC(7).

***N*-(4-Nitrobenzylidene)aniline (1c):** For **1c**, a torsion angle similar to BA is predicted from UV results,[17] which means $\Phi \approx 55°$. HMO calculations by Minkin[18] give Φ=44°. We find the value of $\Phi = \pm 30°$ from present calculations. The energy barrier with respect to the planar structure is 1.51 kcal mol^{-1}. However, it is seen from Table 1 that the region $\Phi = \pm 60°$ is only of 0.06 kcal mol^{-1} higher energy. Since an energy barrier of this magnitude can easily be overcome in the solution or solid state, it may be concluded that the experimental (UV) and the theoretical conformations lead to the same result.

***N*-(4-Dimethylaminobenzylidene)aniline (1d):** From the UV spectral study, **1d** is found to be more or less planar. The results are, however, not unambiguous. The present calculation shows that the aniline ring is twisted out of plane by ±30° with a rotational energy barrier of 1.54 kcal mol^{-1}. The low energy region is indicated by $\Phi = \pm 60°$, which is only of 0.16 kcal mol^{-1} higher energy.

It can be seen from Table 1 that the results with respect to **1b**—**d** are strikingly similar. This implies that perhaps there is a common mechanism that determines the conformational characteristics of these molecules and it appears most rational that this mechanism is the interaction between the ortho hydrogen HC(2) and HC(7), since in all the three cases, CT 1 (π-electron delocalization between the substituents) and CT 2 (delocalization of the nitrogen lone pair to the substituent in the aniline ring) will either be extremely weak or altogether absent. This hypothesis is supported by the results obtained with respect to **Ia**. In this molecule there can be a substantial overlapping of the *N*-lone pair with the aniline ring bearing the strongly electron-withdrawing NO_2 group (CT 2) which reinforces the nonplanar structure due to ortho hydrogen interaction leading to a greater twist angle Φ (=60°).

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