Photoelectron Spectroscopy of Substituted N-Benzylideneanilines

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N-Benzylideneanilines, Photoelectron Spectroscopy

The electronic structure and conformation in the gas phase of N-benzylideneaniline, its para-nitro and -methoxy as well as the ring perfluorinated derivatives were investigated by photoelectron (PE) spectroscopy and semiempirical molecular orbital (HMO) calculations.

The π-ionizations were assigned and it is shown that these compounds in the gas phase are in a nonplanar conformation.

Introduction

The electronic structure of N-benzylideneaniline and especially its conformation in the gas phase and in solution has been the subject of several investigations1–3. Recently we have studied the conformation of a related class of compounds, the 11H-dibenzo(b,e)azepine analogues, in the gas phase and in solution by means of photoelectron spectroscopy (PE) and charge transfer (CT) spectra measurements4. Contrary to the 5H-dibenzo(a,d)cycloheptene analogues investigated earlier5,6 the electronic structure of these compounds was only slightly dependent upon conformational changes thus not allowing to determine the gas phase conformation with accuracy. Therefore it seemed worthwhile to investigate the N-benzylideneanilines using also electron pushing methoxy- and electron withdrawing nitro-substitution in para position as to produce changes in electronic structure, as well as perfluorination of the phenyl rings to prove the assignment of π-ionizations (“perfluoro effect”)7. Here we report these assignments which are also supported by Hückel MO calculations and give insight into the gas phase conformation of the title compounds.

Experimental

The following compounds: N-benzylideneaniline (1), m.p. 53 °C, N-benzylidene-(p-methoxyaniline) (2), m.p. 72 °C, N-benzylidene-(p-nitroaniline) (3), m.p. 143 °C, p-methoxybenzylideneaniline (4), m.p. 62–63 °C, p-nitrobenzylideneaniline (5), m.p. 93 °C, p-nitrobenzylidene-(p-methoxyaniline) (6), m.p. 136 °C, p-methoxybenzylidene-(p-nitroaniline) (7), m.p. 124–125 °C, 2,3,4,5,6-pentafluorobenzylidene-(2,3,4,5,6-pentafluoroaniline) (8), m.p. 92 °C, 2,3,4,5,6-pentafluorobenzylideneaniline (9), m.p. 115 °C, and N-benzylidene-(2,3,4,5,6-pentafluoroaniline) (10), m.p. 126 °C, have been prepared by standard procedure8. Although our melting point for 8 is much higher than reported in the literature9, our analytical data as UV spectrum, mass spectrum as well as the PE spectrum leave no doubt about the structure of 8. All compounds were of high purity and recrystallized before use. The PE spectra of 1–10 were recorded on a Vacuum Generators UV G3 spectrometer11 using He I (21.22 eV) radiation. All spectra were recorded under low resolution of about 30 meV and have been calibrated in situ with argon and xenon. Enhanced temperatures of the sample inlet system (40 °C, 140 °C, 140 °C, 150 °C, 150 °C, 200 °C, 180 °C, 100 °C, 100 °C and 100 °C for 1–10, respectively) were employed as to produce satisfactory spectra. The quoted ionization energies (Ei/eV) are accurate to ± 0.03.

Results and Discussion

The PE spectra of 1–8 are reproduced in Figs. 1–3, where the vertical ionization energies (Ei/eV)
Fig. 1. The HeI photoelectron spectrum of N-benzylideneaniline (1) and 2,3,4,5,6-pentafluorobenzylidene-(2,3,4,5,6-pentafluoraniline) (8).

are given at the top of the corresponding band systems. The assignment of the low energy ionizations is also indicated according to standard spectroscopic notation. The investigated compounds were for better comparison divided into following classes: (I) compounds 1, 8, 9 and 10, with PE spectra of the former two given in Fig. 1, (II) compounds 2, 5 and 6 with their PE spectra given in Fig. 2 and (III) compounds 3, 4 and 7, with their PE spectra reproduced in Fig. 3. Thus, Fig. 1 shows the electronic structure of the parent molecule and the effect of ring perfluorination resulting in a smaller and stronger shift of $\pi(n)$- and $\sigma$-ionizations, respectively. This effect is also observable in the PE spectra of 9 and 10 given here only as numerical data. In Fig. 2 the effect of methoxy substitution at one end of the molecule or nitro substitution at the other as well as the simultaneous action of their effects in the corresponding disubstituted compound on the PE spectrum is shown. The result for the same situations but for the opposite orientation of substituents is shown in Fig. 3. Besides the measurement of PE spectra, a set of HMO calculations for compounds 1–7 was performed using the following model (vide infra) and heteroatom parameters$^{12,13}$.

In the calculation the effect of nonplanarity was taken into account by rotating the phenyl ring attached to the nitrogen around the C–N bond by $\theta$ degrees and allowing the lone pair electrons of nitrogen to interact with the $\pi$-electrons. This was done by assuming an additional virtual bond between the nitrogen and the nearest ring carbon $C_r$ (Fig. 4). Thus, two of the bond parameters (re-
sonance integrals) \( \beta_{CX} \) were changed as a function of \( \theta \), namely the actual C-N bond by \( \beta_{CS} = 0.7 \cos \theta \beta_{CC} \) and the virtual one by \( \beta_{CS} = 0.9 \cos (90^\circ - \theta) \beta_{CC} \) (Table I).

A variation of \( \theta \) indicated that \( \theta \approx 35^\circ \) is a good approximation for all the compounds studied. In the correlation between calculated HMO energies and the PE band systems assigned to the corresponding \( \pi \)-ionizations (Koopmans' theorem) \( \theta = 35^\circ \) for all compounds was assumed. This value of \( \theta \) is in agreement with predictions for the conformation of 1 by other methods.

The assignment of \( \pi \)-ionizations of 1 is very easy to obtain from a comparison of its PE spectrum with PE spectra of stilbene\(^{14} \), \( 5 \)-H-dibenzo(a,d)cycloheptene\(^{6} \), \( 11 \)-H-dibenzo(b,e)azepine\(^{4} \) and especially with those of the fluorinated compound 8 (Fig. 1), 9 and 10. The vertical ionization energies and assignment for 9 are: 8.68(\( \pi \)); 9.55(\( \pi \)); 9.71(\( \pi \)); 10.41 (\( \pi(n) \)); 11.69(\( \pi \)); 12.29(\( \sigma(onset) \)) and for 10: 8.83(\( \pi \)); 9.55(\( \pi \)); 9.77(\( \pi \)); 9.70(\( \pi(n) \)); 12.07(\( \pi \)); 12.40(\( \sigma(onset) \)) eV. This is also qualitatively confirmed by earlier SCF MO\(^{4-6} \) and the present HMO calculations.

Experimentally, an especially lucky circumstance is that in the decafluoro compound 8 all the eight

\[ \pi \]-type ionizations (Systems \( \tilde{X} \) to \( \tilde{G} \) in Fig. 1) corresponding to the parent \( \pi \)-system and to the nitrogen lone pair appear as the lowest energy ionizations. Thus, the shape of the unresolved systems between 11 and 13 eV of 1 can be obtained by adding systems \( \tilde{E}, \tilde{F} \) and \( \tilde{G} \) to the stronger shifted \( \sigma \)-systems \( \tilde{H}, \tilde{I}, \tilde{J} \) and \( \tilde{K} \) of 8. A comparison with \( 11 \)-H-dibenzo(b,e)azepine reveals that system \( \tilde{D} \) in 1 can be attributed to ionization from the delocalized lone pair electrons of nitrogen indicated as \( \pi(n) \), whereas system \( \tilde{E} \) has a high contribution of the C=N-bond \( \pi \)-electrons. The energy difference between the latter and the lowest energy \( \tilde{X} \) system was claimed to be a measure of planarity of the molecule\(^{6,14} \) being maximum in planar conformation. However, in case of strongly

![Fig. 3. The PE spectra of p-methoxybenzylideneaniline (4), p-methoxybenzylidene-(p-nitroaniline) (7) and N-benzylidene-(p-nitroaniline) (3).](image)

![Fig. 4. Assumed conformation change of N-benzylideneanilines as a function of \( \phi \).](image)

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**Table I. Parameters of the HMO calculation.**

<table>
<thead>
<tr>
<th>Car-OCH₃</th>
<th>Car-NO₂</th>
<th>Car</th>
<th>C=⁻N⁺Car</th>
</tr>
</thead>
<tbody>
<tr>
<td>hₓ</td>
<td>0.5</td>
<td>1.5</td>
<td>hₓ</td>
</tr>
<tr>
<td>hₓ</td>
<td>1.0</td>
<td></td>
<td>hₓ</td>
</tr>
<tr>
<td>kₑ₋ₓ</td>
<td>0.9</td>
<td>kₑ₋ₓ</td>
<td>0.7 cos ( \phi )</td>
</tr>
<tr>
<td>kₑ₋ₓ</td>
<td>0.9</td>
<td>kₑ₋ₓ</td>
<td>0.9</td>
</tr>
<tr>
<td>kₑ₋ₓ</td>
<td>0.9</td>
<td>kₑ₋ₓ</td>
<td>0.9 cos (90°-( \phi ))</td>
</tr>
</tbody>
</table>
acting para substitution electronic effects especially on the energy of the \( \bar{X} \) system are also expected. These effects should generally in case of nitro substitution enhance the ionization energy ("nitro-effect")\(^{15} \) and lower it in methoxy substituted compounds. Both is found to hold in the mono-substituted compounds, whereby, the effect of the methoxy group is more pronounced if it is substituted on the aniline side of the molecule (Figs. 2 and 3). The substituents also bring new \( \pi \)-ionizations in the low energy part of the PE spectra. The methoxy group brings one new \( \pi \)-ionization resulting from the delocalized "lone pair" electrons of oxygen appearing at about 11.5 eV (\( \bar{P} \) in 2 and 4, \( \bar{H} \) in 6 and 7) and in addition the nitro group brings two new \( \pi \)-ionizations in the low energy part, one (\( \sigma_0 \)) arising from the in plane (\( \bar{E} \) in 3, 5, 6 and 7) and the other (\( \pi_0 \)) from the out of plane (\( \bar{P} \) in 3, 5, 6 and 7) combination of the oxygen \( p \)-electrons. The \( \pi \)-ionization which predominantly arises from the electrons located at the NO\(_2\) group is expected as \( \pi_1 \) in the region \( E_1 > 16 \) eV.

Besides in the fluorinated N-benzylideneanilines the ionization attributed to the delocalized lone pair of the imino nitrogen appears at 10.0 ± 0.3 eV. In the ring fluorinated N-benzylideneanilines 8, 9 and 10 these values are shifted considerably by > 0.5 eV to higher ionization energies. The splitting between the \( \bar{X} \) and the systems with a high contribution of the C=N-bond \( \pi \)-electrons in 1–10 is not much changed. It is difficult to stress if these changes are the effect of the difference in electronic structure or include a contribution of a change in conformation. Anyhow, the changes are rather small and besides the statement that the investigated N-benzylideneanilines in the gas phase are in a non planar conformation, the PE spectra do not allow an exact determination in each case. However, a plot of the assigned \( \pi \)-ionizations in 1–7 versus the \( m_k \) coefficients from the HMO calculation with an angle of \( \theta = 35^\circ \) for the conformation of the N-benzylideneanilines defining the energy \( E_k \) of the molecular orbital by

\[
E_k = ac + m_k \beta_{CC}, \quad k = 1, 2, \ldots, n
\]

gives a fairly good linear correlation (Fig. 5).

A least square estimation of the Hückel parameters \( ac \) and \( \beta_{CC} \) from the correlation in Fig. 5 gave

\[
ac = 6.70 \pm 0.13 \text{ eV and } \beta_{CC} = 2.77 \pm 0.09 \text{ eV}
\]

in good agreement with the results obtained previously on indene analogues\(^{16} \).

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