Vibrational and NMR Spectra of Protonated trans-N-Benzylideneanilines*

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Infrared and Raman spectra of protonated trans-N-benzylideneaniline (tBA) show significant shifts of vibrational modes of the azomethine group as compared to the neutral form. The most pronounced increase is due to the C=N stretching vibration but also the CH stretching and CH in-plane deformation appear at higher frequencies. Similarities with and differences from other protonated Schiff bases are discussed. $^{13}$C NMR spectra of protonated tBA confirm the change of hybridization around the host nitrogen atom, displaying the downfield shift of the imine carbon atom (increased p-content of the C=N bond) and a greater direct carbon-hydrogen coupling constant (increased s-content of the CH bond). Effects of fluorine substituted in phenyl ring(s) upon imine carbon chemical shifts and carbon-hydrogen coupling constants are discussed.

INTRODUCTION

Schiff bases and their derivatives play an important role in several fields of research, including biological systems and liquid crystals. The Schiff base linkage in its protonated form is present in rhodopsin and related systems during the visual cycle. The functionality of the imine or azomethine group can be followed by numerous spectroscopic techniques.

Babcock and coworkers¹² reported on the C=N stretching frequency in neutral and protonated forms, as well as on the rehybridization of the C=N bond upon protonation in a number of Schiff bases with different alkyl and aryl groups bound to the central imine moiety. They have found out that in all cases the C=N stretching frequency increases upon protonation, but they did not report on any Schiff base with aryls linked to both sides of the central group. Therefore, we consider it worthwhile to analyze the spectroscopic behaviour of the prototype aromatic Schiff base trans- N-benzylideneaniline or trans-benzalanilnine (tBA). It is a relatively simple molecule with one phenyl ring on each side of the azomethine group. Having in hand a number of

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* Dedicated to Professor D. Hadži on the occasion of his 70th birthday.

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specifically labelled isotopomers, one can follow changes of spectral features of the protonated form and compare them to those in the neutral molecule. In this way, one can get more information on the protonation reaction of Schiff bases because its mechanism is not completely understood. On the other hand, it is interesting to compare the vibrational dynamics of protonated tBA with that of structurally related trans-stilbene, for which an extensive vibrational analysis has been undertaken. Thus, it is expected to learn more about the behaviour of the azomethine group and its interactions with the rest of the molecule in both neutral and protonated form.

In their theoretical study, Lopez-Garriga et al. stated that upon protonation of methylamine the rehybridization of the C=N bond takes place. It is well known that hybridization parameters are closely related to coupling constants in NMR spectra. Therefore, we have measured $^{13}$C NMR spectra of neutral and protonated tBAs studied here. A change of NMR parameters, like chemical shifts and coupling constants, upon protonation indicates differences in the structure of the two forms of a Schiff base. Since changes in a vibrational spectrum are very complex, an insight into a $^{13}$C NMR spectrum can give a direct measure of structural changes.

The aim of this paper is to point to the spectral features in both vibrational and NMR spectra of protonated Schiff bases which can help to understand their structure. A number of available isotopomers of tBA enables us to assign characteristic vibraional modes of the imine moiety in its protonated form. A comparison with the vibrational spectrum of neutral tBA, as well as with other protonated Schiff bases, gives an insight into conformational changes upon protonation of the nitrogen lone pair. On the other hand, the data from NMR spectra help in determining the changes in hybridization around the host nitrogen atom. A combination of both data gives an insight into structural changes of the protonated imine group in comparison with the neutral form.

NMR spectra of selected fluorinated trans-N-benzylideneanilines in the neutral and protonated form give important information on the substituent effects on the imine group through the $\pi$-electron system of the phenyl rings. The $\pi$-electron delocalization and possible conjugation in tBA enable a long range transfer of substituent effects along the molecular skeleton. Fluorine is a particularly suitable substituent due to its electronegativity and relatively small steric requirements in comparison with other substituents. To the best of our knowledge, no fluorine substituted tBAs in their protonated forms have been investigated by NMR so far.

**EXPERIMENTAL**

The preparation of trans-N-benzylideneaniline, its deuterated isotopomers and the $^{15}$N labelled species have already been described. Fluorinated tBAs have been prepared from appropriate, freshly distilled, benzaldehydes and anilines according to standard procedures. The products have been recrystallized from ethanol. $p$-Fluorobenzaldehyde, $p$-fluoroaniline, 2,3,4,5,6-pentafluorobenzaldehyde and 2,3,4,5,6-pentafluoroaniline were commercial products (Aldrich) of reaction grade.

Protonated species were obtained by introducing dry HCl(g) into chloroform solutions of the corresponding tBAs, which were previously recrystallized from ethanol:
For vibrational analysis, equivalent amounts of HCl(g) were bubbled into the corresponding solutions. After evaporating the solvent, the crystals were used for either solid state or solution infrared and Raman spectra. Details about the preparation of protonated tBAs will be published elsewhere. The procedure for samples for NMR measurements was the same, but HCl(g) was bubbled into CDCl₃ solutions only in subequivalent amounts. In this way, a mixture of both neutral and protonated species was obtained, so that changes in chemical shifts were determined more precisely. In the case of 4-F-tBA and 4'-F-tBA, solid hydrochlorides were created immediately and were thereafter dissolved in DMSO-d₆.

Infrared spectra of neutral and protonated tBAs were recorded from solutions in chloroform, methanol and carbon tetrachloride, as well as from KBr pellets with a Digilab FTS-20C interferometer equipped with a TGS detector and a NOVA-3 computer. Spectra were measured at 2 cm⁻¹ resolution. Raman spectra of both forms of tBAs were recorded from powders and methanol solutions on a Dilor Z24 spectrometer with a triple monochromator coupled to an IBM AT computer. The 514.5 nm line of a Coherent INNOVA-165 argon ion laser was used for excitation. The spectra were measured in the sequential mode under 2 cm⁻¹ resolution. Data were processed by the Dilor software.

Carbon-13 NMR spectra were measured with a Varian Gemini 300 spectrometer at 75 MHz also from CDCl₃ solutions in 5 mm tubes and the digital resolution was 0.573 Hz (0.008 ppm).

RESULTS AND DISCUSSION

Solid state and solution vibrational spectra of both neutral and protonated tBAs were recorded in the 4000–400 cm⁻¹ range. However, only characteristic vibrational modes, relevant to structural changes of the azomethine group will be discussed here. On the other hand, ¹³C NMR solution spectra of mixtures of neutral and protonated species were recorded for comparison with vibrational data.

Vibrational Spectra

It was already shown that the vibrational spectrum of tBA can be analyzed in terms of its local or group vibrational coordinates. Using a series of isotopomers, we have demonstrated that most of the azomethine vibrational modes can be treated separately from those belonging to both rings. However, there are features that indicate a considerable mixing of vibrational coordinates of the imine group with those of the phenyl rings, a situation similar to isoelectronic molecule of trans-stilbene. A comparison of solid state infrared spectra of tBA and tBA·HCl (Figure 1) shows that the majority of vibrational bands changed both their positions and intensities. A change in molecular symmetry is hard to assume and, according to the C₁ point group selection rules, all modes should be infrared and Raman active for both forms. Most of infrared bands of the protonated tBA are shifted to higher frequencies by 4 to 12 wavenumbers. However, a few bands below 1000 cm⁻¹, belonging to phenyl ring deformations, are shifted to lower values by approximately 10 cm⁻¹. Both features indicate a change of interaction between both phenyl rings and the central group, and very probably a change in conformation of the molecule. In a previous paper, it was claimed that the interaction of the central CH deformation is stronger with the aniline (A) than the benzylidene (B) ring.

The azomethine CH stretching band, which was found at 2889 cm⁻¹ in the infrared spectrum of neutral tBA², was assigned to the 2924 cm⁻¹ weak band in the spectrum of the protonated species. This change indicates an increase of the CH bond strength, but shows that this bond is still weaker than the usual CH bond at an unsaturated
carbon atom. However, it was not possible to assign the NH stretching band and further experiments are under way.\textsuperscript{8}

The solid state infrared spectra of both forms of tBA are presented in Figure 1. The greatest increase in frequency upon protonation is attributed to the strong band at 1626 cm\textsuperscript{-1} in the solid, which now appears at 1671 cm\textsuperscript{-1}. The shift of 38 cm\textsuperscript{-1} for the Nujol mull spectrum has been reported earlier.\textsuperscript{8} The difference of 45 cm\textsuperscript{-1} in the present case in the solid is appreciably higher than that in solution, which is only 32 cm\textsuperscript{-1} (Table I). The latter value is in agreement with those obtained for other Schiff bases, including retinylidene-N-butylamine\textsuperscript{1}, implying that it is of no importance whether the substituent is an aryl or alkyl group. The difference, depending on the state of aggregation, indicates slightly different conformations in the dissolved protonated Schiff bases and solid hydrochloride. Table I contains a selection of data for the C=N stretching frequencies in solution for different isopropomers of tBA in the two forms.
TABLE I

Comparison of C=N stretching frequencies (cm⁻¹) for neutral and protonated species of some isotopomers of trans-N-benzylideneaniline

<table>
<thead>
<tr>
<th>Isotopomersᵃ</th>
<th>neutralᵇ</th>
<th>protonatedᶜ</th>
<th>Δν = (νₚ - νₙ)ᵈ</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBA</td>
<td>1629</td>
<td>1661</td>
<td>32</td>
</tr>
<tr>
<td>Dₛ₁₂ₐ-tBA</td>
<td>1629</td>
<td>1661</td>
<td>32</td>
</tr>
<tr>
<td>Dₛ₁₂₄ₐ-tBA</td>
<td>1626</td>
<td>1659</td>
<td>33</td>
</tr>
<tr>
<td>D₁₁₀ₐ-tBA</td>
<td>1626</td>
<td>1658</td>
<td>32</td>
</tr>
<tr>
<td>¹⁵N-tBA</td>
<td>1612</td>
<td>1645</td>
<td>33</td>
</tr>
</tbody>
</table>

ᵃ A-aniline ring, B-benzylidene ring. ᵇ Infrared spectra of CCl₄ solutions. ᶜ Infrared spectra of CHCl₃ solutions. ᵈ n-neutral, p-protonated.

Another important vibrational mode is the imine CH in-plane deformation, which is assigned to the medium band at 1367 cm⁻¹ in the solution infrared spectrum of tBA.³ It was found at 1378 cm⁻¹ in the solution Raman spectrum of neutral N-benzylidene-n-butylamine, but not in its protonated or deuterated form.¹ A candidate for the corresponding vibration in the protonated form of tBA is the band at 1388 cm⁻¹ in solid (see Figure 1b) and 1387 cm⁻¹ in solution. The band at 1427 cm⁻¹ could be assigned to the in-plane deformation mode of the newly created NH bond. In solution Raman spectra of other protonated Schiff bases, it was found between 1425 and 1420 cm⁻¹ but it is absent in spectra of deuterated species, i.e. upon introducing DCl(g) instead of HCl(g).¹ We also deuterated the tBA solution, and the medium band at 1427 cm⁻¹ decreased. However, it is not quite clear where this band was shifted. In the range between 1120 and 1000 cm⁻¹, where it is expected, it cannot be assigned with certainty.

Among other imine group modes, the out-of-plane CH deformation was assigned to the medium band at 975 cm⁻¹ in the infrared spectrum of tBA.³ This assignment was based on band shifts of the deuterated imine group, CD=N. A quite recent ab initio calculation³ assigns the band at 997 cm⁻¹ as a mode with the greatest contribution from this vibrational coordinate. However, the same calculation resulted in six more vibrational frequencies in the range between 1000 and 960 cm⁻¹. The infrared band at 976 cm⁻¹ (Figure 1a) disappears upon protonation, and a new one of the similar intensity appears at 1030 cm⁻¹ (Figure 1b). However, since there is a weak band at 1021 cm⁻¹ in neutral tBA, this assignment can be treated only as tentative. Although this change is obviously caused by the protonation of the Schiff base, this important point must be further investigated.

The stretching modes of both bonds linking the central group to the aromatic rings, i.e. C-Ph and N-Ph, cannot be assigned unambiguously to any particular band in the vibrational spectra of neutral tBA.³ These two coordinates rather contribute to several modes in the 1300–1150 cm⁻¹ range. The same arguments hold for the protonated form too.

Consideration of the experimental data and the general valence bond calculation for methylimine showed that upon protonation the C=H bond is shortened and the stretching force constant increased by 0.51 mdyn/Å. This is a result of rehybridization at the nitrogen site of the Schiff base. On the other hand, theoretical calculations predict an increase of the C=N bond length, but yet with a shift of the s-character from the host (N) atom into the neighbouring bond, and an increase of the C=N stretching force constant in some cases.¹⁰ It seems that in the case of tBA the protonation strengthens both C=N and CH bond.
NMR Spectra

From the discussion of vibrational spectra it came out that, upon protonation of the nitrogen lone electron pair, a change of hybridization from the host atom to both neighbouring bonds, i.e. C=N and CH, takes place. Therefore, it seemed worthwhile to check this point by analyzing the NMR spectra. It is well known that e.g. the direct carbon-hydrogen coupling constant is proportional to the s-character of the corresponding CH bond. An increase of one bond carbon-hydrogen coupling constant means that s-character of the CH bond is enhanced. A change of $^1J_{CH}$ of the imine CH bond in tBA confirms the rehybridization around the host atom which can help in understanding what happens upon protonation.

As already mentioned, $^{13}$C NMR spectra were recorded from a mixture of tBA and tBA·HCl in CDCl$_3$ solution. Thus, a more exact determination of both differences in chemical shifts and coupling constants has been achieved. Since the imine carbon chemical shift is clearly separated from the others, no significant higher order effects are expected. Table II contains data about the azomethine carbon atom from $^{13}$C NMR spectra of tBA and a few of its isotopomers. In the first column, one can see a significant deuterium isotope effect on $^{13}$C chemical shift in neutral tBA. The difference for deuterated tBAs can be attributed to isotope effects whose real nature is not quite understood. Deuterium isotope effects on $^{13}$C chemical shifts in tBA are not relevant here and will be discussed elsewhere. In protonated species, a substantial deshielding of over 32 ppm was observed for the imine carbon atom. This effect can be explained by a significant increase of the local paramagnetic contribution to the total shielding value at the imine carbon site. In other words, a higher $\pi$-electron density and consequently a higher bond order for the C=N bond takes place upon protonation. The actual value of the chemical shift is here between those for alkenes and allenes, indicating an increase of conjugation in the protonated tBA as compared to the neutral form.

For testing the changes of hybridization in the protonated azomethine group it is interesting to determine $^1J_{CH}$ values. A number of correlations between the direct carbon-hydrogen coupling constant and the s-character of the bond have appeared in the literature. The most recent correlation of Gil, which holds for molecules other than hydrocarbons, is as follows:

$$^1J_{CH} = 769\rho^{3/2} + 6.5 \text{ Hz}$$

(1)

where $\rho = 1/n$, and $n$ is the carbon coordination number in terms of carbon hybrid orbitals sp$^{n-1}$. Standard deviation for Eq. 1 is stated to be 5.9 Hz.

Using Eq. 1, we have calculated s-characters of the imine CH bond for tBA and tBA·HCl from the experimentally determined $^1J_{CH}$ values (Table III). For the neutral

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>$\delta$/ppm</th>
<th>SCS$^a$/ppm</th>
<th>$^1J_{CH}$/Hz</th>
<th>$^1J_{CH}$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBA</td>
<td>160.29</td>
<td>32.11</td>
<td>158.1</td>
<td>174.3</td>
</tr>
<tr>
<td>D$_{6A}$·tBA</td>
<td>159.75</td>
<td>33.08</td>
<td>158.2</td>
<td>173.6</td>
</tr>
<tr>
<td>D$_{10}$·tBA</td>
<td>159.75</td>
<td>32.51</td>
<td>157.8</td>
<td>173.5</td>
</tr>
</tbody>
</table>

$^a$SCS – substituent chemical shift.
tBA, the value is close to the standard sp² hybrid. This is actually an overestimation of the s-content, since the observed CH stretching frequency is only 2889 cm⁻¹, and the *ab initio* calculated one 2927 cm⁻¹.¹⁰ It is interesting to compare here the CH stretching frequency and s-character of the CH bond on the α-carbon atom of benzaldehyde. Green and Harrison¹⁷ have deduced the CH stretching frequency from combination bands in infrared spectra to be 2817 cm⁻¹. We have determined the corresponding value for d₅-benzaldehyde at 2833 cm⁻¹. Both values are lower than that for tBA. The carbon-hydrogen coupling constant is 173.7 Hz, corresponding to a sp¹.¹⁷ hybrid and 36.2% of s-character according to Eq. 1. This disagreement between tBA and benzaldehyde should be checked.

The calculated hybrid for the protonated form of tBA is sp¹.⁷⁶, corresponding to 36.2% of the s-character. However, the observed CH stretching frequency is 2924 cm⁻¹, which is still much lower than the usual value for olefinic and related methine groups but higher than in benzaldehyde, although the hybrids seem to be the same. The linear relationship by van Alseneoy *et al.*⁴ gave practically the same results with an overestimated s-character of the CH bond.

For an unsymmetric system like *trans-N*-benzylideneaniline, a substitution-dependent change of conformation is observed.¹⁸,¹⁹ On the other hand, protonation brings about also conformational changes. Therefore, we have chosen some specifically fluorinated tBAs and measured their ¹³C NMR spectra, to obtain parameters for estimating hybridization in the imine moiety.

Neutral fluorinated tBAs display a relatively wide range of 20 ppm for imine ¹³C chemical shifts (Table IV). In comparison with the parent compound, a single fluorine atom in either of the para-positions induces a small shielding effect. This effect is more pronounced if fluorine is in the B-ring due to the closer position of the substituent to the imine carbon atom and approximate coplanarity of the ring and azomethine group plane. Since the A-ring is twisted (θ_N is about 45°), and the imine carbon atom in 4'-F-tBA is six bonds away from fluorine, the effect is rather small. However, the perfluorinated aniline ring (A) causes a significant deshielding, and perfluorinated benzylidene ring an even stronger shielding effect on the imine carbon atom. No additivity of substituent effects in either of the cases, including F₁₀-tBA, has been observed. This fact implies that in all fluorinated tBAs, electronic effects, which are usually additive, take place in combination with steric effects.
TABLE IV

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>$\delta$/ppm neutral</th>
<th>$\delta$/ppm protonated</th>
<th>SCS$^c$/ppm</th>
<th>$^{1}J_{\text{CH}}$/Hz neutral</th>
<th>$^{1}J_{\text{CH}}$/Hz protonated</th>
<th>$\Delta^{1}J_{\text{CH}}$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>4'-F-tBA$^a$</td>
<td>160.00</td>
<td>192.27</td>
<td>32.27</td>
<td>158.7</td>
<td>175.3</td>
<td>16.6</td>
</tr>
<tr>
<td>4-F-tBA$^b$</td>
<td>158.39</td>
<td>190.54</td>
<td>32.15</td>
<td>158.7</td>
<td>173.5</td>
<td>14.8</td>
</tr>
<tr>
<td>F$_{5A}$-tBA$^a$</td>
<td>168.60</td>
<td>192.37</td>
<td>23.77</td>
<td>161.1</td>
<td>173.8</td>
<td>12.7</td>
</tr>
<tr>
<td>F$_{5B}$-tBA</td>
<td>148.28</td>
<td>181.58</td>
<td>33.33</td>
<td>167.2</td>
<td>190.9</td>
<td>23.7</td>
</tr>
<tr>
<td>F$_{10}$-tBA</td>
<td>157.60</td>
<td>192.27</td>
<td>34.67</td>
<td>172.9</td>
<td>186.9</td>
<td>14.0</td>
</tr>
</tbody>
</table>

$^a$ Position 4' is equivalent to the para-position of the aniline ring (A).

$^b$ Position 4 is equivalent to the para-position of the benzylidene ring (B).

$^c$ SCS – substituted chemical shift.

However, the chemical shifts for protonated Schiff bases are rather close to each other (Table IV), indicating fewer differences in conformation between protonated forms than between compounds in the neutral form. It is probable that the A-ring is now less twisted than in neutral compounds, as already indicated in the discussion on infrared spectra. The only exception is F$_{5B}$-tBA•HCl, where the imine carbon atom is significantly more shielded than in tBA•HCl. The same effect holds for the neutral form. One can assume that a simultaneous action of different fluorine effects upon the $\alpha$-position to the ring is present.

A more direct insight into rehybridization is obtained by determining the carbon-hydrogen coupling on the imine carbon atom (Table III). For monofluorinated tBAs, the sp$^{\text{2-3}}$ hybrids and, consequently, s-characters are only slightly different from the parent molecule for both neutral and protonated Schiff bases. However, perfluorinated benzylidene ring (B) induces a significant increase of the s-character of the CH bond. This effect is also reflected in F$_{10}$-tBA. This is again the most pronounced effect of fluorine substituents, as in the case of $^{13}$C chemical shifts. The shares of s-electrons in this bond are overestimated for all fluorinated compounds, like in the case of tBA itself.

CONCLUSION

The protonation of trans-$N$-benzylideneaniline brings significant changes in the structure of the imine moiety, which are reflected in vibrational and NMR spectra. Thus, the C=N stretching frequency in vibrational spectra is increased by 45 cm$^{-1}$ in the solid hydrochloride and by 32 cm$^{-1}$ in the dissolved Schiff base. This phenomenon is interpreted in terms of rehybridization at the host atom site, like in other protonated Schiff bases.$^{1,2,10}$ The change of hybridization is confirmed here by the simultaneous increase of the imine CH stretching frequency by about 35 cm$^{-1}$ Moreover, the increase of the direct carbon-proton coupling constant by 16.2 Hz means a higher s-character of the CH bond by about 2%, using the relationship of Gil.$^{15}$ However, the calculated s-contents seem to be too high for both the neutral and protonated species. On the other hand, the deshielding effect upon protonation is 32.11 ppm in the $^{13}$C NMR spectrum. This indicates that a higher contribution from p-electrons, is now present in the C=N bond.

Other vibrational modes of the azomethine group are also changed upon protonation, like e.g. the CH deformation modes. Bands belonging to C-Ph and N-Ph stretchings cannot be assigned unambiguously, implying a strong mixing with phenyl vibrations. On the other hand, most of phenyl modes changed both their positions and
intensities in the spectra of the protonated form. Since no significant vibrational coupling between the azomethine and phenyl groups is present in neutral tBA, these changes indicate different conformation in the protonated Schiff base. The infrared and Raman spectra enable an assignment based on vibrational spectra of neutral tBA.

$^{13}$C NMR spectra of fluorinated tBAs in their protonated forms show similar changes to the parent tBA. However, there are differences, depending on whether fluorine is substituted in the aniline (A) or benzyldiene (B) ring. Each of the fluorinated Schiff bases requires a more detailed investigation.

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SAŽETAK

Vibracijski i NMR spektri protoniranih trans-N-benzilidenanilina

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Infracrveni i Ramanov spektro protoniranih trans-N-benzilidenanilina (tBA) pokazuju znatne pomake vibracijskih vrpki u odnosu na neutralni oblik. Najznatniji porast odnosi se na vibraciju istezanja veze C=N, ali se povećavaju i valni brojevi istezanja veze CH i sviranja CH u ravnini. Raspravljaju se sličnosti i razlike drugih protoniranih Schifflovih baza. $^{13}$C NMR spektro protoniranih tBA potvrđuju promjenu hibridizacije oko domaćinskog atoma dušika, pokazujući pomak prema nižem polju za iminski ugljik atom (porast p-sadreža veze C=N) i višu konstantu sprege ugljik vodik (porast s-sadreža veze CH). Na taj način su vibracijski i NMR spektro u skladu, potvrđujući strukturne promjene iminske skupine u protoniranom obliku. Raspravljaju se i učinci fluora, supstituiranog u fenilnim prstenima, na kemijske pomake i sprege ugljik-vodik.