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## Isotope effects in $^{13}\text{C}$ NMR spectra of monodeuteriated *trans*-N-benzylideneanilines

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### Abstract

Deuterium isotope effects on  $^{13}\text{C}$  chemical shifts have been determined in a series of monodeuteriated *trans*-N-benzylideneanilines. The effects over two bonds ( $^2\Delta$ ) observed at C-1 and over three bonds ( $^3\Delta$ ) observed at C-2,6 are sensitive to steric interactions involving nitrogen lone-pair electrons and C-Ph *ortho*-protons. Like in similar  $\pi$ -electron systems, the effect over six bonds ( $^6\Delta$ ) is related to molecular conformation.

### 1. INTRODUCTION

High-field NMR spectrometers and new measuring techniques have recently enabled very precise determination of small changes in chemical shifts (in the ppb range) induced by introduction of an isotopic nucleus into molecule.

It is generally accepted that these isotope shifts arise from slight changes of averaged molecular geometry caused by rovibrational perturbations on isotopic substitution [1]. Deuterium isotope effects on  $^{13}\text{C}$  chemical shifts have attracted much attention because of their long range and relationships with different molecular parameters [2]. Long range deuterium isotope effects, which can be detected over up to twelve C-C bonds, are often of alternating sign and magnitude and might be related to molecular conformation [3].

There are few comprehensive reviews [1,2,4] on isotope effects in NMR spectroscopy but new experimental data are still needed to help a more scrutinised theory of long-range isotope effects to be developed.

*trans*-N-Benzylideneaniline (tBA) is a prototype aromatic Schiff base (Fig. 1) which has for a long time been studied by different spectroscopic techniques, but very little by NMR. We have recently shown that the magnitude and the sign of deuterium isotope effects in monodeuteriated benzaldehydes depend on the position of deuterium in the molecule as well as on molecular geometry [5]. To investigate the dependence of isotope effects on molecular

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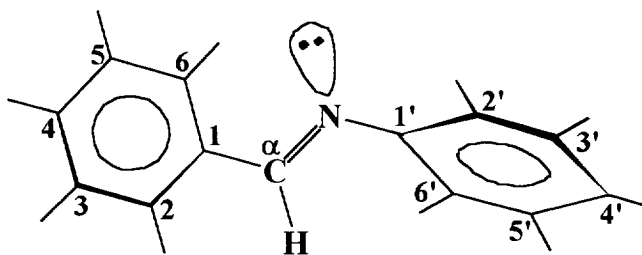


Figure 1. Numbering of C-atoms in *trans*-N-benzylideneaniline.

structure and conformation of tBA we have prepared a series of monodeuteriated species:  $\alpha$ -D-, 2-D-, 3-D-, 4-D- and 4'-D-*trans*-N-benzylideneaniline.

## 2. EXPERIMENTAL

$^{13}\text{C}$  proton-decoupled NMR spectra were recorded with a Varian XL 400 and a Bruker WM 360 spectrometer retrofitted with digital frequency synthesis, operating at 100.58 and 90.56 MHz, respectively. Sample concentrations were 30 mg/ml. Carbon-13 signals were referred to  $\text{CDCl}_3$  which was also used as a solvent and lock signal. All spectra were recorded at ambient temperature in 5 mm NMR tubes. Digital resolution was better than 0.1 Hz per point. Deuterium isotope effects were determined from mixtures of deuteriated and nondeuteriated compounds prepared in different ratios.

The synthesis of deuteriated *trans*-N-benzylideneanilines was described elsewhere [6]. The deuterium contents were determined by mass spectrometry.

## 3. RESULTS AND DISCUSSION

Deuterium isotope effects in tBA isotopomers are collected in Table 1. Positive sign denotes upfield deuterium induced  $^{13}\text{C}$  chemical shifts. All effects are given in ppb units.

Effects over one ( $^1\Delta$ ) and two bonds ( $^2\Delta$ ) have all the positive sign and are similar in magnitude to those observed in other conjugated systems [3,7]. However  $^2\Delta$  at the quaternary C-1 atom in 2-D- and  $\alpha$ -D-tBA is considerably smaller (Table 1) than usually found (ca. 110 ppb). We ascribed it to steric interactions between nitrogen lone-pair electrons and *ortho*-protons of the C-phenyl ring. It was determined by different theoretical and experimental methods [8] that in the tBA molecule (Figure 1) C-Ph and N-Ph dihedral angles are  $0\text{-}20^\circ$  and  $40\text{-}55^\circ$ , respectively, the latter due to  $n\pi$ -interaction. Therefore, nonbonding electrons are closer to C-Ph than to N-Ph *ortho*-protons.

The only negative three-bond effect was observed at C-1' in  $\alpha$ -D-isotopomer where lone-pair interaction with C-1' is significant. The absence of  $^3\Delta$  at C-2,6 in 4-D-tBA is due to steric interaction involving lone-pair and C-Ph *ortho*-protons which is consistent with the

Table 1  
Deuterium isotope effects<sup>a</sup> ( $^n\Delta$ /ppb)<sup>b</sup> on  $^{13}\text{C}$  chemical shifts in *trans*-N-benzylideneaniline isotopomers

Isotopomer	$\alpha$ -D-tBA	2-D-tBA	3-D-tBA	4-D-tBA	4'-D-tBA
Carbon	$^n\Delta$ /ppb				
C- $\alpha$	$^1\Delta = 260.0$	$^3\Delta = 24.5$	$^4\Delta = -4.5$	$^5\Delta = -6.5$	$^6\Delta = 7.0$
C-1	$^2\Delta = 73.0$	$^2\Delta = 73.0$	$^3\Delta = 9.0$	$^4\Delta = -3.5$	
C-1'	$^3\Delta = -5.0$			$^7\Delta = -3.0$	
C-2	$^3\Delta = 21.5$	$^1\Delta = 305.0$	$^2\Delta = 112.0$		
C-6	$^3\Delta = 21.5$	$^3\Delta = 8.5$	$^4\Delta = 14.5$		
C-2',6'	$^4\Delta = -9.0$				$^3\Delta = 7.0$
C-3		$^2\Delta = 111.0$	$^1\Delta = 288.0$	$^2\Delta = 110.0$	
C-5			$^3\Delta = 13.0$	$^2\Delta = 110.0$	
C-3',5'					$^2\Delta = 110.0$
C-4	$^5\Delta = -6.0$	$^3\Delta = 4.0$	$^2\Delta = 107.5$	$^1\Delta = 296.0$	
C-4'	$^6\Delta = 6.5$				$^1\Delta = 286.0$

<sup>a</sup>Standard errors are less than 0.5 ppb.  $\text{CDCl}_3$  was used as solvent.

<sup>b</sup> $n$  is the number of bonds separating the deuterium substitution site and observed nucleus.

results found in similar  $\pi$ -electron systems where a heteroatom with nonbonding electrons is placed at the  $\beta$ -position to the phenyl ring (e.g. benzophenone). On the contrary in 4'-D-*trans*-N-benzylideneaniline, where the heteroatom is at the  $\alpha$ -position to the ring, three-bond effect at C-2',6' was observed having the same value as in 4-D-*trans*-stilbene (7.0 ppb).

Effects over four bonds ( $^4\Delta$ ) range from -9.0 to 14.5 ppb. In  $\alpha$ -D-tBA  $^4\Delta$  at C-2',6' has the value of -9.0 ppb, while in 3-D-tBA both positive at C-2,6 (14.5 ppb) and negative at C- $\alpha$  (-4.5 ppb) four-bond effects were detected. On the other hand, no effect over four bonds in 4'-D-tBA at C-1' was found, probably due to the influence of nitrogen lone-pair electrons, since in 4-D-tBA  $^4\Delta$  at C-1 is -3.5 ppb.

The effects over five bonds determined at C- $\alpha$  in 4-D-tBA and at C-4 in  $\alpha$ -D-tBA are negative (Table 1), i.e. deshielding. Contrary to it, six-bond effects are positive, which is in agreement with results obtained in other extended aromatic molecules. We have recently found that  $^6\Delta$  is related to the conformation of binuclear aromatic molecules [9]. For instance, in planar tolane [3] or nearly planar *trans*-stilbene [10]  $^6\Delta$  amounts to 15.0 ppb and 10.6 ppb, respectively, while in 4'-D-tBA  $^6\Delta$  of only 7.0 ppb reflects rather large N-Ph dihedral angle (40-55°). Such an angle considerable reduces transmission of isotope effects throughout the

$\pi$ -electron system, decreasing magnitude and extent of isotope effects in tBA as compared with those in nearly planar *trans*-stilbene where even a ten-bond effect was observed [10]. The six-bond effects observed at C- $\alpha$  in 4'-D-tBA and at C-4' in  $\alpha$ -D-tBA, i.e. effects acting in opposite directions have almost the same value, corroborating again conformational dependence of  $^6\Delta$ .

The longest range isotope effect found in deuteriated *trans*-N-benzylideneanilines is the one over seven bonds ( $^7\Delta$ ) observed in 4-D-tBA at C-1', i.e. in the N-Ph ring. In 4'-D-tBA no seven-bond effect at C-1, i.e. in C-Ph ring, was revealed. Different N-Ph and C-Ph dihedral angles and lone-pair influence at C-1 and C-1' are the most probable cause for it.

## CONCLUSION

The magnitude and sign of deuterium isotope effects in tBA reflect the position of deuterium substitution in the molecule, spatial orientation of nitrogen lone-pair electrons as well as different dihedral angles of C-Ph and N-Ph moieties of tBA. Further work on multideuteriated tBA's is in progress.

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