

Deuterium isotope effects in ^{13}C NMR spectra of *trans*-azobenzene

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Abstract

Deuterium isotope effects on ^{13}C chemical shifts have been determined in a series of deuteriated *trans*-azobenzene isotopomers. The longest effect observed is the one over ten bonds ($^{10}\Delta$) in 4- ^2H -isotopomer at C-4' atom amounting to 3.3 ppb. The magnitude and the extent of isotope effects in *trans*-azobenzene are related to those observed in isoelectronic and conformationally similar *trans*-stilbene. The sign alternation pattern of the long-range isotope effects in *trans*-azobenzene parallels that in isoelectronic *trans*-stilbene, *cis*-stilbene and *trans*-N-benzylideneaniline. © 1997 Elsevier Science B.V.

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1. Introduction

Isotope effects on NMR chemical shifts are interpreted in terms of dynamic factor, i.e. vibrational and rotational averaging of nuclear shielding, and electronic factor, i.e. changes in nuclear shielding with bond extension or bond angle deformation [1]. A specific feature of deuterium labelling of aromatic molecules is the existence of long-range deuterium isotope effects (LRDIE) on ^{13}C chemical shifts, sometimes even through more than ten bonds [2]. The pattern of the sign alternation of LRDIE parallels that of π -polarization [2–4]. Subtle charge redistribution upon the isotopic substitution, successfully simulated by ab initio calculations [5], is in accord with the observation of pure rotational spectra of monodeuteriated benzene, acetylene, etc. [6].

We have recently investigated isotope effects in *trans*-N-benzylideneaniline (tBA), which consists of

the two phenyl rings connected via the azomethine bridging group [7]. The present work is focused on *trans*-azobenzene (tAB), where the phenyl rings are linked via the azo group. We have prepared a series of deuteriated *trans*-azobenzene (Fig. 1) isotopomers: 2- ^2H -, 3- ^2H -, 4- ^2H -, 4,4'- $^2\text{H}_2$ -, $^2\text{H}_5$ - and $^2\text{H}_{10}$ -tAB, recorded their ^{13}C MR spectra and analyzed isotope effects.

2. Experimental

The synthesis of deuteriated *trans*-azobenzene isotopomers and deuterium contents was reported elsewhere [8]. ^{13}C proton decoupled (Waltz-16) NMR, spectra were recorded with Varian spectrometers: Gemini 300, XL 400 and VXR 500S, operating at 75.4, 100.6 and 125.7 MHz, respectively. Sample concentrations were ca. 20 mg ml $^{-1}$. ^{13}C chemical shifts were referred to TMS. Acetone- d_6 was used as a solvent and for the lock signal. Spectra were recorded at 293 K in 5 mm NMR tubes. LRDIE were measured at

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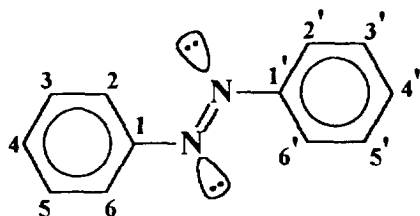


Fig. 1. Molecular model and numbering of C-atoms in *trans*-azobenzene.

narrow spectral widths (1000–3000 Hz), with zero filling giving the digital resolution less than 0.01 Hz per point.

3. Results and discussion

Deuterium isotope effects were determined from mixtures of deuteriated and undeuteriated compounds prepared in different ratios. Deuterium isotope effects (in ppb) observed in tAB isotopomers are given in Table 1. The negative sign denotes a deshielding effect due to deuterium.

One- ($^1\Delta$) and two-bond effects ($^2\Delta$) have the usual positive sign and similar magnitude as those in related conjugated systems [2,4,7]. The only exception is $^2\Delta$ at the quarternary carbon (C-1) in 2- ^2H -tAB which has a ca. 50% lower magnitude (51.7 ppb) than that usually observed in aromatic compounds (ca. 110 ppb). In related 2- ^2H -*trans*-N-benzylideneaniline

(tBA), $^2\Delta$ is also considerably smaller (73.0 ppb) [7]. The decrease of $^2\Delta$ at C-1 is assumed to arise from steric interactions between nitrogen lone-pair electrons and phenyl *ortho*-protons [7], thus the reduction of $^2\Delta$ being greater in tAB (two N-atoms) than in tBA (one N-atom).

The only negative $^3\Delta$ was observed at C-6 (–8.2 ppb) in 2- ^2H -tAB (Table 1) which is ascribed to the nitrogen lone-pair influence at this position.

Seven-bond effect, $^7\Delta$, was observed at C-1' in 4- ^2H -tAB, being twice as great (–6.5 ppb) as in 4- ^2H -tBA (–3.0 ppb). Beside the effect of the second N-atom in tAB, the increase in magnitude of $^7\Delta$ in tAB, relatively to that in tBA, reflects the smaller N–Ph dihedral angle in the former (0–20°) than in the latter molecule (40–55°).

The longest deuterium isotope effect observed here is $^{10}\Delta$ (Fig. 2), in 4- ^2H -tAB at C-4'. This $^{10}\Delta$ amounts to 3.3 ppb, which is similar (within the digital resolution) to $^{10}\Delta$ (2.8 ppb) in 4- ^2H -*trans*-stilbene (tSB), but greater than $^{10}\Delta$ (2.0 ppb) in 4- ^2H -*cis*-stilbene (cSB) [4]. $^1\Delta$ (see Table 1) at C-4' in $^2\text{H}_5$ -tAB and $^2\text{H}_5$ -tSB (both ca. 11.0 ppb) are also greater than those in $^2\text{H}_5$ -tBA and $^2\text{H}_5$ -cSB, amounting to 5.1 ppb and 6.0 ppb, respectively [4,7]. The lower $^{10}\Delta$ and $^1\Delta$ at C-4' in 4- ^2H -cSB and $^2\text{H}_5$ -cSB compared with the corresponding tAB's and tSB's are also related to the larger molecular dihedral angle in cSB (C–Ph ca. 50°) than that in tSB (C–Ph 0–20°) and tAB (N–Ph 0–20°). In accord with this, the extent of LRDIE in nearly planar

Table 1
Deuterium isotope effects, $^n\Delta$ (ppb),^a on ^{13}C NMR chemical shifts in *trans*-azobenzene isotopomers^b

Isotopomer	2- ^2H -tAB	3- ^2H -tAB	4- ^2H -tAB	4,4'- $^2\text{H}_2$ -tAB	$^2\text{H}_5$ -tAB	$^2\text{H}_{10}$ -tAB
Carbon	$^n\Delta$ (ppb)					
C-4	$^3\Delta = 4.4$	$^2\Delta = 106.2$	$^1\Delta = 281.3$	$^{n(1)}\Delta = 290.1$	$^{n(1)}\Delta = 502.0$	$^{n(1)}\Delta = 522.1$
C-3	$^2\Delta = 106.9$	$^1\Delta = 268.8$	$^2\Delta = 109.8$	$^{n(2)}\Delta = 111.4$	$^{n(1)}\Delta = 502.8$	$^{n(1)}\Delta = 504.0$
C-5	$^4\Delta = 5.5$	$^3\Delta = 4.7$	$^2\Delta = 109.8$	$^{n(2)}\Delta = 111.4$	$^{n(1)}\Delta = 502.8$	$^{n(1)}\Delta = 504.0$
C-2	$^1\Delta = 296.9$	$^2\Delta = 104.1$			$^{n(1)}\Delta = 402.6$	$^{n(1)}\Delta = 407.2$
C-6	$^3\Delta = -8.2$	$^4\Delta = 3.1$			$^{n(1)}\Delta = 402.6$	$^{n(1)}\Delta = 407.2$
C-1	$^2\Delta = 51.7$	$^3\Delta = 8.0$		$^{n(4)}\Delta = -6.7$	$^{n(2)}\Delta = 91.6$	$^{n(2)}\Delta = 83.5$
C-1'			$^7\Delta = -6.5$	$^{n(4)}\Delta = -6.7$	$^{n(5)}\Delta = -8.8$	$^{n(2)}\Delta = 83.5$
C-2',6'					$^{n(6)}\Delta = 3.3$	$^{n(1)}\Delta = 407.2$
C-3',5'				$^{n(2)}\Delta = 111.4$		$^{n(1)}\Delta = 540.0$
C-4'			$^{10}\Delta = 3.3$	$^{n(1)}\Delta = 290.1$	$^{n(8)}\Delta = 11.1$	$^{n(1)}\Delta = 522.1$

^a n is the number of intervening bonds between ^2H -atom and observed C-atom. In polydeuteriated isotomers the total isotope effect is denoted by t , where the number in brackets (n) denotes the shortest through-bond distance between the ^2H -atom and the observed C-atom.

^b Standard errors for $^1\Delta$ are less than 3 ppb, while for $^n\Delta$ are 0.5 ppb. Acetone- d_6 was used as a solvent.

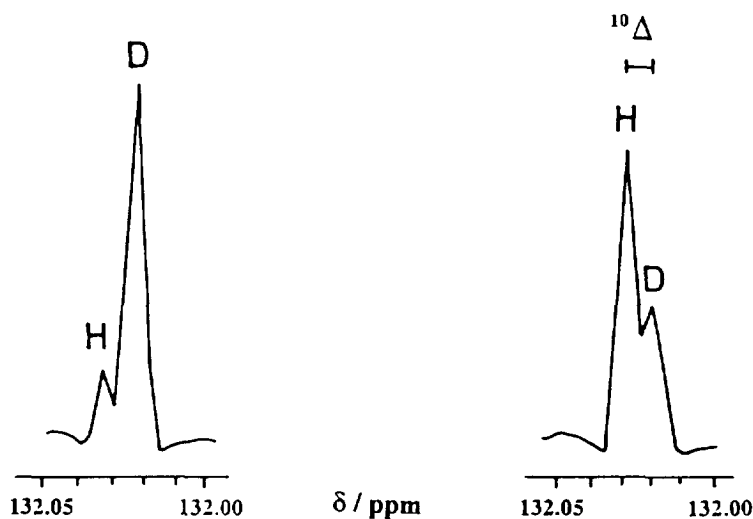


Fig. 2. The ^{13}C spectra of C-4' in 4- ^2H -tAB (at 100.6 MHz), displaying $^{10}\Delta$. The spectrum on the right was measured with a greater amount of undeuterated species.

4- ^2H -tAB (the longest effect is $^{10}\Delta$) is greater than in distorted 4- ^2H -tBA (the longest effect is $^7\Delta$) [7]. The relation of LRDIE with molecular conformation was previously also observed for $^6\Delta$ [4]. In toluene, which is planar, $^6\Delta$ amounts to 15.0 ppb [2], while in 4'- ^2H -tBA (N-Ph dihedral angle 40–55°) it is only 7.0 ppb [7]. The pattern of the sign alternation of LRDIE in tAB is the same as in tBA, tSB, cSB and benzophenone (BPN), resembling π -electron polarization [4,7]. Thus, in $^2\text{H}_5$ -tAB the total isotope effect at C-1' is –8.8 ppb, at C-2',6' is 3.3 ppb, at C-3',5' was not observed and at C-4' is 11.1 ppb. It has been previously assumed that the parallelism of LRDIE with the π -polarization is related to the existence of the conformationally independent contribution to isotope effects, in addition to the conformationally dependent one [2,3]. The observation of LRDIE in BPN ($^7\Delta$, $^8\Delta$ and $^9\Delta$), where conjugation between phenyl rings is interrupted by the insulating C=O group, is in agreement with this model [9].

4. Conclusion

The magnitude of deuterium isotope effects in isotopomers of tAB is similar to those observed in isoelectronic tSB, corresponding to similar dihedral angles in both molecules. The extent of isotope effects in tAB is longer (over 10 bonds) than in tBA (over 7

bonds), whereas it is the same as in tSB and cSB. The sign alternation of LRDIE in tAB parallels that in tSB, cSB, tBA and BPN. Some variations in isotope effects between tAB and tBA are a consequence of different conformation and symmetry of the two molecules.

Acknowledgements

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