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Direct detection of intramolecular Sb···N nonbonded interaction by ^1H – ^{13}C and ^1H – ^{15}N heteronuclear multiple bond correlation spectroscopy

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Abstract

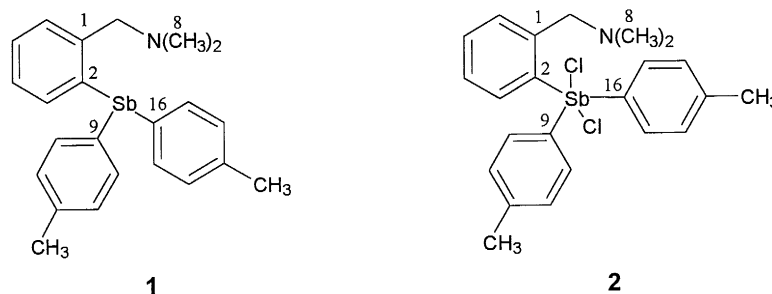
Direct evidence of intramolecular Sb···N nonbonded interaction was obtained by means of ^1H – ^{13}C and ^1H – ^{15}N heteronuclear multiple bond correlation (HMBC) experiments. The long-range coupling constants between ^1H and ^{13}C nuclei through antimony and nitrogen were also determined by the J–HMBC 2D method. © 2000 Elsevier Science Ltd. All rights reserved.

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Many papers have appeared on the intramolecular nonbonded interaction between atoms of the 14, 15, and 16 main group elements and its effect on structure and chemical properties.¹ However, the main evidence for such interaction is the distance between the two hetero atoms determined by X-ray crystallography.² NMR spectroscopy has been of limited value because of the low natural abundance of ^{15}N and ^{17}O nuclei and the difficulty of treating nuclei not having a nuclear spin $I=1/2$ with conventional methods.³ In the case of Sb ($I=5/2$ for ^{121}Sb and $7/2$ for ^{123}Sb), it has been almost impossible to observe NMR signals because of the line shape broadening caused by the large quadrupole moment. This situation has been changed by the dramatic sensitivity enhancement of the inverse detection method owing to the introduction of the pulse field gradient (PFG) technique, making it possible to detect small long-range correlations.⁴ Recently, we have prepared various triaryl-antimony(III,V) and -bismuth(III) compounds bearing a phenyl substituent with $-\text{CH}_2\text{NMe}_2$, $-\text{CH}_2\text{OMe}$, $-\text{CH}_2\text{SMe}$, or $-\text{CH}_2\text{CH}_2\text{SMe}$ in the *ortho*-position in order to investigate the origin of the above interaction. We have now employed this powerful tool to study Sb···N intramolecular interactions in 2-(*N,N*-dimethylaminomethyl)phenyl bis(4-methylphenyl)stibine **1** and its dichloride(V) **2**, which are free from steric constraints (Scheme 1).

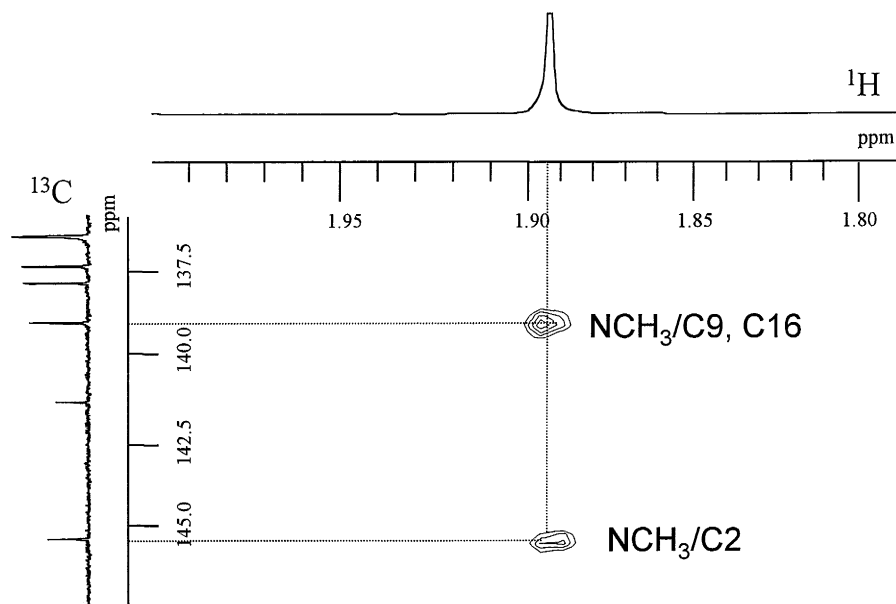
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We report here the existence of $\text{Sb}\cdots\text{N}$ nonbonded interaction, confirmed by a through antimony and nitrogen ^1H - ^{13}C long-range coupling correlation observed by heteronuclear multiple bond correlation (HMBC) experiments, as well as the differences of ^{15}N chemical shift values of **1** and **2** compared with *N,N*-dimethylbenzylamine as a reference.



Scheme 1.

The triaryl-stibene **1** was prepared by condensation of *o*-lithiated *N,N*-dimethylbenzylamine with $(p\text{-tol})_2\text{SbBr}$ in moderate yields. The pentavalent antimony compound **2** was synthesized from the trivalent compound **1** by treatment with SO_2Cl_2 . The ^1H NMR signals of the two tolyl groups of **1** are equivalent. A long-range coupling correlation between the *N*-methyl protons (8-H) and the quaternary carbons (C-9, C-16) of the tolyl groups linked to the antimony atom was seen in a ^1H - ^{13}C HMBC experiment (Fig. 1). Such a long-range coupling correlation through seven bonds seems highly improbable. It is more reasonable to interpret this coupling in terms of a four-bond correlation via $\text{Sb}\cdots\text{N}$ through Fermi-contact interaction. Considering these results, it is suggested that **1** takes a distorted tetragonal structure in solution.

Fig. 1. ^1H - ^{13}C HMBC spectrum of **1**

In the ^1H NMR spectrum of **2**, the tolyl groups are not equivalent, and NOE was observed between the *N*-methyl protons and one tolyl group. This strongly suggests that the antimony center has a pseudo-

octahedral structure, like that in the solid state. The tolyl group showing NOE with the *N*-methyl protons occupies the *cis* position and the other lies in the *trans* position. Long-range coupling correlations with the *N*-methyl protons (8-H) were observed for two quaternary carbons (C-1, C-16) bound to antimony (Fig. 2). One is the carbon of the tolyl group at the *cis* position and the other is that of the dimethylaminobenzyl group. On the other hand, no long-range coupling constant was observed for the quaternary carbon (C-9) of the tolyl group lying in the *trans* position. The difference between C-1, C-16 and C-9 probably arises from the torsion angle dependence of the coupling constant. Again, the long-range coupling correlation can be attributed to intramolecular Sb···N nonbonded interaction as discussed above. The fact that the intramolecular Sb···N distances in **1** [2.824(8) Å] and in **2** [2.584(5) Å] obtained by X-ray structure analysis are shorter than the van der Waals radii (3.59 Å) also supports the existence of Sb···N nonbonded interaction.⁵ ORTEP diagrams of the structures **1** and **2** showing Sb···N short contact are given in Fig. 3.

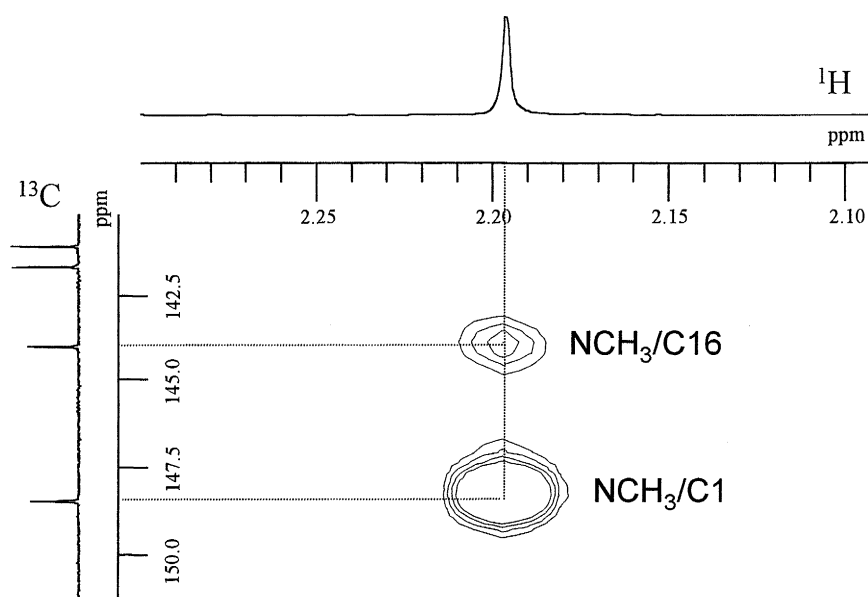


Fig. 2. ^1H - ^{13}C HMBC spectrum of **2**

The chemical shift of amino nitrogen in **1** and **2** was determined by taking advantage of the ^1H - ^{15}N HMBC correlation peak between the *N*-methyl protons and the *N*-methyl nitrogen (natural abundance). The chemical shifts (δ) of the ^{15}N nuclei of **1** and **2** appeared at -350.7 and -342.9 ppm, respectively.⁶ The significant downfield shifts of the ^{15}N NMR signals for **1** by 2.9 ppm and for **2** by 10.7 ppm relative to the signal of *N,N*-dimethylbenzylamine ($\delta -353.6$ ppm) confirm the existence of a nonbonded interaction, since delocalization of the nitrogen lone pair is known to cause downfield shifts.⁷ The Sb···N interaction of **2** may be stronger than that of **1** because of increased Lewis acidity of antimony as a result of chlorination.

Finally, the long-range coupling constants between the *N*-methyl protons and quaternary carbons bound to antimony were determined by J-HMBC 2D experiments.^{8,9} The obtained coupling constants are $^4J_{(\text{NCH}_3, \text{C-9})}$, $^4J_{(\text{NCH}_3, \text{C-16})}=2.3$ Hz for **1**, and $^4J_{(\text{NCH}_3, \text{C-1})}=4.6$ Hz, $^4J_{(\text{NCH}_3, \text{C-16})}\leq 1.0$ Hz for **2**.

In summary, ^1H - ^{13}C and ^1H - ^{15}N HMBC analyses of 2-(*N,N*-dimethylaminomethyl)phenyl bis(4-methylphenyl)stibine **1** and its dichloride **2** have provided direct evidence of the existence of intramolecular Sb···N nonbonded interaction. The detection of long-range coupling correlations by HMBC

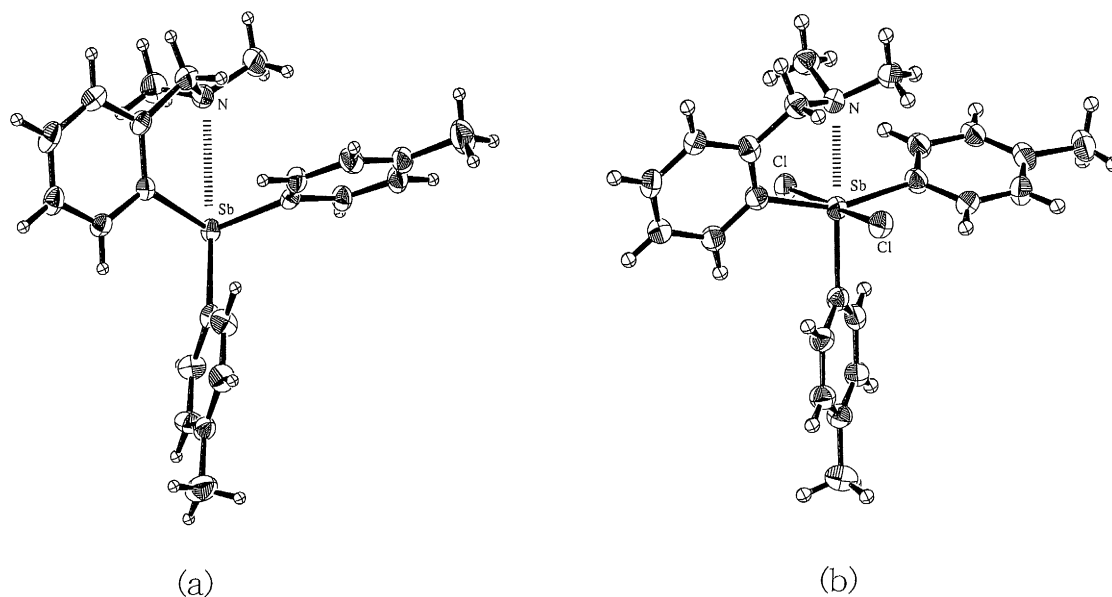


Fig. 3. ORTEP diagrams of **1** (a) and **2** (b)

experiments and the observation of chemical shift changes in heteronuclear NMR seem to be effective methods to investigate such nonbonding interactions.

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5. Crystal data for **1**: empirical formula $C_{23}H_{26}NSb$; triclinic; space group $P\bar{1}$; $a=11.0727(9)$ Å, $b=20.111(1)$ Å, $c=10.0956(8)$ Å; $\alpha=104.358(6)^\circ$, $\beta=105.936(6)^\circ$, $\gamma=80.861(6)^\circ$; No. of observations 5855; R 0.047; R_w 0.054. Crystal data for **2**: empirical formula $C_{23}H_{26}Cl_2NSb$; monoclinic; space group $P2_1/n$; $a=14.689(9)$ Å, $b=9.90(1)$ Å, $c=16.47(1)$ Å; $\beta=113.35(1)^\circ$; No. of observations 3396; R 0.050; R_w 0.054.
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9. All experiments were performed at 303 K using solutions of **1** (22 mg) and **2** (25 mg) dissolved in 0.5 ml of CD_2Cl_2 on a JEOL LA600 spectrometer equipped with a 5 mm NALORAC HX inverse probe. Fifteen J–HMBC 2D spectra were acquired with 64 scans per increment for a 2048 (F2) \times 64 (F1) data matrix with a 300 msec constant time (τ_{max}) and varying the evolution time (Δ) from 10 to 290 msec in 20 msec steps. All spectra were processed with shifted Blackman Harris window for the F2 and F1 dimensions after zero filling to the F1 dimension.