

# Using Proton NMR to Characterize Functionalized Single-Walled Carbon Nanotubes

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## ABSTRACT

Single-walled carbon nanotubes (SWCNTs) can be functionalized covalently at SWCNT ends, covalently at SWCNT sidewalls, or by complexation with SWCNT sidewalls. Each type of product has a wide range of applications, but sometimes their full development is hindered by incomplete product characterization. A convenient method for analysis of these products by solution phase proton NMR has been developed and is reported herein. In each case, protons in the vicinity of the covalent bond to the SWCNT or the SWCNT-complexed functional group are shifted downfield in the NMR. This enables determining the position of covalent bond or complex formation..

**Keywords:** single-walled carbon nanotubes, SWCNT, nuclear magnetic resonance, NMR, characterization

## 1 INTRODUCTION

Select amides have been widely used to suspend nanoarchitectures in organic solvents. In order to determine factors enabling these suspensions, interactions of single walled carbon nanotubes (SWCNTs) with representative amides, aminoalcohols, an aminoketone, and an oxime were examined.  $^1\text{H}$  NMR spectra gave evidence for two types of associations, formed after evaporation of the reaction mixture to a wet paste, and followed by sonication in NMR solvent. NMR spectra after evaporation to concentrated solution show broadening and small downfield changes, suggesting weak interactions. The magnitude of  $^1\text{H}$  NMR chemical shift change upon SWCNT:organonitrogen complex formation represents the strength of the association. Magnitudes of changes in NMR signals of different protons in the organonitrogen reveal which protons are in close proximity to SWCNTs. Results reveal that (1) in amides and aminoketones, SWCNT association with carbonyls is stronger than with nitrogen, (2) in aminoalcohols, SWCNT association with nitrogen is stronger than with oxygen, and (3) protons bonded to heteroatoms have greater changes in their chemical shifts than those bonded to carbons. Changes (broadening and downfield shifts) in  $^1\text{H}$  NMR signals of these compounds, which accompany SWCNT association, depend upon (1) degree of evaporation of residual amide and organic solvent, (2) organic and NMR solvent combination, (3) type of proton in R, (4) proximity effects to the carbonyl (R-CO versus  $\text{NR}_2$ ), (5) steric requirements of R, (6) electronic

effects of alkyls, and (7) effects of tethering two ends of a molecule. These data have important uses in SWCNT solvation, adsorption of molecules, and characterization by NMR.

## 2 RESULTS AND DISCUSSION

Representative organonitrogen compounds **1–4** in this study are shown below. SWCNTs associated with these organonitrogens can be compared among themselves in order to explore differences in the effects of a range of structural variations. (1) Compounds **1** and **2c** are isoatomic in C, O, and N; their comparison gives the effects of tethering together the ends of **2c**. (2) Increasing the steric requirements of groups bonded to C=O in compounds **2** has been reported, but some pertinent data and information are reproduced here for convenience. (3) Comparing compounds **2b** and **3** contrasts the effects of having the carbonyl bonded to nitrogen versus isolated from nitrogen by 3 methylene units. (4) The series represented by **4** explores the effects of increasing steric requirements of groups bonded to nitrogen. NMR spectra of organonitrogen compounds **1–4** in NMR solvent, with and without SWCNTs, enables exploring the above effects upon and trends in these associations, SWCNT:**1–4**. These NMR data are shown in Table 1.

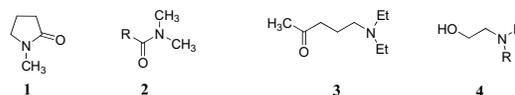


Figure 1. Representative organonitrogen compounds used in SWCNT associations: 1-methyl-2-pyrrolidone (NMP) **1**; *N,N*-dimethylamides **2**, in which R = H (**2a**), Me (**2b**), Et (**2c**), *i*-Pr (**2d**), *t*-Bu (**2e**), Ph (**2f**); 5-diethylamino-2-pentanone **3**; 2-aminoethanols **4** in which R = H (**4a**), Me (**4b**), Et (**4c**).

### 2.1 Steric effects and cyclization

Compounds **1** and **2c** are isoatomic in C, H, and O; their structural difference is that the two ends of **1** forms **2c** are tethered. The difference in magnitudes of downfield NMR shift changes of these compounds, upon association with SWCNT, explores the differences in their interactions with SWCNTs and the origins for the differences. Therefore,  $^1\text{H}$  NMR signals for organonitrogens **1** and **2** were measured in the absence and in the presence of HiPco or SWeNT brand SWCNT. Downfield chemical shift changes upon association were calculated and compared.

Values for **2a**, **2b**, **2d**, **2e** and **2f** were used for comparison when appropriate.

NMR chemical shift values of protons  $\alpha$  to carbonyl in SWCNT:**1** are shifted downfield 0.08 ppm (2.28 – 2.36 ppm) for HiPco, and 0.09 ppm (2.28 – 2.37 ppm) for SWeNT SWCNTs. In SWCNT:**2c**, NMR signals for protons  $\alpha$  to carbonyl are shifted downfield 0.08 ppm (2.24 – 2.32 ppm) for HiPco and 0.10 ppm (2.24 – 2.34 ppm) for SWeNT SWCNTs. In SWCNT:**2d**, NMR signals of protons  $\alpha$  to carbonyl are shifted downfield 0.01 ppm (2.79 – 2.80 ppm) for HiPco and 0.06 ppm (2.79 – 2.85 ppm) for SWeNT. All of these chemical shift changes upon complexation are rather small.

The protons  $\beta$  and  $\gamma$  to carbonyl in SWCNT:**1** are each shifted downfield 0.07 ppm (1.94 – 2.01 ppm, 3.30 – 3.37 ppm) for both HiPco and SWeNT, and NMe protons are shifted downfield 0.07 ppm (2.76 – 2.83 ppm) for HiPco and 0.08 ppm (2.76 – 2.84 ppm) for SWeNT brands. The  $\beta$  protons of SWCNT:**2c** are shifted downfield 0.10 ppm (1.03 – 1.13 ppm) for HiPco and 0.23 ppm (1.03 – 1.26 ppm) for SWeNT brands, and NMe<sub>2</sub> protons are shifted downfield 0.08 ppm for HiPco and 0.02 ppm for SWeNT respectively. The  $\beta$  protons of SWCNT:**2d** are shifted downfield 0.02 ppm (1.08 – 1.10 ppm) for HiPco and 0.20 ppm (1.08 – 1.28 ppm) for SWeNT samples, and NMe<sub>2</sub> protons are shifted downfield 0.02 ppm (2.97 – 2.99) for HiPco and 0.10 ppm (2.97 – 3.07 ppm) for SWeNT SWCNTs. The  $\beta$  protons in **2c** and **2d** show more change in chemical shift upon association of **2c** and **2d** with SWCNTs than do the other protons in **2c** and **2d**, especially when using the SWeNT brand.

Chemical shift changes, for  $\beta$  protons in **1**, **2c**, and **2d** upon association with SWCNTs, are 0.07 ppm, 0.10 ppm and 0.02 ppm respectively for the HiPco brand, and 0.07 ppm, 0.23 ppm, and 0.20 ppm respectively for the SWeNT brand. The general trend for chemical shift upon SWCNT association is in the order **1** < **2d** < **2c**. This indicates that the heteroatom corresponding to the  $\beta$  protons of **1** associates less than those of **2c** and **2d** with SWCNTs, suggesting that the conformational freedom of **2c** and **2d** enables them to be more accommodating sterically and enabling a stronger association than in cyclic, rigid **1**. Therefore, in compounds **2c** and **2d** the heteroatoms corresponding to the  $\beta$  protons can more effectively associate with SWCNTs than that of **1**.

In SWCNT:**2** wet paste samples, downfield changes (Table 1) in amide NMR values are greatest for aldehydic protons (**1a**, R= H, 0.30 ppm), compared to protons  $\alpha$  to C=O (**2b**, R=Me, 0.13 ppm), protons  $\beta$  to C=O (**2c**, R=Et, 0.23 ppm), and NMe<sub>2</sub> protons (**2a**, R=H, 0.20 ppm). This interaction in SWCNT:DMF (**2a**, R= H) was so strong, that the aldehydic proton signal (8.28 ppm, compared to 7.98 ppm for free DMF) broadened sufficiently to obfuscate the NMR chemical shift value. NMR signals for protons in SWCNT:**2b** – **2f** (R = Me, Et, *i*-Pr, *t*-Bu, and Ph) were less broadened than those for SWCNT:**2a** (R = H); broadening decreased with increasing steric requirements of R and with

increasing distance of the proton from C=O. Downfield changes for protons  $\alpha$  to C=O generally show a decreasing trend in the order R = Me (**2b**) > Et (**2c**) > *i*-Pr (**2d**). When there are no  $\alpha$  protons, R = *t*-Bu (**2e**) or Ph (**2f**), the  $\alpha$  and phenyl protons are changed only slightly upon association of the molecule with SWCNTs. NMe<sub>2</sub> signals of SWCNT:amides with larger NMR value changes ( $\geq \sim 0.10$  ppm) coalesced into one broader peak. Relative to the unassociated amide **2**, most signals of NMe<sub>2</sub> in SWCNT:**2** are moved downfield by  $\leq \sim 0.10$  ppm.

## 2.2 Cyclic versus acyclic compounds

Comparing **1** and **3** also explores the effects of SWCNT:organonitrogen formation upon the three methylene units of these cyclic and acyclic analogs. In Table 1, <sup>1</sup>H NMR chemical shift changes of free versus SWCNT-associated **3** are compared versus those for compound **1** above. NMR signals of SWCNT:**3** protons  $\alpha$  to carbonyl are shifted downfield 0.47 ppm for HiPco and 0.08 ppm for SWeNT brands, protons  $\beta$  to carbonyl are shifted 0.24 ppm for HiPco and 0.08 ppm for SWeNT. Protons  $\gamma$  to carbonyl are shifted 0.30 ppm for HiPco and 0.02 ppm for SWeNT SWCNT. Similarly, protons  $\alpha'$  to nitrogen are shifted 0.38 ppm for HiPco and 0.07 ppm for SWeNT, and  $\beta'$  protons are shifted 0.27 ppm for HiPco and 0.08 ppm for SWeNT SWCNT. Position labels  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\alpha'$ ,  $\beta'$  in **3** are identified in Table 1.

The <sup>1</sup>H NMR chemical shift change differences in compound **1** upon association with SWCNTs of either brand, are downfield  $\sim 0.07$  – 0.09 ppm. Association with SWeNT SWCNTs produces a similarly small downfield shift in compound **3**. These small changes indicate a weak association of **1** and **3** with the SWeNT brand. But greater NMR signal changes for all protons of compound **3** as compared to **1**, upon HiPco SWCNT association, indicates more association with (1) increased separation between the carbonyl and amino functionalities and (2) greater conformational freedom of the acyclic molecule. Thus, association with HiPco SWCNTs effects the greatest change in NMR shifts upon protons  $\alpha$  to carbonyl. Again, acyclic **3** has conformational freedom which enables it to be more accommodating sterically and have a stronger association with SWCNTs than **1** does.

## 2.3 Carbonyl versus nitrogen complexation

Compounds **2b** and **3** have the same functionalities, but differ in intervening methylene groups (**2b**,  $n = 0$ ; **3**,  $n = 3$ ). Compound **1** is analogous to **2c**, with the ends tethered. These compounds offer the opportunity to compare changes in NMR chemical shifts of protons  $\alpha$  to carbonyl versus those  $\alpha$  to nitrogen. Upon association with SWCNTs, compounds **1**, **2b**, and **2c** show only a marginally greater proton chemical shift change at protons  $\alpha$  to carbonyl rather than  $\alpha$  to nitrogen. The same trend is observed in compounds **3**, but much larger in magnitude, 0.47 ppm for

protons  $\alpha$  to carbonyl versus 0.38 ppm for those  $\alpha$  to nitrogen. Hence, these results reveal that protons closer to the carbonyl functionality are closer to the major point of association with SWCNTs than those near nitrogen, regardless of SWCNT brand. This supports the hypothesis that amide compounds show a marginally greater association with SWCNTs at the carbonyl end under wet paste conditions, as found previously for simple amides.<sup>8b</sup> Compound **3** experiences the greatest change upon association with SWCNTs, probably due to its conformational flexibility.

It should be mentioned that compound **3** has no protons  $\beta$  to the carbonyl, which are remote to nitrogen, as do compounds **2c** and **2d**. In compounds **2c** and **2d**, it is these  $\beta$  protons, remote to nitrogen, which show the greatest NMR shift changes.

### 2.3 Association with C=O or N electron pairs

The 2-aminoethanol series **4** (Figure 1) explores steric effects due to increasing substituents in  $\text{NR}_2$  ( $\text{R} = \text{H}$  **4a**,  $\text{Me}$  **4b**,  $\text{Et}$  **4c**). For each, NMR proton shift changes in **4a** – **4c** were measured upon association with SWCNTs. The greatest changes in NMR shifts upon SWCNT association were in hydroxyl and amino protons. The  $^1\text{H}$  NMR shift for the hydroxyl functionality in each compound **4** at 1:40 concentration (**4a**, 2.55 ppm; **4b**, 3.53 ppm; **4c**, 3.20 ppm) is comparable to its literature value<sup>28</sup> (**4a**, 2.76 ppm; **4b**, 3.67 ppm; **4c**, 3.41 ppm). It should be noted that an alternate literature report<sup>25a</sup> for **4c** incorrectly assigns the hydroxyl proton to the spurious signal at 7.35 ppm, which is actually due to the typically-observed slight  $\text{CHCl}_3$  contamination in  $\text{CDCl}_3$  NMR solvent. Similarly to the literature reports, NMR spectra of the uncomplexed hydroxyl compounds herein usually do not show a well-defined separate hydroxyl proton signal. One reason for this is because the NMR signals for hydroxyl protons in compounds **4** often accidentally coincide with or overlap another signal. For example, in compound **4a**, the signal for OH overlaps that for  $\text{NH}_2$ , as revealed by the signal integration values.

In compound **4a**, hydroxyl and amino proton signals accidentally coincide, and both are shifted downfield upon complexation with SWCNT: 1.91 ppm (2.55 – 4.46 ppm) for HiPco, and 3.63 ppm (2.55 – 6.18 ppm) for SWeNT. The hydroxyl proton signal for neither **4b** nor **4c** associated with SWeNT SWCNT was observed, but they were shifted 0.73 ppm and 3.96 ppm respectively, upon HiPco complexation. The other protons experienced considerably smaller NMR shift changes, as discussed below. The greater chemical shift changes of heteroatom-bonded protons, is due to these protons being closer to the points of associated with SWCNTs than are those bonded to carbons.

Changes in NMR chemical shifts of the protons  $\alpha$  to OH in the presence, versus the absence, of SWCNTs can also be compared to those  $\alpha$  to  $\text{NR}_2$  ( $\beta$  to OH). This can reveal the relative contributions of lone pairs on O, versus

lone pairs on N, to SWCNT:**4** association. Protons  $\alpha$  to nitrogen experience greater chemical shift change regardless of substituents on nitrogen and regardless of SWCNT brand, which indicates a stronger SWCNT association with N lone pairs than with O lone pairs. Signals for protons  $\alpha$  to hydroxyl in **4a** are shifted downfield 0.12 ppm (3.48 – 3.60 ppm) for HiPco and 0.17 ppm (3.48 – 3.65 ppm) for SWeNT brands;  $\beta$  protons are shifted downfield 0.15 ppm (2.70 – 2.85 ppm) for HiPco and 0.19 ppm (2.70 – 2.89 ppm) for SWeNT. In **4b**, protons  $\alpha$  to OH are shifted downfield 0.11 ppm (3.53 – 3.64 ppm) for HiPco and 0.63 ppm (3.53 – 4.16 ppm) for SWeNT;  $\beta$  protons are shifted 0.16 ppm (2.39 – 2.55 ppm) for HiPco and 1.09 ppm (2.39 – 3.48 ppm) for SWeNT. Dimethyl protons in **4b** are shifted 0.15 ppm (2.19 – 2.34 ppm) for HiPco and 1.14 ppm (2.19 – 3.33 ppm) for SWeNT. Protons  $\alpha$  to OH in **4c** are shifted downfield 0.28 ppm (3.48 – 3.76 ppm) for HiPco and 0.64 ppm (3.48 – 4.12 ppm) for SWeNT;  $\beta$  protons 0.35 ppm (2.53 – 2.88 ppm) for HiPco and 0.87 ppm (2.53 – 3.40 ppm) for SWeNT. In **4c**, both sets of methylene protons  $\alpha$  to N are shifted downfield 0.36 ppm (2.50 – 2.86 ppm) for HiPco and 0.88 ppm (2.50 – 3.38 ppm) for SWeNT and methyl protons are shifted downfield 0.26 ppm (0.97 – 1.23 ppm) for HiPco and 0.38 ppm (0.97 – 1.35 ppm) for SWeNT.

Thus, the trend in NMR chemical shift changes for CH protons in free versus HiPco SWCNT associated with **4a**, **4b**, and **4c** ( $\text{R} = \text{H}$ ,  $\text{Me}$ , and  $\text{Et}$  respectively) is 0.12 ppm, 0.11 ppm, and 0.28 ppm for  $\alpha$  to OH, and 0.15 ppm, 0.16 ppm, and 0.35 ppm for  $\beta$  protons. Similarly, magnitudes of NMR signal changes of SWeNT SWCNT associated with **4** are 0.17 ppm, 0.63 ppm, and 0.64 ppm respectively for protons  $\alpha$  to OH, and 0.19 ppm, 1.09 ppm, and 0.87 ppm respectively for  $\beta$  protons. Protons  $\alpha$  to  $\text{NR}_2$  experience greater chemical shift change than those  $\alpha$  to OH, in order to determine the relative degrees of association of the two functionalities. However, the changes in CH protons both near OH and near N are significant, suggesting that both groups are associating with SWCNT, as portrayed in Figure 2.

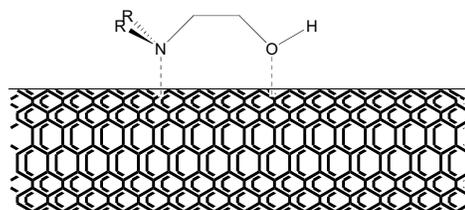


Figure 2. Association of 2-aminoethanol **4** involving SWCNT with lone pairs of both N and O.

Changes in chemical shifts of protons bonded to carbon generally increase with increasing size of the group on nitrogen, in the order  $\text{Et} > \text{Me} > \text{H}$ . These associations with SWCNTs might be expected to be increasingly hindered by increasing steric requirements, as they were in series **2**, but the opposite is observed in series **4**. Upon association with

SWCNTs, greater changes in NMR proton shifts are observed for **4b** and **4c** which have larger substituents than **4a** regardless of SWCNT brand. This indicates that electronic effects of groups on nitrogen are overriding the steric effects of these substituents here, increasing donation

of electrons by R to N in the general order Et > Me > H. Note that this is opposite to the results found for amides,<sup>8b</sup> in which steric effects outweighed electronic effects in these wet paste samples of SWCNT complexes.

**TABLE 1. <sup>1</sup>H NMR CHEMICAL SHIFT VALUES FOR ORGANONITROGENS 1 – 4 IN THE ABSENCE OF SWCNTS AND IN THEIR PRESENCE AS A WET PASTE**

complexing agent	SWCNT brand	chemical shift (ppm)											
		protons near C=O or COH						NR <sub>2</sub> protons				OH protons	
		α	Δα	β	Δβ	γ	Δγ	amino/α'	Δα'	β'	Δβ'	α	Δα
 <b>1</b>	none	2.28		1.94		3.30		2.76					
	HiPco	2.36	0.08	2.01	0.07	3.37	0.07	2.83	0.07				
	SWeNT	2.37	0.09	2.01	0.07	3.37	0.07	2.84	0.08				
 <b>2a</b>	none	7.98						2.88					
	HiPco	-						-					
	SWeNT	8.28	0.30					3.08	0.20				
 <b>2b</b>	none	2.02						2.92					
	HiPco	2.08	0.06					2.97	0.05				
	SWeNT	2.15	0.13					3.03	0.11				
 <b>2c</b>	none	2.24		1.03				2.88					
	HiPco	2.32	0.08	1.13	0.10			2.96	0.08				
	SWeNT	2.34	0.10	1.26	0.23			2.90	0.02				
 <b>2d</b>	none	2.79		1.08				2.97					
	HiPco	2.80	0.01	1.10	0.02			2.99	0.02				
	SWeNT	2.85	0.06	1.28	0.20			3.07	0.10				
 <b>2e</b>	none			1.28				3.04					
	HiPco			-				-					
	SWeNT			1.32	0.04			3.08	0.04				
 <b>2f</b>	none			7.44				3.08					
	HiPco			-				-					
	SWeNT			7.44	0.00			3.09	0.01				
 <b>3</b>	none	2.08		1.65		2.39		2.43		0.93			
	HiPco	2.55	0.47	1.89	0.24	2.69	0.30	2.81	0.38	1.20	0.27		
	SWeNT	2.16	0.08	1.73	0.08	2.41	0.02	2.50	0.07	1.01	0.08		
 <b>4a</b>	none	3.48		2.70				2.55				2.55	
	HiPco	3.60	0.12	2.85	0.15			4.46	1.91			4.46	1.91
	SWeNT	3.65	0.17	2.89	0.19			6.18	3.63			6.18	3.63
 <b>4b</b>	none	3.53		2.39				2.19				3.53	
	HiPco	3.64	0.11	2.55	0.16			2.34	0.15			4.26	0.73
	SWeNT	4.16	0.63	3.48	1.09			3.33	1.14			b	-
 <b>4c</b>	none	3.48		2.53				2.50		0.97		3.20	
	HiPco	3.76	0.28	2.88	0.35			2.86	0.36	1.23	0.26	7.16	3.96
	SWeNT	4.12	0.64	3.40	0.87			3.38	0.88	1.35	0.38	b	-

## CONCLUSION

Magnitudes of changes in NMR chemical shift values indicate the degree to which SWCNTs associate with compounds such as amino alcohols and amides. NMR data for amides **1 - 3** indicate that that carbonyl association with SWCNTs is a stronger interaction. Changes in NMR shifts of aminoalcohols, which occur upon association with SWCNTs, reveal that SWCNTs interact with nitrogen lone pairs in **4a - c**. In amides, steric effects appear to be more important to forming a stronger association, while electronic effects are more important in aminoalcohols. Therefore, compounds with these structural characteristics

are expected to associate more strongly and better disperse nanostructures generally as individual molecules.

In compounds associated with SWCNTs, three characteristics generally have the greatest effect on NMR chemical shifts and therefore are predicted to disperse SWCNTs best: (1) multiple atoms and  $\pi$  bonds, which possess lone pairs for donation to the SWCNT surface, (2) such functional groups separated by a number of methylene units, so they can associate with SWCNTs independently of each other, and (3) a linear molecular framework, as opposed to a cyclic one, in order to enable greater conformational freedom in the molecule, increasing its ability to interact and associate with the SWCNT surface.