Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2010 May 14; 114(22): 10140–10147. doi:10.1021/jp1017746.

Effect of Single-Walled Carbon Nanotube Association upon ^1H NMR Spectra of Representative Organonitrogen Compounds

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Abstract

This report is important to achieving SWCNT solvation, understanding adsorption of molecules on SWCNT surfaces, and SWCNT characterization by NMR. Complexation of 1-methyl-2-pyrrolidone (NMP) and other selected organonitrogens with single-walled carbon nanotubes (SWCNTs) was studied by proton nuclear magnetic resonance (NMR). The magnitude of ^1H 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 ^1H NMR signals of the organonitrogen compounds, which accompany SWCNT:organonitrogen association, are dependent upon (1) type of proton within R (α , β , etc.), (2) proximity to the carbonyl (R-CO versus NR_2), (3) steric effects of alkyls, (4) electronic effects of alkyls, and (5) effects of tethering two ends of a molecule.

Introduction

Single-walled carbon nanotubes (SWCNTs) have recently gained considerable attention due to their wide range of applications^{1a–e} and anticipation of their further development in additional fields.^{1f–7h} SWCNTs are promising candidates for semiconductors in field effect transistors,² sensors for highly sensitive and selective molecular detection,^{3a} specific protein detection^{3b} and memory elements.⁴ However, due to strong van der Waals interactions between SWCNT sidewalls, they exist as bundles,^{1g} so a key challenge for exploiting SWCNTs widely is overcoming their nonpolar nature, which fosters a solvation problem and restricts their stable dispersion, solubilization, and separation.^{5–7} Different and improved dispersal techniques are needed in order to increase SWCNT reactivities, take advantage of their novel structural, electrical, and mechanical properties,⁸ attain higher purities,^{6d,f} and enable their alignment for molecular device development.⁴

A better understanding of the interactions of molecules with SWCNT surfaces would benefit some important applications of SWCNTs, such as molecular sensing,³ which involve adsorption of molecules onto SWCNT surfaces, as well as their dispersal in solvent. Much recent effort has been committed to improving SWCNT solubility by using ionic^{11a,c} or nonionic surfactants,^{11b,c} frequently combined with covalent¹² or noncovalent¹³ side-wall

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Supporting Information Available

Literature²⁶ NMR chemical shift values of uncomplexed organonitrogen compounds are compared versus values from this study taken of solutions at 1:40 concentration (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

functionalization. However, many of these procedures^{6b–d,9,11–13} can disrupt the electronic structure of SWCNTs and cause problems in their subsequent applications.

SWCNTs display exceptional adsorption properties because of their high surface area to volume ratio.¹⁴ Recent adsorption studies of SWCNTs with molecules, such as amines,¹⁵ aminoacids,¹⁶ ketones,¹⁷ amides,^{1d,e,18} CO₂,¹⁹ NH₃,¹⁴ hydroxyl,²⁰ and water,²¹ show that the functionalities in those molecules have a great tendency to associate with SWCNTs. Understanding associations with these simple groups will help understand and design interactions with other molecules containing such functional groups, such as surfactants, which disperse SWCNTs in solvent by forming a lamellar pattern on their surfaces.²² Larger molecules such as DNA²³ and polymers²⁴ are reported to interact with SWCNT either by wrapping^{23,24b–d} or linear associations.^{24a,e}

The organic solvents *N,N*-dimethylformamide (DMF)^{1a–e} and 1-methyl-2-pyrrolidone (NMP)¹ are known to increase the solubility of SWCNTs, and both have been used as solvent in ultrasonic debundling of SWCNTs.¹ Recently, the effect of SWCNT association upon amides was investigated,^{5b} in order to ascertain the molecular characteristics giving rise to the unusual capability of amides, especially DMF, to solvate SWCNTs. It is desirable to compare and contrast these characteristics of DMF versus those of NMP. Recent studies reveal that the solvating capability of NMP is not restricted to SWCNTs, but that solubilities of nanomaterials in general is increased in the presence of NMP,^{1b,g,h,10} as was the case for DMF.^{5b} Therefore, identifying and comparing such molecular characteristics of both NMP and DMF, which facilitate complexing with and solvating SWCNTs, could be applicable to nanomaterials generally. However, the role of NMP has not been fully investigated in any of the above systems.¹ The unusual solvating capabilities of DMF and other amides upon SWCNTs were explored^{5b} in two physical states of samples; the organic solvent and amide were evaporated from the reaction mixture to give either a concentrated solution or a wet paste, followed by sonication in an NMR solvent. NMR value differences between pure amide and wet paste sample were up to 10 times those observed in concentrated solution samples, suggesting that the wet paste sample preparation method effects a stronger SWCNT:amide association, which would be more conducive to solvation.^{5b}

A major deterrent to the use of NMR to analyze SWCNTs has been peak broadening, which most likely arises from residual paramagnetic metal catalysts used in the SWCNT synthesis.^{13b} However, NMR can be a powerful tool in SWCNT characterization, with advantages, such as that over Raman spectroscopy for quantifying the degree of SWCNT functionalization.²⁵ Nevertheless, there are reports of achieving narrower signals in liquid phase NMR spectra^{5b,15c} and using 2D-NMR as a primary tool to characterize products of SWCNT covalent sidewall functionalization.^{5a} Therefore, NMR is a promising tool, undergoing further developments for SWCNT characterization.

Accordingly, we report the use of ¹H NMR spectroscopy to explore the effect of SWCNTs upon NMP and related organonitrogen compounds. The degree and type of SWCNT complexation was measured by comparing NMR spectra of NMP and related organonitrogen compounds in the presence and absence of SWCNTs. The wet paste conditions and methodology, which were shown to afford the strongest interactions between SWCNTs and amides,^{5b} are used in the studies reported herein.

Results and discussion

Representative organonitrogen compounds **1–5** in this study are shown in Figure 1. 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 **2b** are isoatomic in C, O, and N; their comparison gives the effects of tethering together the ends of **2b**. (2) Increasing the steric requirements of groups bonded to C=O in compounds **2** has been reported,^{5b} but some pertinent data and information are reproduced here for convenience. (3) Comparing compounds **2a** 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. (5) Comparing compounds **4** and **5** gives the effects of having hydroxyl isolated from nitrogen by 2 methylene units versus bonded to nitrogen. NMR spectra of organonitrogen compounds **1–5** in NMR solvent, with and without SWCNTs, enables exploring the above effects upon and trends in these associations, SWCNT:**1–5**. These NMR data are shown in Table 1.

Effect of NMP concentration upon NMR chemical shift

Differentiating among and assigning NMR signals of free, unassociated organonitrogen compounds versus those associated with SWCNTs was essential to this study. NMR signal shifts of amides are dependent upon their concentrations.²⁷ Therefore, it was necessary to establish a threshold concentration of NMP in NMR solvent, below which a constant NMR signal shift would be obtained.²⁷ In order to determine the threshold concentration for accurate NMR signal acquisition, NMR signal values of various concentrations (v:v) of NMP **1** in an NMR solvent CDCl₃ were measured (Table 2). The NMR spectrum of NMP at each concentration showed sharp peaks for methyl and methylene protons. For each signal, the difference between the proton chemical shift at each concentration, was calculated versus that at the concentration of 1:2. The data in Table 2 reveal that at concentrations of 1:40 and below (more dilute), NMP signal shifts are constant. Therefore, the concentration of 1:40 (v:v) was used in taking NMR spectra of **1**, and a more dilute concentration (1:150,000) was used for SWCNT:**1**. Literature values for ¹H NMR signals of **126a** and of **2–5** are given in Table 1 and Table S1 (Supporting Information) respectively for comparison and assignment of some peaks with accidental coincidence. For each compound, in spectra from the two sources, proton signals are in the same order and distance apart in the two, and generally the entire spectrum seems to be shifted downfield slightly. Therefore, differences between the literature values and those established in this study are probably merely due to differences in instrument calibration or sample temperature. Concentrations analogous to those used for **1** and SWCNT:**1** were used in taking ¹H NMR spectra of compounds **2–5** and of SWCNT:**2–5**.

Forming SWCNT:organonitrogens (SWCNT:**1–5**)

SWCNT:organonitrogen associations were effected by the procedure reported earlier.^{5b} The conditions which gave the strongest associations there^{5b} were selected for use in this study; these selections were toluene as reaction solvent, CDCl₃ as NMR solvent, and wet paste as physical state. This wet paste method and the judicious choice of complexing agent, reaction solvent, and NMR solvent minimize complications for NMR signals and expose maximally the SWCNT associated organonitrogen compound signals, as discussed in great detail earlier.^{5b} Therefore, in this study, SWCNTs (either HiPco or SWeNT brand) and a small amount of each complexing agent (one organonitrogen **1–5**) were suspended in a small amount of toluene by sonication, in order to achieve SWCNT debundling, dispersion, and association with the complexing agent. The SWCNT:**1–5** solution was allowed to evaporate for 3–5 days at ambient temperature, giving a wet paste.

A small amount of the wet paste sample was then dissolved by sonication in the NMR solvent CDCl₃, and the proton chemical shift values (ppm) were then measured by using ¹H NMR. The results are compiled in Table 1. The NMR spectra of compound **1** are shown in Figure 2 as representative examples of the NMR spectra of compounds **1–5**. NMR data for

SWCNT:**1** – **5** wet paste samples are compared to NMR data for free organonitrogen compounds **1** – **5** in Table 1. The near-complete removal of solvent and free complexing agent from SWCNT:**1** – **5** samples simplify their NMR spectra, but signals for SWCNT:**1** – **5** are nevertheless small and somewhat obscure. Similarly to the previous report,^{5b} changes (broadening and downfield shifts) in ¹H NMR signals of the organonitrogen compounds, which accompany SWCNT:organonitrogen association, were found to be dependent upon (1) type of proton within R (α , β , etc.), (2) proximity to the carbonyl (R-CO versus NR₂), (3) steric effects of alkyl substituents, (4) electronic effects of alkyl substituents, and (5) tethering effects.

A. Compounds 1 and 2: Steric effects and cyclization—Compounds **1** and **2b** are isoatomic in C, H, and O; their structural difference is that the two ends of **1** forms **2b** are tethered, as shown in Figure 3. 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, ¹H 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. Data for **2a** and **2c** were used for comparison when appropriate.

NMR chemical shift values of protons α 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:**2b**, NMR signals for protons α 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:**2c**, NMR signals of protons α 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.

Protons β and γ 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 β protons of SWCNT:**2b** 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 NMe₂ protons are shifted downfield 0.08 ppm for HiPco and 0.02 ppm for SWeNT respectively. The β protons of SWCNT:**2c** 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 NMe₂ 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 β protons in **2b** and **2c** show more change in chemical shift upon association with SWCNTs than do the other protons in **2b** and **2c**, especially when using the SWeNT brand.

Chemical shift changes, for β protons in **1**, **2b**, and **2c** 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** < **2c** < **2b**. This indicates that β protons of **1** associate less than those of **2b** and **2c** with SWCNTs, suggesting that the conformational freedom of **2b** and **2c** enables them to be more accommodating sterically and enabling a stronger association than in cyclic, rigid **1**. Therefore, in compounds **2b** and **2c** the heteroatom(s) near the β protons can more effectively associate with SWCNTs than those of **1**.

B. Compounds 1 and 3: Cyclic versus acyclic—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, ¹H NMR chemical shift changes of free versus SWCNT-associated **3** are compared versus those for compound **1** above. NMR signals of SWCNT:**3**

protons α to carbonyl are shifted downfield 0.47 ppm for HiPco and 0.08 ppm for SWeNT brands, protons β to carbonyl are shifted 0.24 ppm for HiPco and 0.08 ppm for SWeNT. Protons γ to carbonyl are shifted 0.30 ppm for HiPco and 0.02 ppm for SWeNT SWCNT. Similarly, protons α' to nitrogen are shifted 0.38 ppm for HiPco and 0.07 ppm for SWeNT, and β' protons are shifted 0.27 ppm for HiPco and 0.08 ppm for SWeNT SWCNT. Position labels α , β , γ , α' , β' in **3** are identified in Table 1.

The ^1H 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 α 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.

C. Compounds **1**, **2a**, **2b**, and **3**: Carbonyl versus nitrogen complexation—

Compound **1** is analogous to **2b**, with the ends tethered. These compounds offer the opportunity to compare changes in NMR chemical shifts of protons α to carbonyl versus those α to nitrogen. Upon association with SWCNTs, compounds **1**, **2a**, and **2b** show only a marginally greater proton chemical shift change at protons α to carbonyl rather than α to nitrogen.

Compounds **2a** and **3** have the same atomic groupings at their molecular termini, but they differ in a number of ways, which make these groupings similar but not identical functionalities. Compound **3** is an aminoketone with three methylene groups in between the functional groups, while **2a** is an amide with essentially one functional group. This difference manifests itself in several ways, which are detailed below.

1. The number of methylene groups intervening between the carbonyl group and the amino group is different (**2a**, $n = 0$; **3**, $n = 3$) for the two molecules (Figure 3). The increased linearity of the molecule **3** increases its flexibility and allows it to wrap around the SWCNT and associate via two heteroatoms, rather than merely to associate with SWCNT linearly along one side parallel to its axis. This should enable **3** to interact with the SWCNT more effectively than **2a**.
2. The presence of methylene units between the carbonyl group and the nitrogen group breaks the amide moiety into ketone and amine functionalities. The carbonyl oxygen of **3** has less electron density available due to the lack of carbonyl conjugation with nitrogen. The lone pairs on oxygen are more shared with carbon in **3** than in **2a**, making the carbonyl oxygen of **3** less effective at interacting with the SWCNT. This should make **2a** interact with the SWCNT more effectively than **3**.
3. The nitrogen in **3** receives more electron density from the three electron donating hydrocarbon substituents bonded to the nitrogen than does the nitrogen in **2a** from the two hydrocarbon substituents. This should cause **3** to interact with the SWCNT more effectively than **2a**.
4. The amide **2a** is sp^2 -hybridized and has a delocalized pi-system; its electrons are shared between the carbonyl and nitrogen. Because oxygen is more electronegative, it has a higher electron affinity and a more negative charge than the nitrogen. This leads to the association of amides to SWCNTs through the carbonyl as reported

earlier for the small acyclic amides.^{5b} This should also make **2a** interact with the SWCNT more effectively than **3**. However, this does not predict whether compound **3** should associate with SWCNT more strongly through the carbonyl or the amino functionality.

5. Compound **3** has an NEt_2 functionality, while **2a** has NMe_2 . This difference can have two competing effects upon association of N with SWCNT. Ethyl is more electron-donating than methyl, which will increase the electron density on N, enabling **3** to associate more strongly with SWCNT. Simultaneously, Et is larger than Me, so NEt_2 will incur more steric hindrance for nitrogen association with SWCNT than NMe_2 , which would reduce the ability of **3** to associate with SWCNT. This should make **2a** interact with the SWCNT more effectively than **3**. However, we found previously^{5b} that acyclic small amides complex most strongly with SWCNTs under wet paste conditions, through the carbonyl functionality rather than NR_2 ; therefore, this comparison of factors favoring complexation of SWCNT with NEt_2 in **3** more than NMe_2 in **2a** is a secondary consideration.

Only experiment can reveal which of the above predictions are correct: (A) whether **3** or **2a** associates with SWCNT more strongly and (B) whether stronger association of SWCNT with **3** will be via the carbonyl (as it was in **2a**) or via the amino functionality.

Experiment reveals that a preference for complexation of SWCNT with carbonyl over complexation with nitrogen is observed in compound **3**, which is revealed by the relative magnitudes of the protons nearby, 0.47 ppm for protons α to carbonyl versus 0.38 ppm for those α to nitrogen. Hence, the results in Table 1 reveal that protons in **3**, which are closer to the carbonyl functionality have a greater change in chemical shift than those near nitrogen, regardless of SWCNT brand. This supports the hypothesis that aminoketones show a marginally greater association with SWCNTs at the carbonyl end under wet paste conditions, as found previously for simple amides.^{5b}

Experiment reveals further that upon association with SWCNTs, the protons of **3** experience greater change in NMR shift than those of **2a**. Factors favoring complexation with **3** are (a) the greater conformational flexibility of **3** and (b) nitrogen bearing 3 alkyls instead of 2. However, the greater chemical shift of protons near the carbonyl than near nitrogen indicates that changing characteristics of nitrogen should be of secondary importance. Therefore, the preference for SWCNT complexation with **3** over **2a** is probably due mainly to the conformational flexibility of the former.

It should be mentioned that compound **3** does not have protons β to the carbonyl, which are remote to nitrogen, as do compounds **2b** and **2c**. In compounds **2b** and **2c**, it is these β protons, remote to nitrogen, which show the greatest NMR shift changes.

D. Compounds 4: Association with oxygen and/or nitrogen electron pairs—

The 2-aminoethanol series **4** (Figure 1) explores steric effects due to increasing substituents in NR_2 ($\text{R} = \text{H}$ **4a**, Me **4b**, Et **4c**). For each, NMR proton shift changes in **4a–c** were measured upon association with SWCNTs. The greatest changes in NMR shifts upon SWCNT association were in hydroxyl and amino protons. The ^1H 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 in Table S1 (**4a**, 2.76 ppm; **4b**, 3.67 ppm; **4c**, 3.41 ppm). It should be noted that an alternate literature report^{26a} for **4c** incorrectly assigns the hydroxyl proton to the spurious signal at 7.35 ppm, which is actually due to the typically-observed slight CHCl_3 contamination in 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 NH₂, 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, indicates that these protons are more strongly associated with SWCNTs than are those bonded to carbons.

Changes in NMR chemical shifts of the protons α to OH in the presence, versus the absence, of SWCNTs can also be compared to those α to NR₂ (β to OH). This can reveal the relative contributions of lone pairs on O, versus lone pairs on N, to SWCNT:**4** association. Protons α 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 α 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; β 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 α 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; β 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 α 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; β 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 α 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 **4a**, **4b**, and **4c** (R = H, Me, and Et respectively) is 0.12 ppm, 0.11 ppm, and 0.28 ppm for α to OH, and 0.15 ppm, 0.16 ppm, and 0.35 ppm for β protons. Similarly, magnitudes of NMR signal changes of SWeNT SWCNT associated **4** are 0.17 ppm, 0.63 ppm, and 0.64 ppm respectively for protons α to OH, and 0.19 ppm, 1.09 ppm, and 0.87 ppm respectively for β protons. Protons α to NR₂ experience greater chemical shift change than those α to OH, which can be used 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 4.

Changes in chemical shifts of protons bonded to carbon generally increase with increasing size of the group on nitrogen, in the order Et > Me > H. The associations of nearby heteroatoms with SWCNTs might be expected to be increasingly hindered by increasing steric requirements, as they were in series **2,5b** 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. This trend

is opposite to the results found for amides, **5b** in which steric effects at carbonyl outweighed electronic effects in these wet paste samples of SWCNT complexes.

E. Compounds **4c and **5**: Effects of O to N proximity**—It was desirable to compare interactions with SWCNTs of both N and O, when they are remote versus directly bonded to each other. NMR data for compound **5**, both SWCNT-associated and unassociated, are shown in Table 1. The NMR signals for **5** after complexation with SWCNTs are somewhat approximate or undetectable, due to signal broadening, as well as accidental coincidence and signal overlapping, as discussed earlier for **4c**. In **5**, the hydroxyl peak overlaps those of the aromatic protons, in both this study and the literature report (Table S1).^{26a}

In SWCNT:**5**, the proton directly attached to oxygen is shifted 0.90 ppm (7.00 – 7.90 ppm) for SWeNT tubes, and not observed with HiPco tubes. The relative magnitudes of chemical shift changes in **4c** versus **5** upon complexation should compare the effects of proximity to O and to N in **4c** versus **5**. However, it is very hard to draw any comparison, because neither SWeNT nor HiPco tubes produced OH signals with both **4c** and **5** upon association. SWCNT:**4c** gave no OH signal with SWeNT tubes, and SWCNT:**5** gave no OH signal with HiPco tubes. Thus, the only comparison of **4c** and **5** available uses observations with different types of SWCNTs; SWCNT:**4c** is with HiPco, while SWCNT:**5** is with SWeNT. Nevertheless, a very rough approximation is possible by considering data from SWCNT:**4a**, which gave a OH signal both with SWeNT and with HiPco tubes. Upon complexation, the OH signal of **4a** was shifted downfield more with SWeNT (3.63 ppm) than HiPco (1.91 ppm) nanotubes. This raises the possibility that complexation with the SWeNT brand may usually effect greater change in the NMR signal shifts, because this is the case with all compounds studied herein, except **3**.

Comparing **4c** vs **5**, the chemical shift change for hydroxyl in **4c** (3.96 ppm with HiPco) is greater than that of **5** (0.90 ppm with SWeNTs). The observations from SWCNT:**4a** with both types of tubes indicates that SWeNTs can be expected to effect greater change than HiPco upon complexation. Therefore, because the SWeNT-effected change in **5** is so much less than that of HiPco, one could predict that complexation of OH in **5** will be less than in **4c**. This suggests a possibility that heteroatoms separated by 2 methylene units are more associated than when they are directly bonded. However, both suggestions from these data are very tentative, due to incorporating a rough approximation, which is based on an observation using a correction that has not been shown to be general.

NMR chemical shift changes of protons β to nitrogen in **4c** and **5**, upon association with SWCNTs, were compared. Their values were 0.26 ppm and –0.01 ppm respectively for HiPco SWCNTs and 0.38 ppm and 0.37 ppm for SWeNT SWCNT; the NMR chemical shift of protons β to nitrogen are marginally less than that of **4c**. It raises the question whether remote heteroatoms (as in **4c**) will generally enhance the association of organonitrogen compounds more than directly-bonded ones (as in **5**). One more reason for this is that **4c** has more conformational flexibility than rigid **5**, which allows the organonitrogen to associate effectively. This strengthens the concept that conformational flexibility enhances the association of protons β to nitrogen.

SWCNT:1 – 5 Raman studies

The Raman spectrum of each compound studied herein, SWCNT:**1**, SWCNT:**2**, SWCNT:**3**, SWCNT:**4** and SWCNT:**5**, has both D-band and G-band identical in appearance to those of pristine SWCNT (p-SWCNT). They evidence no covalent bond formation to SWCNT and support the concept that the interaction between SWCNTs and complexing agents **1** – **5** herein are associations, similar to those reported previously.^{5b,13a}

Association

The previous report^{5b} on the effect of SWCNT association upon representative dimethylamides **2**, (R = H, Me, Et, *i*-Pr, *t*-Bu, and Ph) indicates that chemical shift change is a measure of degree of adsorption. A stronger association with SWCNTs produces a larger NMR chemical shift change; a small change indicates weak association with SWCNTs. Raman spectral analysis of the SWCNT:complexing agent reveals that there is no bond formation, which confirms the interaction between these two is purely association.

The proton chemical shift change upon association of compounds **2b** and **2c** with SWCNTs is larger for protons β to carbonyl than in compound **1**, indicating a greater degree of heteroatom association with SWCNTs. This suggests that molecules with greater conformational freedom generally associate more strongly with SWCNTs. Another example of this can be seen by comparing the proton shift changes of compounds **1** versus **3**, which has more conformational flexibility; the greater change in **3** upon association reveals that the effect of separation by a long chain between the functionalities permits greater functional group association with SWCNTs.

In compound **4**, protons bonded to the heteroatoms show a higher magnitude of change than other carbon bonded protons, due to their proximity to the heteroatoms which are associating with the SWCNT. It is possible to determine which region of the molecule is associated to the SWCNT more strongly by examining relative magnitudes of NMR chemical shift changes for different protons in a molecule upon SWCNT association. SWCNT:**4a**, SWCNT:**4b**, and SWCNT:**4c** each shows greater change in shifts of protons α to the amino group than those α to the alcohol functionality. This indicates that 2-aminoalcohols **4** form stronger associations at the amino nitrogen than at the hydroxyl oxygen. However, in SWCNT:**4a** the shift changes of protons α to nitrogen are only marginally greater than those α to oxygen. Increasing the size of R on nitrogen in **4** increases its association. This is because increasing the size of the alkyl group on N has a significant inductive effect; this increases the availability of the nonbonding pair on N, outweighing the steric effect.

In summary, the protons do not themselves interact or associate with the SWCNT, but their chemical shift changes arise from changes in their chemical environments. This is due to their being directly bonded to the heteroatoms, which are interacting or associating with the SWCNT. It is these associations which enable these compounds to disperse SWCNTs and effect SWCNT debundling and dispersion.

Effecting dispersion

Recent studies on the degree of a compound's association with SWCNTs conclude that it directly relates to the degree of SWCNT dispersion.^{5b,28} Formation of stronger associations of compounds **1** – **5** with SWCNTs are accompanied by greater NMR value changes, which are caused by an increased SWCNT:organonitrogen interaction. Therefore, the magnitude of change in an NMR spectrum of a compound, after its association with SWCNTs, also helps predict its capability to disperse SWCNTs and effect SWCNT debundling. Thus, association of SWCNTs with carbonyl end in **1**, **2**, and **3**, nitrogen in **4**, and oxygen in **4** and **5** enables those compounds to disperse SWCNTs, which effects SWCNT debundling and dispersion. Because NMP is known to increase nanomaterial solvation generally,^{1b,g,h,10} a similar phenomenon may also be occurring with other nanostructures in order to disperse them as individual molecules.

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** – **2** and the aminoketone **3** indicate that that oxygen lone pair association with SWCNTs is a stronger interaction. Changes in NMR shifts of aminoalcohols, which occur upon association with SWCNTs, reveal that SWCNTs interact more 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) having multiple atoms and π bonds, which possess lone pairs for donation to the SWCNT surface, (2) having such functional groups separated by a number of methylene units, so they can associate with SWCNTs independently of each other, and (3) having an acyclic long-chain molecular framework, as opposed to a cyclic or smaller one, in order to enable greater conformational freedom in the molecule and to increase its ability to interact and associate with the SWCNT surface.

Experimental Section

Chemicals

Complexing agents **1** – **5** were purchased from Aldrich Chemical Co. Purified powder p-SWCNTs were purchased from Unidym, Inc (HiPco PO 279).^{29a} and donated from Southwest Nanotechnologies, Inc.^{29b} All were used without further treatment.

Evaporation of SWCNT:1 – 5 samples to wet paste

The procedure for formation of SWCNT:NMP is given as an example. Adapting procedures reported previously,^{5b} NMP association with SWCNTs was explored by horn sonicating (30 min) p-SWCNT (0.5 mg), NMP (30 mg), and toluene solvent (4 mL). The p-SWCNT/NMP solution was evaporated to wet paste consistency (~5 days). Then a solution of the residual wet paste (~0.1 mg) in *d*-chloroform (10 mL) was prepared by horn sonication (30 min). SWCNT:5 contains a mixture of the complex and starting materials.

NMR spectra

Each sample of free **1** – **5** was prepared for NMR spectrum acquisition by dissolving a small amount (0.25 mL) in *d*-chloroform (~10 mL). Each sample of SWCNT:1 – 5 was prepared by dissolving a small amount of the wet paste (~0.1 mg) in *d*-chloroform (10 mL). The resulting solution was added by pipette into a 5 mm NMR tube (Wilmad, 503-PS). NMR measurements of free **1** – **5** (1:40 concentration (v:v) of sample:solvent) and SWCNT:1 – 5 (1:150,000 concentration (w:w)) were acquired on a Varian VXR-300 or a Varian VMX-400 Spectrometer, with a typical run time of about 30 min (~1000 transients). The typical error in NMR shifts reported herein is $\leq \pm 0.00098$ ppm.

Raman spectra

Raman spectra were measured using microscope laser Raman spectroscopy with a Jobin Yvon-LabRam spectrometer. The laser excitation wavelength was 632 nm with a spectral resolution of 4 cm^{-1} .

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We acknowledge the National Science Foundation and National Institute of Health for support of this research. We are grateful to SouthWest NanoTechnologies for a donation of pristine single-walled carbon nanotubes. We appreciate the assistance of Susan Nimmo in arranging NMR acquisition.

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Figure 1.

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

Figure 2. ^1H NMR spectra of (A) 1-methyl-2-pyrrolidone (NMP) **1** in CDCl_3 , (B) HiPco SWCNT:**1** wet paste sample using toluene and CDCl_3 solvents, and (C) SWeNT SWCNT:**1** wet paste sample using toluene and CDCl_3 solvents.

Figure 3.
Structural similarities in exploring tethering (**1** vs **2b**) and functional group proximity (**2a** vs **3**)

Figure 4.
Representation of association between 2-aminoethanols **4** and SWCNT, by using lone pairs of both N and O.

Table 1
¹H NMR Chemical Shift Values for Organonitrogens **1–5** in Presence and Absence of SWCNTs.

complexing agent	SWCNT brand	chemical shift (ppm)											
		protons near C=O or COH						NR ₂ protons			OH protons		
		α	$\Delta\alpha$	β	$\Delta\beta$	γ	$\Delta\gamma$	amino/ α'	$\Delta\alpha'$	β'	$\Delta\beta'$	α	$\Delta\alpha$
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
none	2.02						2.92					
	HiPco	2.08	0.06					2.97	0.05				
	SWeNT	2.15	0.13					3.03	0.11				

complexing agent	SWCNT brand	chemical shift (ppm)											
		protons near C=O or COH						NR ₂ protons					
		α	$\Delta\alpha$	β	$\Delta\beta$	γ	$\Delta\gamma$	amino/ α'	$\Delta\alpha'$	β'	$\Delta\beta'$	OH protons	α
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				
	none	2.79		1.08				2.97					
	HiPco	2.80	0.01	1.10	0.02			2.99	0.02				

complexing agent	SWCNT brand	chemical shift (ppm)											
		protons near C=O or COH						NR ₂ protons			OH protons		
		$\Delta\alpha$	β	$\Delta\beta$	γ	$\Delta\gamma$	amino/ α'	$\Delta\alpha'$	β'	$\Delta\beta'$	α	$\Delta\alpha$	
		α
SWeNT	2.85	0.06	1.28	0.20		3.07	0.10					
	none	2.08		1.65	2.39		2.43		0.93				
	HiPco	2.55	0.47	1.89	2.69	0.30	2.81	0.38	1.20	0.27			
	SWeNT	2.16	0.08	1.73	2.41	0.02	2.50	0.07	1.01	0.08
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
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			<i>b</i>	-	-
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	<i>b</i>	-	-
none								2.29			7.00 ^a	
	HiPco								2.28	-0.01		<i>b</i>	-
	SWeNT								2.66	0.37		7.90	0.90

^aRef. 26a.

b_q No signal observed.

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Table 2

¹H NMR Chemical Shifts of NMP **1** with various concentrations of CDCl₃.

concentration (NMP:CDCl ₃)	chemical shift (ppm) for protons in NMP									
	α		Δ		β		Δ		γ	
	α	Δ	α	Δ	β	Δ	β	Δ	γ	Δ
1:2	1.64		1.36		2.74		2.15		0.42	
1:10	2.08	0.44	1.76	0.40	3.13	0.39	2.56	0.42		
1:20	2.21	0.13	1.87	0.11	3.24	0.11	2.68	0.12		
1:30	2.29	0.08	1.95	0.08	3.31	0.07	2.76	0.08		
1:40	2.28	-0.01	1.94	-0.01	3.30	-0.01	2.76	0.00		
1:50	2.27	-0.01	1.93	-0.01	3.29	-0.01	2.75	-0.01		
1:10 ^a	2.36	0.28 ^b	2.04	0.28 ^b	3.41	0.28 ^b	2.85	0.29 ^b

^aRef 26a.

^bDifference between 1:10 concentration values of literature and this study.