

Interaction of Tetraaza[14]annulenes with Single-Walled Carbon Nanotubes: A DFT Study

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As predicted at the B3LYP/LANL2MB level of theory, the adsorption of tetraaza[14]annulene ligands (simple analogues of porphyrins and phthalocyanines) on single-walled carbon nanotubes is insignificantly influenced by the presence of aliphatic (methyl) or/and aromatic (benzo) substituents on the macrocyclic molecules. On the contrary, the adsorption dramatically increases in the case of metal (cobalt) complexes, resulting in substantial changes in their geometry and electronic structure. An increase in negative electrostatic potential at the exposed macrocycle side was found for the Co(II) complexes. It might give rise to an enhanced reactivity toward electrophilic agents, which, along with the strong adsorption predicted, is an encouraging prerequisite for the preparation of new hybrid carbon-nanotube-based catalysts.

I. Introduction

Chemical derivatization (or functionalization) is an efficient and widely used tool to modify the chemical and physical properties of carbon nanotubes (CNTs) and to expand in this way application areas of the latter. All the existing derivatization methods belong to one of two large groups, covalent and noncovalent derivatization.^{1–5} While covalent derivatization can be equally applied to both CNT tips and side walls, the noncovalent technique relies essentially upon physisorption on CNTs (through hydrophobic, π -stacking interactions, etc.) and therefore takes place predominantly on CNT side walls. Both approaches have their advantages and drawbacks, depending on the application area. The main “pro” of noncovalent functionalization is that it does not alter the geometric and electronic structure of CNTs and allows for the introduction of higher concentrations of modifying groups.

Within a short time, aromatic compounds have gained special attention as reagents for noncovalent CNT derivatization. Substituted pyrenes are first to be mentioned, which were primarily employed as molecular anchors^{6–10} as well as for increasing CNT solubility.¹¹ Interaction of other aromatic molecules with CNTs has been recently studied, such as benzene and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone,^{12,13} photoluminescent anthracene derivatives,¹⁴ and 1,2-dichlorobenzene.¹⁵

A very peculiar case of aromatic compounds is tetraazaannulenes. While this generic name by itself might sound unusual, such tetraazaannulenes as porphyrins, porphines, and phthalocyanines are commonly known. These compounds, which are all tetraaza[18]annulenes, along with their simpler tetraazamacrocyclic analogues (including tetraaza[14]annulenes) have been studied extensively for many decades, due to a number of unique structural and electronic properties, allowing for versatile catalytic, optical, electronic, sensor, biomedical, and many other applications.

Thus, it is not surprising that during the three last years, carbon nanotube chemistry has been enriched with the research on new hybrid materials composed of CNTs and tetraazaannu-

lenes. The compounds studied are mainly transition-metal complexes of phthalocyanines,^{16–21} with a focus on photoconductivity properties of the CNT-based hybrids.^{20,21} A smaller number of publications involve porphyrins,^{22–24} describing noncovalent porphyrin-functionalized single-walled carbon nanotubes in solution and the formation of porphyrin–nanotube nanocomposites,²² chemical bonding of hemin to CNTs for oxygen detection,²³ and photophysical properties of chemically bonded porphyrins.²⁴ As regards simpler tetraazaannulenes, the only example we are aware of is our preliminary report on adsorption of tetramethyldibenzotetraaza[14]annulene Ni(II) and Cu(II) complexes on single-walled carbon nanotubes (SWNTs).²⁵ At the same time, further more detailed studies of tetraaza[14]annulene interactions with CNTs are highly desirable, justified by their unique structural and electronic properties,^{26–31} resembling those of porphyrins and phthalocyanines (some relevant comparative data can be found in a recent paper by Bell et al.^{31b} and references therein).

All the above studies were essentially phenomenological, whereas a rational approach to noncovalent CNT derivatization with tetraazaannulenes requires first of all a detailed knowledge of the forces driving the tetraazamacrocyclic attachment to CNT side walls. A way to approach this knowledge is to study the effect of different (aliphatic and aromatic) substituents in the ligand, as well as of the central metal ion in the corresponding complexes, on the adsorption energy. In the present paper, we attempted a systematic theoretical study of interaction of a series of tetraaza[14]annulene ligands and their Co(II) complexes with short SWNT models.

II. Computational Details

The macrocyclic compounds (Figure 1) studied in the present work were [14]annulene (A; contains no heteroatoms), tetraaza[14]annulene ligand (H₂TAA) and its cobalt(II) complex (Co-TAA), tetramethyldibenzotetraaza[14]annulene ligand (H₂TMTAA), dibenzotetraaza[14]annulene ligand (H₂DBTAA), and tetramethyldibenzotetraaza[14]annulene ligand (H₂TMDBTAA) and its cobalt(II) complex (CoTMDBTAA). In this way, we were able to study the effect of adding nitrogen donor atoms to [14]annulene and, subsequently, methyl, benzo groups, and a central

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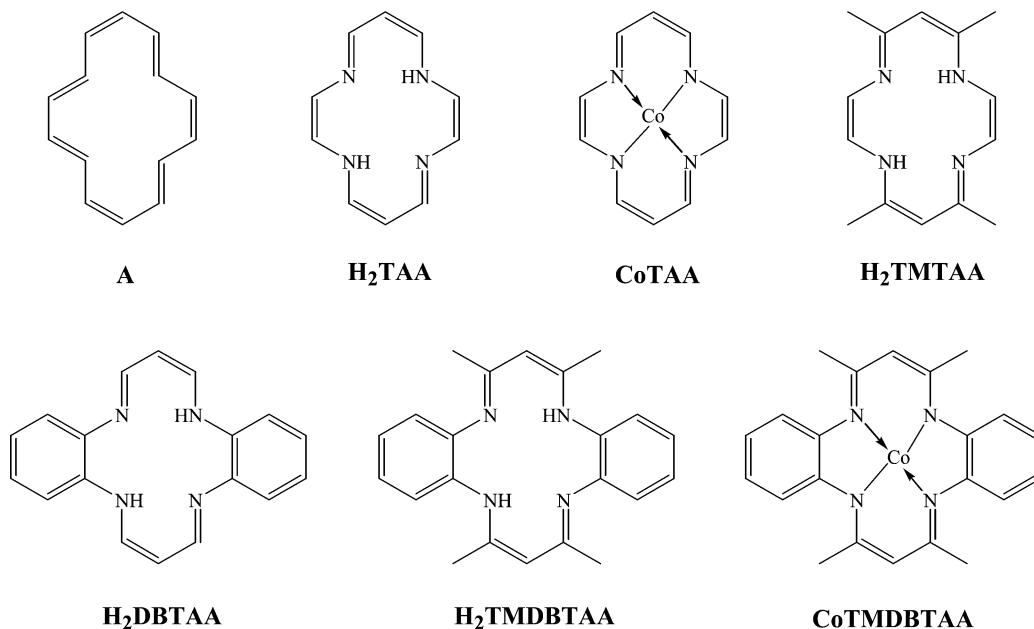


Figure 1. Structures of the compounds studied in the present work: [14]annulene (A), tetraaza[14]annulene ligand (H₂TAA) and its cobalt(II) complex (CoTAA), tetramethyltetraaza[14]annulene ligand (H₂TMTAA), dibenzotetraaza[14]annulene ligand (H₂DBTAA), and tetramethyldibenzotetraaza[14]annulene ligand (H₂TMDBTAA) and its cobalt(II) complex (CoTMDBTAA).

Co(II) atom. These tetraaza[14]annulenes are not hypothetical compounds, being the subject of versatile experimental studies for three decades (see, for example, refs 26–31).

SWNT models employed were armchair (5,5) and zigzag (8,0) nanotubes (Figure 2), referred to as ANT and ZNT, respectively. They included five aromatic-ring belts; this length was sufficient for SWNT models to accommodate [14]annulene molecules without approaching too close to the nanotube edges (dangling bonds filled with hydrogen atoms). We were not able to use more realistic, longer, and wider SWNT models, since they are highly computationally demanding. For the same reason, we focused mainly on the adsorption complexes with ZNT, adding only a few examples with ANT for comparison.

The Gaussian 03W suite of programs was used.³² All the computations were performed with Becke's three-parameter hybrid method³³ and the exchange functional of Lee, Yang, and Parr (B3LYP)³⁴ included in the program package. The B3LYP method was used in conjunction with the LANL2MB basis set, which is STO-3G^{35,36} on the first row and Los Alamos ECP plus MBS on Na–Bi.^{37,38} The choice of the LANL2MB basis set was because of the need to calculate cobalt(II) complexes of tetraaza[14]annulenes. The geometries were fully optimized, meeting the default convergence criteria set in Gaussian 03W. Formation energies $\Delta E_{\text{complex}}$ for the complexes were calculated according to the following formula

$$\Delta E_{\text{complex}} = E_{\text{complex}} - (E_{\text{SWNT}} + E_{\text{annulene}})$$

where E are absolute energies.

III. Results and Discussion

With the set of seven [14]annulenes shown in Figure 1, we were able to estimate an effect on adsorption strength of the following structural elements and factors: (1) nitrogen donor atoms in the macrocyclic ring, (2) aliphatic (methyl) substituents, (3) aromatic (benzo) substituents, (4) central metal ion Co(II) in the complexes, and (5) what side of the molecule contacts the SWNT model, for saddle-shaped ligand H₂TMDBTAA and its complex CoTMDBTAA.

Adsorption of the parent [14]annulene A is very weak and only slightly exothermic (0.1 kcal mol^{−1}) (Figure 2). In the resulting complex A + ZNT, the shortest distance H–C_{ZNT} between hydrogen atoms of A and carbon atoms of ZNT turns to be as long as 4.467 Å. The annulene molecule in A + ZNT is not flat, which is natural, taking into account the steric hindrance between four H atoms directed inside the macrocyclic ring. (One should note that we found a local minimum for an isolated flat molecule of A; however, the corresponding energy is higher by 7.7 kcal mol^{−1} as compared to that for the nonflat, “normal” conformation.)

Adding nitrogen donor atoms into the annulene molecule produces a relatively insignificant effect in terms of both energy and geometry of the adsorption complex. The process is equally slightly exothermic (formation energy of −0.1 kcal mol^{−1}) for H₂TAA + ZNT. At the same time, H₂TAA approaches the nanotube much closer, with the two shorter distances of 2.961 and 2.994 Å between H atoms and carbon atoms of the nanotube side wall. For comparison, formation energy for H₂TAA + ANT is −1.4 kcal mol^{−1}, although the closest contact is as long as 4.479 Å.

Both adsorption complexes of the cobalt complex of tetraaza[14]annulene, CoTAA + ZNT and CoTAA + ANT, behave in a strikingly different way. In the previous two cases the formation of adsorption complexes was due to van der Waals interactions between the ligand “edge” H atoms and SWNT side walls, and correspondingly, the free ligands were inclined with respect to the nanotubes. What can be seen in the case of CoTAA is that the macrocycle approaches ZNT and ANT with its central part, with the separations between two interacting molecules being about 3.5–3.6 Å. While isolated CoTAA molecule is totally flat, with *trans*-N–Co–N and β -C–Co– β -C angles of 180°, it noticeably bends in CoTAA + ZNT and CoTAA + ANT, where the above angles reduce to ca. 177.5° (Figure 2). Despite general geometric similarities, one cannot say the same about the formation energy of the adsorption complexes: it drastically drops to −54.7 kcal mol^{−1} for CoTAA + ZNT and only to −7.0 kcal mol^{−1} for its armchair counterpart. So far we cannot provide a detailed explanation for such a big

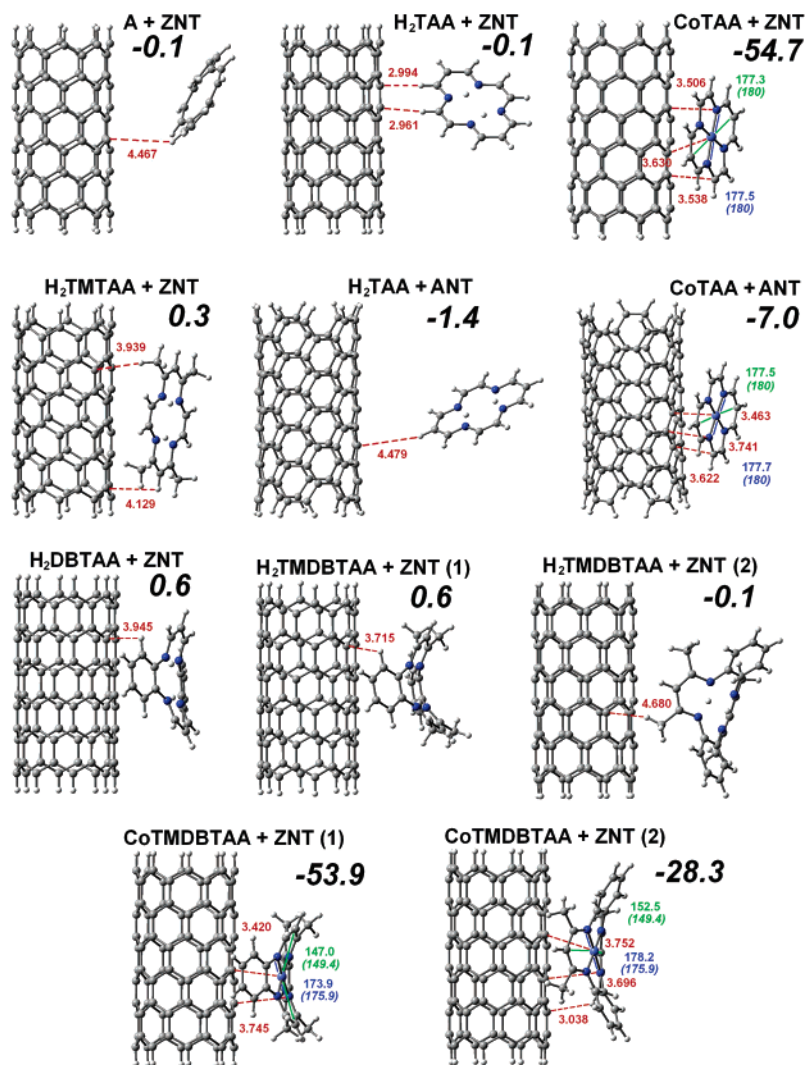


Figure 2. Optimized structures of ZNT and ANT complexes with [14]annulenes. The closest distances (in Å) between tetraazamacrocyclic molecules and NT walls are shown in red. *trans*-N–Co–N and β -C–Co– β -C angles and their values in the NT complexes are shown in blue and green, respectively, with the corresponding values for isolated optimized CoTAA and CoTMDBTAA in parentheses. Note the existence of isomeric adsorption complexes for H₂TMDBTAA and CoTMDBTAA, depending on what side of the annulene approaches the nanotube wall. Binding energy values (in bold italics) are in kcal mol⁻¹.

difference; it has apparently to do with the electronic structure of zigzag and armchair nanotubes.

A similar orientation effect is produced by adding four methyl or/and two benzo substituents to H₂TAA. Nevertheless, none of the resulting H₂TMTAA, H₂DBTAA, or H₂TMDBTAA is capable of approaching the ZNT surface closer than CoTAA is. The shortest distance of 3.715 Å was found in H₂TMDBTAA + ZNT(1) complex, one of two possible isomers, in which the benzo groups are turned toward and methyl groups away from the nanotube. If otherwise oriented, that is, in H₂TMDBTAA + ZNT(2), the separation drastically increases to 4.680 Å. On one hand, a logical explanation of this observation is that the π -stacking interactions are more favorable for the tetraazaannulene adsorption than simple hydrophobic interactions of aliphatic substituents with the nanotube surface. On the other hand, none of the adsorption complexes shows an energy gain, since all the values calculated for formation energies remain close to 0.

The situation dramatically changes again for the cobalt complex CoTMDBTAA. Similarly to H₂TMDBTAA, we considered two orientation isomers. The saddle-shaped complex “accommodates” better on the nanotube, due to a cooperative effect of Co–SWNT and ligand–SWNT interactions. The latter

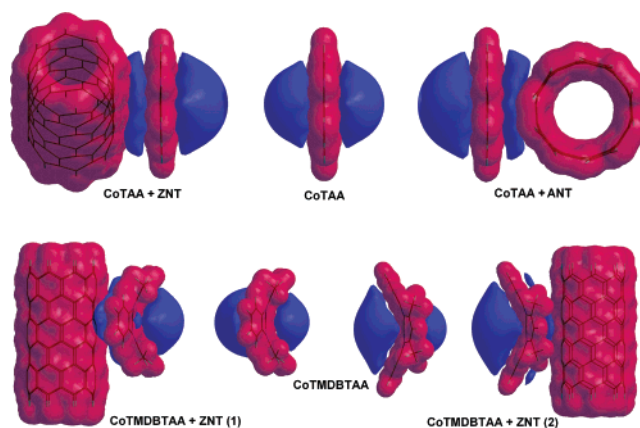


Figure 3. Isosurfaces (at 0.5 au) for molecular electrostatic potential in isolated CoTAA and CoTMDBTAA and in their complexes with ANT and ZNT (two isomeric adsorption complexes exist for CoTMDBTAA, depending on what side of the annulene approaches the nanotube wall). The positive and negative potential is shown in red and blue, respectively.

are mainly due to π -stacking interactions of two aromatic rings (isomer 1) and due to hydrophobic interactions of four methyl

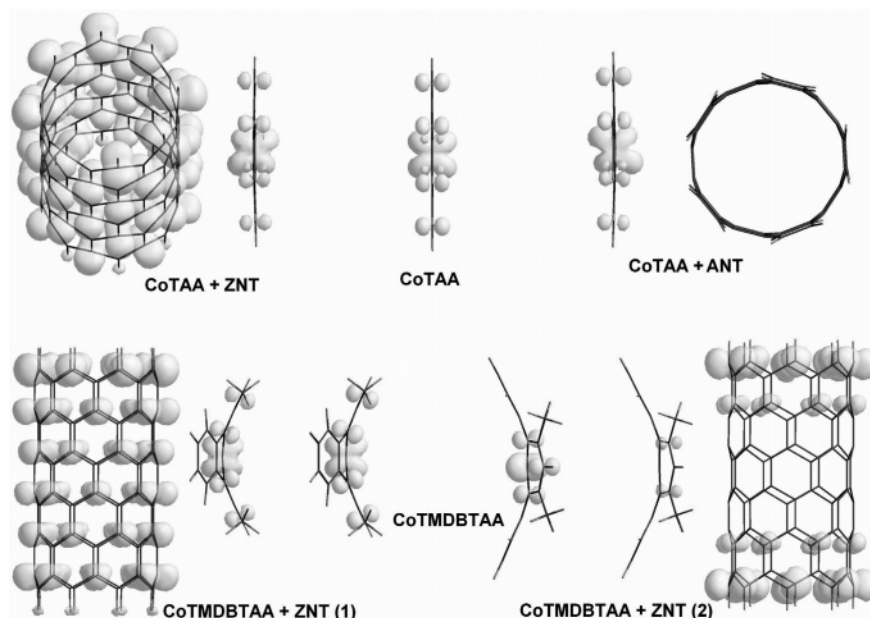


Figure 4. Spin density distribution (isosurface at 0.002 au) in isolated CoTAA and CoTMDBTAA and in their complexes with ANT and ZNT (two isomeric adsorption complexes exist for CoTMDBTAA, depending on what side of the annulene approaches the nanotube wall).

groups (isomer 2) with the nanotube. Benzo groups are flat and do not create such a steric hindrance as methyl groups do. As a result, the distance Co–C_{ZNT} of 3.420 Å for CoTMDBTAA + ZNT(1) increases to 3.752 Å for CoTMDBTAA + ZNT(2). In addition, the macrocyclic ring bends, naturally, to opposite directions, depending on the isomer. As can be seen from the values of *trans*-N–Co–N and β -C–Co– β -C angles specified in Figure 2, both angles exhibit more pronounced changes in CoTMDBTAA + ZNT(2) (2.3° and 3.1°, respectively) than in CoTMDBTAA + ZNT(1) (2.0° and 2.4°, respectively). The more strained structure of CoTMDBTAA in the isomer 2 can explain why its formation energy (–28.3 kcal mol^{–1}) is much higher than the formation energy of isomer 1 (–53.9 kcal mol^{–1}). This observation favors our earlier idea²⁵ on how saddle-shaped NiTMDBTAA and CuTMDBTAA molecules are accommodated on the SWNT surface.

Strong interaction of the cobalt complexes with SWNTs influences not only their geometries but also electronic structure. To demonstrate these changes, in Figure 3 we plotted isosurfaces (at 0.5 au) for molecular electrostatic potential in isolated CoTAA and CoTMDBTAA and in their complexes with ANT and ZNT (where two isomeric adsorption complexes exist for CoTMDBTAA). Negative potential (shown in blue) is always associated with the coordination sphere, that is, with the nitrogen donor atoms and metal ion. In isolated, undistorted CoTAA, negative electrostatic potential is distributed symmetrically with respect to the macrocyclic plane, whereas it is squeezed out from the lobe contacting the nanotube surface in CoTAA + ZNT and CoTAA + ANT. Correspondingly, the opposite lobe becomes notably bigger. A similar picture can be seen for isomeric CoTMDBTAA + ZNT adsorption complexes as compared to isolated CoTMDBTAA molecule (where the molecular electrostatic potential is distributed asymmetrically with respect to the CoN₄ plane). In the case of [14]annulene and metal-free tetraaza[14]annulenes, no visible alterations in the 0.5-au isosurfaces were found.

Since Co(II) complexes are paramagnetic, it was possible also to visualize spin density distribution. In Figure 4, the isosurface plots at 0.002 au are shown. In isolated CoTAA, as observed for electrostatic potential, spin density is distributed symmetrically with respect to the macrocyclic plane. It concentrates

on the cobalt ion and at the same time can be found at N and β -C atoms of the six-membered chelate rings. As a whole, CoTAA + ZNT and CoTAA + ANT keep the above feature, but in other regards they are strikingly different. While a high positive spin density can be found on carbon atoms in ZNT, its armchair counterpart exhibits no appreciable transfer of unpaired electron to ANT. A similar, but not such a contrasting, difference can be seen for two CoTMDBTAA + ZNT isomers. From the examples presented, the following trend can be seen: the lower the formation energy (that is, the stronger the adsorption), the higher spin density is transferred to the nanotube.

IV. Conclusions

Our theoretical study predicts that adsorption of tetraaza[14]-annulene ligands on SWNTs is not noticeably influenced by the presence of aliphatic (methyl) or/and aromatic (benzo) substituents in the macrocyclic molecules. On the contrary, the adsorption dramatically increases in the case of metal (cobalt) complexes, resulting in substantial changes in their geometry and electronic structure. The increase in negative electrostatic potential at the exposed macrocycle side might imply an enhanced reactivity toward electrophilic agents, which, along with the strong adsorption predicted, is an encouraging prerequisite for the preparation of new CNT-based catalysts.

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