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SUBSTITUTION BY HETEROATOMS VERSUS FULLERENIC CAPPING AS REMEDIES FOR DANGLING BONDS IN GRAPHENE TUBULENES

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Abstract. Dangling bonds at the edges of graphene tubules are normally avoided by capping with fullerenic hemispheres. The present paper describes an alternative way for achieving the same result by replacing the dicoordinated carbon atoms at the edges of the tubules by nitrogen heteroatoms. Molecular mechanics calculations are provided for two types of such tubules.

Introduction

Graphite, the thermodynamically stable carbon allotrope, owes its lower energy than that of diamond to electronic delocalization within a bidimensional sheet of condensed benzenoid rings. However, both these "classical" allotropes have dangling bonds at the periphery of the 2- or 3-dimensional carbon nets. For large single crystals, these dandling bonds have negligible effects. However, for systems with smaller numbers of carbon atoms, as one obtains when vaporizing graphite, the system minimizes its number of dangling bonds : when this vaporization is carried out under certain conditions of temperature, pressure, and in an atmosphere of noble gas such as helium, one obtains fullerenes [1,2] and/or graphene tubules ("buckytubes").[3,4]

Buckytubes were first described by Ijima ;[3] later, Ebbesen et al.[4] described a method for preparing buckytubes in large amounts ; these tubulenes are now available commercially [5] at prices comparable to those of fullerenes C_{60} and C_{70}.

Electron microscopy showed that buckytubes are long, hollow cylindrical multi-layered graphitic sheets of sp^2-hybridized carbon atoms, capped at their two ends by fullerenic structures. According to Euler's theorem, a total of 12 five-membered rings is necessary for closure of any polyhedral structure formed from 6- and 5-membered rings, in which each vertex has three neighboring vertices.

The 5-membered rings are more easily oxidized, and on his basis one can open the ends of buckytubes, and "peel off" sequentially the outer sheaths, ending up in sungle tubules. When these are capped at both ends, they are called "capsules".

We shall now consider another theoretically attractive possibility for avoiding dangling bonds : replacement of carbon atoms with free valency at the ends of the buckytube by heteroatoms. Here we shall consider only nitrogen as heteroatom, and the resulting structures will be called "aza-buckytubes" for convenience. In previous papers we have discussed fullero-polycoronands [6] and the related corona-tubulenes,[7] where oxygen was the heteroatom substituting carbon atoms at the edges of holes in the graphitic honeycomb structure.

When at the ends of an open buckytube a carbon atom is connected only to two other carbon atoms, its replacement by a nitrogen heteroatom "cures" the dangling bond by replacing the singly occupied sigma-orbital by an electron lone pair. Thus the nitrogen-bordered open ends of a buckytube may coordinate metal atoms or ions, similarly to what is assumed to happen in fullero-polycoronands or in corona-tubulenes.

Aza-buckytubes

Buckytubes have a helical/rotational structure.[7] A rectangular piece of graphitic sheet can be rolled into a cylinder in two extreme ways, and a multitude of intermediate possibilities. We shall consider here only the two extreme ways with some C—C bonds oriented either in parallel or orthogonal fashion to the cylinder axis. In the former case, after aza-substitution, the

benzenoid rings at the ends of the buckytube are replaced by pyridinic rings, and the electronic structure leads to quinonoid formulas with two double bonds inside each ring, which are energetically unfavorable (cf. Fig. 1). In the latter case, many rings have three double bonds inside each ring as in Clar-structures, but the end-rings are pyridazinic, with two adjacent nitrogen heteroatoms. Such rings with *cis*-azo structures have higher energy than isomeric diazinic (pyrimidinic or pyridazinic) rings, but for aza-buckytubes which are long enough this effect will be counterbalanced by the aromatic stabilization of the whole structure.

Pyridinic aza-buckytubes

If the pyridinic aza-buckytube has fewer than six pyridinic rings at each end, the cylinder does not have a circular cross-section : with five pyridinic rings at each end, after energy minimization, the cross-section of the cylinder is an ellipse with the ratio between the two axes of about 1.6 (Fig. 1).

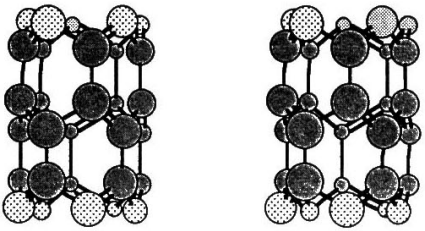

FIG. 1. Stereo-view of an aza-buckytube with five pyridinic rings at each end. In this and subsequent figures, carbon atoms are grey, and nitrogen atoms are dotted.

Therefore we shall discuss in more detail only aza-buckytubes with circular cross-sections. In figures 2 and 3 we present such aza-buckytubes ending in six and ten pyridinic rings, respectively. In addition to electronic factors, one must also consider ateric strain. By means of molecular mechanics (MM2 program, contained in the CSC Chem3D Plus program which minimizes the bond-stretch energy) it was

possible to obtain strain energies for the aza-buckytubes presented in Figures 2 and 3 for systems with 6 and 10 pyridinic rings at each end, respectively. Numerical results are shown in Table 1 ; the numbers of rings are indicated in round brackets.

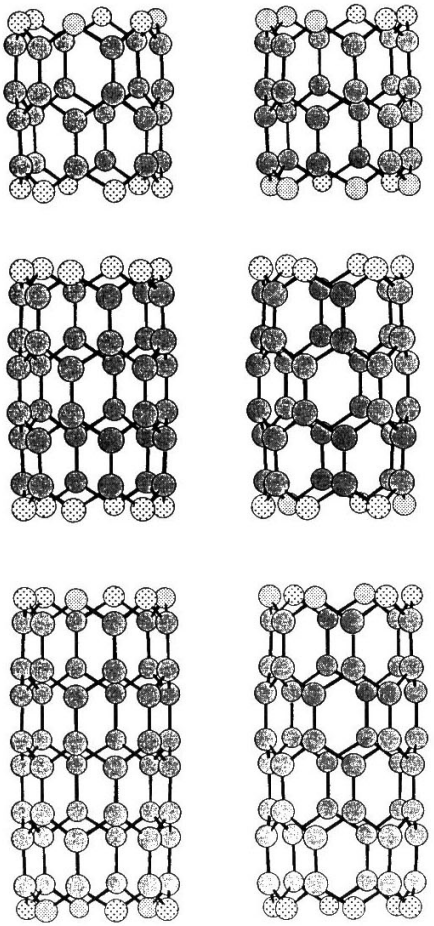

FIG.2. Three aza-buckytubes (1 - 3 from top) with six pyridinic rings at each end.

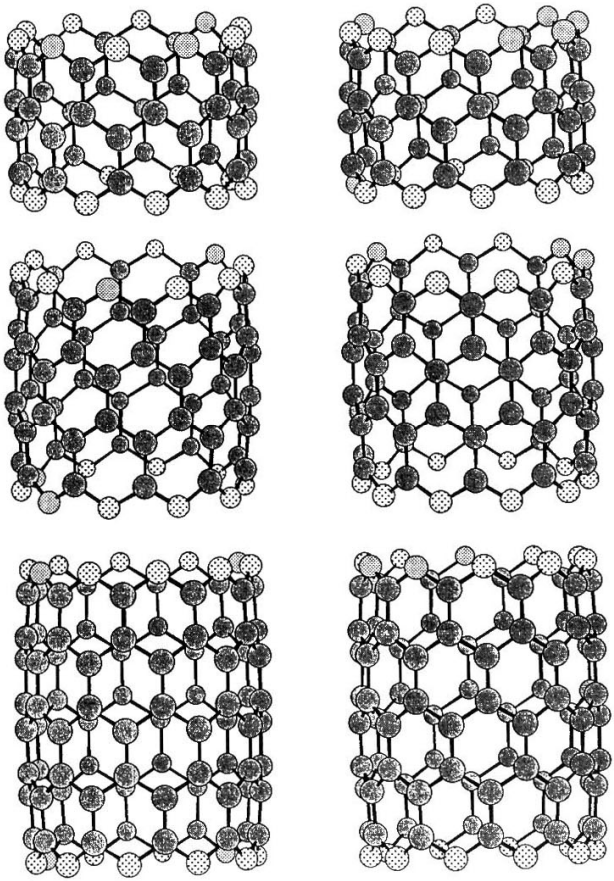

FIG. 3. Aza-buckytubes (**4** - **6** from top) with ten pyridinic rings at each end.

TABLE 1. Strain energies (kcal/mol) for pyridinic aza-buckytubes **1** - **6**.

Type of strain	**1**(12)	**2**(18)	**3**(24)	**4**(20)	**5**(30)	**6**(40)
Stretch :	41.6	4.4	4.4	21.2	9.4	9.1
Bend :	49.6	68.4	87.3	32.8	42.0	52.4
Stretch-Bend :	7.3	-1.5	-1.1	-2.3	-2.5	-2.9
Torsion :	41.2	270.6	358.7	303.9	225.4	247.4
Non-1,4 VDW :	306.9	110.7	120.3	128.1	120.5	111.5
1,4 VDW :	43.1	62.6	76.4	54.2	77.1	97.9
Dipole/Dipole :	18.1	19.5	15.2	30.1	29.2	27.2
Total :	**507.9**	**534.7**	**661.2**	**568.1**	**501.2**	**542.6**
Total / ring :	**42.3**	**29.7**	**27.6**	**28.4**	**16.7**	**13.6**

From Table 1 one can see that the main contributors to the steric strain are torsion and non-1,4-Van der Waals energies. As expected, in the longer pyridinic aza-buckytubes the total steric strain and the total steric energy per ring are lowered when the diameter of the tube is larger, i. e. lower in **5** and **6** than in **2** and **3**. Interestingly, the total strain energy alternates in the series **4** - **6** (this alternance is also observed for torsion energies in this series), but increases steadily in the series **1** - **3**. The total steric energy per ring decreases steadily in both series, and for **4** - **6** is about half of that for **1** - **3**.

Pyrimidinic aza-buckytubes

Aza-buckytubes **7** and **8** with five pyrimidinic rings at each end are presented in Fig. 4, and aza-buckytubes **9** and **10** with six pyrimidinic rings at each end are presented in Fig. 5. All have circular cross-sections.

Results of calculations for steric strain are presented in Table 2.

The non-1,4-Van der Waals interactions become significant only in the longer aza-buckytubes **8** and **10**. Otherwise, the values from Table 2 show again that the total strain energy in the aza-buckytubes **9** and **10** with larger diameter is lower than in **7** and **8** with smaller diameter ; however, the values

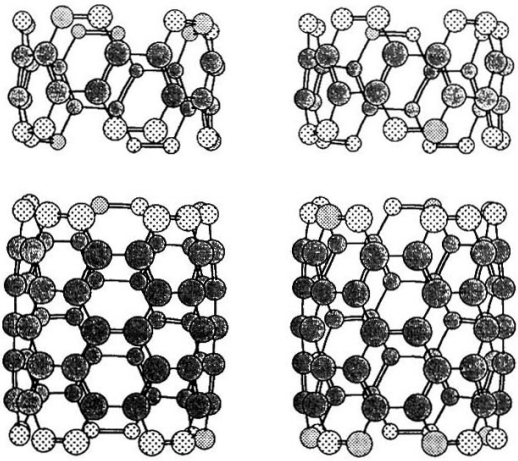

FIG. 4. Aza-buckytubes **7**, **8** (from top) with 5 pyrimidinic rings at each end.

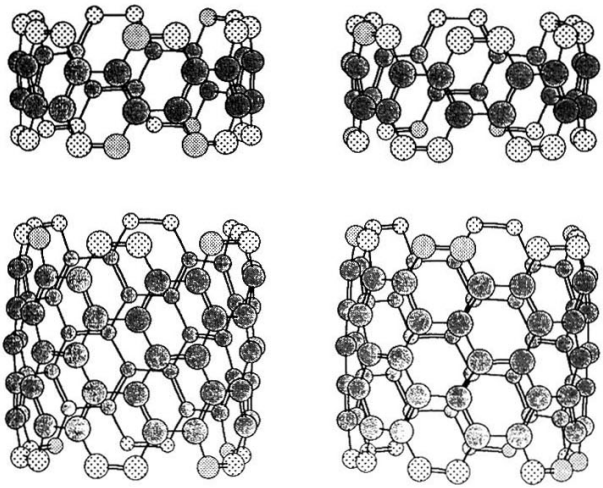

FIG. 5. Aza-buckytubes **9**, **10** (from top) with 6 pyrimidinic rings at each end.

TABLE 2. Strain energies (kcal/mol) for pyrimidinic aza-buckytubes **7** - **10**.

Type of strain	**7**(10)	**8**(25)	**9**(12)	**10**(30)
Stretch :	21.5	23.1	18.8	18.9
Bend :	47.0	58.4	43.6	59.4
Stretch-Bend :	5.2	5.1	4.1	3.8
Torsion :	188.8	142.7	199.7	192.9
Non-1,4 VDW :	2.6	523.5	1.7	469.7
1,4 VDW :	49.7	89.4	46.2	83.8
Dipole/Dipole :	40.7	32.0	34.5	27.0
Total :	**355.5**	**874.2**	**348.6**	**855.5**
Total / ring :	**35.6**	**35.0**	**29.1**	**28.5**

are much closer to one another, when comparing systems with different diameters but with comparable numbers of rings, than for similar comparisons in Table 1. Another difference from Table 1 is the practically constant value of the total steric energy per ring for systems with the same diameter.

Conclusions

The possibility of avoiding dangling bonds by having aza-heterocyclic rings at the ends of buckytubes is an interesting alternative to capping these buckytubes. In practice, for achieving the introduction of nitrogen heteroatoms one may consider either adding gaseous nitrogen or nitrogen-containing precursors such as cyanogen to the noble gas during the preparation of buckytubes, or (probably a better strategy) breaking oxidatively the end-caps of multi-layered capsules with a mixture of gaseous oxygen and nitrogen or nitrogen-containing precursors such as nitric oxides.

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References

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature, 318,* 162-163, **1985**.

2. W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature, 347,* 354-358, **1990**.

3. S. Ijima, *Nature, 354,* 56-58, **1991** ; P. M. Ajayan and S. Ijima, *Nature, 361,* 333-334, **1993** ; P. M. Ajayan, T. Ichihashi and S. Ijima, *Chem. Phys. Lett., 202,* 384-388, **1993** ; S. Ijima and T. Ichihashi, *Nature, 363,* 603-605, **1993.**

4. T. W. Ebbesen and P. M. Ajayan, *Nature, 358,* 220-222, **1992** ; D. Dujardin, T.W. Ebbesen, H. Hiura and K. Tanigaki, *Science, 265,* 1850-1852, **1994** ;T. W. Ebbesen, P. M. Ajayan, H. Hiura and K. Tanigaki, *Nature, 367,* 519, **1994**.

5. Strem Chemicals Catalog, Newburyport, Massachusetts, USA.

6. A. T. Balaban, H. Zhu and D. J. Klein, *Fuller. Sci. Technol., 3,* 133-150, **1995**.

7. A. T. Balaban, *Bull. Soc. Chim. Belges* (in press).