ON THE CHEMISTRY OF NITROGEN IN THE GRAPHENE STRUCTURE

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Introduction

Decreases in oxidative gasification rates and catalytic activity for the reduction of nitrogen oxides are reported in the literature for nitrogen containing and nitrogen doped porous carbons. At low temperatures (<750 K) nitrogen may be present in carbons as aliphatic species such e.g. amine, amide etc. However, these structures are thermally unstable and at higher carbonization temperatures evidence indicates that the majority of nitrogen becomes incorporated into the ring structures of the carbon. Pyrrolic, pyridinic/acridinic and the so called quaternary aromatic structures have been identified in various carbons by XPS [1][2][3] and XANES [4]. Atomic nitrogen possesses 7 electrons (*1s2, 2s2 ,2p3*) and in the ground state has a covalency of 3. To attain a covalency of 5 requires unpairing of the *2s* electrons to produce an exited *sp³d* hybridised system. This study is based on results from previous work in which acridinic and quaternary nitrogen species were identified by XPS in Kevlar and Nomex chars. In this paper we comment upon the likely chemical and structural implications of incorporating a nitrogen atom into a graphene ring.

Experimental

Chars were produced by carbonization of Kevlar or Nomex at 1123 K in an argon flow of 80 cm³/min. XPS was carried out using a Kratos HSi 5-channel, monochromated system with Al kα radiation of energy 1486.6 eV and a pass energy of 20 eV for nitrogen 1s spectra. Binding energies were referenced to the main carbon (C-C/C-H) peak at 284.6 eV. Modelling work has been carried out using Web Lab Viewer Pro Chem software.

Results and Discussion

Nitrogen 1s spectra from Kevlar [2] or from Nomex [5] polymers contain only a single peak at a binding energy of 399.8 eV due to the amide nitrogen. Nitrogen 1s peak envelopes from the chars of these materials clearly contain two prominent peaks with binding energies of 398.2 eV and 400.8 eV which have been assigned as due to acridinic and quaternary nitrogen respectively. For the chars studied so far the ratio of the 400.8/398.2 peak areas is 2:1.

Since oxidation resistance and catalytic activity (NO reduction) have been reported for carbons with similar structures the chemical and physical structures of these species is of interest. Palmer proposed that for the Pyrrolic 5-membered ring structure the nitrogen atom contributes 2 lone-pair electrons to the π system to complete the aromatic sextet and forms sigma bonds with the 2 adjacent carbons plus 1 hydrogen. This molecule is planar. For the 6-membered pyridinic/acridinic structure, the lone pair resides in an *sp* hybridised orbital in the plane of the ring and 1 *p* electron is contributed to the π system [6].

Figure 1 shows the usual proposed structures for quaternary nitrogen (top, centre and valley). Here we comment upon how the incorporation of nitrogen of this type affects bond angle, length and electron distribution assuming these structures to be part of a graphene array.
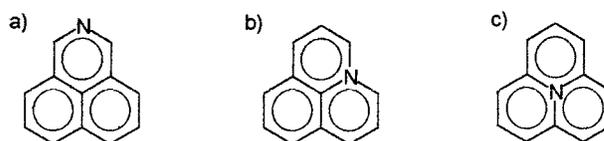

Figure 1: Proposed Structures for quaternary structures a) Top, b) Valley and c) Central

The structure shown in Figure 1 for 'top' nitrogen will have 14 conjugated π electrons of which nitrogen will donate 2. Figure 2 shows 2 alternative structures: the first with nitrogen retaining a lone pair of electrons and therefore not being part of the aromatic structure since the π system only contains 13 electrons and the 4n+2 stability from Huckel Theory is not achieved. In the second structure the nitrogen looses the lone pair by donating 1

electron to the π system (now 14 e-) and forming a N-H sigma bond with the other. However, the stability gained from achieving the 4n+2 π structure could be lost by sigma bond distortion out of the normal $sp2$ 120 degrees.
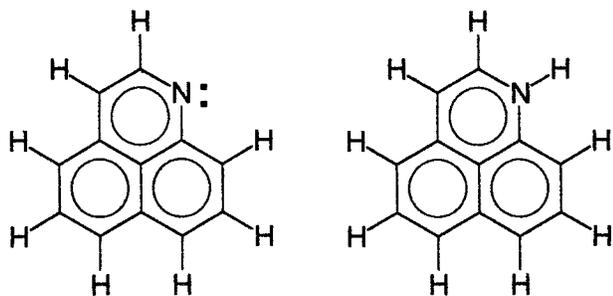
13 pi-electrons   **14 pi-electrons**

Figure 2: Two alternative nitrogen ring structures

Central nitrogen (Figure 1) is symmetrical leading to equal forces between the 3 neighbouring carbons. There are 3 types of carbon in the molecule as shown (i) carbons bonded to nitrogens, (ii) carbons bonded to type (i) carbons, and (iii) carbons bonded only to type (ii) carbons. The bond angles are fractionally less (our model gives 119.9 degrees) than the 120 degrees observed for benzene and the C-N bonds are likely to be shorter than C-C (1.415 Å) bonds of the graphite/graphene structure. Our calculation of this distance is 1.340 Å between C-N and a distance of 1.380 Å between Type (i) and Type (ii) carbons. The distance between Type (ii) and Type (iii) is 1.40Å which is close to the graphite C-C distance i.e. the shortening effect of the N atom on bond length decreases with distance from the nitrogen. There is also torsion of 0.3 degrees around the C-N bonds. This would suggest that the ring is subject to structural tension and would therefore tend to bend out of plane. Our models so far suggest that this strain is very slight and, assuming that the structure is aromatic, might be accomodated by the 'elasticity' of the structure. For the valley structure the distortion is likely to be greater because there is no centre of symmetry. By loss of it's lone pair of electrons nitrogen in a graphene structure is likely to posses a positive charge which may explain it's oxidation resistance. It will also act as an electron acceptor making it an oxidising site within the carbon structure.
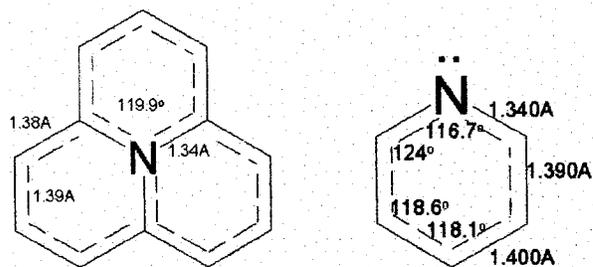

Figure 3: Calculated Bond Lengths and Bond Angles for nitrogen atoms in ring structures

Conclusions

Incorporation of amide nitrogen into the carbon graphene structure structure is observed when Kevlar or Nomex are carbonized. The resulting acridinic and quaternary structures have distinct photoelectron binding energies. For quaternary nitrogen we propose that the C-N bond internuclear distance is 1.34 Å and for next neighbour C-C bonds a distance of 1.380 Å. Both of these values are shorter than the C-C graphite distance (1.415 Å). This may cause some ring strain. Electron loss by the aromatic nitrogen results in a residual positive charge.

References

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