PRF# 57236 – ND 6
Project Title: Unraveling the Interactions between Molecular Species and Two-Dimensional Materials
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The main goal of this project is to present a fundamental study of the mechanisms of molecular interactions with holey 2D structures with a variety of hole sizes as well as passivating chemical groups. Over the past year, the research focus related to this grant has been placed on Density Functional Theory calculations on novel graphene-like 2D sheets based on heterocycles. Below, we elaborate on our findings in these areas.

Novel 2D sheets based on heterocyclic molecular units (Carbon, 152 (2019) 128-133)

Our previous results on the interaction of graphene with specific molecules in the presence of edges (or holes) indicated that sensitivity of these sites is not high enough and thus separation will be dominated by self-diffusion processes. However, the development of new holey structures can potentially increase selective interactions with molecular species. Encouraged by the synthesis of novel two-dimensional (2D) materials through bottom-up approaches, we investigated the structural properties and stability of a variety of 2D monolayers constructed from aromatic six-membered rings using density functional theory methods. We study benzene, single heteroatom heterocycles, as well as borazine, 1,3-diazine, and 1,3,5-triazine as building blocks of graphene-like monolayers that naturally present a holey structure. Our study focused on understanding the stability of novel 2D sheets based on the molecular units shown in Figure 1. We utilized these molecular units as building blocks for 2D sheets as shown in the schemes of Figure 2. The relative stability of these sheets with respect to the molecular constituents sheds light on the feasibility of synthesizing these structures in the lab. Indeed, the 2D sheet with benzene molecules as molecular units has been already synthesized.[1]

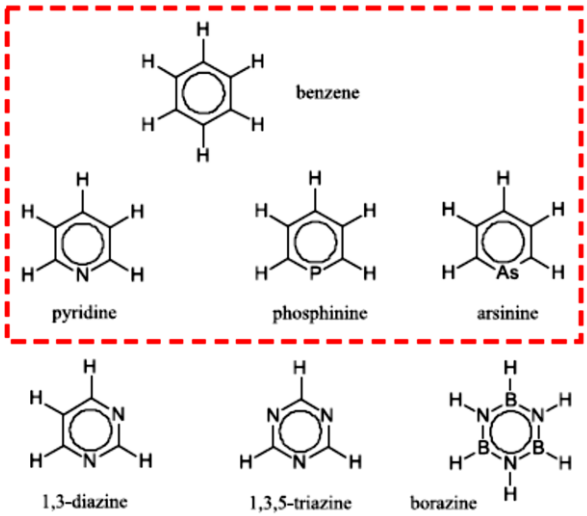


Figure 1: Scheme of the molecular units considered in this work as building blocks of 2D graphene-like sheets. Inside the box we consider benzene and heterocycles with a single heteroatom as our first case of study. Additionally, we extend our work to consider 1,3-diazine, 1,3,5-triazine, and borazine.

Summary

We analyze the cohesive energy, bandgap, and lattice parameters of all these structures. Importantly, we consider their relative stability with respect to their corresponding molecular constituents and H_2 molecules (Figure 3). Through this analysis, we find that diazine and borazine monolayers present the greatest stability of all studied compounds although other monolayers that are meta-stable have relative energies comparable to graphene and are thus likely to be isolated in experiment. These large bandgap holey materials open the possibility of a whole family of 2D sheets based on seamlessly connected six-membered rings that could find applications in, for instance, catalysis and gas separation. These results have been recently published in *Carbon*.[2]

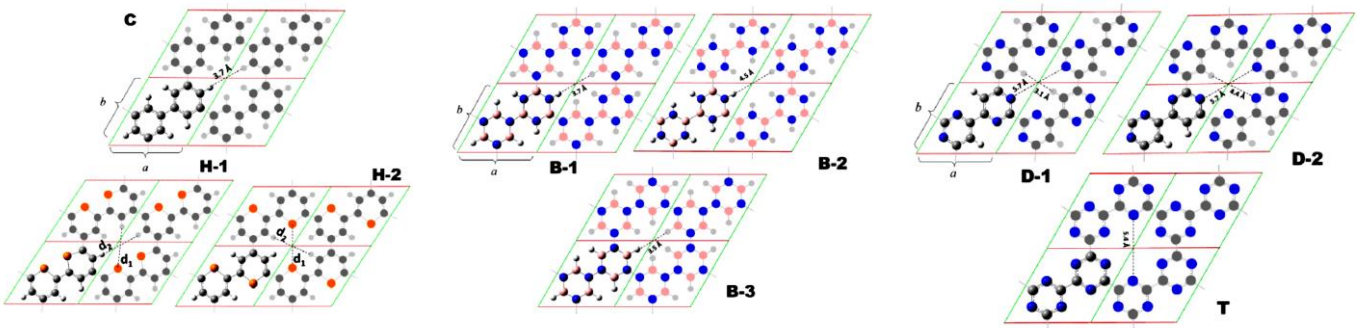
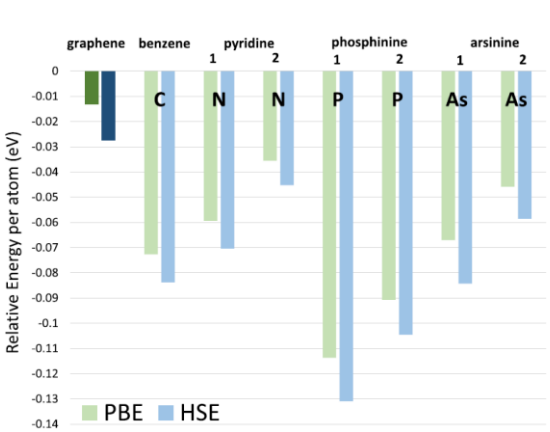
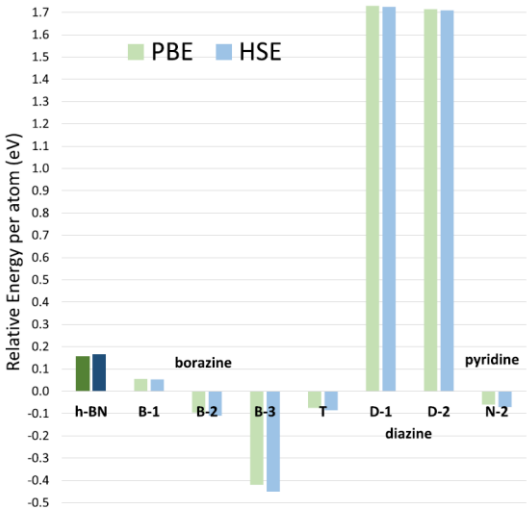


Figure 2: Scheme of the 2D molecular monolayers considered in this work. **A**: lattices formed by seamlessly connected benzene molecules (C) as well as the two non-equivalent configurations of single-substituted heterocycles H-1 and H-2 (where H¼N, P, or As). Grey, white, and orange balls represent C, hydrogen, and the H substituent (H¼N, P, or As), respectively. **B**: lattices formed by seamlessly connected borazine molecules in the three non-equivalent configurations studied here. Blue, pink, and white balls represent N, B, and H, atoms respectively. **C**: lattices formed by seamlessly connected triazine molecules (T) as well as the two non-equivalent configurations of diazine studied here (D-1 and D-2). Grey, blue, and white balls represent C, N, and H atoms, respectively.
Translation vectors *a* and *b* are indicated in the scheme while replicated unit cells are shown dull to indicate the holey nature of the structures.



A: compounds from Fig.2 A



B: compounds from Fig.2 B and C

Figure 3: Calculated relative energies with respect to molecular constituents with PBE and HSE functionals. For comparison, the corresponding values for graphene as well as hexagonal boron nitride are included.

References:

[1] M. Bieri, M. Treier, J. Cai, K. Ait-Mansour, P. Ruffieux, O. Gröning, P. Gröning, M. Kastler, R. Rieger, X. Feng, K. Müllen, Porous graphenes: two-dimensional polymer synthesis with atomic precision, Chem. Commun. 45 (2009) 6919-6921.
[2] Barone and Moses, Structure and stability of graphene-like layers built from heterocyclic units, Carbon, 152 (2019) 128-133.