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THE ADSORPTION OF BENZOTRIAZOLE ON COPPER AND CUPROUS OXIDE

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A brief account is given of the bonding of benzotriazole to a model of a Cu(III) surface. Perpendicular adsorption is favored over parallel, and an oxidized surface exhibits heightened adsorbate-surface interaction.

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The Adsorption of Benzotriazole on Copper and Cuprous Oxide

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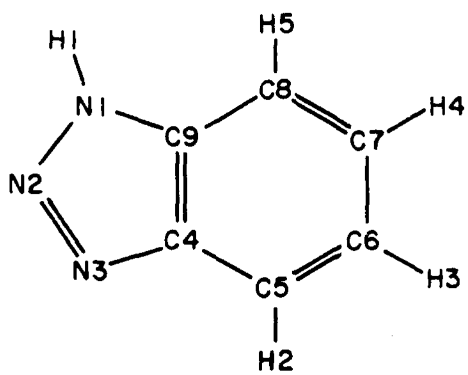
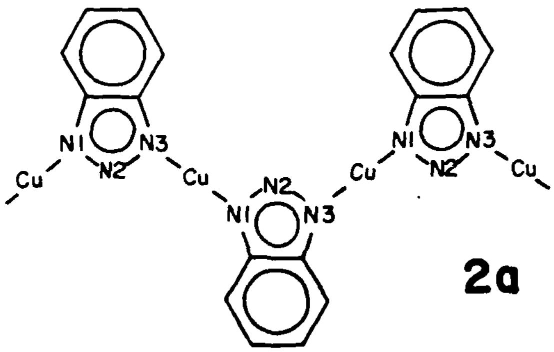
Copper surfaces are commonly treated with benzotriazole (BTA), **1**, to inhibit corrosion. $H1^+$ is thought to be lost to the oxide coating, which is present on commercially available copper, through the formation of water[1]. BTA^- is proposed to bind to the surface through the nitrogen lone pairs, rather than through the π orbitals of the rings. By analogy to organometallic copper chemistry, pyridine ligands (as examples of nitrogen containing aromatic rings) show a marked preference to coordinate through the

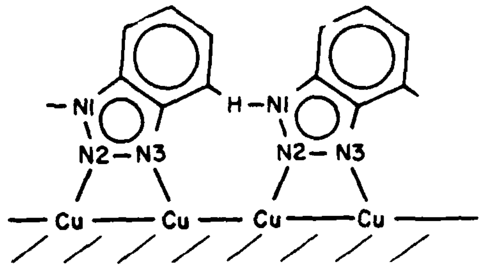


1

nitrogen lone pair[2]. Hundreds of examples of N-bound copper-pyridine complexes exist, but only a few π-bound species have been found. It is however unclear whether BTA^- lies parallel or perpendicular to the copper surface. Roberts[3a] and Orville-Thomas[3b] propose a polymeric Cu-BTA structure, **2a**, which could lie flat on the surface. The copper atoms of the polymer would lie above the Cu surface; the exact registry of these



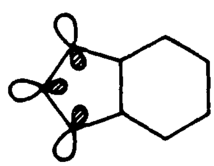
2a



2b

metal atoms to the surface is not specified. A contrasting theory is expounded in a recent photoemission study on clean Cu(111) by Lynch[4]. It is suggested that BTA^- stands upright, bridging the Cu-Cu nearest neighbor contact of 2.55Å via N2 and N3, and hydrogen-bound at N1 to the adjacent BTA^-, **2b**. To allow for a reasonable N-H distance of 1.2Å, the adsorbates must be tilted 6° away from the surface normal in alternating directions. The UPS spectra obtained on clean and oxidized Cu(111) surfaces are nearly identical, implying that oxygen does not play a direct role in BTA chemisorption.

To better understand the electronic factors governing the binding of BTA^- to copper surfaces, we have carried out extended Hückel tight-binding calculations on a one layer Cu(111) slab[5]. Because the calculations are limited by the size of the unit cell and



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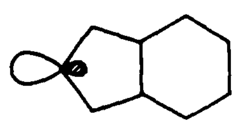

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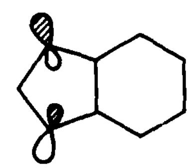
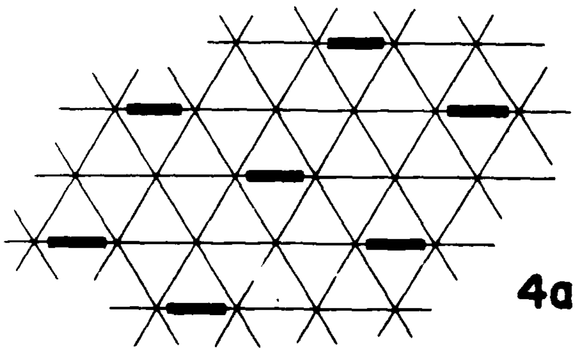


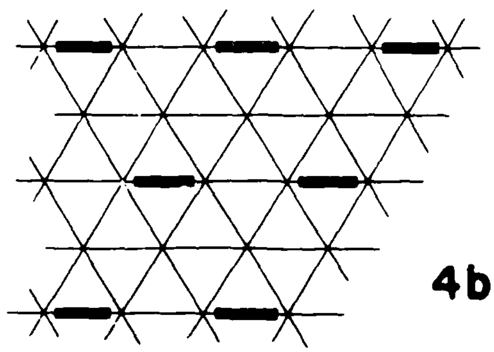
3c

as this particular adsorbate is so large, only one layer could be include if the BTA^- lies parallel, and this slab size is retained in the perpendicular modes for the sake of consistency. Our analysis allows for a decomposition of the crystal orbitals and density of states (DOS) in terms of either an atomic orbital basis set or a basis set of the molecular orbitals (MO's) of fragments of the unit cell — in this case, the two fragments are the BTA^- molecule and the copper unit. The BTA^- MO's of interest in chemisorption can be divided into two groups: the π system orbitals perpendicular to the rings, and the three nitrogen lone pair orbitals N_1, N_2 and N_3, respectively **3a**, **b** and **c**.

The first step to the analysis of the rather complex structure of **2b** is to address the simple perpendicular bonding mode through N2 and N3, without lateral BTA-BTA interaction. An arrangement of BTA^- adsorbates on the hexagonal Cu(111) net shown in **4a** (BTA^- as dark bars) avoids close interadsorbate contacts. The Cu-N distance is taken to be 2.0Å, a typical value for copper-nitrogen bonds in organometallic complexes[6]. The calculated binding energy is 1.67eV. The pertubation of chemisorption on most of the BTA^- orbitals is very small; typically ~90% of the MO density remains



4a



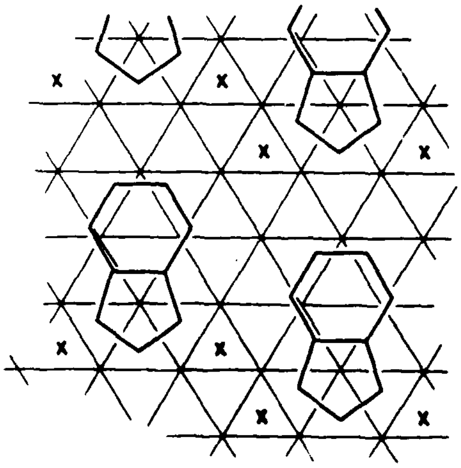
4b

in a "molecular", or majority, peak and little is lost due to the dispersion induced by chemisorption. N_2 and N_3 are the exceptions. The coupling between these orbitals and Cu z^2, which points out of the surface, pulls ~12% of the N_3 levels and ~18% of the N_2 levels down into the d block.

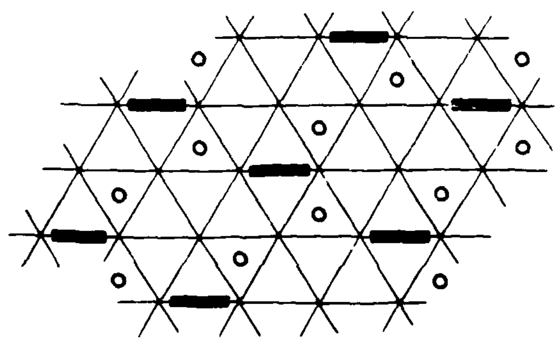
As expected, the BTA^- bridged Cu-Cu bond is greatly weakened as observed in the 54% reduction in the Cu-Cu overlap population (o.p.), a number scaling as bond strength. More interesting are the changes found in a number of the unbridged Cu-Cu bonds. The bonding and antibonding nature of any interaction can be analyzed as a function of energy with a Crystal Orbital Overlap Population (COOP) curve[7]. The COOP curve is created by weighting the density of states by the contribution of the states at that energy to the Cu-Cu o.p. Analysis of the curves indicates that ~70% of the bonding copper states are localized in a sharp Cu s state ~2eV below ϵ_f. In contrast, the bonding s states of the bare surface are dispersed over a 6.5eV wide region. The localization of these orbitals may be a manifestation of the corrosion inibition characteristic of BTA.

If the BTA^- are subsequently tilted 6° away from the surface normal, the binding energy is reduced by 1.0eV. A split in the N_3 peak is observed. The third step in the analysis of **2b** is to allow for H-bonding between the alternately tilting BTA^- species by moving to the chemisorption pattern in **4b**. The binding energy becomes extremely favorable, rising to 6.7eV. Although the π system remains relatively unaffected, the dispersion of the nitrogen lone pairs is heightened. Only ~32% of N_3 remains in molecular peak, the remainder is lost to the d block (~35%) and to a disperse series of N-H bonding states. The N-H COOP curve indicates strong N-H bonding in the N_3 molecular peak region and strong N-H antibonding in a second mainly N_3 peak above ϵ_f. It is also noted that the strength of the BTA^- N2-N3 (bridged) and N1-N2 bonds decreases from the free molecular o.p. value of 0.838 to 0.716 and 0.732 for **4a** and to 0.676 and 0.626 for **4b**. Bond weakening within the adsorbate rings is thus fairly substantial for the H-bonded system.

Chemisorption of the polymeric **2a** can artificially be broken into adsorption of BTA^- parallel to the surface followed by the introduction of additional copper atoms at the same level as the BTA species. The BTA^- ring is positioned 2.00Å above the surface in each case. If it is placed so that the nitrogen containing ring is centered over a Cu (see **5a**, disregarding the "x's"), the interaction between the π orbitals of the ring and the Cu is very weak. The sum of the o.p.'s is 0.014. However, this arrangement places C5 and C8 directly over Cu atoms in the hexagonal net. Each C-Cu o.p. is 0.202. This strong interaction can be traced to the π orbital localized mainly at these carbons, which is the highest occupied molecular orbital (HOMO) of BTA^-. The arguments are much the same if instead the all-carbon 6-membered ring is centered over a surface atom. The ring-Cu interaction is weak, but now N1 and N3 can lie above copper



5a



5b

atoms. Again, the largest dispersion is found in the π orbital localized at these atoms. However, both geometries produce a repulsive interaction between adsorbate and substrate whereas the previously described perpendicular modes are attractive.

As the size of the unit cell needed to treat the chemisorption of the polymer **2b** (2 BTA^- + 2 polymeric Cu + 20 surface Cu) is beyond our limitations, the problem is simplified by treating peices of the polymer. Two Cu are placed 2.00Å above the 3-fold hollows adjactent to N1 and N3 of each BTA^-; the "x's" in **5a** mark the positions of the additional metal atoms. Planar Cu-BTA-Cu units are formed in this manner. Without the additional copper atoms, the dispersion of the nitrogen lone pairs was minimal. But with them, over 1/4 of N_2, for example, is pulled down into the Cu d block. The stong interaction within the polymer-like units is also responsible for the large N-Cu o.p. of 0.460 (d(N-Cu)=1.82Å). In comparison, the perpendicular **4a** produces N2-Cu $\approx$ N3-Cu = 0.338 with a slightly longer N-Cu distance of 2.0Å. The closest contact C-Cu o.p. remains 0.202. In spite of these stabilizing features, the binding energy increases only 1eV, but remains repulsive.

A last point is to consider the effects of coadsorbed oxygen on BTA^- chemisorption. We consider only one case in which the BTA^- is positioned perpendicular to the surface, no H-bonding, with 2 oxygens per BTA^- positioned over 3-fold hollows, **5b**. The direct interaction of N_2 and N_3 with the oxygen p orbitals lying in the plane of the surface accounts for a marked increase in the dispersion of these orbitals. Recall that these BTA^- orbitals were primarily responsible for bonding onto clean Cu(111). In particular, a 7eV region must be taken to account for 90% of the N_2 states on the oxide surface, whereas only 4eV is needed on the clean surface. The coupling is particularly strong because the oxygen p states lie within ~2eV of the N_2 and N_3 levels. In addition, the binding energy increases by 4.6eV, although remaining 2.1eV below that of the H-bonded perpendicular system.

By comparison of both the binding energies and the strength of the adsorbate-substrate interaction as measured by the extent of dispersion of the BTA^- MO's, perpendicular adsorption is favored over parallel adsorption on clean Cu(111). The single example of an oxided surface exhibits a heightened adsorbate-substrate interaction than the comparable clean surface. Clearly many more examples should be considered before the adsorption and corrosion inibition of BTA on copper surfaces is thoroughly understood.

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