Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Using Polarised, Ultra-Soft X-Ray Absorption Spectroscopy to Probe Molecular Orientation in Benzotriazole Films Adsorbed on Partly Oxidised Copper

Joy Johnstone [a] & Kevin J. Roberts [a b]

[a] Dept. of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, U.K.

[b] CLRC Daresbury Laboratory, Warrington, WA4 4AD, U.K.

Version of record first published: 24 Sep 2006.

To cite this article: Joy Johnstone & Kevin J. Roberts (1996): Using Polarised, Ultra-Soft X-Ray Absorption Spectroscopy to Probe Molecular Orientation in Benzotriazole Films Adsorbed on Partly Oxidised Copper, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 278:1, 27-36

To link to this article: http://dx.doi.org/10.1080/10587259608033654

Mol. Cryst. Liq. Cryst., 1996, Vol. 278, pp. 27–36
Reprints available directly from the publisher
Photocopying permitted by license only

USING POLARISED, ULTRA-SOFT X-RAY ABSORPTION SPECTROSCOPY TO PROBE MOLECULAR ORIENTATION IN BENZOTRIAZOLE FILMS ADSORBED ON PARTLY OXIDISED COPPER

JOY JOHNSTONE & KEVIN J. ROBERTS*
Dept. of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, U.K.
*also at CLRC Daresbury Laboratory, Warrington, WA4 4AD, U.K.

Abstract Data are presented of polarisation studies carried out to elucidate the orientation of the benzotriazole molecule adsorbed onto copper thin films. Spectra were obtained at the carbon K-edge. Comparisons are made between this and the orientations of structurally similar molecules; indazole, methyl benzotriazole and benzimidazole. Different copper film thicknesses and degrees of oxidation were investigated, and a film of benzotriazole on silver was also examined. All of the molecules were found to be oriented normal to the substrate, except benzimidazole on copper, which showed no orientation dependence.

INTRODUCTION

Benzotriazole (BTAH) has, for over 50 years, been established as a corrosion inhibitor for copper and its alloys. It is used to prevent tarnishing in the packaging, storage and transport industries, and as an additive in antifreezes, detergents, lubricants etc. However, despite numerous studies, the interfacial chemistry involved has never been satisfactorily established - indeed a number of conflicting results have emerged. The exact structure of the inhibiting film remains the subject of debate.

All copper is covered in a native oxide layer, therefore, it is reasonable to suppose that it is with the oxide that BTAH interacts. It is thought that this inhibitive effect is due to the adsorption of BTAH on the copper surface. Chadwick et al[1] outlined two distinct possibilities - the formation of a cuprous (Cu(1)BTA) complex,

or of a cupric (Cu(2)BTA) complex. XPS showed that it was the cuprous form which most commonly occurred in a wide variety of environments. They reported that the species formed "in situ" was a cuprous complex, consisting of linear polymeric chains, lying flat on the surface but which quickly oxidised to a Cu(2) species on removal from solution. This Cu(2) complex can be wiped off using a tissue, leaving the Cu(1) species behind - evidence that the compound formed "in situ" is Cu(1). Hope et al describe the formation of this cuprous complex as possibly being preceded by a reaction between BTA^- and copper, or by the adsorption of BTAH on the surface.

SEM has shown the structure at the surface to be $Cu/Cu_2O/$ Cu(1)BTA^2. Cotton and Scholes[3] compared the inhibitive effects of BTAH with those of molecules in which N_1 and/or N_2 were replaced by carbon, or in which the labile H was replaced by a bulky methyl group (fig. 1). It was found that only BTAH and indazole prevented staining and,

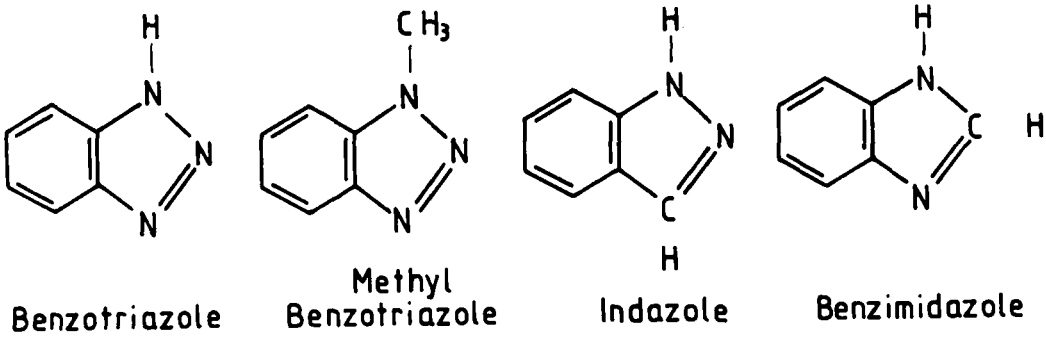

FIGURE 1

while both were impervious to washing with water, indazole was removed by organic degreasants. This is strong evidence to suggest that a true chemical bond is formed between BTAH and the copper surface, involving chelation via the nitrogen atom containing the labile H atom and one or more of the N atoms.

For many years it was thought that BTAH would not bond to "clean" copper. Subsequently, Fang et al[4] found this to be untrue, although the presence of the oxide facilitates the formation of the film, and allows thicker films to form. Moreover, the structure of the film formed on "clean" copper was found to be very similar to that on

oxidised copper, and this means that the presence of oxygen is not strictly necessary for the formation of bonds between BTAH and copper i.e. no OH bonds are formed on the surface copper atoms, rather the labile H atom is lost from BTAH before chemisorption. It was this study which first suggested that the molecules did not lie flat on the surface. Photo-emission of BTAH on "clean" copper, showed no chemical shift for the π orbitals of BTAH upon chemisorption. This implied that the molecule does not lie flat on the surface. A new structure was proposed in which each BTAH is bonded to two Cu atoms thus tying up all the copper atoms on the surface and accounting for the necessity of having three nitrogen atoms - two adjacent to each other for binding to Cu and a third for hydrogen bonding to a hydrogen on a neighbouring molecule. This explains quite neatly the lack of protection afforded by benzimidazole, indazole and methyl benzotriazole, which lack adjacent N's or which cannot form hydrogen bonds. This means that, due to steric effects, only every second copper atom is bonded. The hydrogen bonding is thought to be the factor which makes the Cu-BTAH complex insoluble, and requires that the bonding molecules be neither too close, nor too far apart. For the above model, this means that the molecules cannot all be "in plane" as shown, but that alternate molecules must be "tipped" above and below the plane by at least 9° to put the N and H atoms indicated at a distance of 1.2Å from each other - acceptable for H-bonding. Note that this angle is the bare minimum required.

Xu, Lau and Bohn[5] performed semi-empirical calculations on the molecular structure of free BTA^-. From these it was deduced that it has a planar structure and, since it is thought to be similar to the structure of BTAH adsorbed on copper, the results for free BTA^- were used to calculate the saturation BTA^- density for different bonding geometries. These results indicate that the molecule is oriented "edge on" and suggest that bonding occurs via the lone pairs of N_1 or N_3. Fang et al used photo-emission to obtain spectra of BTAH on clean and oxidised copper. The two sets of results were found to be very similar and the disappearance of N lone pair shifts on chemisorption indicated that they were involved in the bonding process. It is in the determination of precisely which N atoms are involved in the bonding and the related issue of orientation, and in the determination of the exact chemical nature of the protective film that contention arises.

In order to gain structural information about the surface Cu-BTA complex it is necessary to probe the local environment of those surface copper atoms to which benzotriazole is co-ordinated. Pizzini et al[6,7] used EXAFS spectroscopy at the copper K-edge to do this. In order to minimise the contribution to the spectra of uncoordinated copper atoms, spectra of surface samples of Cu-BTA and of 4 and 5 bromo-substituted Cu-BTA complexes were obtained using glancing angle and total reflection geometries and compared with the transmission spectra of their bulk-counterparts. There are only two distinguishable sites on the triazole ring to which copper atoms can co-ordinate - N_1 and N_2 (fig 2). EXAFS simulations show that in model 2 carbon atoms 6-9 are too far away from the central Cu atom to make a significant contribution to the EXAFS spectrum. In model 1, on the other hand, carbon 6 is significant. Analysis of the bulk Cu-BTA sample show that carbon 6 does not make any contribution to the spectrum and so it would seem that model 2 is acceptable. Examination of the surface Cu-BTA sample found

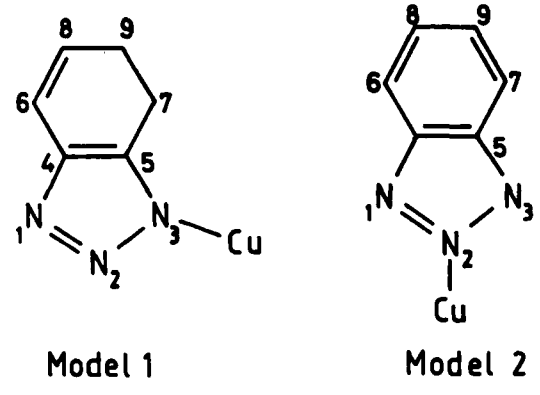

FIGURE 2 Binding sites distinguishable by EXAFS spectroscopy

that the layer of Cu-BTA was too thin to prevent contributions from uncoordinated copper atoms in the bulk of the film. The results of the analysis of the 4 and 5-bromo substituted surface samples at the Cu K-edge and Br K-edge again indicate that bonding to copper is via the N_2 atom.

This study has its limitations, as indicated, particularly in the surface sample of unsubstituted Cu-BTA due to the interference of the bulk copper atoms. The ideal probe would be to examine the environs of the nitrogen and carbon atoms in the

triazole ring itself. This requires ultra-soft x-rays, which was beyond the scope of Pizzini's work but which is available to us. Therefore the aim of this series of experiments is to use polarised ultra-soft XANES spectroscopy at the carbon and nitrogen K-edges to determine the effect of copper film thickness and degree of oxidation of the copper film and to compare the orientation of the benzotriazole molecule on copper with its orientation on silver. Also to examine a series of substituted benzotriazole molecules for comparison. In this paper, the carbon K-edge data are presented.

EXPERIMENTAL

Sample Preparation

Glass squares (1×1cm) were cleaned by immersion in chromic acid for a minimum of 24 hours. The glass was then thoroughly rinsed with deionised water and dried in air before being coated with thin films of copper or silver, using a Edwards evaporation unit, operating at a pressure of 1×10^{-3} Torr. Copper films approximately 100,200,500,1100 and 2000 Å thick were prepared, as well as a 1000 Å film of silver. One 1100 Å sample was placed in an oven at 150 °C for two hours in order to oxidise it. The samples were then immersed in 0.5 wt% solutions of benzotriazole, indazole, benzimidazole or methyl benzotriazole in ethanol, maintained at 50 °C in a water bath, for 30 minutes, then rinsed with ethanol and allowed to dry, before storing in petri dishes. In order to be able to use electron yield detection, the sample needs to conduct electricity, therefore, the back and edges of the glass were coated with silver-loaded epoxy resin, which was allowed to dry for 24 hours before the sample was placed in the beamline.

Data Acquisition

The spectra were recorded over the regions 275-320 eV (C K-edge) on beamline U1A at the NSLS at Brookhaven National Laboratory using an extended range grasshopper monochromator. The experimental chamber provides for measurements to be made in electron yield and fluorescence yield modes, while the sample is maintained under vacuum conditions. A conventional channeltron electron yield detector and a fluorescence yield detector were used. The sample chamber, which is separated from the UHV beamline by a differentially pumped aluminium window (typically 0.1-0.4 μm thick) is maintained at moderate pressures (ca 1×10^{-6} mbar) and is thus suitable for examination of high molecular weight organic thin films. Spectra were obtained at angles of x-ray incidence ranging from glancing angle (10°) to normal (90°) with respect to the substrate in increments of 10°, or, when beam time was limited, at larger intervals; 20,30,50,70 and 90°.

Data Reduction

The spectra were normalised to an edge step of 1.0 using the plotting/analysis program PLOTEK (Daresbury Laboratory). The approximate orientations were determined visually and by comparison of peak intensities.

RESULTS & DISCUSSION

1.Benzotriazole

A pressed powder sample of benzotriazole was placed in the beam, and a fluorescence yield spectrum was obtained at the carbon K-edge (since the sample was non-conducting, data could not be obtained in electron yield). To prevent the sample subliming, liquid N_2 was poured into the sample manipulator. The spectrum is shown in fig. 3a along with a 90° incidence electron yield spectrum for the 1100Å sample of Cu-BTA (fig. 3b). The benzotriazole shows three main peaks, which correspond in shape and relative position approximately to the first three peaks in the Cu-BTA spectrum. In the latter, however, they are shifted to higher energy by about 4 eV. The

differences between the spectra of pure benzotriazole and benzotriazole on copper, indicate disruption of the atomic orbitals upon chemisorption, i.e. the formation of a chemical bond between Cu and benzotriazole.

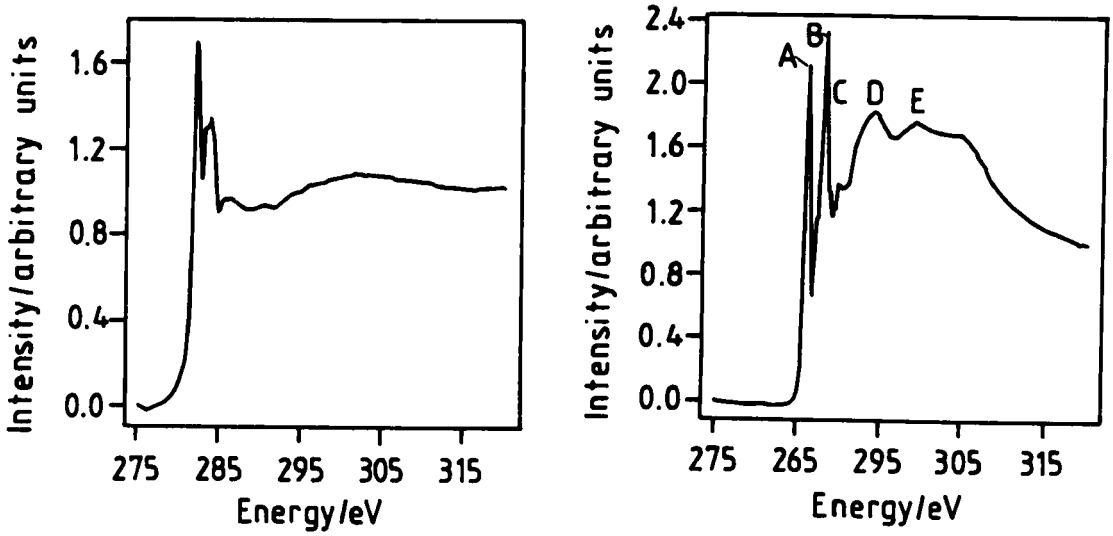

FIGURE 3 (a) Fluorescence yield spectrum of bulk benzotriazole (b) Electron yield spectrum of benzotriazole on 1100Å copper thin film.

2. The Orientation of Copper Benzotriazole:

(a) Cu-BTAH Carbon K-edge Spectra

In analysing the Cu-BTAH samples, it was not necessary to introduce liquid N_2 into the sample manipulator. This suggests that BTAH is strongly bonded to the copper film. There are five main peaks apparent in all of the spectra, labelled A to E (fig. 3b) at energy values 285.7, 287.8, 289.5, 293.3 and 299.9 eV respectively. Peaks A and B are very sharp, which is characteristic of π^* resonances. The remaining peaks are somewhat broader and may be attributable to σ^* or to a mixture of π^* and σ^* components. In order to assign these peaks to specific transitions within the benzotriazole molecule we need to consider first its structure. From figure 1, we can see that carbon is involved in four different types of bond; the C=C σ^* and C=C π^* bonds, the C-H and C-Nσ^* bonds.. Stohr[8] recorded the spectrum of aniline adsorbed on Ag(110). This showed four π orbitals at 285.5, 287.5, 289.5 and 290.5 eV. The first of these is very much stronger than the other three. The spectra of benzene and

various other, similar molecules[8] also indicate that the main C=C π^* transition can be expected at around 285.5 eV, therefore, we can attribute peak A to this transition. Peaks B and C also tie in positionally with two of the C=C π^* energies observed in aniline. However, the C-H transition is also expected at around 289.5 eV[9] and the C-N transition at about 291 eV[7]. Since peak C is approximately as strong in all of the spectra as peak A, while the π^*_2 transition is expected to be substantially weaker than π^*_1, it seems more likely that the C-H transition is the main contributor to this peak. The predicted sigma intensities, also from the aniline spectrum, are at energies around 294 and 302 eV. The first of these coincides with the position of peak D. The assignment of peak E is less obvious.

Visual inspection of the normal (90°) and glancing (10°) incidence spectra, for each of the copper film thicknesses, shows a marked change in the relative peak intensities with changing angle. This indicates that the surface copper-benzotriazole (Cu-BTA) film is oriented with respect to the bulk copper substrate. In each case, peaks A and B dominated at 90° and diminish in intensity with decreasing angle of incidence. Peaks C and D show the opposite polarisation dependence, increasing in intensity as peaks A and B decrease, although the change in their overall intensities is less dramatic than for A and B. Peak E shows no polarisation dependence. As previously noted, peak A is attributable to the first and most intense of the C=C π^* transitions associated with the benzene ring. This peak has its maxima between 70° and 90° for the various film thicknesses. This indicates that the π orbitals of the benzene ring are approximately parallel with the substrate i.e. the benzotriazole molecule is standing roughly upright on the surface. Since the assignment of this particular peak is certain, we can use it as a comparitor for the assignments made for the other peaks. Firstly, let us consider the expected polarisation dependence of the σ^* transition of the benzene ring. The sigma plane is parallel to the π bonds, therefore this transition should show the opposite polarisation dependence to that of the π^* transitions. Referring to the plot of intensity vs angle of incidence, peak D does indeed have opposite dependence to peak A. Peak B, which, it has been suggested above, may be due to a combination of C=C π^* and C-H transitions, shows the same dependence as peak A. This is consistent with its being a second C=C π^* transition,

however, the peak is a good deal more intense than would be expected for this transition alone. This is probably due to the contribution of the C-H bonds. Peak C has the opposite dependence to the first two. As with peak B it may owe some of its intensity to a C=C π^* transition, however, the situation is reversed in that it cannot be the main contributor. It is possible that this peak may be due to the C-N σ^* transition, which would be expected to show the same orientation dependence as the C=C σ^* bonds.

The orientations of the BTAH molecule on the copper films of all thicknesses and degrees of oxidation were determined by comparing the intensities of peak A as the angle of x-ray incidence. Although the overall trend was easily observed in this way, at times the change in intensity was very small, or indeed fluctuated slightly. Therefore, it was also necessary to take into account the relationship between A and the other peaks in the spectrum. All were found to be oriented at 90° with respect to the substrate.

(b) Comparison with Methyl Benzotriazole, Benzimidazole and Indazole

The structures of the three benzotriazole-like compounds used for comparison are shown in figure 1. Methyl benzotriazole is almost identical to BTAH. The carbon K-

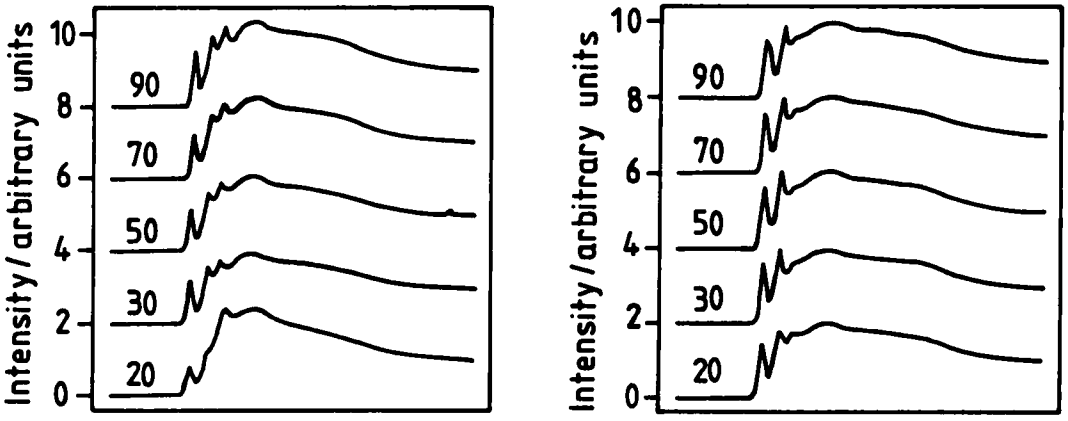

FIGURE 4 Orientation scans for: (a) BTAH on 2000Å Cu (b) Benzimidazole on 1000Å Cu

edge spectra show the same peaks as for Cu-BTA, as we would expect, and indicate that the molecule is oriented normal to the substrate. The same is true for indazole. Benzimidazole, however, shows no orientation dependence.

(c) Silver Benzotriazole

The same peaks are apparent in the Ag-BTA carbon K-edge spectra as for Cu-BTA. From the C K-edge orientation scans, the orientation of the molecule appears to be at around 80° with respect to the substrate.

CONCLUSIONS

The carbon K-edge spectra show that the benzotriazole molecule is generally oriented at 90° with respect to the substrate on all thicknesses of copper film. The presence of more oxide does not appear to influence the orientation. Indazole and methyl benzotriazole are also oriented normal to the substrate. Benzimidazole displays no orientation dependence.

REFERENCES

1. D. Chadwick & T. Hashemi, Corrosion Science, 18, 39, (1978).
2. A.D. Modestov, G.-D. Zhou, H.-H. Ge and B.H. Loo, J. Electroanalyt. Chem., 375, 293, (1994).
3. J.B. Cotton & I.R. Scholes, British Corrosion Journal, 2, 1, (1967).
4. B.-S. Fang, C.G. Olson & D.W. Lynch, Surface Science, 176, 476, (1986).
5. Z. Xu, S. Lau & P.W. Bohn, Surface Science, 296, 57, (1993).
6. S. Pizzini, K.J. Roberts, I.S. Dring, R.J. Oldman & D.C. Cupertino, J. Mater. Chem., 3(8), 811, (1993).
7. S. Pizzini, PhD Thesis, Strathclyde University, (1990).
8. J. Stohr, NEXAFS Spectroscopy, Springer Series in Surface Science 25, Springer-Verlag, Berlin Heidelberg, 199-205, (1992).
9. J. Stohr & D.A. Outka, Phys. Rev. B, 36 (15), 7891 (1987).