NEXAFS and XPS of p-Aminobenzoic Acid Polymorphs: The Influence of Local Environment

J S Stevens[1], A Gainar[1], C Jaye[2], D A Fischer[2], S L M Schroeder[3,4]

[1]School of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK
[2]Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, 20899, USA
[3]School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK
[4]DIAMOND Light Source Ltd., Chilton, Didcot, OX11 0QX, UK

E-mail: joanna.stevens@manchester.ac.uk; s.l.m.schroeder@leeds.ac.uk

Abstract. Nitrogen K-edge XPS and NEXAFS of the two polymorphic forms of para-aminobenzoic acid (PABA) are significantly different reflecting variation in hydrogen bonding. Alteration in hydrogen bonding at the amino group leads to a shift to high energy for both the XPS N 1s core level and the $3\pi*$ NEXAFS resonance with β-PABA. Participation of the amine group in the aromatic system causes the $1\pi*$ resonance to be sensitive to the nature of the intermolecular bonding at the *para*-carboxylic acid group, and a shift to low energy for α-PABA is observed due to hydrogen-bonded carboxylic acid dimer formation. FEFF calculations also successfully reproduce both the energy and intensity variations observed for the σ* shape resonance associated with the C−N bond, with the majority of the decrease in energy observed for β-PABA arising from the longer C−N bond.

1. Introduction

The local 3-dimensional environment and interactions of a molecule in the solid-state can have a substantial influence on physical and chemical properties, such as stability, solubility, melting temperature, and reactivity [1]. The ability to characterize and identify such forms (polymorphs) with identical chemical composition but variations in crystal structure (structural packing, interactions, and bonding) is thus extremely important. Understanding or insight into the electronic nature of these materials could provide the basis for investigating how they form in solution, and therefore ultimately how to control the outcome of crystallization [2]. Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS) are ideal for this purpose, as they intrinsically probe the local environment of X-ray absorbing atoms. The effects of the local environment and interactions were initially investigated for *para*-aminobenzoic acid (PABA), an intermediate for folic acid synthesis with pharmaceutical applications, by nitrogen NEXAFS and *ab initio* density functional theory (DFT) [3]. Comparison of the crystalline α-form and an isolated molecule revealed substantial differences for the extreme case of removing all effects of the surroundings, and this was especially notable for the calculated N K-edge NEXAFS [3]. XPS and NEXAFS of the nitrogen moiety in PABA have therefore been collected for the two different crystalline polymorphs (α- and β-, Figure 1) [4,5] to investigate their sensitivity to more subtle

variations in local environment and intermolecular interactions. This is complemented by investigation into the influence of relatively minor alteration in bond length with FEFF calculations.

2. Methods

2.1. Materials
-PABA was used as supplied (>99% purity, Sigma-Aldrich UK) and β-PABA was formed through an aqueous slurry of -PABA at 5°C. Powder samples were used for analysis.

2.2. X-ray Photoelectron Spectroscopy (XPS)
N 1s XP spectra were recorded with a Kratos Axis Ultra instrument, employing a monochromatic Al K_α source (1486.69 eV) operating at 180 W (15 kV and 12 mA) [3]. Samples were fixed using double-sided tape and measurements were obtained in constant analysis energy mode below 10^{-8} mbar, with a pass energy of 20 eV, 0.1 eV steps, and 500 ms dwell time per data point. Analysis of the data was carried out with CasaXPS software using a Shirley background and GL(30) lineshape [6]. Samples were referenced to the C 1s photoemission C=C at 284.8 eV.

2.3. Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy
N K-edge partial electron yield (PEY) NEXAFS measurements were performed on the U7a beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY with the sample at 54.7°, a 600 l/mm monochromator grating, and an entrance grid bias of -150 V [3]. Spectra were normalized by the simultaneously recorded I_0, and the monochromator energy scale was calibrated using the 400.6 eV 1st π* of a titanium nitride grid using the Athena software [7,8]. Repeatability of resonance positions is <0.1 eV.

2.4. FEFF calculations
FEFF8.2 [9] was used to simulate the * shape resonance in the N K-edge NEXAFS for a molecule from the crystal structure of α- and β-PABA following geometry optimization of the crystal structure with CASTEP [3]. The SCF (7.0), XANES (4.0), and FMS (10.0) cards were used, and the calculated data were rigid shifted by +2.3 eV. To identify the influence of the CóN bond length, calculations were also run in which the average CóN bond length of α-PABA was increased by 0.035Å relative to the equilibrium value in the crystal structure so that it matched that of β-PABA (1.399 Å).

3. Results and Discussion
The nitrogen XPS and NEXAFS for the α- and β-PABA polymorphs yield characteristic spectra (Figures 1 and 2), with NEXAFS clearly differentiating between the two forms. For N 1s XPS, a small yet reproducible increase of around 0.2 eV in binding energy is observed for β-PABA (Figure 1). This follows the change in intermolecular hydrogen bonding with the additional hydrogen-acceptor effect at the amine nitrogen in β-PABA (Figure 1), reducing the electron density on nitrogen.
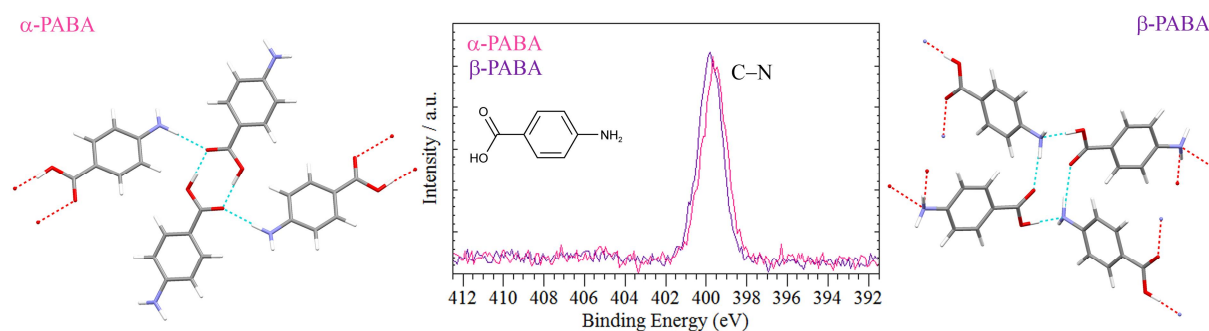
Figure 1. Nitrogen 1s XPS and intermolecular interactions of the α- and β-PABA polymorphs.

In the N K-edge NEXAFS spectra, both energy and intensity shifts occur for each of the peaks (Figure 2), reflecting the influence of variations in the local environment (intermolecular H-bonding, electron density distribution) and geometry (such as bond lengths) between the polymorphs. Visualization of the associated unoccupied π^* molecular orbitals (MOs) shows the first energy resonance ($1\pi^*$) involves promotion from the core N 1s level into the lowest unoccupied molecular orbital (LUMO), which is delocalized across the amine, aromatic ring and *para*-carboxylic acid group (Figure 2) [3]. The chemical state and interactions at the opposite end of the ring to nitrogen appear to influence the position of this $1\pi^*$ resonance, with successively increasing absorption energy reflecting the carboxylic acid dimer in α-PABA, hydrogen bonding to the amino group of another molecule in β-PABA (Figure 1), and the carboxylate COO^- in the anionic form [10]. In contrast, the second resonance ($3\pi^*$) involves the LUMO+2 (Figure 2), which is much more concentrated around the nitrogen atom [3]. This leads to it being more sensitive to the nature of the interactions at nitrogen, with the additional hydrogen-acceptor effect at the amine nitrogen in β-PABA (Figure 1) increasing the energy of this $3\pi^*$ MO in addition to that of the N 1s core level (Table 1). The O K-edge π^* resonances are correspondingly decreased in energy with the accompanying additional hydrogen-donor at oxygen.
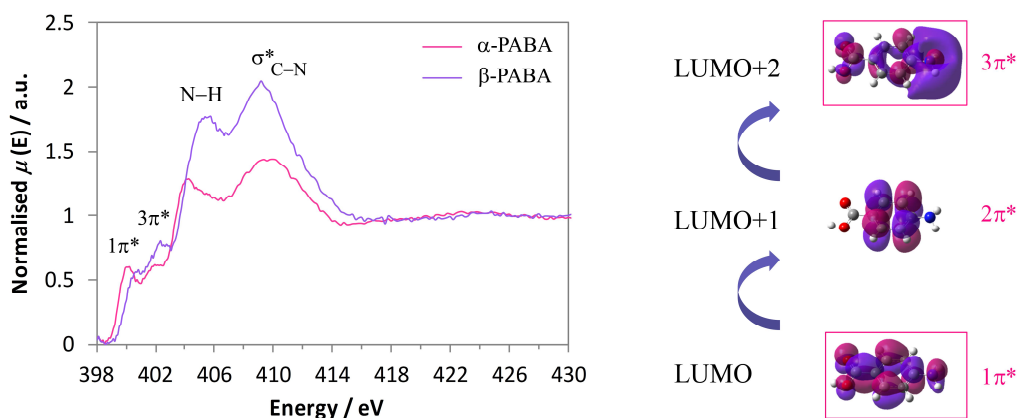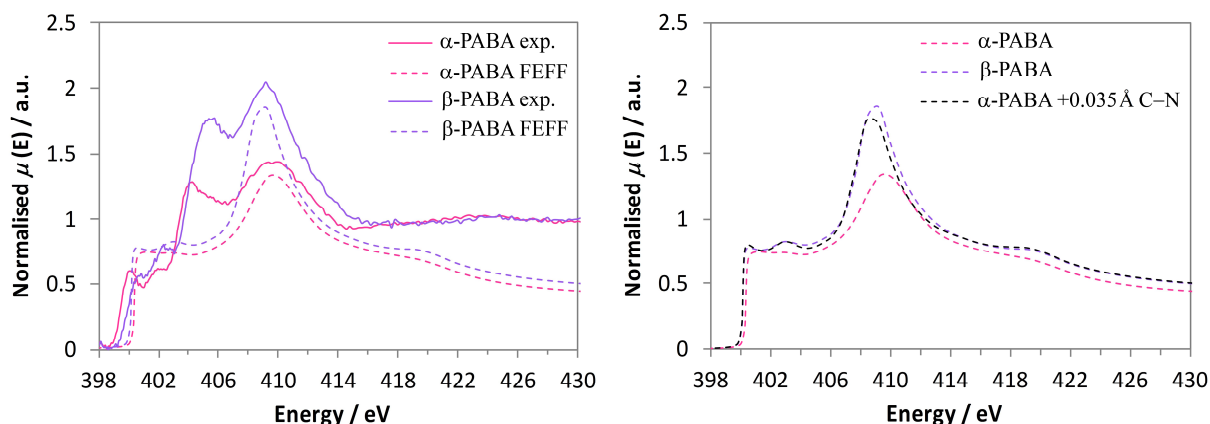

Figure 2. Nitrogen K-edge NEXAFS for the α- and β-PABA polymorphs, and unoccupied MOs involved in the first two resonances (outlined with boxes). Significant promotion to LUMO+1 ($2\pi^*$) is not expected as it has no density at N.

Table 1. Nitrogen K-edge NEXAFS features

NEXAFS features		α-PABA / eV	β-PABA / eV
IP (aromatic NH_2)		403.30	403.60
N 1s	$1\pi^*$	400.00	400.58
N 1s	$3\pi^*$	401.70	402.30
N 1s	N–H	404.09	405.11
N 1s	σ^*_{C-N}	409.61	409.09

Following the edge step (ionization potential, IP) and third resonance associated with N–H, the broader post-edge fourth resonance is a σ^* shape resonance for the C–N bond [3,10]. This σ^*_{C-N} peak shows a shift to lower energy for β-PABA, in contrast to the increased π^* and IP positions (Table 1). This is investigated for the two polymorphs using the FEFF code (as it predicts the post-continuum resonances) [9]. The results for α- and β-PABA show significant differences in both energy and intensity for the two polymorphs (Figure 3). Comparison of the FEFF output with the experimental data (Figure 3) shows excellent correlation, successfully predicting both the relative energy and intensity variations.

The dependence of this σ* resonance on the C−N bond was further investigated through variation of the C−N bond length for α-PABA. Lengthening of the C−N bond to that for β-PABA (+0.035 Å), leads to a decrease in σ* energy relative to the IP, accounting for the majority of the energy and intensity shifts between α- and β-PABA (Figure 3).

Figure 3. Comparison of experimental (solid line) and FEFF-calculated (dashed line) nitrogen K-edge NEXAFS for the two polymorphs of PABA, and the impact of variation in C−N bond length.

4. Conclusions

Insights into the electronic and structural nature of the two polymorphs of PABA are obtained with nitrogen K-edge NEXAFS and XPS. A small shift in core level N 1s energy is attributed to the variation in intermolecular hydrogen bonding. Significantly different, highly characteristic NEXAFS spectra arise from the changes in local surroundings and bonding, with the π* shifts related to the nature of the MOs and local environment, and the σ* shape resonance primarily influenced by the C−N bond length. This demonstrates the sensitivity of XPS and NEXAFS to the relatively minor changes in local environment despite their identical chemical composition.

Acknowledgements

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