Characterization of Hexacarbonitrile–Triimidazo–Triazine (HTT) Using Experimental and Modeled Ultrasoft X-ray Absorption Spectra

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The characterization of a large oligomeric molecule containing primarily carbon and nitrogen using ultrasoft X-ray absorption spectroscopy (USXAS) above the carbon and nitrogen K edges is discussed. Specifically, we have used carbon and nitrogen 1s core level USXAS spectra to characterize the electronic structure of hexacarbonitrile–triimidazo–triazine (HTT) for the first time. The electronic spectrum above the carbon and nitrogen edges allowed us to distinguish between several potential geometric structures. Core spectra of several potential structures for HTT were simulated using a linear combination of core level spectra from several smaller constituent molecules including imidazole (IM), 4,5-dicyanoimidazole (DCIM), and *s*-triazine (TZ). By starting with smaller molecules which contain delocalized π-systems, we propose that a building block approach to USXAS spectral modeling, commonly used in the analysis of nonconjugated systems, can be used for molecules containing extended π-systems. The comparison of HTT simulated spectra with the experimental spectrum provides substantial insight into the complex HTT structure and eliminates alternate C_5N_4 structural possibilities.

Introduction

The characterization of solid polymers and polymeric films has traditionally involved the use of X-ray photoelectron spectroscopy (XPS)[2–4] and secondary ion mass spectroscopy (SIMS).[5,6] Since XPS is a core-level method, elemental compositions can be determined in solid materials. However, XPS cannot generally provide detailed information about carbon-, nitrogen-, and hydrogen-containing covalent solids because the core level shifts commonly observed in these materials are not large enough to allow resolution of chemically distinct local structures. SIMS provides detailed information about the functional groups on the surface, but the information about the connectivity of these functional groups is often ambiguous. Ultrasoft X-ray absorption spectroscopy (USXAS), also known as NEXAFS, is an element specific technique which can provide substantial detailed information concerning electronic structure, connectivity, and functional group identification.[7,8] USXAS is more sensitive to chemical structure than XPS since dipole transitions from core levels to all the unoccupied molecular orbitals can generally be observed and resolved. The size and complexity of polymeric materials, coupled with the scarcity of electronic structure calculations and reference spectra often make assignment of spectroscopic transitions challenging. Spectra of simple, well-understood structural constituents, or building blocks, have been used previously to simulate the spectra of larger systems. These simulations can then be compared to the experimental spectra, and similar spectral features easily assigned. This technique of linearly combining spectra from model compounds to simulate more complex spectra is commonly used in USXAS spectral interpretation, and is discussed in detail in Stöhr's book *NEXAFS Spectroscopy*.[1] In this paper we will show the advantage of using experimental data from smaller heterocyclic compounds in the interpretation of the experimental spectrum of a more complex system, namely triimidazo[1,2-*a*:1,2-*c*:1,2-*e*]-1,3,5-triazine-2,3,5,6,8,9-hexacarbonitrile (HTT). This type of compound is interesting because it contains no hydrogen and is viewed as a precursor to a carbon–nitrogen material.

To help elucidate the goals of these experiments, some introduction to the specific problem addressed in this work follows. A compound with the molecular formula C_5N_4, as determined by elemental analysis, was synthesized at the University of Michigan.[9] Preliminary mass spectrometry, NMR, and IR data all gave inconclusive structural information. Distinct products could have been made from the DCIM-based starting material. A mechanism involving cyclization of the nitrile groups[10–12] could yield a hyperbranched oligomeric structure containing cyano end groups, or a 1–2 cycloaddition of the starting material could yield a cyclic trimer with the HTT structure (see Figure 1 for diagram of both HTT and alternate C_5N_4 structure). The inconclusive data and two possible C_5N_4 products

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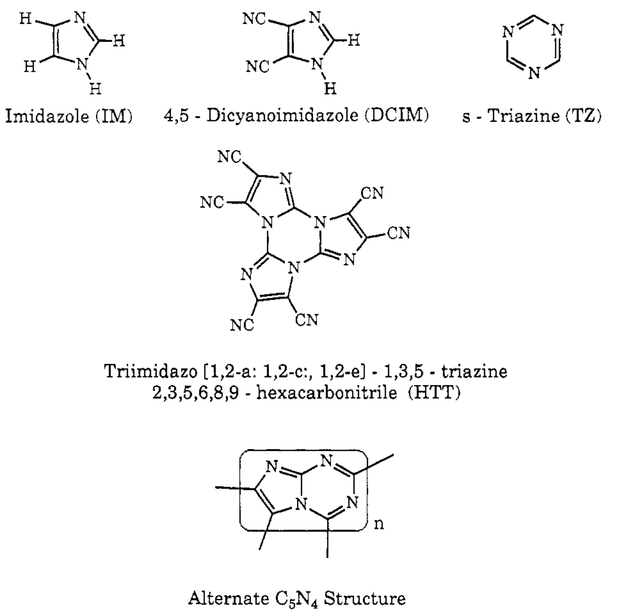


Figure 1. Molecular structures for the compounds used in these studies. Two alternative structures are given for the compound with empirical formula C_5N_4, later determined to be the HTT structure.

made definite structural determination difficult. The two similar structures in Figure 1 were distinguished using the USXAS data on the actual C_5N_4 compound combined with spectral modeling using smaller heterocycles. This type of building-block spectral modeling is being promoted here not as an alternative to the traditional methods of spectral interpretation but as a complementary process which can greatly aid in the interpretation of complex spectra.

Experimental Section

The electron yield, or EY-USXAS, spectra for HTT were recorded on the U1 beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. All spectra presented in this paper were taken at normal incidence. The total electron yield was measured above the carbon and nitrogen K edges with a channeltron located above the sample plane. The resolution at the carbon edge was 0.7 eV, and at the nitrogen edge was 1.2 eV. The total photon flux was estimated at 1×10^{11} photons/s at a photon energy of 300 eV for a ring current of 100 mA. In these experiments, ring currents were typically 400–600 mA.

The incident flux (I_0) spectrum was simultaneously recorded as the photocurrent to a gold grid. All USXAS spectra were normalized by I_0, and an exponential background was subtracted. The two characteristic dips in the I_0 carbon edge spectrum were used to calibrate the energy scale.[13] The agreement between the HTT spectra and previously recorded IM, DCIM, and TZ spectra[14] reinforces our confidence in this energy calibration.

The HTT used in these experiments was synthesized at the University of Michigan following the procedure outlined elsewhere.[9] The synthesis of HTT is pictured in Scheme 1. The samples described in this paper were synthesized using *N*-iodo-2-bromo-4,5-dicyanoimidazole as the starting material. The solid USXAS samples were formed by using 2000–6000 psi to press a 1-cm pellet in a modified KBr pellet press. The pellet thickness was approximately 0.25 mm.

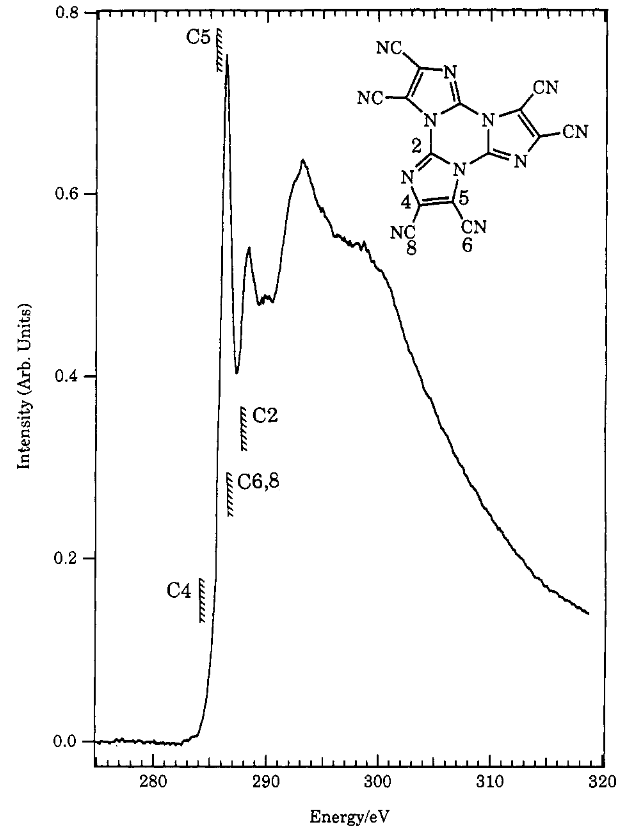
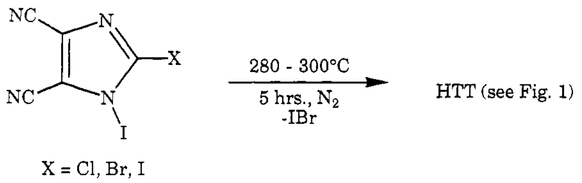


Figure 2. Carbon 1s EY-USXAS spectrum. Solid-state IPs are denoted by the lines labeled C2, C4, C5, and C6,8. The numbers refer to the inset molecular diagram.

Scheme 1



The USXAS and ISEELS (gas phase) spectra of IM, DCIM, and TZ discussed here have been discussed in detail previously[14] and are included here as building blocks for modeling the HTT USXAS spectra.

Results and Discussion

This article is focused on the carbon and nitrogen USXAS spectra of HTT and the use of the USXAS spectra from smaller heterocyclic molecules to distinguish between several potential structures with similar stoichiometries. Spectra for a series of structural constituent model compounds (i.e., IM, DCIM, and TZ) have been linearly combined to provide reference spectra for several potential structures for the C_5N_4 molecular formula unit. The reference provided spectral information in the absence of detailed electronic structure calculations over the required energy range. The spectral differences observed between the experimental spectrum and the reference spectrum obtained using a linear combination of the model molecular building blocks is discussed in terms of nonlocal electronic effects. All spectral assignments for the gas-phase and solid-state IM, DCIM, and TZ model compounds have been discussed in ref 14.

The HTT carbon 1s EY-USXAS spectrum is shown in Figure 2. The USXAS spectrum has been normalized to the I_0 signal and an exponential background has been subtracted. The major spectral features are positioned at 286.4, 288.4, 293.1, and 298.6 eV. Specific assignments

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Table 1. C 1s Peak Positions and Assignments for Hexacarbonitrile–Triimidazo–Triazine (HTT)

		assignment			
	energy	C2	C4	C5	C6,8
1	286.4	$1\pi^*$	$1\pi^*$	$1\pi^*$	C≡N π^*
2	288.4	$2\pi^*$	$2\pi^*$	$2\pi^*$	
IP[15]		287.8	284.0	285.4	286.4
3	289.9				
4	293.1	C–N σ^*	C–N, C–C σ^*	C–N, C–C σ^*	C–N, C–C σ^*
5	298.6	C–N σ^*	C–N, C–C σ^*	C–N, C–C σ^*	C–N, C–C σ^*

for the carbon edge features can be found in Table 1 and will be discussed in detail later. The K shell ionization potentials (IPs) are indicated by the lines marked C2, C4, C5, and C6,8 in Figure 2. The numbers refer to the molecular diagram inset in the figure. The correct IUPAC ring numbering system is not being used here in order to easily compare specific atoms in the HTT molecule with the analogous atoms in the DCIM and IM model compounds. The solid state IPs were directly determined by XPS measurements described in a separate paper.[15]

The first π^* resonance in the HTT C 1s spectrum, positioned at 286.4 eV, is dominated by the C 1s → $1\pi^*$ transition from the C6 and C8, or nitrile, carbon atoms. Contributions from the C2, C4, and C5 carbon atoms are present in this transition as well but are overshadowed by the transitions from the nitrile carbon atoms to the $1\pi^*$ level. The C 1s → $1\pi^*$ transitions from the nitrile carbons are expected to dominate the spectrum, because the nitrile carbon atoms, if grouped together, are present in the molecule in a two to one ratio when compared to other types of carbon atoms. The fwhm of the first transition is 1.5 eV, while the core level splitting for all carbon atoms as determined by XPS measurements[15] is 3.5 eV (see Figure 2 and Table 1). These shifts are similar to the shifts observed in the DCIM USXAS spectrum.[14] The C 1s IPs and π^* orbital shifts compensate for each other, resulting in a peak with a smaller fwhm than expected.

The second feature in the C 1s spectrum is positioned at 288.4 eV. The transition is assigned to an overlap of 1s → $2\pi^*$ for all carbon atoms in the HTT ring system. This assignment is based on the DCIM and IM data where the $2\pi^*$ transitions occur at 288.9 and 288.4 eV, respectively. Because of the close agreement with the IM and DCIM data, we do not attribute this peak to C–H σ^* transitions due to hydrocarbon surface impurities which are commonly found in this energy range.[16]

The continuum region contains two broad resonances at 293.1 and 298.6 eV. These are assigned to C–N σ^* and C–C σ^* transitions from all carbon atoms in the HTT molecule. The transitions are similar in energy and peak shape to IM (292.5 and 297.5 eV) and DCIM (293.4 and 300.0 eV),[14] supporting this assignment.

The HTT nitrogen 1s EY-USXAS spectrum (Figure 3) has been normalized by I_0, and an exponential background has been subtracted. The major spectral peaks occur at 399.4, 402.1, 407.6, 412.1, and 414.6 eV. The spectral assignments are in Table 2 and will be discussed below. The K shell IPs,[15] indicated by the lines marked N1, N3, and N7,9, refer to the numbers inset in Figure 3.

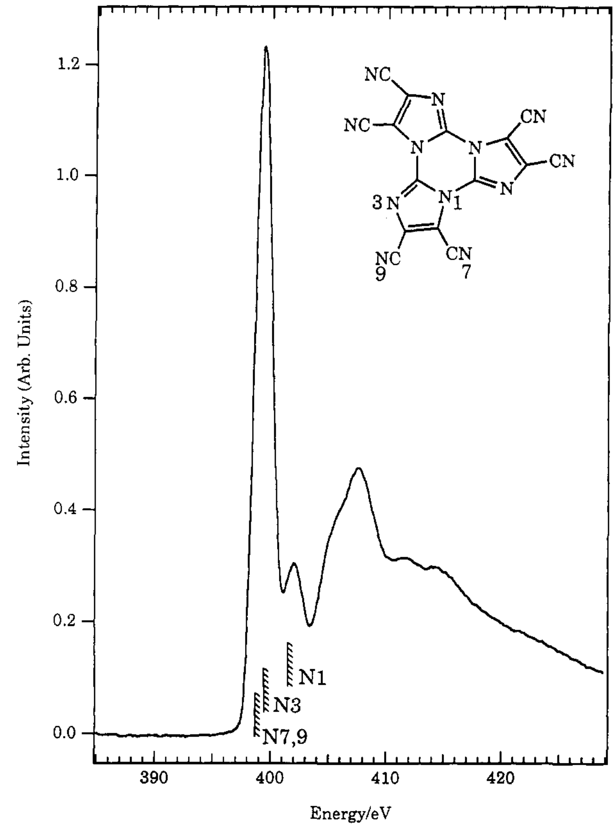

Figure 3. Nitrogen 1s EY-USXAS spectrum. Solid-state IPs are denoted by the lines labeled N1, N3, and N7,9. The numbers refer to the inset molecular diagram.

Table 2. N 1s Peak Positions and Assignments for Hexacarbonitrile–Triimidazo–Triazine (HTT)

		assignment		
	energy	N1	N3	N7,9
1	399.4		$1\pi^*$	C≡N π^*
2	402.2	$1\pi^*$	$2\pi^*$	
IP[15]		401.6	399.4	398.6
3	405.8	continuum onset/double excitation		
4	407.6	C–N σ^*	C–N σ^*	C–N σ^*
5	412.1	C–N σ^*	C–N σ^*	C–N σ^*
6	414.6	C–N σ^*	C–N σ^*	C–N σ^*

The first major feature in the HTT N 1s USXAS spectrum is positioned at 399.4 eV and has a fwhm of 2.0 eV, which is greater than the instrumental resolution. In analogy with DCIM,[14] HTT has four π^* orbitals, the $1\pi^*$ and $2\pi^*$ orbitals associated with the ring system and the C≡N π^* orbitals parallel (‖) and perpendicular (⊥) to the ring system. Compounds such as acetonitrile (CH_3CN)[17] and HCN[18] have transitions attributed to C≡N π^* positioned at 399.9 and 399.7 eV, respectively. In these compounds, the ‖ and ⊥ π^* components are degenerate while in HTT they are not. The ⊥ component can interact with the ring system causing a loss of degeneracy. The splitting for the ‖ and ⊥ components in systems such as propiolic acid where the C=O interacts with the adjacent C≡N bond is about 1.0 eV.[13] The splitting of approximately 1 eV to lower energy shifts the centroid of the peak to slightly lower energy than in a system where the ‖ and ⊥ component are degenerate, e.g., CH_3CN[17] and HCN.[18] This effect is seen in the HTT system. The splitting also accounts for the larger fwhm of the main π^* resonance compared to degenerate C≡N systems. The other component of this first major feature comes from the 1s → π^* transition for the N3 nitrogen, the N atom in the triazine-like ring of the HTT molecule. The N1 1s

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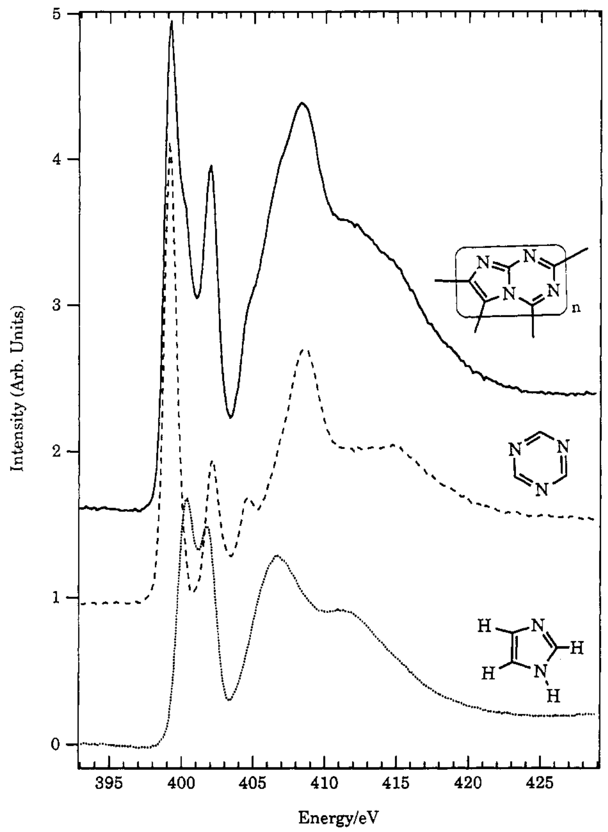

Figure 4. N 1s modeled spectrum of the alternate C_5N_4 structure and the experimental data for its component parts, imidazole (solid phase) and *s*-triazine (gas phase). IM and TZ data from ref 14.

→ $1\pi^*$ transition and position are discussed below. The analogous feature in DCIM occurs at 399.4 eV. Due to the good agreement between the DCIM and HTT data, the 399.4 eV feature is assigned to the overlap of the N3 1s → $1\pi^*$, 1s → $C{\equiv}N$ (∥) π^*, and 1s → $C{\equiv}N$ (⊥) π^* transitions.

We propose that the feature at 402.1 eV in the HTT spectrum is the result of the overlap of several π^* transitions. For IM and DCIM the π^* transitions are positioned at 401.8 and 401.3 eV, respectively. Therefore the lower energy component in this broad peak may be the N1 1s → $1\pi^*$ transition. The higher energy component in this broad transition may result from the N3 1s → $2\pi^*$ transition which is observed at 403.0 eV in DCIM. It could be argued that this peak might also be the 1s → $2\pi^*$ transition for all nitrogen atoms in the ring system with the peak energy shifted 1 eV to lower energy due to the stabilization of the extended π-system in the HTT molecule. However if this were the case, an analogous shift to lower energy of the $1\pi^*$ transition should also be observed. Since the $1\pi^*$ transition for HTT and DCIM occur at the same energy, i.e., there is no shift of the $1\pi^*$ peak and therefore the extension of the π-system does not have a great effect on the spectrum. We therefore attribute the peak at 402.1 eV to the overlap of the N1 1s → $1\pi^*$ and N3 1s → $2\pi^*$ transitions. The N1 1s → $2\pi^*$ transition may be hidden under the onset of the continuum.

The continuum region contains three broad resonances at 407.6, 412.1, and 414.6 eV. These are attributed to 1s → C–N and C–C σ^* transitions based on the TZ and DCIM data. DCIM has σ^* transitions at 406.9 and 414 eV, while TZ has σ^* transitions at 409.2 and 415.3 eV.[14]

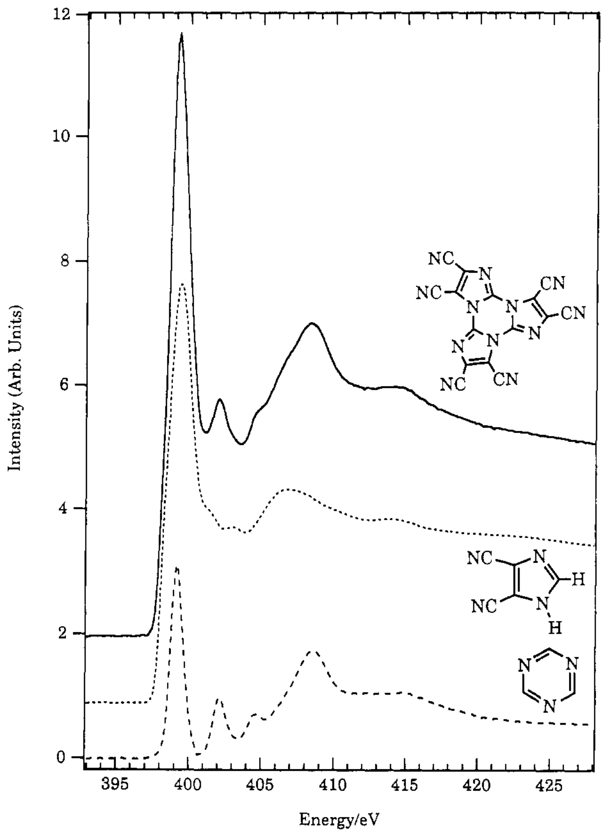

Figure 5. N 1s modeled spectrum of the HTT structure and the experimental data for its component parts, 4,5-dicyanoimidazole (solid phase) and *s*-triazine (gas phase). DCIM and TZ data from ref 14.

Modeling the HTT Spectra Using Experimental Data from Model Compounds

In his book *NEXAFS Spectroscopy*,[1] Stöhr describes an interesting building block approach to modeling the spectra of large molecules. Well characterized molecules such as ethane and HCN are used to model the C 1s NEXAFS spectrum of acetonitrile (CH_3CN).[1] Stöhr also discusses the limitations in the application of this method, namely the effect of conjugation through π-bond interaction. As a result of conjugation, a splitting of the π-system into two antibonding π^* orbitals can occur. This phenomenon is observed in butadiene[19] and in IM, DCIM, and TZ.[14] When the spectra of molecules are modeled with delocalized π-systems from nonconjugated diatomic molecules, for example, this π^* splitting is not observed.[1] We believe that this limitation clearly exists when constructing conjugated systems from nonconjugated building blocks. For example, modeling the IM molecule from a linear combination of methylamine (CH_3NH_2), ethylene (C_2H_4), and methyleneimine (CH_2NH) would most likely not yield the spectrum of IM. (No USXAS data has been collected on the CH_2NH molecule to date, probably due to the instability of the molecule.) We propose, however, that *starting* with building blocks that already contain delocalized π-systems largely circumvents the limitation of the building block approach to modeling molecules with extended π-systems. That is, beginning with molecules which already contain the π^* splitting which results from conjugation will increase the accuracy of the spectral model.

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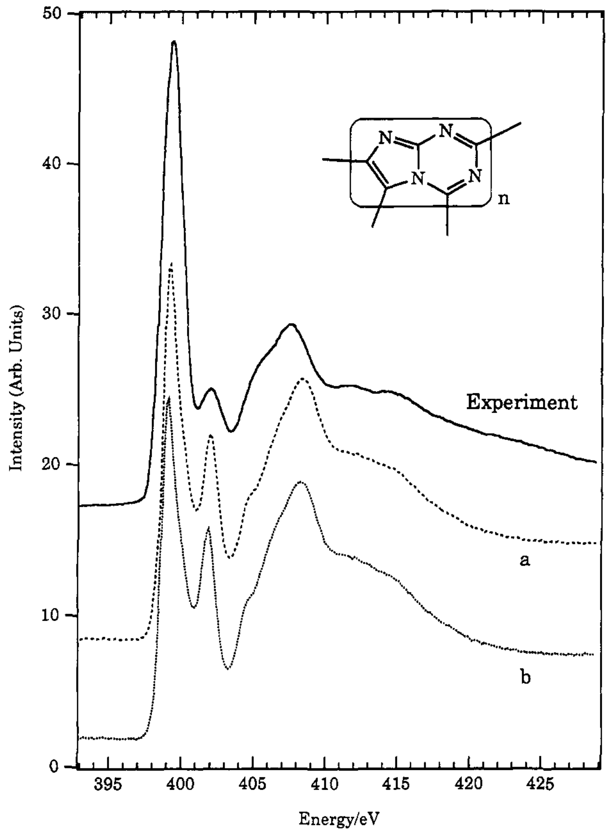

Figure 6. Modeled nitrogen 1s spectra for the alternate C_5N_4 structure where $n = 6$ and linear combination of (a) 6TZ + 4IM + 2DCIM or (b) 6TZ + 5IM + 1DCIM were used to model the inset structure. Inclusion of the cyano end groups (through addition of DCIM) provides a better approximation of the alternate C_5N_4 structure.

The building block approach to spectral modeling is illustrated using the data and simulated spectra above the nitrogen K edge. Similar information can be obtained from the carbon edge. For the alternative C_5N_4 hyperbranched structure shown in Figure 1, the structure could be considered to be a linear combination of an IM molecule and a TZ molecule. The simulated spectra for that structure would simply be the sum of the nitrogen 1s spectra for IM and TZ as shown in Figure 4. Note that the simulation for the alternate C_5N_4 structure has two prominent π^* resonances at 399.2 and 402.0 eV. The approximate position of the HTT N 1s peaks are well simulated, but the intensity ratio of the two π^* resonances does not match the N 1s experimental data in Figure 3. For HTT, the molecular structure can be simulated by using a TZ molecule and 2.5 DCIM molecules. The HTT N 1s spectra was simulated by adding 2.5 times the DCIM N 1s spectrum with the TZ spectrum (Figure 5). This simulated spectrum which models one potential HTT structure contains only one prominent π^* resonance at 399.2 eV, with a smaller π^* peak at 402.0 eV. Both the position and the intensity of the experimental data (Figure 3) are simulated using this structure. The accurate prediction of the position of the two π^* resonances in both models demonstrates the ability of the building block approach to adequately model molecules with extended π-systems. The differences in π^* intensity ratios demonstrates the ability of this particular model system to predict the correct structure for HTT.

The formation of C_5N_4 via the reaction mechanism involving the cyclization of nitrile groups, which could yield the alternate C_5N_4 structure shown in Figure 1, could contain some cyano end groups. To better model this event, spectra were simulated using combinations of IM, DCIM, and TZ. Figure 6 shows the linear combination of TZ, IM, and DCIM in 6:5:1 and 6:4:2 ratios. As with the IM and TZ model shown in Figure 4, these simulations adequately model the π^* peak positions but do not give the proper intensity ratios for the π^* peaks. A comparison of the modeled spectra with the experimental data can be found in Figure 7. It is clear that the HTT model is a better approximation to the actual experimental data than the alternate C_5N_4 structure. Further recent support of this conclusion was found using mass spectral analysis.[9] The use of a direct chemical ionization (DCI) probe for electron ionization (EI) mass spectral analysis produced a spectrum with the 348 MW parent peak[9] which clearly defines the HTT structure. A similar result was also obtained via chemical ionization (CI) using methane.[9] Previous EI studies using a solid probe and CI studies using ammonia failed to produce the parent HTT peak.[9]

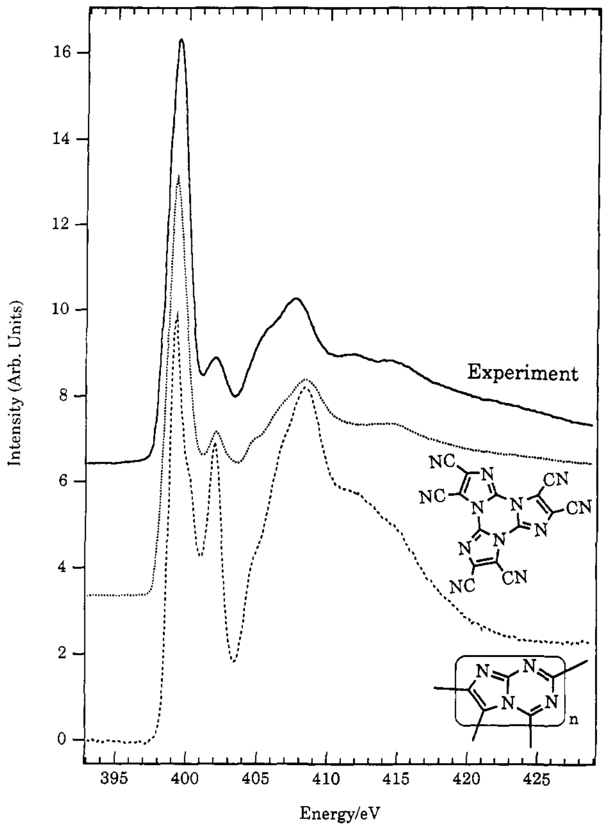

Figure 7. Comparison of modeled spectra for both the HTT and the alternate C_5N_4 structures with the experimental EY-USXAS data.

Conclusions

The USXAS carbon and nitrogen 1s spectra of the HTT molecule have been obtained and interpreted. Peaks in this complex spectrum were assigned by comparison with spectra from smaller model compounds such as IM, DCIM, and TZ. Spectra from smaller compounds can be combined linearly in order to simulate the experimental data from more complex systems. The use of molecules which contain delocalized π-systems to model molecules with extended π-systems circumvents the limitations to the building block approach to modeling USXAS spectra. Modeling the HTT structure using the DCIM and TZ model approximates the experimental HTT spectra quite well, while the alternate C_5N_4 structural possibility was eliminated by comparison with the IM and TZ model.