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He I Photoelectron Spectra and Gas-Phase Electronic Structures of End-Functionalized [3]- and [5]-Ladderanes

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[3]- and [5]-ladderanes obtained by way of template-controlled syntheses conducted in the organic solid state have been characterized *via* He I photoelectron (PE) spectroscopy. The results provide a first correlation with X-ray crystallographic structure data and establish the reliability of quantum chemical DFT (B3LYP/6-31G*) and *ab initio* HF calculations in predicting geometrical and electronic structures of molecular ladder frameworks.

Introduction

Molecules with covalent frameworks based on *n* edge-fused cyclobutane rings (*i.e.*, [*n*]-ladderanes [where *n* = 3, 4, 5, ...]) are attracting increasing attention in several research areas.[1] In the context of biology, [3]- and [5]-ladderanes have recently been discovered as lipids in intracellular membranes of *anammox* bacteria, which are largely responsible for the denitrification step of the oceanic nitrogen cycle.[2,3] These ladderane lipids have been suggested to be essential for the metabolic cycle of the bacterium by providing extraordinary rigidity to the cellular membranes.[1] In the context of theoretical chemistry, recent computational studies suggest that such frameworks exhibit novel forms of fluxional behavior.[4,5] The introduction of a structural defect within a ladderane framework is expected to result in the formation of sigmatropic shiftamers, which are fluxional molecules in which the defect can move throughout the ladderane framework. Ladderanes have also been implicated as potential rod-shaped building blocks in molecular electronics applications.[6,7]

Whereas the chemistry of ladderanes is gaining increasing attention, such significance is underscored by a lack of experimental data that characterizes the ladder frameworks, an issue expected to become increasingly important as ladderanes continue to be synthesized and discovered. This lack of data is largely related to a general difficulty of synthesizing such edge-fused cyclobutane moieties.[8,9] This difficulty is illustrated by two recent total syntheses of a naturally occurring ladderane, which were each achieved in approximately 1% overall yield. The main difficulty encountered in the synthesis was the construction of the ladder portion of the molecule.[10]

In this context, we have recently described a method to synthesize all-*trans*-ladderanes regiospecifically and in quantitative yield.[11] The method employs molecules, in the form of linear templates, that assemble and preorganize conjugated polyenes, *via* hydrogen bonds, in the organic solid state for stepwise [2+2] photodimerizations. We have used this method to generate gram quantities of end-functionalized [3]- and [5]-ladderanes, namely, 1,2,7,8-tetrakis(4-pyridyl)-[3]-ladderane **1** and 1,2,11,12-tetrakis(4-pyridyl)-[5]-ladderane **2** (Scheme 1).[12]

TABLE 1: Calculated $-\epsilon_{DFT}$ and $-\epsilon_{HF}$ (eV) Energies and Assignments for 1 and 2

	1				**2**			
orbital	$-\epsilon_{DFT}$	assign	$-\epsilon_{HF}$	assign	$-\epsilon_{DFT}$	assign	$-\epsilon_{HF}$	assign
h	6.76	n_N	9.62	π	6.69	n_N	9.56	π
h-1	6.8	n_N	9.63	π	6.71	n_N	9.56	π
h-2	6.82	n_N	9.84	π	7.10	n_N	9.82	π
h-3	6.86	n_N	9.98	π	7.10	n_N	9.9	π
h-4	7.15	π	10.08	π	7.52	π	10.04	π
h-5	7.28	π	10.27	π	7.52	π	10.08	π
h-6	7.32	π	10.27	π	7.53	π	10.18	π
h-7	7.42	π	10.34	π	7.68	π	10.26	π
h-8	7.54	π	11.23	n_N	7.77	π	10.94	σ_{ladd}
h-9	7.72	π	11.31	n_N	7.8	π	10.96	$\sigma_{ladd} + n_N$
h-10	7.71	π	11.36	n_N	7.82	π	11.27	n_N
h-11	7.8	π	11.39	n_N	7.92	π	11.3	n_N
h-12	8.13	σ_{ladd}	11.64	σ_{ladd}	8.0	σ_{ladd}	11.37	n_N
h-13	8.84	σ_{ladd}	12.08	σ_{ladd}	8.21	σ_{ladd}	11.47	$n_N + \sigma_{ladd}$
h-14	9.03	σ_{ladd}	12.65	σ_{ladd}	8.55	σ_{ladd}	11.66	σ_{ladd}

Having achieved the synthesis of **1** and **2**, we now wish to report the He I photoelectron spectra of these ladder frameworks. By combining the PE spectra of **1** and **2** and the knowledge gained from our X-ray structure data, we have been able to assess the ability of computational chemistry to predict the ionization bands and electronic structures of the ladderanes. Our studies have allowed us to discuss the only previously reported electronic structure of a ladderane molecule.

Experimental and Computational Details

Compounds **1** and **2** were prepared according to the literature report.[11] He I PE spectra of **1** and **2** were recorded on a Vacuum Generators UV-G3 instrument[13] with spectral resolution of 30 meV when measured at the full width at half-maximum (fwhm) of the Ar^+ $^2P_{3/2}$ calibration line. Sample inlet temperatures of 210 and 180 °C were necessary for **1** and **2**, respectively, to achieve sufficient vapor pressure in the ionization region. The energy scale of the spectra was calibrated using small amounts of Xe gas added to the sample flow. Stability of **1** and **2** in the vapor phase was checked by mass spectrometry following PES measurements. Electronic structure calculations were performed using the GAUSSIAN 03 program package,[14] including full geometry optimization of the neutral molecule using the density functional method (DFT) with the B3LYP functional[15−17] and 6-31g* basis set as the first step. The combination of this

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SCHEME 1

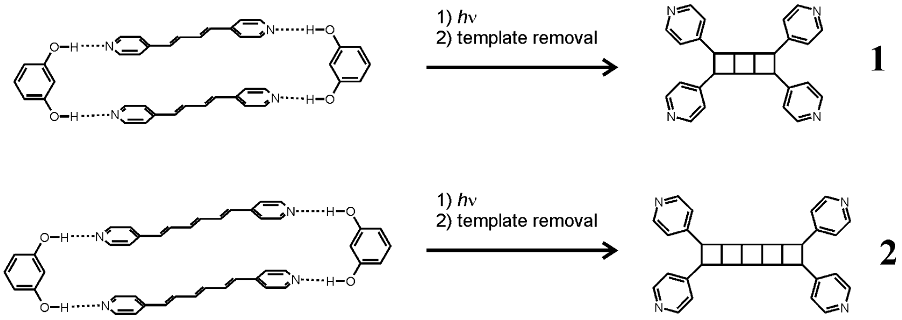


TABLE 2: Computed $-\epsilon_{DFT}$, $-\epsilon_{HF}$, $-\epsilon_{rovgf}$ and Experimental E_i Values (eV) of Orbital Energies for [3]-Ladderane, [3]-Ladderene, and [3]-Ladderdiene

	[3]-ladderane (C_{2h})				[3]-ladderene (C_s)				[3]-ladderdiene (C_{2h})			
orbital	$-\epsilon_{DFT}$	$-\epsilon_{HF}$	$-\epsilon_{rovgf}$	E_i[a]	$-\epsilon_{DFT}$	$-\epsilon_{HF}$	$-\epsilon_{rovgf}$	E_i[a]	$-\epsilon_{DFT}$	$-\epsilon_{HF}$	$-\epsilon_{rovgf}$	E_i[a,b]
homo	7.18	10.23	9.74	9.23	6.84 π	9.25	9.26	9.25	6.58 π^-	8.88	8.93	8.96[a] 8.90[b]
homo-1	7.38	10.49	9.9	9.66	7.15	10.57	10.02	9.66	7.54 π^+	10.04	10.01	9.93[a] 9.93[b]
homo-2	8.09	11.28	10.73	10.47	7.89	10.98	10.32	10.1	7.76	10.84	10.33	10.13[a] 10.27[b]
homo-3	8.31	11.79	11.05	-	8.60	12.10	11.31	10.95	8.22	11.57	10.73	10.57[a] 10.56[b]

[a] Reference 29. [b] Reference 28.

functional, which takes into account the electron exchange−correlation effects, and the polarized basis set offers a good compromise between the size of the calculations and the accuracy of the theoretical predictions. KS orbital energies are known to be lower than the experimental vertical ionization energies, but their ordering provides correct sequence of ionic states for spectral assignment. This notion is confirmed in Table 1 where KS energies are in only a fair agreement with experimental values. Harmonic frequency calculations were performed for all the optimized structures to confirm that the resulting geometry was a true minimum (no imaginary frequencies). The deficiency of such Koopmans-type approximation can be circumvented by performing single point calculation with outer valence Green's function[18] (rovgf) method. The method obviates the need for Koopmans approximation and provides vertical ionization energies with typical deviation of 0.2−0.4 eV from the experimental value.[19] However, owing to the size of our molecules, we could not perform this calculation for **1** and **2**. We have, instead, performed rovgf calculations for [3]-ladderane, [3]-ladderene, and [3]-ladderdiene (Table 2). Full geometry optimization was performed using the DFT method at B3LYP/6-311g* level followed by single point outer valence Green's function[18] (rovgf) calculation at 6-311g** level. The MO energies were also estimated by single-point calculations at the HF/6-311g* level for comparison. The quality of the calculated molecular geometry parameters was successfully checked by comparing the results of X-ray crystal structure analysis with DFT/B3LYP calculation results *via* a least-squares method approach.

Results and Discussion

The He I PE spectra of **1** and **2** are shown in Figure 1. The spectra consist of strongly overlapping band systems. The assignment of the bands to a nitrogen lone pair (n_N), aromatic (π), or skeleton (σ) electron ejection within Koopmans' theorem is a difficult issue. In particular, the difficulty arises in the four pendant 4-pyridyl substituents with expected contribution of 12 ($8\ \pi + 4\ n_N$) ionization events to the low-energy region of the spectrum, which are expected to be very close or degenerate in energy. Thus, to analyze the PE spectrum and deduce the electronic structures of **1** and **2**, we made use of the composite molecule method of Rabalais,[20,21] as well as quantum chemical density functional theory (DFT) and *ab initio* HF calculations.[15−17,22] As composite molecules, we considered and used the PE spectra of pyridine,[18,20] 4-methylpyridine,[23] 4,4′-bipyridyl,[24] 4,4′-dipyridylethene,[25] cyclobutane,[26] bicyclo[2.2.0]hexane[27] (BCH), and pure 3-ladderane[26,28,29] (*i.e.*, *anti*-tricyclo[4.2.0.0$^{2.5}$]octane) for assignment.

In particular, the lowest energy band system in the PE spectrum of pyridine has been shown to correspond to two overlapping ionization events, one at 9.6 eV from the n_N orbital and the other at 9.8 eV from the π_3 orbital (of a_2 symmetry in C_{2v}). Higher in energy at 10.5 eV is the ionization from the $\pi_2(b_1)$ orbital, followed by a σ-ionization at 12.44 eV and the lowest π_1-ionization at 13.2 eV. In 4-methylpyridine, the inductive effect shifts the n_N, π_2, and π_1 assigned bands to 9.41, 10.06, and 12.86 eV, respectively, with the π_3 band at 9.61 eV nearly unchanged in energy, but below the n_N-ionization. In the PE spectrum of 4,4′-dipyridyl, a strong deviation from simple additivity shows the splitting of the two $\pi_2(b_1)$ orbitals into one bonding and one antibonding combination at 11.13 and 9.43 eV, respectively. The two n_N levels are slightly split at 9.6 and 9.8 eV and the two $\pi_3(a_2)$ orbitals assigned to the band at 9.70 eV are practically degenerate owing to the rotational freedom around the C−C bond that connects the aromatic moieties. Such behavior is also evident in the PE spectrum of 4,4′-dipyridylethene where the π-electrons from two orbitals that correspond to linear combinations of $\pi_3(a_2)$ orbitals of the pyridine moiety do not interact with the central double bond. Consequently, their positions at 9.50 and 9.75 eV remain similar to 4,4′-dipyridyl. On the other hand, the combinations of π_2-(b_1) orbitals will interact with the double bond π-electrons (in ethylene at 10.51 eV)[30] in an antibonding, nonbonding, or bonding manner, as indicated by observed ionization band systems at 8.83, 10.56, and 11.56 eV, respectively.

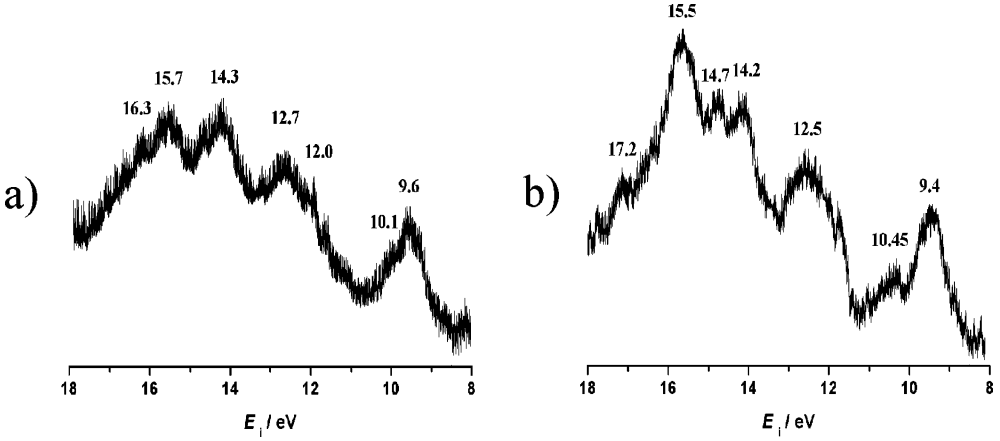


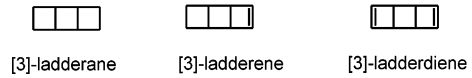
Figure 1. He I photoelectron spectra of (a) **1** and (b) **2**.

In the case of **1** and **2**, 4-pyridyl groups are attached to each end of the aliphatic ladderane ring system. Thus, we expect the pyridines to produce multiple, overlapping bands as in the case of 4-methylpyridine. Specifically, the bands are expected to appear in the region from 8.5 to 10.5 eV, corresponding to 4 π_3 + 4 n_N and 4 $\pi_2(b_1)$ orbitals, respectively. This behavior is observed, as demonstrated by the bands at 9.6 and 10.1 eV for **1**, and 9.4 and 10.45 eV for **2**, respectively, with onsets below 9 eV for both ladderane molecules (Figure 1).

The assignment of the pyridine ring bands allows further interpretation of the bands in the PE spectra corresponding to the ladderane skeletons. Because of the gap in the spectra for ionization energies between 10.5 and 11.5 eV, the lowest energy bands of the ladderane frameworks must either coincide with the 4 π_2 (b_1)-ionizations, or appear at the onset of the 12 and 12.5 eV features of the PE spectra of **1** and **2**. To assist the interpretation of the spectra of **1** and **2**, we anticipated a useful reference would be the PE spectra of cyclobutane,[26] cyclohexane, [2.2.0]bicyclohexane[27] (a [2]-ladderane, BCH) and [3]-ladderane.[29] The respective lowest σ-ionization energies for these molecules were found to be 10.7, 10.3, 9.6, and 9.23 eV. The spectra indicate that both BCH and [3]-ladderane ionization energies do not fall in the range for compounds with normal carbon−carbon (C−C) bonds (*e.g.*, cyclobutane and cyclohexane). We recognized that, as a consequence, mixing of lowest energy orbitals of the ladderane C−C bond framework with the lowest energy orbitals of pyridine may yield an alternative assignment of the PE spectra of **1** and **2**. In that assignment, the ladderane framework ionizations would be contributing to the 10.1−10.5 eV bands in each PE spectrum. Nevertheless, our original assignment is supported by the presence of four *N* atoms per molecule, which are expected to increase the energy needed to release electrons from the orbitals of the ladderane C−C bond framework. The PE spectrum of **2** additionally favors the original assignment, demonstrating only a slight shift to lower ionization energies as a result of the increase in the length of the ladderane framework.

The two possible assignments for the PE spectra of **1** and **2** urged us to analyze the order of orbitals and electron distributions (*i.e.*, within the ionic states in Koopmans' model) in **1** and **2** *via* DFT and HF computational methods. The accuracy of the result calculated using DFT is supported by a more than satisfactory agreement between calculated and observed molecular geometries because the standard deviations for all bonds in **1** and **2** amount 2.01 and 2.21 pm, respectively. Our DFT calculations support the first assignment by predicting ladderane skeleton orbital energies to be higher than those of attached pyridine moieties described as 4 n_N + 8 π. Such ordering of molecular orbitals also support HF results for **1**, although here the 4 n_N orbitals are predicted to be somewhat higher in energy than the 8 π orbitals. For **2**, HF calculations predict two of the ladderane orbitals to appear between the 4 n_N and 8 π levels (Table 1). Both the DFT and HF computational approaches predict the ionization energies for the [3]-ladderane framework to be higher than originally measured for this hydrocarbon.[29] The close agreement of the computational and experimental data for **1** and **2** led us to conclude that the PE spectrum originally ascribed to the [3]-ladderane[29] might have been missassigned. We, therefore, decided to conduct DFT, HF, and rovgf calculations of the [3]-ladderane, [3]-ladderene, and [3]-ladderdiene hydrocarbons (Scheme 2) and compare these results to the original PE data.

SCHEME 2



As Table 2 shows, rovgf calculations for [3]-ladderane, [3]-ladderene, and [3]-ladderdiene yield HOMO values of 9.74, 9.26, and 8.93 eV, respectively, for the lowest ionizations. The lowest ionization energies for the unsaturated [3]-ladderene and [3]-ladderdiene are excellently predicted (Δ < 0.1 eV), but that of the parent [3]-ladderane differs by 0.5 eV. Furthermore, the calculations indicate a significant decrease of 0.5 eV in ionization energy on introducing the first double bond to the ladderane system. That this decrease is not observed in the previously reported experimental data further supports the suggestion that the PES data reported for the [3]-ladderane hydrocarbon was missassigned and likely belongs to the unsaturated [3]-ladderene.[31]

Conclusion

He I photoelectron spectra of readily available end-functionalized [3]- and [5]-ladderanes obtained from template-controlled solid-state reactions have been reported. The molecular geometries and electronic structures obtained using DFT, as well as *ab initio* HF calculations, are in good agreement with the results obtained from X-ray structure analyses. Although it can be difficult to compare solid-state molecular geometries with those calculated for isolated molecules, the agreement is pleasing and likely facilitated by the rigid structures. The ordering of molecular orbitals, obtained using DFT calculations, enabled us to interpret the PES data with the aid of Koopmans' theorem. Further investigation of ladderane and cyclobutane structures is currently underway, using the experimental and computational approaches described in this contribution.

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Supporting Information Available: Numbering schemes and experimental and calculated structural parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Such a conclusion is also consistent with preliminary experimental and computational results involving cyclobutane, cyclobutene, and 1,2,3,4-tetrapyridylcyclobutane (the “[0]-ladderane” analogue of **1** and **2**), which support the ordering of orbitals obtained using DFT calculations.