1,4-Dihydropyrrolo[3,2-*b*]pyrrole: The Electronic Structure Elucidated by Photoelectron Spectroscopy

Shoji TANAKA, Tsutomu KUMAGAI, Toshio MUKAI,* and Tsunetoshi KOBAYASHI*,†
Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980
†The Institute of Physical and Chemical Research, Wako, Saitama 351-01
(Received December 2, 1986)

The electronic structures of 1,4-dihydropyrrolo[3,2-*b*]pyrrole and some of its alkyl derivatives were studied by means of He(I) photoelectron spectroscopy combined with the MNDO calculation and a first-order perturbation theoretical method. The first five bands of the parent pyrrolopyrrole are assigned, from the top, to the $\pi_5(a_u)$, $\pi_4(a_u)$, $\pi_3(b_g)$, $\pi_2(b_g)$, and $\sigma(a_g)$ bands respectively. The MO model, which explains well the spectral data, indicates that the nitrogen lone-pair electrons are mainly delocalized in the π_4, π_2, and π_1 orbitals. The ionization potentials of the HOMO levels of these compounds, which are characterized by the large p_z contributions from the α-carbons, are the lowest among the hitherto known π-electron-excessive heteroaromatic compounds. 1,4-Dihydropyrrolo[3,2-*b*]pyrrole is concluded to be the system with the most efficient π-electron-donating ability among 10π-electron systems.

The purpose of this work is to elucidate the electronic character of 1,4-dihydropyrrolo[3,2-*b*]pyrrole in comparison with pyrrole and indole. Dihydropyrrolopyrroles are fundamentally important heteroaromatic compounds. These heterocycles are expected to be new candidates for conducting polymers and are also of interest from the standpoint of pharmacology.[1] Their electronic structures, however, have not been explored in detail. Although the photoelectron spectrum of the parent [2,3-*b*] isomer has been measured and analyzed by Gleiter et al.,[2] recent MNDO and ab initio MO calculations suggest that the proposed assignments of the first and the second bands are questionable.[1] Here, the He(I) photoelectron (PE) spectra of 1,4-dihydropyrrolo[3,2-*b*]pyrroles **1a—d** are reported and compared with the results of semiempirical MO calculations. In addition, the shifts of the bands induced by the alkyl substitutions are analyzed by a first-order perturbation method. This approach gives information on the assignments of ionizations and on the validity of the MO models used.

Experimental

Materials. The pyrrolopyrroles **1a** and **1c** were synthesized as has been reported formerly.[3] Their 1,4-dimethyl derivatives **1b** and **1d** were obtained by the reduction of the corresponding 1,4-bis(methoxycarbonyl) derivatives[3] with lithium aluminium hydride-aluminium chloride (3 : 1) in ether.

Measurements. The vapor phase He(I) photoelectron spectra of **1a—d** were measured with the PE spectrometer described in Ref. 4. Xe gas was used as the internal standard for the calibration of the energy scale.

Results and Discussion

The He(I) photoelectron spectra of the pyrrolopyrroles **1a—d** are shown in Fig. 1. The vertical ionization potentials and the results of MO calculations for the parent compound **1a** using the HMO[5] and MNDO[6] methods are listed in Table 1.

According to the empirically parameterized method

Table 1. Comparison of the Observed Vertical Ionization Potentials of **1a** with the Orbital Energies Calculated by the HMO and MNDO Methods

Band	I_v/eV	$-\varepsilon^{HMO}$/eV	$-\varepsilon^{MNDO}$/eV
[1]	7.27	7.51 $\pi_5(a_u)$	7.85 $\pi_5(a_u)$
[2]	8.00	8.20 $\pi_4(a_u)$	8.36 $\pi_4(a_u)$
[3]	9.42	9.65 $\pi_3(b_g)$	9.82 $\pi_3(b_g)$
[4]	11.42	11.59 $\pi_2(b_g)$	12.44 $\sigma(a_g)$
[5]	12.10	—	12.66 $\pi_2(b_g)$

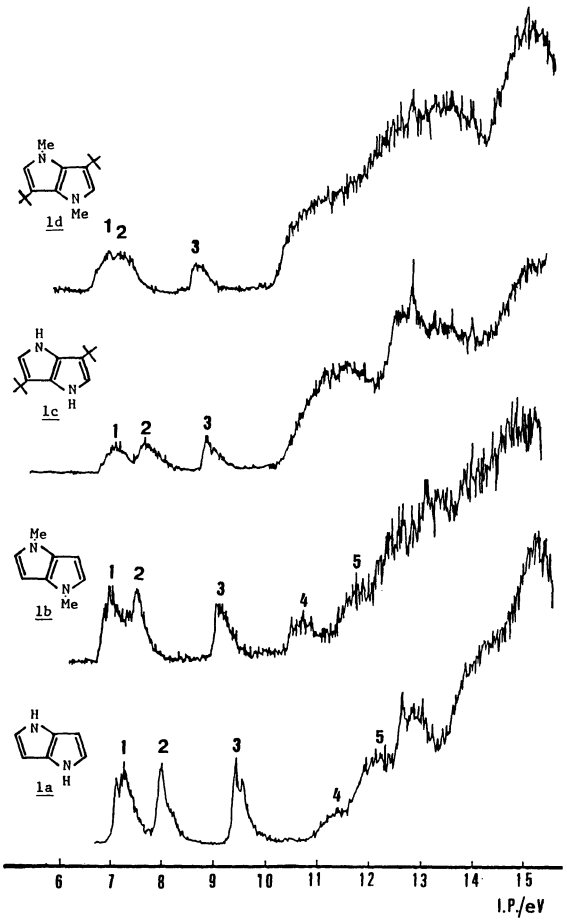

Fig. 1. Vapor phase He(I) photoelectron spectra of 1,4-dihydropyrrolo[3,2-*b*]pyrroles **1a—d**.

Table 2. Comparison of the Observed Vertical Ionization Potentials (I_v) of **1b—d** with Those Calculated by the Perturbation Methods

Compound		I_v/eV				
	Band	[1]	[2]	[3]	[4]	[5]
	Obsd	6.95	7.48	9.00	10.67	11.68
1b	Calcd[a]	6.94	7.43	9.16	10.57	—
		$\pi_5(a_u)$	$\pi_4(a_u)$	$\pi_3(b_g)$	$\pi_2(b_g)$	
	Obsd	6.92	7.49	8.68	—	—
1c	Calcd[a]	6.66	7.43	8.53	—	—
		$\pi_5(a_u)$	$\pi_4(a_u)$	$\pi_3(b_g)$		
	Obsd	6.76	6.98	8.42	—	—
1d	Calcd[b]	6.59	6.92	8.42	—	—
		$\pi_5(a_u)$	$\pi_4(a_u)$	$\pi_3(b_g)$		

a) Calculated by the perturbation method. The reference standard compound is **1a**; $I_v^{calcd}=I_v^{obsd}$ (**1a**)$+\Delta I_v^{calcd}$.
b) Calculated by the perturbation method. The reference standard compound is **1c**; $I_v^{calcd}=I_v^{obsd}$ (**1c**)$+\Delta I_v^{calcd}$.

based on the first order perturbation theory, the vertical ionization potential changes (ΔI_v) of π bands induced by alkyl substitutions can be estimated by using the following formula:[7]

$$-\Delta I_{v,j}=a(\sum_{\alpha} C_{\alpha j}^2+m\sum_{\beta} C_{\beta j}^2)+b$$

where j denotes the j-th MO corresponding to the certain PE spectral band in question, $C_{\alpha j}$ is the AO coefficient of the atom α in the j-th MO at which a certain substitution is introduced, and $C_{\beta j}$ is the AO coefficient of the atom β just adjacent to the atom α. The a, b, and m are the empirical parameters for a certain substitution. The parameter m is a kind of damping factor and is put equal to 1/3, as in Ref. 7. The parameters a and b are reevaluated by the least-squares method using the ionization energy data of hydrocarbons and the AO coefficients obtained by the MNDO method.[8] The ionization potentials estimated by this method and the corresponding experimental values are summarized in Table 2.

For the first three bands of the parent compound **1a**, the orbital energies calculated by the HMO and the MNDO methods correlate reasonably well with the observed ionization potentials. Therefore, these bands are assigned, from the top, to the ionization from the π orbitals, $\pi_5(a_u)$, $\pi_4(a_u)$, and $\pi_3(b_g)$ respectively. In the cases of **1a** and **1b**, the 4th and the 5th bands are rather well resolved. The HMO calculation predicts that the ionization potentials for the $\pi_2(b_g)$ and the $\pi_1(a_u)$ orbitals of **1a** are 11.59 and 13.58 eV respectively. The former is close to the observed value of the 4th band, while the latter is much higher than that of the 5th band. From these results, the 4th and the 5th bands may be ascribed to the ionizations from the $\pi_2(b_g)$ orbital and the σ orbital respectively. On the other hand, our MNDO calculation and the ab initio calculation reported by Verbist et al.[1] predict that the 4th and the 5th bands should correspond to the ionizations from the $\sigma(a_g)$ and $\pi_2(b_g)$ orbitals respectively. It is difficult to assign these bands only on the basis of the MO calculations, but additional information can be obtained from a consideration of the substituent effects on the ionization potentials.

As is shown in Table 2, the perturbation method reproduces reasonably well the observed changes for the first three bands of the alkyl-substituted derivative **1b**. This finding supports both the above assignments of the first three bands of **1a** and the applicability of this method in the assignments of the spectra of the pyrrolopyrroles. In the PE spectrum of **1b**, shifts of 0.75 and 0.42 eV were observed for the 4th and 5th bands relative to those of **1a** respectively. The shift of the $\pi_2(b_g)$ band of the parent compound **1a** by *N,N'*-dimethylation is estimated to be 0.85 eV. (This value is very close to the energy difference between the 4th band of **1a** and that of the 1,4-dimethyl derivative **1b**, 0.75 eV.) Therefore, the 4th bands of these compounds are ascribed to the ionizations from their $\pi_2(b_g)$ orbitals. As a result, the 4th and the 5th bands of the pyrrolopyrroles (**1a** and **1b**) are assigned to the $\pi_2(b_g)$ and the $\sigma(a_g)$ orbitals, and their first three bands, to the $\pi_5(a_u)$, $\pi_4(a_u)$, and $\pi_3(b_g)$ orbitals from the top, respectively. In the case of compounds **1c** and **1d** also, the first three bands are unambiguously ascribed from the top to the ionizations from the $\pi_5(a_u)$, $\pi_4(a_u)$, and $\pi_3(b_g)$ orbitals respectively, based on the perturbation theoretical calculations. Furthermore, the reasonable correspondence between the observed band shifts and those calculated by the perturbation method supports the validity of the delocalized MO pictures for these compounds given by the MO calculations. Figure 2 shows the AO coefficients of the occupied π orbitals in **1a** with the HOMO levels of pyrrole [$\pi_3(a_2)$] and indole [$\pi_5(a'')$].

The above MO model indicates that the nitrogen lone-pair electrons of **1a** are mainly delocalized in the π_4, π_2, and π_1 orbitals. The HOMO level of the pyrrolopyrrole is characterized by large p_z contributions from the α-carbon atoms. This is similar with the nature of the pyrrole HOMO level and is in contrast with that of the indole HOMO level, which has large p_z contributions from the β-carbon atom. Consistent with these results, we have found that some electrophilic substitution reactions, which are known to occur at the β-position of indoles, take place selectively at the α-position of the pyrrolopyrroles.[9] The ionization potential of the HOMO level of the parent pyrrolopyrrole **1a** (7.27 eV) is lower than those of pyrrole (8.21 eV)[10] and indole (7.91 eV).[11] In the case of indole, the oxidation potential and basicity are almost the same as those of pyrrole, although the ionization potential is appreciably lower. In contrast with this, the oxidation potential of **1a** (0.51 V vs. SCE) is much lower than those of pyrrole (1.2 V) and indole (1.2 V).[3]

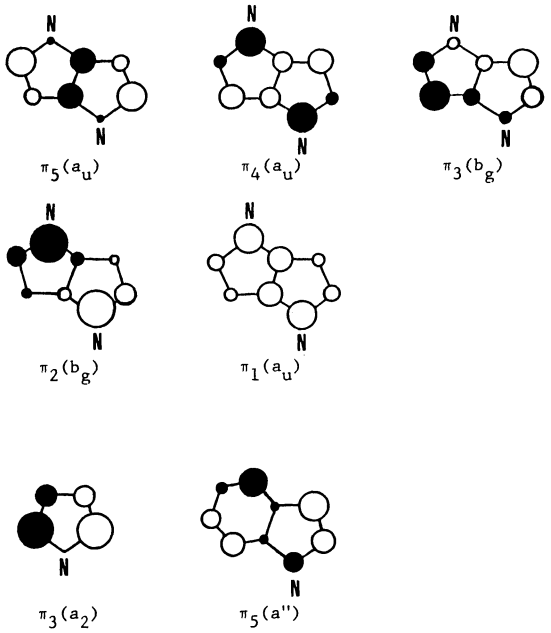

Fig. 2. Schematic representation of the occupied π molecular orbitals of 1,4-dihydropyrrolo[3,2-*b*]pyrrole, pyrrole, and indole given by the MNDO calculations.

The basicity (the pK_a value of the conjugate acid) of the pyrrolopyrrole **1c**, a stable derivative in acidic media, is +3.6; this value is much higher than those of pyrrole (−3.8)[12] and indole (−3.6).[13] In addition, it should be noted that the first ionization potential of **1a** is lower than those of the previously reported π-electron-excessive heterocycles; furan[5] (8.90 eV), thiophene[14] (8.90 eV), 1,6-dihydropyrrolo[2,3-*b*]pyrrole[2] (7.46 eV), thieno[2,3-*b*]pyrrole[2] (7.97 eV), thieno[3,2-*b*]pyrrole[2] (7.70 eV), thieno[2,3-*b*]thiophene[14] (8.32 eV), and thieno[3,2-*b*]thiophene[14] (8.10 eV). In conclusion, all the experimental results are consistent with the description of 1,4-dihydropyrrolo[3,2-*b*]pyrrole as a 10π-heteroaromatic compound possessing a more efficient π-electron-donating ability compared to the previously known π-electron-excessive heteroaromatic compounds.

References

1) R. Lazzaroni, J. P. Boutique, J. Riga, J. J. Verbist, J. G. Fripiat, and J. Delhalle, *J. Chem. Soc., Perkin Trans. 2*, **1985**, 97; H. Hemetsberger and D. Knittel, *Monatsh. Chem.*, **103**, 194 (1972); H. Prinzbach, *Chimia*, **33**, 332 (1979).

2) This parent [2,3-*b*] isomer was synthesized in 1975, but its properties have not been explored except for some spectral data. K. N. Java, S. Soth, M. Farnier, and C. Paulmier, *C. R. Acad. Sci., Ser. C*, **281**, 793 (1975); R. Gleiter, M. Kobayashi, J. Spanget-Larsen, S. Gronowitz, A. Konar, and M. Farnier, *J. Org. Chem.*, **42**, 2230 (1977).

3) T. Kumagai, S. Tanaka, and T. Mukai, *Tetrahedron Lett.*, **25**, 5669 (1984); K. Satake, T. Kumagai, and T. Mukai, *Chem. Lett.*, **1984**, 2033.

4) T. Kobayashi, K. Yokota, and S. Nagakura, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 449 (1973); T. Kobayashi, T. Kubota, and K. Ezumi, *J. Am. Chem. Soc.*, **105**, 2172 (1983).

5) J. H. D. Eland, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 471 (1969).

6) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977).

7) T. Kobayashi, T. Kubota, K. Ezumi, and C. Utsunomiya, *Bull. Chem. Soc. Jpn.*, **55**, 3915 (1982); T. Kobayashi, T. Arai, H. Sakuragi, K. Tokumaru, and C. Utsunomiya, *Bull. Chem. Soc. Jpn.*, **54**, 1658 (1981), and the references cited therein.

8) The parameters *a* and *b* for methyl substitution were evaluated on the basis of the ionization energy data of the ethylene, butadiene, benzene, and naphthalene derivatives as reported in Ref. 7. The values are as follows: a=1.019±0.024 eV, b=0.043±0.016 eV. The standard deviation of $\Delta I_{v,j}$ is 0.036 eV. We applied these parameters for the assignments of the π bands of pyrrolopyrroles in this paper. These parameters are able to reproduce the shifts of the bands of pyrroles and indoles induced by *N*-methylations with a standard deviation of 0.044 eV. The parameters (a=1.316± 0.076 eV and b=0.042±0.069 eV) for *t*-butyl substitution were also estimated based on the data for ethylene, propene, and benzene derivatives. The standard deviation of $\Delta I_{v,j}$ is 0.087 eV. We did not estimate the band shift of the σ orbital by the perturbation method because of the complicated treatment. The photoelectron spectral datum of the parent [2,3-*b*] isomer has been published in 1977; at that time, the first and the second bands were assigned to the a_2 and the b_1 orbitals respectively.[2] Recent ab initio calculations, however, have called the proposed assignments into question.[1] Additional research using a perturbation method will be needed for the exact assignment.

9) T. Mukai, S. Tanaka, T. Hirano, and T. Kumagai, 52nd Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1986, Abstr., No. 1R40.

10) P. J. Derrick, L. Åsbrink, O. Edqvist, B.-Ö. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 191 (1971).

11) H. Güsten, L. Klasinc, J. V. Knop, and N. Trinajstić, *Excited States Biol. Mol. Proc. Int. Conf.*, **1974**, 45.

12) Y. Chiang and E. B. Whipple, *J. Am. Chem. Soc.*, **85**, 2763 (1963).

13) R. L. Hinman and J. Lang, *J. Am. Chem. Soc.*, **86**, 3796 (1964).

14) P. A. Clark, R. Gleiter, and E. Heilbronner, *Tetrahedron*, **29**, 3085 (1973).