195. The Photoelectron Spectra of 4,13-Diaza- and 4,16-Diaza $[2_4](1,2,4,5)$cyclophanes[1]

by **Yang Zhong-zhi**[2][3], **Edgar Heilbronner**[3], **Hee Chol Kang**[4] and **Virgil Boekelheide**[4]

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

Department of Chemistry, College of Arts and Sciences, University of Oregon, Eugene,
Oregon 97403, U.S.A.

(10.VII.81)

Summary

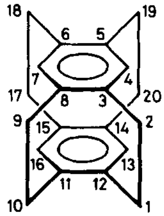
A tentative assignment is proposed for the He(Iα) photoelectron (PE.) spectra of the title compounds. It is based on the assumption that the first four π-bands occupy the same position in both spectra, as suggested by a qualitative correlation with the PE. spectrum of $[2_4](1,2,4,5)$cyclophane and by a previously proposed molecular orbital model. If this is accepted, then the bands due to electron ejection from the lone-pair orbitals are split by roughly 0.8 eV in the case of the 4,13-diaza isomer, whereas no split can be detected in the case of the 4,16-diaza isomer.

---

1. Introduction. - The PE. spectra of pyridine [1-3] and of benzene [2] differ in that the e_{1g}^{-1} band of the latter (at 9.25 eV) is split in the spectrum of pyridine into two bands at ~9.7 and 10.5 eV, corresponding to $a_2(\pi)^{-1}$ and $b_1(\pi)^{-1}$ ionization processes, respectively. In addition, there is a band at ~9.7 eV due to the removal of an electron from the lone-pair orbital $a_1(n)$. In this note we investigate,

---

[1] The nomenclature refers to the following convention for the numbering of the centres in $[2_n]$cyclophanes, in particular in $[2_4](1,2,4,5)$cyclophane:



However, for the sake of convenience and simplicity we shall depart from this convention within the text of the present contribution.

[2] Permanent address: Theoretical Chemistry Institute, Jilin University, Chang Chun, Jilin, People's Republic of China.

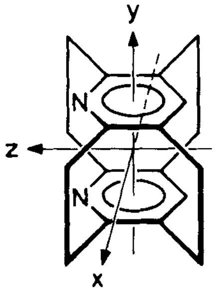
[3] Universität Basel.

[4] University of Oregon.

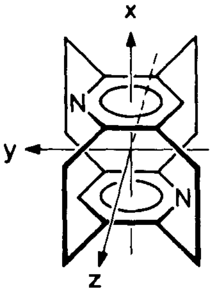
0018-019X/81/7/2029-07$01.00/0

how the above ionization energies are affected when two pyridine nuclei are held closely together in a cyclophane system. This should provide ancillary information concerning previous assignments of cyclophane PE. spectra [4-6].

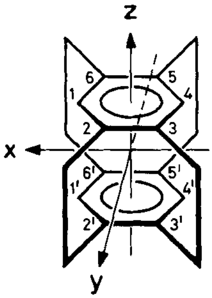
2. Experimental Results. - In *Figure 1* are presented the $\mathrm{He}(\mathrm{I}\alpha)$ PE. spectra of 4,13-diaza$[2_4]$(1,2,4,5)cyclophane (**1**), 4,16-diaza$[2_4]$(1,2,4,5)cyclophane (**2**) [7] and of $[2_4]$(1,2,4,5)cyclophane (**3**) [4]. To simplify the ensuing discussion, we renumber the centres of the upper (u) and lower (l) deck in **3**, and thus in **1** and **2**, as indicated below, so that corresponding π-centres carry the same numbers μ, μ'.



1 (C_{2v})



2 (C_{2h})



3 (D_{2h})

In the ionization energy interval $8\,\mathrm{eV} < \mathrm{I} < 10\,\mathrm{eV}$, the PE. spectrum of the *syn*-isomer **1** consists of three maxima with integrated intensity ratios of 3:2:1, whereas the *anti*-isomer **2** shows four maxima with ratios 1:3:1:1. The positions of these maxima and thus, approximately, the ionization energies I_j^m corresponding to the underlying individual bands, are given in *Table 1*, together with the relevant data for the parent hydrocarbon **3** [4] and with the tentative assignment to be discussed below.

3. Discussion. - Clearly the problem of assigning the bands in the interval $8\,\mathrm{eV} < \mathrm{I} < 10\,\mathrm{eV}$ is made difficult by their strong overlap and, in fact, the following analysis leads to a sequence of the radical cation states for $\mathbf{1}^+$ and $\mathbf{2}^+$ which should be regarded, at best, as a plausible working hypothesis.

We begin by discussing those orbitals of **1** and **2** which consist essentially of the linear combinations of the semi-localized π-orbitals of the two pyridine rings. In the following we designate the π-orbitals $a_2(\pi)$ and $b_1(\pi)$ of the upper and lower pyridine nuclei by S_u, S_l and A_u, A_l respectively, these orbitals being symmetric (S) or antisymmetric (A) relative to a mirror-plane containing the centres 1,1' and 4,4'. (The analogue nomenclature has been used in the previous contributions [4] [5], to which the reader is referred for further details.) From these we form symmetry adapted linear combinations $S_\pm = (S_u \pm S_l)/\sqrt{2}$ and $A_\pm = (A_u \pm A_l)/\sqrt{2}$. In turn, these are the major contributors to the following molecular orbitals of **1** and **2**, the symmetry labels of which refer to the coordinate systems included in formulae **1**-**3** (see *Table 2*).

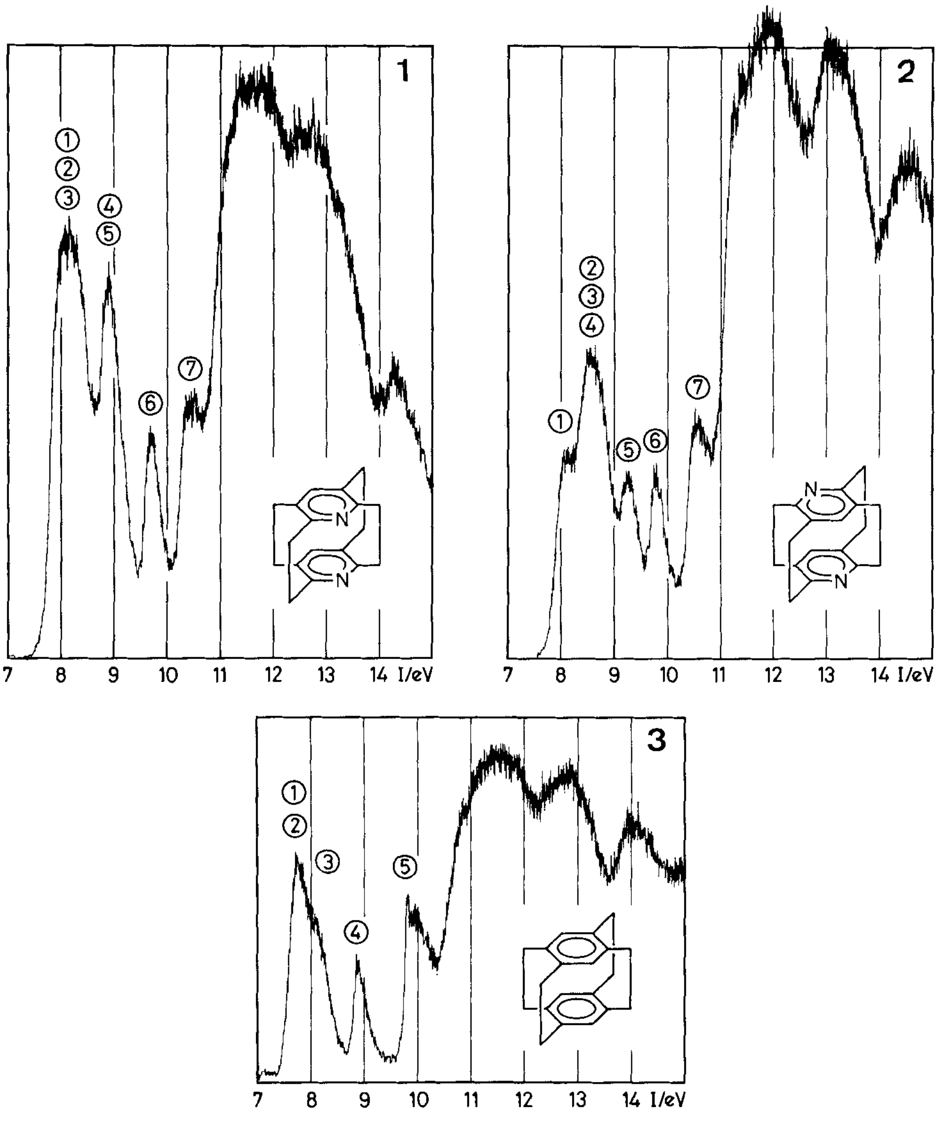


Fig. 1. *He(Ia) PE. spectra of 4,13-diaza[2_4](1,2,4,5)cyclophane* (**1**), *4,16-diaza[2_4](1,2,4,5)cyclophane* (**2**) *and of [2_4](1,2,4,5)cyclophane* (**3**)

For comparison, the corresponding orbitals of the parent hydrocarbon **3** have been included, in which case $A_{\pm}$ and $S_{\pm}$ refer to the linear combinations of the benzene π-orbitals. Note that A_{+} and S_{+} are antisymmetric, A_{-} and S_{-} symmetric, with respect to a reflection in the plane passing between the two decks.

Two ways present themselves for the assignment of orbital energies to the orbitals of **1** and **2** listed in *Table 2*. The first one is entirely empirical and based

Table 1. *Tentative assignment and ionization energies of the PE. spectra of* **1**, **2** *and* **3**

Band	**1**		**2**		**3** [4]	
	Orbital	I^m/eV	Orbital	I^m/eV	Orbital	I^m/eV
①	$a_2(\pi)$	~ 8.2	$b_g(\pi)$	8.1	$b_{3g}(\pi)$	7.7
②	$b_1(\pi)$; $b_2(n)$		$a_u(\pi)$	8.6	$b_{2g}(\pi)$	
③			$a_g(n)$; $b_u(n)$		$b_{2u}(\pi)$	8.1
④	$a_1(n)$	8.9			$b_{3u}(\pi)$	8.8
⑤	$b_2(\pi)$		$a_g(\pi)$	9.3		9.8
⑥	$a_1(\pi)$	9.7	$b_u(\pi)$	9.8		
⑦		10.5		10.5		

on a first-order perturbation argument, starting with the orbitals of **3** [4] *(cf. Table 1)*. Replacement of a CH-unit in benzene ($I(e_{1g}^{-1}) = 9.25$ eV) by N, to yield pyridine ($I(a_2^{-1}) = 9.7$ eV; $I(b_1^{-1}) = 10.5$ eV) shifts the orbital A by -0.45 eV and orbital S by -1.25 eV [1-3]. Similarly, the A and S orbitals of *m*-xylene ($I(a_2^{-1}) = 8.5$ eV; $I(b_1^{-1}) = 9.0$ eV [8]) are shifted by -0.4 and -1.0 eV respectively, if the CH-group in position 2 is replaced by N to yield 2,6-dimethylpyridine ($I(a_2^{-1}) = 8.9$ eV; $I(b_1^{-1}) = 10.0$ eV [3]). Assuming in a crude approximation that similar shifts affect the π-orbital energies of **3** when two N-atoms are introduced to yield **1** or **2**, then the orbital energies given by the expressions 1 are approximately expected for the latter molecules.

$$\begin{array}{lllll}
\textbf{1} & \textbf{2} & \textbf{3} & & \\
\varepsilon(a_2) = & \varepsilon(b_g) = & \varepsilon(b_{3g}) - 0.4\ \mathrm{eV} = & -8.1\ \mathrm{eV} & \\
\varepsilon(b_1) = & \varepsilon(a_u) = & \varepsilon(b_{2u}) - 0.4\ \mathrm{eV} = & -8.5\ \mathrm{eV} & \quad (1) \\
\varepsilon(b_2) = & \varepsilon(a_g) = & \varepsilon(b_{2g}) - 1.2\ \mathrm{eV} = & -8.9\ \mathrm{eV} & \\
\varepsilon(a_1) = & \varepsilon(b_u) = & \varepsilon(b_{3u}) - 1.2\ \mathrm{eV} = & -10.0\ \mathrm{eV} &
\end{array}$$

The major shortcomings of this naive procedure, which necessarily predicts the same energies for corresponding orbitals of **1** and **2**, are that it assumes the same geometry for all three compounds and that it neglects second-order terms which one might feel to be important. To take these factors into account we performed model calculations along the lines described previously [4-6].

To this end we have first parametrized a *Hückel*-type model for pyridine, to reproduce its observed π^{-1}-ionization energies. This yields *ad hoc* the atomic *Coulomb* integrals $\alpha_N = -9$ eV, $\alpha_{C(\mathit{ortho}\ \mathrm{to\ N})} = -6.7$ eV and the resonance integral $\beta_{CN} = -2.5$ eV, if all other values are kept unchanged, as described previously [5]: $\alpha_C = -5.8$ eV; $\beta_{C,C} = -3.2$ eV; $\alpha_{CH_2CH_2\text{-bridge}} = -14.0$ eV; $\beta_{C,CH_2CH_2\text{-bridge}} = -2.4$ eV.

Table 2

Type	**1** (C_{2v})	**2** (C_{2h})	**3** (D_{2h})
A_+	a_2	b_g	b_{3g}
A_-	b_1	a_u	b_{2u}
S_+	b_2	a_g	b_{2g}
S_-	a_1	b_u	b_{3u}

The crystal structure analysis of the compounds **1** [9], **2** [10], **3** [11] reveals that in all three compounds the centres 1,1′ and 4,4′ are further apart than the bridged ones: **1**: 1,1′, 284 pm; 4,4′, 294 pm; mean of others 265 pm; **2**: 1,1′ and 4,4′, 287 pm; others 264 pm; **3**: 1,1′, 295 pm, 2,2′, 269 pm. Using these experimental geometries and the parameters given above leads again to the result that the positions of the first four π-bands in the PE. spectra of **1** and **2** should be the same within rather narrow limits of error (see *Table 3*).

Table 3

1	Orbital	a_2	b_1	b_2	a_1
	ε/eV	−8.28	−8.57	−8.66	−10.29
2	Orbital	b_g	a_u	a_g	b_u
	ε/eV	−8.27	−8.57	−8.71	−10.03

In other words, the relative orientation of the two pyridine rings in the molecules **1** and **2** is predicted to have only a negligible influence on the orbital energies. The same phenomenon has already been observed in the case of the *syn-* and *anti*-[2.2](1,6)azulenophanes [6]. This makes the naive perturbation model underlying the results 1 more palatable and it is indeed surprising that both treatments yield the same sequence of orbitals and rather close-lying orbital energies.

Taking the above results at face value and postulating that the first four π-bands occupy the same positions in the PE. spectra of **1** and **2**, the following procedure suggests itself. We first normalize the spectra of **1** and **2** in the interval 7 eV < I < 10.5 eV in such a way that the integrated intensity is the same for both. This is equivalent to the assumption that the intensities of corresponding pairs of the six bands ① to ⑥ is the same *(cf. Fig. 2)*. Then the two spectra are shifted by 0.1 eV relative to each other, matching the onsets, and then subtracted, *i.e.* the spectrum of **2** from that of **1**. In the difference curve labeled **1**-**2** in *Figure 2*, the positive maxima should then correspond to the lone-pair bands in the PE. spectrum of **1**, the negative minimum to the corresponding bands in **2**. For rather obvious reasons such a treatment is very crude, but the result seems pleasingly clear-cut. The difference curve suggests that in **1** the two lone-pair orbitals, *i.e.* those molecular orbitals which are dominated by the linear combinations $n_{\pm} = (n_1 \pm n_{1'})/\sqrt{2}$, are split by ~0.8 eV, whereas the corresponding orbitals in **2**, based on $n_{\pm} = (n_1 \pm n_{4'})/\sqrt{2}$ exhibit the same orbital energy within narrow but unspecified limits. In contrast to what the smoothed curves of *Figure 2* suggest, the procedure

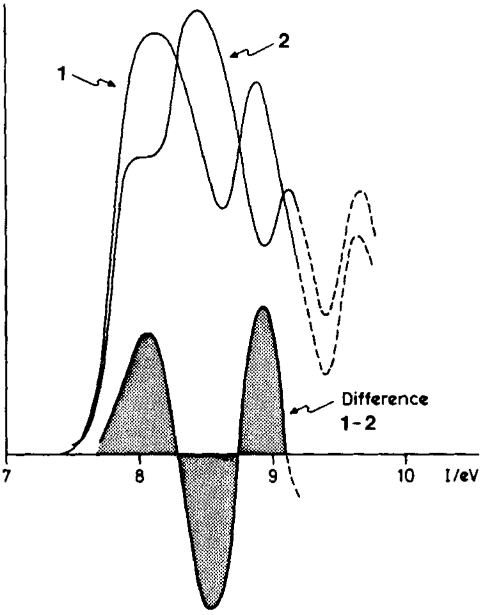


Fig. 2. *Normalized PE. spectra of* **1** *and* **2** *and the difference spectrum* **1-2**

outlined above depends critically on the numerous assumptions implied and not too much significance can be attached to the positions of the maxima (8.1 eV; 8.9 eV) and the minimum (8.5 eV) of the difference curve **1-2**. Notwithstanding the rather large uncertainties, the values are of the size expected, if compared to the positions of the lone-pair bands in the PE. spectra of alkyl-substituted pyridines [1] [3].

Intuitively it seems reasonable that the two lone-pair orbitals n_1, $n_{4'}$ do not interact appreciably in **2**, whereas an interaction, yielding a split of ~0.8 eV exists between n_1 and $n_{1'}$ in **1**, where the two lone-pairs face each other across a distance of 284 pm [9]. Interactions of this size between lone-pair orbitals have been observed in [2.2](2,6)metapyridinophane [12] and are also suggested by the PE. spectra of other heterocyclic [2.2]cyclophanes [13]. However, the origin of a split of ~0.8 eV is by no means obvious. From the computed overlap $S_{nn} = \langle n_1 | n_{1'} \rangle \approx 0.01$ to 0.02, depending on the assumptions made, one would expect a 'through-space' contribution of 0.2 to 0.4 eV towards the observed split, *i.e.* about 1/4 to 1/2 of its size. The difference must then be assigned to a 'through-bond' interaction involving five intermediate C,C-bonds on each side of the pair n_1, $n_{1'}$. Once more, the magnitude of such a contribution is in keeping with expectation based on previous experience [14].

The resulting, tentative assignment is summarized in *Table 1*. It is obvious from the preceeding discussion that it must be taken with more than only one grain of salt and that it should be accepted, at best, as a reasonable working hypothesis, which we hope is not too far from the truth.

We thank Prof. *A. W. Hanson* (National Research Council of Canada) for kindly making the results of his x-ray structure analyses available prior to publication.

This work is part No. 144 of project No. 2.622-0.80 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. (Part 143, *cf.* ref. [5]).

Support by *Ciba-Geigy SA*, *F. Hoffmann-La Roche & Cie. SA* and *Sandoz SA* (Basel) is gratefully acknowledged.

REFERENCES

[1] *B.-O. Jonsson, E. Lindholm & A. Skerbele*, Int. J. Mass Spectrom. Ion Phys. *3*, 385 (1969); *A.D. Baker & D.W. Turner*, Phil. Trans. Roy. Soc. *A 268*, 131 (1970); *G.H. King, J.N. Murrell & R.J. Suffolk*, J. Chem. Soc. Dalton *1972*, 564.

[2] *D.W. Turner, C. Baker, A.D. Baker & C.R. Brundle*, Molecular Photoelectron Spectroscopy, Wiley-Interscience, London, 1970.

[3] *E. Heilbronner, V. Hornung, F.H. Pinkerton & S.F. Thames*, Helv. Chim. Acta *55*, 289 (1972).

[4] *B. Kovač, M. Mohraz, E. Heilbronner, V. Boekelheide & H. Hopf*, J. Amer. Chem. Soc. *102*, 4314 (1980).

[5] *B. Kovač, M. Allan & E. Heilbronner*, Helv. Chim. Acta *64*, 430 (1981); *Z.-Z. Yang, B. Kovač, E. Heilbronner, S. Eltamany & H. Hopf*, Helv. Chim. Acta *64*, 1991 (1981).

[6] *B. Kovač, M. Mohraz, E. Heilbronner, S. Itô, Y. Fukazawa & P.M. Keehn*, J. Electron Spectrosc. *22*, 327 (1981).

[7] *H.C. Kang & V. Boekelheide*, Angew. Chem., *93*, 587 (1981).

[8] *M. Klessinger*, Angew. Chem. Int. Ed. *11*, 525 (1972); *J.P. Maier & D.W. Turner*, Faraday Trans. II *69*, 196 (1973); *T. Kobayashi & S. Nagakura*, Bull. Chem. Soc. Japan *47*, 2563 (1974); *M.H. Palmer, W. Moyes, M. Spiers & J.N.A. Ridyard*, J. Mol. Struct. *49*, 105 (1978).

[9] *A.W. Hanson*, Cryst. Struct. Comm., in press.

[10] *A.W. Hanson*, Cryst. Struct. Comm. *10*, 313 (1981).

[11] *A.W. Hanson*, Acta Cryst. *B 33*, 2003 (1977).

[12] *F. Bernardi, F.P. Colonna, P. Dembech & P. Vivarelli*, Chem. Phys. Letters *36*, 539 (1975).

[13] *F. Bernardi, A. Bottoni, F.P. Colonna, G. Distefano, U. Folli & P. Vivarelli*, Z. Naturforsch. *33a*, 959 (1978); *B. Kovač, M. Allan, E. Heilbronner, J.P. Maier, R. Gleiter, M.W. Haenel, P.M. Keehn & J.A. Reiss*, J. Electron Spectrosc. *19*, 167 (1980).

[14] *R. Gleiter*, Angew. Chem. *86*, 770 (1974).