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Photoelectron Spectroscopic Evidence concerning Ground-state Through-σ-bond Interaction in the 1,3-Diaza-adamantan-6-one System

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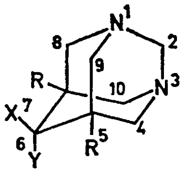
Summary Photoelectron spectroscopic and INDO calculation studies on the 1,3-diaza-adamantan-6-one system are reported; the results clearly indicate through-σ-bond interactions between the nitrogen lone pairs and the carbonyl π-system.

APPLICATIONS of photoelectron spectroscopy (PES) to the study of ground-state interaction between formally non-conjugated π- or *n*-electron system have been reported.[1–3] We report our results of a PES study on the 1,3-diaza-adamantan-6-one system, in which the lone electron pair on nitrogen and the π-orbitals of the C=O group are postulated to interact with the same C–C bond.



(**1**) **a**; R = Ph, X, Y = O, **b**; R = H, X, Y = O.
(**2**) **a**; R = Ph, X = Y = H, **b**; R = H, X = Y = H.
(**3**) R = Ph, X = H, Y = OH.

The measured vertical ionization potentials (IP's) of (**1a**), (**2a**), and (**3**) are given in the Table. IP_1 and IP_2 of (**2a**) at 7·54 and 8·60 eV are assignable to ionizations from the two nitrogen nonbonding levels, $n_N(A)$ and $n_N(S)$[†] respectively. The *S* below *A* ordering is predictable by considering the rigid arrangement of the lobes of nitrogen lone pair and N–C–N σ-bonds.[1] Our INDO calculation results on (**2b**) indicates that the *S* level comes 0·63 eV below *A* [the observed value for (**2a**) is 1·06 eV]. IP_3 at 9·15 eV is assigned to ionization from the highest occupied π-level of the phenyl ring.[7] IP_1 and IP_3 of (**1a**) at 7·87 and 8·75 eV are assigned to the $n_N(A)$ and $n_N(S)$ levels respectively. IP_2 (8·44 eV) is assigned to an oxygen nonbonding level.[8] IP_4 at 8·98 eV is assignable to ionization from the π-level of the phenyl group. Calculations on (**1b**) indicate $n_N(A) < n_O < n_N(S)$. Similarly, IP_1 (7·51 eV) and IP_2 (8·70 eV) of (**3**) are assigned to the $n_N(A)$ and $n_N(S)$ levels, and IP_3 to the π-level of phenyl. IP_4 (10·27) appeared as a sharp band and is assigned to the oxygen nonbonding level of alcohol.[8]

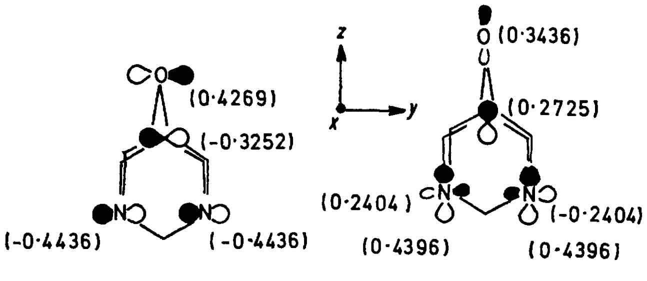
TABLE. Vertical ionization potentials (eV)[a]

	IP_1	IP_2	IP_3	IP_4
(**1a**)	7·87	8·44	8·75	8·98
(**2a**)	7·54	8·60	9·15	
(**3**)	7·51	8·70	9·13	10·27

[a] ± 0·03; from He-I (584 Å) PE spectra measured on JASCO PE-3 spectrometer.

Comparison of the IP's of (**1a**) and (**2a**) indicates stabilization of the n_N levels of (**1a**); 0·33 eV for $n_N(A)$ and 0·15 eV for $n_N(S)$ respectively [the calculated stabilization between (**1b**) and (**2b**) is 0·36 and 0·50 eV for $n_N(A)$ and $n_N(S)$

[†] *A* and *S* designate symmetry with respect to a plane of symmetry (*xz* plane in the Figure), (**1**) and (**2**) have $C_{2}v$ symmetry.



(a) (b)

FIGURE. The $n_N(A)$ (a) and $n_N(S)$ (b) orbitals of (**1b**). The directions of nitrogen partial atomic dipoles of the above two MO's are outside the cage. The coefficients of atomic orbitals are given in parentheses.

respectively]. This stabilization is due to the presence of the C=O group and must be the through-bond type because of the impossibility of direct orbital overlap. From the INDO calculation results on (**1b**), $n_N(A)$, and $n_N(S)$ the orbitals can be pictured as in the Figure. The highest occupied $n_N(A)$ shows electron delocalization between Np_y, C_5p_y, Op_y. The electron density of $n_N(A)$ of (**1b**) is 0·46 compared with 0·56 for $n_N(A)$ of (**2b**), $n_N(S)$ of (**1b**) is 0·52 while $n_N(S)$ of (**2b**) is 0·57.

The PES results and the INDO calculations on (**1**)—(**3**) indicate through-σ-bond interaction between the N lone pair and the C=O π-orbital of (**1**) at the ground state, assuming Koopmans' theorem to be valid.

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