BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1597—1598 (1970)

On the Valence State Energy of the Carbon and Nitrogen Atoms

Hideyuki NARUMI and Kimio OHNO

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received December 5, 1969)

Several years ago, one of the present authors (K.O.) reported calculations on the energies of the carbon and nitrogen atoms in their valence states.[1] The valence state energies were those defined by Van Vleck.[2] A single Slater-type orbital (STO) was used for each atomic orbital (AO) and orbital exponents δ of the $1s$, $2s$, $2p\sigma$, and $2p\pi$ AO's were varied to make the energy minimum. It turned out that this approximation is especially inadequate for negative ions. Calculated electron affinities for carbon and pyridine-type nitrogen were -4.3 and -5.2 eV, respectively. A semi-empirical estimate[3] gives the value of 0.03 eV for C and 1.8 eV for N. The reason for this failure is probably that a single STO is not adequate for describing the long tail of the charge distribution of a negative ion, especially of the $2p\pi$ orbital.

In this note, results obtained by using two STO's to express the $2p\pi$ AO, instead of one STO, are reported. A very similar calculation was carried out on C by Silverstone and Joy,[4] namely Basis III calculation given in their Table III. However, their valence state was defined for hydrocarbon whose π-electrons were described in terms of molecular orbitals. Thus their energies differ from ours by an extra term, that is one fourth of the π Coulomb integral. Orloff and Sinanoğlu[5] have performed very extensive calculations on the valence state of C. Although their sets of basic orbitals are much bigger than ours, our calculations differ from theirs in that the $2p\sigma$ and $2p\pi$ AO's are allowed to differ. On pyridine-type and pyrrole-type nitrogens, there seems to be no calculation more detailed than our previous one.[1]

Results and Discussion

The numerical results are collected in Table 1. The coefficients and orbital exponents of the two STO's in the $2p\pi$ orbital are denoted as C_1, C_2, δ_1 $(2p\pi)$ and $\delta_2(2p\pi)$. The π one-electron energy W is defined by

$$W(n, q) \equiv \left\langle 2p\pi(q) \middle| -\frac{1}{2}\Delta + V(n, q) \middle| 2p\pi(q) \right\rangle,$$

where V is the potential due to the σ-core, n is the

TABLE 1. VALENCE STATE ENERGY OF C, PYRIDINE-TYPE N, AND PYRROLE-TYPE N (eV)

	C			Pyridine-type N			Pyrrole-type N		
	C^+	C	C^-	N^+	N	N^-	N^{++}	N^+	N
Electron config.	$(sp^2)^3$	$(sp^2)^3\pi$	$(sp^2)^3\pi^2$	$(sp^2)^4$	$(sp^2)^4\pi$	$(sp^2)^4\pi^2$	$(sp^2)^3$	$(sp^2)^3\pi$	$(sp^2)^3\pi^2$
$\delta(1s)$	5.66	5.66	5.67	6.65	6.66	6.66	6.65	6.65	6.65
$\delta(2s)$	1.75	1.65	1.62	2.04	1.95	1.90	2.17	2.06	1.98
$\delta(2p\sigma)$	1.75	1.58	1.53	2.07	1.89	1.80	2.27	2.09	1.94
$\delta_1(2p\pi)$	—	2.17	1.86	—	2.71	2.42	—	2.67	2.72
$\delta_2(2p\pi)$	—	1.03	0.56	—	1.26	0.78	—	1.44	1.19
C_1	—	0.466	0.488	—	0.462	0.492	—	0.532	0.450
C_2	—	0.614	0.691	—	0.622	0.670	—	0.525	0.644
Total energy	-1007.98	-1017.27	-1015.25	-1454.68	-1466.55	-1464.42	-1428.05	-1455.04	-1464.57
σ-Core energy	-1007.98	-1007.05	-1006.52	-1454.68	-1453.33	-1451.73	-1428.05	-1427.02	-1424.71
W	—	-10.22	-9.04	—	-13.22	-12.85	—	-28.02	-28.75
$(\pi\pi\|\pi\pi)$	—	15.05	9.35	—	18.47	13.00	—	21.05	17.64

---

[1] K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964). Unfortunately there was an error in the calculation and the corrected results will be published as an erratum in the same journal shortly.

[2] J. H. Van Vleck, *J. Chem. Phys.*, **2**, 20 (1934).

[3] J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

[4] H. J. Silverstone and H. W. Joy, *J. Chem. Phys.*, **47**, 1384 (1967).

[5] M. K. Orloff and O. Sinanoğlu, *ibid.*, **43**, 49 (1965).

Table 2. Pi-electron ionization potential (in eV)

	C	Pyridine-type N	Pyrrole-type N	
			First	Second
Calculated with one STO for π AO	8.69	10.87	7.62	26.43
Calculated with two STO for π AO	9.29	11.87	9.52	27.00
Semi-empirical estimate[3,6]	11.16	14.12	11.96	28.71

difference between the nuclear charge and the number of σ-electrons (*e.g.* $n=1$ for C and pyridine-type N, and $n=2$ for pyrrole-type N) and q is the π-electon charge on the atom ($q=1$ for C, 2 for C^-).

These results show that the effect of q on W is not very big, less than 1.2 eV. The usual assumption in the Pariser-Parr-Pople method

$$W(n, 1)=W(n, 2)=-I_n$$

is valid within an error of about 2 eV. These general conclusions were reached in the previous treatment[1] and do not change under the extended calculations.

On the other hand, the use of two STO's for the π orbital improved somewhat the calculated π-electron affinities. They are -2.0 eV for C and -2.1 eV for pyridine-type N. The errors were reduced to about one half but still the correct sign could not be obtained.

The calculated and semi-empirically estimated π-ionization potentials are compared in Table 2. Here again, by using a better approximation, the calculated values come closer to the semi-empirical estimate but the differences could still be as large as 2.5 eV.

In conclusion, these simple variational calculations of valence state energies show that the deformation of the σ and π orbitals due to the change in the number of π electrons is considerable, but their effects on W apparently cancel each other and the net effect is not large. On the other hand, using two STO's for the π orbital is not good enough for calculating the π-electron ionization potentials and electron affinities for C and N more accurately than 2—3 eV.

The authors are grateful to Dr. J. H. Gallagher and Professor R. McWeeny for reading the manuscript.

---

6) J. Hinze and H. H. Jaffé, *J. Phys. Chem.*, **67**, 1501 (1963).