Theoret. Chim. Acta (Berl.) 67, 271-274 (1985)

THEORETICA CHIMICA ACTA

Ab initio valence bond calculations and the spin-paired diradical character of S_4^{2+}

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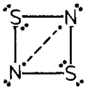
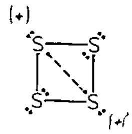
The results of some *ab initio* valence bond calculations, with STO-6G basis sets for the *s* and *p* orbitals, are reported for the ground state of cyclic S_4^{2+}. The sum of the weights for two "long-bond" (or spin-paired diradical) structures is approximately 50% of the total.

Key words: Valence bond—S_4^{2+}—Increased valence

The geometries for numerous molecular systems with cyclic 2-electron 4-center bonds have now been reported [1]. Of them, only S_2N_2 has been subjected to quantitative valence bond (VB) studies. For this molecule, both INDO [2] and *ab initio* [3] VB calculations, with sulphur 3*d* atomic orbitals (AOs) omitted, indicate that the dominant Lewis-type VB structure is the spin-paired diradical structure (**1**), with a "long" or formal N-N π-bond. The results of similar (STO-6G) [4] *ab initio* calculations for cyclic S_4^{2+}, which we here report for the experimental geometry [5], also indicate that important Lewis structures for this ion have a "long" or formal π-bond, as in (**2**).


(**1**)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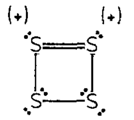
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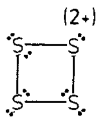
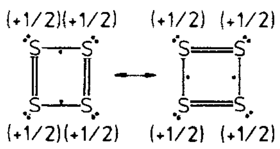

(**4**)


(**5**) (**6**)

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Ten Lewis VB structures were included in the singlet-spin ($S=0$) VB calculations, namely (**2**), (**3**) and (**4**), together with seven equivalent structures which differ in the locations of six valence shell π-electrons amongst four overlapping $p\pi$ AOs. Three sets of AO exponents were used for the $3p\pi$ AOs of S and S^+, namely "best atom" [6], (b) "best atom" and "best ion" [6], and (c) $\frac{1}{2}(S+S^+)$ from (b). The remaining 24 core orbitals were assigned either "best atom" S or $\frac{1}{2}(S+S^+)$ exponents with no *s-p* hybridization. The eight S-S σ-bonding electrons in each of the VB structures were located in four 2-center bonding molecular orbitals (MOs), which were constructed from the in-plane $3p_x$ and $3p_y$ AOs. Details of the VB program, which was originally prepared by Roso [7] and redimensioned by one of us (F.L.S.), are described in Refs. [3] and [7]. STO-6G MO calculations were also performed using the Gaussian 80 program [8]. Total energies (E, a.u.) and VB weights (W_i) [9] for both the $S=0$ ground state and the lowest-energy $S=1$ state (with parallel spins for the two electrons that form the S-S π-bonds of structures (**2**), (**3**)+four equivalent structures) are reported in Table 1.

As is the case for S_2N_2 in Ref. [3], the MO energies are slightly lower than the VB energies. No doubt this arises because the MO description allows for both *s-p* hybridization and a greater delocalization of the core electrons than does our VB description of the core. However, better (valence-shell) π-electron correlation occurs in the VB calculations; for the *same* π-electron core and "best atom" exponents, we have calculated $E(\mathrm{VB})-E(\mathrm{MO})=-0.2943$ a.u.

Each of the VB calculations gives largest individual weights to the "long bond" (or spin-paired diradical) structures of type (**2**) (cf. (**1**) for S_2N_2 [2, 3]). This result shows little sensitivity to the values that are assigned to the AO exponents. The sum of the weights for the four standard structures of type (**3**) and the two

Table 1. Energies (E, a.u.) and VB weights (W_i) for S_4^{2+}

$E+1584$	W_2^e	W_3^e	W_4^e
-0.9804^a	0.463	0.482	0.055
-0.9998^b	0.473	0.471	0.057
-1.0427^c	0.469	0.479	0.052
-1.0325^c	0.509	0.491	—
$-0.9531^{c,d}$	0.608	0.392	—
-0.9287^c	—	0.863	0.137

$E(\mathrm{MO})$: -1585.2039^a, -1585.3029^c.

[a] "Best S" exponents.

[b] "Best S and S^+" exponents for $3p\pi$ AOs.

[c] $\frac{1}{2}(S+S^+)$ exponents.

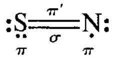
[d] Lowest energy $S=1$ state.

[e] Sum of weights for equivalent structures. The $1s$, $2s$, $2p$, $3s$, and $3p$ exponents for S and S^+ from Ref. [6] are 15.5350, 15.5437, 5.3101, 5.3034, 5.9866, 5.9972, 2.1230, 2.1952, 1.8270 and 1.9676. The "best atom" exponents of Ref. [13] give a VB energy of −1584.9800 a.u.

"long-bond" structures of type (**2**) are similar, and together account for more than 90% of the total weight. Resonance between these six structures is equivalent [3, 10] to resonance between the "increased-valence" structures (**5**) and (**6**), and provides a substantially lower energy (−1585.0325 a.u.) than the −1584.9012 a.u. obtained from the usual VB representation—namely resonance between the four standard Lewis structures of type (**3**). Omission of the "long-bond" structures from the $S = 0$ VB calculations gives an energy of −1584.9287 a.u., which is higher than the −1584.9531 a.u. for the lowest-energy $S = 1$ state.

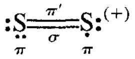
These calculations provide further quantitative support for the inclusion of "long-bond" structures in qualitative VB descriptions of many electron-rich molecules (cf. Refs. [3, 7, 10, 11]). Of course, "long-bond" structures contribute to the VB resonance descriptions of the ground-states for all polyatomic molecules; the Dewar structures for benzene provide a well-known example. However, the extent to which such structures contribute is quite variable. For the ground-state of benzene, the Dewar structures have been calculated to be of minor importance [12]. But for numerous electron-rich molecules (of which S_4^{2+} and S_2N_2 are examples), the nature and spatial arrangements of the atomic formal charges for the standard and "long-bond" Lewis structures help to stabilize the "long-bond" structures relative to the standard structures, and this is the primary reason why the "long-bond" structures are often calculated to make significant contributions to the ground-state resonance descriptions of many electron-rich molecules [3, 7, 10, 11].

For S_2N_2 and S_4^{2+}, "long-bond" Lewis structures with either two



$:\underset{\pi}{\underset{\cdot\cdot}{S}}\overset{\pi'}{\underset{\sigma}{=\!=\!=}}\underset{\pi}{\underset{\cdot}{N}}:$

or two



$:\underset{\pi}{\underset{\cdot\cdot}{S}}\overset{\pi'}{\underset{\sigma}{=\!=\!=}}\underset{\pi}{\underset{\cdot}{S}}:^{(+)}$

moieties have the same arrangements of formal charges and π-electrons as have the Lewis structures of types (**1**) and (**2**). These additional structures have two σ-bonds and two in-plane π'-bonds instead of four σ-bonds, and they would be included in more extended VB studies.

Acknowledgements. We thank members of the University of Melbourne Computer Center for their generous cooperation. One of us (F.L.S.) acknowledges the award of a University of Melbourne Postgraduate Scholarship.

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Received October 1, 1984