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Can Aromaticity Coexist with Diradical Character? An Ab Initio Valence Bond Study of S_2N_2 and Related 6π-Electron Four-Membered Rings E_2N_2 and E_4^{2+} (E = S, Se, Te)

Benoît Braïda,*[a] Aurélien Lo,[a] and Philippe C. Hiberty*[b]

A series of 6π-electron 4-center species, E_2N_2 and E_4^{2+} (E = S, Se, Te) is studied by means of ab initio valence bond methods with the aims of settling some controversies on 1) the diradical character of these molecules and 2) the radical sites, E or N, of the preferred diradical structure. It was found that for all molecules, the cumulated weights of the two possible diradical structures are always important and close to 50%, making these molecules comparable to ozone in terms of diradical character. While the two diradical structures are degenerate in the E_4^{2+} dications, they have on the contrary strongly unequal weights in the E_2N_2 neutral molecules. In these three molecules, the electronic structure is dominated by one diradical structure, in which the radical sites are the two nitrogen atoms, while the other diradical structure is much less important. The ordering of the various VB structures in terms of their calculated weights is confirmed by the relative energies of individual VB structures. In all cases, the major diradical structure (or both diradical structures when they are degenerate) is (are) the lowest one(s), while the covalent VB structures lie higher in energy. The vertical resonance energies are considerable in S_2N_2 and S_4^{2+}, about 80% of the estimated value for benzene, and diminish as one goes down the periodic table ($S \rightarrow Se \rightarrow Te$). This confirms the aromatic character of these species, as already demonstrated for S_2N_2 on the basis of magnetic criteria. This and the high weights and stabilities of one or both diradical structures in all systems indicates that aromaticity and diradical character do not exclude each other, contrary to what is usually claimed. Furthermore, it is shown that the diradical structures find their place in a collective electron flow responsible for the ring currents in the π system of these species.

1. Introduction

Disulfur dinitride S_2N_2 is probably the most widely studied prototype of tetraatomic square planar 6π-electron ring molecules or ions, owing to its postulated aromaticity, controversial diradical character and, on the experimental side, to its role in the synthesis of the superconducting polymeric sulfur nitride $(SN)_x$.[1] Most of the analogous isoelectronic species of the type E_2N_2 and E_4^{2+} (E = S, Se, Te) have been characterized experimentally.[1–5] All these molecules or ions possess square or quasi-square geometries and their electronic structures involve four σ bonds and six delocalized π electrons,[6–8] which makes them isoelectronic to cyclobutadiene dianion $C_4H_4^{2-}$ and suggests some aromatic character, according to Hückel's $(4n + 2)$ electron counting rule. In accord, the magnetic criterion for aromaticity, namely the nuclear independent chemical shift (NICS) criterion, was found to be satisfied by S_2N_2 in a recent theoretical study of Head-Gordon et al.[9] However this study also involved $C_4H_4^{2-}$, complexed by two lithium cations to avoid electron detachment, and showed that the two molecules are not strictly comparable. First, a significant aromatic stabilization energy (ASE) was calculated for $Li_2C_4H_4$, 29.2 kcal mol^{-1}, while a rather modest value, 6.5 kcal mol^{-1}, was found for S_2N_2. Second, the total NICS(0) was negative for $Li_2C_4H_4$, as expected for an aromatic compound, while a small positive value was found for S_2N_2, suggesting a weak antiaromaticity. In contrast, the individual π-orbital contributions to the total NICS(0) are all negative and very similar for the two molecules. Remarkably, the lowest occupied π orbital of S_2N_2 shows a strong negative NICS contribution while the two higher occupied π orbitals contribute very weakly. This, together with the fact that the latter π orbitals are non-bonding, led Head-Gordon et al. to conclude that S_2N_2 displays a 2π-electron aromaticity, rather than 6π-electron as a simple π-electron counting would suggest. Incidentally, the non-bonding character of two out of three occupied π orbitals in S_2N_2 leads to a rather low theoretical bond order, only 1.25,[9] which contrasts with the S–N bond length (1.654 Å) which is nearly half-way between those of a single N-S (1.74 Å) and a double N=S (1.54 Å) bond.[10,11] Such S–N bond lengths would thus be more consistent with bond orders closer to 1.5, suggesting that the π system of this molecule is stabilized in some unconventional fashion.

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Another intriguing aspect of E_2N_2 and E_4^{2+} rings is their electronic structures, which have often been discussed in terms of valence bond (VB) structures.[12–18] For a system of six electrons in four orbitals on four centers, ten VB structures are necessary in all rigor to form a complete and non-redundant basis including all covalent and ionic contributions, however only six VB structures contribute significantly to the ground states as shown below. These VB structures are displayed in Scheme 1 for E_2N_2 and E_4^{2+}, respectively. It can be seen that for each system, two out of six VB structures are diradicals, suggesting some possible significant diradical character for both E_2N_2 and E_4^{2+}, a proposal that has stirred up much controversy.
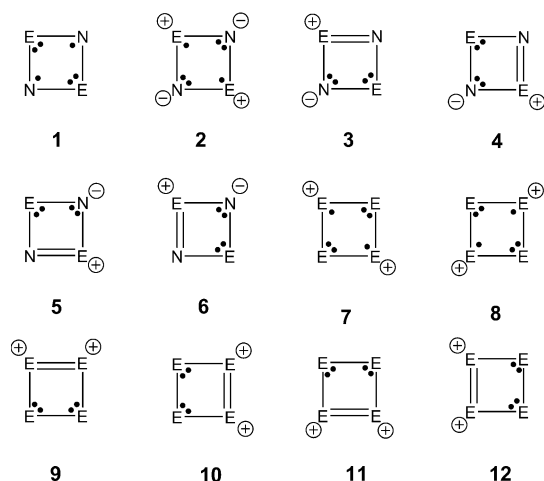
Scheme 1. VB structures for the E_2N_2 molecules (**1**–**6**) and E_4^{2+} cations (**7**–**12**).

Several theoretical studies have addressed the diradical character of S_2N_2 by different means. It is to be noted that this latter property has often been considered as incompatible with aromaticity, the two properties excluding each other, a statement that we do not consider as self-evident and that is discussed below. Be it as it may, Head-Gordon et al. have denied any significant radical character in S_2N_2 on the basis of a large HOMO–LUMO gap (5.2 eV), a large singlet–triplet vertical transition energy (3.6 eV), and the lack of a spin-unrestricted solution at the level of density functional theory (DFT), using the B3LYP functional.[9] On the other hand, these authors found the LUMO occupation number of S_2N_2 to be relatively large (up to 0.20 e^- at the CASSCF level), compared to normal closed-shell molecules (~0.03 e^-).

An opposite point of view is held by Tuononen et al., who showed that all RHF solutions for E_2N_2 and E_4^{2+} (E = S, Se,Te) contain negative values in the stability matrix.[19,20] This implies that symmetry-broken solutions UHF should have lower energies than RHF ones, which suggests that all molecules have significant singlet diradical character. These authors also estimated the diradical character of E_2N_2 by means of the index B in Equation (1), introduced long ago by Laidig and Schaefer,[21] where C_2 is the coefficient of the most important diexcitation in a CI or MCSCF calculation, here a CAS(22,16) one:

$$B = 2 C_2^2 \times 100\% \qquad (1)$$

This popular diradical index, which is based on the fact that B would be 100% for a perfect diradical, yields the values 6% for S_2N_2 and 10% for Te_2N_2.[19] Note however that an analysis of the same CASSCF wave function in terms of VB structures yields weights of 34% for **1** and 14% for **2** in S_2N_2. This latter analysis, which implies that diradical structures account to almost 50% of the CAS(22,16) wave function of S_2N_2, shows that the index B in Equation (1) does not give us much information about the description of the ground state in terms of VB structures. We return to this point below.

Still other theoretical studies have directly investigated the electronic structures of S_2N_2 and S_4^{2+} by VB ab initio methods of various kinds. Thus, Gerratt et al., using the spin-coupled VB method, described S_2N_2 as a unique predominant structure similar to **2** (Scheme 1), with the radical sites on the S atoms which consequently bear a substantial positive charge, while the N atoms bear a complementary negative charge.[17] This interpretation was confirmed by a further calculation using the CASVB method.[18] However it might be argued that the semi-delocalized nature of some of the orbitals involved in the VB wave function preclude the non-ambiguous interpretation of the results in terms of weighted VB structures. A different assessment of the radical sites was proposed by Harcourt et al.,[13,14] who computed the weights of the complete set of VB structures, **1**–**6** in Scheme 1, by a nearly classical ab initio VB method using strictly local AOs in the STO-6G basis set. On the basis of these calculations, Harcourt proposed structure **1** to be the major one, with the radical sites on the N atoms, in agreement with an early INDO calculation of Fujimoto.[12] However Harcourt's calculations, which were carried out in minimal basis set, were not really comparable to Gerratt's ones,[17] which used a larger basis set. Recently, Harcourt and Klapötke (HK) repeated their calculations in a basis set of double-zeta type (without polarization functions), on S_2N_2 and S_4^{2+}.[16] These calculations are close to classical VB type, in that they explicitly involve all relevant covalent and ionic VB structures. However these VB structures are constructed with orbitals of semi-delocalized type, albeit delocalized differently from Gerratt's earlier calculations. HK conclude to a weight of 47% for the diradical structure **1** in S_2N_2, and weights of 23% each for structures **7** and **8** in S_4^{2+}, confirming earlier VB studies in minimal basis set.[15] Thus, HK and Gerratt's VB calculations agree on the importance of a diradical structure for S_2N_2, but strongly disagree on the radical sites.

It appears from the literature perusal that there still exists no consensus on the electronic structures of S_2N_2 and related E_2N_2 and E_4^{2+} molecules and ions. Different opinions are expressed on the magnitude of the diradical character, a concept that is difficult to quantify from MO-CI or DFT calculations (see the discussion below). More insightful, in our opinion, is the description of the electronic states of these species in terms of VB structures, since ab initio VB methods allow the comparison of the various VB structures in terms of their relative specific energies, or in terms of their relative weights that are extracted from variationally computed coefficients in the VB wave func-

tion (see Theoretical Methods Section below). Unfortunately, the VB calculations that have appeared as yet still do not provide a unified picture. This is because the VB orbitals in some of these structures are defined with semi-localized orbitals, and different ways of delocalizing the orbitals lead to different weights for the VB structures.

This lack of consensus motivated us to perform a VB study of the generic E_2N_2 and E_4^{2+} species (E = S, Se, Te) in terms of VB structures, with the aims of 1) quantifying the diradical character of these molecules in terms of diradical structure weights, which we believe is a clear quantitative criterion, 2) settling the controversy on the radical sites of the preferred diradical structures, and 3) estimating the resonance energies so as to quantify the aromaticity of these moelecules from the energetic point of view. In order to reach these goals, we chose to define our VB structures *with strictly one-center atomic π orbitals* with no tail of any kind onto other atomic centers, so that the correspondence between the bonding schemes (Lewis structures) and the mathematical expressions of the VB structures are perfectly clear and nonambiguous. Moreover, the calculations were performed at two levels of sophistication: the standard VBSCF level, which provides static electron correlation, and the more accurate BOVB level, which includes additional dynamic correlation. This latter level has been amply shown to provide reliable descriptions of electronic systems (as providing, e.g., reasonable bonding energies), and will allow us to estimate the effects of dynamic correlation on the weights and relative energies of the VB structures.

Theory and Methodology

A many-electron system wave function Ψ in VB theory is expressed as a linear combination of Heitler–London–Slater–Pauling (HLSP) functions, Φ_K in Equation (2):[22]

$$\Psi = \sum_K C_K \Phi_K \tag{2}$$

where Φ_K correspond to "classical" VB structures, and C_K are structural coefficients. The weights of the VB structures are defined by the Coulson–Chirgwin formula,[23] Equation (3), which is the equivalent of a Mulliken population analysis in VB theory.

$$W_K = C_K^2 + \sum_{L \neq K} C_K C_L \langle \Phi_K \mid \Phi_L \rangle \tag{3}$$

Here the VB structures are those displayed in Scheme 1, that is, **1–6** for E_2N_2 and **7–12** for E_4^{2+}. For each of these molecules, four additional VB structures belong in principle to the full VB basis set. These structures, which all display three doubly occupied π AOs and an empty one, were found to have a weight of the order of 0.01, and were discarded for the sake of simplicity.

There are several computational approaches for VB theory at the ab initio level.[24] In the VBSCF procedure,[25,26] both the VB orbitals and structural coefficients are optimized simultaneously to minimize the total energy. As such, the VBSCF method takes care of the static electron correlation; but it lacks dynamic correlation. Among the electrons and orbitals, one distinguishes an active space, here the π orbitals and their electrons, from an inactive

space (all the rest). The active space is treated at the VB level and its electrons are explicitly correlated, while the inactive part of the molecule is described as a set of doubly occupied orbitals, so that the correlation of inactive electrons and the active-inactive correlation are not explicitly taken into account. An important feature of our VB calculations is that all the active orbitals are strictly localized on a single atom, like in the classical VB method, so as to ensure a clear correspondence between the mathematical expressions of the VB structures and their physical meaning, ionic or covalent.

The breathing-orbital valence bond method (BOVB)[27] improves the accuracy of VBSCF without increasing the number of VB structures Φ_K. This is done by allowing each VB structure to have its specific set of orbitals, different from one VB structure to the other, during the optimization process. In this manner, the orbitals can fluctuate in size and shape so as to fit the instantaneous charges of the atoms on which these orbitals are located. This specificity of the BOVB method ensures its accuracy by bringing some dynamic correlation to the wave function. As with VBSCF, the coefficients and orbitals of the VB structures are optimized simultaneously, so as to minimize the total energy of the multistructure wave function. In the present work, only the active orbitals are allowed to be different from one VB structure to the other, while the σ orbitals are kept common to all VB structures.

The energies of the individual VB structures are computed separately, by minimizing the energy of this VB structure alone, in the absence of the other ones.

Computational Details

Systematically convergent triple-zeta basis sets of Burkatzi et al.,[28] including two sets of d and one set of f polarization functions, have been used together with corresponding pseudopotential for all elements (N, S, Se and Te) in this study. For all species, we have used the geometries optimized at the CCSD(T) level in a previous study by Tuononen et al.[19] The VB calculations have been carried out with the Xiamen Valence Bond (XMVB) package of programs.[29,30]

2. Results

2.1. Weights of VB Structures

The weights of the various VB structures, **1–6** for E_2N_2 and **7–12** for E_4^{2+}, are displayed in Table 1, as calculated at the VBSCF and BOVB levels. Let us comment the VBSCF results first. It is

Table 1. Weights of the VB structures for E_2N_2 and E_4^{2+} as calculated at the VBSCF and BOVB levels.

	VBSCF			BOVB		
	1	**2**	**3–6**	**1**	**2**	**3–6**
S_2N_2	0.473	0.075	0.113	0.349	0.097	0.139
Se_2N_2	0.567	0.052	0.095	0.415	0.085	0.125
Te_2N_2	0.649	0.034	0.079	0.468	0.074	0.115
	7	**8**	**9–12**	**7**	**8**	**9–12**
S_4^{2+}	0.247	0.247	0.128	0.221	0.221	0.139
Se_4^{2+}	0.257	0.257	0.121	0.232	0.232	0.134
Te_4^{2+}	0.258	0.258	0.121	0.234	0.234	0.133

immediately clear that the diradical structure **1**, with the radical sites on the nitrogens, is by far the most important one for S_2N_2 as well as Se_2N_2 and Te_2N_2 molecules. By contrast, the other diradical structure, **2**, with the radical sites on the group-16 atoms (S, Se, Te), is much less important. For E_2^{4+}, the two diradical structures **7** and **8** are degenerate, and their weights are relatively constant from one molecule to the other, summing up to nearly 50% of the total VBSCF wave function. These results are qualitatively and even quantitatively in agreement with the VB studies of Harcourt et al.[16] for S_2N_2 and S_4^{2+}, despite the fact that these authors have used semi-localized orbitals instead of strictly localized ones as we did.

It is interesting to visualize the effect of dynamic electron correlation, in terms of VB weights, by comparing the VBSCF weights to the ones calculated at the more accurate BOVB level (see Table 1). For all E_2N_2 molecules, going from VBSCF to BOVB decreases the weight of **1**, increases the weights of the covalent structures **3–6**, and increases even more (relatively) the weight of the diradical structure **2**. As an outcome, our BOVB description of S_2N_2 still finds structure **1** to be the major one, though slightly less prevailing than at the VBSCF level, and finds structure **2** to be, at least, not negligible. On the other hand, the weights of the VB structures in E_4^{2+} molecules are practically unaffected by inclusion of dynamic correlation, as they remain nearly unchanged from VBSCF to BOVB levels. This dual strong/weak effect of dynamic correlation can be qualitatively explained by the fact that VBSCF tends to disfavor the minor structures, because the unique set of orbitals necessarily comes out as better adapted to the major structure(s) after the optimization process. A fully detailed analysis of this effect is given in the Supporting Information.

Another tendency can be seen in Table 1. As E goes down the periodic table (S→Se→Te), the weight of **1** significantly increases to the detriment of the covalent structures **3–6**. By contrast, the diradical (**7–8**) and covalent (**9–12**) weights do not show such variations in the E_4^{2+} cations, and remain nearly independent of the nature of E. The reasons for these contrasted tendencies will become clear by considering the relative energies of the VB structures in the next subsection.

All in all, the cumulated diradical weights are quite significant for all the E_2N_2 and E_4^{2+} species, and account for nearly 50% of the electronic structures as expressed in VB form. Incidentally, it is interesting to note that our BOVB weights for S_2N_2 are close to the estimations of Tuononen et al.,[19] based on an analysis of their [22,16]-CAS wave function. However, before drawing definitive conclusions, it is interesting to address the question from a different point of view, that of the relative energies of the various VB structures.

2.2. Relative Energies of VB Structures and Resonance Energies

The relative energies of the individual VB structures, or restricted combinations of them, are represented in Figure 1 and Table 2 for the E_2N_2 and E_4^{2+} species. As far as the individual VB structures are concerned, it is seen that the diradical structure **1** for E_2N_2 and the degenerate diradical structures **7** and **8**
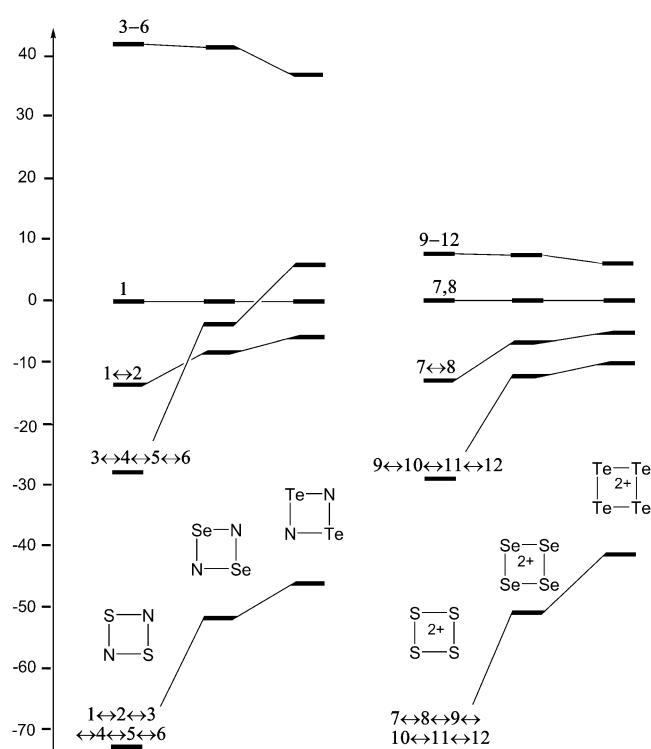

Figure 1. Relative energy levels of individual VB structures, restricted combinations of them, and complete combinations for the E_2N_2 molecules and E_4^{2+} cations. Energies in kcal mol^{-1}, calculated at the BOVB level.

Table 2. Relative energies [kcal mol^{-1}] of some individual diradical structures and combinations of radical structures, relative to the 6-structure ground state of E_2N_2 and E_4^{2+}.

	VBSCF 6-structure	**1**[a]	**1↔2**	BOVB 6-structure	**1**[a]	**1↔2**
S_2N_2	0	53.3	47.8	0	72.8	58.7
Se_2N_2	0	37.2	34.2	0	52.9	44.3
Te_2N_2	0	26.5	24.8	0	40.0	34.6

	6-structure	**7**[b]	**7↔8**	6-structure	**7**[b]	**7↔8**
S_4^{2+}	0	56.3	52.4	0	74.2	61.6
Se_4^{2+}	0	37.7	35.5	0	51.4	44.5
Te_4^{2+}	0	29.8	28.0	0	42.1	36.3

[a] These energies are also the vertical resonance energies of E_2N_2.
[b] These energies are also the vertical resonance energies of E_4^{2+}.

for E_4^{2+} are always the lowest ones, whatever the nature of the atom E. For E_2N_2, the covalent structures **3–6** lie consistently higher in energy than **1** by some 40 kcal mol^{-1}, in agreement with the weight of **1** being much larger than the weights of **3–6** (0.35-0.47 vs 0.14-0.12). On the other hand, the energy gap from diradical structures (**7,8**) to covalent ones (**9-12**) is smaller for the E_4^{2+} cations, in agreement with the corresponding weights being less contrasted (typically 0.23 vs 0.13) than in E_2N_2.

It is also interesting to consider the energies of restricted combinations of VB structures displaying the same type of bonding pattern (covalent or diradical). Thus, the resonance

energy associated with the mixing of the covalent structures **3**–**6** to form the 4-structure resonating combination (**3**↔**4**↔**5**↔**6**) is large in S_2N_2 (ca. 73 kcal mol^{-1}) but smaller in Se_2N_2 (53 kcal mol^{-1} and even smaller in Te_2N_2 (40 kcal mol^{-1}). As a consequence, the resonating combination (**3**↔**4**↔**5**↔**6**) lies below the diradical combination (**1**↔**2**) in S_2N_2, but the order of these two energy levels is reversed in Se_2N_2 and Te_2N_2. By contrast, no such crossing of energy levels occurs in the E_4^{2+} series. In full agreement with these detailed energetic considerations, the cumulated diradical weights are lower than 50 % in S_2N_2, equal to 50 % in Se_2N_2, and larger than 50 % in Te_2N_2. The weights of E_4^{2+} also follow the relative energies of (**7**↔**8**) vs (**9**↔**10**↔**11**↔**12**), with the cumulated BOVB diradical weights being slightly smaller than 50 % in all three cases.

It can also be seen in Figure 1 that the mixing between diradical structures (e.g. **1**↔**2**) and covalent ones (e.g. **3**↔**4**↔**5**↔**6**) is quite stabilizing in all cases, and does not much diminish as E goes down the periodic table, especially from E = S to E = Se. As a consequence, the 6-structure ground state lies significantly lower in energy than any one of the individual structures or restricted combination of covalent structures, in all the E_2N_2 and E_4^{2+} species. This indicates that the diradical structures play an important role in the resonance energies of these 6e–4c systems, an important point to which we return below.

Classically, the vertical resonance energy (VRE) of a molecule is estimated by comparing the energy of its most important VB structure to that of the full multi-structure ground state, at fixed geometry. Let us recall in passing that the VREs are very different from the aromatic stabilization energies, the first quantities being always much larger than the second.[31] For the cases at hand, the VREs correspond to the energies of **1** and **7**, respectively for E_2N_2 and E_4^{2+}, relative to the 6-structure ground states. These VREs are reported in Table 2, as calculated at the VBSCF and BOVB levels.

The BOVB resonance energies are larger than the VBSCF ones, a tendency which is always observed. This is generally due to the fact that VBSCF deals with a unique set of orbitals, and thus has to make a compromise between maximizing the resonance energy and lowering the energies of the individual structures, whereas BOVB can optimize both at the same time. Moreover, in the present case, simple VBSCF level disfavors the minor structures, and hence underestimates the mixing between the major structures and the minor ones. Be that as it may, since the VREs are not experimental observables, the reported values should not be considered as absolute values, but rather as orders of magnitude to compare trends in series of molecules at a given computational level. In that respect, it can be seen that the VREs of the E_2N_2 and E_4^{2+} systems are remarkably close to each other for a given atom E, suggesting that the two systems are comparable from the aromaticity point of view. The VREs decrease down the periodic table but are quite significant for S_2N_2 and S_4^{2+}, with values of 72.8 and 74.2 kcal mol^{-1}, respectively, at the BOVB level. This is in agreement with the significant aromatic character of S_2N_2 according to the magnetic criteria, with a large negative NICS value for the π system (−26.2 ppm) for this molecule,[9] and suggests

that a large negative NICS value should be also found for S_4^{2+}. By comparison, the π system of benzene displays a NICS value of −25.4 ppm,[9] and estimations of the VRE of benzene are in the range 88–92 kcal mol^{-1} in basis sets comparable to ours.[31]

3. Discussion

3.1. Stability of the Diradical Structures

It is clear from what precedes that the stability of the above 4-membered rings does not arise from covalent bonding, since the individual covalent structures all lie above one "no-bond" diradical structure or both. Furthermore, all individual structures lie way above the ground state in all cases, showing that the stability largely arises from resonance between the various VB structures. Yet, it may seem counterintuitive that diradical structures be more stable than covalent ones, especially in the E_4^{2+} systems in which both types of structures display the same number of formal charges. This situation is however less surprising if one notes that a diradical structure, such as **7** in E_4^{2+}, puts the two lone pairs far apart from each other, which is preferable to a covalent structure such as **9**, which has a covalent bond but suffers from the strong Pauli repulsion of two neighboring lone pairs. This is reminiscent to the electronic structure of dioxygen, another 6-electron-4-orbital system, which prefers to separate the two π lone pairs by putting together one π lone pair and one single electron in each π plane, thus forming a diradical $\pi_{ux}^2\pi_{uy}^2\pi_{gx}^1\pi_{gy}^1$ as in the $^3\Sigma_g^-$ state. The alternative, a $\pi_{ux}^2\pi_{uy}^2\pi_{gy}^2$ configuration as in the $^1\Delta_g$ state, lies higher in energy despite the fact that it displays a covalent π bond. Thus, in analogy with O_2, as well as the isoelectronic NF molecule,[32] the 6π-electron 4-membered rings prefer the diradical structures over the covalent ones.

3.2. Couplings between VB Structures and Aromaticity

As noted above, it is remarkable that the resonance between covalent and diradical structures remains important as one goes down the periodic table, while at the same time the 4-structure resonance between covalent structures diminishes, especially from sulfur to selenium. This can be understood by considering the reduced Hamiltonian matrix elements between VB structures. These integrals, which control the stabilization energies that arise from mixing of VB structures, have approximate expressions[33] in terms of orbital overlaps, S, and β integrals which have the same meaning as in Hückel or Extended Hückel theories (neglecting β and S between non-neighbor orbitals). Thus, as shown in Scheme 2a, the reduced Hamiltonian matrix element that couples two covalent structures is $2\beta S$, as is the rule when two VB structures differ from each other by a double electron transfer between neighboring orbitals,[33] and this quantity gives an order of magnitude of the resonance energy arising from the mixing of **3**–**6** or **9**–**12**. A similar matrix element couples together the diradical structures (Scheme 2b). On the other hand, the matrix element that couples a diradical structure to a covalent one is β, because these two structures are now connected to each other by a *single* electron transfer.
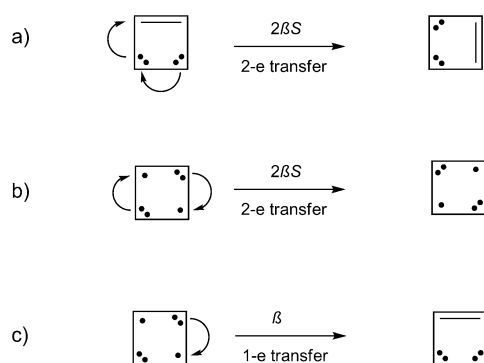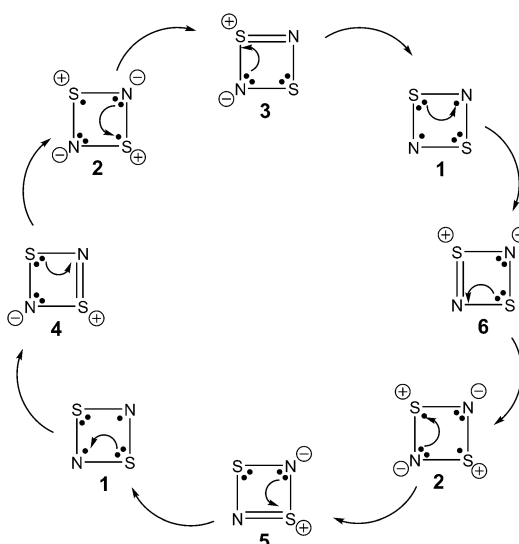
Scheme 2. Qualitative VB expressions for the reduced Hamiltonian matrix elements between VB structures.

Scheme 3. Collective electron flow in the π system of S_2N_2 by means of successive one-electron transfer steps.

Which one of these two matrix elements is the largest one? As β is approximately proportional to S, the former matrix element is proportional to S^2 while the second is simply proportional to S. Thus, as we go down the periodic table, the overlap S between neighboring orbitals diminishes and 2βS dimishes faster than β. It follows that the diradical-covalent mixing (ruled by β) strongly contributes to the overall resonance energy whatever the atom E, whereas the covalent-covalent resonance energy (ruled by 2βS) strongly diminishes from E=S to E=Se.

This explains, for example, the inversion of energy levels of (**1↔2**) and (**3↔4↔5↔6**) from S_2N_2 to Se_2N_2 (Figure 1). For more details, the reduced Hamiltonian matrix elements are tabulated in the Supporting Information document for all E_2N_2 and E_4^{2+} species.

The importance of diradical structures and their one-electron coupling to covalent ones also sheds some light on the type of bonding that takes place in E_2S_2 and E_4^{2+}. As has been said, most of the stability of these rings arises from resonance, and this resonance is due, for an important part, to the interaction between diradical and covalent structures, as illustrated in Scheme 2c. Such an interaction corresponds to the exchange of an electron between a doubly occupied orbital and a neighboring singly occupied one, which is precisely the type of interaction that takes place in a three-electron bond, a type of interaction that can be quite stabilizing, as can be seen in, for example, the dioxygen molecule, whose considerable bond strength is due for the most part to a couple of three-electron π bonds.

The one-electron transfer that couples diradical to covalent structures is also relevant to the magnetic properties of 6π-electron rings, as it is compatible with, or even facilitates, the appearance of ring currents under the influence of an external magnetic field. Indeed, diamagnetic ring currents, as the ones that are revealed by negative NICS values,[9] are associated with a collective circulation of the electrons across the perimeter of an aromatic ring. The result of this motion behaves in accord with the classical Lenz–Biot–Savar law and induces an internal magnetic field which opposes an external field.[34] In a VB model, the electron circulation takes place by means of a passage from one VB structure to the other, and the probabili-

ty of this passage depends on the reduced Hamiltonian matrix element between the two VB structures, as has been conjectured and put to use in previous semiempirical VB studies.[34–36] Scheme 3 illustrates such a cascade of transitions for E_2N_2 and E_4^{2+}, involving the complete set of VB structures. It can be seen that the diradical structures nicely find their places in a collective electron flow around the ring, in which all steps are single electron jumps that occur in the same clockwise direction and are mediated by large reduced Hamiltonian matrix elements β.

As has been said, the reduced Hamiltonian matrix elements (β) that allow such one-electron transfer are always large, at pair or larger than the matrix elements that couple two covalent structures together (2βS). It follows from the preceding discussion that the importance of diradical structures is fully compatible with aromaticity in 6π-electron four-membered rings from the dual point of view of resonance energy and ring currents.

3.3. Diradical Character

The importance of diradical structures, which has been demonstrated herein in terms of calculated weights or relative energies, contrasts with the rather low "diradical character" that has been concluded to in other studies.[9, 19] Let us consider the qualitative arguments first. The moderately large singlet-triplet gap (3.6 eV for S_2N_2) which is frequently taken as an indication of low diradical character, is not incompatible with the importance of diradical VB structures in cases of conjugated molecules. Indeed, the mixing of diradical structures with covalent ones strongly stabilizes the singlet ground state, which is not the case for the triplet state. Besides, the argument of the large HOMO–LUMO gap does not really apply to conjugated molecules, as even the Hartree–Fock configuration of E_2S_2 or E_4^{2+} already contains some diradical VB structures with signifi-

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cant weights, as a mapping of this configuration to VB structures (which can easily be done by hand[33]) would show.

Let us now consider the quantitative index B that is sometimes used to measure the diradical character of a molecule, Equation (1). One first criticism that could be made against this index is that it appears to be dependent on the level of calculation. Thus, in a series of MCSCF calculations on ozone, Schaefer showed that the B index in Equation (1) would take the values 46%, 5% and 23% according as the calculation involves 2, 6825 or 13414 configurations.[21] More recently, the B index for ozone has been estimated to 26% in a large-space CASSCF calculation by Tuononen et al.,[19] a value that contrasts with the estimated weigth of 49.5% for the diradical structure in ozone, recently estimated by Houk et al. by means of a BOVB calculation.[37] Thus, not only does the B index fail to reflect the weight of the diradical structure(s), but molecules that have comparable diradical weights, for example, ozone and E_2N_2 (E = S, Se, Te) have widely different B indexes (respectively 26% and 6–10%). Another problem with the B index is that it only considers the coefficient of the most important diexcitation. As such, it cannot apply to the ground state of E_4^{2+}, which involves three important configurations, among which two degenerate diexcitations. Of course, the corresponding excitations are not degenerate in E_2N_2, however given the similarity of electronic structures in E_4^{2+} and E_2N_2, one may wonder about the validity of the B index in the latter case. Thus, the diradical index in Equation (1) is probably a useful one in 2-electron–2-orbital cases, but we think that its validity is questionable for multi-electron conjugated systems, and that in such cases low B values are not incompatible with significant diradical weights. In the specific case of conjugated molecules (actually the type of electronic systems for which the question of the diradical character is most often addressed), the criterion of the weights and/or the criterion of the relative energies of VB structures have the advantage to be clear and well defined. Moreover, these two distinct criteria are fully consistent with each other, and have the further advantage to specify where exactly in the molecule the diradical sites are preferentially located.

The importance of diradical structures and the relatively high energy of the covalent ones suggests that covalent bonding is not the main factor that stabilizes the above studied 6π electronic systems, in accord with the rather low theoretical bond order (1.25) that is estimated for these systems, based on the bonding/non-bonding characters of the occupied MOs. This is to be related to the apparent paradox that has been mentioned about the S–N bond lengths in S_2N_2.[9] On the one hand, the fact that these bond lengths lie nearly half-way between the standard values for single and double S–N bonds is indicative of strongly bonding interactions in the π system, but on the other hand the low bond order would lead one to expect the S_2N_2 bond lengths to be closer to single bond values. However, a VB view of the electronic structure of this molecule provides a simple answer to the riddle: yes, the π system of S_2N_2 is strongly bound, but the strong bonding does not mainly arise from π-covalent bonding, nor even from resonance between covalent structures alone, but from resonance between the full set of VB structures, including the diradical ones.[38]

3.4. Reconciling the Spin-Coupled and VBSCF/BOVB Views?

It may appear as surprising that different high-level VB calculations, Gerratt's spin-coupled calculations of the one hand, and the present work or Harcourt's ones on the other hand, provide different pictures for S_2N_2. As has been said, the discrepancy arises from the semi-delocalized nature of the orbitals in the spin-coupled theory vs the strictly localized orbitals used herein. However, it is insightful to look at the spin-coupled wave function in more detail.

In this latter method, all VB orbitals are singly occupied, so that the π system of S_2N_2 is described with six electrons in six orbitals, ϕ_1–ϕ_6. The shapes of these orbitals are shown in Figure 1 of ref. [17]. Four of these orbitals (ϕ_1, ϕ_2, ϕ_4 and ϕ_5), are pretty much localized and closely resemble the π atomic orbitals that are labeled S_1, N_2, S_3 and N_4 in Scheme 4, respectively localized either on S or on N atoms [Eq. (4)]:

Scheme 4. The π atomic orbitals of S_2N_2.

$$\phi_1 \approx S_1; \quad \phi_2 \approx S_3; \quad \phi_4 \approx N_2; \quad \phi_5 \approx N_4 \tag{4}$$

On the other hand, ϕ_3 and ϕ_6 are both mainly delocalized on S_1 and S_3, with a small component on a nitrogen atom [Eq. (5)]:

$$\phi_3 \approx S_1 + S_3 + \varepsilon N_2 : \quad \phi_6 \approx S_1 + S_3 + \varepsilon N_4 \tag{5}$$

As indicated in ref. [17], the spin-coupled wave-function is quasi-perfect-pairing and is made of the singlet-coupled orbitals pairs (ϕ_1–ϕ_2), (ϕ_3–ϕ_4), and (ϕ_5–ϕ_6). In terms of determinants, such a wave function can be written as Equation (6):

$$\Psi_{sc} = \left(|\phi_1\bar{\phi}_2| + |\phi_2\bar{\phi}_1|\right)\left(|\phi_3\bar{\phi}_4| + |\phi_4\bar{\phi}_3|\right)\left(|\phi_5\bar{\phi}_6| + |\phi_6\bar{\phi}_5|\right) \tag{6}$$

Now the interpretation of this wave function can be greatly simplified if one notices that ϕ_3 and ϕ_6 orbitals, albeit not being coupled in a bond pair, strongly resemble each other, with a mutual overlap of 0.825.[17] If one neglects the small nitrogen tails in Equation (5), this overlap becomes unity and ϕ_3 and ϕ_6 orbitals becomes one and the same. The spin-coupled wave function can then be rewritten as follows, setting $\phi_3 \approx \phi_6$ and eliminating products of identical spin-orbitals [Eq. (7)]:

$$\Psi_{sc} \approx \left(|\phi_1\bar{\phi}_2| + |\phi_2\bar{\phi}_1|\right)\left(|\phi_3\bar{\phi}_3|\right)\left(|\phi_4\bar{\phi}_5| + |\phi_5\bar{\phi}_4|\right) \tag{7}$$

Replacing now the ϕ_i orbitals by their approximate expressions in terms of S_i and N_i, one gets Equation (8):

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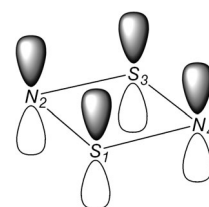
$$\Psi_{sc} \approx \left(|S_1\bar{S}_3| + |S_3\bar{S}_1|\right)|(S_1 + S_3)(\bar{S}_1 + \bar{S}_3)|(|N_2\bar{N}_4| + |N_4\bar{N}_2|)$$

$$(8)$$

Expanding Equation (8) and eliminating once again products of identical spin-orbitals, one gets Equation (9):

$$\Psi_{sc} \approx |S_1\bar{S}_1S_3\bar{S}_3|(|N_2\bar{N}_4| + |N_4\bar{N}_2|)$$

$$(9)$$

in which the orbitals S_1 and S_2, located on sulfur atoms, are both doubly occupied while N_2 and N_4 display a single long π bond, which represents nothing else but structure **1** in Scheme 1, as in VBSCF/BOVB calculations !

The outcome of this development is that our VBSCF or BOVB wave functions, constructed with local orbitals, are maybe not so different from Gerratt's spin-coupled wave function. Thus, we believe that the spin-coupled description of S_2N_2 is correct, even if we disagree with Gerrat et al. on the interpretation of the spin-coupled wave function.

4. Conclusions

The question of the diradical character of S_2N_2 has been addressed in many ways, ranging from VB calculations with semi-delocalized orbitals, VB analysis of CASSCF calculations, or by a diradical index based on the two most important CI coefficients in an MO-based wave function. Here we adopt a definition which has the merit of, we think, clarity, as it directly estimates the weights of all the relevant VB structures of the electronic system, by means of a VB method that takes care of dynamic correlation and that uses strictly local one-center orbitals. While former VB calculations using semi-delocalized orbitals disagree on the nature of the diradical structure, our study unambiguously shows that the preferred diradical structure is the one that bears radical sites on the nitrogen atoms, the other one being much less important. This result carries over to the isoelectronic species, Se_2N_2 and Te_2N_2. Incidentally, the controversy on the radical sites is resolved if one re-interprets the spin-coupled wave function for S_2N_2 after an expansion of the latter in terms of VB structures with localized orbitals. The electronic structure of the E_4^{2+} dications resemble that of the neutral E_2N_2 molecules, except that the diradical structures are now degenerate. In all cases, neutral and cationic, the cumulated weights of the diradical structures are close to 50%, comparable to the diradical weight of ozone, a molecule whose strong diradical character is well accepted. These results illustrate the importance of diradical structures in 6-π-electron 4-center systems, and are at variance with a commonly used index [Eq. (1)] for estimating the diradical character, based on the two most important coefficients of a MO-based CI wave function.

The ordering of the various VB structures in terms of their calculated weights is confirmed by the relative energies of individual VB structures. In all cases, the major diradical structure (or both diradical structures when they are degenerate) is the lowest one, while the covalent VB structures lie higher in energy. Thus, the stability of the above studied 6-π electronic systems does not mainly arise from π-covalent bonding, nor even from resonance between covalent structures alone, but from resonance between the full set of VB structures, including the diradical ones. In accord, the vertical resonance energies are considerable in S_2N_2 and S_4^{2+}, about 80% of the estimated value for benzene, while they somewhat diminish as one goes down the Periodic Table (S→Se→Te). This confirms the aromatic character of these species, as already demonstrated for S_2N_2 on the basis of magnetic criteria.[9] This and the high weights and stabilities of one or both diradical structures in all systems indicates that aromaticity and diradical character do not exclude each other. Furthermore, consideration of reduced Hamiltonian matrix elements show that the diradical structures find their place in a collective electron flow that can mediate ring currents in the π system, as has been found in S_2N_2. In accord, we predict that comparable ring currents should also exist in Se_2N_2, Te_2N_2 and the E_4^{2+} cations (E = S, Se, Te).

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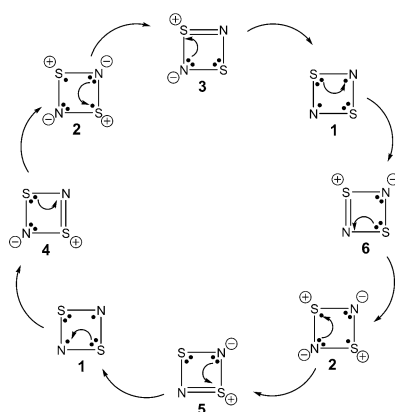
ARTICLES

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■■ – ■■

🖥 **Can Aromaticity Coexist with Diradical Character? An Ab Initio Valence Bond Study of S_2N_2 and Related 6π-Electron Four-Membered Rings E_2N_2 and E_4^{2+} (E = S, Se, Te)**

Radical ideas about diradicals: A series of 6π-electron 4-center species, E_2N_2 and E_4^{2+} (E = S, Se, Te; see picture) is studied by means of ab initio valence bond methods. It is shown that aromaticity and diradical character do not exclude each other, contrary to what is usually claimed.