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Electronic Structure of N–S Compounds. *Ab initio* and INDO/S-CI Investigation of $S_4N_4H_4$

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Ab initio *closed and unrestricted open-shell molecular orbital calculations of STO-3G quality are reported for $S_4N_4H_4$ and some anionic states of $S_4N_4H_4$, S_4N_4 and S_2N_2.*

Molecular orbital energies and overlap populations were used to investigate the electronic structure of $S_4N_4H_4$. The results are compared with those of the related compounds S_4N_4 and S_2N_2. By comparing theoretical data with available dipole moment values of the related compounds $S_{8-x}(NH)_x$ it is inferred that STO-3G calculations give reasonable charge distribution on the investigated compounds.

The search in $S_4N_4H_4^-$ for a ring structure of symmetry lower than C_{4v} to account for Jahn–Teller distortion was unsuccessful. On the contrary, a ring structure of C_s symmetry gives a Jahn–Teller stabilization of 24.7 and 20.5 kcal·mol^{-1} for $S_4N_4^-$ and $S_4N_4^{2-}$, respectively.

The calculated electron affinity of $S_4N_4H_4$ is predicted to be about three times and four times lower than that of S_2N_2 and S_4N_4, respectively. The energy of the disproportionation reaction $2R^- \rightarrow R + R^{2-}$ is reported for $S_4N_4^-$ and $S_2N_2^-$. INDO/S-CI calculations predict for $S_4N_4H_4$ no UV–VIS absorption up to 6 eV as a consequence of the high energy value of its lowest unoccupied molecular orbital.

Introduction

The work carried out on the molecular structure of cyclic sulphur–nitrogen compounds is noteworthy [1]. Since the discovery of the peculiar physical and electronic properties of the inorganic conductor $(SN)_x$ the interest in the electronic structure of these compounds has greatly increased [2–9]. The variability of the molecular conformation is a typical feature of cyclic N–S compounds. This is, of course, closely connected with their electronic structure. An example is offered by S_4N_4, $S_4N_4O_2$ and $S_4N_4H_4$. The first compound has a cradle-like structure of D_{2d} symmetry [10], which in $S_4N_4O_2$ is greatly flattened [11]. $S_4N_4H_4$ has a crown shape structure [12, 13] very similar to that of the isoelectronic molecule S_8 [14, 15]. Accordingly, the photoelectron spectra of S_4N_4 and $S_4N_4O_2$ show marked differences in the band structure and composition [5]. Unfortunately, the photoelectron spectrum of $S_4N_4H_4$ is not known, so that a comparison with that of S_4N_4 [2, 5] cannot be made.

The present work is a contribution to the knowledge of the electronic structure of $S_4N_4H_4$ by means of *ab initio* and INDO/S-CI calculations. *Ab initio* calculations were also performed on the anion $S_4N_4H_4^-$ and were extended to anionic species of the related compounds S_4N_4 and S_2N_2 for comparison. Recently X-α and CNDO/BW calculations on $S_4N_4H_4$ have been reported [6]. Cassoux *et al.* [9] have evidenced through a partitioning of the total electronic molecular energy the absence of cross-ring S–S interactions in $S_4N_4H_4$, contrary to the case of S_4N_4.

Calculations

Calculations were performed with the Gaussian 70 set of programs [16] using the minimal STO-3G basis set, and with an INDO/S-CI program whose parameterization was described elsewhere [17, 18]. The first 60 monoexcited singlet transitions have been considered in the CI calculations. The experimental geometry of $S_4N_4H_4$, slightly idealized to give a C_{4v} point group symmetry (Fig. 1), was used

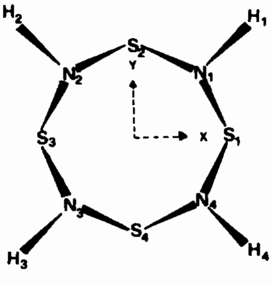

Fig. 1. Molecular structure $S_4N_4H_4$. S–N = 1.653 Å; N–H = 1.049 Å; $N\hat{S}N$ = 111.3°; $S\hat{N}S$ = 128.2°; $S\hat{N}H$ = 115.3°.

TABLE I. Molecular Orbital Data for $S_4N_4H_4$.

STO-3G			INDO/S-CI		
Orbital type[a]	Symmetry	Energy	Orbital type[a]	Symmetry	Energy
Virtual molecular orbitals					
a(S–N), a(N–H)	$6a_1$	10.82	a(S–N), a(N–H)	7e	1.82
a(S–N), a(N–H)	7e	10.38	a(S–N), a(N–H)	$6a_1$	1.48
Occupied molecular orbitals					
b(N–H), n(S)	$5a_1$	–6.36	n(N)	6e	–10.16
n(S)	$3b_1$	–7.15	n(S, N)	$5a_1$	–10.21
n(S)	6e	–7.29	n(N)	$3b_2$	–10.53
n(S, N)	5e	–7.56	n(S)	$3b_1$	–11.09
n(N)	$3b_2$	–9.24	n(S)	5e	–11.25
n(S, N)	$2b_1$	–10.22	n(S, N)	$4a_1$	–12.38
n(S, N)	$4a_1$	–10.65	n(S)	$2b_1$	–13.89
b(S, N)	4e	–12.75	b(S–N)	4e	–15.31
b(S, N)	$3a_1$	–14.37	b(S–N)	$3a_1$	–16.70
b(S, N)	$1a_2$	–14.77	b(N–H)	$2b_2$	–18.03
b(N–H)	$2b_2$	–15.35	b(S–N)	$1a_2$	–18.43
b(S–N), b(N–H)	3e	–16.08	b(S–N), b(N–H)	3e	–19.57
s(S), b(N–H)	$2a_1$	–19.51	b(N–H)	$2a_1$	–22.25
s(S, N, H)	2e	–21.27	n(S, N), s(H)	2e	–22.44
s(S)	$1b_1$	–24.83	s(S), n(N)	$1b_1$	–25.13
s(N)	$1b_2$	–28.83	s(N, H), n(S)	$1b_2$	–35.25
s(S, N, H)	1e	–31.05	s(S, N, H)	1e	–38.03
s(S, N, H)	$1a_1$	–32.41	s(S, N, H)	$1a_1$	–41.20

[a] a = antibonding; b = bonding; n = non bonding; s = *s*-type orbital. Figures are in eV.

throughout the calculations of the neutral molecule. Calculations at STO-6G level gave practically the same results as STO-3G calculations for molecular orbital energies, ordering of symmetries and population analysis.

Results and Discussion

The eigenvalue spectrum of $S_4N_4H_4$ at *ab initio* STO-3G and INDO/S-CI level of calculations is reported in Table I. In the *ab initio* scheme the outermost occupied molecular orbitals (MOs) have a prevailing S_{3p} lone-pair character. The highest occupied $5a_1$ MO (HOMO) (orbital number 48) also shows appreciable contributions from N–H bonding interactions. Next MOs are of mixed N_{2p} and S_{3p} lone-pair composition; they are followed by a bonding S–N and N–H region. The innermost MOs are mainly *s*-(S, N, H) atomic orbitals.

The eigenvalue ordering in $S_4N_4H_4$ is in some respect different from that found in S_4N_4 by the same type of calculation [7]. A major difference in the latter compound is that the lower energy ionizations have more N character than in $S_4N_4H_4$.

The INDO/S-CI results indicate that the higher energy region of the eigenvalue spectrum of $S_4N_4H_4$ is dominated by S_{3p} and N_{2p} lone-pairs. However, contrary to the *ab initio* data, ionizations from N_{2p} orbitals are predicted to occur at a lower energy than ionizations from S_{3p} orbitals. The remaining MOs of the eigenvalue spectrum reasonably agree with the *ab initio* results, apart from some inversion in the ordering of MO symmetries.

Since wide-scale use is made of Koopmans' theorem in interpreting photoelectron spectra, a comparison between the present results and those reported by Whitehead *et al.* [6] on $S_4N_4H_4$ may be useful. This comparison, diagrammatically shown in Fig. 2, indicates that the ordering of the MO symmetries differs in many instances in the various methods of calculation. Moreover, some MOs of the same symmetry show different composition (see also Table II of ref. 6). For example the $3b_1$ MO is predicted to be centered on nitrogen atom in X-α and CNDO/BW calculations [6], but on the sulphur atom in the present *ab inito* and INDO/S-CI calculations.

It is worth noting that, in contrast with the present *ab initio* results, X-α and CNDO/BW data both predict that the highest three occupied MOs are essentially N_{2p} lone-pairs and that S_{3p} lone-pair levels at a lower energy. This, one the other hand, agrees with our INDO/S-CI results.

TABLE II. Total Energies and Mulliken Population Analysis of S–N Compounds. STO-3G Results.

	E_T	q(N)	q(S)	q(H)	w(S–N)	w(S••S)	w(N–H)
$S_4N_4H_4$ (C_{4v})	−1789.878195	−0.569	0.417	0.153	0.435	0	0.666
$S_4N_4H_4^-$ (C_{4v})	−1789.495454	−0.562	0.246	0.065	0.263	−0.012	0.571
S_4N_4 (D_{2d})	−1787.225249	−0.551	0.551		0.416	0.113[a]	
$S_4N_4^-$ (D_{2d})	−1787.140691	−0.639	0.354 0.423[b]		0.382 0.423[b]	0	
$S_4N_4^-$ (C_s)[c]	−1787.180108						
$S_4N_4^{2-}$ (D_{2d})	−1786.768455	−0.695	0.219		0.425	−0.029	
$S_4N_4^{2-}$ (C_s)[c]	−1786.801273						
S_2N_2 (D_{2h})	−893.663064	−0.459	0.459		0.468	−0.245	
$S_2N_2^-$ (D_{2h})	−893.517920	−0.630	0.130		0.394	−0.218	
$S_2N_2^{2-}$ (D_{2h})	−893.001812	−0.817	−0.183		0.313	−0.199	

[a] Overlap population between the two sulphur atoms across the ring. [b] Alternation is found in charge densities and overlap populations, see text. [c] For the Mulliken population analysis in this ion see Table IV.

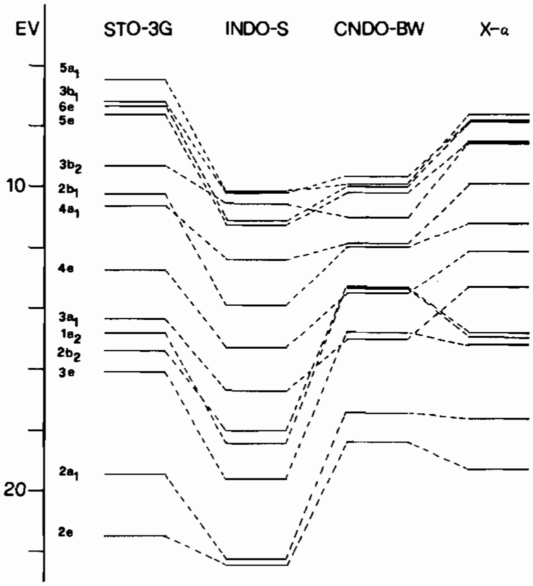

Fig. 2. Correlation by symmetry of orbital energies for $S_4N_4H_4$. CNDO/BW and X-α data from ref. [6].

On this subject we may note that the symmetry ordering of the MOs of S_4N_4 in STO-3G calculations [7] and in *ab initio* calculations with a much more extended basis set [2] are similar: only one inversion ($4b_2$ for $2a_2$) occurs in STO-3G data [7] with respect to the results of *ab initio* calculations of double-ζ spd quality [2]. MO composition also shows a good agreement. Although the agreement between the two levels of calculations is less good as far as the spacing of the energy levels is concerned, the above comparison makes the present STO-3G results appear reliable enough. In any case, the availability of the photoelectron spectrum of $S_4N_4H_4$ under He(I) and He(II) radiation would appear to be very useful. This approach, in fact, has been successfully applied by Palmer *et al.* in the case of S_4N_4 [2].

In the *ab initio* calculations the lowest unoccupied MO (LUMO) of $S_4N_4H_4$ is an antibonding S–N and N–H orbital of *e* symmetry. The next orbital has a_1 symmetry and the same composition as the 7e orbital (Table I). The INDO/S-CI calculations give an inverse ordering but the same MO composition. Both *ab initio* and INDO/S-CI calculations assign a positive value to the LUMO. The gap between the LUMO and the HOMO is 16.74 and 11.64 eV in the *ab initio* and INDO/S-CI calculations, respectively. The corresponding figures in S_4N_4 were 9.13 [7] and 5.16 eV [8], respectively. The noticeable difference in the energy gap between the two compounds (about 7 eV) is connected with the higher energy of the LUMO in $S_4N_4H_4$ than in S_4N_4: 10.38 (Table I) and 2.68 eV [7], respectively, at *ab initio* 3G level; 1.48 (Table I) and −3.50 eV [8], respectively, at INDO/S-CI level. This difference must be reflected in the relative UV absorption characteristics of the two compounds. The UV spectrum of S_4N_4 has been measured by Braterman [19] and most recently by Apter *et al.* [20]. It is characterized by a strong absorption at about 39,000 cm^{-1}. Its experimental features are reasonably reproduced by INDO/S-CI calculations [8]. Unfortunately, the UV spectrum of $S_4N_4H_4$ is not known. However, in consequence to this very large $E_{LUMO}-E_{HOMO}$ energy gap, INDO/S-CI calculations predict no UV/VIS absorption for $S_4N_4H_4$ up to 6 eV. The first weak allowed transition (f = 0.08) polarized along the z-axis, is computed to lie at 6.67 eV.

Anionic States

The position of the LUMO is important in determining the conductivity properties of S–N compounds, so that we decided to carry out some *ab initio* STO-3G open-shell unrestricted SCF calculations on negative ions of $S_4N_4H_4$ and on the related molecules S_4N_4 and S_2N_2, to provide information on their *relative* electron affinity (EA), and to evaluate the energy of the formal disproportionation reaction in the gas phase, E_D

$$2R^- \longrightarrow R + R^{2-}$$

E_D can be envisioned as the energy required to move one electron from one R^- unit to another. This is a useful parameter in band calculations of stks [21].

Calculations on the anions were performed on the fixed geometry of the neutral molecule, corresponding to the vertical attachment of the extra electron. However, the LUMO of S_4N_4 and $S_4N_4H_4$ is a double degenerate orbital of *e* symmetry, so that a Jahn–Teller distorsion towards a structure of a lower symmetry must occur in their anions.

$S_4N_4^{2-}$ is isoelectronic with S_8^{2+}, which has an *exo-endo* structure of C_s symmetry [22]. Calculations on this structure (Fig. 3) give a Jahn–Teller stabilization of 24.7 kcal•mol^{-1} for S_4N_4 and 20.5 kcal•mol^{-1} for $S_4N_4^{2-}$.

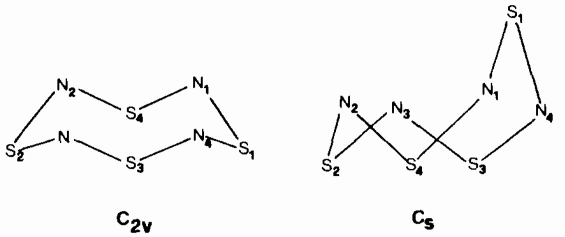

Fig. 3. C_{2v} and exo-endo molecular conformations of S_4N_4.

The radical anion $S_4N_4^-$ was identified in the chemical [23, 24] and electrochemical [25, 26] reduction of S_4N_4. $S_4N_4^-$ is stable at temperatures below *ca.* –25 °C, while above 0 °C it rapidly decomposes *via* an intramolecular rupture [25]. The electrochemical reduction of S_4N_4 in ethanol at 23 °C gives $S_3N_3^-$ [26]. Very recently [27] a two-step polarographic reduction of S_4N_4 in acetonitrile was reported, with $E_{1/2}$ values of –0.93 and –2.58 V for the first and second wave, respectively. In the presence of proton donors the reduction of S_4N_4 seems to give $S_4N_4H_4$ [27]. $S_4N_4^-$ produce a nine-line ESR spectrum with four equivalent nitrogens, which suggests a C_{2v} structure (Fig. 3) for this ion [24]. It is a pity that STO-3G calculations on this structure do not converge, therefore a very useful comparison with experimental data cannot be made. For $S_4N_4H_4^-$ we were unable to find a stable structure of symmetry lower than C_{4v}. In particular, calculations carried out on C_s structures with coplanar sulphur or nitrogen atoms give total energies slightly higher than those of C_{4v} structure. On the other hand the great stability of the C_{4v} structure in $S_4N_4H_4$ can be foreseen owing to the large HOMO–LUMO energy gap. We tentatively conclude that the Jahn–Teller stabilization in $S_4N_4H_4^-$ is achieved through non-equivalent bond lengths, or through a ring opening probably due to high ring strain energies in the anion. So far we have not investigated this point further; however, some indications may be drawn from the population analysis reported below. Note that non-equivalence of bond lengths in the $(SN)_x$ chains is probably to be ascribed [28] to the Jahn–Teller effect. The instability of $S_4N_4H_4^-$ seems to be supported by the electrochemical reduction of $S_4N_4H_4$ [27], which shows a polarographic reduction wave at *ca.* –2.80 V, corresponding to the formation of $S_4N_4H_4^-$, which decomposes in coulometric experiments by further addition of electrons.

From the total electronic energies of neutral molecules and ions reported in Table II we have calculated the figure shown in Table III. It can be seen that the highest EA value is exhibited by S_4N_4. Accordingly, S_4N_4 shows the lowest E_D value.

TABLE III. Electron Affinity EA (eV) and Disproportionation Energy E_D (eV) for S–N Compounds. STO-3G Results.

	EA Koopmans	EA ΔSCF	E_D
$S_4N_4H_4$ (C_{4v})	–10.38	–10.41	
S_4N_4 (D_{2d})	–2.68	–2.30	7.83
S_4N_4 (C_s)^a	–2.68	–1.23	6.93
S_2N_2 (D_{2h})	–3.95	–3.95	10.09

^{a}The symmetry notation refers to the structure of the ion, see text.

A quantitative comparison between EA and $E_{1/2}$ values for S_4N_4 and $S_4N_4H_4$ cannot be made owing to the irreversibility of the corresponding reduction processes [27]. Qualitatively, however, electrochemical results [27] confirm that $S_4N_4H_4$ has an EA lower than S_4N_4.

$S_4N_4H_4$ and S_2N_2 do not show electron reorganization on electron addition, while the formation of $S_4N_4^-$ involves a significant electron reorganization also in the rigid D_{2d} structure. The peculiar characteristics of S_4N_4, which, among the present compounds, is the one showing a molecular structure near to that of $(SN)_x$ chain, are worth noting.

Mulliken Population Analysis

Charge densities and overlap populations for the studied compounds are reported in Tables II and IV.

TABLE IV. Mulliken Population Analysis in $S_4N_4^-$ (C_s) and $S_4N_4^{2-}$ (C_s)[a]. STO-3G Results.

	q(N)	q(S)	w(S–N)	w(S••S)
$S_4N_4^-$ (C_s)	$N_1 = -0.598$	$S_1 = 0.197$	$N_1{-}S_1 = 0.326$	$S_1{-}S_2 = 0$
	$N_2 = -0.458$	$S_2 = 0.306$	$N_4{-}S_1 = 0.326$	$S_3{-}S_4 = -0.06$
	$N_3 = -0.458$	$S_3 = 0.305$	$N_1{-}S_3 = 0.420$	
	$N_4 = -0.598$	$S_4 = 0.305$	$N_3{-}S_4 = 0.420$	
			$N_2{-}S_3 = 0.364$	
			$N_3{-}S_4 = 0.364$	
			$N_2{-}S_2 = 0.332$	
			$N_3{-}S_2 = 0.332$	
$S_4N_4^{2-}$ (C_s)	$N_1 = -0.698$	$S_1 = 0.136$	$N_1{-}S_1 = 0.356$	$S_1{-}S_2 = 0$
	$N_2 = -0.728$	$S_2 = 0.101$	$N_4{-}S_1 = 0.356$	$S_3{-}S_4 = 0.08$
	$N_3 = -0.728$	$S_3 = 0.308$	$N_1{-}S_3 = 0.447$	
	$N_4 = -0.698$	$S_4 = 0.308$	$N_4{-}S_3 = 0.447$	
			$N_2{-}S_3 = 0.412$	
			$N_3{-}S_4 = 0.412$	
			$N_2{-}S_2 = 0.339$	
			$N_3{-}S_2 = 0.339$	

[a] See Fig. 3 for numbering.

The polarity of the S–N bond is of central importance for the understanding of the physical properties of inorganic cyclic S–N compounds. As an example, it was argued [29] that the geometry and the mechanism of the ring opening in S_2N_2 to give $(SN)_x$ is closely dependent on the S–N bond polarity. Unfortunately the available experimental charge densities on nitrogen and sulphur atoms, as obtained from chemical shifts of the binding energies in X-ray photoelectron experiments, disagree with each other: values of ±0.25 [5] and ±0.6 [28] were quoted for the charge separation in S_4N_4. This certainly does not help in evaluating the reliability of the various theoretical calculations, which also disagree with each other.

The STO-3G calculations predict in $S_4N_4H_4$ charge densities on sulphur and nitrogen atoms of 0.42 and −0.57e, respectively. They are slightly higher than those found in S_4N_4 (Table II) owing to the electron donation of the hydrogen atom.

The charge density similarity in S and N atoms in the two compounds is in agreement with the very close S_{2p} and N_{1s} core electron binding energy value in S_4N_4 (164.5 and 397.9 eV respectively) [5] and in cyclic sulphur imides (164.8 and 398.8–399.5 eV, respectively) [30].

Barrie *et al.* [30] deduce from Siegbahn's correlation curves between chemical shift and q, a charge density on sulphur in $S_4N_4H_4$ of 0.17e. They also suggest that in compounds of the type $S_{8-x}(NH)_x$ a small positive charge of about 0.1e resides on sulphur, and of −0.1e on the NH group, in agreement with the Pauling electronegativity difference between nitrogen and sulphur of 0.08. Our STO-3G results disagree with these proposals. The INDO/S-CI results, on the contrary, do agree. In fact they predict q(S) = 0.08e, q(N) = −0.21e and q(H) = 0.13e. The corresponding X-α figures are [6]: q(S) = 0.184e, q(N) = −0.419e and q(H) = 0.235e; while CNDO/BW calculations give [6]: q(S) = 0.310e, q(N) = −0.532e and q(H) = 0.222e. So X-α results agree with the proposals of Barrie *et al.* [30]. Clearly the various theoretical methods disagree with each other in predicting the charge separation in $S_4N_4H_4$. Independent indications on this matter may come from the analysis of the available dipole moment values of $S_{8-x}(NH)_x$ compounds [31]. Of direct interest is the dipole moment of 1,5-hexasulphurdiimide (Fig. 4), 1.74 D. This compound has a molecular structure [32] very similar to that of $S_4N_4H_4$ [12, 13]. By considering that the dihedral angle between the S_1–NH–S_2 plane and the plane of the four S_1, S_2, S_3, S_4 sulphur

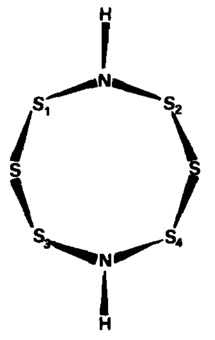

Fig. 4. Dipole moment of 1,5-hexasulphurdiimide.

atoms is evaluated to be 43.6° in 1,5-$S_6(NH)_2$ and 38° in $S_4N_4H_4$, a simple vector analysis gives a value of 1.20 D for the group dipole moment S–NH–S in 1,5-$S_6(NH)_2$. By transfering this quantity into $S_4N_4H_4$ we obtain for this molecule a dipole moment of 3.80 D, to be compared with the calculated STO-3G value of 2.92 D. Thus STO-3G calculations underestimate the S–NH–S group moment by about 0.22 D. The agreement may be considered moderately good, so that, on this basis, we may infer that STO-3G calculations predict reasonable charge distribution in the present compounds.

The excess electron in $S_4N_4H_4^-$ is essentially localized on the sulphur and hydrogen atoms. This reflects the S–N and N–H antibonding composition of the LUMO in $S_4N_4H_4$. Accordingly the S–N overlap population is greatly reduced in the anion. The addition of the extra electron should thus favour ring opening. In $S_2N_2^-$ there is much less decreasing than in $S_4N_4H_4^-$ in the S–N overlap with respect to the neutral molecule. The ring structure in this case probably is preserved.

A relevant feature of the overlap population in $S_4N_4^-$ and $S_4N_4^{2-}$ (Tables II and IV) is the loss of the positive cross-ring interaction. This again is a consequence of the S–S antibonding character of the LUMO in S_4N_4. The decreasing in the cross-ring bonding interaction is consistent with the evolution of the geometry of S_4N_4 towards the *exo-endo* form in the anion.

Tables II and IV show non-uniform charge distribution and bond order in $S_4N_4^-$ and $S_4N_4^{2-}$. This may indicate that a stable ring structure of these ions is unlikely. This is also supported by the fact that salts of $S_4N_4^{2-}$ are very likely to be unstable [26].

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