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Hartree Fock instabilities in the $S_4N_4^{2+}$ dication

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The HF singlet stability of the $S_4N_4^{2+}$ dication is investigated. At the experimental bond length, $R_{SN} = 1.545$ Å, the D_{4h} solution is stable but at 2.00 Å a C_{2v} broken symmetry solution is of lower energy. Population analysis shows that C_{2v} solution has a nitrogen "π-hole" on one of the unique nitrogens. The sulphur π-hole (found for the anion $S_3N_3^-$ at this distance) is not a local minimum.

Key words: Instability — Sulfur — Nitrogen systems — Electron-rich systems

1. Introduction

The synthesis of the $S_4N_4^{2+}$ dication was first reported in 1977 by Gillespie and coworkers [1]. They proposed several structures including a planar cyclic D_{4h} species with equal bonds and a planar species with alternate long and short bonds. Their later crystallographic X-ray studies [2] have been interpreted in terms of the D_{4h} planar structure with all bonds equal to $R_{SN} = 1.545$ Å and theoretical studies [3, 4] have also assumed equal bond lengths. In this study we investigate the stability of the D_{4h} Hartree-Fock solution of $S_4N_4^{2+}$.

We have already carried out HF instability calculations for the $S_3N_3^-$ anion with 10 π electrons [5] and our calculations confirmed that the D_{3h} symmetry adapted solution is stable at the experimental bond length of $R_{SN} = 1.60$ Å. However, a close lying instability, triggered by only a 15% increase in the bond length provided several novel features. The first broken symmetry was C_{2v} (rather than the more usual bond alternation of a C_{3h} broken symmetry solution [6]) and led to two non-equivalent solutions. In each of the C_{2v} broken symmetry solutions the 10 π electrons are confined to a five atom sequence leaving, in one case, a sulphur atom stripped of π electrons and, in the other case, a nitrogen centre without its π electrons. Further, in the lower energy of these (the "N $-\pi$ hole" case), the overlap population between the NSN and the SNS fragments (which have been suggested as thermolysis products of $S_3N_3^-$ [7]), is markedly reduced.

The absence of a bond alternating broken symmetry solution for $S_3N_3^-$ is a direct consequence of the π electron richness of the symmetry adapted species. It is of interest to test this principle in the π electron rich $S_4N_4^{2+}$ dication for which a bond alternating structure has been suggested. Further the generation of *two* non-equivalent broken symmetry $S_3N_3^-$ solutions by the lowest stability root can be rationalized in terms of the difference between S and N atoms and it is important to extend these arguments to the dication. The relation between characteristics of broken symmetry solutions, such as overlap population, and chemical properties is under debate [5], and consequently the broken symmetry solutions of $S_4N_4^{2+}$ are of interest in this connection also.

2. The stability equations

In order to establish notation we will review briefly some of the ideas associated with symmetry breaking of self-consistent Hartree-Fock wavefunctions. The Hartree-Fock operator, H_{SCF}, is defined in terms of the self consistent field given by a density distribution of electrons. It is a non local operator and in principle need not commute with the point group operators of the nuclear framework. In turn the calculated Hartree-Fock (HF) wavefunction need not be an eigenfunction of the symmetry operators. As a result the HF *wavefunction* may exhibit "broken-symmetry" - a lower symmetry than that of the nuclear framework.

The variational procedure ensures that the solution is a stationary point of the energy, i.e., $\delta^1 E = 0$, where $E = \langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle$. However this stationary point can have complex character, for example, the stationary point can be a maximum or a saddle point with reference to a wider class of variations, i.e., to other symmetries. To determine whether a solution would break symmetry one needs to calculate $\delta^2 E$ in the neighbourhood of the stationary point without imposing any symmetry restriction. The appropriate formulation of the problem dates back to the work of Thouless in 1960 [8] and a tractable method for spin-independent Hamiltonians was developed by Cizek and Paldus [9] in the late sixties.

One constructs a variational function, ψ_{BS} for the potentially broken symmetry solution using, as a basis, the symmetry adapted solutions obtained at the stationary point of interest. ψ_{BS} can be expressed as a sum of the symmetry adapted function, ψ_{SA}, and the functions ψ_1 and ψ_2 generated by single and double excitations $\psi_{\mathrm{SA}}(i \to j)$ and $\psi_{\mathrm{SA}}\binom{i\to j}{k\to l}$ as in:

$$\psi_{\mathrm{BS}} = \psi_{\mathrm{SA}} + \psi_1 + \psi_2, \text{ where } \psi_1 = \sum d_{ij}\psi_{\mathrm{SA}}(i \to j), \text{ and } \psi_2 = \sum d_{ij} d_{kl} \psi_{\mathrm{SA}}\binom{i\to j}{k\to l}.$$

The second variation, $\delta^2 E$, can be written as a quadratic form in d_{ij}

$$\delta^2 E = \sum \{d_{ij}d_{kl}A_{ijkl} + \tfrac{1}{2}d_{ij}d_{kl}B_{ijkl} + \tfrac{1}{2}d_{ij}d_{kl}B^{\dagger}_{ijkl}\} \tag{1}$$

where the matrix elements A_{ijkl} and B_{ijkl} are defined by

$$A_{ijkl} = \langle i \to j|\mathrm{H} - \mathrm{E}_{\mathrm{SA}}|k \to l\rangle, \qquad B_{ijkl} = \langle (\substack{i \to j \\ k \to l})|\mathrm{H} - \mathrm{E}_{\mathrm{SA}}|\rangle, \tag{2}$$

where H is the Hamiltonian and E_{SA} is the energy of the symmetry adapted solution at the stationary point of interest. The sign of $\delta^2 E$ can be determined by calculating the eigenvalues λ_n of the characteristic matrix of the quadratic form given in Eq. (1).

As shown by Cizek and Paldus [9] this problem can be broken into a number of subproblems depending on the constraints placed on the broken symmetry solution. In this work we require that the broken symmetry solution be a singlet and write the *singlet stability* problem as

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^{\dagger} & \boldsymbol{A} \end{pmatrix} \begin{pmatrix} \boldsymbol{D} \\ \boldsymbol{D}^{\dagger} \end{pmatrix} = \lambda \begin{pmatrix} \boldsymbol{D} \\ \boldsymbol{D}^{\dagger} \end{pmatrix} \tag{3}$$

where the elements of $\boldsymbol{A}$ and $\boldsymbol{B}$ are defined by Eq. (2) and D_n are vectors giving the mixing coefficients d^n_{ij} corresponding to the broken symmetry solution $\psi_{\mathrm{BS},n}$. In addition the singlet stability problem can be separated into a number of symmetry subproblems according to the representation generated by the excitation being considered. A positive value of λ_n indicates stability of the symmetry adapted solution whereas a negative λ_n indicates the existence of a broken symmetry solution of lower energy.

3. Calculations

For our stability calculations we have utilized a Hartree-Fock solution obtained with a minimal basis set for the internal shells and a double-zeta basis set for the valence shell. The basis sets used were those of Huzinaga [10] contracted as appropriate, e.g., 11.7 to 5.3 for a sulphur centre and a 9.5 to 4.2 for nitrogen. The stability calculations involved all excitations arising from a set of 13 doubly occupied and 29 unoccupied molecular orbitals. Since the stability calculation is considerably simplified if carried out in a non degenerate representation we utilized D_{2h} symmetry and on this basis the stability problem could be split into 8 subproblems each involving about 60 excitations.

In each case we first calculated the HF symmetry adapted solution for a given value of the molecular parameters. From these orbitals the matrix elements $\boldsymbol{A}$, $\boldsymbol{B}$ for each symmetry subproblem could be obtained and Eq. (3) solved for λ_n and D_n. If negative λ_n are found the HF solutions for the broken solutions can be obtained using the D_n as a guide in constructing the starting vector.

4. Results

(*i*) *The symmetry adapted solution*

Since the HF solution for the D_{4h} symmetry adapted $S_4N_4^{2+}$ dication with equal bond lengths (see Fig. 1) is the basis for our stability analysis we briefly review

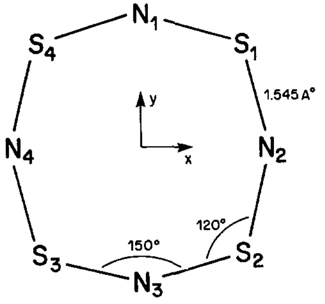

Fig. 1. Geometry and numbering sequence for $S_4N_4^{2+}$

its features in the context of our current calculations. This planar dication has 42 valence electrons and ten of these are π electrons. As there are only eight centres this system is considered "π electron-rich" [12]. Since a non-degenerate representation is a convenient basis for the stability calculation we performed our symmetry adapted calculations within D_{2h} symmetry.

The ordering of the higher energy molecular orbitals is given in Fig. 2. As Fig. 2 indicates the HOMO and LUMO are π orbitals and there is a significant band gap between occupied and virtual orbitals. Examination of the self atom populations of the symmetry-adapted solution at 1.545 Å reveals that the HOMO π is a sulphur based lone pair orbital and the HOMO-1 π is a nitrogen lone pair orbital. This ordering of the π orbitals is the same as that obtained in the HFS calculation [4] although the position of the σ orbitals relative to the π orbitals in the two calculations is different (e.g., in HFS several σ orbitals lie between the two highest occupied π orbitals). The nitrogen lone pair π orbital is strongly destabilized as R_{SN} is increased and at $R_{SN}=2.00$ Å is the HOMO. Similar destabilization of the σ N and S lone pairs ($11a_1$ and $7b_{1g}$) is observed as $R_{SN} \rightarrow 2.00$ Å and results in low-lying π and σ excitations for the stability calculations at 2.00 Å.

Table 2 provides the calculated charges and p^π populations. The net charges associated with the sulphur and nitrogen, $q_S=1.52$ and $q_N=-1.01$, are large, as expected for DZ basis calculations (cf. the smaller charges for the HFS results using a DZ+polarization basis [4]) but this charge separation decreases at $R=2.00$ Å, to $q_S=1.01$ and $q_N=-0.51$. The π population, on the other hand, becomes more disparate, going from $p_S^\pi=1.19$, $p_N^\pi=1.32$ at $R_{SN}=1.545$ Å to $p_S^\pi=1.62$ and $p_N^\pi=0.88$ at $R_{SN}=2.00$ Å.

(ii) The stability eigenvalues

The eigenvalues for this stability problem are given in Table 1. At the experimental bond length $R_{SN}=1.545$ Å all eigenvalues of the symmetry adapted solution are positive indicating that this solution is singlet stable. However, as Table 1 shows, the three lowest eigenvalues do become negative as r_{SN} is increased to 2.00 Å implying that the symmetry adapted solution is no longer singlet stable. A sketch of λ vs R_{SN} indicates that instability first occurs at $R_{SN} \simeq 1.90$ Å.

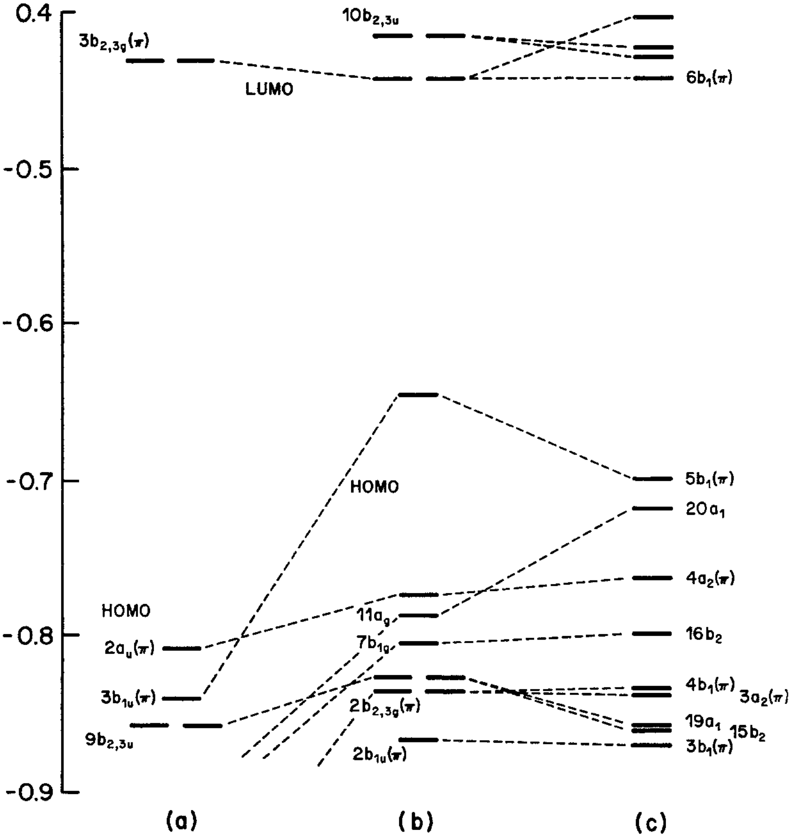

Fig. 2. Energy levels (au) and correlation. **a** $S_4N_4^{2+}$ at $R_{SN} = 1.545$ Å symmetry adapted*; **b** $S_4N_4^{2+}$ at $R_{SN} = 2.00$ Å symmetry adapted*; **c** $S_4N_4^{2+}$ at $R_{SN} = 2.00$ Å broken symmetry. *Energy levels for the symmetry adapted D_{4h} system are denoted in D_{2h} notation

Table 1. Lowest instability roots

Subproblem (d_{2h})	Broken symmetry	$R = 1.54$ Å λ	$R = 2.00$ Å λ
b_{2u}, b_{3u}	C_{2v}[a]	0.13	−0.035
b_{2g}, b_{3g}	C_{2h}[b]	0.18	−0.021
b_{1u}	C_{2v}[b]	0.16	−0.01

[a] Principal axis through two nitrogens and nuclear plane of symmetry retained

[b] Loss of nuclear plane as a symmetry element

At $R_{SN} = 2.00$ Å the lowest stability eigenvalue $\lambda = -0.035$ is degenerate [13] and occurs in the b_{2u} and b_{3u} symmetry subproblems of D_{2h} for which the basis is respectively the x and the y axis. Consequently this root corresponds to removal of either the x or y element of symmetry so that the broken symmetry solutions

Table 2. Charges and atomic populations

Symmetry adapted	S_1, S_2, S_3, S_4				N_1, N_2, N_3, N_4					
	q		p^π		q			p^π		
$R_{SN} = 1.545$ Å	1.52		1.18		−1.01			1.32		
$R_{SN} = 2.00$ Å	1.01		1.61		−0.51			0.89		
Broken (C_{2v})	S_1	S_2	S_3	S_4	N_1	N_3	N_2		N_4	
Symmetry	q	p^π	q	p^π	q	p^π	q	p^π	q	p^π
$R_{SN} = 2.00$ Å	0.83	1.60	0.95	1.80	−0.37	0.50	−0.50	1.92	−0.31	0.27

implied are C_{2v} with the symmetry axis going through either one pair of nitrogens or the other pair of nitrogens.

The important role of the σ electrons (particularly the lone pair orbitals, cf. [14]) in the HF instabilities of these systems is emphasized by noting that when only π excitations were considered the lowest stability root, at $R_{SN} = 2.00$ Å was 0.12 compared to a value of −0.035 when both σ and π electrons were considered.

Examination of the eigenvectors D_1 for the lowest root indicates that the excitations responsible are from the highest occupied π orbitals ($3b_{1u}$) to the lowest empty π ($3b_{3g}$) i.e., a $\pi \rightarrow \pi'$ excitation and from the highest occupied σ ($11a_g$) to a low-lying empty σ ($10b_{2u}$) i.e., a $\sigma \rightarrow \sigma'$ excitation.

The second lowest root $\lambda_2 = -0.020$ occurs in the b_{2g} subproblem and involves excitations from π to σ' and from σ to π'. The third root, which is barely negative (−0.006) occurs in the b_{1u} symmetry subproblem and again $\pi \rightarrow \sigma'$ and $\sigma \rightarrow \pi'$ excitations are responsible.

(iii) The broken symmetry solution

For $R_{SN} = 2.00$ Å we have calculated the C_{2v} broken symmetry solution suggested by the lowest negative eigenvalue. It is, as expected, a 10 π system and the energy of this solution is approximately 30 kcal/mol lower than that of the symmetry adapted solution at $R_{SN} = 2.00$ Å. The orbital eigenvalues are displayed in Fig. 2 and, it is to be noted, the band gap has increased as the HOMO-π is stabilized. The stability of this C_{2v} solution was probed by performing the calculation in C_s symmetry (i.e., requiring only that the plane of the eight nuclei remain a symmetry element) and the broken symmetry solution retained its C_{2v} character when $R_{SN} = 2.00$ Å. The broken symmetry solutions suggested by the other two instability roots have energies higher than this C_{2v} solution but of course also below the symmetry adapted solution.

As Table 2 shows, the π electrons in the C_{2v} broken symmetry solution are no longer evenly distributed on the four nitrogens. Rather, as with the lowest broken symmetry solution for $S_3N_3^-$, the π electrons are preferentially stripped from one of the nitrogens; that is, there is a nitrogen "π-hole". This represents a polarization of the π network, relative to the symmetry adapted distribution, along the C_{2v} symmetry axis through two of the nitrogens. The net charges and the π populations for each centre are given in Table 2 and it is worth emphasizing that the polarization of σ population is in the opposite sense to that of the π system. The overlap populations suggest a weakened bond between the nitrogen with the nitrogen π-hole and the rest of the framework.

5. Discussion

These calculations show that the symmetry adapted HF description of $S_4N_4^{2+}$ is singlet stable at the "experimental" bond length of $R_{SN} = 1.545$ Å. However, with a relatively small (i.e., a 20%) increase in R_{SN} the symmetry adapted solution is no longer stable. The principal excitation at $R_{SN} = 2.0$ Å, for the lowest negative stability eigenvalue involves mixing b_{1u} and b_{3g} i.e., a π nitrogen lone pair and the π' orbital. Since $b_{1u} \times b_{3g} = b_{2u}$ one expects a C_{2v} broken symmetry solution and indeed the first broken symmetry solution in this π-electron rich system is of a C_{2v} symmetry which retains the plane of the S and N nuclei and the axis through two nitrogens as elements of symmetry.

A C_{2v} symmetry of course implies that a bond alternating HF solution would not occur. This is a direct consequence of the π electron richness of $S_4N_4^{2+}$ for, in a similar 8 centre 8 π electron D_{4h} system, the first excitation would be from $2a_u$ to $3b_{1u}(a_u \times b_{1u} = b_{1g})$ which would imply C_{4h}, i.e., a bond alternating solution. However in the π electron rich system this excitation is not available since $3b_{1u}$ is already occupied.

It is also worth pointing out that the lowest stability root, λ_1, does not generate two distinct solutions via the plus and minus combination; i.e., $3b_{1u} + 3b_{2g}$ and $3b_{1u} - 3b_{2g}$ are degenerate. This is because in $S_4N_4^{2+}$ the C_{2v} symmetry axes pass either through only nitrogen (or through only sulphur centres). This in contrast to the case of $S_3N_3^-$ where the symmetry axes may pass through both sulphur and nitrogen centres with the result that nondegenerate solutions are generated by the plus and minus combinations.

We should emphasize that, in principle, there could be C_{2v} broken symmetry solutions with the principal axis passing through sulphur centres. These solutions would produce a "sulphur π-hole". However at a 2.00 Å the sulphur lone pair π orbital ($2a_u$) is not as destabilized as the nitrogen lone pair π orbital ($3b_{1u}$). The excitation associated with the sulphur π hole therefore remains high and does not generate a negative root in the instability problem (this root corresponds to the second lowest root ($\lambda_2 = 0.11$) of the same symmetry subproblem which contains the nitrogen lone pair π-excitation). It is interesting to note that when *only* π excitations are allowed; the eigenvector corresponding to λ_1 has a much larger contribution of the π sulphur lone pair to π' excitation. In other words the appearance of a well defined N-π hole (or a well defined S-π hole) requires the σ electrons to redistribute themselves.

The weakly bonded "N π-hole" of the broken symmetry solution is consistent with the role of a unique nitrogen in reactions of S_4N_4 (15).

Conclusions

Since the HF single determinant description of the $S_4N_4^{2+}$ dication is singlet stable at $R_{SN} = 1.545$ Å and first breaks symmetry to a C_{2v} form, we would not expect a low energy bond alternating structure. In the lowest broken symmetry solution the π electrons are distributed over seven centres leaving a nitrogen "N-hole" which is only weakly bonded to its neighbour sulphur centres. The appearance of a nitrogen π-hole broken symmetry rather than a sulphur π-hole is due to the strong destabilization of the symmetry adapted nitrogen lone pair π orbital as R_{SN} is increased. This is in contrast to the $S_3N_3^-$ anion where both solutions appear simultaneously.

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