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The Electronic Structure of the Trisulfur Trinitride Anion

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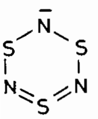
Introduction

The trisulfur trinitride anion, $S_3N_3^-$, is the first example of a planar cyclic S–N anion among the known binary sulfur–nitrogen species. Its electronic structure has been the subject of recent discussion and debate [1–5]. According to the suggestions of Banister [6, 8] this compound should be a 10π electron Huckel-type system. However, in recent publications, Turner and coworkers [2, 5] concluded on the basis of the results of a CNDO/2 L(ocalized) M(olecular) O(rbital) study that $S_3N_3^-$ is a four π-electron system with six out-of-plane lone pair electrons. The authors [2, 5] also claim that symmetry breaking occurs and produces a set of inequivalent sulfur atoms and a set of inequivalent nitrogen atoms despite the full symmetry (D_{3h}) assumed. Chivers and coworkers [4] suggested that this was due to the non-uniqueness of the Edmiston and Ruedenberg [9] transformation to localized orbitals used by Turner *et al.* [2], the Turner structure, *1*, being recognized as one of the canonical structures, *1–3*. They also pointed out [4] that they did not find symmetry breaking when they required only C_{2v} symmetry (with the nuclei still in their D_{3h} positions). In their reply, Turner *et al.* [5] pointed out that the two non-equivalent sets of sulfur and nitrogen atoms occurred already in the Mulliken population analysis based on canonical orbitals, *i.e.* prior to the transformation to LMO s. They contended as well that their LMO structure *1*, did not imply the delocalized representation *4*, based upon the three canonical structures *1–3*. Chivers *et al.* [1, 4] also found a clear π-electron picture of the molecule in their DVM-Xα calculations.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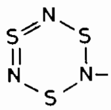
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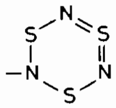
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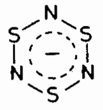
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In order to clarify these points, we have made calculations by means of the SCF-Xα-S(cattered) W(ave) method as well as new CNDO/2 calculations of both C(anonical) MO and LMO types.

SCF-X-SW Calculations

Our $S_3N_3^-$ electronic structure calculations have been carried out by means of the SCF-Xα-SW method, a basically first principles procedure with a few structural parameters [10, 11]. We determined the geometry of $S_3N_3^-$ from the averaged structural data [1, 12] namely a planar symmetric six-member ring (D_{3h}) with bond distances equal to 1.6 Å and bond angles equal to 120°. The atomic sphere radii have been chosen according to Norman's rule [13] with 20% degree of overlap and the touching outersphere. The atomic exchange parameters (α_{HF}) have been taken from Schwarz [14] with the simple average of the atomic values used in the intersphere and outersphere regions. Partial waves up to $l = 2$ were used in the S and N atomic spheres and up to $l = 4$ in the outersphere. The spin-restricted, frozen-core version of the method has been used.

The results are summarized in Table I, where we have listed the valence and virtual energy levels together with their respective group symmetry labels, occupancy and the charge contained in the sulfur, nitrogen, outer and interspheres respectively. The order of the levels is generally the same as that obtained by Chivers *et al.* [1, 4] using the DVM-Xα method. The only reordering is between the $1a_2''$ and $3a_1'$ levels which are very close in energy to each other. However, the description of the valence $2a_1'$ and $3a_1'$ orbitals is different as can be seen after inspection of the wavefunction plots given in Fig. 1. We found the $2a_1'$ level to be a slightly bonding p-type combination, in contrast to the sulfur lone pair classification of Chivers and coworkers [1, 4]. The $3a_1'$ level appears to be a strongly antibonding combination of sulfur and nitrogen s orbitals with some p admixture, which is similar to the Chivers' description. Thus we would suggest the picture of four strong σ bonds ($1a_1'$ $1e'$, and $1a_2'$) with the weaker σ bonding contributions of $2e'$, $2a_1'$, and $3e'$ being largely offset by the antibonding contribution from the $3a_1'$, and $4e'$ levels. We found the S–N bonds to be distinctly polar, the appropriate charges are: $Q_S = +0.33$ and $Q_N = -0.66$. This may be

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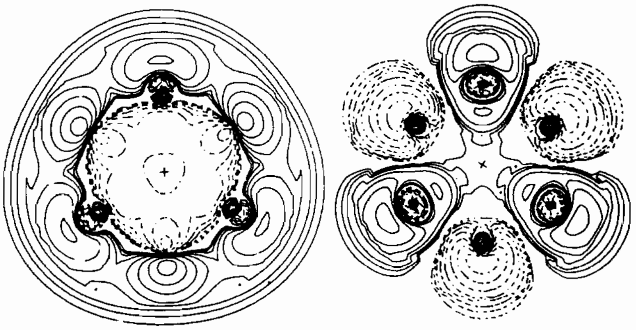
TABLE I. Orbital Energy Levels for Planar (D_{3h}) $S_3N_3^-$ Calculated with the SCF-Xα-SW Method.

Orbital	– Energy [Ry]	Occupancy	Q_S	Q_N	Q_{int}	Q_{out}
$1a_1'$	1.838	2.0	0.147	0.153	0.092	0.007
$1e'$	1.696	4.0	0.131	0.177	0.066	0.009
$2e'$	1.351	4.0	0.185	0.122	0.054	0.020
$1a_2'$	1.055	2.0	0.159	0.163	0.021	0.014
$2a_1'$	0.872	2.0	0.133	0.129	0.151	0.061
$3a_1'$	0.798	2.0	0.131	0.097	0.228	0.087
$1a_2''$	0.788	2.0	0.104	0.096	0.364	0.035
$1e''$	0.647	4.0	0.096	0.119	0.312	0.042
$3e'$	0.640	4.0	0.095	0.150	0.170	0.093
$4e'$	0.603	4.0	0.145	0.132	0.084	0.084
$2e''$	0.366	4.0	0.127	0.094	0.275	0.061
$2a_2''$	0.169	0.0	0.079	0.138	0.235	0.115
$4a_1'$	0.165	0.0	0.015	0.009	0.493	0.432
$5e'$	0.049	0.0	0.118	0.048	0.205	0.296



(a) (b)

Fig. 1. Contour plots of a) $2a_1'$ and b) $3a_1'$ orbitals.

contrasted with the atomic charges $Q_S = 0.56 = -Q_N$ for S_4N_4 and $Q_S = 0.48 = -Q_N$ for S_2N_2 found [15] with the SCF-Xα-SW method.

Another interesting aspect of the $S_3N_3^-$ electronic structure is its π-electron system. There are 3 π-type levels occupied, namely $1a_2''$, $1e''$ and $2e''$. Two of them, $1a_2''$ and the degenerate pair $1e''$ are bonding combinations of S and N p orbitals, the highest occupied orbital, the $2e''$ one, has antibonding character. We provide plots of the charge densities for these three π levels in Figs. 2, 3 and 4, respectively. The pictures to indicate clearly that these levels are entirely π and π* orbitals, not lone pair levels, and thus the $S_3N_3^-$ anion can be described as a 10 π-electron system. However, the occupied π* levels make it different from the usual aromatic system in the sense of Hückel and Banister.

CNDO/2 Calculations

The results of our calculations by means of the CNDO/2 method are presented in Table II while the LMO s are described in Table III. Our LMO s were determined using the Edmiston–Ruedenberg scheme [9]. In the latter table, the atomic orbital coefficients in each LMO are listed together with its percentage localization. For the evaluation of the latter quantity we follow the Turner procedure [2] of

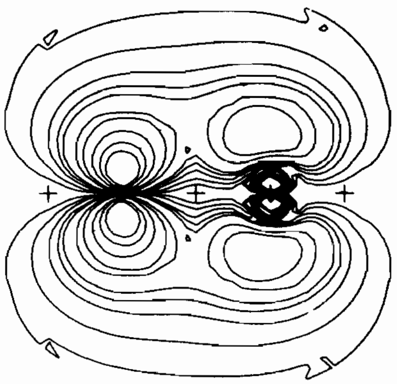


Fig. 2. Contour plot of the $1a_2''$ orbital density.

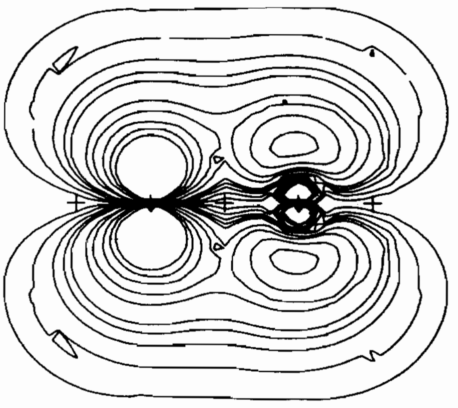


Fig. 3. Contour plot of the $1e''$ orbital density.

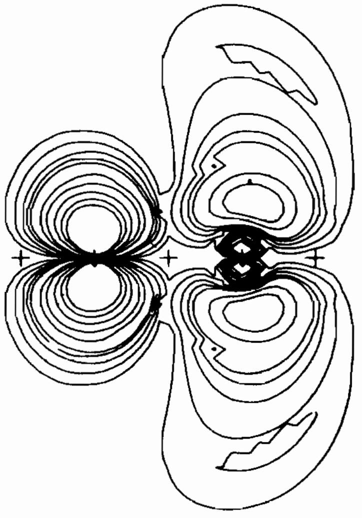


Fig. 4. Contour plot of the $2e''$ orbital density.

TABLE II. Present CNDO/2 Results for $S_3N_3^-$.

d_{NS} = 1.600 Å
Bond angles NSN and SNS = 120°
B.E. = −0.2171 A.U. (136.2 kcal/mol)
E_{total} = −65.7452 A.U.

Net Atomic charges:
S(1) = S(2) = S(3) = 0.041
N(1) = N(2) = N(3) = −0.375

Orbital charges:

	S(1)	S(2) and S(3)	N(2)	N(1) and N(3)
3s	1.6146	1.6146	1.5737	1.5737
$3p_x$	1.4203	1.1089	1.3367	1.0394
$3p_y$	1.0050	1.3165	0.9403	1.2376
$3p_z$	1.6874	1.6874	1.5240	1.5240
$3d_{z^2}$	0.0086	0.0086		
$3d_{xz}$	0.0181	0.0824		
$3d_{yz}$	0.1039	0.0396		
$3d_{x^2-y^2}$	0.0603	0.0454		
$3d_{xy}$	0.0405	0.0553		

TABLE III. Localized Orbitals of $S_3N_3^-$.

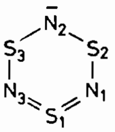
	LMO Type	Atomic Orbital Coefficients				Localization %
		N		S		
1.	$[S(2)]_{lp\sigma}$			3s	−0.7662	99.27
				$3p_x$	0.3172	
				$3p_y$	−0.5491	
2.	$[S(3)]_{lp\sigma}$			3s	0.7667	99.26
				$3p_x$	−0.3172	
				$3p_y$	−0.5469	
3.	$[N(1)–S(2)]_\sigma$	2s	−0.3117	3s	−0.3300	98.41
		$2p_x$	0.6061	$3p_x$	−0.6226	
		$2p_y$	0.0857	$3p_y$	0.0898	
4.	$[N(3)–S(1)]_\sigma$	2s	−0.3109	3s	−0.3297	98.40
		$2p_x$	−0.2285	$3p_x$	0.3890	
		$2p_y$	−0.5683	$3p_y$	0.4945	
5.	$[N(3)]_{lp\sigma}$	2s	−0.7687			97.18
		$2p_x$	0.3091			
		$2p_y$	0.5342			
6.	$[N(2)–S(2)]_\sigma$	2s	−0.3119	3s	−0.3297	98.42
		$2p_x$	−0.3758	$3p_x$	0.2334	
		$2p_y$	−0.4830	$3p_y$	0.5845	
7.	$[N(1)–S(1)]_\pi$	$2p_z$	0.8274	$3p_z$	0.4687	93.05
8.	$[S(1)]_{lp\sigma}$			3s	−0.7657	99.27
				$3p_x$	−0.6347	
				$3p_y$	0.0005	
9.	$[N(3)–S(3)]_\sigma$	2s	−0.3120	3s	−0.3291	98.42
		$2p_x$	0.6059	$3p_x$	−0.6231	
		$2p_y$	−0.0857	$3p_y$	−0.0908	
10.	$[N(3)–S(1)]_\pi$	$2p_z$	0.8298	$3p_z$	0.4612	92.79
11.	$[N(2)]_{lp\pi}$	$2p_z$	0.8648			74.78
12.	$[N(2)]_{lp\sigma}$	2s	−0.7682			97.17
		$2p_x$	0.6177			
		$2p_y$	0.0007			
13.	$[N(1)]_{lp\sigma}$	2s	−0.7679			97.17
		$2p_x$	−0.3082			
		$2p_y$	−0.5358			
14.	$[N(1)–S(1)]_\sigma$	2s	−0.3132	3s	−0.3309	98.42
		$2p_x$	−0.2293	$3p_x$	0.3888	
		$2p_y$	+0.5667	$3p_y$	−0.4941	
15.	$[N(2)–S(3)]_\sigma$	2s	−0.3122	3s	−0.3271	98.40
		$2p_x$	−0.3785	$3p_x$	0.2323	
		$2p_y$	0.4807	$3p_y$	−0.5862	
16.	$[S(3)]_{lp\pi}$			$3p_z$	0.8802	77.64
17.	$[S(2)]_{lp\pi}$			$3p_z$	0.8782	77.30

associating the given LMO with a bond (σ or π) or atom (lone pair) and truncating it in such a way as to include contributions from the atomic orbitals of the atom(s) participating in the bond or lone pair. It should be noted that the coefficients C_{TLMO} of the LMO's truncated in this manner do not necessarily sum to unity. The percent localization is defined by % Localization = $\Sigma_i(C_{TLMO})^2 \times 100$.

Examination of Table II reveals that the present CNDO/2 results differ from those reported previously in two respects. The energy (total) is lower and most importantly, the Mulliken net atomic charges are the *same* for all three sulfur atoms ($q_S = 0.041$) and the *same* for all three nitrogen atoms ($q_N = -0.375$) and are very similar to those found by Chivers *et al.* ($q_S = 0.065$, $q_N = -0.40$). Thus the question of possible symmetry breaking is answered—there is none in this type of calculation. This leads to the question as to why it was found in the previous CNDO/2 calculation. We speculate that the CNDO/2 calculations employed the so-called method B [16] of parameterization for second-row elements. As pointed out by Sabin *et al.* [17], the original method B is not rotationally invariant. The present calculations were rotationally invariant.

We find by inspection of Table III that the seventeen occupied MO's have been transformed into a) six N–S σ-bonding type orbitals for the framework of the ring, *i.e.* numbers 3, 4, 6, 9, 14 and 15; b) six lone-pairs (in the molecular plane) on each of the atoms, *i.e.* numbers 1, 2, 5, 8, 12 and 13; c) three π-type (out-of-plane) lone-pairs on N(1), S(6) and S(5), *i.e.* numbers 11, 16, and 17; and d) two π-bonding orbitals between N(2)–S(4) and S(4)–N(3), *i.e.* numbers 7 and 10. It should be noted that all of these orbitals are more than 92% localized with the exception of the three π-type lone-pair LMO s which are about 75% localized.

The set of LMO's may be represented schematically by the structure *5* which is the same as *1* found by Turner and coworkers.



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Since in our calculation the three sulfurs are equivalent and the three nitrogens are as well, the canonical structures *1*, *2* and *3* may be obtained from one another by the appropriate rotation (120°) and *4* represents a superposition of these three localized structures.

Acknowledgement

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