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CNDO/2 Localized Molecular Orbital Studies of the Trisulfur Trinitride Anion

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Among the several known binary sulfur–nitrogen compounds only tetrasulfur tetranitride, S_4N_4, can be termed well understood from both a bonding and structural point of view. Numerous theoretical [1] and experimental [2] studies have been carried out on this molecule. Although the geometrical structure of disulfur-dinitride, S_2N_2, and tetrasulfur dinitride, S_4N_2, is well known [3–7], the electronic structure was only recently investigated [8, 9] in our laboratory.

We have now carried out a similar localized orbital study for trisulfur trinitride anion, $S_3N_3^-$, a relatively new binary sulfur-nitride anion. Its geometrical structure was recently determined [10]. The molecule is isoelectronic with tetrasulfur dinitride, S_4N_2, *i.e.* the same number of valence electrons.

Calculations

The geometrical structure [10] of $S_3N_3^-$ indicates that the ring is planar and the S–N bond distances vary from 1.580 Å to 1.626 Å. The six intra-ring bond angles vary from 116.5 degrees to 124.2 degrees. We have taken the average bond distances to be 1.600 Å and average intra-ring bond angles to be 120 degrees in our calculations (Fig. 1).

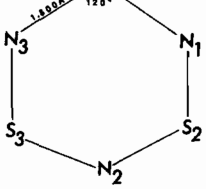

Fig. 1. Structure of $S_3N_3^-$ averaging the experimental bond distances and bond angles.

The symmetry (D_{3h}) of the trisulfur trinitride anion requires that the molecule be in the x–y plane with the z axis (which is the C_3 rotational axis) passing through the center of the S–N ring. The x-axis was chosen so as to pass through S(1) and N(2) and the y-axis bisects the lines joining N(1)–S(2) and N(3)–S(3) (Fig. 1).

The localized molecular orbitals were calculated from the CNDO/2 canonical molecular orbitals using the energy localization method of Edmiston and Ruedenberg [11] as applied to CNDO wave functions by Trindle and Sinanoglu [12]. A convergence criteria requiring two successive iterations to produce no more than 10^{-5} change in the sum of the self repulsion energies was used. The trisulfur trinitride anion converged after eight iterations and required about 6.5 h of computer time (Burroughs 6700).

Results and Discussion

The calculated population analysis for $S_3N_3^-$ is shown in Table I. Table II contains the localized molecular orbitals. We have listed the atomic orbital coefficients in each localized molecular orbital, together with its percentage localization. The latter is evaluated by associating the localized orbital with a bond (σ or π) or atom (lone pair) in the molecule and truncating it so as to include only contributions from the atomic orbitals of the atoms or atom included in the bond or lone pair, respectively. The coefficients of this truncated localized molecular orbital, C^i_{TLMO}, when squared do not sum to unity.

TABLE I. CNDO/2 Results for $S_3N_3^-$.

d_{NS} = 1600 Å
Bond angles NSN and SNS = 120°
B.E = 0.2835 A.U. (177.8 kcal/mol)
E_{total} = –65.2446 hartrees

Atomic charges:

S(1)	+0.385	S(2)	–0.219	S(3)	–0.219
N(1)	+0.240	N(2)	–1.426	N(3)	+0.240

Orbital charges:

S(1)		S(2) and S(3)	
3s	1.6418	3s	1.6940
$3p_x$	1.4129	$3p_x$	1.2588
$3p_y$	0.9919	$3p_y$	1.1469
$3p_z$	1.3971	$3p_z$	1.8590
$3d_{z^2}$	0.0059	$3d_{z^2}$	0.0094
$3d_{xz}$	0.0083	$3d_{xz}$	0.1131
$3d_{yz}$	0.0852	$3d_{yz}$	0.0204
$3d_{x^2-y^2}$	0.0453	$3d_{x^2-y^2}$	0.0310
$3d_{xy}$	0.0265	$3d_{xy}$	0.0867
N(2)		N(1) and N(3)	
2s	1.6884	2s	1.5447
$2p_x$	1.5715	$2p_x$	0.8029
$2p_y$	1.3155	$2p_y$	1.0755
$2p_z$	1.8501	$2p_z$	1.3373

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TABLE II. Localized Orbitals of Trisulfur Trinitride Anion, $S_3N_3^-$.

L.M.O. Type	*Atomic Orbital Coefficients*				*% Localization*
N(2) lone pair (type 1)	N_{2p_z}	0.9611			92.37
N(2) lone pair (type 2)	N_{2s}	−0.7525			98.61
	N_{2p_x}	0.6479			
N(1) & N(3) lone pairs	N_{2s}	0.7931			92.61
	N_{2p_x}	0.2567			
	N_{2p_y}	0.4808			
S(2) & S(3) lone pairs (type 1)	S_{3s}	−0.8001			98.95
	S_{3p_x}	0.3137			
	S_{3p_y}	−0.5009			
S(2) & S(3) lone pairs (type 2)	S_{3p_z}	0.9601			92.18
S(1) lone pair	S_{3s}	0.7715			97.97
	S_{3p_x}	0.6201			
S(1)–N(1) π bond & S(1)–N(3) π bond	S_{3p_z}	0.5415	N_{2p_z}	0.7800	90.16
S(1)–N(1) σ bond & S(1)–N(3) σ bond	S_{3s}	−0.3340	N_{2s}	−0.2914	93.66
	S_{3p_x}	0.3994	N_{2p_x}	−0.2197	
	S_{3p_y}	−0.4884	N_{2p_y}	0.5420	
S(2)–N(1) σ bond & S(3)–N(3) σ bond	S_{3s}	0.3795	N_{2s}	0.2367	98.02
	S_{3p_x}	0.6826	N_{2p_x}	−0.5262	
	S_{3p_y}	−0.1667	N_{2p_y}	−0.0978	
S(2)–N(2) σ bond & S(3)–N(2) σ bond	S_{3s}	0.2312	N_{2s}	0.3702	98.01
	S_{3p_x}	−0.2108	N_{2p_x}	0.4248	
	S_{3p_y}	−0.4937	N_{2p_y}	0.5666	

The percent localization is defined by

$$\% \text{ Localization} = \sum_i (C^i_{\text{TLMO}})^2 \times 100$$

The seventeen occupied molecular orbitals are transformed into a set of six N–S σ bonding type orbitals forming the sigma skeleton of the ring; one lone pair orbital on each of the atoms S(1), N(1) and N(3); two lone pair orbitals on each of the atoms S(2), N(2) and S(3); and two π-bonding orbitals between N(3)–S(1) and S(1)–N(1). This is shown in Fig. 2. All calculated orbitals are more than 90% localized. The d-type atomic orbitals for the sulfur atoms were included in the calculation but are omitted from Table 2 because they enter the localized orbitals with very small coefficients. However, because of some contribution by S(1) d_{yz} (0.1450) and S(2) d_{xz} (0.2031), the S(1)–N(1) π bond (90.16% localized) may be visualized as slightly extended up to S(2) (*i.e.* 6.22% extra localization between S(1)–N(1)–S(2), due to d orbital participation). For the same reason the π bond between S(1) and N(3) (90.18% localized) may be also slightly extended up to S(3). The σ bonds between S(1)–N(1) and S(1)–N(3) are 93.66% localized, but all other σ bonds are more than 98% localized. The lone pairs on N(1) and N(3) are 92.6% localized. However, N(2) has two types of lone pairs, one is extended out of the molecular plane, 92.37% localized and the other with 98.61% localization lies wholly in plane.

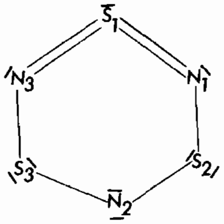

Fig. 2. The electronic structure of $S_3N_3^-$.

One lone pair on each of the atoms S(2) and S(3) is of the same type (type 1) with 98.95% localization. The other lone pairs on the same two atoms (type 2) are only 92.16% localized. This later pair is composed of almost entirely an out of plane p_z orbital. The lone pair on S(1) is different from those of S(2) and S(3), although it also has an in plane charge distribution. The LMOs also indicate that there is no appreciable bonding between intra-ring sulfur atoms (d_{ss}, intra-ring = 2.80–2.82 Å) [10].

Taken together the localized orbitals clearly show the distribution of charge through the molecule. This same type of bonding was exhibited by 1,3 tetrasulfur dinitride. We prefer to view the molecule as possessing four pi type electrons in contrast to the arbitrary counting procedure of Banister [13] and the observations of Chivers and coworkers [10], which predicts a 10π Huckel type system.

The orbital energy diagram does not reflect the symmetric features present in a Huckel type system. However, we have observed that the molecule contains six out-of-plane lone pair electrons (Table II), in addition to the four out-of-plane π-electrons, giving a total of 10 electrons which may be involved in a resonance. Moreover, a ten π-electron system of six centers as described by Chivers and coworkers would be expected to show a S–N bond distance considerably smaller than 1.6 Å. A distance more in the range of 1.40 Å–1.50 Å would probably be appropriate, such as is observed in NS [16] and thionylimide complexes [17]. In a recent publication [18], Chivers and Oakley suggest an electronic structure for $S_3N_3^-$ which is very similar to one calculated herein.

The most interesting feature of the calculated electronic structure is the fact that the three nitrogen atoms are not equivalent to each other in the sense that they do not possess the same electronic environment. The same observations can be made for the three sulfur atoms. The calculations assume that D_{3d} symmetry and the canonical molecular orbitals do transform according to the irreducible representations of the group D_{3d}. Nevertheless, the non-equivalency persists. If the effect is a real one, it should show up in the chemistry of the $S_3N_3^-$ ion. Since the molecule ion contains two electronically equivalent sulfur atoms ((2) and (3)), each adjacent to an electronegative nitrogen atom, N(2), the addition of a Lewis acid, say BF_3, might be expected to produce a 1:1 addition compound with the Lewis acid bonded to N(2). The alternative of forming a 3:1 adduct involving all the electronic rich centers of the molecule ion is probably unlikely for steric reasons.

It is possible that the non-equivalence is a reflection of the localization procedure. Any orbital localization method simply represents the application of a similarity transformation to the original wave function. There is no mathematical guarantee that the point group symmetry will be preserved in the localized orbitals. The symmetry of total wave function will of course be retained. It is not the symmetry of the total wave function that is being examined in this paper.

The sulfur nitrides represent a group of electron rich molecules and ions. It is becoming clear that the 'excess' electronic charge cannot be viewed as simply being present in π type delocalized orbitals but the tendency seems to be more in the direction of forming lone electron pairs on the atoms and at the same time forming islands consisting of 4 π type electrons distributed over three adjacent nuclear centers [8, 9, 14, 15].

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