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CNDO/2 Localized Molecular Orbital Studies for the Isoelectronic Cations *cyclo*-1,3,4-Trithiadiazole(2+) and *cyclo*-2,5-Dithiatriazole(1+)

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The electronic structures of cyclo-*1,3,4-trithiadiazole(2+) and* cyclo-*2,5-dithiatriazole(1+) ions have been studied using energy localized CNDO/2 molecular orbitals.* Cyclo-*1,3,4-trithiadiazole(2+) was found to have five σ-bonds forming the sigma skeleton of the ring, one lone pair orbital on each atom and six π-electrons. No π-bonding was observed between the two adjacent sulfur atoms.* Cyclo-*2,5-dithiatriazole(1+) possesses a sigma bond structure and one lone pair orbital on each atom. It has six π-electrons, two between the adjacent nitrogen atoms and the remaining four delocalized over the SNS segment of the molecule. The enhanced stability of the* $S_3N_2^{2+}$ *cation relative to the isoelectronic* $S_2N_3^+$ *can be attributed to the larger tendency of an apical sulfur atom to participate in three center two electron π bonding relative to the lack of ability of an apical nitrogen to do the same.*

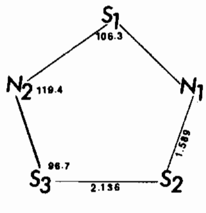


Fig. 1. Structure of $S_3N_2^{2+}$.

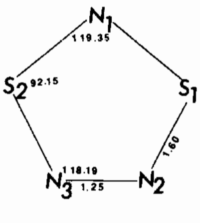
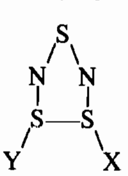


Fig. 2. Structure of $S_2N_3^+$.

Introduction

The electronic structures of a number of sulfur nitrides, *viz.* S_4N_2, $S_3N_3^+$, $S_3N_3^-$, S_3N_2, and S_2N_2 have been studied in this laboratory and others [1–3]. Now we have carried out a similar localized molecular orbital study for the two isoelectronic cations $S_3N_2^{2+}$ and $S_2N_3^+$. The cation $S_3N_2^{2+}$ is the ring moiety of the stable species $[S_3N_2Cl]Cl$ [4], whereas its isoelectronic analogue $S_2N_3^+$ is unstable [5]. The simple 1,3,4-trithiadiazole is not presently known as such but the S_3N_2 ring system has been demonstrated to be present in the compound $S_3N_2Cl_2$ where it exists as $S_3N_2Cl^+$ [6]. It has also been identified as the radical cation $S_3N_2^+$ present in thiodithiazyl hexafluoroarsenate [7] and other salts [8]. Organo derivatives of the ring system S_3N_2XY are also known where X and Y are H, CH_3, C_6H_5, CN, CF_3, or COOH [9]. The structural element S_3N_2 is also believed to be present in 3,4-bis(trifluoromethyl)2,5-*epi*-dithio-1-thiadiazole [10]. The presence of the S_3N_2 structural element in these diverse molecular environments prompted our study of the parent ring system, *cyclo*-1,3,4-trithiadiazole.



CNDO/2 type molecular orbital calculations and energy localized molecular orbitals are presented in this paper in an attempt to elucidate their electronic structures and to study the relative instability [5] of the $S_2N_3^+$ ion.

Calculations

The symmetry of $S_3N_2^{2+}$ ion (C_{2v}) requires that the molecule be in yz plane with the z axis (which is the C_2 rotation axis) passing through S_1 and bisecting the line joining S_2 and S_3. The y axis was chosen so as to pass through the two nitrogen atoms, while the

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TABLE I. CNDO/2 Results for $S_3N_2^{2+}$.

d_{NS} = 1.589 A, d_{SS} = 2.136 A

Angle $N_1S_1N_2$ = 106.3°, Angle $S_1N_1S_2$ = Angle $S_1N_2S_3$ = 119.4°, Angle $N_1S_2S_3$ = Angle $N_2S_3S_2$ = 96.7°

B.E. = 1.1095 A.U. (5787 kJ/mole)

E_{total} = −55.3417 hartrees

Atomic Charges: S(1) +0.737, S(2) +0.622, N(2) +0.010, N(1) +0.010, S(3) +0.622

Orbital Charges:

S(1)		N(1) and N(2)		S(2) and S(3)	
3s	1.6738	2s	1.5753	3s	1.7757
$3p_x$	1.4117	$2p_x$	0.8634	$3p_x$	1.3898
$3p_y$	0.8026	$2p_y$	1.4260	$3p_y$	1.0815
$3p_z$	1.2642	$2p_z$	1.1256	$3p_z$	1.0492
$3d_{z^2}$	0.0265			$3d_{z^2}$	0.0191
$3d_{xz}$	0.0087			$3d_{xz}$	0.0144
$3d_{yz}$	0.0313			$3d_{yz}$	0.0249
$3d_{x^2-y^2}$	0.0205			$3d_{x^2-y^2}$	0.0132
$3d_{xy}$	0.0242			$3d_{xy}$	0.0101

TABLE II. Localized Orbitals of cyclo-1,3,4-Trithiadiazole(2+), $S_2N_2^{2+}$.

L.M.O. Type		Atomic Orbital Coefficients				% Localization
S(3)–N(2)	σ bond	S_{3s}	−0.2531	N_{2s}	−0.3618	
and S(2)–N(1)	σ bond	S_{3p_z}	−0.6130	N_{2p_y}	−0.1479	97.86
				N_{2p_z}	−0.6212	
S(1)–N(2)	σ bond	S_{3s}	−0.2678	N_{2s}	−0.3684	
and S(1)–N(1)	σ bond	S_{3p_y}	+0.4376	N_{2p_y}	+0.5566	97.29
		S_{3p_z}	+0.3988	N_{2p_z}	−0.3243	
S(2)–S(3)	σ bond	S_{3s}	−0.1918	S_{3s}	−0.1918	97.40
		S_{3p_y}	+0.6710	S_{3p_y}	−0.6709	
N(1) and N(2) lone pairs		N_{2s}	−0.7203			
		N_{2p_y}	−0.6153			96.66
		N_{2p_z}	−0.2631			
S(2) and S(3) lone pairs		S_{3s}	−0.8859			
		S_{3p_y}	−0.2549			99.44
		S_{3p_z}	+0.3803			
S(1) lone pair		S_{3s}	−0.8299			99.11
		S_{3p_z}	−0.5499			
S(3)–N(2)	π bond	S_{3p_x}	−0.8151	N_{2p_x}	−0.5374	95.32
and S(2)–N(1)	π bond					
$N_1S_1N_2$ 3-center π bond		S_{3p_x}	+0.8400	$N(1)_{2p_x}$	+0.3498	95.04
				$N(2)_{2p_x}$	+0.3498	

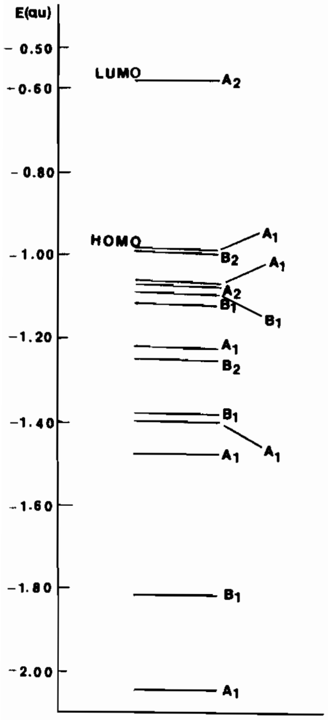


Fig. 3. Molecular Orbital Energy Diagram for $S_3N_2^{2+}$.

x axis is perpendicular to the plane of the molecule (Fig. 1). For $S_2N_3^+$ ion (also C_{2v}), the molecule was placed in the yz plane with the z axis passing through N_1 and bisecting the line joining N_2 and N_3 (Fig. 2).

All the bond distances (d_{NS} and d_{SS}) and bond angles (angle NSN, angle SNS and angle NSS) of $S_3N_2^{2+}$ ion were obtained from the X-ray structure of $S_3N_2Cl_2$ [6]. The calculations were carried out using an average N–S bond distance equal to 1.589 Å.

For the ion $S_2N_3^+$, a series of calculations were completed for the planar structure in orer to detail the geometry. The N–N distance was allowed to vary from 1.20 Å to 1.55 Å, the NSN angles from 91.91° to 98.07° and SNN angles from 118.41° to 112.25°. The angle SNS (119.35°, which was observed [6] in its isoelectronic analogue $S_3N_2^{2+}$) and S–N bond distance (1.60 Å) were not allowed to vary. The geometry of minimum energy was d_{NN} = 1.25 Å, angle NSN = 92.13° and angle SNN = 118.19°.

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. $S_3N_2^{2+}$ converged after 7 iterations and required about 2.4 h of computer time (Burroughs 6700). $S_2N_3^+$ converged in 8 iterations and required about 1.9 h of computer time.

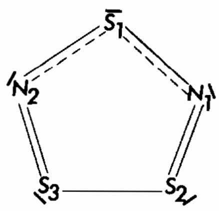


Fig. 4. Electronic Structure of $S_3N_2^{2+}$.

Results for *cyclo*-1,3,4-Trithidiazole (2+)

The orbital charges and gross atomic charges are shown in Table I. A molecular orbital energy level diagram is given in Fig. 3. Atomic orbital coefficients for the localized molecular orbitals, together with the percentage localization [13] are listed in Table II. The thirteen occupied molecular orbitals are transformed into a set of five σ-bonding orbitals, one lone pair orbital on each of the atoms, two π-bonding orbitals between N_1–S_2 and N_2–S_3 and one 3-center 2-electron-π-bonding orbital between N_2–S_1–N_1. This is shown in Fig. 4. The d type atomic orbitals for the sulfur atoms were included in the calculation but are omitted from Table II because they enter the localized orbitals with very small coefficients. This seems to be a general character for the cyclic sulfur nitrides.

All σ-bonding orbitals are more than 97% localized. Lone pairs on both the nitrogen atoms are directed in plane with 96.66% localization. All the sulfur lone pairs are also in plane but S_1 lone pair is somewhat different from the pairs on S_2 and S_3. Both S_3–N_2 and S_2–N_1 π orbitals (95.32% localized) are out of the plane of the molecule. The 3-center (N_1–S_1–N_2) 2-electron orbital is also out of the plane of the molecule with 95.04% localization. This orbital is probably of key importance in determining the stability of the $S_3N_2^{2+}$ cation. Its nitrogen analog is distinctly absent in the $S_2N_3^+$ cation (see Discussion). Interestingly it does not involve any appreciable 'd' orbital contributions, but rather is made up almost entirely of the atomic $3p_x$ orbital and involves overlap of $3p_x$ sulfur with the $2p_x$ orbitals of the adjacent nitrogen atoms.

Results for *cyclo*-2,5-Dithiatriazole(1+)

A rather lengthy series of CNDO/2 molecular orbital studies were performed in order to obtain the structure of minimum energy. The CNDO/2 results for $S_2N_3^+$ ion in the preferred geometry is given in

TABLE III. CNDO/2 Results for $S_2N_3^+$.

d_{NS} = 1.60 A; d_{N-N} = 1.25 A
Angle SNS = 119.35°, Angle NSN = 92.13°, Angle SNN = 118.19°
B.E. = 0.4097 A.U. (2137 kJ/mole)
E_{total} = −55.17 hartrees

Atomic Charges: N(1) − 0.089, N(2) +0.006, S(2) +0.538, S(1) +0.538, N(3) +0.006

Orbital Charges:

N(1)		N(2) and N(3)		S(1) and S(2)	
2s	1.5654	2s	1.5502	3s	1.7245
$2p_x$	0.9456	$2p_x$	1.0365	$3p_x$	1.4592
$2p_y$	1.0206	$2p_y$	1.1136	$3p_y$	1.1961
$2p_z$	1.5572	$2p_z$	1.2933	ep_z	0.9923
				$3d_{z^2}$	0.0283
				$3d_{xz}$	0.0218
				$3d_{yz}$	0.0218
				$3d_{x^2-y^2}$	0.0083
				$3d_{xy}$	0.0097

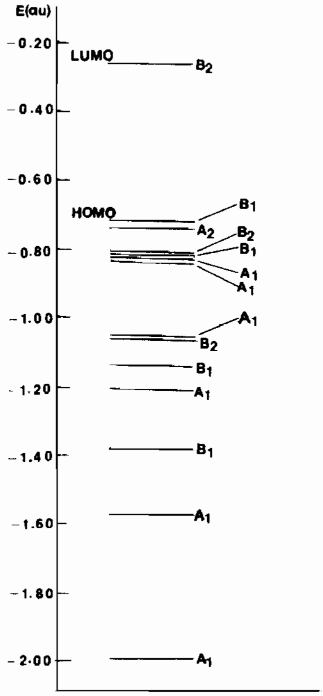


Fig. 5. Molecular Orbital Energy Diagram for $S_2N_3^+$.

Table III. A molecular orbital energy level diagram is shown in Fig. 5. Table IV contains the localized molecular orbitals. We have listed the atomic orbital coefficients in each localized molecular orbital together with its percentage localization. $S_2N_3^+$ was found to have a σ structure and one lone pair orbital on each of the ring atoms. All the five lone pair orbitals are directed in the molecular plane. Pi-type bonding is present between the two adjacent nitrogen atoms (N_2 and N_3) and also between N_1–S_1 and N_1–S_2 (Fig. 6). The π bond between N_1 and S_1 may be slightly extended up to N_2 because of some contribution (coefficient = 0.1334) by N_2–$2p_x$. The same reason accounts for the π bond between N_1 and S_2 being slightly extended up to N_3. The electronic structure is shown in Fig. 6.

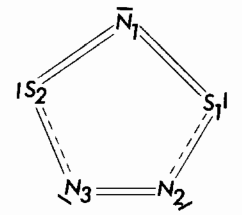
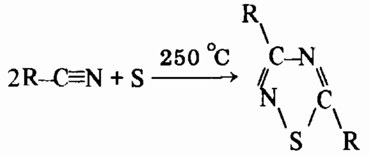


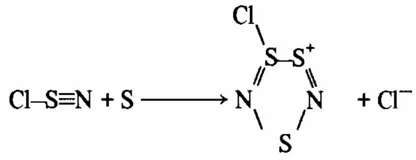
Fig. 6. Electronic Structure of $S_2N_3^+$.

Discussion

As predicted by Banister [5], $S_3N_2^{2+}$ ion was found to have six π-electrons, all of which are out of plane. The electronic structure (Fig. 4) is in reasonable accord with the synthetic routes [5, 14] used in the synthesis of the $S_3N_2^{2+}$ ion. $S_3N_2Cl_2$ can be prepared by the reaction of Cl–S≡N and disulfur dichloride which indicates that a S–N double bond and S–S single bond are to be expected in the $S_3N_2^{2+}$ ring. The following equations illustrate this point.



By analogy



We have calculated a much higher binding energy for $S_3N_2^{2+}$ (5787 KJ/mol) than for $N_3S_2^+$ (2137 KJ/mol). It is well known that the Complete Neglect of Differential Overlap Approximation tend to overestimate the binding energy [16], but nevertheless relative binding energies in an isoelectronic sequence

TABLE IV. Localized Orbitals of *cyclo*-2,5-Dithiatriazole(1+), $S_2N_3^+$.

L.M.O. Type		Atomic Orbital Coefficients				% Localization
S(2)–N(3)	σ bond	S_{3s}	+0.2631	N_{2s}	+0.3085	
and S(1)–N(2)	σ bond	S_{3p_y}	+0.2773	N_{2p_y}	−0.2562	98.21
		S_{3p_z}	−0.5877	N_{2p_z}	+0.5749	
		3				
S(2)–N(1)	σ bond	S_{3s}	+0.2442	N_{2s}	+0.3834	
and S(1)–N(1)	σ bond	S_{3p_y}	+0.5174	N_{2p_y}	−0.5036	98.30
		S_{3p_z}	+0.3397	N_{2p_z}	−0.3737	
N(2)–N(3)	σ bond	N_{2s}	−0.3582	N_{2s}	+0.3582	97.30
		N_{2p_y}	+0.5985	N_{2p_y}	+0.5985	
S(1) and S(2) lone pairs		S_{3s}	+0.8541			
		S_{3p_y}	−0.4943	9		99.77
		S_{3p_z}	+0.1444			
N(2) and N(3) lone pairs		N_{2s}	+0.7400			
		N_{2p_y}	+0.3599			97.64
		N_{2p_z}	−0.5471			
N(1) lone pair		N_{2s}	−0.6973			98.35
		N_{2p_z}	−0.7052			
N(1)–S(1)	π bond	N_{2p_z}	+0.4724	S_{3p_x}	+0.8433	93.44
and N(1)–S(2)	π bond					
N(2)–N(3)	π bond	N_{2p_x}	−0.6874	N_{2p_x}	−0.6874	94.50

of molecules and ions might be considered indicative. From both an experimental and theoretical viewpoint the *cyclo*-1,3,4-trithiadiazole(2+) cation seems to be considerably more stable than the *cyclo*-2,5-dithiatriazole positive ion. This is reflected in the electronic structure based upon localized orbitals. The apical sulfur atom in $S_3N_2^{2+}$ has the ability to enter into 2-electron-3-center-π-bonding with its neighboring nitrogen atoms. A number of other sulfur nitrides are known wherein pi-bonding is developed over the three atom segment NSN, *e.g.* *cyclo*-1,3-tetrasulfurdinitride [3], the cyclic trisulfur-trinitride anion [17], and *cyclo*-1,3,4-trithiadiazole [18]. Much more uncommon is the occurrence of three center pi-bonds over the sequence of atoms S–N–S. The species $S_2N_3^+$ is the only molecule that we have encountered which exhibits such pi-bonds. Although the possibility of developing such bonds exists in molecules such as S_4N_2, $S_3N_3^+$, $S_3N_2^{2+}$, or S_2N_2, it does not occur.

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