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Localized Molecular Orbital Studies of Three-, Four-, Five-, and Six-Membered Ring Molecules and Ions Formed from Sulfur and Nitrogen

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Abstract: Theoretical studies using energy localized CNDO/2 molecular orbitals have been carried out for some three-, four-, five-, and six-membered binary sulfur nitrogen ring systems in an effort to identify generalizations that can be used to analyze the electronic structures of this group of molecules and ions. It has been observed, in contrast to some previous studies, that the electronic charge in these electron-rich systems cannot be viewed as simply being present in π-type delocalized molecular orbitals, but rather that the tendency seems to be more in the direction of forming out-of-plane lone-pair orbitals on the atoms, and that cations generally possess more π-bonds than the corresponding neutral molecules or anions. Generalities such as valence saturation and the role played by the symmetry of the molecular framework are discussed. It is pointed out that compounds of this class cannot be discussed in the classical manner. A σ–π separation is present in their electronic structures but is recognizable only from the localized orbitals, and cannot be detailed a priori. Finally, the use of localized orbital descriptions to predict the chemistry to be expected for a molecule of this class is illustrated.

Research over the last 2 decades on sulfur–nitrogen ring systems has revealed an unexpectedly diverse range of species, many of which possess unusual structural features.[1] While tetrasulfur tetranitride, S_4N_4, the dominant member of this group of compounds, is well understood from both a bonding and structural point of view, owing to numerous theoretical[2–5] and experimental[6–9] studies, very little is known about most of the other ring systems. Some recent work[10,11] has been concerned with materials such as the saturated imides, $S_x(NH)_{8-x}$, the cyclic unsaturated compounds $(NSOX)_3$ (X = halogens), and a few cyclic binary species such as $S_4N_3^+$, $S_3N_3^-$, and $S_5N_5^+$.[12]

We recently have studied the electronic structures of several binary sulfur nitrides, viz., S_2N_2 and S_4N_2,[13,14] $S_3N_3^+$ and $S_3N_3^-$,[15] and S_3N_2, $S_3N_2^{2+}$, and $S_2N_3^+$.[16] The principal difficulty in this group of molecules is the fact that the compounds are all electron-rich species possessing more electrons than are required to develop a simple Lewis-type model. Indeed, for many molecules in this class 40 or more valid Lewis structures are not unusual. Furthermore, preliminary studies have indicated a diversity of structural elements to be present in the electronic structures of this family of molecules and ions. The subject is at a developmental stage at which general rationalizations of electronic structure and reactivity are just beginning to emerge. In this paper we present additional studies on three-, four-, five-, and six-membered cyclic molecules and ions, and attempt to identify the salient electronic structural features prevalent throughout sulfur–nitrogen chemistry.

Calculations

A set of canonical molecular orbitals was calculated for each species, using the CNDO/2 method of Pople et al.[17,18] The geometrical structures employed were taken from experimental diffraction or spectroscopic studies when such information was available. If a structure was unavailable from experimental studies, the structure employed was that which exhibited the lowest total energy in the CNDO/2 approximation subject to the limitation that the system remain planar. The canonical orbitals were transformed to a set of localized molecular orbitals, using the energy-localization method of Edmiston and Ruedenberg[19] as modified by Taylor[20] and Trindle and Sinanoglu.[21] A convergence criteria requiring two successive iterations to produce no more than a 10^{-5} change in the sum of the self-repulsion energies was used. Most of the molecules and ions studied converged within ten iterations. The d-type atomic orbitals for the sulfur atoms were included in the calculations. The percentage localization for a localized orbital was determined 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. The percentage localization is defined by:

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

The specific details of calculations for each of the basic ring systems follow below.

1. Three-Membered Ring Systems. The species SN_2, SN_2^{2+},

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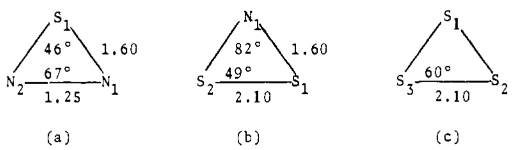

Figure 1. Geometrical structures employed for the MO calculations in three-membered ring systems: (a) SN_2, (b) S_2N, and (c) S_3.

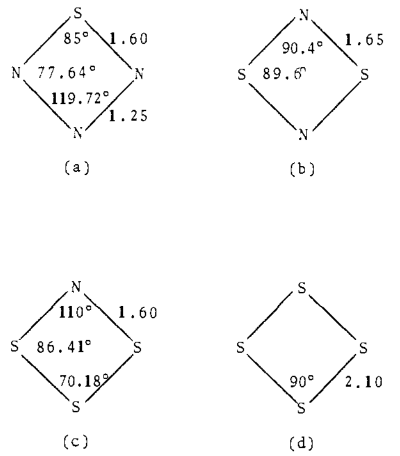

Figure 2. Geometrical structures employed for the MO calculations in four-membered ring systems: (a) SN_3, (b) S_2N_2, (c) S_3N, and (d) S_4.

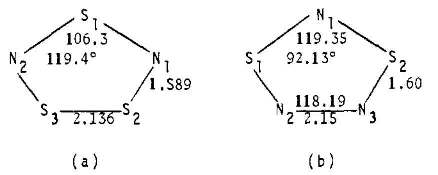

Figure 3. Geometrical structures employed for the MO calculations in five-membered ring systems: (a) S_3N_2 and (b) S_2N_3.

and SN_2^{2-} belong to the C_{2v} point group. The z axis was chosen to pass through the sulfur atom and bisected the N–N distance. Since no stable binary S–N compound with N–N bonding is known, an appropriate N–N bond distance was obtained from a series of calculations. The N–N distance was allowed to vary from 1.20 to 1.40 Å, the NSN angle from 44.04° to 51.89°, and SNN angles from 67.98° to 64.05°. The geometry of minimum energy for the neutral molecule occurred at $d_{N-N} = 1.25$ Å, angle NSN = 45.99°, and angles SNN = 67.00° (Figure 1a). This same geometry was employed for the cation and the anion.

The ions S_2N^+ and S_2N^- belong to the C_{2v} point group. The z axis was selected to pass through the nitrogen atom and bisected the S–S bond. The S–S bond distance was taken to be 2.10 Å as observed in many S–N ring systems.[14,16,22] The N–S bond distances employed were 1.60 Å (Figure 1b).[22,23]

The molecules S_3 and S_3^{2+} belong to the D_{3h} point group. the molecules were placed in the xy plane with the z axis passing through the center of the S_3 ring (Figure 1c), $d_{S-S} = 2.10$ Å.

2. Four-Membered Ring Systems. The four-membered ring systems that we have studied are SN_3^+, SN_3^-, $S_2N_2^{2+}$, $S_2N_2^{2-}$, S_3N^+, S_3N^-, S_4^{2+}, and S_4. The point groups and the geometrical structures employed in the molecular orbital calculations are shown in Figure 2.

3. Five-Membered Ring Systems. All five-membered ring systems studied, viz., $S_3N_2^{2+}$, S_3N^2, $S_3N_2^{2-}$, $S_2N_3^+$, and $S_2N_3^-$, belong to the C_{2v} point group. N–S and S–S bond distances for the species $S_3N_2^{2+}$ were obtained from X-ray structure of $S_3N_2Cl_2$.[22] For the S_2N_3 systems, the d_{S-N} was taken to be equal to 1.60 Å and all other bond angles and bond distances were obtained from a series of CNDO/2 calculations. The structures for which calculations were carried out are presented in Figure 3.

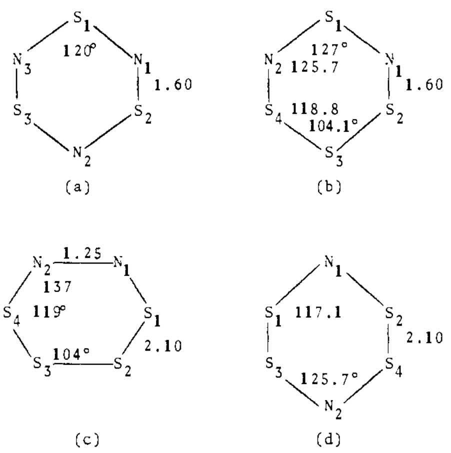

Figure 4. Geometrical structures of: (a) S_3N_3, (b) 1,3-S_4N_2, (c) 1,2-S_4N_2, and (d) 1,4-S_4N_2 systems.

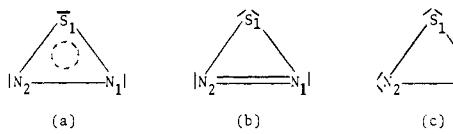

Figure 5. Electronic structures of: (a) SN_2^{2+}, (b) SN_2, and (c) SN_2^{2-}.

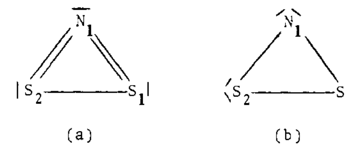

Figure 6. Electronic structures of: (a) S_2N^+ and (b) S_2N^-.

4. Six-Membered Ring Systems. The geometrical structures used for the calculations in six-membered ring systems are shown in Figure 4. Bond distances and bond angles of S_3N_3 and S_4N_2 systems have been obtained from X-ray structure[23] and previous calculations,[14] respectively.

Results

1. Three-Membered Ring Systems. The CNDO/2 results and the localized molecular orbitals for the three-membered ring systems are shown in Table I. It is possible to generalize about the gross distribution of charges in the molecules. In the cations calculated, the sulfur atoms possess more positive charge than the nitrogen atoms, while for anions the sulfur atoms reflect a higher negative charge than the nitrogen atoms.

Among the sulfur dinitride systems the binding energy decreases in the order $SN_2^{2+} > SN_2 > SN_2^{2-}$ and the reasons for this order are reflected in the localized orbital description. Electronic structures (Figure 5) based on the localized molecular orbitals indicate SN_2^{2+} to be a delocalized 2π system; SN_2 to be a 2π system with the π electrons localized between the two nitrogen atoms; and SN_2^{2-} to have no π bonding at all. The cation SN_2^{2+} not only has the highest binding energy, but also satisfies Hückel's $(4n + 2)\pi$ rule ($n = 0$) and can be considered the most stable species of the three sulfur dinitrides studied.

It is interesting to note that when one progresses to the S_2N type of ring systems the disulfur nitride cation, S_2N^+, also has a greater binding energy than the anion S_2N^-. This is because S_2N^+ has two N–S π-bonding orbitals (Figure 6a and Table I), whereas the anion S_2N^- shows a "valence saturated" structure which possesses no π bonding. The term "valence saturated structure" denotes an electronic structure in which the species possesses only σ-type single bonds and lone-pair electrons.

We shall now analyze the electronic structures of this group of molecules and ions one by one in order to clarify what is implied in "pictures"—Figures 5 and 6. In Figure 5a we show the

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Table I. CNDO/2 Results and the Localized Molecular Orbitals for Three-Membered Ring Systems

systems	atomic charges		orbital charges				localized MO type	% localizations
SN_2^{2+}	S_1	1.322	N_1 and N_2		S_1		σ bonds	
	N_1	0.339	2s	1.6516	3s	1.7892	N_1-S_1 and N_2-S_1	96.27
	N_2	0.339	$2p_x$	0.7876	$3p_x$	0.4009	N_1-N_2	98.97
			$2p_y$	1.2199	$3p_y$	1.5269	lone pairs	
			$2p_z$	1.0017	$3p_z$	0.9046		
					$3d_{z^2}$	0.0133	S_1	99.97
					$3d_{xz}$	0.0240	N_1 and N_2	99.32
					$3d_{yz}$	0.0137	π bonds	
					$3d_{x^2-y^2}$	0.0058		
					$3d_{xy}$	0.0000	$S_1N_1N_2$ three-center	98.79
SN_2	S_1	−0.027	N_1 and N_2		S_1		σ bonds	
	N_1	0.013	2s	1.6502	3s	1.8004	N_1-S_1 and N_2-S_1	96.13
	N_2	0.013	$2p_x$	0.9818	$3p_x$	1.9960	N_1-N_2	97.94
			$2p_y$	1.2191	$3p_y$	1.3422	lone pairs	
			$2p_z$	1.1355	$3p_z$	0.8156		
					$3d_{z^2}$	0.0125	S_1 (type 1)	98.64
					$3d_{xz}$	0.0404	S_1 (type 2)	99.80
					$3d_{yz}$	0.0147	N_1 and N_2	89.32
					$3d_{x^2-y^2}$	0.0051	π bonds	
					$3d_{xy}$	0.0000		
							N_1-N_2	98.17
SN_2^{2-}	S_1	−0.816	N_1 and N_2		S_1		σ bonds	
	N_1	−0.592	2s	1.6536	3s	1.7725	S_1-N_1 and S_1-N_2	93.80
	N_2	−0.592	$2p_x$	1.9509	$3p_x$	1.9956	N_1-N_2	99.01
			$2p_y$	1.2193	$3p_y$	1.7599	lone pairs	
			$2p_z$	0.7686	$3p_z$	1.1409		
					$3d_{z^2}$	0.0159	S_1 (type 1)	99.98
					$3d_{xz}$	0.0311	S_1 (type 2)	99.78
					$3d_{yz}$	0.0151	N_1 and N_2 (type 1)	97.59
					$3d_{x^2-y^2}$	0.0107	N_1 and N_2 (type 2)	98.99
					$3d_{xy}$	0.0236		
S_2N^+	N_1	0.145	N_1		S_1 and S_2		σ bonds	
	S_1	0.427	2s	1.6627	3s	1.8271	N_1-S_1 and N_1-S_2	96.93
	S_2	0.427	$2p_x$	0.6493	$3p_x$	1.6500	S_1-S_2	97.77
			$2p_y$	1.1993	$3p_y$	0.8754	lone pairs	
			$2p_z$	1.3433	$3p_z$	1.1541		
					$3d_{z^2}$	0.0131	N_1	99.56
					$3d_{xz}$	0.0035	S_1 and S_2	99.75
					$3d_{yz}$	0.0178	π bonds	
					$3d_{x^2-y^2}$	0.0097		
					$3d_{xy}$	0.0218	N_1-S_1 and N_1-S_2	97.88
S_2N^-	N_1	−0.375	N_1		S_1 and S_2		σ bonds	
	S_1	−0.312	2s	1.6741	3s	1.8282	N_1-S_1 and N_1-S_2	98.78
	S_2	−0.312	$2p_x$	1.9145	$3p_x$	1.9880	S_1-S_2	88.52
			$2p_y$	0.7242	$3p_y$	0.8982	lone pairs	
			$2p_z$	1.0623	$3p_z$	1.5016		
					$3d_{z^2}$	0.0159	N_1 (type 1)	99.20
					$3d_{xz}$	0.0311	N_1 (type 2)	95.73
					$3d_{x^2-y^2}$	0.0151	S_1 and S_2 (type 1)	99.71
					$3d_{xy}$	0.0107	S_1 and S_2 (type 2)	99.40
S_3^{2+}	S_1	0.855	S_1		S_2 and S_3		σ bonds	
	S_2	0.573	3s	1.8436	3s	1.8773	S_1-S_2 and S_1-S_3	95.83
	S_3	0.573	$3p_x$	1.3226	$3p_x$	0.6386	S_2-S_3	97.08
			$3p_y$	1.6300	$3p_y$	1.0098	lone pairs	
			$3p_z$	0.2599	$3p_z$	1.8309		
			$3d_{z^2}$	0.0043	$3d_{z^2}$	0.0057	S_1	95.83
			$3d_{xz}$	0.0251	$3d_{xz}$	0.0019	S_2 and S_3	99.21
			$3d_{yz}$	0.0143	$3d_{yz}$	0.0186	π bonds	
			$3d_{x^2-y^2}$	0.0311	$3d_{x^2-y^2}$	0.0225		
			$3d_{xy}$	0.0156	$3d_{xy}$	0.0222	S_1-S_2 and S_1-S_3	97.91
S_3	S_1	0.0053	S_1		S_2 and S_3		σ bonds	
	S_2	−0.0026	3s	1.8709	3s	1.8638	S_1-S_2, S_1-S_3, S_2-S_3	97.03
	S_3	−0.0025	$3p_x$	0.9191	$3p_x$	1.0880	lone pairs	
			$3p_y$	1.1543	$3p_y$	1.0016	S_1, S_2, S_3 (type 1)	99.65
			$3p_z$	1.9718	$3p_z$	1.9713	S_1, S_2, S_3 (type 2)	98.59
			$3d_{z^2}$	0.0059	$3d_{z^2}$	0.0055		
			$3d_{xz}$	0.0135	$3d_{xz}$	0.0116		
			$3d_{yz}$	0.0092	$3d_{yz}$	0.0168		
			$3d_{x^2-y^2}$	0.0206	$3d_{x^2-y^2}$	0.0220		
			$3d_{xy}$	0.0210	$3d_{xy}$	0.0218		

Table I (*Continued*)

systems	atomic charges	orbital charges				localized MO type	% localizations
S_3^{2-}	S_1 −0.652	S_1		S_2 and S_3		σ bonds	
	S_2 −0.674	3s	1.8934	3s	1.8680	S_1–S_2 and S_1–S_3	96.06
	S_3 −0.674	$3p_x$	0.7187	$3p_x$	1.7463	S_2–S_3	82.59
		$3p_y$	1.9445	$3p_y$	1.0040	lone pairs	
		$3p_z$	1.9722	$3p_z$	1.9712		
		$3d_{z^2}$	0.0065	$3d_{z^2}$	0.0002	S_1 (σ-type 1)	99.55
		$3d_{xz}$	0.0197	$3d_{xz}$	0.0167	S_1 (σ-type 2)	97.22
		$3d_{yz}$	0.0093	$3d_{yz}$	0.0267	S_2 and S_3	99.66
		$3d_{x^2-y^2}$	0.0228	$3d_{x^2-y^2}$	0.0178	S_1, S_2, S_3 (π-type 3)	98.60
		$3d_{xy}$	0.0649	$3d_{xy}$	0.0231		

electronic structure of the SN_2 dipositive ion. The localized orbitals upon which it is based are delineated in Table I. The two σ bonds bonding the sulfur atom S_1 to nitrogen atoms N_1 and N_2, respectively, are shown by a solid line connecting the appropriate atomic centers. These σ-type bonding orbitals are each 96.27% localized. The remaining σ-type orbital bonding N_1 and N_2 (98.97% localized) is similarly denoted. The molecule possesses three lone pairs of electrons one on each atom. These are shown by a single dashed line drawn next to the appropriate atomic center. The lone electron pairs on the two nitrogen atoms are in equivalent orbitals (99.32% localized), while the electron pair on the sulfur atom is unique. The dashed circle denotes a single pair of electrons in an out-of-plane orbital (π type) delocalized over all three centers, which we refer to as a three-center-two-electron π bond. Since the localization procedure is an iterative one the end point of which is determined by the imposition of an arbitrary criteria for convergence (10^{-5} for the sum of the intraorbital repulsion energies) we do not expect to encounter orbitals which are completely localized, i.e. 100%.

The electronic structure of the neutral molecule SN_2 is shown in Figure 5b. this molecule has three σ bonds between S_1–N_1, S_1–N_2, and N_1–N_2, respectively. It also possesses lone-pair electrons: one pair on each nitrogen atom—equivalent to each other—and two electron pairs on the sulfur atom. The localized orbital for the one pair (type 1) on sulfur is composed entirely of atomic orbitals of sulfur which are directed in the molecular plane, while the localized orbital for the other pair (type 2) is made up entirely of sulfur atomic orbitals which are directed entirely out of plane, i.e., p_x, d_{xy}, and $d_{x^2-y^2}$. The electron pairs are denoted by a single dashed line for each electron pair. The "in-plane"—"out-of-plane" distinction is a direct result of the assumption of planarity for the molecule. A calculation in a nonplanar geometry would alter the atomic-orbital composition of the localized lone-pair orbitals, but not change the fact that one electron pair occurs on each nitrogen atom and two electron pairs are present on the sulfur atom. The equivalencies between localized orbitals would also be retained.

The electronic structure of the dinegative anion, SN_2^{2-}, is describable wholly in terms of σ bonds and lone electron pairs. Each atom is singly bonded and also contains the maximum number of lone-pair electrons that it can possibly accommodate. We refer to a structure of this kind as being a "valence saturated structure". The disulfur nitride anion, S_2N^-, is an example of another such structure.

The electronic structure of S_2N^+ is shown in Figure 6a. This ion possesses a σ bond structure, i.e., three σ bonds, N_1–S_1 and N_1–S_2, equivalent to each other, and S_1–S_2. There are three lone electron pairs, one on the nitrogen atom 99.56% localized, and one on each of the two sulfur atoms each equivalent to the other. The ion also possesses four π-type electrons which are pairwise localized into a bonding-type out-of-plane orbital between centers S_1, N_1, and S_2. These two π-type orbitals are equivalent symmetry-wise. We denote their presence by an additional line between the appropriate atomic centers. We could consider this structural element to represent a three-center-four-electron, π-type bond.

In all A_2B-type systems the two A centers are electronically equivalent in the sense that they possess the same distribution of charge within the molecule. The detailed distribution itself, of course, differs from molecule to molecule.

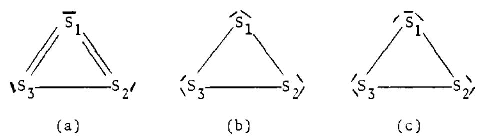

Figure 7. Electronic structures of: (a) S_3^{2+}, (b) S_3, and (c) S_3^{2-}.

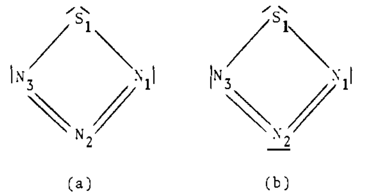

Figure 8. Electronic structures of: (a) SN_3^+ and (b) SN_3^-.

The binding energies in the *cyclo*-trisulfur systems decrease in the same order as observed for the sulfur dinitrides and the disulfur nitrides, namely $S_3^{2+} > S_3 > S_3^{2-}$. The localized molecular orbitals indicate that S_3^{2+} has two S–S π-bonding orbitals, whereas neither S_3 nor S_3^{2-} possess any π bonding (Figure 7). This observation is consistent with the fact that S_3^{2+} seems to be the most stable among the trisulfur ring systems. It should be noted that the addition of an electron pair to S_3^{2+} to form the neutral S_3 causes the molecule to adopt a totally symmetric structure consistent with the point group D_{3h}. This is another "valence saturated" structure. The further addition of an electron pair forces the S_3^{2-} anion to adopt a C_{2v} type of symmetry. An interesting feature in the electronic structure of S_3^{2-} is the presence of three lone-pair orbitals on the apical sulfur atom. This phenomenon is in no way related to the presence of the d-type orbitals on sulfur. Throughout this study it has been observed that the d-orbital charges are extremely small and the lone-pair localized orbitals contain virtually no contributions from the d-type orbitals of the sulfur atoms.

2. Four-Membered Ring Systems. In four-membered ring systems, the sulfur atoms generally exhibit higher positive charges than the nitrogen atoms, the single exception being the sulfur trinitride anion. The population analyses and the localized molecular orbitals for these systems are given in the supplementary material.

We begin our discussion with the four-membered ring materials which contain a single sulfur atom. The two species examined, SN_3^+ and SN_3^-, both contain a pair of adjacent two-electron two-center π-type bonds (alternatively a three-center-four-electron π bond). Unlike the three-membered rings the double bonds do not collapse to a valence saturated structure upon addition of an electron pair (Figure 8). Rather than N–N π bonds seem to contribute sufficient stability to the electronic structure that the additional electron pair is pushed out to the electronegative center in the molecule (N_2). The electron pair on N_2 does exhibit a destabilizing effect in that the binding energy of the anion is less than that of the cation. Once again the presence of d-type orbitals on the sulfur atom seems to be unimportant. Although they do possess the ability to accommodate an electron pair, this does not

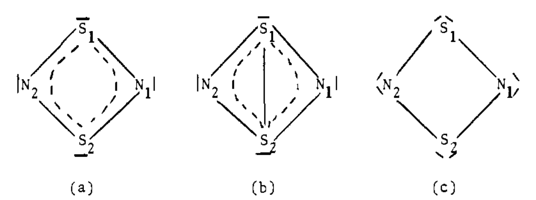

Figure 9. Electronic structures of: (a) $S_2N_2^{2+}$, (b) S_2N_2, and (c) $S_2N_2^{2-}$.

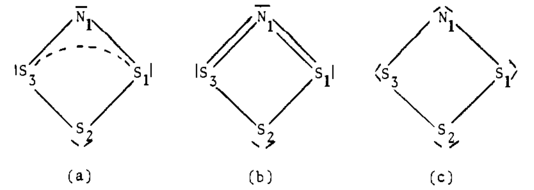

Figure 10. Electronic structures of: (a) S_3N^{3+}, (b) S_3N^+, and (c) S_3N^-.

occur. In each of the molecules the two nitrogen atoms bonded to the sulfur atom are electronically equivalent to each other and in turn different from the third nitrogen atom.

The electronic structure of S_2N_2 has previously been studied[14] in this laboratory (Figure 9) and others.[11,24,25] The results indicate that the neutral molecule contains two three-center (SNS)-two-electron π bonds and one S–S π bond. It has been observed in the present study that when two electrons are removed from the stable 6π Hückel system, the electrons come from the S–S π bond resulting in the formation of a 4π system with two three-center-two-electron π orbitals spanning S–N–S centers. When two electrons are added to the species S_2N_2, the anion $S_2N_2^{2-}$ results, and it has a "valence saturated" electronic structure. Both ions show equivalent electronic charge distributions about the two sulfur atoms in the ring and about the two nitrogen atoms in the ring. All of the four-membered ring systems have been calculated in a planar geometry, thus providing the maximal opportunity for π-bond formation. A distortion to a nonplanar geometry would lessen the degree of π bonding but not alter any of the basic equivalencies observed between equivalent charge regions within the molecule.

In the *cyclo*-trisulfur nitride systems, the binding energy decreases in the order $S_3N^{3+} > S_3N^+ > S^3N^-$. This indicates that S_3N^{3+} is expected to be the most stable among the three systems. Moreover, the ion S_3N^{3+} has two π electrons and satisfied Hückel's $(4n + 2)\pi$ rule (Figure 10). The two π electrons are located in a three-center orbital which spans the SNS segment of the ring. The occurrence of three-center-two-electron π bonds spanning a SNS linkage seems to be prevalent in the cyclic sulfur nitrides. The same structural element occurs in $S_2N_2^{2+}$, S_2N_2, $S_3N_2^{2+}$, and 1,3-$S_4N_2^{2+}$. The calculated localized orbital description indicates that the two sulfur atoms bonded to the nitrogen atom are distinctly different from the remaining sulfur atom, with the later possessing two unshared electron pairs and thus being considerably less electropositive. S_3N^+ contains 4π electrons and thus is not as aromatic-like as S_3N^{3+}. The π electrons occur as two localized electron pairs between N_1 and S_2, and N_1 and S_3, respectively. Once again we observe a collapse of the S–N π bonds into a "valence saturated" structure as electrons are added to S_3N^+ forming S_3N^-. A comparison of S_3N^{3+} and S_3N^+ reflects the tendency for species below the saturation level to follow Hückel's rule where possible and to form SNS three-center-four-electron π bonds where it is not possible. S_3N^+ is isoelectronic with S_4^{2+} and S_2N_2. Unlike S_3N^+, both S_4^{2+} (discussed later) and S_2N_2 are aromatic systems with 6π electrons.

In the *cyclo*-tetrasulfur systems the binding energy is greater for S_4^{2+} compared to S_4. Moreover, S_4^{2+} with 6π electrons satisfies Hückel's $(4n + 2)\pi$ rule $(n = 1)$, whereas S_4, without any π bonding is a "valence saturated" system. The S_4^{2+} cation exists in the compounds[26] $S_4(SO_3F)_2$ and $S_4(SbF_6)_2$. The ultraviolet and Raman spectra of S_4^{2+} indicate the cation to be planar. The compounds $S_4(SO_3F)_2$ and $S_4(SbF_6)_2$ are diamagnetic and do not exhibit ESR spectra. The neutral species, S_4, has so far not been reported. Both experimental and theoretical points of view indicate that a 6π electron system is more stable than the corresponding valence saturated neutral species (see Figure 11). The localized π-type MOs for S_4^{2+} merit some comment. The π electrons are localized into a bonding-type orbital which spans all four centers S_1–S_2–S_3–S_4, and a pair of π-type orbitals which spans three centers, S_1–S_4–S_3 and S_1–S_2–S_3, respecively. Each center is equivalent symmetry-wise and the atom numbering is arbitrary. The three orbitals taken together indicate a 6π electron distribution which is delocalized over the entire ring. This situation is not unlike that encountered in the localization of the π orbitals in benzene.[27]

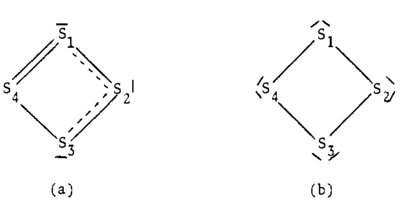

Figure 11. Electronic structures of: (a) S_4^{2+} and (b) S_4.

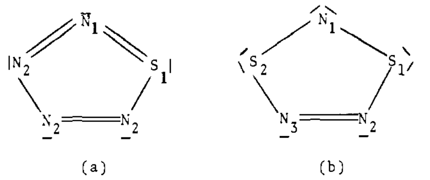

Figure 12. Electronic structures of: (a) $S_2N_3^+$ and (b) $S_2N_3^-$.

3. Five-Membered Ring Systems. We shall first discuss the electronic structure of the planar cyclic system composed of three nitrogen atoms and two sulfur atoms, $S_2N_3^+$ and $S_2N_3^-$. Although $S_2N_3^+$ is isoelectronic with the stable species $S_3N_2^{2+}$ and closely related to $C_2H_2N_2S$,[28] the cation itself has not yet been experimentally observed.[16] When two electrons are added to $S_2N_3^+$, the anion $S_2N_3^-$ results. The localized molecular orbitals indicate that this cation has a σ structure, five electron pairs, and three π-type bonds. The lone-pair electrons on the two sulfur atoms are described by identical localized orbitals, while those on the three nitrogen atoms are not equivalent, the lone pair located on the "bridgehead" nitrogen atom (N_1) being different from the other two pairs, which in turn are described by two equivalent localized orbitals.

The calculated structure thus predicts the one nitrogen lone pair to be different from the remaining two, with the electron-rich center being on the bridgehead nitrogen atom. A localized π-type bond is located between the adjacent nitrogen atoms. The remaining four electrons are located in two adjacent π-type localized orbitals which span the SNS segment of the molecule. The later two orbitals are equivalent to each other and the bonding can best be described as a three-center-four-electron bond over the SNS segment of the ring. Banister[29] has also predicted that the $S_2N_3^+$ ion should have 6 π electrons. A number of sulfur nitrides are known wherein π bonding is developed over the three-atom segment NSN, e.g., 1,3-S_4N_2, $S_3N_3^-$, 1,3,4-$S_3N_2^{2+}$, etc. Much more uncommon is the occurrence of the three-center-four-electron π bonds over the sequence of atoms SNS. $S_2N_3^+$ is one of the rare examples of such π bonds.

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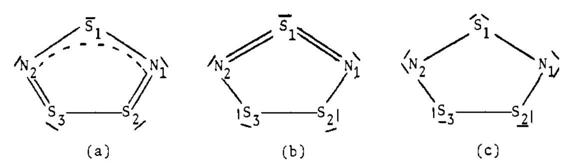

Figure 13. Electronic structures of: (a) $S_3N_2^{2+}$, (b) S_3N_2, and (c) $S_3N_2^{2-}$.

The addition of two electrons to the $S_2N_3^+$ cation produces the corresponding anion $S_2N_3^-$. The calculations indicate that the anion has an electronic structure consisting of five σ bonds, a single π bond located between the two adjacent nitrogen atoms, and ten lone electron pairs. The adjacent nitrogen atoms each possess a single lone electron pair, while the two sulfur atoms and the "bridgehead" nitrogen atom in turn each have two pairs of electrons localized about them. The lone electron pairs on the sulfur atoms are equivalent between sulfur atoms in the sense that each atom exhibits a type 1 and type 2 pair (see Figure 12). The apical or "bridgehead" nitrogen atom is about three time more electron rich than the remaining equivalent nitrogen atom, which in turn appears to carry about the same amount of residual electronic charge as do the sulfur atoms.

The calculated electronic structure of the stable cation $S_3N_2^{2+}$ is shown in Figure 13. The cation $S_3N_2^{2+}$ was initially assumed to be present in $S_3N_2Cl^+$.[22] Recently the discrete $S_3N_2^{2+}$ ion was obtained in the stable compounds $S_3N_2(SbCl_6)_2$ and $S_3N_2(RSO_3)_2$.[30-32] The cation possesses a σ structure, five lone electron pairs, and six π-type electrons. The equivalencies among the lone-pair electrons can be ascertained from the LMO's. The electron pairs located on the two nonapical sulfur atoms are the same, the two pairs on the two nitrogen atoms are equivalent to each other, while the electron pair located in the apical sulfur atom is different from any of the preceeding pairs. The stable $S_3N_2^{2+}$ ion, as predicted by Banister,[29] has 6 π electrons. Four of these are located in two equivalent localized orbitals bonding N_1 to S_2 and N_2 to S_3, respectively, while the remaining electron pair is described by a three-center-two-electron bond over the NSN segment of the molecular ion. When two electrons are added to the cation $S_3N_2^{2+}$, the neutral species S_3N_2 results. 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 many ring compounds.[22,34]

The electronic structure of the neutral 1,3,4-trithiadiazole molecule is shown in Figure 13. The adjacent sulfur atoms are electronically equivalent and each atoms exhibits two pairs of lone-pair electrons. The two nitrogen atoms are also equivalent to each other, each possessing a single lone pair of electrons. The NSN segment of the ring contains a three-center-four-electron π bond which describes the 4π system. In addition, the apical sulfur atom contains a single lone pair making it less electron rich than the other two sulfur atoms, which in turn are the most electronegative centers of the molecule. These inequivalencies have been observed in recent XPS and UPS spectroscopic studies.[33]

The further addition of two electrons to 1,3,4-trithiadiazole leads to the $S_3N_2^{2-}$ anion. These species are predicted to possess a valence saturated structure with two lone electron pairs on each atomic center. The apical sulfur atom is calculated to have a slightly smaller negative charge than the remaining sulfur atoms in the ring, but the proper interpretation of the localized MO results leads us to conclude that the two units of negative charge are rather evenly distributed over the ring.

4. Six-Membered Ring Systems. Two well-known six-membered ring systems are S_4N_2 and $S_3N_3^-$. Tetrasulfur dinitride, S_4N_2, can have three different isomers, namely 1,2-, 1,3-, and 1,4-S_4N_2 depending on the position of the nitrogen atoms in the ring. Among these only the 1,3 isomer has been identified as such, although the other isomers are known as the diimide derivatives $S_4(NH)_2$. The calculated results for six-membered ring systems are presented below. In the cyclic cations the nitrogen atoms possess more negative charge than the sulfur atoms. The generalization does not, however, extend to the neutral molecules or to the anions. The most electron-rich centers in the anions are the two nitrogen atoms in the 1,4 isomer, while in the 1,3 isomer the mid-sulfur atom of the S–S–S linkage is most electronegative, and in the 1,2 isomer the electron-rich centers are located at S_1 and S_4.

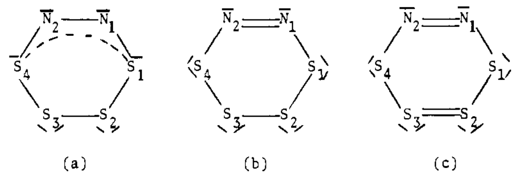

Figure 14. Electronic structures of: (a) 1,2-$S_4N_2^{2+}$, (b) 1,2-S_4N_2, and (c) 1,2-$S_4N_2^{2-}$.

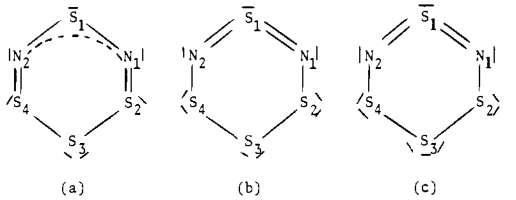

Figure 15. Electronic structures of: (a) 1,3-$S_4N_2^{2+}$, (b) 1,3-S_4N_2, and (c) 1,3-$S_4N_2^{2-}$.

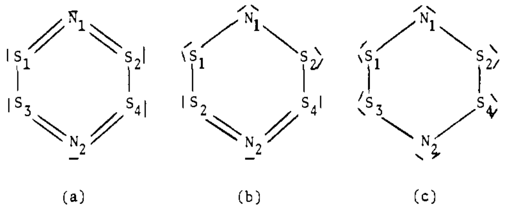

Figure 16. Electronic structures of: (a) 1,4-$S_4N_2^{2+}$, (b) 1,4-S_4N_2, and (c) 1,4-$S_4N_2^{2-}$.

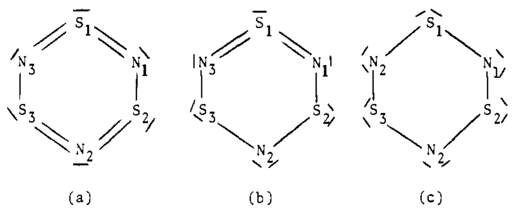

Figure 17. Electronic structures of: (a) $S_3N_3^+$, (b) $S_3N_3^-$, and (c) $S_3N_3^{3-}$.

The electronic structures of the isomers of $S_4N_2^{2+}$, S_4N_2, and $S_4N_2^{2-}$ are diagrammed in Figures 14, 15, and 16. It is apparent that the nuclear skeleton of the molecule is the principal dictate for the electronic structure obtained. Each cation possesses a structure which shows distinctly different structural features. The 1,4 isomer has eight π electrons distributed into four π-type orbitals which span the two SNS regions of the ring. They can be viewed as a collection of two S=N=S islands of structure or, perhaps more satisfactorily, two three-center-four-electron π bonds composed of out-of-plane p-type orbitals of the SNS atomic centers. Each atom of the ring has a single lone-electron pair. The 1,3 isomer of the $S_4N_2^{2+}$ cation shows a different electron distribution. Its π-electron distribution is described as a 6π system composed of a three-center-two-electron π bond over the NSN segment of the ring, together with two isolated S–N double bonds which do not involve the same sulfur atom as occurs in the three-center bond. The "extra" electron pair has migrated to the S_3 atom. The 1,2 isomer has only 4π electrons which in turn are distributed into

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(34) Roesky, H. W.; Janssen, E. *Chem. Ber.* **1975**, *108*, 2531.

two three-center π orbitals which span SNN regions of the ring. These results are quite different from the electronic structure of the $C_4N_2H_6$ systems in carbon chemistry where all isomers can be considered as 6π electron systems.

The electronic structures of the isomer of the neutral tetrasulfur dinitride molecules are also quite distinct. As pointed out previously,[14] the 1,3 isomer is a 4π electron system with the four π-type electrons distributed into a pair of three-center orbitals over the NSN segment of the molecule. The 1,4 isomer is best viewed as a 4π system also, but with the π electrons confined to three-center orbitals which span the SNS segment of the ring, while the 1,2 isomer is a 2π-electron system with a localized N–N double bond. The four sulfur atoms of the 1,4 isomer are "pairwise" equivalent (S_1 equivalent to S_2; S_3 equivalent to S_4). The 1,3 isomer exhibits sulfur in three different environments with only S_2 and S_4 being electronically equivalent. All four of the sulfur atoms of the 1,2 isomer possess the same environment.

The anion exhibits a valence-saturated structure in the case of the 1,4 isomer. 1,3-Tetrasulfur dinitride appears as a 4π system involving two three-center-two-electron π bonds over the NSN region of the ring, while the 1,2 isomer, also a 4π system, shows isolated N–N and S–S double bonds.

The neutral molecule and cation of the 1,2 isomer both show the four sulfur atoms to be in the same electronic environment possessing two unshared electron pairs. The four sulfur centers in the anion are pairwise equivalent, S_1 being the same as S_4 and S_2 being the same as S_3. Among the species derived from the 1,3 isomer, the tendency to maintain multiply bonded electronic structures is pronounced. Both the anion and the neutral molecule show a four-electron-three-center NSN bond. This bond is diminished to a three-center-two-electron bond in the cation. Somewhat surprisingly, the cation shows the highest degree of multiple bonding among the species derived from the 1,4 distribution of nitrogen atoms in the ring. As one progresses from the cation to the anion by the formal addition of electrons, the extent of π bonding diminishes resulting in a valence saturated structure for the 1,4-tetrasulfur dinitride dinegative anion.

The structure of the 1,3,5-trisulfur trinitride anion has been previously discussed.[15] The mononegative anion is a 4π system with the multiple bonding of the three-center-four-electron type over the NSN segment of the ring. The nitrogen atoms are of two distinct types, N_1 being equivalent to N_3 and both in turn being different from the nitrogen atom (N_2) not involved in π bonding. A similar remark holds for the three sulfur atoms. the formal addition of two electrons to create $S_3N_3^{3-}$ has the effect of completely destroying the π network in the ring and leads to a "valence-saturated" electronic structure in which all the nitrogen and all the sulfur atoms are electronically equivalent. The simple $S_3N_3^+$ cation can be expected to have 8π electrons—four of these should be distributed about a NSN segment of molecule and four about the SNS segment. This is the only species that we have encountered which showed both NSN and SNS three-center π-type bonds. The nonequivalency among the three nitrogen atoms and among the three sulfur atoms observed in $S_3N_3^-$ is preserved in the sense that N_1 and N_3 are equivalent to each other but different from N_2 and S_2 and S_3 are equivalent to each other but different from S_1.

Discussion

Having analyzed a number of electronic structures it is appropriate to see if any generalizations concerning the electronic structure of this class of molecules can be identified. Certain features and aspects of the structures are apparent.

(i) The sulfur nitrides represent a group of electron-rich molecules and ions whose electronic structures are not *readily* describable in terms of simple Lewis theory.

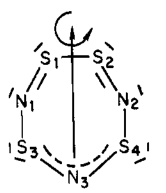
(ii) The electronic structures of this group of molecules and ions can be represented by the superposition of a few basic structural entities. These structural entities are the following: (a) ordinary S–N, N–N, and S–S two-center σ bonds which can be constructed from valence level "s type" and "p type" (in plane) atomic orbitals of the constituent atoms; (b) lone-pair electrons on the constituent atoms which are best described by hybridized valence-level atomic orbitals; (c) two-center π bonds of the classical type constructed of out-of-plane p-type atomic orbitals of sulfur and nitrogen atoms; (d) three-center π bonds which are of two types, either SNS or NSN (These are also constructed from p-type atomic orbitals directed out of the plane of the molecule.); (e) the "higher lying" d-type orbitals of the sulfur atom play no significant role in the development of the electronic structures of this class of molecules and ions; and (f) the structure which results from a localized orbital analysis always reflects the presence of at least one of the C_2 rotational axis possible for a given molecule, usually the C_2 axis which located in the plane of the molecule.

(iii) The change in the electronic structure which results from the addition or substraction of an electron pair to an existing structure is always such that: (a) the addition of electrons to a neutral molecule destroys or reduces the amount of multiple bonding (π type) present in the molecule and replaces it by the generation of more unshared electron pairs (Not infrequently a valence-saturated structure results.); (b) the removal of electrons from a neutral molecule generally increases the extent of π bonding; and (c) the symmetry of the molecule with respect to at least one of the C_2 rotational axis (in plane) is preserved during the addition or the subtraction of electrons from sulfur–nitrogen ring systems, e.g., $S_3N_3^+ \rightarrow S_3N_3^- \rightarrow S_3N_3^{3-}$. The later two points b and c are simply a reflection that, like most systems, the most probable electronic structure for a given species is that structure which utilizes fully all the atomic orbitals present in the valence levels of its composite atoms. This phenomena also has virtually nothing to do with the presence of, or by the invoking of, "higher lying" d-type orbitals on the sulfur atoms.

(iv) A simple electron "counting recipe" for determination of the number of π electrons in a given species cannot be deduced from only the number of sulfur and nitrogen atoms present in the ring system. The number of out-of-plane, π-type orbitals present depends upon both the number of sulfur and nitrogen nuclei present and the symmetry of the nuclear framework of the molecule or ion. In the past this phenomena has been deduced by simply counting the number of electrons necessary to form the σ-bonding framework, then assigning each sulfur and nitrogen atom two or one lone-electron pair, and attributing the remainder of the electrons to π-type MOs. Under this description a molecule like S_3N_2, for example, would be considered an 8π-electron system. Our results suggest it to be a 4π-electron system. Numerous examples of this type of contradiction occur, some of which are: SN_2 (4π electrons vs. 2π electrons), SN_2^{2-} (6π electrons vs. no π electrons), S_3 (6π vs. no π electrons), S_2N_2 (2π vs. no 4π electrons), S_3N^+ (6π vs. 4π electrons), S_4 (8π electrons vs. no π), and $S_2N_3^-$ (8π electrons vs. 2π electrons).

Finally the chemical implications inherent in the predicted structures should be pointed out. We use as our example the trisulfur trinitride anion. The localized orbital based structure shows this anion to possess two different kinds of nitrogen atoms in the sense that N_2 is in an electronic environment distinctly different from that of N_1 or N_3 which in turn have the same electronic environment. This implies that if $S_3N_3^-$ were to be reacted with a Lewis acid like boron trifluoride, BF_3, we could expect to produce a 1:2 adduct where BF_3 adds to N_1 and N_3 in an equivalent way or a 1:3 adduct wherein BF_3 adds to all three nitrogen atoms. If a 1:3 adduct is obtained it should, however, reflect the presence of two different $N{:}BF_3$ bonds. A 1:1 adduct to the most electron-rich center at N_2 is also possible. These differences should be apparent in any structural or spectroscopic study. Succinctly, the localized orbital structures of a given species provide a basis for the prediction of the chemical behavior of the species. Heretofore, it has not been possible to predict the chemistry of the sulfur nitrides with any reasonable degree of reliability.[34]

We illustrate the applicability of the above generalizations by "predicting" the electronic structure of the known ion $S_4N_3^+$. The ion possesses 38 valence electrons and they are predicted to be distributed as diagrammed below.



This is the only structure that can be built from the structural elements listed above which preserves the diagrammed rotational axis. It predicts the molecule ion to be a 6π system. The Banister counting method predicts the ion to contain 10π electrons. The presence of 10π electrons is difficult to accept since the molecule clearly contains no S–S multiple bonds ($d_{S\text{-}S}$ observed = 2.06 Å) and thus the 10π electrons must be equally distributed over the six possible N–S segments of the ring. Our predicted structure resolves this problem. The structure predicted above implies that the electronic environment of N_3 is different from that of N_1 or N_2 which in turn are equivalent to each other. The four sulfur atoms are pairwise equivalent (S_1 is the same as S_2; S_3 is the same as S_4). These equivalencies should be reflected in the photoelectronic spectrum of the molecule ion and also in the chemistry. The molecule also possesses a four-electron-three-center π-type charge distribution ($S_3N_3S_4$) and two isolated S–N normal π bonds.

Supplementary Material Available: CNDO/2 results (population analysis) and atomic orbital coefficient for localized molecular orbitals for all four-, five-, and six-membered ring compounds discussed herein (26 pages). Ordering information is given on any current masthead page.

Kinetic and Thermodynamic Contributions to Energy Barriers and Energy Wells: Application to Proton-Bound Dimers in Gas-Phase Proton-Transfer Reactions

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Abstract: A previously reported equation for predicting energy barriers yields Marcus' equation for electron transfer as a special case and is shown to be suitable for estimating the stabilities of proton-bound dimers of neutral molecules and anions in the gas phase. The average deviation between calculated and experimental well depths of 51 proton-bound dimers is about 0.6 kcal. In many cases, the energy of the proton-bound dimer (A–H–C) is simply the average of the energies of the two symmetrical dimers (A–H–A and C–H–C). In other cases a nonlinear correction becomes important. It is significant that either barrier heights or well depths for group-transfer reactions can be expressed in terms of the thermodynamics of the overall reaction (A–B + C → A + B–C) and the barrier heights (or well depths) of two thermoneutral identity reactions (A–B + A → A + B–A and C–B + C → C + B–C).

I. Energy Barriers and Energy Wells. Some Common Elements

A. General Equation for Describing Energy Barriers. Recently it has been found that energy barriers for group-transfer reactions are closely related to the overall thermodynamics and to the barriers of two related identity reactions.[1] For example, the barrier for a reaction A–B + C → A + B–C can be expressed as:

$$\Delta E^{\ddagger} = \Delta E_0^{\ddagger}(1 - g_2(\tau)) + \tfrac{1}{2}\Delta E(1 + g_1(\tau)) \qquad (1)$$

where $\Delta E_0^{\ddagger}$ (called the intrinsic barrier) is the average of the barriers for the identity reactions A–B + A → A + B–A and C–B + C → C + B–C, ΔE is the difference in energy between products and reactants, and g_2 and g_1 are even and odd functions[2] of τ, which in turn is a function of $\Delta E_0^{\ddagger}$ and ΔE. Possible choices for τ include:

$$\tau = \Delta E/4\Delta E_0^{\ddagger} \qquad |\Delta E/\Delta E_0^{\ddagger}| \leq 4 \qquad (2)$$

$$\tau = \sin\,(\Delta E/2\Delta E_0^{\ddagger}) \qquad |\Delta E/\Delta E_0^{\ddagger}| \leq \pi \qquad (3)$$

$$\tau = (2/\pi)\arctan\,(\pi\Delta E/4\Delta E_0^{\ddagger}) \qquad (4)$$

$$\tau = \tanh\,(\Delta E/2\Delta E_0^{\ddagger}) \qquad (5)$$

These relationships are shown graphically in Figure 1.

B. Marcus' Equation for Electron Transfer Is a Special Case. The simplest odd and even functions of τ are the monomials τ and τ^2, which on substitution in eq 1 give

$$\Delta E^{\ddagger} = \Delta E_0^{\ddagger}(1 - \tau^2) + \tfrac{1}{2}\Delta E(1 + \tau) \qquad (6)$$

Equation 6 is limited to the range $|\Delta E| \leq 4|\Delta E^{\ddagger}{}_0|$ which interestingly enough is also a feature of Marcus' equation.[3] In fact, substitution of eq 2 into eq 6 leads to Marcus' equation:[4]

$$\Delta E^{\ddagger}{}_{\text{Marcus}} = \Delta E_0^{\ddagger} + \tfrac{1}{2}\Delta E + (\Delta E)^2/16\Delta E_0^{\ddagger} \qquad (7)$$

C. τ Is a "Nonadditivity" Parameter. It should be noted that when $\tau = 0$, the energy of A–B–C is simply the average of the energies of A–B–A and C–B–C.[1] Under such conditions the barrier for the reaction A–B + C → A + B–C is given by:

$$\Delta E^{\ddagger}{}_{\text{additive}} = \Delta E_0^{\ddagger} + \tfrac{1}{2}\Delta E \qquad (8)$$

The $^1/_2\Delta E$ term can be regarded as the thermodynamic contribution to the barrier, since it is directly related to the thermodynamics of the overall reaction. The other term, $\Delta E_0^{\ddagger}$, can be

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(1) J. R. Murdoch and D. E. Magnoli, *J. Am. Chem. Soc.*, in press. This material was also presented at the 5th IUPAC Conference on Physical Organic Chemistry, Santa Cruz, Calif., Aug 1980.

(2) An odd function of τ is one which can be expressed in terms of odd powers of τ, and an even function is one which can be expressed in terms of even powers of τ. For $\tau \rightarrow 1$, g_1 and g_2 approach unity, and for $\tau \rightarrow -1$, $-g_1$ and g_2 approach unity. When $\tau = 0$, g_1 and g_2 equal zero. See ref 1 for details.

(3) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

(4) The fact that ΔE is confined to a finite range has troubled certain authors, and this problem has been discussed elsewhere.[1] It can be shown[1] that the choice of $g_1(\tau)$ and $g_2(\tau)$ determines whether ΔE is confined to a finite or to an infinite range. Two choices for $g_1(\tau)$ and $g_2(\tau)$ which lead to an infinite range for ΔE are: $g_1(\tau) = {}^3/_2\tau - {}^1/_2\tau^3$; $g_2(\tau) = \tau^2$ and $g_1(\tau) = \sin \pi\tau/2$; $g_2(\tau) = 1 - \cos \pi\tau/2$.

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