On the Electronic Structure of the Tetrathiazyl Dication

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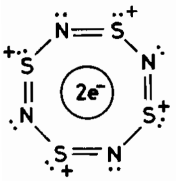
Introduction

The synthesis and structure of the tetrathiazyl dication, $S_4N_4^{2+}$ has recently been reported. In the solid state the ion seems to exist in a planar form possessing equal bond lengths (symmetry D_{4h}) and a non-planar form also presumed to have equal bond lengths [1, 2]. Infrared and Raman studies are in accord with this conclusion, the spectra being interpretable in terms of a somewhat flexible planar ion of symmetry D_{4h} [3]. The electronic structure of the ion is somewhat less clearly understood. A simple electron counting indicates that the ion possess 10 pi electrons, satisfies the 4n + 2 rule and can be expected to show a delocalized, aromatic-like structure. As pointed out previously by ourselves [4] and others [2], one cannot be certain that these magic numbers confer any additional stability to the molecule or ion in SN heterocyclic systems. The distribution of 10 pi electrons into 8 pi type molecular orbitals presents no difficulty. Gillespie and coworkers [2] have suggested that the ion might be described in terms of 8 conventional π type electrons and two electrons which occupy an orbital associated with the four S atoms, *i.e.*:



Paddock, Sharma, and Aubke [3] have studied the system using some empirical M.O. methods based upon the CNDO and Extended Hückel approximations and correlated the M.O.s of the dication with those of tetrasulfur tetranitride as the latter is altered from D_{2d} to D_{4h} symmetry. They found that the alteration of symmetry causes the highest antibonding level in symmetry D_{4h} to drop sharply as one progresses to D_{2d} and acquire significant S–S bonding character in symmetry D_{2d}. Ionization of S_4N_4 to $S_4N_4^{2+}$ causes a stabilizing of all the M.O. levels in either symmetry, but the effect is smaller for the HOMO of the ion than for the neutral S_4N_4. They suggest that the dication possesses some degree of S–S bonding and that it in turn is formed at the expense of a decrease in the strength of the S–N bonds.

TABLE I. MNDO Results for $S_4N_2^{2+}$.

Structure	$d_{N-S} = 1.52$ Å angle SNS = 159° angle NSN = 110 $\Delta H_f^\circ = +676$ Kcal/mol
Atomic Charges	N = 0.82 S = +1.32
Bond Order	N–S = 1.237 S–S = 0.1130 (between S atoms bonded to the same N atom) N–N = 0.1399 (between N atoms bonded to the same S atom)

TABLE II. Localized Orbitals for $S_4N_2^{2+}$.

Number and type of localized MO*		% localization
8 – N–S sigma bonds		98.30
4 – S lone pair		99.35
4 – N lone pair		92.22
5 – π orbitals		
type a.	$N_1-S_8-N_7-S_6$	97.98
type b.	$N_1-S_2-N_3-S_4\cdots S_6-N_7$	99.67
	$N_1-S_2-N_3-S_4\cdots S_6-N_7$	99.94
type c.	$N_7-S_6-N_5-S_4-N_3\cdots N_1$	99.10
	$S_2-N_1-S_8-N_7-S_6\cdots S_4$	99.31

*The numbering system used for the atoms starts by assigning the number one to an arbitrary nitrogen atom and progress clockwise around the 8 membered ring.

We have demonstrated the utility of a localized molecular orbital description to elucidate the nature of the electronic structure of S–N heterocyclic

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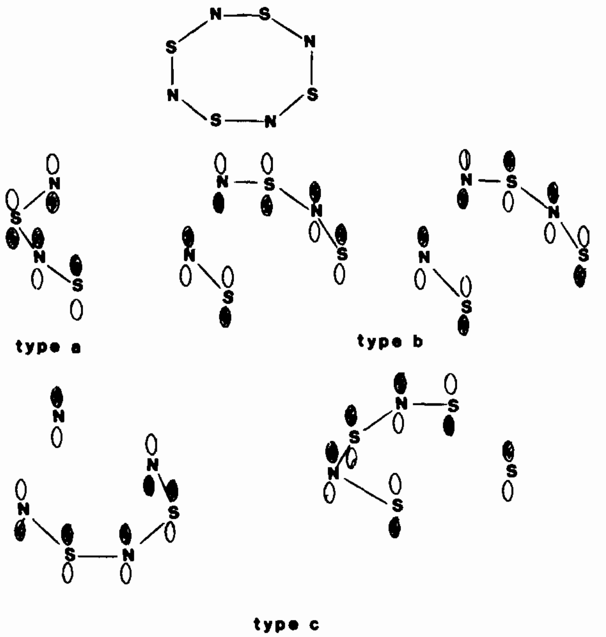


Fig. 1. Localized pi-type Orbitals for $S_4N_4^{2+}$

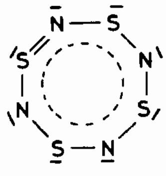
species [4–6]. Below we report the results of a localized orbital calculation for $S_4N_4^{2+}$ based upon a MNDO type molecular orbital wave function.

Calculations and Results

A molecular orbital calculation for the dication was carried out using the MNDO method [7, 8]. The calculation was started from a suitably averaged, observed geometry for $S_4N_4(SO_3F)_2$, d_{N-S} = 1.55 Å, SNS angle = 152°, NSN angle = 118°, symmetry D_{4h}. The results and concomitant population analysis is shown in Table I. The MNDO canonical orbitals were energy localized by a previously published procedure [4] and the resulting localized orbitals are presented in Table II. Diagrams are presented in Fig. 1.

Discussion

The calculations indicated $S_4N_4^{2+}$ to be a highly endothermic material* with the electronic environment of each nitrogen atom the same and each sulfur atom the same**. The canonical M.O.s do not localize to four classical two center pi type bonds and an M.O. which involves only out of plane orbitals of the four sulfur atoms, arguing against the simple Hückel type model. A superposition of the charge densities of the five localized pi type orbitals leads to the following canonical structure:



by which we denote a sigma framework, a lone electron pair on each atom, eight π type electron delocalized about the ring and a 2 center pi bond between N and S. This is but one of eight possible equivalent structures that could be drawn and the eight equivalent structures taken together denote a 10 π electron delocalized system Studies of this kind in the past have generally identified any unique structural features associated with the one electron density function, and thus we must conclude that no such features are to be expected for the tetrathiazyl dication, *i.e.*, it is not necessary to invoke transannular S–S bonding or some similar type feature to account for the present of the 10 π type electrons. A consequence of this delocalization is reflected by the slightly smaller than usual N–S bond distance observed, *i.e.*, 1.55–1.56 Å, as compared to 1.61 Å in S_4N_4.

References

1 R. J. Gillespie, R. R. Slim and J. D. Tyrer, *J. Chem. Soc., Chem. Commun.*, 253 (1977).

2 R. J. Gillespie, J. P. Kent, J. F. Sawyer, D. R. Slim and J. D. Tyrer, *Inorg Chem.*, *20*, 3799 (1981).

3 R. D. Sharma, F. Aubke and N. L. Paddock, *Can J Chem*, *59*, 3157 (1981).

4 A. A. Bhattacharyya, A. Bhattacharyya and A. G. Turner, *J. Am. Chem Soc*, *103*, 7458 (1981).

5 R. R. Adkins and A. G. Turner, *J Am. Chem. Soc*, *100*, 1383 (1978).

6 A. Bhattacharyya, A. A. Bhattacharyya and A. G. Turner, *Inorg Chim. Acta Lett.*, *42*, 69 (1980).

7 M J. S. Dewar and W. Thiel, *J Am Chem. Soc*, *99*, 4899 (1977).
R. Bingham, M. J. S. Dewar and D. H. Lo, *ibid.*, *97*, 1285 (1975).
M. J. S. Dewar and M. L. McKee, *ibid*, *99*, 5231 (1977);
M. J. S. Dewar and H. S. Rzepa, *ibid.*, *100*, 58 (1978).

8 For application to sulfur–nitrogen compounds, see S. Sensarma and A. G Turner, *Inorg. Chim. Acta Lett*, *674*, L182 (1982);
also R. Gleiter and R. Bartetzko, *Z. Naturforsch*, *36*, 956 (1981).

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*Interestingly all sulfur–nitrogen molecules and ions calculated to date using the MNDO or MINDO/3 methods have turned out to have a positive standard enthalpy of formation.

**By this remark we mean that the gross atomic charges are same for each sulfur atom and all four N atom charges are the same. The nitrogen atoms are the electrophilic centers of the ion and the sulfur atoms represent the nucleophilic centers.