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The Molecular Orbital Description of the Trisulfur Trinitride Anion

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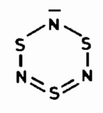
In a recent publication Turner and coworkers [1] report the results of a CNDO/2 localized molecular orbital study on the $S_3N_3^-$ anion. Several of their conclusions are in direct conflict with our concept of this species as suggested by both experiment and *ab initio* Hartree-Fock-Slater (HFS) SCF calculations [2]. We believe that some comments are necessary to clarify the issues.

Symmetry of $S_3N_3^-$

We begin by noting that the calculation of localized orbitals by Turner and coworkers, using the Edmiston and Ruedenberg scheme, [3, 4] indicates that "the three nitrogen atoms are not equivalent to each other in the sense that they do not possess the same electronic environment". We find it surprising that they would draw this conclusion since it is well known that the transformation to localized orbitals using the Edmiston and Ruedenberg approach does not yield a unique set of localized orbitals. This fact was recognized by Edmiston and Ruedenberg themselves as early as 1965 [5]. It would appear that the calculations of Turner and coworkers have only yielded one of the three canonical structures depicted below.



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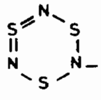

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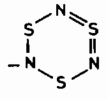

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The inclusion of the other two structures would equalize the charges on the three nitrogen atoms and, in fact, results in charge densities ($q_S = -0.02$, $q_N = -0.32$) not significantly different from those found in our *ab initio* HFS calculations ($q_S = +0.065$, $q_N = -0.40$) [2]. Furthermore, in these latter calculations, the threefold symmetry of the molecular orbitals is maintained even when the restriction of D_{3h} (not D_{3d} as stated by Turner and coworkers) symmetry is lowered to C_{2v}, *i.e.* there is no symmetry breaking due to the non-local character of the SCF Hamiltonian [6]. The near equality of the S–N bond lengths found in the crystal structures of n-Bu_4N^+ $S_3N_3^-$ [2] and PPN^+ $S_3N_3^-$ [7] is certainly not consistent with the notion of inequivalent nitrogens. We also point out that the ^{15}N nmr spectrum of $S_3N_3^-$ (one narrow signal at δ = 148.4 ppm relative to external $NH_{3(l)}$ at 25 °C) gives no indication of inequivalence of the nitrogen nuclei [8].

Considerable caution should therefore be used in the assignment of valence bond formulations to sulfur nitride structures. Although such a caveat was included, as a footnote, in our recent communication on the thermal conversion of $S_3N_3^-$ to S_4N^- [9], Turner and coworkers interpreted the valence bond representation of $S_3N_3^-$ as implying formal bond orders. Such formulations should at best be interpreted like the Kekulé structures of benzene and should not be taken to imply asymmetry in the isolated $S_3N_3^-$ anion. Although it is possible that symmetry breaking changes occur *en route* to reaction products in the thermolysis of $S_3N_3^-$, we suggest that, as with delocalized carbocyclic systems, the valence bond structures should be put to rest in favour of a delocalized representation *e.g.* 4.

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The π-System of $S_3N_3^-$

Turner and coworkers also conclude that $S_3N_3^-$ is a four π-electron system and cite the observed S–N bond length of *ca.* 1.6 Å as evidence in support of their view. By contrast, we [2] and, more recently, Gimarc and Trinajstic [10] have indicated that $S_3N_3^-$ is a 10π electron system consistent with the original prediction by Banister [11]. In our *ab initio* HFS calculation we found, as depicted in Fig. 1, a total of five occupied orbitals which are antisymmetric to reflection in the molecular plane. The overlap populations for these orbitals (Table V, ref. 2) indicate strongly bonding characteristics for the lower three ($1A_2''$ and the degenerate pair $1E''$) and antibonding characteristics for the next highest degenerate pair ($2E''$); hence there are the three π and two π* occupied orbitals. If the unoccupied orbital $2A_2''$ is taken into account, the correspondence of the π/π* system to benzene, for

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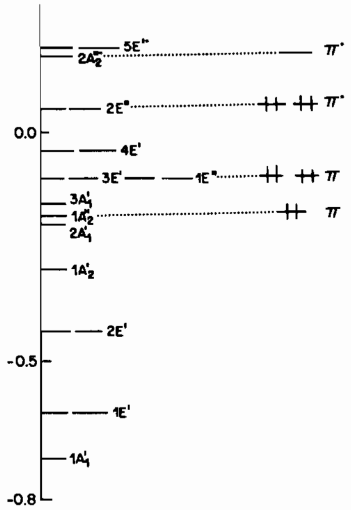

Fig. 1. Orbital energy level diagram for planar (D_{3h}) $S_3N_3^-$ showing the π-energy levels (a.u.).

example, is quite clear. Certainly the expected pattern of bonding and antibonding orbitals is evident. The correctness of this description is further supported by the recent magnetic circular dichroism study of $S_3N_3^-$ by Waluk and Michl [12] who find a negative A term for the 360 nm transition consistent with an excitation of the $\pi^* \rightarrow \pi^*$ type. The presence of ten π-electrons should not, therefore, lead to very short S–N bond lengths, as implied by Turner, since four of these electrons are described by antibonding orbitals. More precisely, the orbital overlap populations of the five occupied levels are 0.024, 0.020, 0.020, –0.012 and –0.012, respectively, giving rise to a net overlap population of 0.16*. Since the overlap population of a full π-bond is about 0.5 it is clear that the π-bond order of each S–N linkage is approximately 1/3 corresponding to a net of four π electrons distributed over six centres**.

Clearly the presence of ten electrons of π-symmetry in $S_3N_3^-$ does not imply a strongly bonding π-network, just as the extra π-electron in the benzene radical anion, $C_6H_6^-$, would not imply a strengthening of the π-system. In electron-rich thiazenes the antibonding, as well as the bonding, nature of the occupied orbitals must be taken into account.

Acknowledgement

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*The net overlap population is four times the sum of the orbital overlap populations, where the factor 4 arises due to doubly occupied orbitals giving a factor of 2 and the quadratic form of the population giving rise to another factor of 2 for the cross terms.

**In ref. 2 we stated, that, on the basis of occupancy, the antibonding orbitals reduce the π bonding to a net of a little over one π bonding orbital. However, a more precise inspection using the orbital overlap populations shows that this statement is inexact due to the fact that the bonding contribution of the 1E" level is not completely cancelled by the antibonding contribution of the 2E" levels.