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The Molecular Orbital Description of the Trisulfur Trinitride Anion Revisited

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In a recent article [1] Chivers, Laidlaw, and coworkers discussed the disagreement they believe to exist concerning the interpretation to be placed upon the electronic structure of the $S_3N_3^-$ anion as discussed by their laboratory [2] and our own [3]. Two basic topics were discussed, the symmetry of the one electron density function, and the nature and extent of the π electrons in the anion. We wish to make additional comments on these topics, having as our goal the further clarification of the questions involved.

Question 1

The Symmetry of $S_3N_3^-$

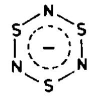
It seems to us that the symmetry of the molecular frame is clear. Both studies have assigned $S_3N_3^-$ to the point group D_{3h}, *i.e.* it has been assumed to be a planar ion.

The symmetry of the one electron density is less clear. The gross atomic charges quoted by ourselves are the result of a classical Mulliken population analysis [4] and as such are calculated directly from the CNDO/2 canonical molecular orbitals. They are in no way related to the localized M.O. calculations as inferred by Chivers, Laidlaw and coworkers, and have nothing to do with the convergence of the localized orbital calculations, to one or more canonical valence bond structures which are members of a symmetry equivalent set. The fact that the three nitrogen atoms were predicted to have two different gross atomic charges (two +0.240; the other one −1.426) surprised us a great deal. For several months we firmly believed that we had made an arithmetic or algebraic error. We were unable to find such an error and thus accepted this inequivalence. Since we have dealt only with a structure which represents an "averaging of experimental bond distances and angles," 1.600 Å and 120°, respectively, the inequivalences appear to be even more surprising, but none the less real. Chivers and Laidlaw suggest that the "near equality" of S–N bond lengths is "certainly not consistent with the notion of inequivalent nitrogen atoms." Two points should be made: firstly, we are not aware of a mathematical theorem which supports the conclusion (perhaps a group theorist can contribute here), and secondly, this observed S–N bond length differs by as much as 0.046 Å a rather large difference that may be attributable to electronic effects. What is needed are some careful NQR measurements in the system.

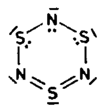
Question 2

The Nature and Extent of the π Electron System

The basic question here is whether or not a simple classical π electron counting system, which if applied in this case leads to prediction of 10 pi electrons, offers an accurate picture of the system [5]. We feel that the answer to this quiry must be no. The mere fact that the orbital energy diagram (see Chivers *et al.*, Fig. 1) requires that electrons be placed into antibonding type M.O.'s negates the simple counting concept. Generally one's interest is in knowing to what extent π type electrons are available in the system for chemical purposes, *i.e.* for π bonding or for spectroscopic considerations. It is only when a localized orbital picture is available that this information becomes transparent. The localized orbitals clearly show the presence of two two-center two electron π bonds or one three-center four electron π bond. The remaining electrons occur only as lone electron pairs (π or π type) on the sulfur or nitrogen atoms, or as sigma bonds. Thus, to write



is not nearly as descriptive as



The localized orbital picture is but one of three possible canonical valence bond structures. The three taken together might imply the presence of four pi type electrons delocalized over the six membered ring. We choose not to do this in this particular case since to do so contributes nothing to the overall

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picture. The concept of π electrons delocalization is illusive, elusive, ill defined, and except in very special situations, not directly experimentally measurable. It is useful when introduced *post facto* to explain experimental fact, and thus is premature here.

We feel that $S_3N_3^-$ possesses only four pi-type electrons that are involved in π bonding, possibly distributed on three adjacent NSN centers, possibly delocalized about the entire ring but most assuredly only four in number.

References

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