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Electron Density Study of Thiotrithiazyl Chloride, S_4N_3Cl

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Abstract: Ab initio restricted Hartree–Fock calculations have been performed for S_4N_3Cl. The aim is to study the bonding between chlorine and the seven-membered S_4N_3 ring, as well as the bonding within the ring. The ring turns out to be significantly influenced by the presence of chlorine, and the system is found to have a 7-ring with bonds bent to the inside and a 3-ring with bonds bent to the outside. The calculated deformation density compares favorably with experimental results.

S_4N_3Cl contains a seven-membered S_4N_3 ring system, which interacts with chlorine via two mutually bonded sulfur atoms. This leads to a triangular S_2Cl arrangement. The S_4N_3 part of the molecule is expected to carry positive charge, and the chlorine, negative. The nature of the bond between the two, as well as the amount of charge transfer, is however disputed,[1,2] and an aim of this paper is to elucidate the interaction from a theoretical point of view.

The molecule shows only small deviations from planarity,[2] which conforms with the 7-ring having an aromatic delocalized 10-electron π-system. It is further a purpose of the investigation to illustrate the strains in the two rings by the use of bent bonds and to compare experimental and theoretical deformation density maps.

Details of Calculations

The calculations use the restricted Hartree–Fock method with a Gaussian basis set of the form (S/12,9,1) (Cl/12,9,1) (N/9,5) contracted as ⟨S/6,5,1⟩ ⟨Cl/6,5,1⟩ ⟨N/4,2⟩. The primitive functions for S and Cl are those reported by Veillard[3] augmented with d functions[4] having exponents 0.54 and 0.68 for S and Cl, respectively. The primitive functions for N are reported by van Duijneveldt.[5] The geometry for the molecule was supplied by R. G. Hazell.[2] It is based upon X-ray structure determination, but C_{2v} symmetry has been enforced (Table I and Figure 1). The resulting wave functions and the corresponding electron density distributions were analyzed with deformation densities, Mulliken populations, and bond paths. The latter were determined with a program supplied by R. Bader, and contour plots were drawn with MOLPLOT.[6]

Results and Discussion

A Mulliken population analysis[7] of the calculated wave function is given in Figure 1. It shows positive sulfur atoms and negative nitrogen atoms in the 7-ring, and the ring carries as a whole a charge of +0.75e. This is quite different from what was found experimentally[1] for $S_4N_3NO_3$, where numbers between −0.4 and +0.2e are listed. The charge of an atom in a molecule is, however, not an observable as such; it relies both theoretically and experimentally on more or less shaky definitions. Thus, the absolute values of populations should not be overinterpreted, whereas trends may be more useful. The overlap population between Cl and S_1 is very small. It results from adding numbers with alternating signs, and even though there is an orbital with a contribution of +0.05e, the interaction seems not to be very covalent in character. In the 7-ring, the largest overlap population is, as expected, found for the shortest S–N bond. All overlap populations in the ring decrease from their respective values in a similarly calculated $S_4N_3^+$ ion, in particular the S_1–N_3 bond, where the decrease is +0.23e. The 7-ring is, therefore, significantly different in $S_4N_3^+$ and S_4N_3Cl, and a noteworthy influence can be attributed to chlorine.

Table I. Coordinates of Symmetry-Independent Atoms in Units of a_0 (a_0 = 52.9166 pm) (Atomic Labels Shown in Figure 1)

atom	*x*	*y*
N_1	2.749 610	3.070 870
N_2	6.748 355	0
S_2	0	1.963 467
S_3	5.623 944	2.738 271
Cl	−5.045 676	0

Figure 2 shows the total electron density for the system with so-called bond paths[8] and atomic fragments indicated. The bonds are all bent, with the 7-ring bending toward the inside and the 3-ring toward the outside, showing their respective strains. The bond paths between chlorine and the sulfur atoms start to curve very close to sulfur, and this shape may be indicative of a fairly weak interaction. There is a (3, +1) critical point in the middle of each ring (the notation signifies that a function of three independent variables has two positive and one negative eigenvalues of the Hessian in the particular point). The critical point for the 3-ring is a very shallow minimum in the molecular plane (a (2, +2) critical point), and an additional contour line has been drawn to make it visible. The interaction between chlorine and the sulfur atoms in the S–S bond is obviously not very covalent in character, and this, together with the Mulliken populations, points toward a fairly ionic type of bond.

The deformation density for the system is shown in Figure 3. It is calculated with reference to neutral spherical atoms, and it is depicted in the molecular plane with bond paths and atomic fragments shown. It is as usual difficult to select a proper reference system, or promolecule, as it is often called. For atoms with more than half filled shells, a hybridization model[9] will often display "chemical features" more clearly. On the other hand, this makes the map more model dependent, in particular for these rather unusual ring systems. For more electron-deficient molecules, which contain atoms like carbon and hydrogen, bonds and lone pairs are more visible. Oxalic acid is here a good example.[10] One could also apply Cl^- instead of Cl in the reference, but with a Mulliken charge for chlorine of −0.75e, this is still not a very clean procedure. A difference density between S_4N_3Cl and $S_4N_3^+ + Cl^-$ was, however, calculated. This shows density increase in the N_1–S_2 and N_1–S_3 type of bonds and more lone pair density for the sulfur atoms. Chlorine is polarized toward the 7-ring, as also appears from Figure 3, and the S_1–S_2 bond has a small density increase toward the interior of the 7-ring and a decrease to the side of the 3-ring. So as for the populations, we find a significant influence from chlorine.

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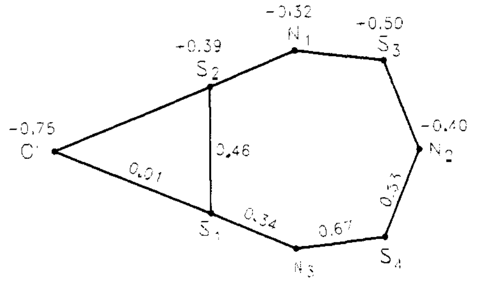

Figure 1. Geometry and labels used for S_4N_3Cl. The numbers shown above atoms are charges, and the numbers shown on bonds are overlap populations, both found from Mulliken population analysis. The molecule is forced to have C_{2v} symmetry.

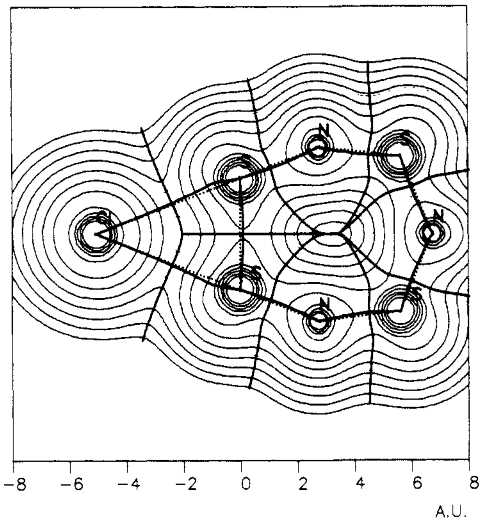

Figure 2. Total electron density for S_4N_3Cl with bent bonds and atomic fragments shown. The lowest contour is 0.0025 e a_0^{-3}, and there is a factor of 2 between adjacent levels (an extra contour with the value 0.24 e a_0^{-3} has been drawn as a thin line).

The deformation density in Figure 3 shows lone pair formation behind all N and S atoms, and there is density accumulation in connection with all the bonds in the 7-ring. The corresponding maxima are found displaced toward the center of the ring, and the displacement is about twice the bond-path displacement. The 3-ring region shows a decrease of density, which correlates well with the outward strain of the ring.

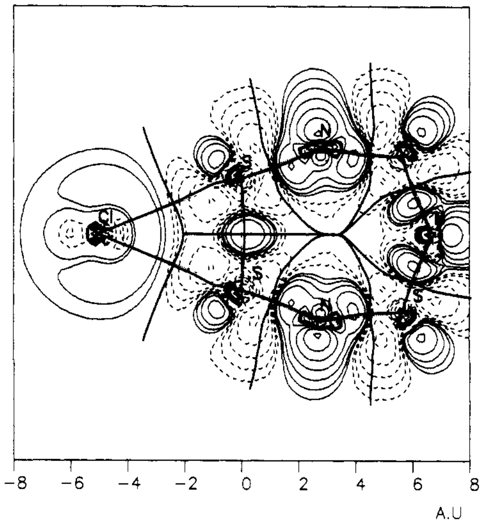

Figure 3. Deformation density for S_4N_3Cl with bent bonds and atomic fragments shown. The lowest contours are ±0.0025 e a_0^{-3}, there is a factor of 2 between adjacent levels, and negative values are dashed.

The structure of S_4N_3Cl has been solved by X-ray diffraction,[2] but an experimental deformation density has so far not been determined. A low-temperature study has, however, been done for the corresponding nitrate,[1] which makes a comparison for the S_4N_3 part possible. The general agreement is good. The experimental map shows accumulation of density on all bonds in the 7-ring, and the S–S bond appears to be bent as was found in the calculation. The other bond peaks are located close to the straight connection lines, and any bending cannot be deduced. The lone pair features for the four sulfur atoms and for the N_2 atom are quite similar in the two maps, whereas a lone pair accumulation is missing for N_1 and N_3 in the experimental map. It is, however, not easy to assess whether the calculation or the experimental determination is most reliable on this point.

Conclusions

The calculations display a strained S_4N_3Cl molecule, which may be considered as a 7-ring bending inward and a 3-ring bending outward. Chlorine is attached to the ring with fairly ionic bonds, but the resulting charge of about −0.75e for the atom indicates significant charge transfer. The deformation density for the 7-ring compares well with experimental results for $S_4N_3NO_3$ on most of the dominant features. It is as usual difficult to select a satisfactory promolecule reference for the deformations, but in order to resolve the current problems with theoretical and experimental deformation densities and to find limits of applicability, it is necessary to study a diverse list of molecules.

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