and is generally obscured by ligand bands.[16] The shoulder at 21 kK in the salicylaldimine spectra may be such a ligand absorption. The assignment of the electronic spectra given here can only be tentative. Circular dichroism measurements on similar optically active complexes will be valuable in making firmer assignments.

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The Electronic Structure of the Thiotrithiazyl Cation[1]

BY PAUL FRIEDMAN

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The thiotrithiazyl cation has been found to possess a planar structure, with very short, approximately equal sulfur–nitrogen bonds.[2] It is unusually stable for a sulfur-nitrogen heterocycle and has well-defined absorptions in the ultraviolet region indicative of $\pi \rightarrow \pi^*$ transitions.[3] These facts imply a well-defined π-electron system and a considerable amount of aromatic character.

Some recent efforts[3] have been made to gain understanding of the physical and chemical properties of this compound by attempting correlations with values determined by calculations using molecular orbital theory. These correlations were of limited utility because the methods which were used, the HMO and free-electron procedures, are too approximate to yield anything but qualitative agreement.

This situation led us to apply the semiempirical SCF–MO procedure developed by Pople,[4] which we had used successfully[5] with thiaaromatic compounds such as thiophene, thiazole, and thiazole derivatives, with the hope of obtaining more useful results for correlation. The known geometry of thiotrithiazyl cation[2] was simplified by assuming equal S–N bond lengths of 1.55 Å. The S–S bond length of 2.06 Å was used (Figure 1). Each sulfur was assumed to donate two electrons to the π system resulting in a ten-π-electron system in the cation. This geometry was used (Figure 1) to calculate the two-center, two-electron repulsion integrals (*ii*/*jj*) by the Mataga method.[6] The complete set of semiempirical parameters is given in Table I.

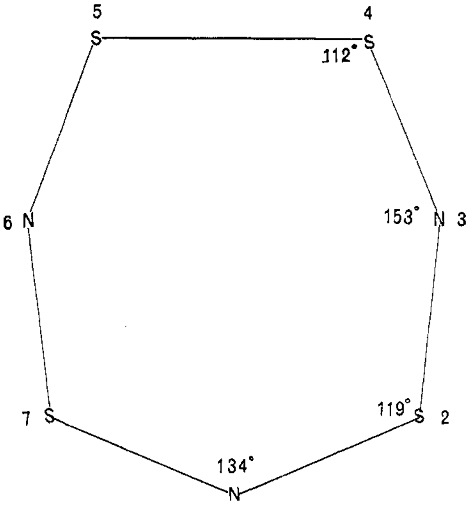

Figure 1.—Modified geometry of $S_4N_3^+$. The N–S bonds are all 1.55 Å; the S–S bond is 2.06 Å.

TABLE I

VALUES OF INTEGRALS USED (IN eV)

11/11	12.27	33/55	3.24
11/22	6.14	33/66	3.09
11/33	3.64	44/55	4.66
11/44	2.59	β_{12}	−2.0
22/22	11.90	β_{45}	−1.2
22/44	3.18	W_S	−23.0
22/55	2.51	W_N	−14.5
22/66	2.89		
22/77	3.42		

No special adjustments, such as calibration against observed spectral values, were made in these parameters in terms of the particular molecule being investigated. Rather, these parameters were carried over from our previous calculations of thiaaromatic compounds, except for β_{NS} and β_{SS}, which, not having been encountered previously, were given reasonable values based on bond lengths. The results of these calculations listed in Table II were correlated with the only available experimental data—ultraviolet[3] and ^{15}N nmr spectra.[7]

Discussion of Results

Uv Spectra.—A strong case has been made for considering both observed uv absorption bonds to be $\pi \rightarrow \pi^*$ in origin.[3] This enhances the significance of our calculations which give only the values of singlet and triplet $\pi \rightarrow \pi^*$ transitions for thiotrithiazyl cation. Our assumption of C_{2v} symmetry for thiotrithiazyl

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[1] Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; see Abstract M44.

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TABLE II

RESULTS OF CALCULATIONS

π-Electron density		Bond order		Transition energy, eV		λ, Å	Oscillator strength	Symmetry	Polarization
q_1	1.4174	P_{12}	0.4954	$^1E_{5\to6}$	3.644	3403	0.49	B_2	Y
q_2	1.3776	P_{23}	0.6426	$^1E_{5\to7}$	4.619	2684	0.72	A_1	X
q_3	1.2496	P_{34}	0.4810	$^1E_{4\to6}$	4.655	2669	0.88	A_1	X
q_4	1.6641	P_{45}	0.2660						

imposes the restriction that a maximum of three types of transition will be symmetry allowed. Our calculations give three transitions that correspond closely with those observed experimentally: $^1E_{5\to6}$, $^1E_{5\to7}$, and $^1E_{4\to6}$. The latter two transitions are very close to each other in energy and intensity and have the same predicted polarization. The observed shorter wavelength band may then possibly be an overlapping doublet. The observed spectra, which show some variation with solvent, are tabulated along with a mean value for the solution spectra. Correlation with the calculated transition energies is remarkably good and may be taken as evidence of a well-developed π-electron system including the disulfide bond. The calculated oscillator strengths are higher than the observed values, particularly for the long-wavelength transition.

TABLE III[3]

OBSERVED UV SPECTRA

Solvent	Band 1[a]	Band 2[a]
HCl (12 M)	3420 (0.051)	2700 (0.40)
H_2SO_4 (18 M)	3320 (0.049)	2600 (0.41)
$HClO_4$ (12 M)	3340	2580
Mean	3360	2627
Calcd	3403 (0.49)	2684 (0.72) 2669 (0.88)

[a] Wavelength given in ångströms; oscillator strength in parentheses.

^{15}N Nmr Spectra.—An nmr study of the ^{15}N thiotrithiazyl cation in 70% nitric acid showed two multiplets that were readily assigned to N(1) and N(3) on the basis of multiplicity and relative areas. The positions of these absorptions, relative to $^{15}NH_4^+$, were −343 ppm for the N(1) triplet and −355 ppm for the N(3) doublet. Qualitatively this implies that N(1) has less π bonding around it and a higher π-electron density. The calculated values support this: N(1) ($P_{12} + P_{27}$), 0.991, q_1, 1.4174; N(3) ($P_{23} + P_{34}$), 1.124, q_3, 1.250.

Bonding.—The dominant features of the structure of thiotrithiazyl are its planarity and its short N–S bonds. The results of our calculations encourage us to accept the assumptions of conjugation throughout the entire ring, although limited in extent across the S–S bond, and of donation of two electrons from each of the sulfurs to the π-electron system. Undoubtedly the 3d orbitals of sulfur must participate in bonding in this molecule, but it does not seem useful at this stage to try to describe a scheme for the bonding based on the geometric requirements of $3d_{xz}$ or $3d_{yz}$ orbitals or to envision a particular hybridization involving 3d (and possibly 4s) orbitals because such speculation is not subject to test or verification. Similarly the assignment of sp hybridization to N(3)[3] does not afford any advantage over sp^2 or some intermediate hybridization in terms of the semiempirical methods being employed in our calculations. The treatment of the disulfide bond that we have used should hopefully be effective in studies of the related 1,2-dithiolium ion systems.[8]

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The Structure of the Oxyhyponitrite Ion

BY DAVID N. HENDRICKSON AND WILLIAM L. JOLLY

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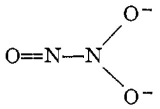
The structure of the anion of Angeli's salt[1] ($Na_2N_2O_3$) has never been unequivocally determined. Three structures have been considered



I

$O{=}N{-}O{-}N^-{-}O^-$

II

$^-O{-}N{=}N{-}O{-}O^-$

III

The ultraviolet spectrum,[2] the infrared spectrum,[3] the heat of formation,[4] and the pK values[5] have all been interpreted as favoring structure I. In this study, we have obtained further evidence for structure I by asymmetrically labeling the $N_2O_3^{2-}$ ion with ^{15}N

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