also give further information. Experiments with this objective have been in progress.

Acknowledgment. Several perceptive comments and criticisms by Professor A. J. Bard and the reviewers of an earlier version of this manuscript helped us to formulate our speculations more clearly.

Registry No. $Fe(CN)_6^{4-}$, 13408-63-4; $Fe(CN)_6^{3-}$, 13408-62-3; PVP, 9003-47-8; graphite, 7782-42-5.

Preparation and Crystal and Molecular Structure of $S_4N_4H^+BF_4^-$. Molecular Orbital Study of the Protonation of Tetrasulfur Tetranitride

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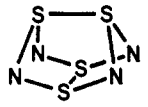
Abstract: The reaction of tetrasulfur tetranitride with tetrafluoroboric acid diethyl etherate in methylene chloride solution produces $S_4N_4H^+BF_4^-$, the first simple salt of S_4N_4. the crystal and molecular structure of $S_4N_4H^+BF_4^-$ has been determined by X-ray crystallography. Crystals of the compound are monoclinic, space group $P2_1/n$, a = 6.563 (2) Å, b = 11.717 (2) Å, c = 11.409 (2) Å, β = 101.63 (2)°, V = 859.3 (6) Å^3, and Z = 4. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares procedures to give a final R of 0.042 for 1428 observed reflections. The structure of the $S_4N_4H^+$ cation consists of a boat-shaped 8-membered ring with approximately coplanar (to within 0.02 Å) sulfur atoms. The reasons for the structural rearrangement which the protonation of S_4N_4 induces are discussed in the light of MNDO molecular orbital calculations on a number of idealized conformations of $S_4N_4H^+$ unit.

In spite of the lack of evidence usually regarded as diagnostic of aromatic behavior, e.g., heats of formation and[2] diamagnetic ring currents,[3] the descriptions of the electronic structures of cyclic binary sulfur nitride derivatives often allude to their aromatic character. The empirical rules devised by Banister[4] and the symmetry-based molecular orbital arguments of Gleiter[5] and of Gimarc and Trinajstić[6] emphasize the preponderance of cyclic π systems containing $4n + 2$ electrons. However, the need for such a complement vanishes in molecules possessing less than 3-fold symmetry.[7] Recently several cyclic molecules containing $4n$ π electrons have been reported.[8,9]

The observed structure of tetrasulfur tetranitride (**1**) has long



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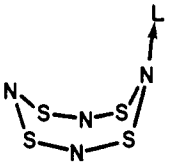

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been regarded as a manifestation of the $4n + 2$ rule. In his extended Hückel analysis of S_4N_4, Gleiter pointed out that the 12-π-electron ground state of a planar S_4N_4 would be orbitally degenerate and as such unstable with respect to Jahn–Teller distortion.[10] However, as indicated above, there is no a priori reason to suppose that the cage shape will be more stable than a cyclic structure if the symmetry of the molecule is lowered by the attachment of an exocyclic ligand. Certainly the structural evidence obtained from numerous Lewis acid adducts, e.g., S_4N_4·A (**2**),[11-17] indicates that the coordination of a lone pair of electrons on nitrogen to an acceptor site is a sufficient perturbation to cause the cage to open. However, the electronic factors that dictate this conformational change have not hitherto been addressed. In order to develop some understanding of this rearrangement we have carried out a synthetic, structural, and molecular orbital (MNDO) study of $S_4N_4H^+BF_4^-$, the first simple salt of S_4N_4 to be structurally characterized. The results provide an insight into the factors that govern the conformational preferences of sulfur–nitrogen rings.

Experimental Section

Reagents and General Procedures. Tetrasulfur tetranitride, S_4N_4, was prepared according to a published method.[18] Fluoroboric acid–diethyl ether complex was obtained commercially (Aldrich) and used without further purification. Methylene chloride (reagent grade) was dried by distillation from phosphorus pentoxide. Infrared spectra were recorded on Nujol mulls (CsI cells) by using a Perkin-Elmer 467 grating spec-

(1) (a) University of Arkansas. (b) University of Calgary. (c) Permanent address: Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.
(2) Only for S_4N_4 has thermochemical data been reported. See: Barker, C. K.; Cordes, A. W.; Margrave, J. L. *J. Phys. Chem.* **1965**, *69*, 334.
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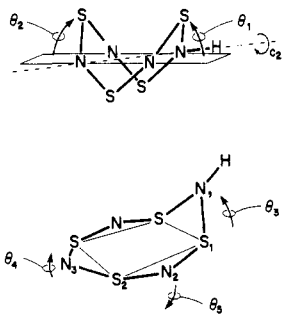

Figure 1. Definition of the atom numbers and dihedral angles θ_1–θ_5 used in the molecular orbital analysis of $S_4N_4H^+$.

trophotometer. UV–visible spectra were recorded on a Cary 219 spectrophotometer. Chemical analyses were performed by MHW Laboratories, Phoenix, AZ.

Preparation of $S_4N_4H^+BF_4^-$. An excess of $HBF_4{\cdot}Et_2O$ (500 mg, 3.01 mmol) was added dropwise via a pipet under a stream of nitrogen to a solution of S_4N_4 (500 mg, 2.72 mmol) in 50 mL of methylene chloride. The deep burgundy red solution so obtained was then cooled to 0 °C overnight. The red crystalline precipitate of $S_4N_4H^+BF_4^-$ (560 mg, 2.06 mmol, 77%) was collected by filtration under nitrogen and dried in vacuo. Crystals of $S_4N_4H^+BF_4^-$ are extremely air sensitive, reverting to S_4N_4 on contact with moisture: IR (Nujol mull) 3180 (s, br), 1303 (w), 1291 (w), 1278 (w), 1132 (s), 1050 (vs, br), 990 (s), 828 (vw), 791 (m), 772 (m), 694 (m), 629 (s), 605 (vw), 570 (w), 525 (vs), 396 (s), 382 (w), 362 (m), 258 (m) cm^{-1}; UV–vis (CH_2Cl_2), λ_{max} (log ϵ) 474 (3.1), 325 (3.7) nm. Anal. Calcd for $S_4N_4HBF_4$: H, 0.37; N, 20.59; S, 47.14. Found: H, 0.6; N, 20.39; S, 46.89.

X-ray Analysis of $S_4N_4H^+BF_4^-$. A crystal suitable for X-ray work was grown from methylene chloride solution and sealed under argon in a glass capillary. All data were collected by using an Enraf-Nonius CAD-4 diffractometer and graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The 0.5 × 0.6 × 0.7 mm crystal used for data collection was mounted with the 3-6-2 vector approximately parallel to the Φ axis. A least-squares calculation using the diffractometer settings for 25 (28° < 2θ < 30°) carefully centered reflections gave the following cell parameters (at 21 °C): a = 6.563 (2) Å, b = 11.717 (2) Å, c = 11.409 (2) Å, β = 101.63 (2)°, V = 859.3 (6) Å^3. For $S_4N_4HBF_4$ with M_r = 272.10 and Z = 4, D_c = 2.10 g cm^{-1} and F_{000} = 536.

Systematic absences of $h0l$ for $h + l$ odd and $0k0$ for k odd uniquely indicated the space group $P2_1/n$. A total of 2448 unique reflections were measured by using θ–2θ scans for values of 2θ ranging from 4 to 60° with h = 0 to 9, k = 0 to 16, and l = −16 to 16. The scan range was 1.2 + 0.35 tan θ and the scan speeds varied from 4 to 20° min^{-1}. A total of 888 reflections had $I < 3\sigma(I)$ and were considered unobserved. The intensities of three reflections (−3,5,−3, −2,−2,−6, 3,−6,−2), which were measured periodically during the data collection, revealed a loss of intensity (total = 14.9%) attributed to crystal decomposition; a simple correction based on the intensities of monitor reflections was made. An empirical absorption correction (μ = 10.85 cm^{-1}) based on ψ scans gave correction factors that varied from 1.00 to 1.03.

The structure was solved by direct methods (MULTAN78)[19] and refined by Fourier and least-squares techniques. The final full-matrix least-squares refinement based on $(|F_o| - |F_c|)^2$ included 1428 observed relections and 122 parameters (positional and anisotropic thermal parameters for all non-hydrogen atoms; positional and isotropic thermal parameters for the hydrogen atom) and a parameter:reflection ratio of 1:11.7. The weighting scheme based on counting statistics (p = 0.05) gave no systematic variation of $\Delta F/\sigma(F)$ as a function of either F or sin θ. No secondary extinction correction was made. In the final cycle of refinement the maximum shift/error was 0.005, R = 0.042, R_w = 0.054, and GOF = 1.61. The final difference map had a maximum value of 0.53 e Å^{-3}. Neutral atom scattering factors corrected for real and imaginary anomalous dispersion corrections were used.[20] The computer programs used were those provided by the Enraf-Nonius SDP program package.

Computational Method and Models. The use of the MNDO (modified neglect of diatomic overlap) method[21] and the DFP geometry optimization algorithm[22] for the study of binary sulfur–nitride molecules has been reported by several groups.[23-25] It reproduces well the molecular orbital energies and compositions obtained by ab initio methods[23] and provides reliable predictions regarding conformational preferences.[23,24] In the study of $S_4N_4H^+$ we have examined a wide range of idealized geometries, all of which could be interconverted by the varition of five dihedral angles θ_1–θ_5. To clarify the meaning of these parameters and the geometries that they generate, we illustrate several examples (see Figure 1). The first model (I) studied possessed C_2 symmetry and consisted of a planar arrangement of nitrogen atoms with the dihedral angles between this plane and the planes of the two symmetry-unrelated NSN planes designated as θ_1 and θ_2. Protonation of S_4N_4 with retention of the cage structure could then be simulated by setting $\theta_1 = \theta_2$ = 90°. All other bond lengths and angles were then released to optimize independently (within the confines of C_2 symmetry). This model could be converted into a planar C_{2v} arrangement (model II) by setting $\theta_1 = \theta_2$ = 0°. A third model (III) was generated from the C_{2v} structure by rotating the plane of the S–N(H)–S group away from the coplanar SNSNSNS fragment, this dihedral angle being defined as θ_3. Finally, a fully optimized C_s geometry (model IV) was obtained by allowing all nitrogen atoms to move independently of the four coplanar sulfur atoms. The dihedral angles θ_3, θ_4, and θ_5 defined these motions. In all the calculations the bonds to the protonated nitrogen were held coplanar. The atom numbering scheme used throughout the discussion is shown in Figure 1.

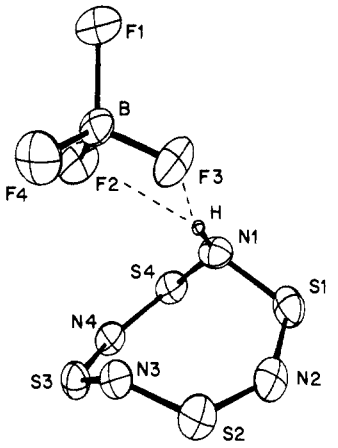

Figure 2. ORTEP drawing of $S_4N_4H^+BF_4^-$ (30% probability ellipsoids) illustrating the orientation of a cation–anion pair and the boat-like conformation of the S_4N_4 ring.

Results and Discussion

Preparation of $S_4N_4H^+BF_4^+$. The reactions of S_4N_4 with Lewis acids have been extensively studied.[26] However, its behavior with protic acids is less well documented. In 1956 MacDiarmid reported the formation of a red solid upon passing dry hydrogen chloride through a solution of S_4N_4 in carbon tetrachloride, but the material rapidly decomposed to give S_4N_3Cl.[27] At the time he suggested that the intermediate compound was $S_4N_4{\cdot}HCl$, but no evidence for this formulation was provided. More recent studies on the reactions of S_4N_4 with fluorosulfuric[28] and trifluoromethanesulfonic[29] acid have also indicated the transitory existence of red solids and solutions, but no protonated materials were isolated. In the course of our work we have found that dilute solutions of tetrafluoroboric acid (as its diethyl ether adduct) in

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Table I. Final Fractional Coordinates and B_{eq} Values for $S_4N_4H^+BF_4^-$ with Esd's in Parentheses

atom	x/a	y/b	z/c	B_{eq}[a]
S1	0.4755 (7)	0.2602 (4)	0.4041 (3)	5.32 (9)
S2	0.3573 (7)	0.1104 (3)	0.5849 (3)	5.22 (9)
S3	0.0003 (6)	0.2563 (3)	0.5875 (3)	4.63 (7)
S4	0.1215 (7)	0.3983 (3)	0.4034 (3)	4.72 (8)
N1	0.367 (2)	0.3713 (9)	0.4596 (8)	4.2 (2)
N2	0.459 (2)	0.147 (1)	0.480 (1)	4.8 (3)
N3	0.211 (2)	0.1982 (9)	0.6316 (8)	4.0 (2)
N4	−0.025 (2)	0.3404 (9)	0.4807 (9)	4.5 (3)
B	0.486 (3)	0.552 (1)	0.239 (1)	4.1 (3)
F1	0.362 (1)	0.4616 (7)	0.2007 (7)	5.5 (2)
F2	0.673 (1)	0.5215 (7)	0.3073 (7)	5.4 (2)
F3	0.384 (1)	0.6240 (7)	0.3060 (6)	5.9 (2)
F4	0.518 (2)	0.6129 (8)	0.1397 (6)	6.9 (2)

[a] B_{eq} = isotropic B values equivalent to the anisotropic ellipsoids = $^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac \cos \beta)$.

Table II. Bond Distances (Å) and Angles (deg) for $S_4N_4H^+BF_4^-$ [a]

atom 1	atom 2	dist	atom 1	atom 2	dist
S1	N3	1.569 (2)	S4	N1	1.643 (3)
S1	N4	1.539 (3)	S4	N4	1.595 (3)
S2	N1	1.656 (3)	B	F1	1.373 (3)
S2	N2	1.582 (2)	B	F2	1.386 (3)
S3	N2	1.573 (2)	B	F3	1.378 (3)
S3	N3	1.555 (2)	B	F4	1.356 (3)
N1	H	0.72 (3)	H	F2	2.38 (3)
			H	F3	2.19 (3)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
N3	S1	N4	118.8 (1)	F1	B	F2	110.0 (2)
N1	S2	N2	109.7 (1)	F1	B	F3	109.1 (2)
N2	S3	N3	119.3 (1)				
N1	S4	N4	111.1 (1)	F1	B	F4	109.7 (2)
S2	N1	S4	118.4 (1)	F2	B	F3	107.0 (2)
S2	N2	S3	138.9 (2)	F2	B	F4	110.4 (2)
S1	N3	S3	138.1 (1)	F3	B	F4	110.6 (2)
S1	N4	S4	138.0 (2)	N1	H	F2	149 (3)
S2	N1	H	113 (2)	N1	H	F3	152 (3)
S4	N1	H	121 (2)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

methylene chloride provide a suitable medium for the clean protonation of S_4N_4; the red crystalline salt $S_4N_4H^+BF_4^-$ readily precipitates upon cooling the mixture. We note that the salt is rapidly hydrolyzed (to S_4N_4) by atmospheric moisture; evidently S_4N_4 is a relatively weak base (i.e., weaker than water).

Molecular Structure of $S_4N_4H^+BF_4^-$. Crystals of the title compound consist of $S_4N_4H^+$ cations and BF_4^- anions linked by hydrogen bonds from H to F2 and F3 (d(H···F) = 2.38 (3) and 2.19 (3) Å, respectively), making N–H···F angles near 150° in each case. The relative orientation of the cation anion pair and the boat-like conformation of the eight-membered ring are illustrated by the ORTEP drawing displayed in Figure 2. Atomic coordinates for both the cation and the anion are listed in Table I, and bond distance and angle information is given in Table II. Table III provides a compendium of the mean values of the structural parameters for all S_4N_4·A structures reported to date. As the data in this latter table indicate, there is a remarkable regularity in the structural features of the different adducts; the conformational consequences of the complexation of S_4N_4 at nitrogen do not appear to depend significantly on steric or packing effects. In the case of $S_4N_4H^+$ the four sulfur atoms are coplanar to within 0.02 Å, with the nitrogen atoms N1–N4 lying respectively −0.845 (2), 0.221 (2), −0.502 (2), and 0.242 (3) Å from this plane. The geometry at the protonated nitrogen is almost planar (sum of angles at N1 = 352°). The reasons for the observed bond length variations, e.g., the long N1–S1 and short

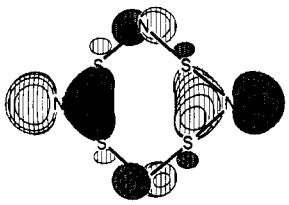
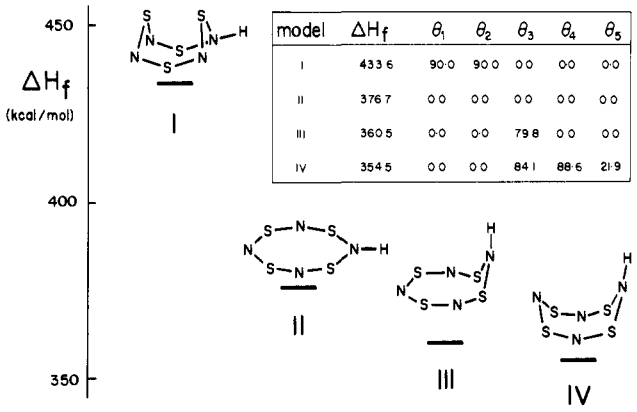


Figure 3. The 4e′ orbital (MNDO) of S_4N_4. It is with this orbital that an incoming proton binds.



model	ΔH_f	θ_1	θ_2	θ_3	θ_4	θ_5
I	433.6	90.0	90.0	0.0	0.0	0.0
II	376.7	0.0	0.0	0.0	0.0	0.0
III	360.5	0.0	0.0	79.8	0.0	0.0
IV	354.5	0.0	0.0	84.1	88.6	21.9

Figure 4. Heats of formation (ΔH_f, kcal/mol) for various idealized conformations of $S_4N_4H^+$.

S2–N2 bonds (see Table III), and the conformation of the 8-membered ring will be discussed in the next section.

Electronic Structure of $S_4N_4H^+$. Many theoretical studies of the S_4N_4 molecule have been carried out.[10,30] While the results differ in detail, the existence of at least a partial cross-ring S–S bond is generally acknowledged. That these transannular interactions are weak is demonstrated by the effect of oxidation of S_4N_4 to $S_4N_4^{2+}$,[31] which causes a collapse of the cage structure to give an essentially planar 8-membered ring. Recent semiempirical[32] and ab initio HFS[33] molecular orbital calculations on the D_{2d} and D_{4h} conformations of $S_4N_4^{2+}$ have determined that the stability of the latter structure is a result of its strong π network. In the case of the Lewis acid adducts **2** and $S_4N_4H^+$, the reasons for the opening of the S_4N_4 cage to give a boat-shaped ring are more subtle. The interpretation of their structures is best approached by an examination of the molecular orbital makeup of a series of key model compounds (models I–IV defined above). A stepwise analysis of this series reveals the electronic factors that mold the final conformation.

We begin our discussion with some comments on the formation of the donor–acceptor bond. The development of a bond between S_4N_4 and a proton involves those orbitals on S_4N_4 that are energetically and directionally disposed to interact with the 1s orbital of an approaching proton, i.e., the high-lying "lone pairs" on nitrogen. In agreement with our earlier prediction[33] it is one of the 4e orbitals of S_4N_4[30c] that is the primary participant in σ-bond formation.[34] However, in addition to exhibiting lone-pair

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(34) Recent X-ray fluorescence studies on S_4N_4 have confirmed that the HOMO of S_4N_4 is localized predominantly on nitrogen. See: Dolenko, G. N.; Zibarev, A. V.; Pykhov, V. *Z. Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1981**, *26*, 795. However, we point out that this orbital $(2a_2)^{30c}$ is not correctly oriented to interact with an approaching proton and makes little contribution to the bonding process.

Table III. Mean[a] SN Distances (Å) and Valence and Dihedral[b] Angles (deg) in Molecules of the Type $S_4N_4 \cdot A$

	A							
	H^+	SO_3	FSO_2NCO	BF_3	$SbCl_5$	$FeCl_3$	AsF_5	$TaCl_5$
N1–S1	1.650	1.678	1.677	1.659	1.69	1.662	1.659	1.65
S1–N2	1.589	1.589	1.589	1.593	1.59	1.578	1.584	1.56
N2–S2	1.538	1.547	1.547	1.546	1.57	1.559	1.540	1.54
S2–N3	1.562	1.578	1.578	1.584	1.58	1.576	1.567	1.60
N1	118.4	116.1	116.3	112.7	113	109.8	113.6	110.7
S1	110.4	108.2	108.1	110.2	112.5	110.7	109.9	110.2
N2	138.4	137.8	138.3	137.5	137	137.6	139.3	139.9
S2	119.0	119.6	120.4	120.7	121	119.5	119.5	119.9
N3	138.1	139.3	140.0	137.9	144	137.3	138.7	133.8
θ_3	88.8	84.0	83.2	86.4	89.9	86.8	87.6	89.6
θ_4	64.4	57.4	50.9	57.4	45.1	59.7	54.6	53.6
θ_5	24.7	23.2	26.5	23.1	29.5	28.1	26.6	31.5
ref	this work	11	12	13	14	15	16	17

[a] Average values of two chemically equivalent parameters. [b] Dihedral angles, as defined in the text, were measured from the mean plane of the four sulfur atoms.

Table IV. Orbital Energies and Bond Orders[a] for the π Molecular Orbitals of $S_4N_4H^+$ (Model II)

		$2c_{ir}c_{is}$			
orbital	ϵ_i, ev	N1–S1	S1–N2	N2–S2	S2–N3
$5b_1$	−5.656	−0.06	−0.19	0.35	−0.36
$3a_2$	−6.784		−0.32	0.39	
$4b_1$	−12.638	−0.40	−0.15	0.08	−0.23
$2a_2$	−15.317		0.02	0.01	
$3b_1$	−15.792	−0.09	0.05	−0.01	0.02
$2b_1$	−18.689	0.44	0.08	−0.05	0.25
$1a_2$	−19.853		0.34	0.37	
$1b_1$	−21.036	0.11	0.22	0.33	0.32
ρ_{SN} (π)		0.00	0.30	0.53	0.13
total ρ_{SN} ($\sigma + \pi$)		0.80	1.22	1.37	1.09

σ and π Charge Densities for $S_4N_4H^+$ (Model II)

	H	N1	S1	N2	S2	N3
$q(\sigma)$	0.23	3.79	3.53	4.49	3.57	4.28
$q(\pi)$		1.97	1.69	1.17	1.34	1.65

[a] See ref 35.

characteristics this orbital (See Figure 3) also provides an antibonding contribution to the transannular S–S bond. Thus, the evolution of this orbital into the strongly localized N–H σ bond of $S_4N_4H^+$ (model I) leads to a net strengthening of the S–S bonds; the S–S bond order[35] increases from 0.29 in S_4N_4 (with $\theta_1 = \theta_2 = 90°$)[36] to 0.34 in $S_4N_4H^+$ (model I). However, despite the increased strength of the S–S bonds, the cage structure of $S_4N_4H^+$ is unstable with respect to the planar conformation (see Figure 4).

The reasons for the relative stability of the planar conformation (model II) can be traced to the influence of the proton on the σ and π networks of the S_4N_4 skeleton. Table IV provides a bond order and charge density analysis of this model. First it should be noted that protonation of S_4N_4 lowers the molecular symmetry and lifts the orbital degeneracy of the 12-π-electron ground state. Examination of the charge densities[30] listed in Table IV reveals an important difference in the polarization of electrons in the σ and π systems. In the σ system, the presence of a proton bound to nitrogen draws charge away from this atom into the N–H σ bond. In response to this perturbation there is a migration of charge in the π system back toward this nitrogen. Thus the π charge at N1 corresponds to a net transfer of 0.97 electron, while the π charges at N2 and N3 suggest the transfer of only 0.17 and 0.65 electron. The bonding characteristics of the individual π orbitals provide further insight into the structure of the π system.

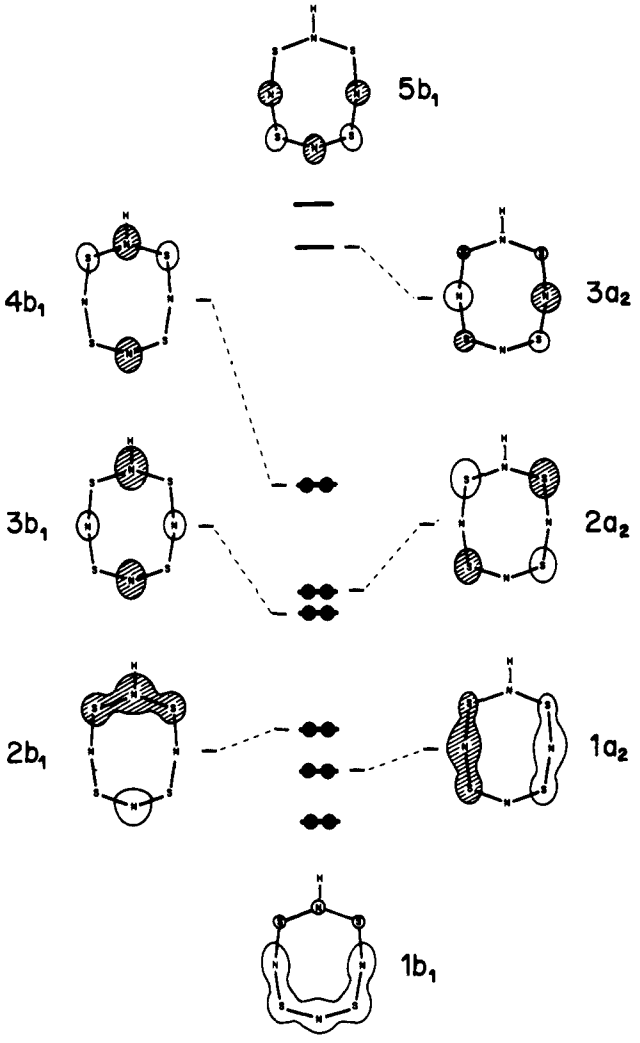

Figure 5. Distributions and relative energies of the π molecular orbitals of $S_4N_4H^+$ (model II). See Table IV for eigenvalues.

Figure 5 illustrates the distributions and nodal properties of these orbitals. There are a total of six occupied orbitals: three bonding ($1b_1$, $2b_1$, $1a_2$), two nonbonding ($3b_1$, $2a_2$), and one antibonding ($4b_1$). As Table IV indicates, the total π bond orders[35] around the ring are determined, in large part, by the contribution of the $4b_1$, which concentrates antibonding electron density into the N1–S1 and, to a lesser extent, the S2–N3 regions and offsets the bonding effects of the $2b_1$. The net π bonding then stems from the contributions of the $1b_1$ and $1a_2$ orbitals, one of which ($1b_1$) is strongly bonding over the entire SNSNSNS fragment, while

(35) Bond orders and charge densities calculated as in: Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Dalton. Trans.* **1973**, 838.

(36) In the structure of S_4N_4 itself the observed dihedral angles range from 87.3° to 88.8°. See: (a) Delucia, M. L.; Coppens, P. *Inorg. Chem.* **1978**, *17*, 2336. (b) Sharma, B. D.; Donohue, J. *Acta Crystallogr.* **1963**, *16*, 891.

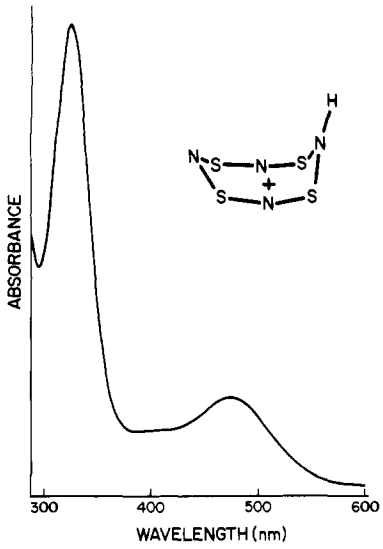

Figure 6. UV–visible spectrum (in CH_2Cl_2) of $S_4N_4H^+BF_4^-$.

the other ($1a_2$) is restricted to the S1–N2 and N2–S2 bonds. As a result, the latter bonds are particularly strong; their π bond orders[35] are commensurate with that found for planar $S_4N_4^{2+}$ (0.36).[37] In essence, the effect of protonation of a planar S_4N_4 is to restrict the influence of the antibonding electrons by localizing them in one region of the molecule, i.e., the N1–S1 bonds. The remainder of the π network is simultaneously strengthened, so that the planar SNSNSNS fragment is sufficiently robust to withstand any potential gains in σ bonding that would accompany a puckering of the molecule into C_2 symmetry (model I).

The above description of the planar model II provides a rationale for its stability relative to model I. However, because of the localized nature of the $4b_1$ orbital, the bonds to the protonated nitrogen are unacceptably weak. A structural modification that alleviates this situation while maintaining the integrity of the π system in the remainder of the ring involves a displacement of the NH group from the molecular plane. At the energy minimum associated with this process (model III), the $2a_2$ orbital of model II is transformed into a lone-pair orbital located primarily on the protonated nitrogen. The remaining π orbitals of II retain their π-like character in III. As a result of the redistribution of electrons between the σ and π networks the N1–S1 bonds are strengthened; the total ($\sigma + \pi$) bond order[35] is increased from 0.80 (model II) to 0.90 (model III). There is also a concomitant weakening of the S1–N2 bonds; their total ($\sigma + \pi$) bond order[35] is reduced from 1.22 to 1.07. The changes in the N2–S2 and S2–N3 bonds are minor. From an energetic standpoint, the heat of formation of the molecule is lowered by ca. 15 kcal mol^{-1}.

Additional structural refinements of model III can be envisaged that further lower the energy of the system. Within the seven-atom SNSNSNS fragment, the S2–N3 π bonds are relatively weak and puckering of the ring in this region is to be expected. Certainly the actual structure of $S_4N_4H^+$ illustrates this effect. A calculation involving the complete optimization of θ_3, θ_4, and θ_5 reduces the value of ΔH_f by a further 6 kcal mol^{-1} and provides a final geometry (model IV) that resembles the observed conformation (see Table III). In fact, in view of the shallowness of the conformational energy surface with respect to changes in θ_4 and θ_5, the correspondence between the predicted and observed conformations is remarkably good.

Electronic Spectrum of $S_4N_4H^+$. Like most Lewis acid complexes of S_4N_4 the protonated salt $S_4N_4H^+BF_4^-$ is deep red in color. The UV–visible spectrum of this compound, as illustrated in Figure 6, exhibits two distinct low energy absorption maxima at 325 and 474 nm. In previous studies of the electronic spectra of planar or nearly planar sulfur–nitrogen ring systems ($S_3N_3^-$,[38] $S_4N_4^{2+}$,[33] $S_4N_3^+$,[39] S_4N_2,[23] and $R_2PS_2N_3$[8]), the electronic transitions responsible for their characteristic colors have been shown to be of the $\pi^* \rightarrow \pi^*$ type. In the present case, a similar description can be invoked, but the designation π can retain only a local significance. A comparison of the frontier orbitals of models II, III, and IV shows that the LUMO($3a_2$) and 2LUMO($5b_1$) and the HOMO($4b_1$) and 2HOMO($2a_2$) of II all evolve, without change in ordering, into predominantly π-like orbitals in III and IV. Thus, while these results do not allow a definite assignment of individual transitions (configuration interaction may well be important[39]), it is reasonable to suggest that the two low-energy absorptions in $S_4N_4H^+$ are $\pi^* \rightarrow \pi^*$ type excitations.

Summary

MNDO molecular orbital calculations indicate that, in contrast to S_4N_4 itself, the 12-π-electron ground state of a planar $S_4N_4H^+$ is more stable than a cage structure. The relative stability of the planar conformation is made possible by the localization of π^* electrons into the skeletal bonds to the protonated nitrogen. In this way the π network of the SNSNSNS fragment is strengthened at the expense of the S–N(H) bonds. Puckering of the ring causes a redistribution of electrons in the σ and π systems and leads to a net stabilization of the molecule. We conclude by noting that it is the molecular orbital distributions of the uppermost antibonding electrons, i.e., those that impart electron-rich character to the molecule, which decide its structural fate.

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Supplementary Material Available: Tables of anisotropic thermal parameters (S1) and observed and calculated structure factor amplitudes (S2) (16 pages). Ordering information is given on any masthead page.

(37) This is an MNDO estimated obtained from a calculation on a D_{4h} model.

(38) (a) Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1979**, *101*, 4517. (b) Waluk, J. W.; Michl, J. *Inorg. Chem.* **1981**, *20*, 963.

(39) Waluk, J. W.; Michl, J. *Inorg. Chem.* **1982**, *21*, 556.