the accumulated experimental evidence is compelling: a β-bromo substituent provides, especially in solution reactions when HBr concentration is minimized, substantial neighboring group participation in radical brominations, facilitating hydrogen abstraction and constraining configuration at the vicinal site. Some product can be formed by other reaction pathways under certain conditions, but the direct, favorable effect of β-bromo accounts for most of the product.

We believe that the controversy over the interpretation of the experimental results should wither, just as has the controversy earlier over the results themselves.

Bromo Bridging: Single or Double Potential Energy Minimum Model?

To date, none of the product studies concerned with bromo bridging has provided evidence that could govern a choice between alternative descriptions of the bridged species: a single potential energy minimum or a double minimum with shuttling between them at rates over 10^{10} s^{-1}. Since data for chloro bridging required a double minimum description with rapid shuttling,[4e] the

same model for bromo bridging seems reasonable for the present.

Although the ESR spectrum published for **17** was

17
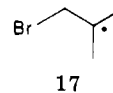
interpreted in terms of an unsymmetrical bridge, with stronger bonding of Br to primary C than to tertiary C,[7a] it provided no evidence for $(CH_3)_2CBrCH_2$· and therefore no guide to the double vs. single minimum dilemna.

A CIDNP experiment indicated that $BrCH_2CH_2$· has an unsymmetrical structure.[8] Although there is no evidence for bridging from this experiment, it is reasonable to ascribe an unsymmetrical bridge, and thus a double-minimum model, to this species. This interpretation makes the description of 2-bromoethyl and 2-chloroethyl[31] systems consistent.

(31) Chen, K. S.; Elson, I. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 5341–9.

Electron-Rich Sulfur–Nitrogen Heterocycles

Tristram Chivers

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received June 2, 1983 (Revised Manuscript Received October 11, 1983)

The chemistry of inorganic heterocycles has a long history. The first representatives of the cyclothiazenes and cyclophosphazenes,[1a] S_4N_4[1b] and $(NPCl_2)_3$,[2] were discovered in the previous century and borazine ($B_3N_3H_6$) was isolated in 1926.[3] One aspect of the behavior of such heterocycles that has particularly intrigued chemists is the extent and consequences of delocalized π bonding in these ring systems. The concept of aromaticity has played a prominent role in these discussions. For example, borazine has been described as the inorganic analogue of benzene. However, the polarization of the π-electron density, which arises from the electronegativity difference between boron and nitrogen, results in much greater chemical reactivity than is observed for aromatic organic compounds. the possibility of aromatic behavior has also been a central issue in studies of cyclophosphazenes, $(NPX_2)_n$, for which an extensive homologous series is known ($n = 3$–17).[4]

Both borazine and the cyclophosphazenes are π-*electron-precise* molecules, i.e., the number of π electrons is equal to the number of atomic centers in the ring. By contrast, cyclothiazenes are π *electron rich*; i.e., the number of π electrons exceeds the number of atomic centers in the ring. In 1972 Banister proposed

that planar sulfur–nitrogen heterocycles belong to a class of "electron-rich aromatics" which conform to the well know Hückel $(4n + 2)$ π-electron rule.[5] On the reasonable assumption that each sulfur contributes two electrons and each nitrogen one electron to the π system, S_2N_2 (6π), $S_4N_3^+$ (10π), and $S_5N_5^+$ (14π) were cited as examples in support of this contention.

Since then our knowledge of electron-rich heterocycles has been considerably enhanced by the discovery of numerous new sulfur–nitrogen rings and heterocyclothiazenes (Figure 1). The development of the subject has been accelerated by the application of physical techniques, particularly X-ray crystallography and, to a lesser extent, ^{15}N NMR and Raman spectroscopy, to structural determinations. Concomitantly, theoretical treatments have reached the stage where a good understanding of the thermodynamic stability, chemical reactivity, and intense colors of these electron-rich compounds has emerged and UV–visible and MCD spectroscopic measurements have provided corroborative evidence for the MO calculations.

Consistent with the philosophy of our research efforts, this Account illustrates the main features of the

Tristram Chivers, a native of Bath, England, received his B.Sc., Ph.D., and D.Sc. degrees all from the University of Durham, England. He did postdoctoral work during the years 1964–1969 at the Universities of Cincinnati, Sussex, and British Columbia. He joined the faculty at the University of Calgary in 1969, was Head of the Chemistry Department (1977–1982), and now continues as Professor of Chemistry.

(1) (a) The terms cyclothiazene and cyclophosphazene refer to ring compounds formed by the oligomerization of the monomer units SN or R₂PN, respectively. (b) Gregory, W. *J. Pharm.* (*Antwerp*) **1835**, *21*, 315; *22* 301.
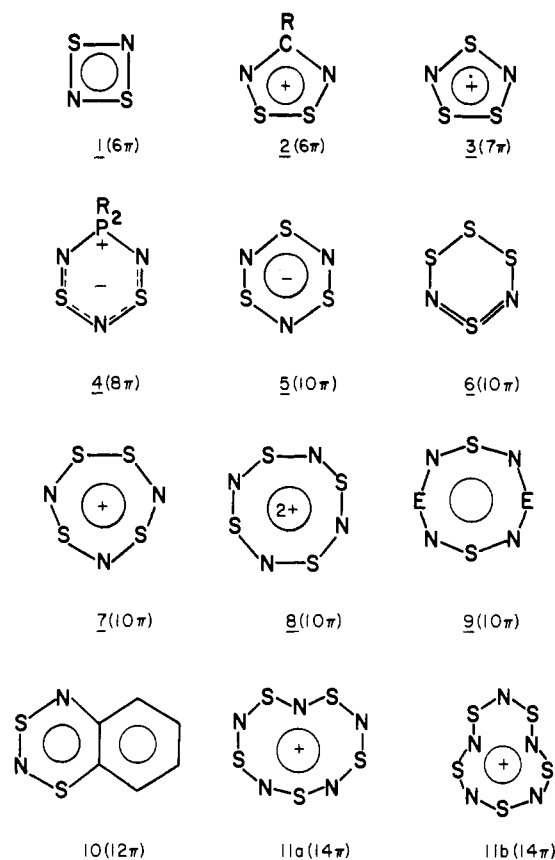(2) Liebig, J.; Wöhler, F. *Liebigs Ann. Chem.* **1834**, *11*, 139. Rose H. *Ibid.* **1834**, *11*, 131.
(3) Stock, A.; Pohland, E. *Chem. Ber.* **1926**, *59*, 2215.
(4) Krishnamurthy, S. S.; Sau, A. C.; Woods, M. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 41.
(5) Banister, A. J. *Nature* (*London*) **1972**, *237*, 92.

Figure 1. Schematic representation of the structures of planar cyclothiazenes and related heterocycles. Details of the X-ray structural investigations can be found in the following references: 1,[9] 2 (R = CCl$_3$,[10a] Cl[10b]), 3,[11] 4 (R = Ph),[12] 5,[13] 6,[14] 7,[15] 8,[16] 9 (E = CPh),[17] 10,[18] and 11[19].

chemistry of electron-rich sulfur–nitrogen heterocycles by reference to the molecular and electronic structures, chemical reactivity, and spectroscopic properties of examples selected because of their importance in advancing our understanding of these fascinating molecules. For details of synthetic methods the reader is referred to recent reviews[6,7] and a book by Heal.[8]

(6) Roesky, H. W. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 239.

(7) Chivers, T.; Oakley, R. T. *Top. Curr. Chem.* **1982**, *102*, 117.

(8) Heal, H. G. "The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen, and Phosphorus"; Academic Press: London, 1980.

(9) Mikulski, C. M.; Russo, P. J.; Saran, M. S.; MacDiarmid, A. G.; Garito, A. F.; Heeger, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6358.

(10) Andreasen, O.; Hazell, A. C.; Hazell, R. G. *Acta Crystallogr., Sect. B* **1977**, *B33*, 1109. (b) Höfs, H. U.; Mews, R.; Noltemeyer, M.; Schmidt, M.; Sheldrick, G. M. *Chem. Ber.* **1983**, *116*, 416.

(11) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3784.

(12) Burford, N.; Chivers, T.; Oakley, R. T.; Cordes, A. W.; Swepston, P. N. *J. Chem. Soc., Chem. Commun.* **1980**, 1204. Burford, N.; Chivers, T.; Cordes, A. W.; Laidlaw, W. G.; Noble, M. C.; Oakley, R. T.; Swepston, P. N. *J. Am. Chem. Soc.* **1982**, *104*, 1282.

(13) Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1978**, 391. Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1979**, *101*, 4517.

(14) (a) Chivers, T.; Codding, P. W.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1981**, 584. (b) Small, R. W. H.; Banister, A. J.; Hauptman, Z. V. *J. Chem. Soc., Dalton Trans.* **1981**, 2188. (c) Chivers, T.; Codding, P. W.; Laidlaw, W. G.; Liblong, S. W.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1983**, *105*, 1186.

(15) See, for example: (a) Moss, G.; Guru Row, T. N.; Coppens, P. *Inorg. Chem.* **1980**, *19*, 2396. (b) Mayerle, J. J.; Wolmershäuser, G.; Street, G. B. *Ibid.* **1979**, *18*, 1161.

(16) Gillespie, R. J.; Slim, D. R.; Tyrer, J. D. *J. Chem. Soc., Chem. Commun.* **1977**, 253. Gillespie, R. J.; Kent, J. P.; Sawyer, J. F.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.* **1981**, *20*, 3799.

(17) Ernest, I.; Holick, W.; Rihs, G.; Schomburg, D.; Shoham, G.; Wenkert, D.; Woodward, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1540.
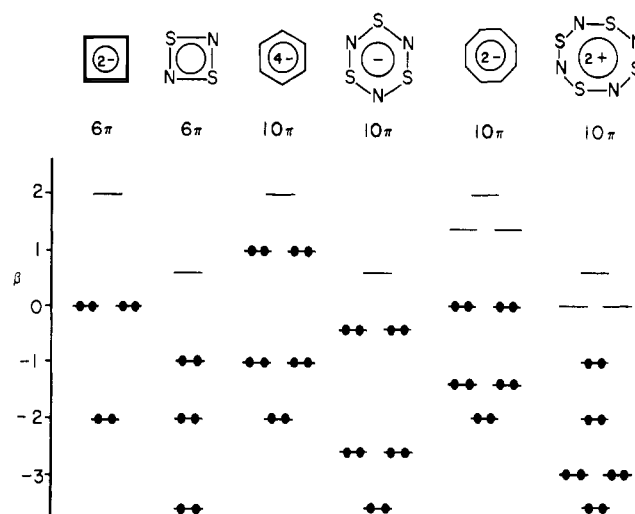
Figure 2. Hückel MO energy levels for S$_2$N$_2$, S$_3$N$_3^-$, S$_4$N$_4^{2+}$, and their hydrocarbon analogues. The carbon p atomic orbital, α_C, is arbitrarily chosen as zero energy and $\alpha_S = -1$, $\alpha_N = -2$, $\beta = -1$.
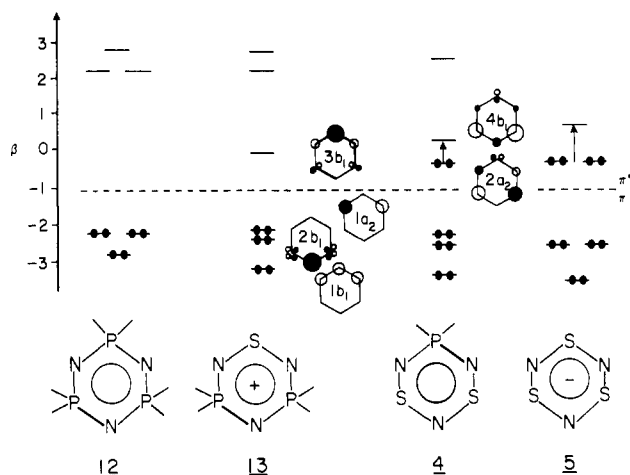
Figure 3. Hückel MO energy levels for the heterocyclic series P$_x$S$_{x-3}$N$_3$ (x = 0–3); α_P = +2, α_S = -1, α_N = -2, β = -1) showing the frontier orbitals for PS$_2$N$_3$ (4) and the three occupied orbitals and the LUMO for P$_2$SN$_3^+$ (13). The dotted line separates π and π^* orbitals.

Molecular and Electronic Structures

Planar Sulfur–Nitrogen Rings and Heterocyclothiazenes. The molecular structures of some electron-rich heterocycles are depicted in Figure 1. With the exception of 4 and 6 (vide infra) all these ring systems are essentially planar. Their electronic structures have been discussed at the simple and extended Hückel levels by Gimarc and Trinajstić[20] and by Gleiter,[21] respectively; Figure 2 compares the π-MO energy levels of S$_2$N$_2$, S$_3$N$_3^-$, and S$_4$N$_4^{2+}$ with those of their hydrocarbon analogues. The principal conclusion to emerge from this comparison is that the lower energies of their π^* molecular orbitals enable sulfur–nitrogen heterocycles to accommodate the additional electrons in π-type orbitals.

The effect of the higher electronegativity of sulfur relative to phosphorus on the π-MO energy levels for the series of

(18) Koenig, H.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1983**, 73.

(19) (a) Gillespie, R. J.; Sawyer, J. F.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.* **1982**, *21*, 1296. (b) Banister, A. J.; Durrant, J. A.; Rayment, I.; Shearer, H. M. M. *J. Chem. Soc., Dalton Trans.* **1976**, 928. (c) Roesky, H. W.; Bowing, W. G.; Rayment, I.; Shearer, H. M. M. *J. Chem. Soc., Chem. Commun.* **1975**, 735. (d) Hazell, A. C.; Hazell, R. G. *Acta Chem. Scand.* **1972**, *26*, 1987.

(20) Gimarc, B. M.; Trinajstić, N. *Pure Appl. Chem.* **1980**, *52*, 1443.

(21) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 444.

six-membered rings, $P_xS_{3-x}N_3$ ($x = 0$–3) is illustrated in Figure 3. It should be noted that the successive replacement of phosphorus by sulfur in the P_3N_3 ring stabilizes the π^* levels substantially and reduces the HOMO–LUMO gap in $(R_2PN)_2(SN)^+$ (13) and $(R_2PN)(SN)_2$ (4). Notice also that there are no degenerate levels in 4 and 13 due to their lower symmetry (C_{2v}) compared to that of 5 and 12 (D_{3h}).

In the π-electron-precise ring $P_2SN_3^+$ (13) (e.g., in $(Cl_2PN)_2(SN)^{+\,22}$ or $(Ph_2PN)_2(NSCl)^{23}$), the P–N bonds connecting the PNP and NSN fragments of the ring are significantly longer (ca. 1.66 Å) than the P–N bonds in the PNP unit (ca. 1.58 Å). At the simple Hückel level, the lowest ($1b_1$) of the three occupied π MO's is primarily NSN bonding while the next ($2b_1$) is bonding with respect to the PNP unit (Figure 3). Above these two is a nonbonding π MO ($1a_2$) located primarily on the equivalent nitrogen centers (the order of $2b_1$ and $1a_2$ is reversed in EHMO calculations).[24] Thus the π bonding is strongest in the NSN segment of the ring and insignificant between the PNP and NSN units as reflected in the long connecting P–N bonds.

While these simple MO pictures give a useful indication of the π-electronic structures of electron-rich rings, the results should be interpreted with caution. All electron calculations provide a more detailed description of the electronic structure of these heterocycles, e.g., the composition of frontier orbitals and the nature of electronic transitions, in addition to confirming the conclusions of the simple Hückel treatment as illustrated by the following examples.

Ab initio calculations have established that disulfur dinitride (1) is a six-π-electron system in which the upper occupied levels are not quite degenerate cf., $C_4H_4^{2-}$ (Figure 2). UV–photoelectron spectra indicate that the HOMO is a nonbonding π MO located on sulfur, which is of slightly higher energy than the nonbonding nitrogen-based MO.[25]

The cyclophosphadithiatriazene ring (4) was confirmed to be an eight-π-electron system by ab initio calculations. The experimental geometry, in which the phosphorus atom is tilted out of the NSNSN plane by 0.28 Å, is slightly lower in energy (ca. 15 kcal mol⁻¹) than a planar PS_2N_3 ring.[12] Both the HOMO and LUMO are strongly antibonding in the NSNSN framework (Figure 3) and their predominant sulfur character is decisive in explaining the course of cycloaddition reactions. Calculations of the π-charge density suggest that the internal salt model $R_2P^+S_2N_3^-$ is a useful approximate description of 4 (cf., λ^5-phosphorins).[26]

The 10-π-electron system of the cyclotrithiazene (trisulfur trinitride) anion (5) has been verified by a variety of ab initio calculations.[13,27] The π-orbital manifold is reminiscent of benzene with the important difference that the degenerate π^* levels are fully occupied in 5 (Figure 3). As a result the π structure is considerably weaker in 5 than in benzene.

According to ab initio calculations,[14c,28] the envelope conformation (C_s) of tetrasulfur dinitride (6) (dihedral angle ca. 55°) is of slightly lower energy (ca. 6–14 kcal mol⁻¹) than the planar conformation (C_{2v}), for which it is possible to assign a 10-π-electron distribution formed by the weak interaction of two pseudo-allyl units, SSS and NSN.[14c] These calculations show that there is significant net π bonding in the NSN moiety

(22) Pohl, S.; Petersen, O.; Roesky, H. W. *Chem. Ber.* 1979, *112*, 1545.

(23) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* 1982, 982 and unpublished results.

(24) Burford, N. Ph.D. Thesis, University of Calgary, 1983, and unpublished results.

(25) (a) Frost, D. D.; Le Geyt, M. R.; Paddock, N. L.; Westwood, N. P. C. *J. Chem. Soc., Chem. Commun.* 1977, 217. (b) Findlay, R. H.; Palmer, M. H.; Downs, A. J.; Egdell, R. G.; Evans, R. *Inorg. Chem.* 1980, *19*, 1307.

(26) Dimroth, K. *Acc. Chem. Res.* 1982, *15*, 58.

(27) Bhattacharyya, A. A.; Bhattacharyya, A.; Turner, A. G. *Inorg. Chim. Acta* 1980, *45*, L13. Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *Ibid.* 1981, *53*, L189. Bhattacharyya, A. A.; Bhattacharyya, A.; Turner, A. G. *Ibid.* 1982, *64*, L33. Smith, V. H., Jr.; Sabin, J. R.; Broclawik, E.; Mrozek, J. *Ibid.* 1983, *77*, L101.

(28) Palmer, M. H.; Wheeler, J. R.; Findlay, F. H.; Westwood, N. P. C.; Lau, W. M. *J. Mol. Struct.* 1981, *86*, 193.
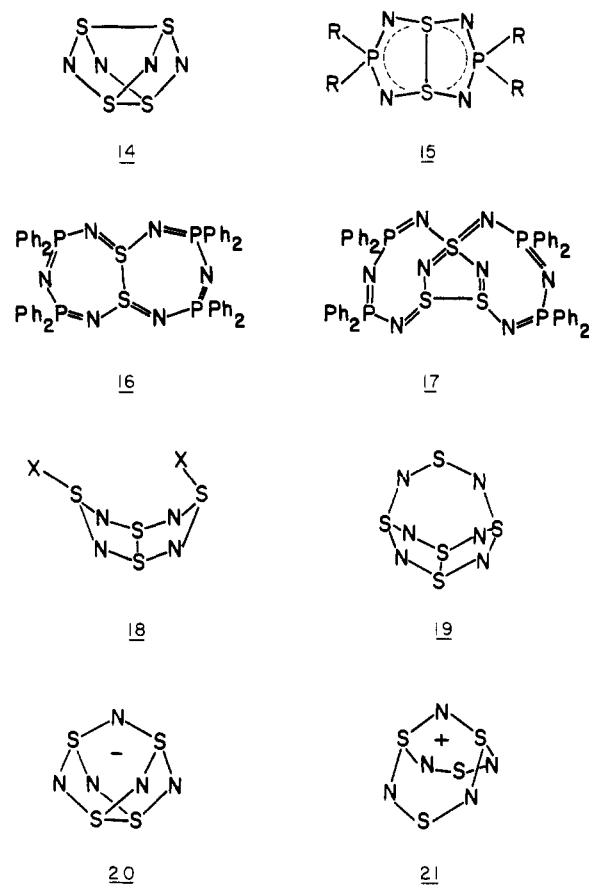
Figure 4. Schematic representation of the structures of bicyclic, tricyclic, and cage S–N and P–S–N molecules. Details of the X-ray structural investigations can be found in the following references: 14,[32] 15,[31] 16,[33] 17,[23] 18,[34] 19,[35] 20,[36] 21.[37]

but essentially no net π bonding in the remaining S–N and S–S bonds. In the envelope conformation the σ system in the SSS and NSN units is strengthened at the expense of weakened connecting S–N bonds. This may account for the thermal instability of 6 and, in part, the length of the latter bonds (1.68 Å) compared to the relatively short S–N bonds (1.56 Å) of the NSN unit.

The cyclotetrathiazyl dication (8) usually has a planar structure with equal S–N bond lengths, but distortions from the regular D_{4h} structure have been observed in certain salts.[16] CNDO and extended Hückel MO calculations indicate that the planar form is stable but easily deformable.[29] This conclusion is supported by ab initio calculations, which also demonstrate that 8 is a fully delocalized 10-π-electron system in which the strong π network is more than sufficient to overcome the loss of S–S σ bonding in the S_4N_4 cage.[30]

The geometry of eight-membered heterocyclothiazenes of the type $E(NSN)_2E$ (9) is markedly dependent on the effective electronegativity of the substituents E. When E = CPh the heterocyclic ring is planar and the C–N and S–N bond lengths are consistent with a delocalized 10-π-electron system.[17] However, if E = $CNMe_2$[17] or PR_2 (15) the molecule adopts a folded (butterfly) structure with a cross-ring S–S bond of 2.4–2.5 Å (vide infra).[31]

Benzo-1,3-dithia-2,4-diazene (10) has an essentially planar structure and can be considered as a sulfur–nitrogen analogue of naphthalene.[18] However, the π manifold of 10 has two more electrons than naphthalene, i.e., it is a 12-π-electron system.

(29) Sharma, R. D.; Aubke, F.; Paddock, N. L. *Can. J. Chem.* 1981, *59*, 3157.

(30) Trsic, M.; Laidlaw, W. G.; Oakley, R. T. *Ibid.* 1982, *60*, 2.

(31) (a) Burford, N.; Chivers, T.; Codding, P. W.; Oakley, R. T. *Inorg. Chem.* 1982, *21*, 982. (b) Burford, N.; Chivers, T.; Richardson, J. F. *Ibid.* 1983, *22*, 1482.

It is important to recall that the Hückel $(4n + 2)$-π-electron rule was devised for cyclic hydrocarbons and is based on Hund's rule of maximum multiplicity coupled with the presence of degenerate levels.[28] The foregoing discussion of the molecular and electronic structures of electron-rich inorganic heterocycles provides several examples that illustrate that the distinction between $4n$- and $(4n + 2)$-π-electron systems is not fundamental for molecules of C_{2v} (or lower) symmetry. Thus, we have examples of stable molecules or ions with 6-, 8-, 10-, 12-, or 14-π-electron systems in all of which the number of π electrons exceeds the number of atomic centers in the ring. The excess of electrons is accommodated in π^* (antibonding) levels that are of low energy compared to their counterparts in hydrocarbon or cyclophosphazene systems. In favorable cases, however, there is a strong tendency for electron-rich inorganic heterocycles to reduce the number of antibonding electrons in the π manifold by the formation of transannular S–S bonds. Some examples, represented in Figure 4, are discussed in the following section.

Bicyclic and Tricyclic Sulfur–Nitrogen Rings and Cages. Cyclotetrathiazene (Tetrasulfur Tetranitride) (14), the prototype of S–N cage or bicyclic molecules, has been the subject of many theoretical discussions at both the semiempirical and ab initio levels in recent years.[7,25b,38] All these calculations elucidate the same fundamental features. There is a substantial cross-ring bonding interaction between opposite pairs of sulfur atoms, little or no N–N bonding, and polar S–N bonds in which ca. 0.3–0.4 electrons are transferred from sulfur to nitrogen. On the basis of electron density measurements the possibility of four-center bonding involving all the sulfur atoms has been suggested.[32]

A planar (D_{4h}) S$_4$N$_4$ molecule would be a 12-π-electron system with an open-shell configuration (Figure 2) unstable with respect to Jahn–Teller distortion. In an extended Hückel analysis of S$_4$N$_4$ Gleiter has correlated the MO's of the hypothetical planar molecule with those of the experimental (D_{2d}) conformation.[39] In the D_{2d} structure, the orbital degeneracy of the ground state is lost and four of the previously π^* electrons are accommodated in S–S σ bonds. According to ab initio calculations, however, the HOMO of 14 is a nitrogen-based lone-pair orbital and not the cross-ring S–S bond, while the LUMO is the S–S (σ^*) orbital.[25b,37b,40] This conclusion is supported by recent measurements of the X-ray fluorescence spectra of S$_4$N$_4$.[41]

Transannular S–S bonds are frequently found in eight-membered (or larger) electron-rich heterocycles and the approach of Gleiter has been adapted to explain the observation of two structural types (9 and 15) for molecules of the type E(NSN)$_2$E.[31] For the planar structure 9 the HOMO is a π^* orbital that can be stabilized by a substituent E with a high effective electronegativity. If E is not sufficiently electronegative, however, the π^* electrons of the planar structure are converted to an S–S σ bond and a folded structure results [e.g., E = CNMe$_2$,[17] PR$_2$(R = Me, Ph)[31]]. Other examples of cross-ring S–S bonds include the cyclophosphathiazenes 16 and 17.[23,33] In the absence of the S–S bond both heterocycles would be π electron rich and the excess of electrons would presumably have to be accommodated in π^* levels. The bicyclic and cage molecules and ions 18–21 can all be considered as examples of 1,5-disubstituted derivatives of S$_4$N$_4$. In 1,5-X$_2$S$_4$N$_4$ (18; X = Cl, NMe$_2$, NPPh$_3$) the X groups adopt exo, endo positions in the solid state and there is a cross-ring bond of ca. 2.45 Å,[34] (cf., 2.43 Å in S$_5$N$_6$ (19)).[35] In S$_4$N$_5^-$ (20) the

fifth edge of the S$_4$ tetrahedron of an S$_4$N$_4$ cage is bridged by nitrogen leaving only one cross-ring S–S bond $(d$(S–S) = 2.71 Å).[36] In the corresponding cation S$_4$N$_5^+$ (21) there is no bonding interacting between these sulfur atoms $(d$(S–S) = 4.0 Å).[37]

For extended Hückel and ab initio calculations the NSN units in 18–21 involving the unbridged (or unsubstituted) sulfur atoms have been treated as two pseudo-allylic five-π-electron fragments.[42] If the substituents X in 18 or the bridging group (19–21) are able to withdraw π^*-electron density from the S$_4$N$_4$ cage, e.g. N$^+$, the S–S σ interaction will be weakened and a large S–S separation is expected and is found for S$_4$N$_5^+$.[37] Ab initio calculations provide further insight into the bonding in S–N cages. In S$_4$N$_5^-$ the introduction of the N$^-$ bridge weakens the S–N bonds in the S$_4$N 4 cage,[37b] as indicated by the thermal instability of the anion.[43]

Spectroscopic Studies

UV–Visible and MCD Spectra. In contrast to unsaturated organic ring systems or cyclophosphazenes electron-rich sulfur–nitrogen heterocycles usually exhibit intense colors ranging from yellow (5) through orange (7) and red (6) to blue (4 and 10). The colors are due to low energy $(\pi^* \rightarrow \pi^*$ or n $\rightarrow \pi^*)$ transitions and in many cases the electronic absorption spectra have been assigned on the basis of ab initio calculations of the transition moments and energies for HOMO $\rightarrow$ LUMO and other low-energy transitions.[44]

For example, the cyclophosphadithiatriazenes (4) exhibit a characteristically intense visible absorption band at ca. 550 nm attributed to the HOMO $(2a_2,\pi^*)$ $\rightarrow$ LUMO $(4b_1,\pi^*)$ transition (Figure 3, calculated value 560 nm).[12] Similarly the strong bands observed at 455 and 377 nm for S$_4$N$_2$ (6) have been assigned to HOMO $(\pi^*) \rightarrow$ LUMO (π^*) and HOMO-1 $(\pi^*) \rightarrow$ LUMO (π^*) excitations, respectively.[14] The pale yellow color of 1,5-(Ph$_2$PN)$_2$(SN)$_2$ (15) is in contrast to the dark orange color $(\lambda_{max}$ 460 nm) of the structural isomer, 1,3-(Ph$_2$PN)$_2$(SN)$_2$. In the absence of a cross-ring S–S bond the latter isomer is π electron rich (10 π electrons) and the strong visible absorption band has been tentatively ascribed to a HOMO $(\pi^*) \rightarrow$ LUMO (π^*) transition.

The intense band at 360 nm in the UV-visible spectrum of S$_3$N$_3^-$ (5) has been assigned to the HOMO (π^*) $\rightarrow$ LUMO (π^*) transition (Figure 3).[14] This assignment has been confirmed by the observation of a negative A term in the MCD spectrum, as predicted by the Platt perimeter model.[45] The MCD spectrum of S$_4$N$_3^+$ (7) reveals the presence of four low-energy transitions with

(32) DeLucia, M. L.; Coppens, P. *Inorg. Chem.* 1978, *17*, 2336.

(33) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* 1983, 186.

(34) (a) Bojes, J.; Chivers, T.; MacLean, G.; Oakley, R. T.; Cordes, A. W. *Can. J. Chem.* 1979, *57*, 3171. (b) Bojes, J.; Chivers, T.; Cordes, A. W.; MacLean, G.; Oakley, R. T. *Inorg. Chem.* 1981, *20*, 16. (c) Zak, Z. *Acta. Crystallogr., Sect. B* 1981, *B37*, 23. (d) Roesky, H. W.; Rao, M. N. S.; Graf, C.; Gieren, A.; Hädicke, E. *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 592 (e) Roesky, H. W.; Pelz, C.; Gieren, A.; Hädicke, E. *Z. Naturforsch.* 1981 *36b*, 1437.

(35) (a) Chivers, T.; Proctor, J. *J. Chem. Soc., Chem. Commun.* 1978, 642. (b) Chivers, T.; Proctor, J. *Can. J. Chem.* 1979, *57*, 1286. (c) Roesky, H. W.; Rao, M. N. S.; Nakajima, T.; Sheldrick, W. S. *Chem. Ber.* 1979, *112*, 3531.

(36) Flues, W.; Scherer, O. J.; Weiss, J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* 1976, *15*, 379.

(37) (a) Chivers, T.; Fielding, L. *J. Chem. Soc., Chem. Commun.* 1978, 212. (b) Chivers, T.; Fielding, L.; Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* 1979, *18*, 3374. (c) Isenberg, W.; Mews, R. *Z. Naturforsch.* 1982, *37b*, 13.

(38) Haddon, R. C.; Wasserman, S. R.; Wudl, F.; Williams, G. R. J. *J. Am. Chem. Soc.* 1980, *102*, 6687 and references cited therein.

(39) Gleiter, R. *J. Chem. Soc. A* 1970, 3174.

(40) Millefiori, A.; Millefiori, S. *J. Chem. Res., Synop.* 1980, 244.

(41) Dolenko, G. N.; Zibarev, A. V.; Pykhov, V. *Z. Zh. Neorg. Khim.* 1981, *26*, 1476.

(42) (a) Bartetzko, R.; Gleiter, R. *Chem. Ber.* 1980, *113*, 1138. (b) Trsic, M.; Wagstaff, K.; Laidlaw, W. G. *Int. J. Quantum Chem.* 1982, *22*, 903.

(43) Chivers, T.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* 1979, 752. Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* 1980, *102*, 5773. Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* 1981, *20*, 1792.

(44) Laidlaw, W. G.; Trsic, M. *Int. J. Quantum Chem.*, in press.

(45) Waluk, J. W.; Michl, J. *Inorg. Chem.* 1981, *20*, 963.

properties matching those expected for $\pi^* \to \pi^*$ excitations in a 10-π-electron system with cyclic delocalization.[46] The electronic spectrum of $S_4N_4{}^{2+}$ provides a classic example of an eight-atom ten-π-electron perimeter. The two major peaks at 346 and 262 nm in the UV–visible spectrum of $S_4N_4{}^{2+}$ (8) have been attributed to $n\pi_S \to \pi^*$ and $n\pi_N \to \pi^*$ transitions, respectively, which should give rise to a pair of positive A terms in the MCD spectrum.[30]

^{15}N NMR Spectra. In principle, ^{15}N NMR spectra can provide useful information about structure and bonding in sulfur–nitrogen heterocycles. However, it is usually necessary to prepare ^{15}N-enriched samples due to the low natural abundance of ^{15}N (0.36%) and poor solubility of many S–N compounds.[47] The observed chemical shifts span a wide range of values and, although there is no obvious correlation with calculated charge densities,[47] the knowledge of these values is helpful in monitoring reactions of S–N compounds and may provide structural information about new compounds. For example, the ^{15}N NMR spectrum gave the first indication that the anions $S_3N_3O^-$ and $S_3N_3O_2{}^-$ were among the products formed when $S_3N_3{}^-$ is oxidized with molecular oxygen.[48]

The fine structure resulting from ^{15}N–^{15}N coupling can also give an indication of the structures of S–N compounds (e.g., $S_4N_3{}^+$ (7)[47] and $(R_2PN)(SN)_2$ (4)[12]). However, this information is only worthwhile in carefully selected cases due to the expense involved in preparing highly enriched samples.

^{15}N NMR spectroscopy would be the technique of choice for the study of fluxional behavior in S–N cages, although no experimental evidence in support of stereochemical non-rigidity has been presented. For example, a series of degenerate intramolecular rearrangements can be constructed leading to equivalence of all five nitrogen atoms in $S_4N_5{}^-$ (18).[42] However, the activation energy for such a process may be sufficient to disrupt the cage, e.g., by loss of N_2S.[43]

Raman Spectra. Raman spectroscopy is a useful probe for detecting transannular S–S interactions in bicyclic or cage molecules.[31a] The strongly Raman active S–S vibrations occur at low frequencies (180–300 cm^{-1}) because the S–S bond lengths (2.4–2.7 Å) are substantially longer than a S–S single bond (ca. 2.06 Å) for which vibrational frequencies of 420–400 cm^{-1} are observed.[49]

Chemical Reactivity

An appreciation of the electronic structures and, in particular, the composition of the frontier MO's of electron-rich sulfur–nitrogen heterocycles is helpful in understanding their versatile chemical behavior. To illustrate this point the following types of reaction will be considered: (a) thermolysis, (b) formation of adducts (including cycloaddition reactions), (c) redox reactions, and (d) reactions with nucleophiles.

Thermolysis. Cyclothiazenes are thermodynamically unstable with respect to N_2 and S_8 and their structural frameworks are weaker than those of hy-

drocarbon analogues due, in part, to the partial occupational of π^* MO's. In many cases (e.g., S_5N_6,[35] $S_4N_5{}^-$ [43]) there is a low kinetic barrier to decomposition via elimination of small molecules, e.g., N_2S and N_2S_2, and caution must be exercised to avoid explosions. Under controlled conditions, however, thermolysis can be employed for the synthesis of S–N compounds. For example, the six-membered rings $S_3N_3{}^-$ (5) and $Ph_3P=N-S_3N_3$ (22) undergo ring-opening reactions in boiling acetonitrile to give S_4N^- [43] and $Ph_3P=NSNSS$,[50] respectively. Both the anion and the neutral molecule
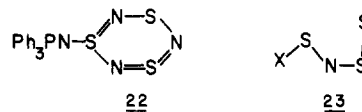
have an open chain cis–trans structure (23) with short (ca. 1.9 Å) polar, terminal S–S bonds. In contrast, the arsenic derivative $Ph_3As=N-S_3N_3$ eliminates S_2N_2 (1) under mild conditions,[50] as does $S_4N_3{}^+Cl^-$.[51]
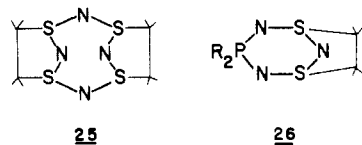
Adduct Formation (Including Cycloaddition Reactions). The formation of adducts between S_4N_4 (or related heterocycles) and Lewis acids (e.g., AsF_5, $TaCl_5$, and $FeCl_3$)[52] and the cycloaddition reactions of conjugated S–N rings with olefins can provide experimental confirmation of the theoretically predicted symmetries of their formation MO's.

For example, in the adducts $S_4N_4 \cdot L$ (24)[52] the site of coordination is a nitrogen atom in agreement with theoretical[25b,37b,40] and experimental evidence[41] which indicate that the HOMO of S_4N_4 is a nitrogen lone-pair orbital. The adducts 24 and $S_4N_4H^+$ show remarkably
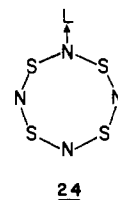
similar structural features. The cage structure of S_4N_4 is opened so that the four sulfur atoms are almost coplanar. The S–N bonds involving the coordinated nitrogen, N(L), are substantially longer (1.65–1.69 Å) than the other S–N bonds in the adducts (1.54–1.60 Å) on account of the localization of π^* electrons into the skeletal bonds to N(L). Thus the π network of the SNSNSNS moiety is strengthened at the expense of the S–N(L) bonds.[53]

In the adduct $S_4N_4 \cdot 2NBD$ (25, NBD = norbornadiene) one C=C bond of the olefin adds across an SNS unit of S_4N_4 to give a five-membered ring.[54]

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

(47) Chivers, T.; Oakley, R. T.; Scherer, O. J.; Wolmershäuser, G. *Inorg. Chem.* **1981**, *20*, 914.

(48) Chivers, T.; Cordes, A. W.; Oakley, R. T.; Pennington, W. T. *Inorg. Chem.* **1983**, *22*, 2429.

(49) Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655.

(50) Chivers, T.; Oakley, R. T.; Cordes, A. W.; Swepston, P. N. *J. Chem. Soc., Chem. Commun.* **1980**, 35. Chivers, T.; Oakley, R. T.; Cordes, A. W.; Swepston, P. N. *Inorg. Chem.* **1981**, *20*, 2376.

(51) Banister, A. J.; and Hauptman, Z. V. *J. Chem. Soc., Dalton Trans.* **1980**, 731.

(52) See, for example: Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Acta Crystallogr., Sect. B* **1980**, *B36*, 655. Thewalt, U.; Albrecht, G. *Z. Naturforsch.* **1982**, *37b*, 1098 and references cited therein.

(53) Cordes, A. W.; Marcellus, C. G.; Noble, M. C.; Oakley, R. T.; Pennington, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 6008.

This mode of addition can be rationalized from a consideration of the LUMO of S_4N_4 which is antibonding with respect to opposite pairs of sulfur atoms.[55] Consequently, the HOMO of the olefin will add concertedly across nearest neighbor pairs of sulfur atoms. Similarly, the concerted addition of a two-electron olefin to 4 in an S,S fashion to give 26 can be easily understood from a consideration of the eigenvector coefficients of the HOMO ($2a_1$) and LUMO ($4b_1$) levels of 4 (Figure 3).[12] Both orbitals are primarily sulfur based, so that efficient overlap in the transition state is best achieved via addition at sulfur as opposed to nitrogen.

Redox Reactions. In view of their surplus of electrons it is not surprising that electron-rich heterocycles are easily oxidized. For example, 4 readily undergoes oxidative addition with Cl_2 to give $(Ph_2PN)(NSCl)_2$.[7,56] Halogens also add across the S-S bond in 15 to give $1,5-(Ph_2PN)_2(NSX)_2$ (X = Br, Cl),[57] while S_4N_4 itself is converted to the dication 8 by an excess of oxidizing agent (e.g., $SbCl_5$ or $S_2O_6F_2$).[16,29]

Perhaps more surprising is the fact that these electron-rich heterocycles are good electron acceptors. As pointed out by Fukui et al.,[58] the energetically low-lying LUMO of S_4N_4 implies *electron-deficient* properties. Indeed 14 readily undergoes a one-electron reduction at −0.93 V (vs. Ag/0.1 M $AgClO_4$) in acetonitrile to give the anion radical $S_4N_4^-$,[59] which is unstable above 0 °C with respect to the formation of 5.[60] Preliminary electrochemical results[61] demonstrate that 4 ($E_{1/2}$ = −1.47 V) is more easily reduced than cyclophosphazenes 12[62] as might be anticipated from consideration of LUMO energy levels (Figure 3).

Reactions with Nucleophiles. The polarity of the S-N bonds in S_4N_4 (vide supra) and related heterocycles results in facile nucleophilic attack at sulfur and subsequent rearrangements to a variety of products.[7] Reactions with anionic nucleophiles, e.g., N_3^-, S^{2-}, produce the anions 5 and 20,[60,63] while Ph_3P converts S_4N_4 to heterocycles containing exocyclic $Ph_3P=N$

groups, 18 and 22.[50,64] However, if the phosphorus nucleophile has a good leaving group, e.g., R_2PX, the phosphorus atom is incorporated in the ring system to give 4 and 15 (X = H, PR_2)[12,31b] or $(Ph_2PN)_2NSCl$ (X = Cl).[23]

The reactions of the P_2SN_3 ring 13 with nucleophiles provide a nice illustration of the importance of frontier MO concepts in understanding the chemical transformations of PNS heterocycles. The low energy π^* LUMO ($3b_1$) in 13 is strongly antibonding with respect to the NSN unit in the ring (Figure 3). Consequently reactions with nucleophiles or reducing agents lead to cleavage of the ring at the S-N bond. For example, $(Ph_2PN)_2(NSCl)$ reacts with Ph_3Sb[33] or $Me_3SiNSNSiMe_3$[23] to give 16 or 17, respectively.

Concluding Remarks

Although the mechanisms involved in the unusual transformations of sulfur-nitrogen heterocycles are poorly understood, many aspects of their chemical behavior, molecular structures, and spectroscopic properties can be explained from a knowledge of their electronic structures. Thus, it is the availability of low-lying π^* orbitals that enables these ring systems to accommodate more electrons than their hydrocarbon analogues and, at the same time, confers on them electron-accepting properties and a susceptibility to nucleophilic attack. The partial occupation of π^* levels results in a weakened π framework (compared to hydrocarbons) and, hence, a tendency to thermal degradation. Where possible, the excess of electrons is minimized by the formation of weak, cross-ring S-S bonds and the removal of π^* electron density via oxidation strengthens the π network.

The possibilities for the preparation of novel binary sulfur-nitrogen heterocycles appear to be limited, but there is considerable scope for imaginative work involving the incorporation of heteroatoms (e.g., B, C, P or transition metals) into sulfur-nitrogen rings and polymers. Such materials may have unusual electrical properties. Photochemical and electrochemical studies should provide alternative synthetic approaches as well as additional insights into the electronic structures of electron-rich heterocycles.

(54) Griffin, A. M.; Sheldrick, G. M. *Acta Crystallogr., Sect B* 1975, *31*, 895. Ertl, G.; Weiss, J. Z. *Anorg. Allg. Chem.* 1976, *420*, 155.

(55) Yamabe, T.; Tanaka, K.; Tachibana, A.; Fukui, K.; Kato, H. *J. Phys. Chem.* 1979, *83*, 767.

(56) Burford, N.; Chivers, T.; Oakley, R. T.; Oswald, T. *Can. J. Chem.*, in press.

(57) Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.*, in press.

(58) Tanaka, K.; Yamabe, T.; Tachibana, A.; Kato, H.; Fukui, K. *J. Phys. Chem.* 1978, *82*, 2121.

(59) Hojo, M. *Bull. Chem. Soc. Jpn.* 1980, *53*, 2856 and references cited therein.

(60) Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* 1977, 453. Bojes, J.; Chivers, T.; Drummond, I.; MacLean, G. *Inorg. Chem.* 1978, *17*, 3668.

(61) Chivers, T.; Hojo, M. *Inorg. Chem.*, in press and unpublished results.

(62) Allcock, H. R.; Birdsall, W. J. *Inorg. Chem.* 1971, *11*, 2495.

(63) Bojes, J.; Chivers, T. *Inorg. Chem.* 1978, *17*, 318.

(64) Bojes, J.; Chivers, T.; MacLean, G.; Oakley, R. T.; Cordes, A. W. *Can. J. Chem.* 1979, *57*, 3171.