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On The Electronic Structure of Tetranitrogen Tetrasulfide

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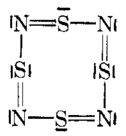
The results of molecular orbital calculations are presented in an attempt to answer four questions concerning the electronic structure of N_4S_4 and its derived ions. The important conclusions are: (1) A geometrical structure involving coplanar nitrogen atoms is to be preferred over one involving coplanar sulfur atoms. (2) Appreciable bonding is to be expected between sulfur atoms located on the same side of the plane defined by the four nitrogen atoms. No bonding is to be expected between nitrogen atoms. (3) Negative ions of N_4S_4 having one to four units of charge ought to exist and exhibit π-electron-delocalized electronic structures. (4) The role played by d-type orbitals on sulfur is a contributing but not a main factor in describing the electronic structure.

Introduction

The electronic and geometrical structure of tetranitrogen tetrasulfide, N_4S_4, has long been of interest to the chemist.[2] After several X-ray diffraction,[3] electron diffraction,[4] and spectroscopic investigations,[5] a structure involving four copolanar nitrogen atoms with two sulfur atoms above and below the plane has generally been accepted.[3a] This structure is shown in Figure 1. The electronic structure of the molecule has been previously described by Lewis-type structures such as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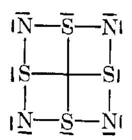
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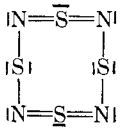
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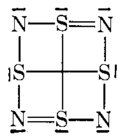
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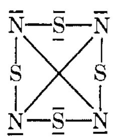
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Interestingly, a reasonable Lewis structure can be drawn containing sulfur–sulfur bonds, nitrogen–nitrogen bonds, or neither of these, but a satisfactory atomic orbital based description is still forthcoming. The coplanar sulfur atom structure posed by Lippincott and Tobin[5] requires the presence of nitrogen–nitrogen bonds. The more recent coplanar nitrogen atom structure does not. Lindqvist[6] has discussed the possibility of sulfur–sulfur bonds occurring across the plane of nitrogen atoms. The possible utilization of d-type orbitals by sulfur atoms has been briefly discussed by Glemser[7] using a recent model of Dewar, Lucken, and Whitehead.[8]

Presently, the following questions can be raised regarding the structure of tetranitrogen tetrasulfide.

(I) What is the preferred geometrical structure of the molecule? Is it Donohue and Sharma's D_{2d} coplanar nitrogen atom structure shown in Figure 1, or is it the coplanar sulfur atom structure first proposed by Lippincott and Tobin?

(II) Is there bonding between sulfur atoms in the molecule and, if so, to what extent? A similar question can be raised for the N–N bonding.

(III) To what extent, if any, does π-electron delocalization occur in the molecule or its related ions giving it properties similar to those of the aromatic hydrocarbons?

(IV) Is it necessary to invoke d-type orbitals on sulfur to explain the electronic structure of the molecule?

This paper addresses itself to these four questions and seeks to answer them using the results of extended Hückel molecular orbital calculations,[9] employing a limited Slater orbital basis which includes 2s- and 2p-type orbitals on nitrogen and 3s-, 3p-, and 3d-type orbitals on sulfur. We address ourselves to the above questions, one at a time.

Question I. The Geometrical Structure of N_4S_4

Two distinct structures have been posed for N_4S_4. The first, a structure of symmetry $42m(D_{2d})$, places the four sulfur atoms in a plane and assigns an S–N distance of 1.74 A, an NSN bond angle of 79.25°, and an SNS angle of 98.2°.[5] The second having the same symmetry requires that the four nitrogen atoms be copolanar, invokes an S–N distance of 1.616 ± 0.010 A, and requires bond angles of 113° at nitrogen and 105° at sulfur.[3a] When the question is one of topology, as it is here, Hückel-type calculations can frequently provide the answer. Relative values of the total electronic energy have been shown to be a good indication of relative stability when the two trial structures are

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(1) (a) Polytechnic Institute of Brooklyn, Brooklyn, N. Y.; (b) Shell Development Co., Emeryville, Calif.

(2) For reviews see M. Becke-Goehring, *Progr. Inorg. Chem.*, **1**, 207 (1959); *Angew Chem.*, **73**, 589 (1961); *Quart. Rev.* (London), **10**, 437 (1956).

(3) (a) D. B. Sharma and J. Donohue, *Acta Cryst.*, **16**, 891 (1963); (b) J. Donohue, *J. Am. Chem. Soc.*, **66**, 818 (1944); D. Clark, *J. Chem. Soc.*, 1615 (1952).

(4) O. Hassel and H. Viervoll, *Tidsskr. Kjemi, Bergvessen*, **3**, 7 (1943).

(5) E. R. Lippincott and M. C. Tobin, *J. Chem. Phys.*, **21**, 1559 (1953).

(6) I. Lindqvist, *J. Inorg. Nucl. Chem.*, **6**, 159 (1958).

(7) O. Glemser, *Angew. Chem. Intern. Ed. Engl.*, **2**, 530 (1963).

(8) M. J. S. Dewar, E. A. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

(9) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2474 (1963).

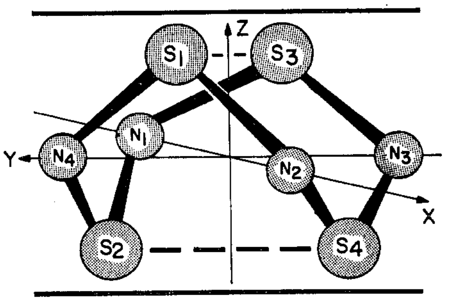

Figure 1.—The geometrical structure of tetranitrogen tetrasulfide. Superimposed upon the structures are the cartesian coordinate axes used in the calculations.

geometrically similar.[9] It has also been shown[10] that the total overlap population from such calculations is closely related to the experimental molecular energy of atomization. By both criteria the coplanar nitrogen structure is favored for N_4S_4. The calculations were performed as described in ref 10, using a Slater-type orbital basis consisting of 3s and 3p orbitals for sulfur and 2s and 2p orbitals for nitrogen. The orbital exponents were those given by Clementi.[11] A complete overlap matrix was calculated. Matrix elements of the Hamiltonian were valence-state ionization potentials[12] or were calculated from them using the Wolfsberg–Helmholtz formula.[13] Values for neutral atoms were entered in the calculation and systematically altered during the calculation to attain a self-consistent set of atomic charges. (We shall refer to these calculations as SCC–MO calculations.) The equation for the valence-state ionization potentials as a function of the charge, q, of the atom used are (H in ev) for N

$$\text{s electrons } H_{ss} = -25.58 - 13.31q - 1.78q^2$$

$$\text{p electrons } H_{pp} = -12.38 - 13.09q - 1.55q^2$$

and for S

$$\text{s electrons } H_{ss} = -21.13 - 10.83q - 1.24q^2$$

$$\text{p electrons } H_{pp} = -11.07 - 10.37q - 1.08q^2$$

The results are given in Table I.

TABLE I

SCC–MO CALCULATION FOR POSED STRUCTURES OF TETRANITROGEN TETRASULFIDE

Structure	N in plane	S in plane
Total energy	−725.81	−724.41
Charge on N	−0.24	−0.08
Charge on S	+0.24	+0.08
N–S bond order	0.774	0.628
S–S bond order	0.109	. . .
Sum of all bond orders	5.29	4.79

The calculations indicate that the structure containing coplanar nitrogen atoms is energetically favored over its sulfur counterpart by 32 kcal/mole. The total overlap population was calculated to be 5.39, which is to be compared with a value of 4.79 for the coplanar sulfur structure. By this criterion the coplanar nitrogen form is favored by *ca.* 70 kcal/mole. The expected error of the prediction based on overlap population should not be larger than 25–30 kcal/mole and is more probably 12–15 kcal/mole.[10] This work, together with that of Donohue and Sharma, leaves little doubt that the coplanar nitrogen structure is to be preferred for N_4S_4. Lippincott and Tobin assigned the coplanar sulfur structure on the basis of the occurrence of a Raman line at 888 cm^{-1} corresponding to an N–N bond (to be compared with a line at 893 cm^{-1} for N_2H_4).[5] The molecular orbital calculations, SCC–MO, show absolutely no tendency for bonding between nitrogen atoms since the calculated overlap population between nitrogen atoms is negative or zero under all parametizations. Hence, both experiment and theory argue against a structure containing a N–N bond. (This point is further discussed in section II.)

Question II. Sulfur–Sulfur Bonding in Tetranitrogen Tetrasulfide

Lindqvist[6] in 1958 suggested, principally on a geometrical basis, that there might be pure pσ bonds between sulfur atoms across the nitrogen plane in N_4S_4. The S–S distance is 2.58 A, intermediate between 2.04 A,[14] the normal sulfur–sulfur single bond distance, and *ca.* 3.7 A, the sum of the van der Waals radii.[15] In addition, the N–S···S angles are all within 2° of 90°. In Table II we list the calculated reduced overlap population ("bond order") between sulfur atoms on the same side of the nitrogen plane as obtained from our molecular orbital calculations under various parametizations.

TABLE II

REDUCED SULFUR–SULFUR OVERLAP POPULATION AND CHARGE

Calculation	n(S,S)	q(S)
(1) SCF—s and p orbitals on sulfur and nitrogen	0.109	+0.243
(2) EHMO excluding d orbitals on sulfur[a]	+0.1152	+0.328
(3) EHMO including d orbitals on sulfur[b]	+0.1901	−0.108
(4) EHMO excluding d orbitals on sulfur[c]	+0.3620	+1.457
(5) EHMO including d orbitals on sulfur[d]	+0.4767	+1.161
(6) EHMO excluding d orbitals on sulfur[e]	+0.1147	+0.321
(7) EHMO including d orbitals on sulfur[f]	0.1621	+0.004

[a] Parameters: nitrogen 3s: $\mathfrak{L} = 1.924, H_{ii} = -23.83$; nitrogen 2p: $\mathfrak{L} = 1.917, H_{ii} = -13.68$; sulfur 3s: $\mathfrak{L} = 2.050, H_{ii} = 24.08$; sulfur 3p: $\mathfrak{L} = 2.050, H_{ii} = -17.32$; H_{ij} obtained by arithmetic mean formula with $K = 2.00$. [b] Same as calculation 2 with d orbital included: $\mathfrak{L} = 2.050, H_{ii} = -7.00$. [c] Parameeters: nitrogen 2s: $\mathfrak{L} = 1.924, H_{ii} = -23.83$; nitrogen 2p: $\mathfrak{L} = 1.917, H_{ii} = -13.68$; sulfur 3s: $\mathfrak{L} = 2.122, H_{ii} = 22.46$; sulfur 3p: $\mathfrak{L} = 1.827, H_{ii} = -9.30$; H_{ij} obtained as in *a* and *b*. [d] Same as calculation 4 with d orbitals included: $\mathfrak{L} = 0.924, H_{ii} = -4.60$. [e] Same as calculation 2 except H_{ij} values were obtained with a geometric mean and $K = -2.00$. [f] Same as calculation 6 except d orbitals were included with parameter values as in calculation 3.

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(10) F. S. Mortimer, presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; Advances in Chemistry Series, to be published.

(11) E. Clementi and D. L. Daimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(12) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955); H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

(13) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

(14) "Table of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(15) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

The bond orders in Table II are strongly suggestive of some bonding between sulfur atoms on the same side of the nitrogen atom plane. The conclusion is apparent from both the SCC calculation using only s and p orbitals on the sulfur atoms and by the extended Hückel calculations. The extended Hückel calculations were carried out with several different sets of parameters. Calculations 2 and 3 in Table II employ the same shielding constants and coulomb integrals for the sulfur orbitals as used by Jordan, *et al.*, in their MO study of the sulfones.[16] The shielding constants for the nitrogen orbitals are taken from Clementi,[11] and the coulomb integrals are those of Pritchard and Skinner.[12] The off-diagonal matrix elements are chosen by an arithmetic mean formula with $K = 2.00$.[9] Calculations 6 and 7 are similar except they employ a geometric mean formula for H_{ij}. All descriptions bond the sulfur atoms to each other. The inclusion of d orbitals enhances the S–S bond order from 0.1152 to 0.1901 using the arithmetic mean formula for computation of H_{ij} and from 0.1147 to 0.1621 using the geometric mean; *however, their presence is not required for a nonzero S–S bond order.* Calculations 4 and 5 in Table II employ the same nitrogen orbital descriptions as above and the orbital exponents and coulomb integrals obtained from the SCC results for the sulfur orbitals. Calculations including and excluding d orbitals on sulfur give rise to S–S bond orders 0.4767 and 0.3620, respectively.

Some insight into the origin of the sulfur–sulfur bonding can be obtained by an examination of overlap population between the various sulfur orbitals. In Table III are shown the overlap populations which resulted from calculation 3 of Table II. The contributions to the S–S bond in order of decreasing importance are the overlap of p_x on one sulfur atom with p_y on the other sulfur atom, p_x–p_x overlap, p_x–d_{xz} overlap, and s–p_x overlap. Most of the total overlap is obtained using only p orbitals on each sulfur, the d orbitals playing only a secondary role. Consequently, the bonding between sulfur atoms is effectively of the pσ type. This result is a direct consequence of the N–S–S angle being within 2° of $\pi/2$.

Table III

Overlap Populations between Orbitals on Two Bonded Sulfur Atoms[a]

Orbital	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	$d_{x^2-y^2}$	d_{yz}	d_{xz}
s	18	0	56	56	10	0	0	0	68
p_z		−7	0	0	0	16	0	16	0
p_x			168	291	17	0	−1	0	114
p_y				168	17	0	−1	0	114
d_{z^2}					9	0	0	0	−13
d_{x^2}						3	0	0	9
$d_{x^2-y^2}$							−25	0	0
d_{yz}								3	0
d_{xz}									27

[a] The overlap populations have been multiplied by 10^4. The sulfur atoms used are those lying above the plane of nitrogen atoms in the quadrants defined by $x > 0$, $y > 0$, $z > 0$ and $x < 0$, $y < 0$, $z > 0$.

In Tables IV and V are given the overlap populations between orbitals on two nitrogen atoms, first, for two nitrogen atoms located along the edge of the plane of nitrogen atoms and, second, for two diagonally opposite nitrogen atoms. These illustrate that there is no tendency for bonding to occur between two edge-adjacent nitrogen atoms. Quite to the contrary, the MO orbitals are antibonding in this region of the molecule. A similar statement can be made with respect to bonding between nitrogen atoms diagonally opposite each other. These atoms are too far removed from each other (~3.6 A) for any appreciable orbital overlap to occur. It is not surprising that all attempts to isolate hydrazines from reactions starting with N_4S_4 have to date failed.

Table IV

Overlap Populations between Orbitals on Two Edge-Located Nitrogen Atoms[a]

Orbital	s	p_z	p_x	p_y
s	−10	0	−25	−58
p_z	0	12	0	0
p_x	−58	0	40	−112
p_y	−25	0	−112	40

Reduced overlap population −0.0262

[a] The overlap populations have been multiplied by 10^4. The nitrogen atoms used are those having coordinates $x < 0$, $y = 0$ and $x = 0$, $y > 0$ in the xy plane.

Table V

Overlap Populations between Orbitals on Two Diagonally Located Nitrogen Atoms[a]

Orbital	s	p_z	p_x	p_y
s	0	0	−3	0
p_z	0	1	0	0
p_x	−3	0	12	0
p_y	0	0	0	−2

Reduced overlap population +0.004

[a] The overlap populations have been multiplied by 10^4. The nitrogen atoms used are those along the positive and negative x axis.

Question III. π-Electron Delocalization in N_4S_4 and Related Ions

The occurrence of a single nitrogen–sulfur distance in tetranitrogen tetrasulfide indicates that all nitrogen–sulfur bonds in the eight-membered ring are equivalent. A nitrogen–sulfur single bond is normally taken to be 1.74 A,[13] while a nitrogen–sulfur double bond is characterized by a distance 1.54 A.[13] The observed distance in N_4S_4 is 1.62 A, intermediate between that of a single bond and a double bond. These two observations have led previous workers to speculate that there may occur appreciable delocalization of electronic charge in π-type orbitals which span in a bonding manner all eight atoms of the nonplanar system, the resulting electronic structure being representative of the π-electron-delocalized type so familiar in planar aromatic molecules. Additional experimental evidence for a delocalized electronic structure is found in the work of Chapman and co-workers,[17] who pointed out

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(16) T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 846 (1963).

(17) D. Chapman and A. C. Massey, *Trans. Faraday Soc.*, **58**, 1291 (1962); D. Chapman, R. M. Golding, A. C. Massey, and J. T. Moelwyn-Hughes, *Proc. Chem. Soc.*, 377 (1961).

that a solution of N_4S_4 and potassium metal in dimethoxyethane exhibits various color changes and gives rise to at least two species having a nine-line esr spectrum. The nine-line spectrum is definitive for the presence of a paramagnetic material having four chemically equivalent nitrogen atoms. This can only be possible if the negative ions possess π-electron-delocalized electronic structures.

In the calculations, the coordinates of the atom were selected so that the nitrogen atoms lie in the xy plane with the following orientations (listed are the algebraic signs of the x, y, and z coordinates of each atom): N_1 $(-, 0, 0)$, N_2 $(+, 0, 0)$, N_3 $(0, -, 0)$, N_4 $(0, +, 0)$, S_1 $(+, +, +)$, S_2 $(-, +, -)$, S_3 $(-, -, +)$, S_4 $(+, -, -)$. Thus, N_1 and N_2 lie on the x axis. N_3 and N_4 lie on the y axis. S_1 and S_3 lie above the plane of the nitrogen atoms and are bonded to nitrogen atoms 2 and 4 and 1 and 3, respectively, while sulfur atoms 2 and 4 lie below the nitrogen plane and are bonded to nitrogen atoms 1 and 4 and 2 and 3, respectively. The molecular orbitals belong to the irreducible representations of the group D_{2d} which in turn are A_1, A_2, B_1, B_2, and E.

The relative energies of the seven highest occupied molecular orbitals are very sensitive to the parameters of the calculations, and arguments based upon the order of the orbitals or the energy differences between them must be avoided. This type of calculation applied to benzene predicts that one π orbital (a_{2u}) will be energetically below three of the σ orbitals (e_{2g}, e'_{2g}, and b_{2u}),[9] a rather unsatisfactory basis for any discussion of π-electron delocalizations. The total atomic charges obtained from a population analysis of the calculation utilizing only s- and p-type orbitals predict that the nitrogen atoms will have an excess of electronic charge of -0.328, while the sulfur atoms will be electron deficient to the same extent. Inclusion of sulfur d orbitals makes the charge on the sulfur atoms negative 0.108 and that on nitrogen positive 0.108. The small charges calculated for the atoms suggest that the electronic charge is about equally distributed among the eight atoms of the ring in both molecules, but refined calculations are necessary before a discussion of its delocalization can be made.

In Figure 2 are shown the relative orbital energies of the molecular orbitals for N_4S_4 for two different calculations. The first calculation utilizes only s- and p-type orbitals; the second includes the d-type orbitals of sulfur as well. Diagrammed are the 24 lowest lying molecular orbitals, the first 22 being occupied in N_4S_4 and the 2 highest lying degenerate orbitals being unoccupied. The number to the left of the line in Figure 2 represents the degeneracy of the orbital. In the calculation which includes only the s and p orbitals, the two lowest lying bonding-type MO's (unoccupied) are degenerate. The calculation involving d orbitals admits a large number of unoccupied molecular orbitals, but, interestingly, again the two lower lying of these are degenerate. Since these orbitals are bonding molecular orbitals, bonding with respect to all eight atoms in the ring, occupancy of them would yield a delocalized charge distribution for negative ions of N_4S_4.

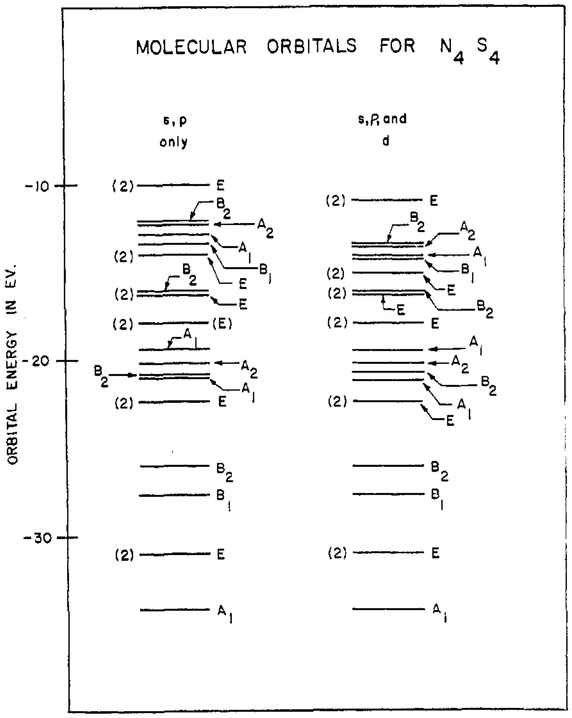

Figure 2.—The molecular orbital energies of tetranitrogen tetrasulfide. Shown are two sets of orbitals; the set on the left is derived from a calculation which excluded the d-type orbitals of sulfur. The right-hand set includes them.

Question IV. The Role of d-Type Orbitals on the Sulfur Atoms

The role played by the d-type orbitals of sulfur in discussing the chemical bonding occurring in sulfur-containing compounds is well known. Frequently, when it is not possible to describe the compound using classical valence theory, the d orbitals are brought into play. This situation is most frequently encountered in cases when no obvious Lewis structure suggests itself, such as SF_6. Tetranitrogen tetrasulfide is such a molecule. Craig has pointed out the role played by d-type orbitals in cyclic inorganic systems and the fact that they enable a continuous d_π–p_π type of overlap to occur, which in turn leads to appreciable π-electron delocalization.[18] In addition, Dewar, *et al.*,[8] have demonstrated that the use of two d orbitals on phosphorus atoms in the phosphonitrilic halides leads to a three-centered-bond description of the form P–N–P. A similar argument is applicable to N_4S_4.

In a rigorous quantum mechanical description of sulfur nitride, properties such as chemical binding energies and accurate charge densities are not obtainable from a wave function composed solely of s- and p-type orbitals on the nitrogen and the sulfur atoms. Indeed, the inclusion of d-type orbitals would also do little to remedy the situation. One would expect that the basic description of the molecule, for example, its geometrical structure, could be deduced from s and p

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(18) D. Craig, *J. Chem. Soc.*, 997 (1959).

orbitals alone. That this is so was clearly demonstrated by the self-consistent-field-type calculations described in section 1. When d orbitals are included in the calculation, one would not expect a marked change to occur. The total electronic energy might fall slightly, some small amount of charge can be expected to shift from s- and p-type orbitals to the d orbitals, and the π structure of the molecule would be changed.

The role of d orbitals can best be ascertained by comparison of two calculations, one including them and one in which they are omitted. Calculations 2 and 3 of Table II constitute such a pair. These calculations differ only in that calculation 3 includes the d orbital of sulfur with the parameters of Jordan, *et al.*[16] The same 2s, 2p, 3s, and 3p orbitals are used in both. Table VI lists the total atomic orbital charges for the two calculations. The effect of the d orbitals upon the π-electron structure of the molecule is visible from Figure 2.

TABLE VI

ORBITAL CHARGE IN N_4S_4

Orbitals	Excluding sulfur d orbitals	Including sulfur d orbitals
2s	1.299	1.295
$2p_z$	1.215	1.064
$2p_x$	1.573	1.411
$2p_y$	1.240	1.122
3s	1.455	1.463
$3p_z$	1.590	1.566
$3p_x$, $3p_y$	1.314	1.299
$3d_{z^2}$		0.094
$3d_{xz}$, 3_{yz}		0.064
$3d_{x^2-y^2}$		0.099
$3d_{xy}$		0.160

First, the sulfur d orbitals play no major role in the molecular description. The orbital charges in the two calculations differ only slightly. The largest d orbital charge computed is 0.160 for d_{xy}. This orbital has lobes of charge density symmetrically distributed between the x and y axes and is thus principally involved in the development of bonds between sulfur and nitrogen atoms and not between the sulfur atoms themselves. It contributes to the p_π–d_π overlap necessary for π-electron delocalization. Since the molecule is nonplanar and we arbitrarily calculate with the nitrogen atom in the xy plane, d_π–p_π overlap can best occur *via* either the d_{z^2}, d_{xz}, or d_{yz} orbitals. The latter two orbitals are the d orbitals which are least important. Since the S–N–N angle is close to $\pi/2$, the d_{z^2} orbital should be more effective than either d_{xz} or d_{yz}, as it will niteract more strongly with the $2p_y$ or $2p_x$ orbitals of nitrogen. This interaction is reflected in the relative energies of the higher occupied molecular orbitals. These orbitals are the only orbitals to which the d orbitals make an appreciable contribution and account for the lowering of the total energy which occurs with d orbital inclusion. The maximum coefficients of these d orbitals are quite small, and thus they are not a major component of the basis set utilized in building the molecular orbital description. *All of the principal conclusions* of this paper *are unaltered* if the *d orbitals* of the sulfur atoms *are omitted* from the calculations.

Discussion

There have been two previous theoretical studies of tetranitrogen tetrasulfide. The free-electron model has been applied by Chapman and Waddington.[19] Braterman[20] has recently applied the simple molecular orbital theory. The free-electron model predicts the existence of S–S and N–N bonds in N_4S_4. The latter conclusion is not in accord with our calculations. With the atomic centers at their equilibrium positions and a selected set of orbital shielding constants, the calculation of the molecular orbitals becomes a symmetry-determined problem when a full overlap matrix is included. The calculated bond orders are not very sensitive to the choice of shielding constants. We feel that the absence of a positive bond order between nitrogen atoms is significant. If bonding occurs between nitrogen atoms, the bonds themselves must be far weaker than the N–S or S–S bonds present. The free-electron model views the molecule as having a spherically symmetrical potential field and correctly predicts the spectral line of N_4S_4 at 2530 A. The observation of a dipole moment (0.72 D.) belies the realistic nature of the model.[21] Our molecular orbital calculations fail to predict the correct spectrum for N_4S_4 by a factor of 2 (calcd, 5248A; obsd, 2530 A), but this is to be expected as spectroscopic predictions based upon crude MO models are of dubious value. The free-electron model most closely resembles the method of the one-center expansion (OCE) in its approach (the correct potential is however ignored).[22] Previous studies have demonstrated that the OCE procedure is successful in calculating total electronic energies when coupled with configuration interaction. It gives rise to artificial charge densities,[23] and, without configuration interaction, it fails to calculate even a correct electronic energy. One cannot help but feel that the agreement obtained by Chapman and Waddington is somewhat fortuitous when N_4S_4 is examined in the light of, say, CH_4.

The results of our calculations are in accord with the somewhat simpler study of Braterman. Whereas Braterman partitions the electronic charge among σ-bonding electrons, nitrogen atom lone pairs, etc., we obviate this necessity by inclusion of the full-overlap matrix. Braterman predicts the spectral assignments for N_4S_4 by the introduction of some S–S bonding and the corresponding antibonding level.

Our calculations lend support to Braterman's assignments in that they give rise to S–S bonding. The lowest lying MO's calculated are of symmetry E and are antibonding with respect to sulfur–sulfur bonds.

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[19] D. Chapman and T. C. Waddington, *Trans. Faraday Soc.*, **58**, 1679 (1962).

[20] P. S. Braterman, *J. Chem. Soc.*, 2297 (1965).

[21] N. L. Phalnikar and B. V. Bhide, *Current Sci.* (India), **8**, 473 (1939).

[22] See R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963.

[23] A. G. Turner, A. F. Saturno, P. Pauk, and R. G. Parr, *J. Chem. Phys.*, **40**, 1919 (1964).