The Electronic Structure and Localized Molecular Orbitals in S_4N_4 by the CNDO/BW Theory

M. S. GOPINATHAN AND M. A. WHITEHEAD[1]
Theoretical Chemistry Department, 1 South Parks Road, Oxford, England

Received September 24, 1974

M. S. GOPINATHAN and M. A. WHITEHEAD. Can. J. Chem. **53**, 1343 (1975).

The energies calculated for tetranitrogen tetrasulfide, S_4N_4, by the CNDO/BW theory favor a structure with coplanar nitrogen atoms and not a structure with coplanar sulfur atoms. Both structures have been proposed from experimental studies. Localized molecular orbitals are calculated for S_4N_4 and used to choose the appropriate Lewis structure for the molecule. The hybridization at the nitrogen and sulfur atoms is discussed. There is electron delocalization in the molecule, the S—N bond is a bent bond involving pure p-orbitals on the sulfur and nitrogen atoms and there is a pure p-bent bond between the sulfur atoms on the same side of the coplanar nitrogen atoms. There is no N—N bond in S_4N_4.

M. S. GOPINATHAN et M. A. WHITEHEAD. Can. J. Chem. **53**, 1343 (1975).

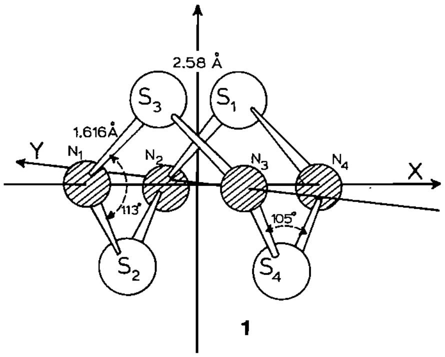
Les énergies calculées pour le tétrasulfure de tétrazote, S_4N_4, par la théorie CNDO/BW favorisent une structure avec des atomes d'azote coplanaires et non pas une structure avec des atomes de soufre coplanaires. Les deux structures avaient été proposées à partir d'études expérimentales. Les orbitales moléculaires localisées peuvent être calculées pour S_4N_4 et utilisées pour choisir la structure de Lewis appropriée pour la molécule. On discute de l'hybridisation aux atomes d'azote et aux atomes de soufre. Il y a une délocalisation des électrons dans la molécule; le lien S—N est un lien courbé impliquant des orbitales p pures sur les atomes de soufre et les atomes d'azote et il y a un lien p courbé entre les atomes de soufre sur le même côté des atomes d'azote coplanaires. Il n'y a pas de lien N—N dans le S_4N_4.

[Traduit par le journal]

Introduction

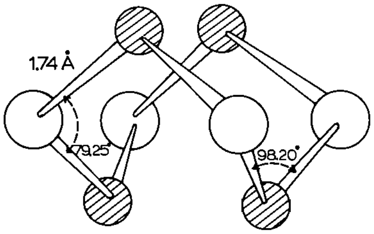
The molecular structure and chemical bonding in tetranitrogen tetrasulfide, S_4N_4, are unresolved (1, 2). X-Ray and electron diffraction studies (3) and vibrational (4) and electronic (5) spectral studies lead to two proposed molecular structures, **1** and **2**, (Figs. 1 and 2). In structure **1** the four nitrogen atoms are coplanar with two sulfur atoms above and two below the plane, while structure **2** has coplanar sulfur atoms with the nitrogen atoms above and below the plane. Both structures have D_{2d} molecular symmetry. An extended Hückel theory study (6) of the energies of the two structures predicted structure **1** to be more stable. The same structures are here studied using SCFMO wavefunctions of the CNDO/BW theory (7).

There is also the problem of the electronic structure of S_4N_4. Many Lewis structures (Fig. 3, **A** to **G**) have been proposed for S_4N_4, which differ in the type of bonds present, the charge on the atoms, the number of lone-pair electrons on each atom, and the presence or absence of S—S



1

FIG. 1. The coplanar nitrogen atom structure of S_4N_4.



2

FIG. 2. The coplanar sulfur atom structure of S_4N_4.

---

[1] Permanent address: Chemistry Department, McGill University, Montreal, Quebec.

and N—N bonds. Experimental and theoretical studies have not provided a unique atomic orbital description. From vibrational spectra, Lippincott and Tobin (4) proposed structure **2** with N—N bonds but no S—S bonds. The electronic spectrum was explained (5) using a weak S—S bond, structure **1**. A free electron treatment (8) suggested the presence of both N—N and S—S bonds, while Lindqvist (9) proposed formula **B**. From an empirical correlation between S—S bond length and s-character of the sulfur hybrid orbitals in other molecules, it was argued that a single bond involving pure pσ orbitals exists in S_4N_4 (9). Extended Hückel calculations (6) gave a negative bond order between the nitrogen atoms and indicated a weak S—S bond of the pσ type. The dispute over the existence of an S—S bond arises from the fact that the observed S—S distance in S_4N_4 is 2.58 Å which is longer than the normal single bond length, of 2.08 Å, and shorter than the sum of the van der Waals radii, 3.70 Å (7). A pure pσ bond between sulfur atoms does not fit (3) with the "double bond character" of the N—S bond inferred from the bond length of 1.616 Å, which is shorter than a "pure single (sp^3)" bond length of 1.764 Å. However this N—S double bond character is not consistent with the observed angles of 113° at nitrogen and 105° at sulfur. Any bonding scheme for the molecule also has to explain the electron delocalization in the S—N ring, indicated by the electronic spectrum (5), and the ^{14}N n.m.r. chemical shifts (10) and explain the unstable nature of the compound.

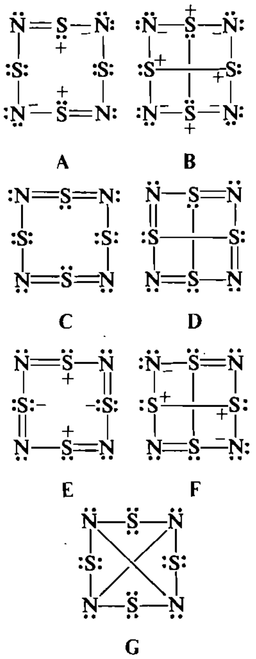


FIG. 3. Possible Lewis structures for S_4N_4.

The conventional form of molecular orbital wavefunctions cannot answer the above questions since the wavefunctions are delocalized over the entire molecular frame, and do not correspond to chemical bonds, lone pairs, etc. However, a single determinantal wavefunction, such as the CNDO/BW wavefunction, is invariant to orthogonal transformation of the occupied molecular orbitals out of which it is formed. Therefore the delocalized molecular orbitals can be transformed into Localized Molecular Orbitals (LMO's) which correspond to chemical bonds and lone pairs. Several criteria have been used to determine the transformation matrix (11) but the most successful and theoretically attractive method is that of Lennard-Jones (12), extensively applied by Ruedenberg and co-workers (13). This method uses the theory that the two electrons forming a localized bond have maximum self-repulsion. This is an intrinsic criterion (14) and does not involve any preconceived model for the electron density distribution. The method successfully describes the electronic structure of a wide variety of molecules including electron deficient molecules (15, 27), and has been applied to the CNDO/BW wavefunctions for S_4N_4 to obtain a quantitative description of the nature of the bonding.

Method of Calculation

The CNDO/BW theory is specifically parameterized to yield the correct equilibrium molecular geometry (7). The parameter set III of Boyd and Whitehead (7) has been used, together with the experimental molecular geometry: structure **1**: N—S 1.616 Å, ∠SNS 113°, ∠NSN 105° (ref. 3); structure **2**: N—S 1.74 Å, ∠SNS 98.2°, ∠NSN 79.25° (ref. 4). Only 2s and 2p functions were used in the basis set; the possibility of d-orbitals on sulfur is discussed later. The localization procedure followed that of CNDO type wavefunctions given by Gopinathan and Narasimhan (16).

Results and Discussion

Geometrical Structure

The total molecular energy calculated by the

TABLE 1. Truncated Localized Molecular Orbitals, TLMO, in S_4N_4. The numbering of the atoms and the coordinate axes refer to structure **1**

Type of LMO	N_s*	N_{p_x}	N_{p_y}	N_{p_z}	S_s†	S_{p_x}	S_{p_y}	S_{p_z}
N_1 lone pair (I)	−0.95299	0.28548	0.00513	0.00756				
S_3 lone pair					0.89418	0.14669	0.15409	−0.38646
N_1—S_3 bond	0.12185	0.39316	−0.31899	0.343203				
					0.23949	−0.29937	0.44656	−0.48681
N_1 lone pair (II)	0.00890	−0.00544	0.65906	0.646042				
				(S_2)	−0.00148	−0.05309	0.18677	0.10042
				(S_3)	−0.00535	0.064929	0.18992	0.10374
S_3—S_1 bond				(S_1)	−0.03571	0.43401	0.49203	−0.13945
				(S_3)	−0.11140	−0.48274	−0.46936	−0.12651

*N_a coefficient of atomic orbtal a on nitrogen.

†S_b coefficient of atomic orbital b on sulfur. The delocalization is given by $d = (1 - \sum_i c_{i\mathrm{TLMO}}^2) \times 100\%$. Thus the delocalization of the N_1 lone pair is $(1 - \sum_{s,p_x,p_y,p_z} c_{N_1\mathrm{TLMO}}^2)$, and the amount of delocalization other than to the adjacent S_2 and S_3 is given by $(1 - \sum_{\substack{\text{nitrogen}\\\text{orbitals}}} c_i^2 - \sum_{\substack{\text{sulfur}\\\text{orbitals}}} c_i^2)$.

CNDO/BW method is −64.72827 a.u. for structure **1** and −64.39302 a.u. for structure **2**. The average calculated S—N bond energy is 70 kcal mol^{-1} for structure **1** and 50 kcal mol^{-1} for structure **2**. Thus the coplanar nitrogen structure is more stable than the coplanar sulfur structure by 0.33525 a.u. (~200 kcal mol^{-1}). Qualitatively similar results were obtained from extended Hückel calculations (6). The latest three-dimensional X-ray diffraction study (3) also supports structure **1**. These results show structure **1** to be the correct one; structure **2** is not considered further.

Electronic Structure

There are 44 valence electrons in S_4N_4 in 22 occupied molecular orbitals. The localized CNDO/BW molecular orbitals for S_4N_4 are highly localized. The degree of delocalization of LMO can be obtained as follows.

While a given LMO approximates a given bond or lone pair in a molecule, it contains coefficients of atomic orbitals on atoms which are not those forming a localized bond or lone pair. If all the coefficients of atomic orbitals, other than those chemically considered to be involved in the bond or lone pair, are neglected, a *Truncated Localized Molecular Orbital*, TLMO (Ψ_{TLMO}) is obtained. This TLMO is not renormalized. The original LMO is normalized, and the difference

$$1 - \int \Psi_{\mathrm{TLMO}}{}^2 \, d\tau$$

measures the delocalization of the original LMO. If the LMO is completely localized it equals the TLMO and the above difference is zero. Within the CNDO/BW theory, where differential overlap is neglected, this difference becomes

$$d = \left(1 - \sum_i c_{i\mathrm{TLMO}}^2\right) \times 100$$

as a percentage of delocalization, and d goes to 0% when the LMO represents a completely localized lone pair or bond, and hence is identical to the TLMO.

The LMO's in S_4N_4 belong to five types, Table 1 and Fig. 4.

(1) Nitrogen Lone Pair (I)

This is a nitrogen 2s orbital, with 99.1% s-character. Thus there is no hybridization at the nitrogen atoms in S_4N_4. The delocalization index, d, is 1.02%; this lone pair is highly localized.

(2) Sulfur Lone Pair

This is predominantly a sulfur 2s orbital, with 80.45% s-character. The d value is 0.85%; the lone pair is highly localized.

(3) N—S Bond

The d value is 2.76%; the bond is highly localized. It is a single bond between almost pure p-orbitals on nitrogen and sulfur. The s-characters of the nitrogen and sulfur orbitals are 3.82 and 9.83% respectively. These orbitals are not directed along the N—S internuclear axis. The p-vector corresponding to the nitrogen orbital (having the x, y, z components given in Table 1) makes an angle of 6.03° with the NS axis at 21.17° to the NSS plane and the corresponding

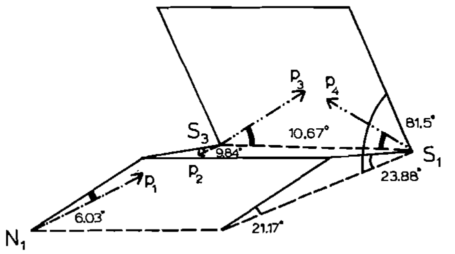


FIG. 4. Atomic orbital representation (schematic) of N—S and S—S bonds in S_4N_4 obtained from LMO's. Only one N—S bond (N_1S_3) and one S—S bond (S_1—S_3) are shown. The angles represent the deviation of the atomic hybrids from the internuclear axes and from the NSS plane. Note that the overlap occurs inside the nuclear frame, as in ref. 27 for the center bond of 1,2-$C_2B_4H_6$. Angle between $\boldsymbol{p}_1$ and N_1—S_3 axis = 6.03°; $\boldsymbol{p}_1$ and N_1—S_3—S_1 plane = 21.17°; $\boldsymbol{p}_2$ and N_1—S_3 axis = 9.84°; $\boldsymbol{p}_2$ and N_1—S_3—S_1 plane = 23.880°; $\boldsymbol{p}_3$ and S_3—S_1 axis = $\boldsymbol{p}_4$ and S_3—S_1 axis = 10.67°; $\boldsymbol{p}_3$ and N_1—S_3—S_1 plane = $\boldsymbol{p}_4$ and N_1—S_3—S_1 plane = 81.5°; where $\boldsymbol{p}_1$ = p-orbital vector on N_1 involved in the N_1—S_3 bond, $\boldsymbol{p}_2$ = p-orbital vector on S_3 involved in the N_1—S_3 bond, $\boldsymbol{p}_3$ = p-orbital vector on S_3 involved in the S_3—S_1 bond, and $\boldsymbol{p}_4$ = p-orbital vector on S_1 involved in the S_3—S_1 bond.

sulfur orbital makes an angle of 9.84° with the NS axis at 23.88° to the NSS plane (Fig. 4). Thus, maximum overlap occurs off the internuclear axis; the N—S bond is bent (17).

(4) S—S Bond

The delocalization index is 6.7% and is over the whole molecule. The orbitals in this LMO are almost pure p-orbitals on sulfur, with 2.0% s-character; the bond is between two sulfur atoms on the same side of the nitrogen plane. The S—S bond is bent, the sulfur p-orbital vectors in this LMO make angles of 10.67° with the S—S axis at 81.5° to the NSS plane.

(5) Nitrogen Lone Pair (II)

The *d* value is 14.82%. The delocalization is mainly (9.89%) to the p-orbitals of the two sulfur atoms to which the nitrogen is bonded. The remaining 5% is to all other atoms. This is a pure p-orbital lone pair on nitrogen, but more delocalized than the nitrogen s-lone pair (I) described above.

These are the only LMO's in S_4N_4. No LMO corresponds to an N—N bond; there is no N—N bond in the molecule, agreeing with the reduction products of S_4N_4 never containing N—N bonds. The LMO's show the molecule to be adequately described by the Lewis structure **B**, suggested by Lindqvist (9).

The atomic charges at nitrogen and sulfur from the present calculations are −0.329 and +0.329 respectively, again supporting structure **B** which has been shown to be consistent with the electronic spectrum of S_4N_4 (5) which requires a polar structure.

The N—S and S—S bonds are bent bonds between almost pure p-orbitals; they are weaker than normal straight bonds involving sp^n hybrids, which explains the classical "strain" in S_4N_4 and its unstable nature (4). Thus S_4N_4 is analogous to P_4 (17) where bent bonding occurs between essentially p-orbitals. The difficulty in reconciling the observed N—S and S—S bond lengths with the valence angles at nitrogen and sulfur disappears; bond lengths are not simply a function of double bond character or bond order. Thus while the N—S bond length in H_3—N—SO_3 is 1.764 ± 0.020 Å, and is assumed to be a single sp^3 bond (3), the observed N—S distance in S_4N_4 is 1.616 ± 0.010 Å. But this does not imply double bond character in the N—S bond in S_4N_4 (bond order greater than 1) nor sp^2 hybrids. The nature of a chemical bond between two atoms is determined by, (*1*) the s and p character of the bonding atomic hybrids, (*2*) the bent or straight overlap of these hybrids, and (*3*) the delocalization of these hybrids to other atoms. The S—S bond in S_4N_4 illustrates these points. The LMO shows pure p-orbitals in the bond, a considerably bent bond, and a delocalization of 6.7% to other atoms in the molecule, causing a considerable weakening of the bond even though it is a two electron single bond. This result agrees with Lindqvist's (9) prediction of a pure p-orbital bond from the correlation of observed S—S distances in S_8, $S_2O_6{}^{2-}$, $S_2O_4{}^{3-}$, and S_4N_4 with the s-character of the sulfur hybrid.

There is no satisfactory definition of bond index to measure the strength of a bond in SCFMO theory (18, 19). However, the bond order index of Wiberg (20, 21) may be used as a measure of bond strength. The index is the sum of the squares of the first-order density matrix elements between orbitals on two atoms. The Wiberg index for the N—S and S—S bonds in S_4N_4, has been calculated using the LMO's in Table 1. For the N—S bond the value is 0.907; there is an additional contribution to the N—S bond order from the delocalized N lone pair (II) of 0.16. Thus the total bond order for the N—S bond is 1.067; that for the S—S bond is 0.869. The N—S bond has little double bond character, and the S—S bond is weaker than a normal single S—S bond.

The diamagnetic ring current in S_4N_4 (10) suggests electron delocalization around the SN ring. From the LMO's the diamagnetic ring current is obviously due to the p-orbital lone pair electrons on nitrogen delocalizing into the p-orbitals on the sulfur atoms to which it is directly bonded. A recent CNDO/2 calculation of the Wiberg bond order for the S—N bonds in $N_4S_4F_4$ and S_4N_4 by Cassoux *et al.* (22) gave the values 1.3 and 1.87 for the two types of bonds in $N_4S_4F_4$ and 1.49 for the bond in S_4N_4. These authors interpreted the bond order in S_4N_4 intermediate between the values for $N_4S_4F_4$, as evidence for electron delocalization in N_4S_4. This is not true; their result is a consequence of using uniform S—N bond lengths in S_4N_4 intermediate between the two S—N bond lengths in $N_4S_4F_4$.

The present LMO picture of the molecule obtained using only s and p functions on sulfur shows electron delocalization in the molecule, and hence it is not necessary to use d-orbitals on sulfur to explain the ring current (10, 15). Turner and Mortimer's extended Hückel theory calculations (6), specifically included d-orbitals on sulfur and showed that d-orbitals do not play any role in the molecular description of S_4N_4. Similarly X_α calculations on SO_4^{2-} and SF_6 (23) have shown that there is no sulfur 3d orbital contribution to the electronic structure of these molecules. Similar conclusions have been reached by Koutecky and Musher (24) from CNDO/2 calculations on sulfur compounds of different valence states.

Conclusion

S_4N_4 has a molecular structure with coplanar nitrogen atoms. The electronic formula for the molecule is the polar Lewis structure **B**. There is no s–p hybridization at nitrogen or sulfur. The N—S and S—S bonds are bent single bonds involving pure p-orbitals. There is no N—N bond. Electron delocalization occurs by delocalization of the p-electrons in a nitrogen lone pair to the p-orbitals on the sulfur atoms to which the nitrogen is bonded. The field gradient direction at the nitrogen atom, and the relation to recent n.q.r. field gradient measurements (25) will be considered in a paper on the n.q.r. field gradients of various SN ring systems (26).

The authors deeply appreciate the warm hospitality and the keen interest in their welfare and scientific work, extended by the late Professor C. A. Coulson, FRS. M.S.G. gratefully acknowledges the award of a Commonwealth Bursary of the Royal Society, London, that made possible his visit to Oxford. M. A. W. acknowledges the award of a National Research Council of Canada Travelling Fellowship 1971–1974.

1. M. B. Goehring. Q. Rev. **10**, 437 (1959); Prog. Inorg. Nucl. Chem. **1**, 207 (1959); Angew. Chem. **73**, 589 (1961).
2. C. S. Lu and J. Donohue. J. Am. Chem. Soc. **66**, 818 (1944).
3. B. D. Sharma and J. Donohue. Acta Cryst. **16**, 891 (1963).
4. E. R. Lippincott and M. C. Tobin. J. Chem. Phys. **21**, 1559 (1953).
5. P. S. Brateman. J. Chem. Soc. 2297 (1965).
6. A. C. Turner and F. S. Mortimer. Inorg. Chem. **5**, 906 (1966).
7. R. J. Boyd and M. A. Whitehead. J. Chem. Soc. Dalton, 73, 78, 81 (1972).
8. D. Chapman and T. C. Waddington. Trans. Faraday Soc. **58**, 1679 (1962).
9. I. Lindqvist. J. Inorg. Nucl. Chem. **6**, 159 (1958).
10. J. B. Mason. J. Chem. Soc. A, 1567 (1969).
11. H. Weinstein, R. Pauncz, and M. Cohen. *In* Advances in atomic and molecular physics, Vol. 7. Academic Press, New York. 1971. p. 40.
12. J. E. Lennard-Jones. Proc. R. Soc. Lond. **A198**, 1, 14 (1949).
13. W. England, L. S. Salmon, and K. Ruedenberg. Top. Curr. Chem. **23**, 31 (1971).
14. K. Ruedenberg. *In* Modern quantum chemistry, Part 1. Academic Press, New York. 1965. p. 85.
15. E. Switkes, W. N. Lipscomb, and M. D. Newton. J. Am. Chem. Soc. **92**, 3847 (1970).
16. M. S. Gopinathan and P. T. Narasimhan. Mol. Phys. **22**, 473 (1971).
17. C. A. Coulson. Valence, 2nd ed. Oxford University Press, London. 1961.
18. R. J. Boyd. Can. J. Chem. **51**, 1151 (1973).
19. J. W. McIver, Jr., P. Coppens, and D. Nowaic. Chem. Phys. Lett. **11**, 82 (1971).
20. K. B. Wiberg. Tetrahedron, **24**, 1083 (1968).
21. C. Trindle and O. Sinanoglu. J. Am. Chem. Soc. **91**, 853 (1969).
22. P. Cassoux, J. F. Labarre, O. Glemsek, W. Kock. J. Mol. Struct. **13**, 405 (1972).
23. K. H. Johnson. *In* Advances in quantum theory, Vol. 7. *Edited by* P. O. Lowdin. Academic Press, New York. 1973. p. 143.
24. V. B. Koutecky and J. I. Musher. Theor. Chim. Acta, Berl. **33**, 227 (1974).
25. D. Benlian, M. Gourdji, and L. Guibe. J. Chem. Phys. **59**, 5382 (1974).
26. M. S. Gopinathan and M. A. Whitehead. To be published.
27. D. A. Kleier, T. A. Halgren, J. H. Hall, and W. N. Lipscomb. J. Chem. Phys. **61**, 3905 (1974).