An *Ab initio* Self-consistent Field Molecular-orbital Study of Novel Stereoelectronic Effects in Linear $R_2S_3N_2$ and Cyclic XS_3N_2 Systems†

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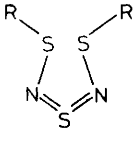
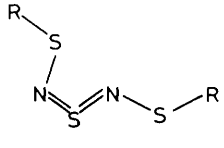
Ab initio self-consistent field molecular-orbital calculations confirm that compounds of the type RSNSNSR (**1**; R = H) exist preferentially as the *syn,syn* isomer in which the S • • • S distance is significantly shorter than the non-bonded van der Waals value, an effect attributed to stereoelectronic interactions involving the terminal sulphur lone-pair orbitals. A five-membered ring valence isomer (**2**) is calculated to be much higher in energy and not a true minimum. A series of related compounds (**4**) in which the two R substituents are replaced by a bridging group (X = S, NH, or CH_2) have similarly short S • • • S distances. To account for this, another novel stereoelectronic interaction is proposed between specifically the equatorial orbitals on X and the adjacent sulphur lone-pair orbitals, which results in bonding electron density in the transannular S • • • S region, and has the greatest effect for X = S. On this basis, it is predicted that the bridging group X = NR will show an axial preference for the R substituent, and that groups such as X = CR_2 could reveal a discrimination between the axial and equatorial substituents.

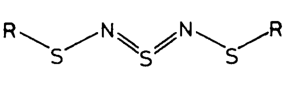
Both organic[1] and inorganic[2,3] sulphur–nitrogen systems are currently the subject of considerable interest. They can display a number of structural features such as bond delocalisation due to aromaticity,[1] close interatomic contacts, or unusual configurations. In sulphur di-imide systems such as (**1**) three possible linear isomers (**1a**)—(**1c**) are possible, of which a preference for the apparently most hindered isomer (**1a**) is displayed with substituents such as R = Ph[4] or p-ClC_6H_4.[5,‡] In a previous paper[6] we discussed these preferences in terms of stereoelectronic interactions between the nitrogen and the sulphur lone-pair orbitals, and also raised the possibility of a contribution from the cyclic form (**2**).



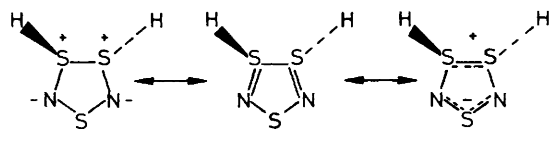
(**1a**)



(**1b**)

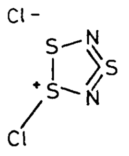


(**1c**)

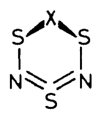


(**2**)

This speculation was prompted by the knowledge that a relatively short S • • • S interaction (3.29 Å) is observed in the *X*-ray structure,[5] compared with the sum of the van der Waals radii of approximately 3.6 Å. However, it was not clear whether forms such as (**2**) were merely resonance contributions, or whether they constituted a separate, and possibly isolable, valence isomer. Superficially at least, (**2**) is similar to stable molecules such as thiophene or 1,2,5-thiadiazole. Although the dichloro analogue (**1a**; R = Cl) is unknown, an ionic isomer (**3**) closely analogous to (**2**) in which a full S–S covalent bond exists is well characterised.[7] The crystal structures of bridging systems such as (**4**) have also recently been determined,[8] and these too reveal unexpectedly short S • • • S interactions. In these however, the bridging group X is not coplanar with the rest of the ring, and moreover the orientation of the sulphur lone pairs is expected to be quite different from *e.g.* (**1a**). In order to understand the quantitative role of structures such as (**2**), and the qualitative nature of the interactions in *e.g.* (**4**), we undertook a self-consistent field molecular-orbital (SCF-MO) study at the *ab initio* level of these systems.



(**3**)



(**4**) X = S, NH, or CH_2

Computational Method

Initial theoretical studies on compounds (**1**) and (**4**) were carried out at the *ab initio* STO-3G* closed-shell SCF-MO level,[9] restricting the geometries to C_{2v} symmetry for (**1a**) and (**1c**) and to C_s symmetry for (**1b**) and (**4**). Within these restrictions, all geometrical variables were fully optimised. In addition structure (**1a**) was explored with a variety of starting values for the S • • • S distance between 2 and 4 Å, and indeed apparent minima corresponding to both (**1a**) and (**2**) were located. However, the Hessian matrix for (**2**) proved to have two negative roots,

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Supplementary data available (No. SUP 56749, 6 pp.): Gaussian archive files. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

† *Non-S.I. units employed:* cal = 4.184 J, Hartree ≈ 4.36 × 10^{-18} J.

‡ Electron-diffraction studies have also revealed that the ground state of the species $(Me_3Si)_2S_2N$ corresponds to the *syn,syn* isomer (D. G. Anderson, H. E. Robertson, D. W. Rankin, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1989, 859).

Table 1. Calculated *ab initio* energies[a] and S $\cdots$ S bond distances[b] for compounds (**1**) and (**2**)

	(**1a**)	(**1b**)	(**1c**)	(**2**)
STO-3G*	−1 288.2321 (3.110)	−1 288.2298	−1 288.2147	−1 287.8699 (2.101)[c]
RMP2/ STO-3G*	−1 288.6942 (3.000)	−1 288.6945	−1 288.6790	−1 288.4442 (2.030)
3-21G*	−1 296.3133 (3.637)	−1 296.3060	−1 296.2835	−1 295.9727 (2.565)
6-31G*	−1 302.4378 (3.466)	−1 302.4364	−1 302.4180	−1 302.0905

[a] In Hartree. [b] Calculated lengths (in parentheses) in Å. [c] Calculated to have two negative roots in the Hessian matrix.

Table 2. Calculated energies and S $\cdots$ S distances for (**4**)

X	Energy[a]	S $\cdots$ S Distance[b]
CH_2	−1 325.6884 (−1 333.9776)	3.049 (3.097)
S	−1 680.3798 (−1 690.8261)	3.083 (3.217)
NH(ax)	−1 341.4465 (−1 349.8749)	2.920 (2.947)
NH(eq)	−1 341.4308[c]	2.945

[a] In Hartree at the STO-3G* basis-set level. Values in parentheses represent 3-21G* energies. [b] In Å at STO-3G* level. Values in parentheses represent 3-21G* lengths. [c] Attempts to locate the equatorial isomer at the 3-21G* level resulted in optimisation to the axial form.

corresponding to out-of-plane and asymmetric distortions, and no true minimum could be located. The calculations were also repeated at the 3-21G* and 6-31G* basis-set levels, which correspond to the addition of polarisation functions to the sulphur and the nitrogen respectively. The inclusion of such functions is known to be essential for reliable geometrical predictions of species containing heteroatoms. Re-optimisation at the RMP2 correlated level was only possible at the STO-3G* level due to disk storage limitations. Complete geometrical details are summarised in the Gaussian-type archive files, which have been deposited as supplementary material (SUP 56749). Molecular orbitals (STO-3G*) were plotted using a locally modified version of the program PSI/77.

Results and Discussion

The calculated *ab initio* energies and geometries of compounds (**1**) and (**2**) (R = SH) are shown in Table 1. The *syn,syn* isomer (**1a**) was calculated to be more stable than (**1b**) by 1.5 (STO-3G*), 4.6 (3-21G*), and 0.9 (6-31G*) kcal mol^{-1}, and its calculated geometry was similar to that found experimentally for R = aryl.[5] As expected, the SCF calculations tend towards a limit in which the calculated bond lengths are longer than the experimental values. The MP2/STO-3G* bond length is shorter than the corresponding SCF value, as expected (Table 1), and we anticipate that the MP2 correction would bring the 6-31G* S $\cdots$ S bond length (3.47 Å) into better agreement with the experimental value for R = aryl (3.29 Å).[5] The alternative valence isomer (**2**) had significantly greater energy at all basis-set levels (> 160 kcal mol^{-1}) than did (**1a**), and at the STO-3G* level, at least, was not a true minimum. These results effectively eliminate the possibility that such an isomer could be experimentally characterised. These quantitative calculations also indicate that the S $\cdots$ S interactions in systems such as (**1a**) are reasonably modelled at the closed-shell SCF level, and that this is not an effect associated with electron correlation.

We have previously attributed the preference for the *syn,syn* arrangement in compound (**1**) to a stereoelectronic interaction between the two in-plane sulphur lone-pair orbitals and the antiperiplanar nitrogen orbital, resulting in bonding electron density in the S $\cdots$ S region.[6,10] In a bridged system such as (**4**) one would expect the sulphur lone pairs to be orientated differently and therefore to result in different interactions. The S $\cdots$ S distances in (**4**) are also shorter than the expected non-bonded distance (X = S, 3.22; CH_2, 3.06 Å)[8] and it is not certain whether these values correspond to any bonding interaction between the two terminal sulphur atoms, or whether the short distances are entirely due to the bridging X groups forcing the two sulphur atoms into close proximity. In order to clarify this aspect of the bonding, we investigated three different bridging groups at the STO-3G* and 3-21G* levels. The predicted STO-3G* S $\cdots$ S distances for compound (**4**) (Table 2) are in good agreement with the experimental values for the two known systems, and in particular are all shorter than the value (3.32 Å) for the linear system (**1a**; R = H).

To ascertain whether the short S $\cdots$ S distances are due to a specific electronic interaction, we inspected the forms of the first four highest-occupied molecular orbitals at the STO-3G* level for (**4**; X = S, NH, or CH_2). The first two π-type orbitals involve the essentially planar SNSNS system, whilst the next two more closely resemble σ-type combinations of lone-pair orbitals. The more stable of these does indeed reveal a stabilising S $\cdots$ S interaction, although of a more complex type to that previously found for (**1a**; R = H). Thus an interaction of the equatorial lone-pair orbital on the bridging sulphur (**3**; X = S) with the two adjacent sulphur atom lone-pair orbitals results in a combination with a prominent in-phase overlap in the S $\cdots$ S region (Figure 1). The topology of this orbital is in fact similar to the corresponding in-phase combination that was previously identified as contributing to the short S $\cdots$ S distance in (**1a**; R = SH).[6]

For (**4**; X = CH_2) a smaller stereoelectronic interaction is evident, involving the equatorial rather than the axial C–H bond (Figure 2). On this basis, we predict that altering the energy of this axial bond (and hence its ability to interact with the sulphur lone-pair orbitals) by systematic variation of one or both of the substituents on the central bridging carbon atom should in turn effect the S $\cdots$ S distance. It is less certain whether these effects would be sufficiently large to detect by *e.g. X*-ray crystallography.[8]

Derivatives of (**4**) bearing a nitrogen bridging group with a simple alkyl or aryl substituent (X = NH or NR) are as yet unknown. Such compounds might exist in either axial or equatorial NR conformations. The calculated S $\cdots$ S distances are shorter (2.920 and 2.945 Å respectively at the 3G* level) and the total energies lower by 9.9 kcal mol^{-1} (Table 2) for the axial form of X = NH relative to the equatorial isomer. The reasons for this are apparent from Figure 3, which illustrates that the stereoelectronic S $\cdots$ S interactions involving the equatorial nitrogen lone pair are much greater than for the equatorial N–H σ bond.

Decreasing the S $\cdots$ S distance *via* a stabilising S $\cdots$ S σ-type interaction is also expected to *increase* the π-type interactions across the S $\cdots$ S region of the essentially planar SNSNS ring. Such an interaction could be described as homo-antiaromatic, and hence destabilising since the formal π-electron count in this ring is eight (4*n*). We note that compounds such as (**4**) are indeed more reactive when compared with a variety of 4*n* + 2 electron aromatic sulphur–nitrogen heterocyclic systems,[1] which could indeed indicate a measure of anti-aromaticity in (**4**).

These stereoelectronic interactions are of quite an unusual type, and we are currently investigating their generality in other heteroatom systems involving third-row elements.

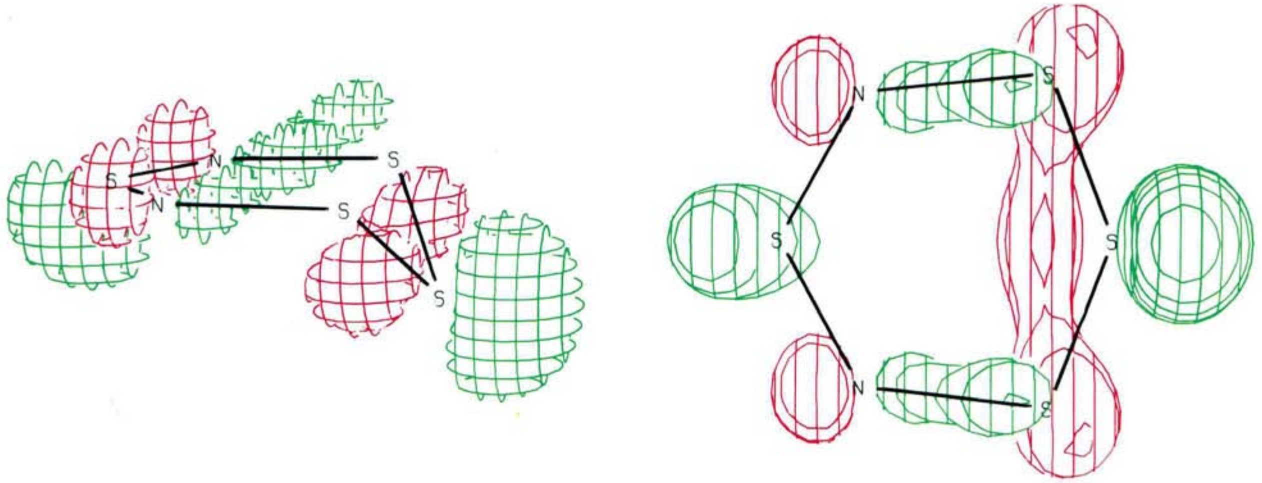

Figure 1. STO-3G* HOMO-3 Molecular orbital for (**4**; X = S). Two different views are given, illustrating the S • • • S transannular interaction

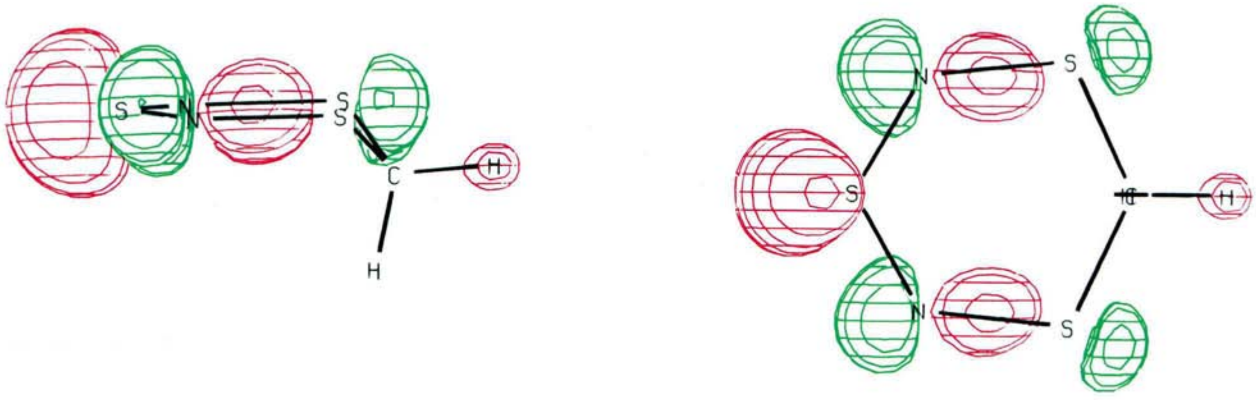

Figure 2. STO-SG* HOMO-3 Molecular orbital for (**4**; X = CH_2). Two different views are given, illustrating the interaction of the equatorial C–H but not the axial C–H bond with the sulphur lone pairs

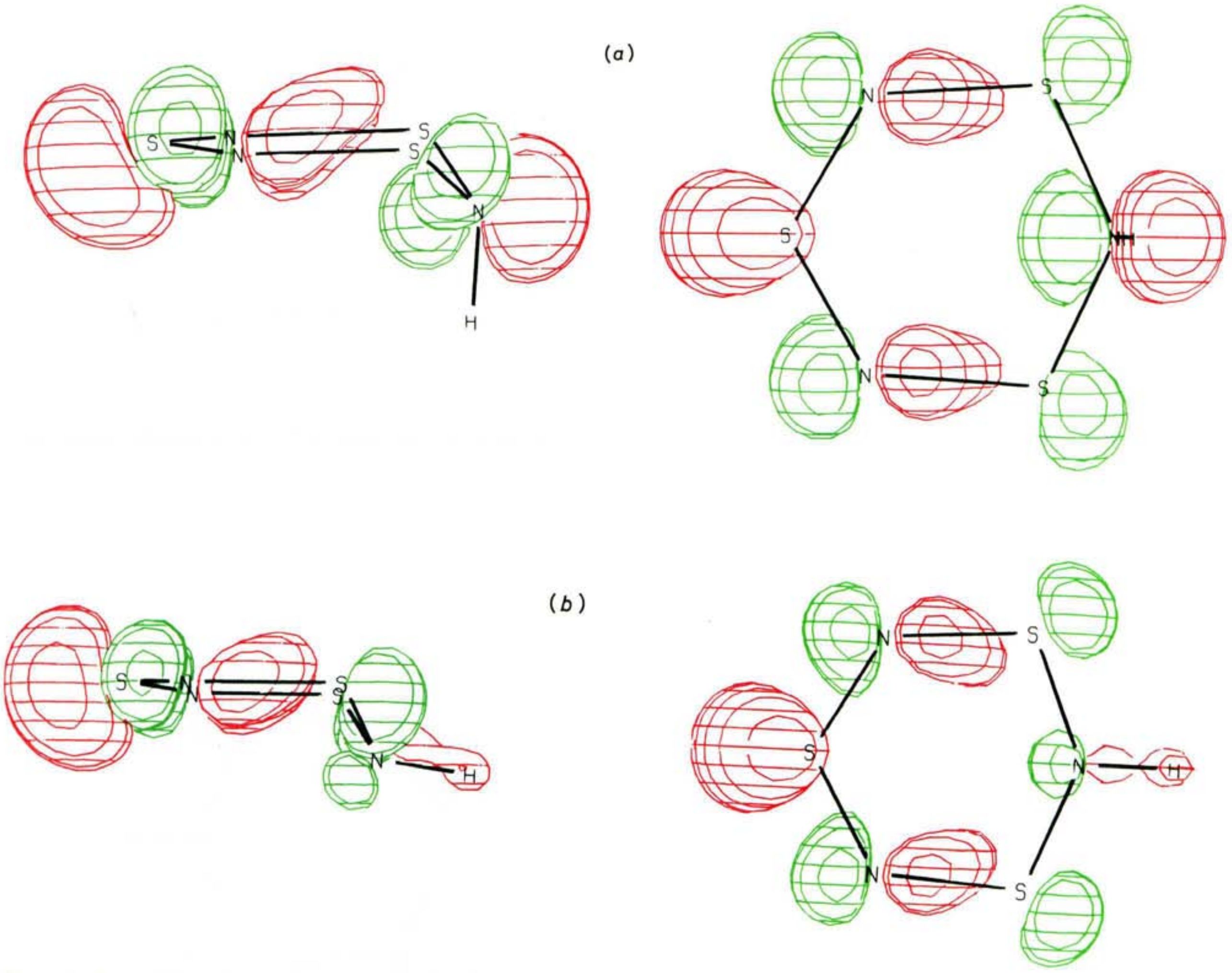

Figure 3. Two different views of the STO-3G* HOMO-3 molecular orbital for (*a*) (**4**; X = NH) axial and (*b*) (**4**; X = NH) equatorial. The transannular S • • • S interactions are significantly more prominent for the axial isomer

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