The Reaction between Tetrasulphur Tetranitride (S_4N_4) and Electron-deficient Alkynes. A Molecular Orbital Study

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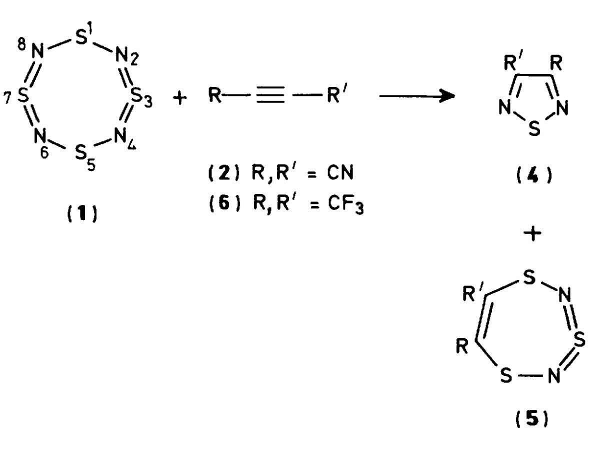
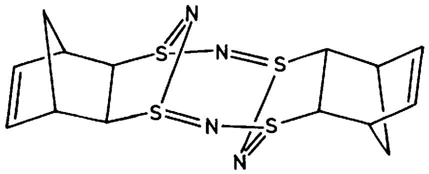
The regioselectivity of the cycloaddition of tetrasulphur tetranitride (**1**) to electron-deficient alkynes such as dicyanoacetylene (**2**) is shown to be largely controlled by interaction between the lowest unoccupied molecular orbital (LUMO) of (**2**) and either the occupied $3a_2$ orbital on (**1**), favouring [2,4]-addition across nitrogen, or the occupied $4b_1$ orbital on (**1**), favouring [1,5]-addition across sulphur. The latter regiochemistry in particular is less readily rationalised by the alternative overlap between the highest occupied orbital (HOMO) of the alkyne and the degenerate LUMO on (**1**). In an alkyne such as (**2**), the LUMO is polarised towards the electron-withdrawing groups, increasing the overlap with the $4b_1$ orbital on (**1**) and enhancing the selectivity for [1,5]-addition across sulphur. These conclusions are consistent with experimental observations and with the most recent calculations on (**1**), which predict the lowest cationic state to correspond to ionisation from the approximately degenerate $3a_2$, $4b_1$, and $8b_2$ orbitals.

It has been known for some time that [1,2] adducts [*cf.* (**3**)] are formed between S_4N_4 (**1**) and strained alkenes such as norbornadiene.[1] This reaction has been previously rationalised by assuming that an energetically low lying doubly degenerate LUMO in (**1**) interacts with the HOMO of the alkene,[2] in such a manner as to lead to [1,3]-cycloaddition across sulphur. It was later reported that the reaction of (**1**) with disubstituted alkynes (R,R′ = Ph, PhCO, *p*-XC_6H_4, *p*-XC_6H_4CO, CO_2CH_3)[3] gives high yields of thiadiazoles (**4**) (40—80%), presumably by an alternative mode involving [2,4]-cycloaddition across nitrogen. Subsequently, it has been noted[3,4] that some electron-poor alkynes (R,R′ = CO_2CH_3; R = Ph, H; R′ = CO_2CH_3) additionally give low yields (2—5%) of what is now characterised[4] as a 1,3,5,2,4-trithiadiazepine (**5**), formally corresponding to [1,5]-cycloaddition across the sulphur atoms of (**1**). Most recently, it has been discovered that the reaction of (**1**) with alkynes bearing more powerful electron-withdrawing groups such as dicyanoacetylene (**2**) or bis(trifluoromethyl)acetylene (**6**) gives (**5**) in substantial yield (52—80%),[5] together with [in the case of (**2**)] a 60% yield of (**4**). Failure to isolate (**4**; R,R′ = CF_3) was thought to have been due to its high volatility.[5] The mechanism of this reaction probably involves consecutive [1,5]- and [2,4]-cycloaddition of the alkyne across sulphur and nitrogen respectively, resulting in the eventual production of both (**4**) and (**5**). The sequence of the two addition reactions is not known.

The factors that control the regioselectivity of this reaction are not well understood, especially where (**1**) acts as an electron donor rather than an electron acceptor. In addition, the selectivity for [1,5]- or [2,4]-attack has not previously been rationalised. We report in this paper a qualitative analysis based on MNDO and *ab initio* molecular orbital calculations for (**1**) and several alkynes.



(**1**)
(**2**) R,R′ = CN
(**6**) R,R′ = CF_3
(**4**)
(**5**)



(**3**)

Computational Procedure.—Calculations were carried out using the MNDO SCF-MO method[6] using a standard *s*/*p* valence basis set and the closed shell single determinantal restricted Hartree–Fock approach, with full optimisation of all geometrical variables. The species (**1**) was calculated by imposing D_{2d} symmetry, since MNDO incorrectly predicts this species to have a lower symmetry in its ground state.[7] Since the MNDO method does not include *d*-type functions, a calculation was carried out using the *ab initio* program GAUSSIAN 82[8] and using the STO-3G * basis set, which includes *d*-functions on sulphur. The form of the calculated orbitals was essentially the same as the MNDO result, and in particular the *d*-functions were found not to contribute significantly to the gross features of the orbitals. The orbitals were plotted using a locally modified version of the program PSI/77.[9] In order to compare the orbitals on the same scale, the wavefunction was obtained in several cases by calculating both (**1**) and the alkyne as one molecule, the latter being orientated parallel to the principal plane of symmetry of (**1**) and located 5 Å away from the centre of the plane defined by the four N atoms.

Results and Discussion

Orbital analysis of the mode of action of (**1**) as an electron donor has in the past been difficult due to the uncertainty in assigning the HOMO of this molecule. Palmer and co-workers[10] in 1980 measured the photoelectron spectrum of this species and, on the basis of *ab initio* calculations, assigned the first ionisation band at 9.4 eV in terms of three energetically equal orbitals, $3a_2$, $8b_2$, and $9a_1$. More recently, by including configuration interactions in their calculations, they concluded[11] that the

Table. Frontier orbital energies (in eV) for substituted alkenes

Compound	HOMO	LUMO
(2)	11.65	−0.74
(6)	13.72	−0.86
CF_3–C≡C–CN	12.48	−0.77
OCH–C≡C–CHO	11.47	−0.82
HO_2C–C≡C–CO_2H	12.03	−0.87
H–C≡C–H	10.98	2.18
HO–C≡C–OH	9.21	1.42

state resulting from ionisation from the $4b_1$ orbital rather than the $9a_1$ orbital, together with $3a_2$ and $8b_1$, corresponded to the observed first ionisation band.

Group theory suggests that of these three orbitals, only $4b_1$ and $3a_2$ possess the correct symmetry to interact with the LUMO of an alkene or alkyne. These two orbitals are shown in Figure 1, superimposed on the LUMO of acetylene. Overlap of the latter with the $4b_1$ orbital, leading to S–C bond formation, is not particularly good (Figure 1a) whereas overlap with the $3a_2$ orbital (Figure 1b), resulting in C–N bond formation, is enhanced as a result of the pronounced 'tilting' of the lobes of this orbital towards the centre of the S_4N_4 ring. Fukui and coworkers[2] have shown previously that interaction between the HOMO of an alkene and the 12e (LUMO) orbitals of **(1)** can lead to [1,3]-addition across sulphur (Figure 2). However, the two lobes on the sulphur are relatively far apart and may only overlap well with a relatively large HOMO orbital such as might be found in a strained alkene. With alkynes, the HOMO is inevitably more compact as a result of the shorter C–C bond length, and such an overlap might not be favoured. However, an alternative linear combination of the 12e orbitals reveals that there are two lobes on the nitrogen atoms that have approximately the correct phase and geometry to result in [2,4]-addition (Figure 3a) to an alkyne. In contrast, there is no combination of the 12e orbitals which is particularly favourable for a [1,5]-sulphur interaction (Figure 3b). This is in part due to an antibonding [3,7]-interaction from the other two sulphur atoms and in part to smaller overlap.

In terms of simple PMO theory, relative orbital energies as well as overlap are important in controlling reactivity. In considering an interaction between an alkene or alkyne acting as an electron donor (first ionisation potential *ca.* 9.0—10.0 eV) and **(1)** as an acceptor, the HOMO–LUMO energy gap is likely to be approximately 9 eV. For the reactivity to be controlled by **(1)** acting as an electron *donor*, the HOMO–LUMO gap must have a similar or smaller value. The MNDO method is known to predict LUMO energies reasonably accurately (by application of Koopmans' Theorem and comparison with known electron affinities).[12] The results for several acetylenes are shown in the Table. These suggest that a species such as **(2)** or **(6)** has a LUMO energy of approximately −0.9 to −0.7 eV, compared with the much more positive value for acetylene itself. Taken with the ionisation potential of **(1)** itself (9.4 eV), this leads to a HOMO–LUMO gap significantly less than 9.0 eV, and certainly small enough to be important in controlling the reactivity.

These results suggest that orbital energies alone might explain why electron-deficient alkynes such as **(2)** or **(6)** form cycloadducts more readily than do simple alkynes, but not the specificity for [1,5]- or [2,4]-addition. There also remains a possible anomaly, because **(6)** is predicted to have a larger electron affinity than **(2)** (Table), and yet gives a lower yield of adduct **(5)**.[5] There are two possible explanations for this observation. A plot of the lowest unoccupied orbitals of **(2)** (Figure 4) reveals that these orbitals are substantially polarised away from the central C–C bond by mesomeric resonance with the two cyano groups. This polarisation significantly facilities overlap with the $4b_1$ orbital of **(1)** (Figure 4a), whilst not enhancing the overlap with the $3a_2$ orbital (Figure 4b). Inspection of the LUMO of **(6)** reveals a similar but smaller polarisation towards the trifluoromethyl groups by a purely inductive mechanism. This particular analysis therefore suggests that the observed reactivity[5] may be rationalised by initial [1,5]-attack of the alkyne on S_4N_4, followed by a subsequent [2,4]-addition across nitrogen with parallel elimination of the thiadiazole **(4)**. An alternative explanation for the observed relative reactivity may be that the HOMO of **(2)** is much less negative than that of **(6)** (Table). There is the possibility therefore that interactions between the HOMO of **(2)** [but not of **(6)**] and the LUMO of **(1)** may also play a role in promoting initial [2,4]-addition across nitrogen, followed by subsequent [1,5]-attack across sulphur. Clearly these two mechanistic possibilities can only be distinguished by further experimental studies.

In conclusion, the observed regioselectivity of the cycloaddition reaction between S_4N_4 and dicyanoacetylene **(2)** can be rationalised in terms of overlap with the occupied $4b_1$ or $3a_2$ orbitals of **(1)** and the relatively small energy gap between these orbitals and the LUMO of the alkyne.

Acknowledgements

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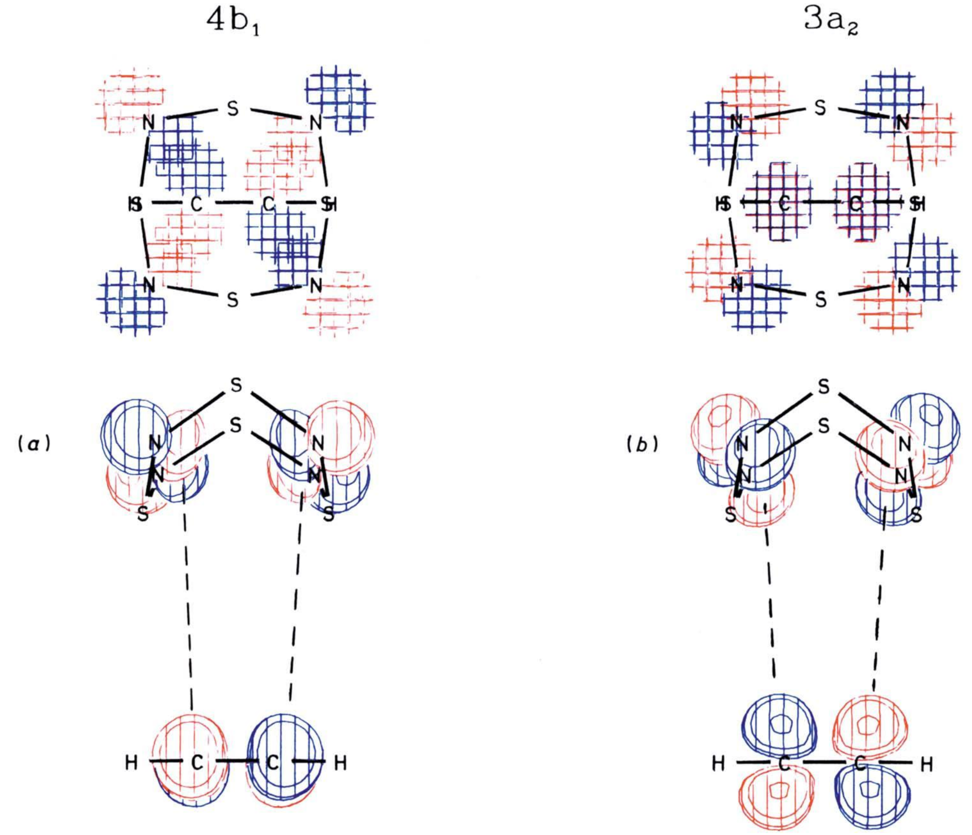

Figure 1. (*a*) Plot of the 4b$_1$ orbital of S_4N_4 and the lowest unoccupied orbital on acetylene, seen from two different views. The interaction leading to [1,5]-cycloaddition across sulphur is shown with dashed lines. (*b*) Plot of the 3a$_2$ orbital of S_4N_4 and the LUMO of acetylene. The interaction leading to [2,4]-cycloaddition across nitrogen is shown with dashed lines

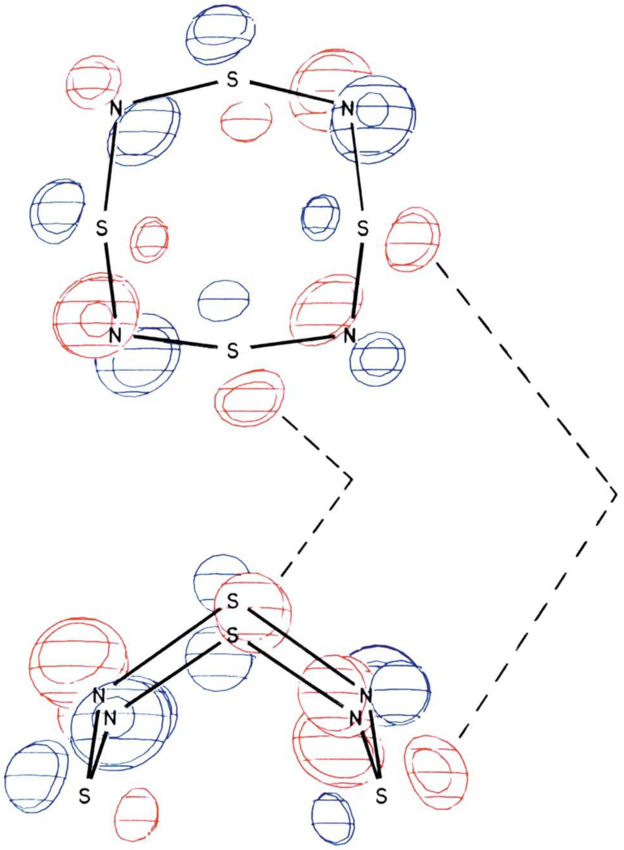

Figure 2. Plot of a linear combination of the degenerate 12e orbitals in S_4N_4, showing the required interaction with the HOMO of an alkene for [1,3]-addition across sulphur

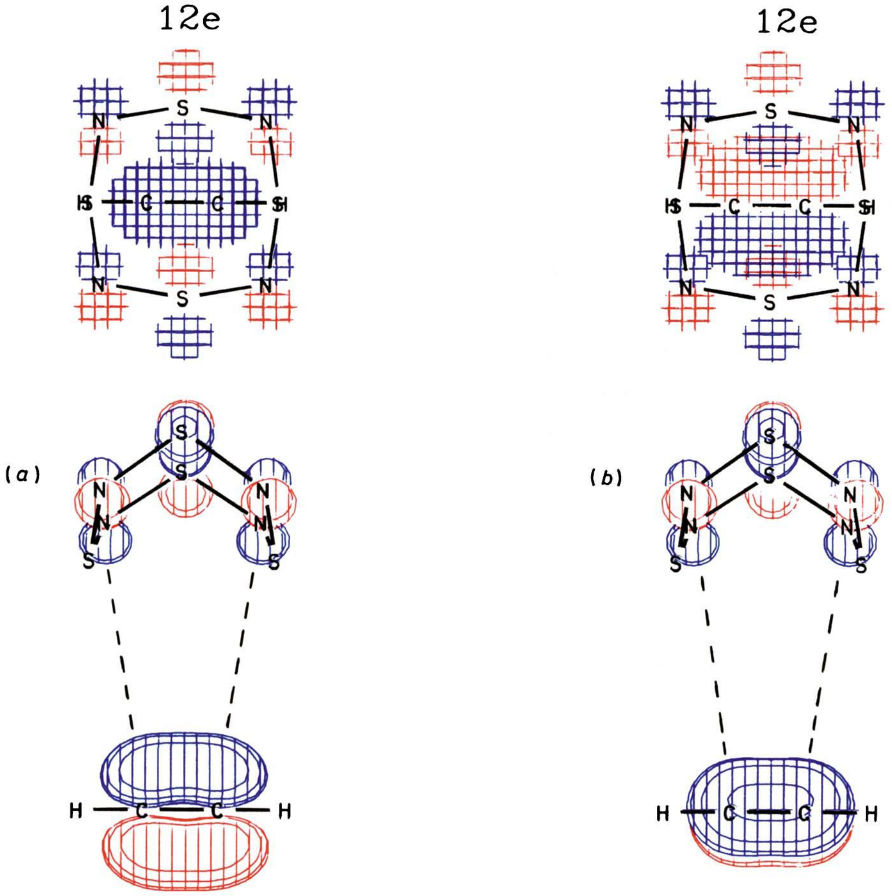

Figure 3. (*a*) Plot showing the interaction between the appropriate linear combination of the degenerate 12e orbitals in S_4N_4 and the HOMO of acetylene. Dashed lines indicate [2,4]-cycloaddition across nitrogen. (*b*) Plot showing the interaction between the 12e orbital and the HOMO of acetylene required for [1,5]-addition across sulphur. Alternative linear combinations of the two 12e orbitals lead to identical conclusions

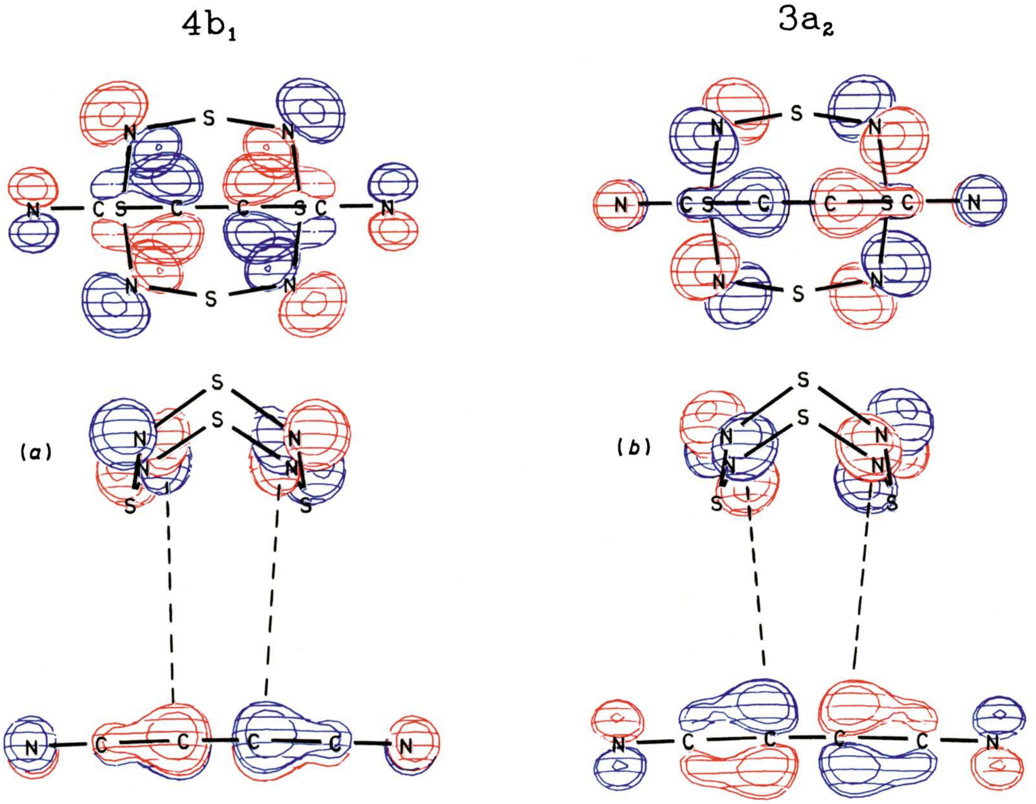

Figure 4. (*a*) Plot showing the interaction between the $4b_1$ orbital of (**1**) and the LUMO of dicyanoacetylene (**2**) resulting in [1,5]-cycloaddition across sulphur. (*b*) Plot showing the interaction between the $3a_2$ orbital of (**1**) and the LUMO of (**2**) resulting in [2,4]-cycloaddition across nitrogen (dashed lines)