Stereoelectronic Effects in R–NSN–R Systems. An MNDO and *Ab Initio* SCF-MO Study

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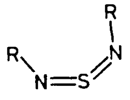
The *syn,syn* configurational preference of compounds of the type R–NSN–R, where the substituent R is $SiMe_3$, is rationalized in terms of anti-periplanar hyperconjugation between the in plane nitrogen lone pairs on the NSN fragment and the electropositive silicon-H/Me σ bonds. MNDO and *ab initio* calculated energies and geometries are reported for a range of electropositive and electronegative substituents R and discussed in terms of stereoelectronic interactions.

There is substantial current interest in the chemistry of sulphur–nitrogen heterocycles. Both organic[1] and inorganic[2,3] ring systems are known, but with the exception of $(SN)_x$[4] our understanding of linear S–N systems is less well developed. Sulphur di-imides, RNSNR, have been known for a number of years. They are iso-electronic with sulphur dioxide and their co-ordination chemistry has been extensively studied.[5] The silyl compound $(Me_3Si)_2N_2S$ is particularly useful in synthesis.[1–3]

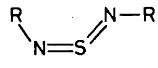
In principle, three configurations are possible for this type of compound, (**1a**)—(**1c**), and n.m.r. studies[5] indicate that the (**1b**) and (**1c**) are in equilibrium in solution for a variety of R groups. When R = Me,[6] *p*-tolyl,[7] or 4-biphenyl[8] the *syn,anti* structure (**1b**) is adopted (from electron diffraction[6] or *X*-ray studies[7,8]). However, when R = SPh[9] or SC_6H_4Cl-*p*,[10] single-crystal *X*-ray studies reveal the *syn,syn* structure (**1a**). In the latter case, a relatively short S ⋯ S interaction (3.29 Å) is observed. Electron diffraction studies[11] on $(Me_3Si)_2N_2S$ also indicate such a configuration for this compound in the gas phase. We report here SCF-MO calculations for the three isomers (**1a**)—(**1c**) which provide a simple stereoelectronic argument for the structural preferences of this class of molecule.

Initial theoretical studies were carried out at the MNDO SCF-MO level, using the MOPAC program system[12] and restricting the geometries to C_2 symmetry for (**1a**) and to C_s symmetry for (**1b**) and (**1c**). Within these restrictions, all geometrical variables were fully optimised. The calculated energies and geometries of the three isomers with R = Me are shown in the Table. The lowest energy isomer was correctly the *syn,anti* configuration (**1b**) and its calculated geometry was in good agreement with that found experimentally.[6]

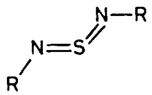
Attempts to locate three distinct isomers at the MNDO level for R = SiH_3 or for R = $SiMe_3$ did not succeed, all initial starting guesses resulting only in optimisation to the *syn,syn* forms (**1a**). The MNDO calculated geometry (R = SiH_3) was also quite different from the methyl analogue in having an unusually large Si–N–S bond angle (165°). The trimethylsilyl derivative (**1a**, R = $SiMe_3$) displayed an even larger angle (171°). Since this result revealed a major difference between a carbon and a silicon substituent, we sought support for the MNDO calculations by carrying out *ab initio* gradient geometry optimisation at a variety of basis set levels (Table).[13] The smallest basis set (3G) reveals a 'normal' bond angle of 132.5° for (**1a**, R = SiH_3) but this angle increases with the quality of the basis set up to the 3-21G* basis set level (164°), which includes *d* functions on both the sulphur and silicon, followed by a decrease when *d* functions are included on the nitrogen (144.6° for 6-31G*). Further calculations at the RMP2 correlated level were precluded by the amount of computer time required. Both the MNDO and *ab initio* procedures are in qualitative agreement in predicting relatively large Si–N–S angles for the *syn,syn* isomers, with an almost exactly planar R–NSN–R framework. For the smaller *ab initio* basis sets, where the Si–N–S angle is 'normal', the energy of the *syn,anti* isomer is clearly lower than the *syn,syn* form, due to steric repulsions in the latter. As the quality of the basis set improves, the predicted angle in (**1a**) increases and the energy difference decreases. At the 3-21G basis set level we calculate the *syn,syn* isomer to be lower in energy than the *syn,anti* (Table), whilst as with MNDO, no distinct *syn,anti* form could be located at the 3-21G* level. At the highest level (6-31G*) two forms could be located, with the *syn,syn* isomer again lowest in energy.



(1a)



(1b)



(1c)

Inspection of the occupied molecular orbitals revealed a possible explanation for the relatively large bond angles indicated by the calculations for the *syn,syn* form.† The two highest energy MNDO orbitals (R = SiH_3) are conventional π systems of little interest, but the next two lower energy occupied orbitals comprise the *in phase* and *out of phase* combinations of the two in-plane nitrogen lone pairs. In order to compare the difference between the isomers (**1a**) and (**1b**), the MNDO wavefunction for the latter was calculated at a fixed *anti* Si–N–S bond angle of 133° (Figures 1 and 2). We find that the relative ordering of these two orbitals is reversed between (**1a**) and (**1b**). This suggests that the apparently greater stability of the *syn,syn* isomer is due to the ability of the nitrogen lone pair to interact with the adjacent electropositive silicon–hydrogen σ bonds, due to their similarity in energy. For the compounds (**1a**/**1b**, R = Me), the methyl C–H σ bonds are of much lower energy and hence less well able to interact with the higher energy nitrogen lone pair. The trends in the MNDO calculated bond lengths for (**1a**—**1c**, R = Me) also support such interactions; the N=S and R–N bond lengths are significantly shorter for the *syn,syn* isomer (**1a**) than for the other two isomers, along with a much greater Me–N–S angle (Table). Such association of the shorter R–N bond with the larger R–N–S bond angle is also found for all the *ab initio* calculations for (**1a**) and (**1b**) (R = SiH_3, Table). These various results are consistent with a contribution from a resonance formulation such as (**2**), which rationalises the

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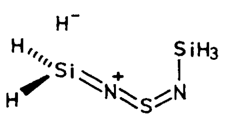
† For a discussion of orbital interactions in the related S_4N_4 system, see ref. 14.

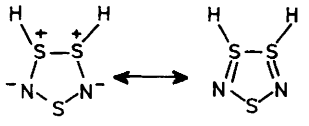
Table. Calculated MNDO and *ab initio* energies and geometries for (**1**). Where two values are given those in parentheses relate to the *syn* bond, those without to the *anti* bond

Compound	Energy[a]	r_{NS}/Å	r_{R-N}/Å	NSN/°	RNS/°
MNDO					
(**1a**) Me	70.6	1.522	1.428	122.4	134.3
(**1b**) Me	67.5	1.531 (1.544)	1.435 (1.436)	109.6	122.4 (129.1)
(**1b**) Me[b]	—	1.532	1.464	113.6	116.5 (124.3)
(**1c**) Me	74.3	1.552	1.440	103.4	119.0
(**1a**) SiH_3	34.2	1.480	1.686	111.6	165.0
(**1b**) SiH_3[c]					
(**1a**) BH_2	46.2	1.494	1.355	110.0	174.4
(**1a**) $Si(CF_3)_3$	−918.3	1.477	1.637	111.6	180.0
(**1a**) GeH_3	77.1	1.480	1.808	111.4	166.61
(**1a**) SH[d]	86.3	1.526	1.605	119.4	132.7
(**1b**) SH	84.2	1.549 (1.533)	1.615 (1.607)	107.1	121.6 (129.2)
(**1a**) Cl	104.7	1.544	1.687	126.2	125.9
(**1b**) Cl	101.4	1.566 (1.545)	1.695 (1.687)	110.0	115.3 (124.3)
Ab initio					
(**1a**) SiH_3					
STO-3G	−1 075.1911	1.588	1.753	121.6	132.5
STO-3G*	−1 075.5587	1.503	1.702	123.8	137.2
3-21G	−1 081.9741	1.568	1.749	119.0	147.8
3-21G*	−1 082.3885	1.476	1.704	119.8	164.0
6-31G*	−1 087.6735	1.489	1.734	122.4	144.6
(**1b**) SiH_3					
STO-3G	−1 075.2161	1.637 (1.597)	1.794 (1.772)	103.1	114.6 (115.4)
STO-3G*	−1 075.5620	1.519 (1.509)	1.725 (1.711)	116.7	121.2 (123.5)
3-21G	−1 081.9736	1.580 (1.578)	1.791 (1.745)	112.3	127.9 (141.9)
3-21G*[c]					
6-31G*	−1 087.6727	1.496 (1.489)	1.753 (1.734)	117.1	131.0 (134.0)

[a] Calculated energy, in kcal mol^{-1} (cal = 4.184J) for MNDO and Hartree for *ab initio*. [b] Experimental geometry (ref. 6). [c] Rearranges without activation to *syn,syn* isomer. [d] S–S distance 3.32 (calc.), 3.29 Å (obs.).[9]



(**2**)



(**3**)

properties of the R–N–S bond in terms of a cumulene type system. In all cases the larger bond angle and shorter R–N bond length is associated with the *syn* R–N–S geometry, indicating greater hyperconjugation for this configuration.

Inspection of the orbitals for (**1a**, R = SiH_3), Figure 1, shows that such hyperconjunction of both combinations of the nitrogen lone pairs with the Si–H bonds is favoured by the larger Si–N–S angle. For the isomer (**1b**), only the *syn* R–S–N nitrogen lone pair interacts with the Si–H σ bonds to any great extent (Figure 2). This effect is also present for (**1a**, R = $SiMe_3$), *via* hyperconjugation with the Si–C bonds.

On the basis of MNDO calculations, we predict that the Si–N–S bond angle for the hitherto unknown compound [**1**, R = $Si(CF_3)_3$] becomes essentially linear, again consistent with structure (**2**) in which H^- is now replaced by a highly stable carbanion, whereas the germanium and boron analogues (R = GeH_3, BH_2) are similar to silicon (Table). Conversely, the sulphur and chlorine derivatives (**1a**, R = SH or Cl) show quite different behaviour, due we think to the presence of additional lone pairs on the electronegative R group which are not present with sp^3 hybridised groups such as SiH_3. Effective antiperiplanar interaction between the nitrogen lone pairs and those on R leads to bonding electron density located between the two R groups (Figure 3). This has the effect of reducing the 'non-bonded' R···R distance and hence the R–N–S angles (Table), an effect represented by contribution from resonance formulations such as (**3**), in which electron density has migrated towards rather than away from the nitrogen atoms. Such a representation rationalises the decrease in the R–N–S valence angle and the stabilisation of the *syn,syn* form. For the *syn,anti* isomers (**1b**, R = SH or Cl), it is noteworthy that the *anti* R group is also associated with the *smaller* bond angle, but a *larger* R–N bond length. However for neither substituent (R = SH or Cl) is (**1a**) lower in energy than (**1b**), contrary to the known experimental structures. This may simply be due to the known error of MNDO in overestimating non-bonded repulsions.[15]

Acknowledgements

We thank the S.E.R.C. for the award of time on the U.L.C.C. Cray system, the University of London for time on the FPS-164 system located at Imperial College, and Professor C. W. Rees for valuable discussions.

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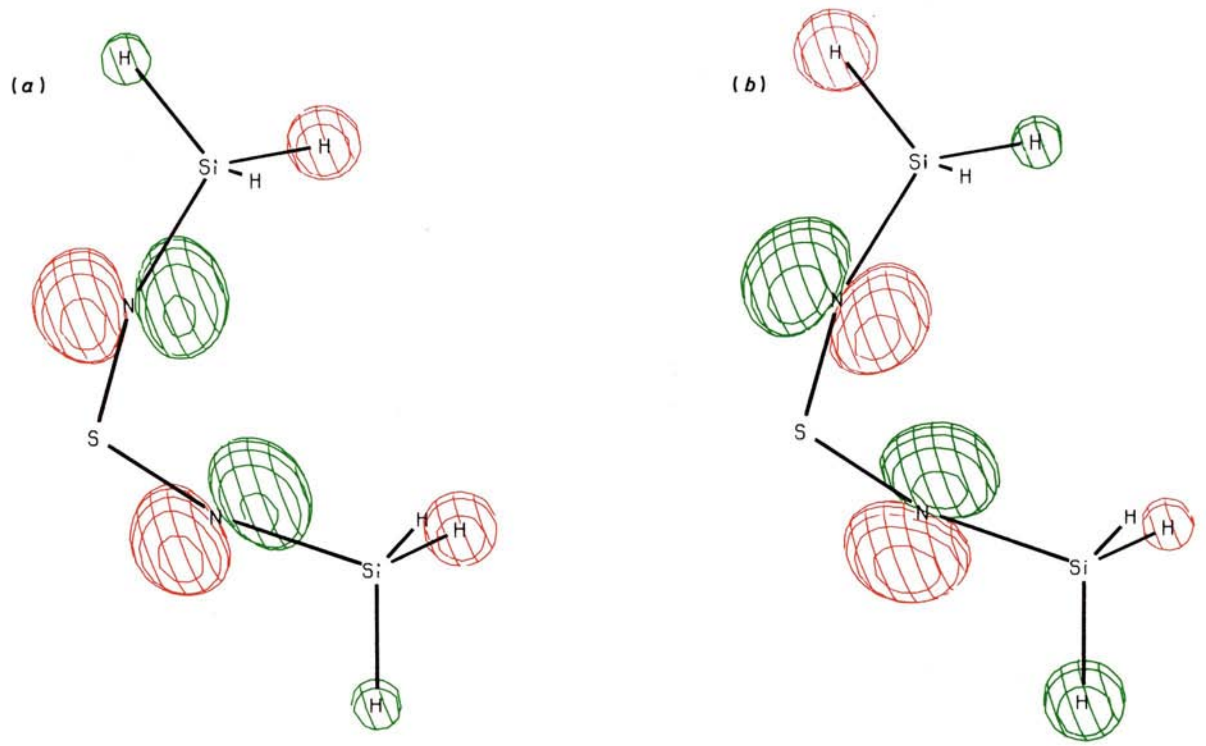

Figure 1. Molecular orbitals corresponding to (*a*) in-phase and (*b*) out-of-phase lone pair orbitals on (**1a**, R = SiH_3). The MNDO orbital energies are -10.17 and -9.88 eV respectively (eV $\approx 1.60 \times 10^{-19}$ J)

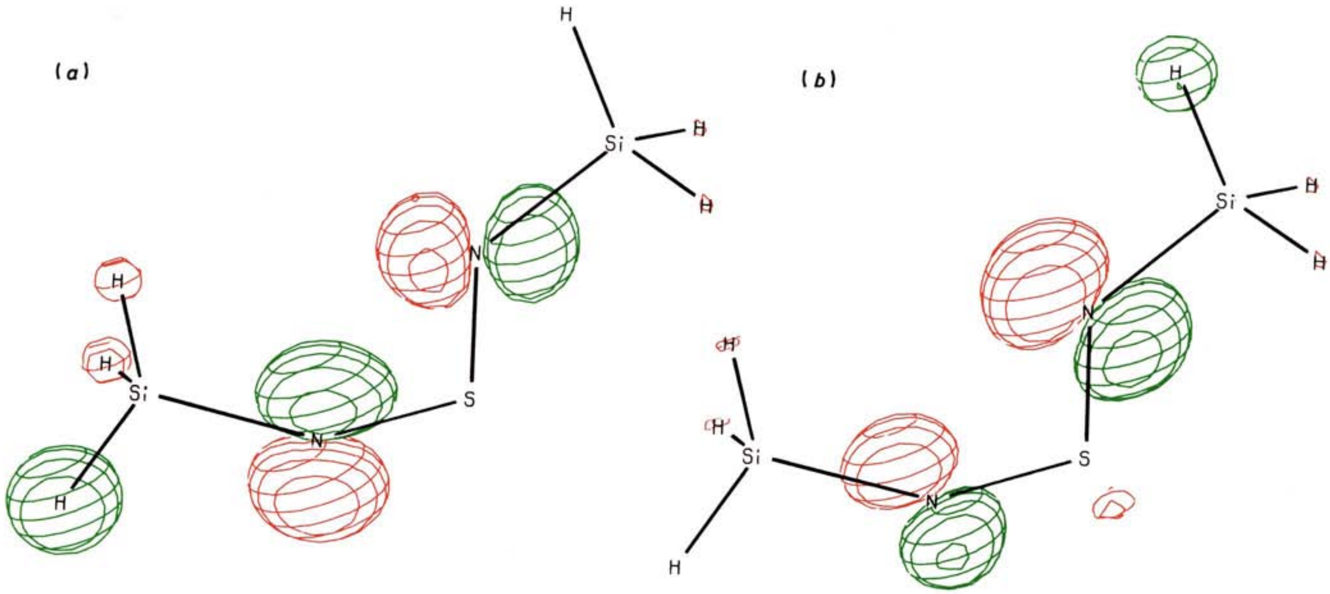

Figure 2. Molecular orbitals corresponding to (*a*) in-phase and (*b*) out-of-phase lone pair orbitals on (**1b**, R = SiH_3). The MNDO orbital energies are -9.97 and -10.37 eV respectively

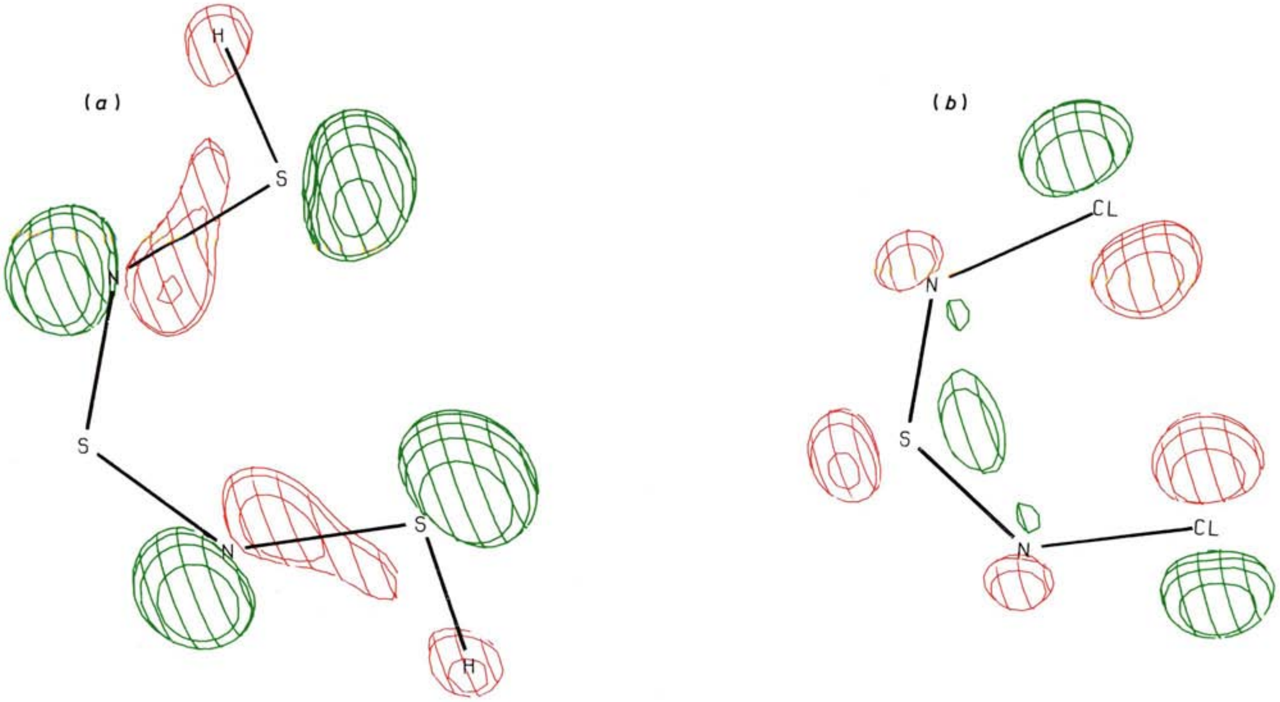

Figure 3. Molecular orbitals corresponding to R • • • R interaction in RNSNR: (*a*) R = SH and (*b*) R = Cl. The MNDO orbital energies are −11.90 and 13.07 eV respectively

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Received 12*th April* 1988; *Paper* 8/01419A