ab initio Molecular Orbital Study of Disulphur Dinitride, S_2N_2

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Summary The structure and ionization spectrum of disulphur dinitride (S_2N_2) is discussed using the *ab initio* molecular orbital method, and the predicted square-planar geometry is in excellent agreement with the experimental geometry; a simple many-body perturbation technique suggests that the lowest ion state arises from removal of a π electron in disagreement with the Koopmans' theorem prediction.

THE chemistry of sulphur–nitrogen compounds has attracted much recent interest[1] and there have been several theoretical calculations, mainly at the CNDO[2] or $X\alpha$[3] level. In the course of a more general theoretical study using *ab initio* molecular orbital techniques, it became attractive to study the smallest ring system S_2N_2, particularly as prior to this study there was little experimental evidence available and so predictions could be made. The only structural evidence, for example, was from a study of the geometry of the S_2N_2–$SbCl_5$ adduct,[4] where one may suppose $SbCl_5$ to have a significant effect on the bonding in the S_2N_2 ring, and some vibrational evidence.[5] A crystallographic study[6] of S_2N_2 itself was published when our calculations were being completed.[3] The geometry is indeed different from that in the $SbCl_5$ adduct and is in remarkable agreement with the theoretical calculations. The photoelectron spectrum of S_2N_2 has not been reported so we predict the ordering of the ion states using a simple many-body perturbation technique improvement to the Koopmans' theorem results.

The basis set used comprised the Basch–Snyder[7] double zeta functions for nitrogen valence orbitals, Clementi–Roetti[8] double zeta STO-3G for sulphur orbitals, Clementi-Raimondi[9] STO-3G single zeta functions for all core orbitals and STO-1G $3p$ and $3d$ orbitals on the nitrogen and sulphur respectively. The latter were optimised for FSN but the effect of such orbitals is very insensitive to their exponent value.

This basis set is much better for the valence orbitals than for the core orbitals. The poor representation of the latter leads to energies somewhat above others in the literature for S–N compounds but studies of several molecules indicate that the bonding is only slightly influenced by the form of the core orbitals. The total energy may be a poor criterion for judging the quality of a basis set and its ability accurately to describe molecular bonding. The error in the energy is due entirely to the failure to fit the cusp condition close to the nuclei. The basis was carefully chosen after a study of several basis sets for smaller S–N compounds and is a useful compromise between accuracy and economy. The presence of the 3*d* orbital on sulphur is crucially important for predicting good geometries. Its absence even from double-zeta basis set computations predicts poor bond lengths and angles in H_2S and FSN. In FSN, for example, R(S–N) = 3·23 a.u.† without the *d*-orbital and 2·85 a.u. with the *d*-orbital, with angles of 108° and 115°, respectively compared with the experimental values R(S–N) = 2·73 a.u. and θ = 116·46°.

In these computations four alternative SN co-ordinated shapes were considered and the structure for each partially optimised. However, the issue of the most stable structure was very clear cut. They were as follows (in increasing order of stability, with molecular energies in parentheses).

Ring structure: several forms considered, and some difficulty experienced in achieving SCF convergence (−894·233 a.u.)
(N–N 2·15, S–S 4·08, N–S 3·78 a.u.)

NS–SN

Syndotactic SN dimer. Idealised SN bond lengths taken, S–S bond distance and bond angle explored (−894.351 a.u.).
(S–N 2·83, S–S 5·50 a.u., ∠NSS 120°).

NS–NS

Endotactic SN dimer. Idealised terminal bond lengths, internal SN interatomic distance and angle examined (−894·637 a.u.).
(N–S 2·83, S–N 3·33, N–S 3·13 a.u., ∠NSN 115°).

Planar and puckered ring structure. Full optimisation (−894·750 a.u.) gives a square-planar structure.
(N–S 3·06 a.u., ∠NSN = ∠SNS = 90°).

The predicted square-planar structure is in good agreement with MacDiarmid's experimental geometry[6] and differs from the rhomboid structure with angles of 85° and 95° found in the $SbCl_5$–S_2N_2 adduct.[4] The S–N distance of 3·06 a.u. agrees well with the experimental results of 3·11 found by MacDiarmid and 3·07 in the adduct. CNDO[2] calculations predict angles of 88° and 92° and an S–N distance of 3·23 a.u. The *ab initio* Mulliken charge on sulphur is +0·33 compared with +0·21 from CNDO results.

TABLE. Summary of calculated state assignments for S_2N_2 (ionization potentials in eV)

Xα	CNDO	*ab initio* KT	Corrected KT
$1B_{3g}$	$1B_{1g}$	$1B_{2g}$ 11·8	$1B_{3g}$ 10·5
$1B_{2g}$	$1B_{2g}$	$1B_{3g}$ 12·5	$1B_{2g}$ 11·0
$2B_{3u}$	$2B_{2u}$	$2B_{3u}$ 14·3	$2B_{3u}$ 12·2
$2B_{2u}$	$1B_{3u}$	$2B_{2u}$ 15·4	$2B_{2u}$ 12·9
$1B_{1u}$	$3A_g$	$1B_{1u}$ 16·8	$1B_{1u}$ 15·7
$3A_g$	$1B_{3g}$	$1B_{1g}$ 17·7	$1B_{1g}$ 15·8
$2A_g$	$1B_{1u}$	$3A_g$ 17·9	$3A_g$ 16·4
$1B_{1g}$	$2A_g$	$2A_g$ 18·6	$2A_g$ 17·3
$1B_{2u}$	$1B_{2u}$	$1B_{2u}$ 20·9	$1B_{2u}$ 19·9

The sequence of ion states predicted by the Xα[3] method and using Koopmans' theorem (KT) and either CNDO[2] or our *ab initio* result are not in accordance. Some of the errors in the Koopmans' theorem eigenvalues, due to relaxation and correlation effects, can be compensated for using a Green's function approach to many-body perturbation theory. We follow here the simple method of Kellerer *et al.*[10] who use CNDO to estimate the electron repulsion integrals along with the *ab initio* orbital energies to evaluate the self-energy matrix, to second order. In this way the so-called Koopmans' defects can be evaluated with reasonable economy. This technique has been used by us for over 30 molecules, some containing sulphur. In nearly every case where Koopmans' theorem fails to predict the correct sequence of ionic states, agreement with the experimental sequence is found. For S_2N_2 only one inversion of the predicted sequence is found (Table). It should be noted that the lowest ionisation is predicted to give a Π state for the ion–$1B_{3g}$. CNDO follows its usual pattern and lowers the $\pi 1B_{3g}$ orbital below several orbitals (we have corrected the published CNDO orbital labels to be consistent with the correct labels used for the Xα results). The Xα results are for the incorrect rhomboid geometry. They agree with our predictions for the lowest five ion states but differ in the position of the $1B_{1g}$ state in the sequence. S_2N_2 appears to be another example of a molecule where Koopmans' theorem fails to predict the correct sequence. These results suggest that an experimental study may be most interesting.

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† 1 a.u. (length) = *ca.* 5·292 × 10^{-11} m. 1 a.u. (energy) = *ca.* 4·359 × 10^{-18} J.

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