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Electronic States of Nitrogen–Sulfur Compounds N_2S_2 and N_4S_4

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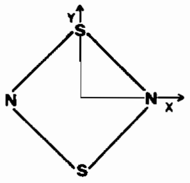
The chemistry and the physics of N–S compounds have attracted much interest since the discovery of the metallic conductivity and superconductivity of the polymer sulfurnitride $(SN)_x$ [1, 2]. N_2S_2 and N_4S_4 are precursors in the formation of $(SN)_x$. Many theoretical calculations, at various levels of sophistication, have been done on the ground-state electronic structure of both compounds [3]. Disagreements, however, between the various MO results are evident. Less information is available on the excited-state properties of N_2S_2 and N_4S_4 [3a, 3f]. The present paper gives the contribution of INDO/S-CI calculations to the knowledge of the electronic states of N_2S_2 (I) and N_4S_4 (II). Calculations are performed on the planar D_{2h} and D_{2d} (nitrogen atoms in the plane) geometry of N_2S_2 [4] and N_4S_4 [5] respectively. In the CI calculations all the occupied molecular orbitals and the lowest four unoccupied molecular orbitals have been considered in N_2S_2, while in N_4S_4 the uppermost twelve occupied and the lowest then unoccupied molecular orbitals have been taken into account. The first 60 monoexcited singlet transitions have been considered. Only transitions having non-zero oscillator strengths are reported in the following.



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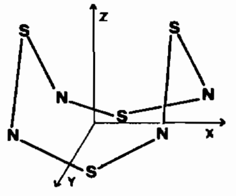

II

Results and Discussion

N_2S_2

The calculated atomic population shows a charge transfer from sulfur to nitrogen of 0.22*e*. Results of previous calculations [3] range from 0.20 to 0.50*e*. Thus, all calculations agree with a prediction of a polar S–N bond. The INDO/S-CI eigenvalues spectrum of N_2S_2 is reported in Table I. The highest occupied $1b_{2g}$ MO is predicted to be an antibonding combination of N_{2p} orbitals; it is followed by a $\sigma 2b_{3u}$ and $\pi 1b_{3g}$ MO s, the latter being an antibonding combination of S_{3p} orbitals. By comparison with *ab initio* results (Table I), the INDO/S-CI calculations show the usual trend to raise the energy of σ MO s above some π-type orbitals and to put the N_{2p}

TABLE I. Molecular Orbital Data for N_2S_2.

Orbital Type	INDO/S-CI		CNDO/S[a]	Xα-SW[b]	*ab initio*[c]
	Symmetry	Energy			
σ^* antibonding	$3b_{3u}$	2.85			
π^* antibonding	$2b_{1u}$	−3.39	$2b_{1u}$	$2b_{1u}$	
π N lone-pair	$1b_{2g}$	−9.64	$1b_{3g}$	$1b_{3g}$	$1b_{3g}$
σ bonding	$2b_{3u}$	−11.33	$1b_{2g}$	$1b_{2g}$	$1b_{2g}$
π S lone-pair	$1b_{3g}$	−12.02	$2b_{3u}$	$2b_{3u}$	$2b_{3u}$
σ bonding	$2b_{2u}$	−12.73	$2b_{2u}$	$2b_{2u}$	$2b_{2u}$
σ bonding	$3a_g$	−15.03	$1b_{1g}$	$1b_{1u}$	$1b_{1u}$
π bonding	$1b_{1u}$	−16.25	$1b_{1u}$	$3a_g$	$1b_{1g}$
σ bonding	$2a_g$	−17.07	$3a_g$	$2a_g$	$3a_g$
σ bonding	$1b_{1g}$	−18.76	$2a_g$	$1b_{1g}$	$2a_g$
lone-pairs	$1b_{2u}$	−22.66	$1b_{2u}$	$1b_{2u}$	$1b_{2u}$
lone-pairs	$1b_{3u}$	−30.30		$1b_{3u}$	
lone-pairs	$1a_g$	−43.73		$1a_g$	

[a] Ref. 3a. [b] Ref 3b. [c] Ref 3c.

TABLE II. Molecular Orbital data for N_4S_4.

Orbital Type	INDO/S-CI		CNDO/S[a]	Xα-SW[b]
	Symmetry	Energy		
S,N non-bonding	$5a_1$	2.95	7e	
S,N non-bonding	$3b_1$	2.89	$3b_1$	
S–S antibonding	6e	−3.50	6e	
N non-bonding	$2a_2$	−8.66	$4b_2$	$4b_2$
S–S bonding	$4b_2$	−8.73	$4a_1$	$2a_2$
S,N non-bonding	$2b_1$	−10.55	$2b_1$	$3b_2$
S,N non-bonding	$4a_1$	−10.59	$3b_2$	$4a_1$
S–N bonding	5e	−10.61	$2a_2$	5e
S–S bonding	$3b_2$	−12.07	5e	$2b_1$
N non-bonding	4e	−12.23	4e	4e
S,N non-bonding	3e	−14.93	3e	3e
S non-bonding	$3a_1$	−17.39	$3a_1$	$3a_1$
S–N bonding	$1a_2$	−19.05	$1a_2$	$2b_2$
S non-bonding	$2b_2$	−19.35	$2b_2$	$2a_1$
S–S bonding	$2a_1$	−19.50	2e	$1a_2$
S,N non-bonding	2e	−21.89	$2a_1$	2e
S non-bonding	$1b_2$	−25.40	$1b_2$	$1b_2$
S,N non-bonding	$1b_1$	−31.09	$1b_1$	$1b_1$
S,N non-bonding	1e	−36.60	1e	1e
S,N non-bonding	$1a_1$	−45.97	$1a_1$	$1a_1$

[a] Ref 3a. [b] Ref 3b.

lone-pair level in the higher-energy spectral region. However, some *ab initio* calculations [3c, 3f] also indicate noticeable disagreement between the various MO calculations in predicting the ordering of the MOs. This will be reflected in the assignment of the photoelectrum (PE) spectrum of N_2S_2 when use is made of the Koopman's approximation. The PE spectrum of N_2S_2 shows [6] ionizations at 10.52, 10.86, 11.05, 12.15, 14.4 and 16.2 eV. It is evident from Table I that INDO/S-CI calculations do not reproduce this spectrum satisfactorily. In particular, the first three calculated ionization energies are within 2.5 eV compared with the experimental value of 0.5 eV. In this respect the CNDO/s method seems to give the best results. The lowest vacant S–N antibonding MO (LVMO) is of b_{1u} symmetry, in agreement with previous calculations [3]. The associated energy level is predicted to be negative (Table I) (high electron affinity) as in previous semi-empirical results [3].

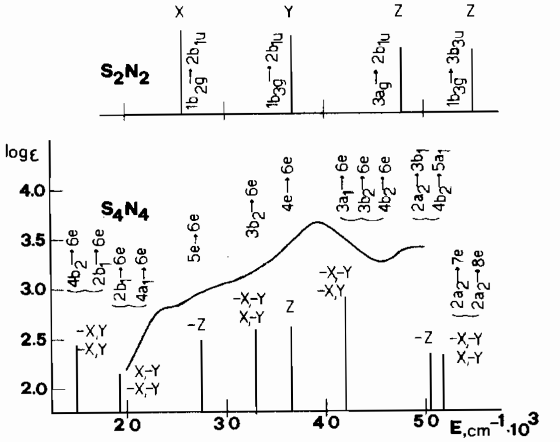

Fig. 1. The UV/visible spectra of N_2S_2 and N_4S_4. The solid line is the Brateman's spectrum [8]. The segments show the calculated INDO/S-CI spectra, and are proportional to logf 10^4. The polarizations of the electronic transitions along the axes are indicated.

Ab calculations, however, predict a positive energy for the LVMO. A negative energy level is considered to agree with the calculated negative Fermi level for $(SN)_x$ by different methods [3d]. This low-lying antibonding π^* MO is a peculiar feature of the electronic structure of the present compounds. It is supposed [3a, 3f] that it plays an important role in determining the metallic properties of $(SN)_x$. The calculated excited states of N_2S_2 are shown diagrammatically in Fig. 1. In the energy range 3–7 eV four excited states are expected: $^1B_{3u}$ (3.19 eV, f = 0.23),

$^1B_{2u}$ (4.56 eV, f = 0.15), $^1B_{1u}$ (5.38 eV, f = 0.04) and ^1A_u (6.80 eV, f = 0.03). The first two states are π–π^* transitions and involve appreciable charge transfer from nitrogen to sulfur and from sulfur to nitrogen, respectively. Experimentally a transition at 5.0 eV with f = 0.02–0.08 was reported [9, 3f] for N_2S_2, which was assigned to a $^1B_{2u}$ state. The calculated INDO/S-CI $^1A_g \rightarrow {}^1B_{2u}$ transition (y-axis polarized) is in agreement with this report. However, our results disagree with *ab initio* calculations [3f]. The latter, in fact, give an inverse ordering of the states; in particular the low-energy $^1B_{1u}$ state is predicted to be a $\pi \rightarrow \sigma^*$ transition arising from the $1b_{2g} \rightarrow 3b_{3u}$ (in our notation) excitation. In the absence of further experimental data on the excited state properties of N_2S_2, the present INDO/S-CI results must be accepted with caution.

N_4S_4

The eigenvalues spectrum of N_4S_4 is reported in Table II, together with CNDO/S [3a] and Xα-SW [3b] data. The first two uppermost MOs are of a_2 and b_2 symmetry respectively, the latter being an S–S bonding orbital. A reverse ordering is obtained by the Xα-SW method. However these orbitals are nearly degenerate and small changes in the molecular geometry are likely to affect their ordering. CNDO/S puts the $2a_2$ orbital under many other orbitals. As in N_2S_2, many other discrepancies exist in the MO sequence predicted by the various calculations (Table II and ref. 3), including also EH calculations. The PE spectrum of N_4S_4 [3a] shows a low-energy band corresponding to two ionizations. When our orbital energies are shifted by +1 eV this feature is well reproduced, but the comparison with the following bands in the spectrum is less satisfactory. INDO/S-CI calculations predict a charge transfer from sulfur to nitrogen of 0.39*e* to be compared with the experimental value of 0.6*e*. The corresponding CNDO/S and Xα-SW figures are 0.47 and 0.55*e*, respectively. There are no clear evidence of N–N bonds. Some N–N interactions can be recognized in the $4b_2$ orbital. The LVMO 6*e* corresponds to an S–S antibonding MO. As in N_2S_2, the energy of this level is predicted to be negative.

The absorption spectrum of N_4S_4 was measured by Braterman [8]. More recently, a single maximum at 256 nm (ϵ = 14.000 mole^{-1} cm^{-1}) was reported [9]. Our calculated UV/visible spectrum of N_4S_4 is reported in Fig. 1 together with Braterman's data. Almost all the excited states are of E symmetry. A$^1B_2$ state is found in the higher-energy spectral region at about 6.25 eV. The most intense ^1E transition arises from a nearly equal contribution of electronic excitations from $4a_1$, $3b_2$ and $4b_2$ orbitals to the S–S antibonding 6*e* orbital. It is predicted to lie at 42.000 cm^{-1} in fair agreement with the experimental value [8] of 38.900 cm^{-1}. This band was attributed by Braterman to a $4b_2 \rightarrow 6e$ transition (^1E symmetry) in reasonable agreement with our results. On the contrary, CNDO/S calculations [3a] put the $4b_2 \rightarrow 6e$ transition in the lower-energy spectral region at about 32.500 cm^{-1}, while the most intense experimental peak is attributed to the $3b_2 \rightarrow 5a_1$ excitation of $^1B_2$ symmetry.

Conclusions

The INDO/S-CI calculations qualitatively predict some peculiar electronic features of N_2S_2 and N_4S_4, such as the polarity of the S–N bond, the existence of low-lying excited states and of S–S bonds across the plane of nitrogen atoms in N_4S_4. The agreement between the eigenvalues spectra and the PE spectra is not satisfactory. Indeed, the ground state electronic structure of N_2S_2 and N_4S_4 is dominated by nitrogen and sulfur lone-pairs, so that it is expected that the Koopman's approximation does not work well in these compounds [3c]. By comparing our results with previous calculations some disagreements have been found in many instances. An experimental study on the polarization of the UV/visible bands could be very useful for the assignment of the excited states of N_2S_2 and N_4S_4.

References

1 M. M. Labes, P. Love and L. F. Nichols, *Chem. Rev., 79,* 1 (1979).

2 R. L. Greene, G. B. Street and L. J. Suter, *Phys. Rev. Lett., 34,* 577 (1975).

3 (a) W. R. Salaneck, J.W-p Lin, A. Paton, C. B. Duke and G. P. Ceasar, *Phys. Rev., B13,* 4517 (1976) and references therein;
(b) D. R. Salahub and R. P. Messmer, *J. Chem. Phys., 64,* 2039 (1976);
(c) M. P. S. Collins and B. J. Duke, *J. Chem. Soc. Chem. Comm.,* 701 (1976);
(d) M. Kertesz, M. Suhai, A. Azman, D. Kocjan and A. I. Kiss, *Chem. Phys. Lett., 44,* 53 (1976);
(e) P. W. Deutsch and L. A. Curtiss, *Chem. Phys. Lett.; 51,* 125 (1977);
(f) J. A. Jafri, M. D. Newton, T. A. Pakkanen and J. L. Whitten, *J. Chem. Phys., 66,* 5167 (1977);
(g) T. Yamabe, K. Tanaka, M. Fukui and H. Kato, *J. Phys. Chem., 81,* 727 (1977);
(h) R. D. Harcourt, *J. Inorg. Nucl. Chem., 39,* 237 (1977);
(i) A. Karpfen, P. Schuster, J. Petkov and H. Lischka, *J. Chem. Phys., 68,* 3884 (1978);
(l) R. R. Adkins and A. G. Turner, *J. Am. Chem. Soc., 78,* 1383 (1978).

4 A. G. McDiarmid, G. M. Mikulski, P. J. Russo, M. S. Saran, A. F. Garito and A. J. Heeger, *J. Chem. Soc. Chem. Comm.,* 476 (1975).

5 B. P. Sharma and J. Donohue, *Acta Cryst.*, *16*, 891 (1963).

6 D. C. Frost, M. R. Legeyt, N. L. Paddock and N. P. C. Westwood, *J. Chem. Soc. Chem. Comm.*, 217 (1977).

7 R. N. Wiener, L. I. Rubin and S. N. Singh, U.S. *At. Energy CoMM. AFCRL-67-0512*, 491 (1966).

8 P. S. Braterman, *J. Chem. Soc.*, 2297 (1965).

9 S. Apter, M. Carruthers and L. H. Sutcliffe, *Inorg. Chim. Acta*, *31L*, 455 (1978).