NOTES

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A Valence Structural Study of the Electronic Structure of S_2N_2

Hiroshi Fujimoto* and Takashi Yokoyama
Faculty of Engineering, Kyoto University, Kyoto 606

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Synopsis. A valence structural analysis of S_2N_2 has been performed within the framework of the INDO approximation. The fractional double-bond character has been suggested to be the consequence of the interaction between nonionic and ionic structures, counterbalanced in part by the overlap repulsions in the ring.

The strength of pi-bonds in polar conjugated systems is a matter of great concern both experimentally and theoretically. For instance, the dimeric sulfur nitride, S_2N_2, decomposes very rapidly above −80 °C to give larger rings and polymeric materials.[1] In order to explain the weak pi-bond character of the four equivalent sulfur–nitrogen bonds, Patton and Raymond proposed that the ionic structures, II, III, IV, and V, shown in Fig. 1 should be dominant in the ground state of the S_2N_2 molecule.[2] In the course of our studies of the mechanisms of the formation and breaking of chemical bonds, we obtained a somewhat different view of the pi-bonds in S_2N_2. In this note, we wish to report the results of our qualitative calculation.

Results of Calculation

The S_2N_2 ring was assumed to be square-planar, with sulfur and nitrogen alternating at the bond distance of 1.619 Å.[3] The 3d atomic orbitals of the sulfur atoms were disregarded tentatively, since their participation has been reported to be insignificant.[4] The distribution of sigma electrons was determined by the INDO MO calculation without configuration interaction.[5] Then, this distribution was used to constitute the sigma core in the evaluation of the diagonal and off-diagonal matrix elements of the secular equation for the pi-electron configurations, I—X, in the valence-bond calculation. Table 1 gives the energies of these structures, as calculated within the framework of the INDO approximation. The nonionic structure, I, was found to lie lower than the other structures. Table 2 indicates clearly that the structures I and VI participate significantly in the ground state of S_2N_2. The linear combination of the structures II, III, IV, and V was found to be a poor representation, yielding an energy which was 7.7 eV higher than the ground state in the present calculation.

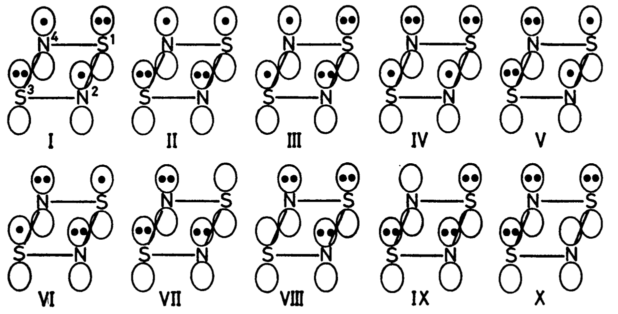

Fig. 1. Pi-electron configurations of S_2N_2.

Table 1. The relative energies of valence structures

Structure	Energy/eV[a]
I	4.30
II, III, IV, V	9.33
VI	9.69
VII, VIII	16.93
IX, X	18.23

a) The ground state of S_2N_2 was taken as the standard.

Table 2. The coefficients of valence structures in the ground-state wave function of S_2N_2

Structure	Coefficient
I	0.710
II, III, IV, V	0.305
VI	0.290
VII, VIII	0.103
IX, X	0.099

The interactions of the valence structures I and VI with the structures II, III, IV, and V are obviously the major source of the pi character of the S–N bonds. The double-bond character is partially lifted because of the overlap repulsions which are inherent in the ring containing six pi-electrons on four centers.[6] In particular, the structures II—V themselves contribute to the weakening of the S–N bonds.

References

1) a) A. G. MacDiarmid, C. M. Mikulski, P. J. Russo, M. S. Saran, A. F. Garito, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, **1975**, 476; b) C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *J. Am. Chem. Soc.*, **97**, 6358 (1975).

2) R. L. Patton and K. N. Raymond, *Inorg. Chem.*, **8**, 2426 (1969).

3) a) J. R. Warn and D. Chapman, *Spectrochim. Acta*, **22**, 1371 (1966); b) M. P. S. Collins and B. J. Duke, *J. Chem. Soc., Chem. Commun.*, **1976**, 701.

4) R. A. Adkins and A. G. Turner, *J. Am. Chem. Soc.*, **100**, 1383 (1978).

5) a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y. (1970); b) The standard parameters were used for nitrogen. As for sulfur, the standard CNDO parameters given by Pople (Ref. 5a) were incorporated with the one-center exchange-repulsion integrals taken from Stevenson and Burkey. See E. Stevenson and D. L. Burkey, *J. Am. Chem. Soc.*, **96**, 3061 (1974).

6) On the role of overlap repulsions, see, for instance, H. Fujimoto, Y. Osamura, and T. Minato, *J. Am. Chem. Soc.*, **100**, 2954 (1978), and the references cited therein.