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Molecular Orbital Study of Sulfur–Nitrogen and Sulfur–Carbon Conjugation: Mode of Bonding in $(SN)_x$ and Related Compounds

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Abstract: Ab initio molecular orbital theory has been used to study sulfur–nitrogen and sulfur–carbon conjugation. The molecules treated include the isomers of $(SN)_2$ and $(SN)_4$, SN oligomers, the $(SCH)_2$ isomers, and their fluoro- and cyano-substituted counterparts. Particular attention is paid to the importance of including sulfur d orbitals in the computational basis set. In quantitative energy comparisons between valent and hypervalent sulfur-containing molecules it is found that the inclusion of sulfur d functions is mandatory. Sulfur d orbitals serve to decrease the ionic character of the S–N bond, increase the overlap populations, and may contribute to extravalent intermolecular interactions. They play a very important role in S_4N_4 where delocalization via the s,p basis set is inhibited by the nonplanarity of the molecule. Even in the planar SN oligomers, about half the sulfur–nitrogen conjugation energy arises from the participation of sulfur d orbitals. They do not contribute to the sulfur–carbon bond to the same extent as a result of the decreased ionicity of this linkage with respect to the sulfur–nitrogen bond. Furthermore, the strength of the C–C bond (relative to the N–N) favors dimerization reactions which convert hypervalent to valent sulfur. These factors seem to militate against the existence of a stable $(SCH)_x$. The substitution of electron-attracting groups for hydrogen in hypervalent $(SCH)_2$ does not facilitate the participation of sulfur d functions.

Sulfur–nitrogen conjugation is of considerable current interest. A large variety of new neutral and charged sulfur–nitrogen compounds have been reported,[3] and some unusual organosulfur- and selenium–nitrogen compounds have been recently synthesized.[4] Polysulfur nitride $[(SN)_x]$ has proved to be metallic and the first superconducting polymer.[5] Furthermore, there has been considerable interest[6-8] in the possibility of obtaining analogues of $(SN)_x$ such as $(SCH)_x$.

The activity in this area has prompted us to initiate a comparative study of sulfur–nitrogen and sulfur–carbon conjugation, using ab initio molecular orbital theory, with particular emphasis on the mode of bonding in linear and cyclic species. There has been a number of theoretical studies of small sulfur–nitrogen compounds,[6,9] and many band structure calculations of $(SN)_x$ have been reported.[7,10] The present work attempts to bridge the important aspects of the two areas, by study of linearly conjugated sulfur–nitrogen oligomers. Extended sulfur–carbon conjugation has received comparatively little theoretical attention.[7,11]

Most of the species studied were structurally characterized by full calculational geometry optimization. We investigated the

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[3] (a) Banister, A. J. *Phosphorus Sulfur* **1978**, *5*, 147. (b) Scherer, O. J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 485. (c) Gillespie, R. J.; Slim, D. R.; Tyrer, J. D. *J. Chem. Soc., Chem. Commun.* **1977**, 253. (d) Chivers, T.; Oakley, R. T. *Ibid.* **1979**, 752. (e) Gillespie, R. J.; Ireland, P. R.; Vekris, J. E. *Can. J. Chem.* **1975**, *53*, 3147. (f) Wolmershäuser, G.; Brulet, C. R.; Street, G. B. *Inorg. Chem.* **1978**, *17*, 3586. (g) Sharma, B. D.; Donohue, J. *Acta Crystallogr.* **1963**, *16*, 891. (h) Sass, R. L.; Donohue, J. *Ibid.* **1958**, *11*, 497. (i) Nabi, S. N.; Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2309.

[4] (a) Cava, M. P.; Schlesinger, R. H. *Tetrahedron Lett.* **1962**, 3815. (b) Dietz, R. *Chem. Commun.* **1965**, 57. (c) Behringer, H.; Leiritz, K. *Chem. Ber.* **1965**, *98*, 3196. (d) Beecken, H. *Ibid.* **1967**, *100*, 2164. (e) Atherton, N. M.; Ockwell, J. N.; Dietz, R. *J. Chem. Soc. A* **1967**, 771. (f) Flowerday, P.; Perkins, M. J.; Arthur, A. R. J. *J. Chem. Soc. C* **1970**, 290. (g) Bertini, V.; DeMunno, A.; Marraccini, A. *J. Org. Chem.* **1972**, *37*, 2587. (h) Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1357. (i) Kowin, A. P.; Street, R. W.; Carmack, M. *J. Org. Chem.* **1975**, *40*, 2749. (j) Kwan, C. L.; Carmack, M.; Kochi, J. K. *J. Phys. Chem.* **1976**, *80*, 1786. (k) Haddon, R. C.; Kaplan, M. L.; Marshall, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 1235. (l) Kaplan, M. L.; Haddon, R. C.; Schilling, F. C.; Marshall, J. H.; Bramwell, F. B. *Ibid.* **1979**, *101*, 3306. (m) Geiren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *Ibid.* **1979**, *101*, 7277. (n) Geiren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *Ibid.*, **1980**, *101*, 5070. (o) Bartetzko, R.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 468.

[5] (a) Walatka Jr., V. V.; Labes, M. M.; Perlstein, J. H. *Phys. Rev. Lett.* **1973**, *31*, 1139. (b) Greene, R. L.; Grant, P. M.; Street, G. B. *Ibid.* **1975**, *34*, 89. (c) Greene, R. L.; Street, G. B.; Suter, L. J. *Ibid.* **1975**, *34*, 577. (d) Mikulski, C. M.; Russo, P. J.; Saran, M. S.; MacDiarmid, A. G.; Garito, A. F.; Heeger, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6358. (e) Cohen, M. J.; Garito, A. F.; Heeger, A. J.; MacDiarmid, A. G.; Saran, M. S.; Kleppinger, J. *Ibid.* **1976**, *98*, 3844. (f) Smith, R. D.; Wyatt, J. R.; DeCorpo, J. J.; Saalfeld, F. E.; Moran, M. J.; MacDiarmid, A. G. *Ibid.* **1977**, *99*, 1726. (g) Geserich, H.-P.; Pintschovius, L. *Festkoerperprobleme* **1976**, *16*, 65. (h) Street, G. B.; Greene, R. L. *IBM J. Res. Dev.* **1977**, *21*, 99. (i) Labes, M. M.; Love, P.; Nichols, L. F. *Chem. Rev.* **1979**, *79*, 1.

[6] Salahub, D. R.; Messmer, R. P. *J. Chem. Phys.* **1976**, *64*, 2039.

[7] Yamabe, T.; Tanaka, K.; Imamura, A.; Kato, H.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 798.

[8] Wudl, F.; Kruger, A. A.; Thomas, G. A. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 79.

[9] (a) Adkins, R.; Dell, R.; Turner, A. G. *J. Mol. Struct.* **1976**, *31*, 403. (b) Kertesz, M.; Suhai, S.; Azman, A.; Kocjan, D.; Kiss, A. I. *Chem. Phys. Lett.* **1976**, *44*, 53. (c) Collins, M. P. S.; Duke, B. J. *Chem. Commun.* **1976**, 701. (d) Salaneck, W. R.; Lin, J. W. P.; Paton, A.; Duke, C. B.; Caesar, G. P. *Phys. Rev. B: Solid State* **1976**, *13*, 4517. (e) Jafri, J. A.; Newton, M. D.; Pakkanen, T. A.; Whitten, J. L. *J. Chem. Phys.*, **1977**, *66*, 5167. (f) Deutsch, P. W.; Curtiss, L. A. *Chem. Phys. Lett.* **1977**, *51*, 125. (g) Yamabe, T.; Tanaka, K.; Fukui, K; Kato, H. *J. Phys. Chem.* **1977**, *81*, 727. (h) Cassoux, P.; Glemser, O.; Labarre, J. F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 41. (i) Karpfen, A.; Schuster, P.; Petkov, J.; Lischka, H. *J. Chem. Phys.* **1978**, *68*, 3884. (j) Adkins, R. R.; Turner, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 1383. (k) Lindquist, I. *J. Inorg. Nucl. Chem.* **1958**, *6*, 159. (l) Gleiter, R. *J. Chem. Soc. A* **1970**, 3174. (m) Gopinathan, M. S.; Whitehead, M. A. *Can. J. Chem.* **1975**, *53*, 1343. (n) Bartetzko, R.; Gleiter, R. *Inorg. Chem.* **1978**, *17*, 995. (o) Bojes, J.; Chivers, T.; Laidlan, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1979**, *101*, 4517.

[10] (a) Chapman, D.; Wam, R. J.; Fitzgerald, A. G.; Yoffe, A. D. *Trans. Faraday Soc.* **1964**, *60*, 294. (b) Walatka, V. V.; Labes, M. M.; Perlstein, J. H. *Phys. Rev. Lett.* **1973**, *31*, 1139. (c) Parry, D. E.; Thomas, J. M. *J. Phys. C* **1975**, *8*, L45. (d) Kamimura, H.; Grant, A. J.; Levy, F.; Yoffe, A. D.; Pitt, G. D. *Solid State Commun.* **1975**, *17*, 49. (e) Rajan, V. T.; Falicov, L. M. *Phys. Rev. B: Solid State* **1975**, *15*, 1240. (f) Friesen, W. I.; Berlinsky, A. J.; Bergerson, B.; Weiler, L.; Rice, T. M. *Bull. Am. Phys. Soc.* **1975**, *20*, 360; *J. Phys. C* **1975**, *8*, 3549. (g) Schulter, M.; Chelikowsky, J. R.; Cohen, M. L. *Phys. Rev. Lett.* **1975**, *35*, 869. (h) Rudge, W. E.; Grant, P. M. *Ibid.* **1975**, *35*, 1799. (i) Zunger, A. *J. Chem. Phys.* **1975**, *63*, 4854. (j) Kamimura, H.; Glazer, A. M.; Grant, A. J.; Natsume, Y.; Schreiber, M.; Yoffe, A. D. *J. Phys. C* **1976**, *9*, 291. (k) Bordas, J.; Grant, A. J.; Hughes, H. P.; Jakobsson, A.; Kamimura, H.; Levy, F. A.; Nakao, K.; Natsume, Y.; Yoffe, A. D. *Ibid.* **1976**, *9*, L277. (l) Berlinsky, A. J. *J. Phys.* 1976, C9, 283. Bright, A. A.; Soven, P. *Solid State Commun.* **1976**, *18*, 317. (m) Kertesz, M.; Koller, J.; Azman, A. *Phys. Status Solidi* **1976**, *77*, K157. (n) Messmer, R. P.; Salahub, D. R. *Chem. Phys. Lett.* **1976**, *41*, 73. (o) Salahub, D. R.; Messmer, R. P. *Phys. Rev. B: Solid State* **1976**, *14*, 2592. (p) Merkel, C.; Ladik, J. *Phys. Lett. A* **1976**, *56A*, 395. (q) Suhai, S.; Ladik, J. *Solid State Commun.* **1977**, *22*, 227. (r) Chelikowsky, J. R.; Schluter, M.; Cohen, M. L. *Phys. Status Solidi B* **1977**, *82*, 357. (s) Ching, W. Y.; Harrison, J. G.; Lin, C. C. *Phys. Rev. B: Solid State* **1977**, *15*, 5975. (t) Batra, I. P.; Ciraci, S.; Rudge, W. E. *Ibid.* **1977**, *15*, 5858. (u) Tanaka, K.; Yamabe, T.; Fukui, K.; Imamura, A.; Kato, H. *Chem. Phys. Lett.* **1978**, *53*, 452. (v) Kertesz, M.; Koller, J.; Azman, A. *Int. J. Quantum Chem.* **1978**, *14*, 239.

[11] George, J. K.; Trindle, C. *Int. J. Sulfur Chem.* **1973**, *8*, 83.

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Table I. Total Energies

mol	total energies,[a] hartree				
	STO-2G	STO-3G	4-31G	STO-3G + 6D	4-31G + 6D
NH_3		−55.455 42 (B)[b]			
SH_2		−394.311 63 (B)[c]		−394.378 43 (B)	
1	−436.212 33 (A)	−448.620 27 (B)		−448.700 17 (B)	
2	−868.903 96 (A)	−893.675 59 (B)	−902.587 96 (C)	−893.931 90 (B)	−902.756 91 (B)
2	−868.891 68 (D)	−893.664 24 (D)	−902.563 47 (D)	−893.950 07 (D)	−902.762 55 (D)
3	−868.999 08 (A)	−893.761 11 (B)	−902.696 14 (C)	−893.942 86 (B)	−902.791 09 (B)
4	−868.907 43 (A)	−893.675 08 (B)	−902.737 47 (C)	−893.802 38 (B)	−902.777 90 (B)
5	−868.914 46 (A)	−893.684 39 (B)	−902.585 06 (B,G)	−893.871 91 (B)	−902.688 05 (B)
6	−870.012 97 (A)	−894.799 48 (A)		−895.053 49 (A)	
7	−1737.779 49 (A)	−1787.293 05 (B)		−1787.748 48 (B)	
7	−1737.706 30 (E)	−1787.225 87 (E)		−1787.943 72 (E)	
8	−1738.001 56 (A)	−1787.505 17 (B)		−1787.918 24 (B)	
9	−1737.666 89 (A)	−1787.210 92 (A)		−1787.786 77[d] (A)	
10	−1737.643 18 (A)	−1787.176 84 (A)		−1787.853 26 (A)	
11	−1737.936 30 (A)	−1787.442 49 (B)		−1787.849 74 (B)	
12	−1737.812 19 (A)	−1787.354 58 (B)		−1787.870 43 (B)	
13	−1738.914 49 (F)	−1788.464 92 (A)		−1788.999 52[d] (A)	
14	−1740.352 40 (F)	−1789.903 14 (F)		−1790.353 28 (F)	
15		−862.165 24 (B)	−870.726 61 (C)	−862.372 95 (B)	−870.853 49 (B)
16		−862.271 45 (B)	−870.837 98 (C)	−862.436 20 (B)	−870.928 93 (B)
17		−862.221 84 (B)	−870.841 73 (C)	−862.363 59 (B)	−870.914 62 (B)
18		−862.223 44 (B)	−870.848 53 (C)	−862.365 39 (B)	−870.922 28 (B)
19		−862.208 84 (B)	−870.775 10 (C)	−862.369 80 (B)	−870.863 59 (B)
20		−1724.597 14 (B)		−1724.919 06 (B)	
21		−1057.069 50 (B)		−1057.280 04 (B)	
22		−1057.188 98 (B)		−1057.357 50 (B)	
23		−1043.304 62 (B)		−1043.504 97 (B)	
24		−1043.378 49 (B)		−1043.547 17 (B)	

[a] For geometries see Table II and footnotes. [b] Reference 14c. [c] Reference 17. [d] Difficulties experienced in obtaining SCF convergence. Results expected to be reliable to stated accuracy.

chemistry of the conjugated species via a consideration of the thermodynamic preferences for π vs. σ bonding and valent vs. hypervalent bonding. Particular attention was paid to the importance of d functions on sulfur in achieving a balanced description of the bonding. This is of some present concern as quantum chemical and band structure studies exhibit some disagreement on this point. Our studies throw further light on the proposed symmetry criterion for the necessity of including atomic d orbitals in computational basis sets[12]—the validity of which has been recently criticized.[13]

Method

Geometries were calculated with the STO-2G, STO-3G, or 4-31G basis sets[14] by using the gradient search program based on Gaussian 70[15] developed by Poppinger.[16] Single calculations using the STO-3G, 4-31G, STO-3G+6D, or 4-31G+6D basis sets were then carried out on these geometries to obtain final energies. The latter bases are identical with those developed by Pople and co-workers[17] for calculations on third-row atoms, except that we employ six Cartesian d functions (exponent 0.39[17]). The calculations including d functions were carried out with the HONDO 76 program[18] and utilized the full molecular point group symmetry. The total energies are given in Table I and the calculated geometries in Table II.

Results

With the exception of the $(SN)_2$ isomers, very few of the molecules treated in the present paper have been previously subjected to theoretical study. As the precursor to $(SN)_x$, **2** has received considerable attention, and CNDO,[9a,b,g,h] X_α,[6] ab initio,[9b,c,e,f] and configuration interaction[9e] calculations on the molecule have been reported. The ring bond angles are quite well described at all theoretical levels with the calculated values for N–S–N lying in the range 85–90°, which may be compared with the experimental result of 89.6°.[5d,e] Calculations of the N–S bond length in **2** gave values of 1.710 (CNDO[9a]), 1.695 (STO-3G[9b]), 1.73 (4-31G[9e]), 1.62 (DZ+D[9c]), 1.646 (PNO-CI[9i]), and 1.672 (CEPA[9i]), which may be compared with the results given in Table II. Among the calculations at the SCF level (that is, without the inclusion of electron correlation effects), there is a clear demarcation between the results obtained with and without the inclusion of d functions in the basis set. The minimal basis set calculations overestimate the N–S bond length (experimental value = 1.654 Å[5d,e]), whereas the calculations including d functions err in the opposite direction. The extended basis set results accentuate the error evidenced by the minimal basis set. As expected, the best geometries are obtained from the most detailed calculations which employ very large basis sets and include electron correlation effects.[9i] The minimal basis set calculations on **7** (Table II) accentuate the trend discussed above. Most of the geometries in the present work were calculated at the minimal basis set level, and it is apparent that there will be a systematic error associated with the bond lengths, although bond angles seem to be adequately described at this theoretical level.

There has only been one previous study[9c] on the relative energies of the $(SN)_2$ isomers. A DZ+D basis set was employed[9c] which for **3** gave bond lengths of 1.14 (N–N), 2.0 (N–S), and 2.16 (S–S) Å and an energy of +324 kcal/mol relative to **2**. These results appear somewhat unlikely (Tables II and III) and it seems that the difficulty experienced in achieving SCF convergence, which was noted by the authors,[9c] may actually have led to the wrong final state for **3**.

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(12) (a) Ratner, M. A.; Sabin, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 3542; **1977**, *99*, 3954. (b) Ball, E. E.; Ratner, M. A.; Sabin, J. R. *Chem. Scr.* **1977**, *12*, 128.

(13) Rodwell, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7209.

(14) (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (b) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *Ibid.* **1971**, *54*, 724. (c) Lathan, W. A.; Hehre, W. J.; Curtiss, L. A.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 6377.

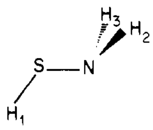
(15) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. Gaussian 70, QCPE Program No. 236.

(16) Poppinger, D. *Chem. Phys. Lett.* **1975**, *34*, 332; *Chem. Phys.* **1976**, *12*, 131.

(17) Collins, J. B.; Schleyer, P. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(18) Dupuis, M.; Rys, J.; King, H. *QCPE*, **1977**, *11*, 338.

Discussion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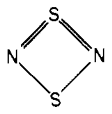
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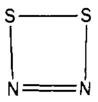
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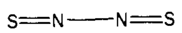
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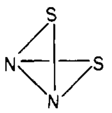
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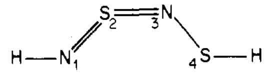
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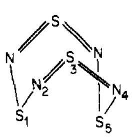
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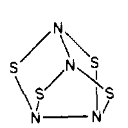
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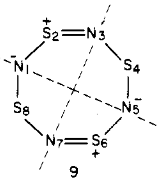
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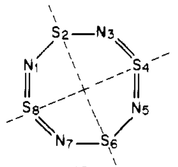
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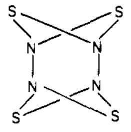
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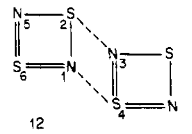
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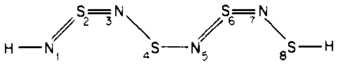
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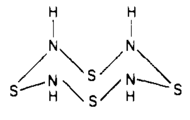
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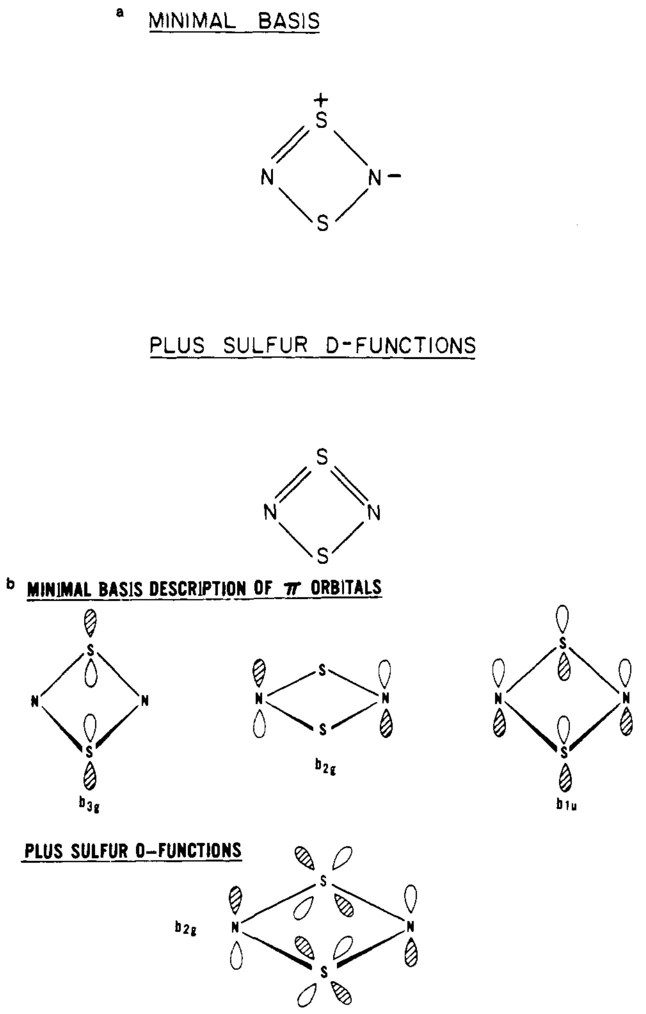

Figure 1. Electronic structure of S_2N_2 (**2**): (a) valence bond theory; (b) molecular orbital theory.

$(SN)_2$ Isomers (2–5) and $(SN)_4$ Isomers (7–12). At the highest theoretical level **3** is found to be the most stable of the $(SN)_2$ isomers. In the calculations, **2** is only competitive with **3** when d functions are included in the basis set. The addition of d functions to both the minimal and extended basis sets favor **2** relative to **3** by about 60 kcal/mol. It is possible that the addition of a second set of d functions[9i] to the 4-31G+6D calculations would actually reverse the order of stability shown in Table III. Nevertheless at the present theoretical level **3** is the global minimum on the potential surface and may prove to be a stable structure; even **4** is found to be more stable than **2**. It is interesting to note that both **3** and **4** require the generation of a head-to-head NS dimer for their formation which may involve an electrostatically unfavorable transition state. Furthermore the vapors over S_4N_4 are richer in $(SN)_2$ moieties than SN fragments,[5f] and it therefore seems that the formation of **2** during the cracking of **7** may result from kinetic factors. At the 4-31G level **5** is not a minimum on the potential surface, and the molecule dissociates to $N_2 + 2S$.

The results for the $(SN)_2$ isomers highlight the importance of including a set of d functions in the basis set in treating hypervalent sulfur (that is, where the octet must be expanded). Our results do not allow a definitive statement on the current controversy regarding the symmetry criterion for the necessity of including atomic d orbitals in computational basis sets.[12,13,19] Nevertheless, from the relative energies of **2** and **3** (irrespective of the degree of contraction of the s and p functions), it seems clear that the inclusion of d functions is mandatory in quantitative comparisons between valent and hypervalent molecules. Figure 1 shows the importance of the d functions on sulfur on the π orbitals of **2**. The same sort of bonding situation obtains in the linear polymers (Figure 2), and on this basis it seems likely that d functions will be important in $(SN)_x$ and will be involved in states near the Fermi level. Other authors[6] have chosen to stress the importance of the dipolar character of the S–N bond in these compounds and $(SN)_x$. A resolution of this apparent conflict in interpretation is provided by the work of Craig and co-workers.[20] They showed that the overlapping power of d orbitals on sulfur could be made compatible with bond formation only if the orbitals were contracted and pointed out that this might well happen if the attached atoms were highly electronegative. Thus sulfur d orbitals may be expected to effectively participate in bonding when the attached atoms

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(19) See also: (a) Brill, T. B. *J. Chem. Educ.* **1973**, *50*, 392. (b) Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1975**, *97*, 2209.

(20) (a) Craig, D. P.; Maccoll, A.; Nyholm, R. S.; Orgel, L. E.; Sutton, L. E. *J. Chem. Soc.* **1959**, 332. (b) Craig, D. P.; Magnusson, E. A. *Ibid.* **1956**, 4895. (c) Craig, D. P.; Zauli, C. *J. Chem. Phys.* **1962**, *37*, 601, 609.

Table II. Geometries

molecule (symmetry)	parameters[a, b]
1 (C_s)	N-S = 1.743, 1.742; N-H = 1.041, 1.033; S-H = 1.327, 1.334; S-N-H = 108.5, 108.5; H-S-N = 95.2, 95.1; H_1-S-N-H_3 = 123.5, 123.5 [A, B]
2(D_{2h})	N-S = 1.705, 1.699, 1.741, 1.654; N-S-N = 87.1, 86.6, 86.0, 89.6 [A, B, C, D]
3 (C_{2v})	N-N = 1.285, 1.279, 1.191; N-S = 1.774, 1.766, 1.888; S-S = 2.093, 2.102, 2.348 [A, B, C]
4 ($D_{\infty h}$)	N-N = 1.172, 1.163; N-S = 1.628, 1.619 [A, B]
5 (C_{2v})	N-N = 1.464, 1.468; N-S = 1.797, 1.791; S-N-N-S = 111.6, 112.1 [A, B, G]
6 (C_s)	N_1-S_2 = 1.669; S_2-N_3 = 1.617; N_3-S_4 = 1.726; N_1-H = 1.056; S_4-H = 1.331; N_1-S_2-N_3 = 102.4; S_2-N_3-S_4 = 113.8; H-N_1-S_2 = 101.1; N_3-S_4-H = 92.2 [A]
7 (D_{2d})	N-S = 1.751, 1.763, 1.616; N-S-N = 100.1, 99.7, 105.0; S-N-S = 103.4, 103.6, 113.0; N$\cdots$N = 2.684, 2.694, 2.564; S$\cdots$S = 2.299, 2.306, 2.605 [A, B, E]
8 (D_{2d})	N-S = 1.795, 1.791; N-N = 1.572, 1.573; N-S-N = 85.3, 84.7; S-N-S = 95.3, 95.8; S$\cdots$S = 2.653, 2.659 [A, B]
9 (D_{2h})	vertical symmetry planes through atoms 1-5 and 3-7; N_1-S_2 = 1.760; S_2-N_3 = 1.604; N_1-S_2-N_3 = 127.0; S_2-N_3-S_4 = 159.1; S_4-N_5-S_6 = 126.9 [A]
10 (D_{2h})	vertical symmetry planes through atoms 2-6 and 4-8; N_1-S_2 = 1.708; N_3-S_4 = 1.591; N_1-S_2-N_3 = 119.9; S_2-N_3-S_4 = 142.6; N_3-S_4-N_5 = 134.9 [A]
11 (D_{2h})	N-N = 1.564, 1.566; N-S = 1.812, 1.808; NSN planes = 122.5, 122.3 [A, B]
12 (C_{2h})	intramolecular parameters taken from 2 [B]; $N_1\cdots N_3$ = 2.841; $N_1\cdots S_4$ = 3.011; $S_2\cdots S_4$ = 3.985 [B]
13 (C_s)	N_1-S_2 = 1.672; S_2-N_3 = 1.616; N_3-S_4 = 1.706; S_4-N_5 = 1.748; N_5-S_6 = 1.656; S_6-N_7 = 1.627; N_7-S_8 = 1.728; H-N_1 = 1.056; S_8-H = 1.330; N_1-S_2-N_3 = 101.4; S_2-N_3-S_4 = 113.1; N_3-S_4-N_5 = 100.7; S_4-N_5-S_6 = 116.8; N_5-S_6-N_7 = 100.6; S_6-N_7-S_8 = 112.6; H-N_1-S_2 = 101.8; N_7-S_8-H = 92.3 [A]
14 (C_{4v})	N-S = 1.674; N-H = 1.01; N-S-N = 108.4; S-N-S = 122.2 [F]
15 (D_{2h})	C-S = 1.710, 1.746; C-H = 1.069, 1.058; C-S-C = 81.8, 82.6 [B,C]
16 (C_{2v})	C-C = 1.319, 1.314; C-S = 1.769, 1.847; S-S = 2.099, 2.296; C-H = 1.080, 1.065; C-C-H = 131.1, 130.9 [B, C]
17 (C_{2v})	C-C = 1.489, 1.452; C-S = 1.591, 1.638; C-H = 1.092, 1.074; C-C-S = 126.4, 127.5; C-C-H = 112.4, 113.7 [B, C]
18 (C_{2h})	C-C = 1.487, 1.445; C-S = 1.590, 1.641; C-H = 1.092, 1.073; C-C-S = 124.8, 123.5; C-C-H = 113.0, 115.0 [B, C]
19 (C_{2v})	C-C = 1.465, 1.413; C-S = 1.789, 1.891; C-H = 1.080, 1.061; S-C-C-S = 119.0, 114.2; C-C-H = 128.8, 135.9 [B, C]
20 (D_{2h})	C-C = 1.610; C-S = 1.833; C-H = 1.089; CSC planes = 128.8; C-C-H = 111.5 [B]
21 (D_{2h})	C-S = 1.715; C-F = 1.351; C-S-C = 80.5 [B]
22 (C_{2v})	C-C = 1.330; C-S = 1.784; S-S = 2.098; C-F = 1.346; C-C-F = 132.1 [B]
23 (D_{2h})	C-S = 1.713; C-C = 1.409; C-N = 1.162; C-S-C = 81.2 [B]
24 (C_{2v})	C_1-C_2 = 1.340; C_1-S = 1.769; S-S = 2.098; C_2-C_3 = 1.444; C-N = 1.158; C_1-C_2-C_3 = 130.4 [B]

[a] A = STO-2G; B = STO-3G; C = 4-31G; D = exptl, ref 5d, e; E = exptl, ref 3g; F = exptl, ref 3h,i; G = no 4-31G minimum; dissociation to N_2 + 2S. [b] A-B = bond lengths (Å); A-B-C = bond angles (deg); A-B-C-D = dihedral angles (deg).

Table III. Relative Energies (kcal/mol)

		theoretical level: energy//geometry[a]			
mol	rel to	STO-3G// STO-3G	STO-3G +6D// STO-3G	4-31G// 4-31G	4-31G +6D// STO-3G
3	2	−60.8	4.5	−79.3	−18.0
4	2	−6.8	92.7	−105.2	−9.7
5	2	−12.4	49.0	13.6	46.8
7	2(2)	64.4	−27.4		
8	2(2)	−110.8	−11.4		
11	2(2)	−71.4	30.6		
12	2(2)	−2.1	−4.2		
8	7	−175.3	16.0		
9	7	9.4	98.5		
10	7	30.7	56.8		
11	7	−135.9	59.0		
16	15	−66.6	−39.7	−69.9	−47.3
17	15	−35.5	5.9	−72.3	−38.4
18	15	−36.5	4.7	−76.5	−43.2
19	15	−27.3	2.0	−30.4	−6.3
20	2(15)	−167.3	−108.7		
22	21	−75.0	−48.6		
24	23	−46.4	−26.5		

[a] Experimental geometries (Table II) are employed for 2 and 7, with the exception of the energy of 12 relative to 2(2). The STO-3G geometry is used for 5 throughout: see footnote *a* [G] to Table II.

remove inner-shell electron density and thereby decrease the shielding of the nuclear charge. It is therefore not surprising to find a parallel between the participation of d orbitals in a bond and the ionic character of the bond: indeed it is doubtful if the two concepts are truly separable. It is apparent from the valence bond (Figures 1a and 2a) and molecular orbital (Figures 1b and 2b) pictures that the inclusion of d functions on sulfur decreases the ionic character of the N-S bond in hypervalent molecules.

Turning to the $(SN)_4$ isomers, we find another dramatic example of the importance of d orbitals, in the comparison between the energies of **2** and **7**—both of which are hypervalent molecules. Molecule **7** gains 31.2 kcal/mol/sulfur atom more than **2** on addition of the polarization functions to the basis set. This is related to the lower symmetry at sulfur in the case of **7** where the nonplanarity of the ring does not allow efficient delocalization without the inclusion of d functions (cf the calculated bond lengths of **7**).

The structure calculated for S_4N_4 (**7**) (Table II) shows that the transannular S···S bonding interaction which is present in this molecule is manifested at the minimal basis set level and in fact overestimated. At this theoretical level the transannular extravalent S···S interaction is primarily pσ in character,[9k-m] but it is clear from Table V that when d functions are present in the sulfur basis set, they make an important contribution to the S···S bonding in **7**.

The relative energies of **2** and **11** allow a comparison between the strength of the N-S hypervalent bond and N-N σ bond. Again, the inclusion of d functions is critical and brings about a reversal in the calculated order of stability for **2** and **11**. There is no chemical evidence for the existence of **11** (in contrast to **2**). Among the $(SN)_4$ isomers themselves we see further dramatic examples of the importance of d orbitals in achieving a balanced description of valent and hypervalent bonding. Thus both **8** and **11** are found to be over 100 kcal/mol more stable than **7** at the minimal basis set level, while the addition of d orbitals to the basis set completely reverses this order of stability. The relative energies of the valent isomers **8** and **11** are insensitive to the presence of polarization functions. The planar $(SN)_4$ isomers **9** and **10** are

Table IV. Calculated Atom Charge Densities from Mulliken Population Analysis

mol	atom	STO-3G	STO-3G + 6D
2	N	−0.421	−0.286
	S	0.421	+0.286
3	N	−0.180	−0.129
	S	+0.180	0.129
4	N	−0.101	−0.042
	S	0.101	0.042
5	N	−0.257	−0.162
	S	0.257	0.162
7	N	−0.551	−0.370
	S	0.551	0.370
8	N	−0.324	−0.213
	S	0.324	0.213
9	N_1	−0.469	−0.349
	N_3	−0.441	−0.290
	S	0.455	0.319
10	N	−0.529	−0.331
	S_2	0.388	0.258
	S_5	0.671	0.404
12	N_1	−0.432	−0.301
	N_5	−0.423	−0.286
	S_2	0.443	0.310
	S_6	0.413	0.277
6	N_1	−0.469	−0.366
	N_3	−0.410	−0.287
	S_1	0.542	0.364
	S_4	0.274	0.163
	H(N)	0.083	0.099
	H(S)	−0.020	0.026
13	N_1	−0.470	−0.405
	N_3	−0.455	−0.276
	N_5	−0.488	−0.384
	N_7	−0.410	−0.254
	S_2	0.530	0.365
	S_4	0.385	0.252
	S_6	0.575	0.419
	S_8	0.273	0.150
	H(N)	0.081	0.105
	H(S)	−0.020	0.027
14	N	−0.571	−0.416
	S	0.405	0.242
	H	0.163	0.173
15	C	−0.375	−0.215
	S	0.316	0.165
	H	0.059	0.050
16	C	−0.175	−0.113
	S	0.105	0.051
	H	0.071	0.062
17	C	−0.179	−0.083
	S	0.123	0.036
	H	0.056	0.047
18	C	−0.177	−0.080
	S	0.117	0.029
	H	0.060	0.051
19	C	−0.246	−0.125
	S	0.163	0.052
	H	0.084	0.072

Table V. Mulliken Two-Center Overlap Populations

mol	atoms	STO-3G	STO-3G + 6D
7	N_2-S_1	0.209	0.373
	$S_1 \cdots S_5$	0.053	0.106
12	N_1-S_2	0.230	0.323
	$N_1 \cdots N_5$	−0.043	−0.032
	$S_2 \cdots S_6$	−0.089	−0.048
	$N_1 \cdots N_3$	−0.000	−0.000
	$S_2 \cdots S_6$	−0.000	−0.000
	$N_1 \cdots S_4$	−0.000	0.001
6	N_1-S_2	0.220	0.376
	S_2-N_3	0.277	0.419
	N_3-S_4	0.219	0.298
	$N_1 \cdots S_4$	0.001	0.004
13	N_1-S_2	0.217	0.369
	S_2-N_3	0.276	0.419
	N_3-S_4	0.215	0.307
	S_4-N_5	0.193	0.285
	N_5-S_6	0.224	0.375
	S_6-N_7	0.269	0.413
	N_1-S_8	0.219	0.300
	$N_1 \cdots S_4$	0.001	0.004
	$N_3 \cdots S_6$	0.000	0.000
	$N_5 \cdots S_8$	0.000	0.005

not enegetically competitive at any theoretical level—in contrast to the situation found for the dication.[3c]

The strong intermolecular interactions which occur in sulfur-nitrogen compounds[4m,n] prompted us to consider dimer **12**. This arrangement is present in the (011) plane of crystalline **2**, and it is polymerization between such pairs of molecules which gives rise to $(SN)_x$.[5d,e] These molecules lie along the *a* axis, and even as discrete $(SN)_2$ units they are characterized by short N···S contacts which ultimately become N–S bonds in $(SN)_x$.[5d,e] In dimer **12**, the calculated N···S contact distance is 3.011 Å which may be compared with the value of 2.890 Å found in the crystal structure of **2**. Given the fact that the sum of the van der Waals radii of sulfur and nitrogen is 3.35 Å, it is clear that **2** possesses strong intermolecular interactions and that these are at least partially accounted for at the SCF level. The addition of d functions to the basis set doubles the dimerization energy. It has already been noted that d functions reduce the ionic character of the N–S hypervalent bond, and this presumably works to decrease the coulombic component of the binding energy (Figure 1). Thus it may well be that the attraction between molecules of **2** (and other sulfur–nitrogen species) arises from the formation of weak intermolecular bonds which are peculiar to such species, and there is other evidence in the literature[4m,n] which supports this idea of "extravalent" bonds in such compounds.

$H(SN)_2H$ (6) and $H(SN)_4H$ (13). As molecular models for $(SN)_x$ (**25**), we included the oligomers **6** and **13** where the terminal valencies are annealed with hydrogen atoms. The calculated bond lengths accord well with the valence bond representation of **6** and **13** in which divalent and tetravalent (or hypervalent) sulfurs alternate along the chains (Figure 2a). This is in contrast to the structure found for $(SN)_x$ in which this periodicity does not exist, either in bond lengths or valency. Rather, the bond lengths in $(SN)_x$ are very similar to values of 1.628 Å (inner) and 1.593 Å (outer).[5d,e] The bond angles calculated for **6** and **13** are similar to the values found for $(SN)_x$ (S–N–S = 119.9°, N–S–N = 106.2°).[5d,e]

The presence of bond length alternation in the oligomers **6** and **13** and its absence in $(SN)_x$ provide an interesting contrast to the situation in $(CH)_x$[21] and the linear polyenes[22] where alteration in bond lengths persists throughout. The metallic and superconductive properties of $(SN)_x$ are intimately related to the absence of bond alternation (which leads to a finite density of states at the Fermi level). Given our results for **6** and **13**, this may well be related to the 3-D environment of the crystal lattice. If **12** may be used as a model for the intermolecular interactions which occur between $(SN)_x$ chains, then the extravalent N···S bond, in which d functions are heavily involved, may well be the determining factor in raising the electronic band structure of $(SN)_x$ above 1-D.

We now turn to a consideration of the energy of the linearly conjugated N–S bond. Specifically we consider the conjugation across the S_4–N_5 bond in **13** via the isodesmic reaction 1.

$$\mathbf{1} + 2(\mathbf{6}) \rightarrow NH_3 + SH_2 + \mathbf{13} \qquad (1)$$

$$\Delta E = -8.0 \text{ (STO-3G)}, -16.5 \text{ (STO-3G+6D) kcal/mol}$$

This result may be compared with the value of −13 kcal/mol calculated[22] for the conjugation energy across the partial C–C double bond in linear polyenes. Clearly for the N–S bond, d

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(21) (a) Temkin, H.; Lichtmann, L. S.; Fitchen, D. B. "Symposium on the Structure and Properties of Highly Conducting Polymers and Graphite"; IBM: San Jose, California, March 1979. (b) Heeger, A. J., personal communication.

(22) (a) Haddon, R. C.; Starnes Jr., W. H. *Adv. Chem. Ser.* **1978**, *No. 169*, 333. (b) See also: Haddon, R. C. *Chem. Phys. Lett.* **1980**, *70*, 210.

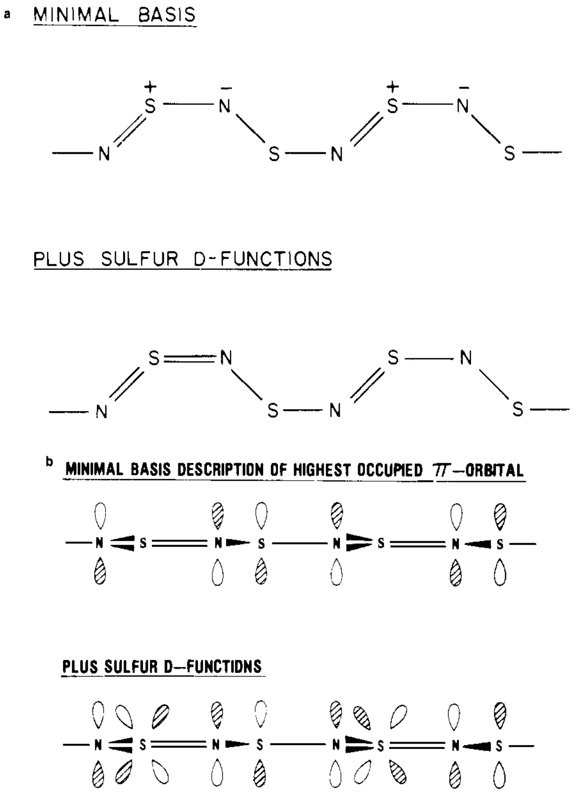
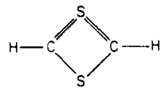


Figure 2. Electronic structure of $(SN)_x$ (**25**): (a) valence bond theory; (b) molecular orbital theory.

functions make a large contribution to the energy of conjugation.

If we adopt **13** as a model for $(SN)_x$ (**25**), we can obtain an estimate of the charge densities in the polymer chain by taking an appropriate average. With this approximation we obtain for **25** atomic charges of 0.449 (STO-3G) and 0.323 (STO-3G+6D) (positive on sulfur and negative on nitrogen). This gives for the charge density ordering **7** > **25** > **2** (Table IV) which is in accord with XPS studies.[23]

$(HCS)_2$ Isomers (15–19) and $(HCS)_4$ (20). Considerable interest is attached to the $(HCS)_2$ isomers as a result of suggestions[7,8] of an $(SN)_x$-like polymer based on $(HCS)_x$, in which the nitrogen atoms are replaced by C–H groups. By analogy with the $(SN)_2$ isomers, the $(HCS)_2$ isomers might be expected to play a role in the formation of $(HCS)_x$ and to provide a convenient model for the type of bonding which would occur in such a polymer.



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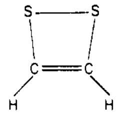

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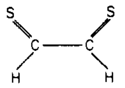

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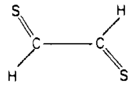

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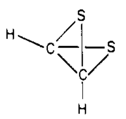

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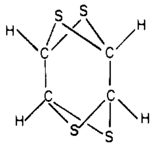

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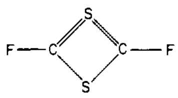
Particularly with regard to the homologous pairs **2**/**3** and **15**/**16** the nitrogen and carbon heterocycles provide an interesting contrast. We have already mentioned that the hypervalent (tetravalent) state of sulfur makes an important contribution to the electronic structure and stability of $(SN)_x$, and it would be expected that the same situation must prevail in $(SCH)_x$ if it is to be a viable material. The results obtained for **15**/**16** (Table III) are not encouraging in this regard. In the comparison between hypervalent and valent heterocycles (**2**/**3** and **15**/**16**), the carbon compound is found to be at a small disadvantage with respect to the nitrogen compound at both the minimal and extended basis set levels. This relative stability gap is considerably widened on introduction of d functions, and the hypervalent carbon–sulfur compound experiences less than half the energy gain of the nitrogen heterocycle with respect to their valent counterparts. As a result, the final energy difference between the hypervalent and valent carbon compounds is more than twice that of the nitrogen heterocycles. The ineffective utilization of sulfur polarization functions in the case of **15** (relative to **2**) probably stems from the electronegativity differences between carbon (2.5) and nitrogen (3.0) relative to sulfur (2.5). This is reflected in the lower charge densities in **15** and, as mentioned previously, without removal of inner-shell electron density, the d-functions on sulfur are too shielded to effectively participate in bonding. The stability of –HC=S=CH– vis à vis the –N=S=N– unit is further militated against by a consideration of the N–N and C–C single bond energies (38 and 83 kcal/mol,[24] respectively). This shows up in the dimerization reactions 2(**2**) → **7** and 2(**15**) → **20** (Table III). Although this reaction is favored at the minimal basis set level for the nitrogen compound, the addition of d functions reverses this trend. This is not the case for the carbon heterocycles, and the dimerization reaction is heavily favored at all theoretical levels. Experimental work[8,25] also suggests the instability of the –HC=S=CH– linkage.

Dithione isomers **17** and **18** are calculated to be energetically competitive with **15**, and this is in agreement with experimental studies[26] on substituted isomers which have shown that the ground state structure may be of type **17**/**18** or **15**. Although lying higher in energy than the other isomers, **19** was found to be a potential minimum on the potential surface at the 4-31G level, in contrast to the corresponding nitrogen compound (**5**).

$(FCS)_2$ Isomers (21,22) and $(NCCS)_2$ Isomers (23,24). As we have already noted, hypervalent bonds to sulfur (–X=S=X–) are stabilized by removal of inner-shell electron density from S to X. Accordingly we considered **21**/**22** and **23**/**24** in which X = C—F and C—CN, respectively, in the hope that these electron-attracting substituents might facilitate the hypervalent bonding in **21** and **23**. Some stabilization does occur in the **23**/**24** comparison relative to the **2**/**3** couple, but this energy is gained



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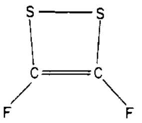

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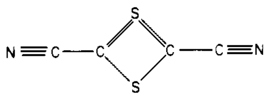

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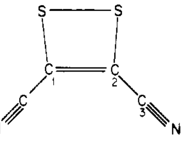

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[23] Brant, P.; Weber, D. C.; Ewing, C. T.; Carter, F. L.; Hashmall, J. A. "Symposium on the Structure and Properties of Highly Conducting Polymers and Graphite"; IBM: San Jose, California, March 1979.

[24] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 85.

[25] (a) Ponticello, I. S.; Schlesinger, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 4190. (b) Cava, M. P.; Pollack, N. M.; Mamer, O. A.; Mitchell, M. J. *J. Org. Chem.* **1971**, *36*, 3932.

[26] (a) Küsters, W.; de Mayo, P. *J. Am. Chem. Soc.* **1973**, *95*, 2383; **1974**, *96*, 3502. (b) Hencher, J. L.; Shen, Q.; Tuck, D. G. *Ibid.* **1976**, *98*, 899.

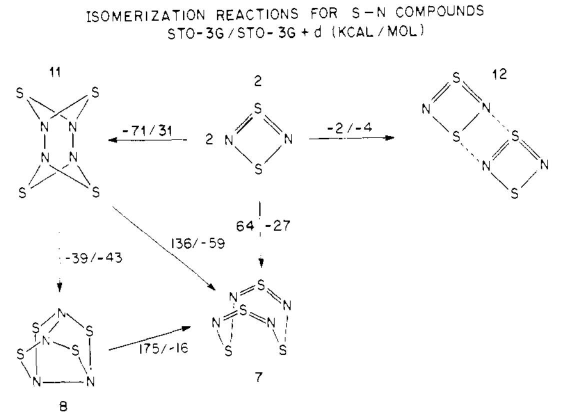

Figure 3. Highlights of the importance of d functions on sulfur in describing various bonding situations.

at the minimal basis set level and presumably results from dipolar bonding (cf. Figure 1a). Remote substituents therefore do not seem effective in increasing the participation of the d orbitals in bonding to sulfur via the hypervalent state. The results of the present study are not encouraging with respect to the prospects for the production of an $(HCS)_x$ polymer.

Conclusion

(i) With regard to energetic (and to some extent structural) comparisons between sulfur-containing molecules, the inclusion of d functions in the sulfur basis set is found to be (a) relatively unimportant in comparisons between structures containing only valent sulfur, (b) important in comparisons between molecules containing the same number of hypervalent sulfur atoms, and (c) mandatory in comparisons between molecules which contain unequal numbers of hypervalent sulfur atoms. These points are illustrated in Figure 3.

(ii) The conjugation energy of the linear N-S bond is found to be 8 kcal/mol at the minimal basis set level and 17 kcal/mol with the inclusion of d functions.

(iii) The hypervalent state of sulfur (with d-orbital participation) is only about half as effective in bonds to carbon as it is in bonds to nitrogen when energetic comparisons are made with valent isomers. This factor, together with the greater strength of the C-C single bond as against the N-N single bond, militates against the viability of $(SCH)_{2n}$-type structures.

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Excitation Profiles, Absorption and Resonance Raman Spectra of the Carotenoprotein Ovorubin, and a Resonance Raman Study of Some Other Astaxanthin Proteins

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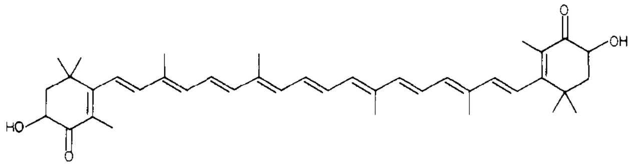
Abstract: The resonance Raman spectrum of ovorubin, excited by irradiation within the contour of the lowest $\pi^* \leftarrow \pi$ absorption band, has been observed and compared to those of some other astaxanthin proteins. The excitation profiles and relative intensities of the three most intense bands in the resonance Raman spectrum of ovorubin, together with those of a number of their combination tones and overtones, have been measured and analyzed by using a simple model applied previously to free carotenoids. The results lead to estimates of the elongation of the C═C and shrinkage of the C—C bonds in the resonant excited state. The correlation, for ovorubin and a number of other astaxanthin proteins, between the ν_1 wavenumber and $1/\lambda_{max}$ of the $\pi^* \leftarrow \pi$ absorption band is investigated and discussed in terms of current ideas on the binding of astaxanthin in astaxanthin proteins.

Introduction

The carotenoid astaxanthin (I) has been shown to occur in a variety of carotenoproteins from invertebrates such as *Pomacea canaliculata* (ovorubin), *Hommarus gammarus*, and *Velella velella*.[1-4]



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The visible absorption spectrum of free astaxanthin in organic solvents[5] shows a strong band at 480 nm; at low temperature this band exhibits vibronic structure. In common with that of other carotenoids the band is caused by a $\pi^* \leftarrow \pi$ type transition of the π electrons delocalized along the polyene chain.[6] On association of astaxanthin with protein, the absorption maximum may be subjected to large wavelength shifts.[1,2,4] The type of binding, the conformation of the carotenoid and the state of astaxanthin aggregates are important factors in the perturbation of the π-electron system and so may be expected to account for these shifts. In this respect, resonance Raman spectroscopy is an important analytical tool since the technique is capable of probing vibrational properties of a carotenoid, even if the latter is situated within carotenoproteins of large molecular weight.[7-12]

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(1) D. F. Cheesman, W. L. Lee, and P. F. Zagalsky, *Biol. Rev. Cambridge Philos. Soc.*, **42**, 131 (1967).
(2) P. F. Zagalsky, *Pure Appl. Chem.*, **47**, 103 (1976).
(3) D. F. Cheesman, *Proc. Roy. Soc. London, Ser. B* **149**, 571 (1958).
(4) O. Isler, Ed., "Carotenoids", Halsted Press, New York, 1971.
(5) V. R. Salares, R. Mendelsohn, P. R. Carey, and H. J. Bernstein, *J. Phys. Chem.*, **80**, 1137 (1976).
(6) J. Dale, *Acta Chem. Scand.*, **8**, 1235 (1954).

0002-7863/80/1502-6693$01.00/0