(planar) **11** is calculated to be exothermic by only 1 kcal/mol[11] and the cyclization of (*Z*)-3-hexene-1,5-diyne to 1,4-dehydrobenzene is inherently endothermic ($\Delta H_0 = +14$ kcal/mol).[2a] This potential ground-state stabilization may be reflected in the transition state for cyclization of **1**, perhaps by twisting of the allenic methylene group toward the plane of conjugation.

Alkyl substitution of the allene terminus of **1**, and thereby the benzylic carbon of the corresponding dehydroaromatic intermediate, is found to accelerate the cyclization reaction. (*Z*)-3,5,6-Octatrien-1-yne (**12**), synthesized in analogy to **1**, produces ethylbenzene (45%) and combination products **13** and **14** (1:1, 55%) in quantitative yield upon thermolysis in 1,4-cyclohexadiene (0.001 M, 100 °C, 30 min). Kinetic analysis shows the loss of **12** to be first-order and approximately 6-fold faster than loss of **1** under the same conditions ($k = 3.24 \pm 0.75 \times 10^{-3}$ s^{-1} at 78 °C). The facility of both cyclizations is striking ($t_{1/2}$ of **1** at 37 °C ~ 24 h) and raises the intriguing possibility that these simple structures may themselves form the basis for the design of new antibiotics.

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(10) ΔH_f (**1**) is calculated to be 117.9 kcal/mol by using group additivities (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976). The ΔH_f of the planar, biradical form of α,3-dehydrotoluene is estimated to be 103 kcal/mol by subtraction of the bond dissociation energy of molecular hydrogen (104.2 kcal/mol: Herzberg, G. *J. Mol. Spectrosc.* **1970**, *33*, 147) from the sum of ΔH_f (toluene) (11.95 kcal/mol: Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969) and the two relevant CH bond dissociation energies (85 and 110 kcal/mol).

(11) Calculated as in ref 10: ΔH_f (**10**) = 152.13, ΔH_f (**11**) = 151 kcal/mol [35 (ΔH_f of styrene) + 2 × 110 (BDE of ArH) − 104.2 (BDE of H_2)].

The Role of d Functions in Sulfur Oxide Molecules

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An empirical observation that has provoked much debate and interest is the important role that higher angular momentum basis functions play in predicting accurate bond lengths and angles for *some* molecules containing second-row atoms. Associated with this observation is an anomalously large lowering of the calculated total energy when, for example, d functions are included in the basis set as compared to the total energy calculated when only an sp basis set is employed. In this communication we provide new insight regarding these observations by considering the kinds of bonding found for sulfur in sulfur oxides and hydrogen sulfide.

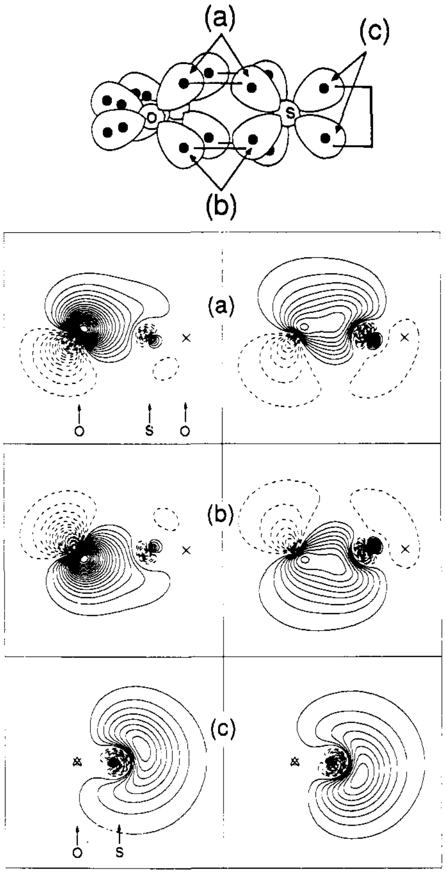

Figure 1. GVB orbitals for SO_2 using a DZ+d(O,S) basis set. (a, b) Orbitals representing the S=O double bond. (c) Angularly correlated S lone pair. Contours are separated by 0.04 au in both figures.

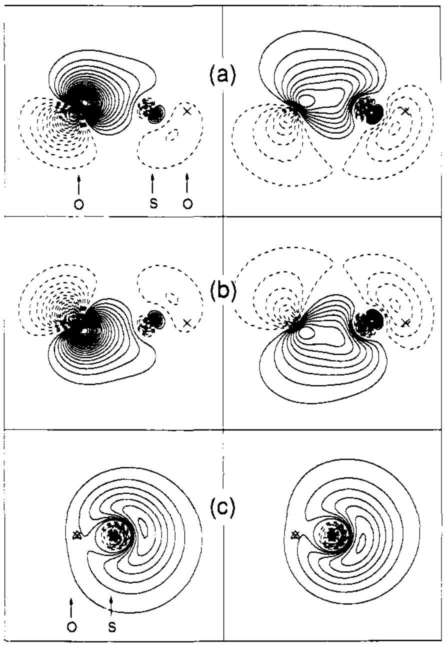

Figure 2. GVB orbitals for SO_2 using an unpolarized DZ basis set. (a, b) Orbitals representing the S=O double bond. (c) Angularly correlated S lone pair.

In a recent paper we presented a new description of the bonding in sulfur dioxide and other sulfur oxide molecules.[1] For these molecules it was found that there are six valence orbitals on the sulfur atom arranged in a trigonal prism which form covalent bonds to oxygen atoms or, if unbonded, combine as lone pairs. This is illustrated schematically at the top of Figure 1. Results of generalized valence bond (GVB) calculations on sulfur dioxide using a double-ζ sp basis set and the same basis set augmented by single-ζ d basis functions on each atom are shown in Figures

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(1) Patterson, C. H.; Messmer, R. P. *J. Am. Chem. Soc.* Submitted. Calculations were performed within the strong orthogonality and perfect pairing (SOPP) approximations to the GVB wave function. The form of this wave function is described in the following: Bobrowicz, F. W.; Goddard, W. A., III *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 4.

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2 and 1, respectively, and we use this representation of the molecule to explain the role of d functions.

In the absence of d functions, significant probability amplitudes of the bond orbitals centered on the sulfur atom (right panels in Figure 2a,b) lie outside the region of the bond, but when d functions are included, these parts of the orbitals are considerably reduced (Figure 1a,b). The other orbital in the bond, centered on the oxygen atom, changes to a much smaller extent. The angularly correlated lone-pair orbitals also show major changes in shape when d functions are included. In Figure 1c, the lone pair is significantly separated angularly and effectively "wraps around" the sulfur core, but in Figure 2c, the orbitals are not so effective in producing angular separation.

In these calculations[1] and those of others who have considered this question,[2] the orbitals of different electron pairs are required to be mutually orthogonal.[3] Thus in the present description of sulfur dioxide there are six lobes (or "hybrid" orbitals) which must be orthogonal to one another[4] *about the sulfur atom*. When only a double-ζ sp basis set is used, the functions centered on the sulfur atom can only remain orthogonal by having large proportions of each orbital on the opposite side of a node at the nucleus to the lobe forming a bond. This raises the kinetic energy of the electrons because of the increased curvature of the one-electron wave functions and increases their potential energy because they cannot achieve their optimum electron-nuclear attraction. We conclude that the importance of d basis functions on sulfur is in providing sufficient flexibility in the basis set to allow for six *angularly distinct* orbitals when required. Further evidence for this conclusion is provided by the following observation: a population analysis shows that the coefficients of the d basis functions in these calculations are small even though they play an important energetic role. In addition, when the coefficients of the d basis functions are set to 0 after the wave function has already been converged (contour plots in Figure 1) and the renormalized orbitals are plotted, there is essentially *no change* in the contours. This contrasts with the situation when the wave function is converged without the d functions and major changes in the contours are observed (Figure 2). The double-ζ sp basis functions therefore can reasonably describe the six sulfur orbitals, but the role of the d functions is to enable these orbitals to remain orthogonal to one another while attaining their optimum shapes, i.e., when d functions are included, charge is moved into the bond region *and* orbitals more effectively "wrap around" cores, thereby increasing their electron-nuclear attraction.[5]

The GVB description of hydrogen sulfide, on the other hand, has only four angularly distinct lobes centered on the sulfur atom because there are two bonds and two radially correlated lone pairs. A double-ζ sp basis set has adequate flexibility to describe this arrangement of electron pairs, and so there is no anomalously large energy lowering (0.98 eV for H_2S compared to 5.52 eV for SO_2) when d functions[6] are included in the O and S basis sets. However, when the electron-withdrawing potential of the hydrogen atoms is artificially increased, the GVB description of the electron pairs in hydrogen sulfide changes from tetrahedral to octahedral.[1] Lone pairs are now angularly correlated, and this description can only be obtained when at least two sets of d functions are included in the S atom basis set.[1] Hence it is the arrangement of electron pairs about an atomic site that dictates whether calculations on a molecule will have anomalously large energy lowerings when d functions are included in the basis set.

In summary, a combination of orthogonality constraints and an arrangement of electron pairs with more than four angularly distinct lobes in molecules containing second-row atoms require that calculations performed on these molecules should have better than double-ζ sp basis set flexibility. The importance of d functions in sulfur dioxide arises from this ability to provide additional spatial flexibility so that orbitals can remain orthogonal *and* attain their optimum shapes.

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(2) (a) Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 114. (b) Schmiedekamp, A.; Cruickshank, D. W. J.; Skaarup, S.; Pulay, P.; Hargittai, I.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2002. (c) Stromberg, A.; Wahlgren, U.; Pettersson, L.; Siegbahn, P. E. M. *Chem. Phys.* **1984**, *89*, 323. (d) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. (e) Cruickshank, D. W. J. *J. Mol. Struct.* **1985**, *130*, 177. (f) Cruickshank, D. W. J.; Eisenstein, M. *J. Mol. Struct.* **1985**, *130*, 143. (g) Cruickshank, D. W. J.; Eisenstein, M. *J. Comput. Chem.* **1987**, *8*, 6. (h) Magnusson, E.; Schaeffer, H. F. *J. Chem. Phys.* **1985**, *83*, 5721. (i) Yadav, A.; Surjan, P. R.; Poirier, R. A. *J. Mol. Struct.* (*THEOCHEM*) **1988**, *165*, 297.

(3) This is enforced by the strong orthogonality approximation to the GVB wave function. Relaxation of the strong orthogonality constraint can be achieved within the GVB model while independent particle interpretability is retained: Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1988**, *110*, 8258. Schultz, P. A. Ph.D. Thesis, University of Pennsylvania, 1988. This is a major task for sulfur dioxide and and has not been carried out so far.

(4) GVB-SOPP orbitals of the angularly correlated lone pair overlap because they belong to the same electron pair. Although this pair of orbitals may overlap, both must be orthogonal to all other orbitals.

(5) There may be a parallel between the latter observation and the "penetration effects" introduced by d functions of second-row atoms referred to in the recent literature.[2e,g]

(6) d function exponents were $\zeta = 0.53$ for S and $\zeta = 0.80$ for O in each case where single-ζ d functions were employed.

Photodehalogenation of 4-Haloindoles

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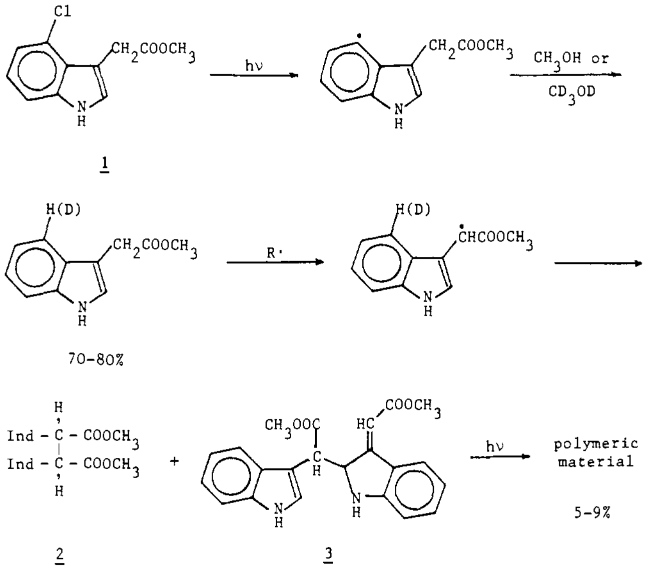
L-Tryptophan is an essential amino acid containing a bicyclic aromatic group, indole, which is highly hydrophobic in nature and often occupies critical positions in proteins.[1] Tryptophan also exhibits unique spectroscopic properties, which enables it to serve as an intrinsic probe for protein structures, protein dynamics, and intermolecular interactions between proteins and other molecules.[2] Fluorotryptophans may be incorporated into proteins via methods of molecular biology.[3] Tryptophan, 5- and 6-fluorotryptophan, and their derivatives exhibit a strong fluorescence with a quantum efficiency up to 0.25;[2,4] however, 4-haloindoles, including 4-fluorotryptophan, proteins containing 4-fluorotryptophan, and methyl 4-chloroindole-3-acetate, do not exhibit a measurable fluorescence.[5] This observation suggests that there is a unique nonradiative decay pathway present in 4-haloindoles that is not

Scheme I



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