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(5) The synthetic potential of heteroatom-directed photoarylation has been noted in recent reports from this laboratory; for example, see A. G. Schultz and R. D. Lucci, *J. Chem. Soc., Chem. Commun.*, 925 (1976). The synthesis of *dl*-lycoramine represents our first application of the methodology to natural products total synthesis.
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(7) The isomeric mixture **5a** and **5b** is easily separated by silica gel chromatography. See P. M. McCurry and R. K. Singh, *J. Org. Chem.*, **39**, 2316 (1974), and S. Danishefsky and A. Zimmer, *ibid.*, **41**, 4059 (1976), for recent studies of the factors controlling the direction of base-catalyzed aldol cyclizations of 1,4 and 1,5 diketones, respectively.
(8) The rationale for designing a synthetic intermediate to **1** with a ketone carbonyl positioned as shown in **5a** will be considered in a full paper dealing with heteroatom-directed photoarylation in aryl vinyl ethers.
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(11) The carbonyl transposition described here is similar to that used by J. A. Marshall and H. Roebke, *J. Org. Chem.*, **34**, 4188 (1969). An essential modification is the incorporation of keto mesylate **11a** (rather than an α-acetoxy ketone) into the sequence. With the ring system considered here, α-acetoxy ketones failed to undergo reductive cleavage under a variety of conditions and chromous chloride was found to be required for reductive cleavage of **11a**; see ref 9.
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(14) We wish to thank Professor William C. Wildman for a generous sample of authentic (−)-lycoramine.
(15) Compounds **5a**, **8a**, and **10a** gave satisfactory elemental analyses.
(16) NOTE ADDED IN PROOF. *dl*-Lycoramine has been obtained in 8.1% overall yield from **2a**.

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Electron Deformation Density Distribution for Cyclic Octasulfur by the SCF-Xα-SW Method

Sir:

We wish to report the first application of the self-consistent-field-Xα-scattered-wave method[1,2] to the calculation of electronic deformation density distributions, $\Delta\rho(\mathbf{r})$, i.e., the difference between a molecular electronic density distribution and the superposition of spherically averaged atomic distributions.[3] The orbital energies and wave functions calculated in the SCF-Xα-SW method have been employed successfully in a wide variety of applications;[4] however, no comparison has heretofore been made between the electron density distribution calculated with this method and experimental distributions determined by x-ray diffraction. Such comparisons provide a stringent test of the quality of the calculated wave functions.

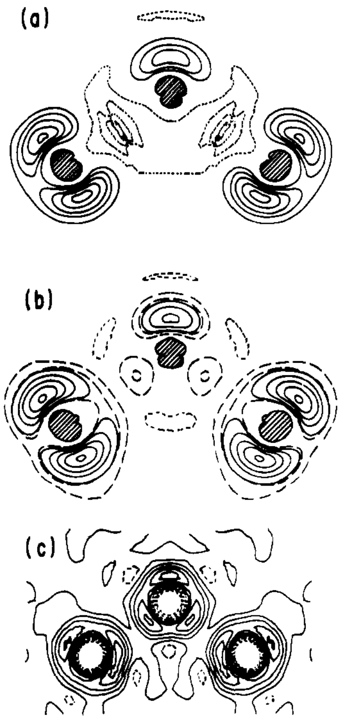

Figure 1. Deformation density for S_8 in an S-S-S face: (a) SCF-Xα-SW, s, p basis; (b) SCF-Xα-SW, extended (s, p, d, f) basis; (c) experimental, from ref 5. Contours at 0.10 e Å^{-3} (solid, positive $\Delta\rho$; short dashed, negative $\Delta\rho$). Long dashed contours in b are +0.067 and +0.007 e Å^{-3}. See ref 5 for effect of temperature parameters and differences between x-ray and neutron atomic parameters.

Coppens et al.[5] have recently reported $\Delta\rho(\mathbf{r})$ distributions for orthorhombic sulfur (S_8 molecules) derived from x-ray scattering experiments. Their results for the deformation density in a triangular S-S-S face are reproduced in Figure 1c. In Figures 1a and 1b are shown deformation densities calculated with the SCF-Xα-SW method in the muffin-tin (nonoverlapping sphere) approximation for two different basis sets. For Figure 1a, s and p waves were included in the sulfur spheres, while s, p, and d waves were used on the outer sphere; for Figure 1b, d and f waves were added to the sulfur spheres. Two intermediate cases with d waves in the sulfur spheres and waves up to $l = 2$ and $l = 4$ on the outer sphere were also examined. The results are intermediate to those shown in Figures 1a and 1b. In all cases the molecular wave functions were generated in the usual manner[6] and the electron density was calculated as the sum over contributions from all of the occupied valence levels for a mesh of 6400 points. The frozen core approximation was used throughout. A second distribution was generated by superposing the spherically averaged valence densities for s^2p^4 sulfur atoms, placed at the positions of the atoms in S_8, calculated by the Herman-Skillman method[7] (the atomic Xα method) for the same value of α (0.72475)[8] as for the molecule. A point by point subtraction was then carried out to yield the deformation density.

The comparison of Figure 1a and 1b with Figure 1c involves a number of assumptions and possible uncertainties which space restrictions do not allow us to discuss in detail. These include (i) the neglect of crystal packing effects; (ii) the neglect of molecular and crystal vibrations, i.e., temperature effects (see ref 3, 5, 9, and 10 for a discussion); (iii) possible systematic errors remaining in the experimental data (see ref 3 and 5 for

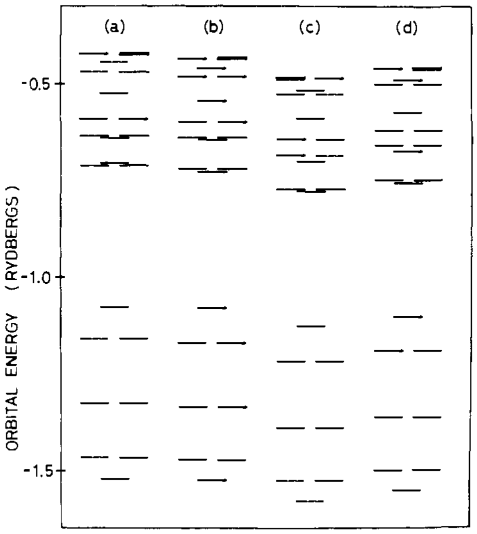

Figure 2. SCF-Xα-SW orbital eigenvalues (Rydbergs) for S_8 using various basis sets (l_{max} on S, l_{max} on outer sphere); (a) (1,2); (b) (2,2); (c) (2,4); (d) (3,3).

a discussion). Further work is required to assess the importance of each of these factors; however the degree of agreement between Figures 1b and 1c discussed below indicates that, for the qualitative purposes with which we are concerned, the comparison is valid.

For the purpose of discussion we will divide the plane into three regions (i) the core region, near the sulfur nuclei, (ii) the region further removed from the nuclei perpendicular to the S-S line, and (iii) the bond region along the S-S line.

For region i the experimental results are "notoriously unreliable" [3a] and, since we have used the frozen core approximation in our calculations, this region will not be discussed in detail. The hatched areas on Figures 1a and 1b correspond to regions of large valence electron deformation density and yield a rough indication of the extent of the core area.

Region ii is also rather easily dealt with. Experimentally one finds "lone-pair" lobes with a maximum density difference of $\sim$0.5 e Å^{-3} which is precisely what we have found in our calculations for all basis sets considered. There is relatively little effect of the higher partial waves for this region. The agreement is very good and therefore promotes optimism as to the accuracy of the Xα wave functions.

Region iii, along the S-S line, is more complicated. Here Coppens et al.[5] found a complicated double maximum distribution with a remarkably small electron surplus at the midpoint of the bond. The minimum basis set calculation, Figure 1a, is completely unsatisfactory for this region, almost all of the S-S line having a negative deformation density. A similar lack, or underestimate, of electron density gain in the bonding region for other molecules has previously been noted[3,11] if small basis sets are used in the approximate Hartree-Fock or the discrete variational-Xα method. For example the CO molecule shows a negative deformation density throughout the bonding region if a minimum basis set of Slater orbitals is used in a Hartree-Fock-type calculation.[11]

In the present case the bond region can be systematically improved by adding further partial waves to the basis set, first d waves (not shown) and then both d and f waves (Figure 1b). The large negative area of Figure 1a shrinks and by the time one has f waves it is reduced to a number of small regions along the border of the muffin-tin sphere which surrounds the atom. It is clear that at this stage the negative regions are unphysical but are rather a result of slight discontinuities in the wave functions which would disappear if calculations were performed with an even larger set of partial waves. For the calculations including f waves the deformation density is now positive for most of the interatomic region although it is still much smaller than the experimental values.

Overall the qualitative features of the change in electron density upon formation of the S_8 molecule from eight sulfur atoms are reasonably well accounted for in the extended basis set calculation. Partial waves of high angular momentum quantum number are necessary in order to account for the details of the deformation density. Spectroscopic results, i.e., the positions of the orbital eigenvalues, are much less sensitive to the changes in basis set as shown in Figure 2. Clearly the same overall pattern of energy levels is obtained for all of the sets of partial waves considered, typical energy level shifts being of the order of at most a few tenths of an electron volt. The spectroscopic results for S_8 will be discussed elsewhere.[12]

In conclusion the electron density distribution for S_8 as calculated by the SCF-Xα-SW method with an extended basis set is found to be remarkably accurate, especially in light of the approximations (muffin-tin potential, truncated partial wave expansion etc.) made in the method.

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A Novel Class of Alkylating Reagent, $RCu{\cdot}BF_3$. Substitution of Allyl Halides with Complete Allylic Rearrangement

Sir:

Substitution of allylic substrates with (or without) complete allylic rearrangement is still a challenge for chemists.[1] We now wish to report that the substitution with complete allylic rearrangement is achieved by using a new alkylating reagent, $RCu{\cdot}BF_3$ (eq 1). To our knowledge, this is the first example