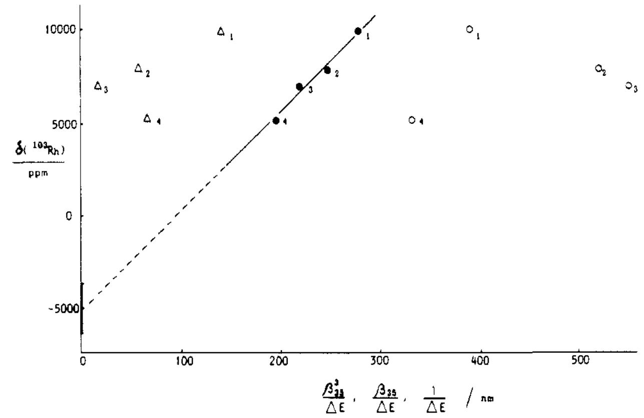

Figure 2. Correlation of the rhodium chemical shift of rhodium(III) complexes {1, $[Rh(OH_2)_6]^{3+}$; 2, $[RhCl_6]^{3-}$; 3, $[RhBr_6]^{3-}$; 4, $[Rh(NO_2)_6]^{3-}$} with the ligand field parameters ($1/\Delta E$ (○), $\beta_{35}/\Delta E$ (●), and $\beta_{35}{}^3/\Delta E$ (▲)). Relevant spectroscopic data for complexes 1–3 have been collected in ref 1b. For the hexanitrorhodate(III) complex, the chemical shift[16] and excitation energy[17] have been reported, while for the nephelauxetic parameter (not experimentally available) the value of the tris(ethylenediamine)rhodium(III) complex[9] is applied based on the evidence that in cobalt(III) complexes the nephelauxetic effect of nitro and ethylenediamine ligands is the same.[2]

origin only for the correlation of the chemical shifts with $\beta_{35}/\Delta E$. Hence, interpretation of the metal chemical shifts in terms of eq 1 is supported also by data on rhodium(III) complexes.

In the analysis of the metal NMR chemical shifts there remain the question as to whether there is any higher energy contribution to the magnetic shielding, besides that from d–d spin-allowed transitions. In the view of the good linearity, and the correct slope value, of the correlation of the chemical shifts with $\beta_{35}/\Delta E$,[1,3] these contributions should be very small or, very unlikely, invariant on complex composition.

Appendix

For "double-zeta" 3d radial wave functions:

$$R_{3d} = c_1\frac{(2\zeta_1)^{7/2}}{(6!)^{1/2}}r^2e^{-\zeta_1 r} + c_2\frac{(2\zeta_2)^{7/2}}{(6!)^{1/2}}r^2e^{-\zeta_2 r}$$

the following expression for the Racah parameter B is obtained:

$$B = c_1{}^4B(\zeta_1) + c_2{}^4B(\zeta_2) + c_3{}^4B(\zeta_3) + 2c_1{}^2c_2{}^2B(\zeta_1,\zeta_2) + 2c_1{}^2c_3{}^2B(\zeta_1,\zeta_3) + 2c_2{}^2c_3{}^2B(\zeta_2,\zeta_3)$$

where:

$$c_3{}^2 = 2c_1c_2\frac{(\zeta_1\zeta_2)^{7/2}}{\zeta_3{}^7}$$

$$\zeta_3 = (\zeta_1 + \zeta_2)/2$$

$$B(\zeta_i) = 389.15\zeta_i$$

$$B(\zeta_i,\zeta_j) = 4180\zeta_i a^2\left\{1 - \frac{25a^2}{3}[1 - (1 + a^{-1})^{-2}] + \frac{50}{3}a(1 + a^{-1})^{-3} + \frac{1}{3}(1 + a^{-1})^{-4}[72 + 88(1 + a)^{-1} + 95(1 + a)^{-2} + 90(1 + a)^{-5}]\right\}$$

$$a = \zeta_i/\zeta_j$$

Electron Transfer via Dithiaspiroalkane Linkages. Nature of Long-Range Through-Bond Electronic Coupling in Disulfoxide Radical Cations and Bis(metal) Complexes and Implications for the Characterization of the SO Bond

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Abstract: Electron transfer in bis(ruthenium pentaammine) complexes III–V of the single-, double-, and triple-ring dithiaspiroalkanes is known to be surprisingly facile. The mechanism of donor–acceptor interaction with these rigid nonconjugated bridges is thus of considerable interest. The electronic structure of the series of disulfoxides VI and VII for which photoelectron spectroscopic data are available has been studied in order to investigate this. Ab initio SCF calculations using a variety of basis sets have been carried out, and the ionization potentials (IP's) at Koopmans' theorem, ΔSCF, and projected broken-symmetry levels of approximation, obtained. Calculations were also performed for the related dithiaspiroalkanes, for the single-ring sulfide X and monosulfide IX, for dimethyl sulfoxide, and for ethylene sulfoxide, at the experimental or interpolated geometries. The use of a polarized (3-21G*) rather than an unpolarized (3-21G) basis for IX and the double-ring disulfoxide VI resulted in comparatively small changes in calculated IP's and orbital character. Thus, orbital assignments obtained without the inclusion of 3d functions are judged to be justified. The SO bond is then considered as an essentially semipolar link ($>S^{\delta+}—O^{\delta-}$) rather than as one involving hypervalent S ($>S=O$). The observed near constancy of the first IP of dithiaspiroalkanes and their mono- and disulfoxide derivatives is shown to be accidental. The trends in the experimental IP's are well reproduced by calculations, and the nature of the through-bond interaction is related to orbital type. An SO bond lying out of the plane of the thiaspiroalkane ring is necessary for nonzero interaction. Implications for electron transfer in metal complexes and relationships with transfer through rigid hydrocarbon chains are discussed. Through-space effects are equally important in the radical cation of the double-ring molecule VI.

The concept of through-space and through-bond interactions was first introduced by Hoffmann and co-workers nearly 20 years ago, in interpreting the results of their extended Hückel molecular orbital[1,2] calculations on diradical systems in terms of these types

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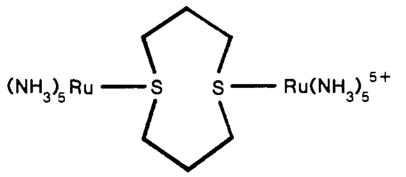
of coupling. In such a conceptual dissection of the interaction of two functional groups or chromophores, through-space effects are envisaged as arising from the direct spatial overlap of the orbitals associated with each functional group, while through-bond coupling requires the mutual mixing of the functional group orbitals with those of some communicating framework.[2,4] As a result, the effects of through-space interactions should decrease rapidly with increasing separation of the functional groups, while the through-bond couplings are expected to be less strongly distance dependent.[5]

In 1978 Stein and Taube[6] reported a surprisingly facile intramolecular electron transfer in the pair of dinuclear ruthenium complexes I and II. This was a strong indication that there was significant interaction between the two sulfur atoms, and since the ease of electron transfer was greater for compound I, in which the S–S separation was smaller, the interaction was considered to occur primarily by a through-space mechanism. Following these initial investigations further studies were carried out, in particular on the dinuclear ruthenium complexes (III–V) that are formed when the bridging ligand is a dithiaspiroalkane.[7,8] In accord with the results for the earlier compounds (I and II), the rate of electron transfer was again found to be surprisingly fast, in spite of the substantially larger formal separation of the sulfur atoms and the σ-bond character of the interconnecting framework. The interaction between the sulfurs was therefore considered to occur via a primarily through-bond rather than through-space mechanism.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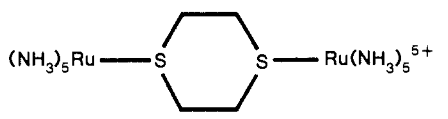
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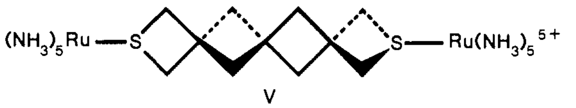
III


IV


V

In a further investigation of the through-bond interactions in these dithiaspiroalkane complexes, Stein et al.[9] recorded the photoelectron spectra of the isolated bridging ligands contained in III–V and carried out semiempirical (CNDO) self-consistent-field molecular orbital (SCF MO) calculations to aid with the assignment of the bands. Thus, they concluded that the first band in the spectrum was due to ionization from the two degenerate sulfur lone-pair orbitals, while the next band was attributed to ionization from an orbital strongly delocalized throughout the molecule, which was thought to provide a relaying pathway for the through-bond interaction. To mimic the effects of complex formation between these ligands and ruthenium atoms, Baker et al.[10] studied the corresponding series of dithiaspiroalkane sulfoxides VI–VIII. In these compounds the coordination about the sulfur is pyramidal and might be considered similar to the typically pyramidal conformation found in crystalline ruthenium compounds where a ruthenium atom directly bonds to a sulfur[11] (Figure 1). In reporting the photoionization spectra of these sulfoxides, Baker et al.[10] first discussed the photoionization spectrum of the single-ring thiacyclobutane sulfoxide (IX). The

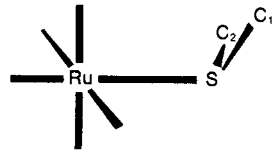


Figure 1. Typical pyramidal coordination of the sulfur atom in a ruthenium complex, e.g. in the tribromobis(dipropylsulfide)nitrosylruthenium(II) $[Ru(NO)Br_3(n\text{-}Pr_2S)_2]$ molecule $\angle$Ru–S–C$_1$ = 102.3° and $\angle$Ru–S–C$_2$ = 98.4°.[11]

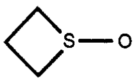
Table I. Comparison of the Experimentally Determined[10] Ionization Potentials (eV) of the Sulfoxides (Compounds VI–IX) and the Corresponding Parent Sulfides

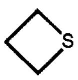
		ionization potential		
no. of rings	sulfide or sulfoxide	1st	2nd	3rd
one	sulfide	8.65	10.7	
	sulfoxide	8.90	10.1	
two	sulfide	8.71	10.04	
	sulfoxide	8.75	9.60	10.45
three	sulfide	8.75	9.55	
	sulfoxide	8.78	9.16	10.10
four	sulfide	8.75	9.45	
	sulfoxide	8.75	9.00	10.15


VI


VII


VIII


IX


X

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first two bands, at 8.9 and 10.1 eV, were clearly distinguishable from the rest of the valence shell ionization spectrum. By comparison with the photoelectron spectrum of the parent thiacyclobutane (X), in which the first band is at 8.65 eV and corresponds to ionization of a sulfur lone-pair electron, and because of its relatively small half-width, the band at 8.9 eV in thiacyclobutane sulfoxide was assigned to ionization from a sulfur lone-pair orbital. The second band at 10.1 eV was found to be somewhat broader than the first, suggesting that the orbital associated with this ionization process possessed more bonding character; following the work of Bock and Solouki,[12] who also interpreted sulfoxide photoelectron spectra in terms of CNDO molecular orbital calculations, Baker et al.[10] assigned it to ionization from a π_{SO} orbital. A summary of the observed first and second ionization potentials of the sulfide and sulfoxide compounds is given in Table I.

In this paper, we primarily report the results of ab initio SCF calculations of the ionization energies of the sulfoxide systems VI, VII, and IX and also discuss the electronic structures of the parent sulfides that result when the oxygens are removed and hence serve as difunctional ligands in the formation of bis(pentammineruthenium) complexes. To investigate the spectral assignments and the nature of the relevant molecular orbitals, ab initio SCF calculations on the dimethyl and ethylene sulfoxides were also carried out and the results compared with those of the earlier CNDO calculations of Bock and Solouki;[12] as some notable differences were found, a new orbital assignment scheme is suggested.

The magnitude of the orbital splitting in the disulfoxide systems has been found to be particularly sensitive to the angle between the S–O bond and the attached carbon framework. In particular, for S–O bonds lying in the plane of the ring, an extremely small splitting would be expected. The mechanism for the splitting is explored, as are the relative through-space and through-bond contributions. The conclusions reached can be qualitatively generalized to systems where atoms or groups other than oxygen are attached to the sulfur centers.

Theory and Computational Methods

Koopmans and ΔSCF Ionization Potentials. For a closed-shell system the first approximation to the ionization potentials (IP) is given by Koopmans' theorem,[13] as the negative of the canonical orbital energies. The basic physical approximations inherent in the Koopmans method are that both the initial and final states of the system are described by single-determinantal wave functions (i.e., electron correlation effects are implicitly neglected) and that the occupied molecular orbitals do not relax on ionization; it is therefore often described as a frozen-orbital approximation. However, despite these failings Koopmans IP's are frequently more accurate than may at first have been expected, as the effects of orbital relaxation and electron correlation generally tend to cancel to some extent. In any case, Koopmans IP's are often sufficiently accurate to predict the correct order of the ionization energies and therefore to assign the experimentally observed bands.

Describing an ionization process as the removal of an electron from an occupied orbital of the parent molecule is a common and widespread practice, and we, too, often use it in this work. It is important however to keep in mind that the use of such terminology implicitly assumes that Koopmans' theorem is at least qualitatively valid, and consequently it implies that the orbitals from which we ionize are canonical SCF MO's.

To account for the relaxation of the molecular orbitals, it is necessary to optimize the wave functions of the ionized species by carrying out an open-shell SCF calculation. A given IP is then evaluated as the difference between the total energies of the parent molecule and the positive ion in a particular quantum state ($IP_{\Delta SCF}$). Since open-shell wave functions are strictly variationally stable only in the case of ionization from the highest occupied molecular orbital of each symmetry, it is usually only possible to include relaxation effects for a small number of the ionic states. In this work the open-shell SCF calculations needed to obtain the ΔSCF estimates of the ionization energies were carried out by the spin- and symmetry-restricted formalism.[14,15]

An alternative approach to ΔSCF is to formulate the ion wave functions as limited configuration interaction (CI) expansions in terms of the MO's of the neutral parent molecule.[16,17] Hence, the relaxation effects are resolved mainly through the inclusion of singly excited configurations of the Koopmans determinants. The implicit advantage of such CI methods is that all valence ionizations can be treated simultaneously.

The incorporation of electron correlation effects into the evaluation of a specific IP can be achieved in a manner similar to the inclusion of relaxation effects, i.e., by performing independent correlated calculations on both the initial and final states; consequently, it requires considerably greater computational effort. Alternatively, using electron propagator, viz. Green's function methods,[18,19] ionization potentials can be obtained directly, implicitly including both relaxation and correlation effects; these techniques have proved to be very successful in quantitative interpretations of photoelectron spectra.

When the ionization spectra of the various sulfoxide species of interest here are analyzed, we find that the computational methods have been limited by the size of the systems. Therefore, no attempt has been made to include the effects of dynamical electron correlation; instead, we focus on the evaluation of the Koopmans ionization energies and the effects of orbital relaxation. When "relaxed" wave functions for the ions were calculated with the spin-restricted open-shell SCF formalism, it was expected (and indeed found) that "symmetry breaking"[20] of the open-shell SCF wave functions of the symmetric disulfoxides would occur, leading to a significant increase in the relaxation energy. A brief discussion of the effects and interpretation of such symmetry breaking, including an outline of the method used for the resymmetrization of broken-symmetry wave functions, is given below.

Symmetry Breaking of Open-Shell SCF Wave Functions. The potential instability of an open-shell SCF wave function with respect to the relaxation of the spatial-symmetry constraints in the context of ionization energy calculations was first demonstrated by Bagus and Schaefer,[21] who found that removal of the interchange symmetry between the two oxygen atoms in a core-ionized oxygen molecule resulted in a substantial lowering of the total energy. Since then, so-called symmetry breaking has been observed and discussed on numerous occasions in the calculation of core[22–27] as well as valence[27–33] ionization energies.

An electronic wave function with broken symmetry is really a linear combination of two or more wave functions whose symmetries are consistent with the symmetry properties of the molecule's nuclear framework. Consequently, if symmetry breaking is observed, it is an indication of the presence of near-degeneracy effects and the basic inadequacy of a symmetry-adapted single-configuration treatment. Therefore, in such a case the zeroth-order wave function for the ionized molecule should be calculated by resymmetrization of the broken-symmetry SCF wave functions, i.e. by projecting out the components with the appropriate symmetry, or immediately formulated as a multiconfigurational SCF (MCSCF) wave function, in which case the orbitals as well as the total wave function transform as irreducible representations of the molecule's point group.[28,31,34–37] If we now consider the former method and take

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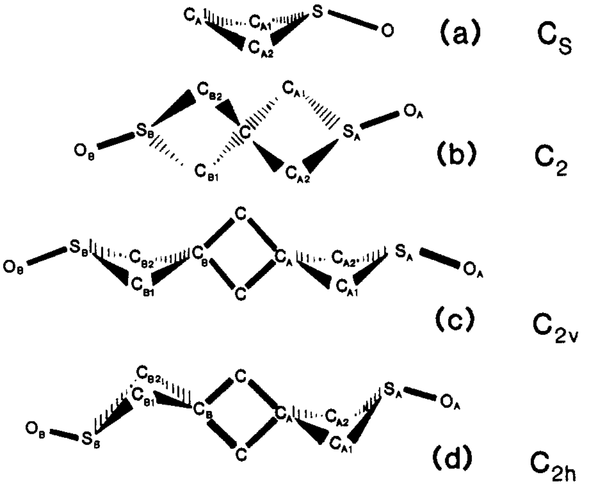

Figure 2. Structures, conformations, and symmetries of (a) thiacyclobutane sulfoxide, (b) 2,6-dithiaspiro[3.3]heptane disulfoxide, and (c,d) 2,8-dithiaspiro[3.1.3.1]decane disulfoxide.

the specific case of the double-ring disulfoxide molecule (Figure 2b), which belongs to the C_2 point group, the highest occupied molecular orbital (HOMO) and the next highest occupied molecular orbital (NHOMO) transform according to the b and a irreducible representation, respectively. Hence, the symmetry-adapted single-determinantal wave functions corresponding to ionization from the HOMO and NHOMO can be denoted by eq 1 and 2 where A is the antisymmetrizer. When

$$\Psi_B^+ = A[...(a)^2(b)^1] \tag{1}$$

$$\Psi_A^+ = A[...(a)^1(b)^2] \tag{2}$$

the molecular orbitals are allowed to break symmetry, two new degenerate wave functions are obtained, constructed from the MO's $\{\varphi_L\}$ and $\{\varphi_R\}$, respectively, and they correspond to localization of the positive hole to the left or right side of the molecule (eq 3 and 4). Resymmetrization

$$\Psi_L^+ = A[...(\varphi_L^{n-1})^2(\varphi_L^{n})^1] \tag{3}$$

$$\Psi_R^+ = A[...(\varphi_R^{n-1})^2(\varphi_R^{n})^1] \tag{4}$$

of these degenerate localized wave functions is achieved by taking symmetric and antisymmetric combinations of Ψ_R^+ and Ψ_L^+ that will transform as A and B, respectively (eq 5), which have the energies in eq

$$\Psi_\pm = \Psi_R^+ \pm \Psi_L^+ \tag{5}$$

$$E_\pm = (\langle\Psi_R^+|H|\Psi_R^+\rangle \pm \langle\Psi_R^+|H|\Psi_L^+\rangle)/(1 \pm \langle\Psi_R^+|\Psi_L^+\rangle) \tag{6}$$

6. In deriving eq 6 we used the fact that Ψ_L and Ψ_R are related to each other by symmetry, hence

$$\langle\Psi_L|H|\Psi_L\rangle = \langle\Psi_R|H|\Psi_R\rangle \tag{7}$$

and that $\langle\Psi_L|H|\Psi_R\rangle$ is real. As remarked earlier, such a resymmetrization process is equivalent to projecting out the component with the appropriate symmetry from a broken-symmetry wave function, Ψ_L^+ or Ψ_R^+; hence, we refer to this technique as the projected broken-symmetry self-consistent-field (PBS–SCF) method. Evaluation of the energies $E_\pm$ therefore requires the computation of the overlap and Hamiltonian matrix elements between the two nonorthogonal wave functions Ψ_R^+ and Ψ_L^+. To perform this, we have implemented the procedure outlined by Bacskay et al.,[22] which uses the atomic one- and two-electron integrals, i.e. without recourse to a full integral transformation. This is of considerable advantage in the systems studied here, since a full four-index transformation, in addition to the raw numerical work, would necessitate the simultaneous storage of at least two very large files of two-electron integrals that is beyond the capabilities of our current computing facilities.

Hence, having obtained the energies E_+ and E_-, we have an additional estimate of the energy splitting between the lowest A and B states of the disulfoxide ion, as well as improved values for the corresponding IP's.

Table II. First Two Ionization Potentials and Their Separation (eV) Calculated for the Thiacyclobutane Sulfoxide Molecule with Koopmans' Theorem and the ΔSCF Method

	1st		2nd		separation	
basis	Koopmans'	ΔSCF	Koopmans'	ΔSCF	Koopmans'	ΔSCF
STO-3G	5.73	2.90	6.22	3.52	0.49	0.62
3-21G	9.32	7.06	10.30	7.74	0.98	0.68
3-21G*	9.27	7.35	10.56	8.17	1.29	0.82
DZ	9.69	7.31	10.64	7.96	0.95	0.65
DZP	9.68	7.74	11.00	8.54	1.32	0.80
expt	8.9		10.1		1.2	

Cederbaum and Domcke[23] have performed a detailed analysis on the effects of reduced symmetry in correlated calculations on core hole states, concluding that a significant proportion of the correlation energy obtained from a symmetry-restricted calculation could be accounted for in a localized SCF calculation. This is simply because in a symmetry-restricted calculation a large proportion of the correlation energy is due to the configuration interaction expansion resolving the near-degeneracy effects, rather than accounting for true dynamical correlation. Allowing the SCF wave function to break symmetry can therefore be considered as allowing additional relaxation to occur, beyond that accounted for in a symmetry-restricted open-shell calculation.

Basis Sets and Computer Programs. Due to the size of the systems studied, the basis sets used had to be modest in size; they range from the minimal STO-3G basis,[38] through the split-valence 3-21G,[39,40] to the double-ζ (DZ) basis. The double-ζ set for the first-row element atoms and hydrogen is derived from the primitive Gaussian (9s, 5p; 4s) set of Dunning and Hay,[41] while for sulfur the (11s, 7p) set of Huzinaga[42] is used, contracted to [6s, 4p]. Two polarized basis sets, labeled 3-21G* and DZP, were also used; these contained polarization functions on the heavy atoms (S, C, and O) with exponents as recommended by Ahlrichs and Taylor.[43]

The calculations were performed with the MOLECULE[44] integral programs interfaced with the quadratically convergent SCF programs of Bacskay.[45,46] In addition, some of the larger calculations were performed with the direct SCF program DISCO,[47] which recalculates the necessary integrals during each iteration of the SCF procedure and consequently is not limited by lack of disk space or slow input/output.

Results

The geometry used in the thiacyclobutane sulfoxide (Figure 2a) calculations is an experimental geometry, as determined from microwave spectroscopy by Bevan et al.[48] For the double-ring 2,6-dithiaspiro[3.3]heptane disulfoxide (Figure 2b) and the triple-ring 2,8-dithiaspiro[3.1.3.1]decane sulfoxide (parts c and d of Figure 2), no experimental geometries have, to our knowledge, been obtained. Consequently, we had to resort to employing approximate structures. The geometry of the double-ring compound was arrived at by combining two thiacyclobutane sulfoxide molecules with the planes described by CB2, CB1, C and CA1, CA2, C (Figure 2b) perpendicular. The resulting species is of C_2 symmetry; i.e., a rotation of 180° around the axis of symmetry interconverts rings A and B. For the triple-ring sulfoxide, the central ring was constrained to be planar, with C–C bond lengths equal to those in the cyclobutane[49] molecule. Two possible ar-

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Table III. Total SCF Energy (E_h) and Ionization Potentials (eV) of 2,6-Dithiaspiro[3.3]heptane Disulfoxide Calculated with Koopmans' Theorem, the ΔSCF, and the Projected Broken-Symmetry SCF (PBS–SCF) Methods

		1st			2nd			3rd	4th	splitting $IP_2 - IP_1$		
basis	SCF energy	Koopmans'	ΔSCF	PBS–SCF	Koopmans'	ΔSCF	PBS–SCF	Koopmans'	Koopmans'	Koopmans'	ΔSCF	PBS–SCF
STO-3G	−1125.378437	5.859	4.913	2.995	6.253	5.192	3.188	6.529	6.529	0.394	0.279	0.193
3-21G	−1132.609988	9.402	8.741	7.146	10.124	9.378	7.575	10.705	10.783	0.722	0.632	0.428
3-21G*	−1133.227511	9.244	8.678		10.063	9.433		10.908	10.969	0.819	0.755	
DZ	−1137.910828	9.975	9.260	7.612	10.588	9.776	7.940	11.218	11.270	0.613	0.516	0.328
					Planar Ring Conformation							
3-21G	−1132.601505	9.284	8.642		10.201	9.349		10.621	10.623	0.917	0.707	
expt			8.75			9.60		10.45	10.45		0.85	

rangements for the sulfoxide rings now exist: one isomer has a plane of symmetry between each sulfoxide ring and is of C_{2v} symmetry (Figure 2c) while the second has an axis of symmetry and belongs to the C_{2h} point group (Figure 2d). The effects of geometry variation on the calculated IP's have been investigated and will be discussed in the later sections.

Single-Ring Thiacyclobutane Sulfoxide. The calculated first and second IP's (IP_1^s and IP_2^s) of the single-ring thiacyclobutane sulfoxide molecule, obtained with all five basis sets, are given in Table II. The photoelectron spectrum was recorded by Baker et al.,[10] and the two lowest energy bands were interpreted as ionizations from a sulfur lone pair (n_S) and a sulfur-to-oxygen π orbital (π_{SO}), respectively.

On examining the theoretically calculated IP's, we find that with the STO-3G basis the absolute magnitudes of the two IP's as well as their separation are substantially underestimated by both the Koopmans and ΔSCF calculations. When greater flexibility is allowed in the valence region by using the split-valence 3-21G basis, a marked increase in the calculated IP's results. The theoretical values are now slightly higher than the experimental ones when calculated within the Koopmans approximation and fall below the experimental values when relaxation effects are included via the ΔSCF process. As already mentioned, this is the expected behavior, since the inclusion of correlation effects usually leads to an increase in the calculated IP. A further increase in the basis set to double-ζ (DZ) does not produce any significant changes in the IP's.

Since the sulfur atom is believed to be capable of hypervalency, the addition of 3d functions to the basis set may be expected to result in substantial changes in the IP's. However, the differences between the values calculated with the 3-21G and 3-21G* or the DZ and DZP results are not particularly large. This is especially so for the first IP, where there is hardly any change in the Koopmans ionization energies while the ΔSCF values differ by about 0.3 eV. The second IP shows a more substantial variation, and, consequently, the separation between the two peaks is calculated to be slightly larger when the polarized bases are used.

Double-Ring 2,6-Dithiaspiro[3.3]heptane Disulfoxide. The results of our calculations on the 2,6-dithiaspiro[3.3]heptane disulfoxide are given in Table III. Since the system is of C_2 symmetry, only the first two IP's could be obtained by the ΔSCF method. In relation to the previously calculated IP's for the single-ring sulfoxide (IP_1^s and IP_2^s), the first and second IP's are due to ionizations from molecular orbitals that qualitatively are antisymmetric and symmetric combinations of the single-ring molecular orbitals associated with IP_1^s. Similarly, the third and fourth IP's are due to the removal of an electron from molecular orbitals that are antisymmetric and symmetric combinations of the NHOMO in the single-ring sulfoxide.

As expected on the basis of the single-ring sulfoxide results, the IP's of the double-ring sulfoxide $\{IP_i^d\}$ obtained with the STO-3G basis are substantially below experiment. However, even these results clearly indicate that there is a substantial difference between IP_1^d and IP_2^d, while IP_3^d and IP_4^d are nearly equal. A moderate improvement in the quality of the basis set to the 3-21G or DZ level again shows a marked increase in the IP's. Within the Koopmans approximation, all the calculated IP's are now higher than the experimental values, while at the ΔSCF level IP_1^d and IP_2^d are very close to the observed values and actually fall below them when calculated with the 3-21G basis. When the wave function is allowed to break symmetry, a further relaxation of considerable magnitude occurs; energetically it is comparable to the relaxation of the frozen-orbital (Koopmans) wave function to the symmetry-restricted SCF one. (The energy corresponding to the localized, broken-symmetry wave function is, to a good approximation, just the average energy of the symmetric and antisymmetric states; hence, the intrinsic lowering in the calculated first and second ionization potentials due to symmetry breaking is $\approx$1.4 eV, calculated with the 3-21G and DZ bases). The resulting first and second ionization potentials are now well below experiment, irrespective of basis set.

The effect of d functions on the calculated IP's could only be evaluated for the 3-21G basis set within the Koopmans and ΔSCF approximations. The results obtained with the polarized 3-21G* basis show very little difference from those obtained with the unpolarized 3-21G basis; indeed the changes observed are even smaller than those found for the single-ring sulfoxide discussed above.

Examining the splitting between IP_1^d and IP_2^d, we observe a consistent decrease with level of theory calculated with the same basis set. The addition of polarization functions increases the separation. In all cases the calculated splitting is less than that observed experimentally. Although it is not clear to us why the PBS–SCF method yields splittings that appear inferior to those obtained by the simpler, symmetry-adapted techniques, we note that Martin[31] reported similar behavior in the excitation energies of pyrazine, where PBS–SCF consistently underestimates the u–g splittings by $\approx$0.5 eV.

Triple-Ring 2,8-Dithiaspiro[3.1.3.1]decane Disulfoxide. The results obtained for both the C_{2v} and C_{2h} theoretical structures of 2,8-dithiaspiro[3.1.3.1]decane disulfoxide are given in Table IV. The two conformers are found to be almost isoenergetic, irrespective of basis, although a definitive comparison cannot be made unless the individual geometries are optimized. The calculated IP's for the two structures differ only slightly, indicating that they are relatively insensitive to variations in the geometry of the mediating σ framework.

In agreement with experiment, the calculated first and second IP's (IP_1^t and IP_2^t) are not equal; they can be described as ionization from MO's that are antisymmetric and symmetric combinations of the single-ring HOMO's, respectively, i.e., those associated with the first ionization peak in thiacyclobutane sulfoxide. The third and fourth IP's (IP_3^t and IP_4^t), which, because of the higher point group symmetry, can now also be determined by the ΔSCF method, are found to be very nearly the same. The orbitals, ionization from which gives rise to these bands, can again be related to antisymmetric and symmetric combinations of the single-ring NHOMO's.

The trends observed in the absolute magnitudes and separations between the ionization energies as the basis set and method of calculation are varied are similar to those found in the double-ring sulfoxide. While symmetry-breaking calculations could not be carried out for these systems, the fact that the ΔSCF IP's, IP_1^t

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Table IV. Total SCF Energies (E_h) and Ionization Potentials (eV) for the C_{2v} and C_{2h} Conformers of 2,8-Dithiaspiro[3.1.3.1]decane Disulfoxide, Calculated with Koopmans' Theorem and the ΔSCF Method

		1st		2nd		3rd		4th		splitting $IP_2 - IP_1$	
basis	SCF energy	Koopmans'	ΔSCF	Koopmans'	ΔSCF	Koopmans'	ΔSCF	Koopmans'	ΔSCF	Koopmans'	ΔSCF
					C_{2v} Structure						
STO-3G	−1239.931 756	5.763	4.698	5.961	4.803	6.331	5.328	6.350	5.338	0.198	0.105
3-21G	−1245.876 222	9.217	8.567	9.642	8.850	10.374	9.517	10.447	9.556	0.425	0.283
DZ	−1253.786 773	9.713	9.013	10.075	9.235	10.835	9.913	10.894	9.939	0.362	0.222
					C_{2h} Structure						
STO-3G	−1239.931 932	5.789	4.714	5.938	4.791	6.338	5.334	6.345	5.334	0.149	0.079
3-21G	−1247.876 327	9.256	8.591	9.602	8.833	10.389	9.530	10.434	9.545	0.346	0.242
DZ	−1253.787 678	9.745	9.035	10.045	9.224	10.844	9.918	10.894	9.944	0.300	0.189
expt		8.78		9.16		10.10		10.10		0.38	

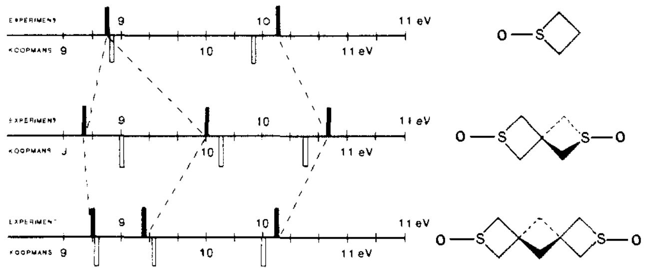

Figure 3. Comparison of the first two ionization potentials of the single-ring sulfoxide (IX) with the first four ionization potentials of the double- and triple-ring sulfoxides (VI and VII). The experimental results are shown above the axes while the theoretical (3-21G, Koopmans) values are below them (shifted down by 0.4 eV for easier comparison).

and $IP_2{}^t$, calculated with the DZ basis, are larger than the experimental values indicates that the corresponding ion wave functions are very likely to be unstable with respect to a lowering in symmetry.

Energy Levels of the Sulfoxides. To summarize the results obtained for the sulfoxide ring systems, the first two IP's of the single-ring sulfoxide and corresponding four IP's of the double- and triple-ring sulfoxide are compared in Figure 3. When the experimentally observed trends are examined as the molecular size is increased, the most striking feature we note is the near-constancy of the first IP with the number of rings. This trend is also well reproduced by the theoretical calculations, although in absolute sense the calculated IP's are higher than the experimental values. The splitting observed between the first two bands in the photoelectron spectrum of the double- and triple-ring sulfoxides consequently results almost exclusively from an increase in the second IP. Theory and experiment agree further in that the magnitude of the splitting decreases as we go from the double- to the triple-ring sulfoxide; the calculated splitting for the double-ring compound is slightly below experiment, but comparable with experiment in the case of the triple-ring system.

If we now compare the second IP of the single-ring sulfoxide with those of the double- and triple-ring disulfoxides, we find, in agreement with experiment, that on forming the double- and triple-ring compounds virtually no splitting occurs; i.e., the two orbitals from which the second ionization takes place are very nearly degenerate. The shift in this IP as we go from the single-ring to the double- and triple-ring sulfoxides is also well reproduced by the theoretical calculations, although again the absolute values are all moderately displaced to higher energies when compared with experiment. For all three compounds, however, the separations between these bands and the first and second IP's are only slightly underestimated by the theoretical treatment. In summary, taking into account the limitations of the calculations and the approximate geometries used, the overall agreement between experiment and theory is reasonably satisfactory.

Orbital Assignment. The interpretation and assignment of the bands in the photoelectron spectra of the dithiaspiroalkane sulfoxides requires some consideration of the nature of the bonding in the sulfoxide group, in particular, whether the sulfoxide bond should be considered as a semipolar bond in which a formal electron transfer takes place between the sulfur and the oxygen or, at the other extreme, whether the sulfur exists in a tetravalent state, i.e.,

$>S^{\delta+}—O^{\delta-}$ semipolar sulfur

$>S{=}O$ tetravalent sulfur

In the former case, the standard 3s and 3p valence orbitals of sulfur would suffice to describe the bonding, while in the latter, it would be necessary to invoke 3d orbital participation. This problem has received considerable attention and has been approached in a number of different ways.[50-55] The inclusion of 3d functions in the sulfur basis, e.g. in dimethyl sulfoxide (DMSO), results in a considerable drop in the energy and a decrease in the SO bond length. These effects have been interpreted as resulting from the formation of a sulfur-to-oxygen double bond,[51] although they are also consistent with the view that d functions act purely as polarization functions. Bond lengths,[56] calculated at the SCF level, generally decrease when polarization functions are introduced, although the changes observed for bonds between first-row atoms are not as large as, for example, those found in the SO bond.[55] In an effort to answer the question of whether d functions are actually incorporated into the hybrid orbitals that need to be formed if sulfur were tetravalent or whether they are simply polarization functions, Wallmeier and Kutzelnigg[53] carried out population analyses, using the Heinzmann and Ahlrichs[57] method, for a number of molecules that contain a semipolar X–O bond, where X is a nitrogen, phosphorus, or sulfur atom. The results indicated that the typical d orbital population was substantially smaller (0.3 electron) than that which may be expected for a hypervalent species, and they therefore concluded that the "traditional valence AO's of s and p type are, when appropriately deformed, able to describe the bonding". The results obtained here indicate that relatively little change in the calculated IP's takes place when 3d functions are included in the sulfur, oxygen, and carbon basis sets, although owing to the size of the systems, an extensive study of d orbital participation was not possible. Hence, provisionally, we believe that an orbital assignment based on the results obtained with an unpolarized basis set may be justified.

In Table V, the atomic and overlap populations, calculated by the Mulliken[58] procedure with the 3-21G basis set, are given for the two highest lying molecular orbitals of the single-ring sulfoxide and the corresponding four orbitals of the double- and triple-ring compounds. For the HOMO of the single-ring sulfoxide, we observe a substantial electron population located on the oxygen, slightly less on the sulfur, and a progressively decreasing con-

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Table V. Mulliken Population Analysis for the Highest Occupied MO's of the Single-, Double-, and Triple-Ring Sulfoxides Using the 3-21G and DZP Basis Sets

		orbital	net atomic and overlap populations						
basis	sulfoxide molecule	energy, eV	O	O–S	S	S–C	C	C–C	C
3-21G	single ring	−9.32	1.122	−0.093	0.942	−0.216	0.417	−0.102	0.142
	double ring	−9.40	0.547	−0.049	0.434	−0.076	0.243	−0.047	0.176
	double ring	−10.12	0.572	−0.039	0.510	−0.150	0.220	−0.078	0.133
	triple ring 1	−9.22	0.506	−0.048	0.419	−0.079	0.211	−0.058	0.140
	triple ring 1	−9.64	0.564	−0.045	0.503	−0.124	0.222	−0.055	0.083
	triple ring 2	−9.26	0.513	−0.047	0.424	−0.080	0.211	−0.057	0.139
	triple ring 2	−9.60	0.553	−0.047	0.506	−0.121	0.235	−0.057	0.085
3-21G	single ring	−10.30	1.306	0.013	0.023	−0.006	0.531	−0.006	0.025
	double ring	−10.70	0.655	0.006	0.018	0.021	0.242	−0.013	0.046
	double ring	−10.78	0.655	0.007	0.015	−0.050	0.345	−0.009	0.046
	triple ring 1	−10.37	0.627	0.003	0.039	0.002	0.284	−0.003	0.035
	triple ring 1	−10.45	0.641	0.003	0.066	0.000	0.326	−0.003	0.013
	triple ring 2	−10.39	0.628	0.003	0.038	0.003	0.284	−0.003	0.037
	triple ring 2	−10.43	0.641	0.002	0.068	0.000	0.327	−0.003	0.016
DZP	single ring	−9.68	1.148	−0.169	0.807	−0.014	0.217	−0.039	0.145
	single ring	−11.00	1.279	−0.048	0.146	0.069	0.385	0.000	0.000

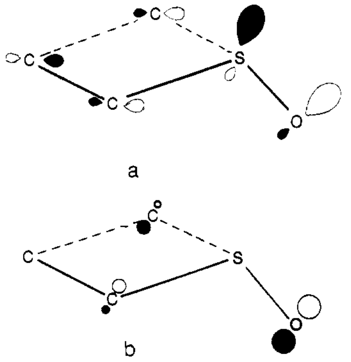

Figure 4. Diagrammatic representations of the (a) HOMO and (b) NHOMO of thiacyclobutane sulfoxide.

tribution from the carbon atoms of the ring. To assess whether any major changes in this picture occur when d functions are included in the basis, the results obtained for the single-ring sulfoxide with the DZP basis set are also given. Comparison of the populations obtained with the 3-21G and DZP bases for the HOMO reveals only minor differences, with the major contributions in each case coming from the oxygen and sulfur atoms.

Following the examination of the molecular orbital coefficients for the HOMO of the single-ring sulfoxide, a diagrammatic illustration of the molecular orbital is shown in Figure 4a. The principal components of this MO are the atomic p orbitals of the sulfur and oxygen atoms with some participation from the ring atoms, via a bonding combination of essentially in-plane sp hybrid orbitals. Overall, from the population analysis and the orbital coefficients, this orbital is best described as an antibonding combination of sulfur and oxygen lone pairs (n_S–n_O), which, however, extends into the carbon ring, rather than as a pure sulfur lone pair as proposed by Baker et al.[10]

The NHOMO of the single-ring sulfoxide is antisymmetric with respect to the single plane of symmetry. With the 3-21G basis set the electron population is predicted to reside almost totally on the oxygen atom with some minor contributions, from the first two ring–carbon atoms. When the basis is enlarged to DZP, the sulfur atom plays a more important role, as revealed by its increased atomic population. However, the major features are still the same as those at the 3-21G level. A schematic representation of the orbital would therefore overemphasize the participation of the d orbitals on the sulfur; instead, we propose that this orbital is better described as an oxygen lone pair with some π_{SO} character, i.e. $n_O(+\pi_{SO})$.

Considering now the effect of forming the double- or triple-ring disulfoxides from the single-ring sulfoxide (Table V), we observe that the electron density is split between the symmetry-related atoms. The two highest molecular orbitals are again principally located on the sulfur and oxygen atoms with some delocalization onto the carbon atoms of the ring system, while the third and fourth highest molecular orbitals are distributed largely on the oxygens. The assertion that these two pairs of orbitals correspond to antisymmetric and symmetric combinations of the HOMO's and NHOMO's of the parent single-ring systems, therefore, appears to be correct. A diagrammatic representation of the HOMO and NHOMO in the double-ring sulfoxide is shown in Figure 5.

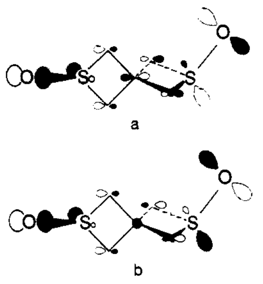

Figure 5. Diagrammatic representations of the (a) HOMO and (b) NHOMO of 2,6-dithiaspiro[3.3]heptane disulfoxide.

Dependence of Ionization Potentials on Geometry. To assess the sensitivity of the IP's to changes in the geometry, a series of calculations on the double-ring disulfoxide were carried out at a number of conformations. With the 3-21G basis set, the IP's were recalculated at the Koopmans and ΔSCF levels for a structure in which the two sulfoxide rings were taken to be planar. The total SCF energy for this structure, given in Table III, is about 0.23 eV higher than that for the conformation adopted on the basis of the experimental single-ring geometry, where the ring dihedral angle is ≈35°. The first and second IP's are, however, within about 0.1 eV of their previous values, although due to their opposite movement their separation has increased by slightly more than this. The third and fourth IP's show a similar shift, except they both decrease, and therefore remain nearly equal. Overall, the use of an approximate geometry for the mediating framework between the two sulfoxide groups is unlikely to change the trends that have been found or the conclusions reached.

The effects of local conformation variations about each sulfur atom on the orbital energies were investigated by performing a series of calculations on the planar double-ring sulfoxide described above, in which the angle (θ) between the sulfur-to-oxygen bond and the plane of each ring was progressively altered. The resulting orbital correlation diagram calculated with the 3-21G basis set for a range of θ values, plotted as Koopmans' IP's, is shown in Figure 6. In addition to the Koopmans IP's, the ΔSCF ionization energies corresponding to ionization from the uppermost two molecular orbitals are also marked by the dashed line. Considering first the highest lying MO's, we note that these are degenerate when the two oxygen atoms lie in the plane of the rings (i.e. $\theta = 0$). At this D_{2d} geometry the sulfur and oxygen lone pair p orbitals in one ring are orthogonal to those in the second ring and also

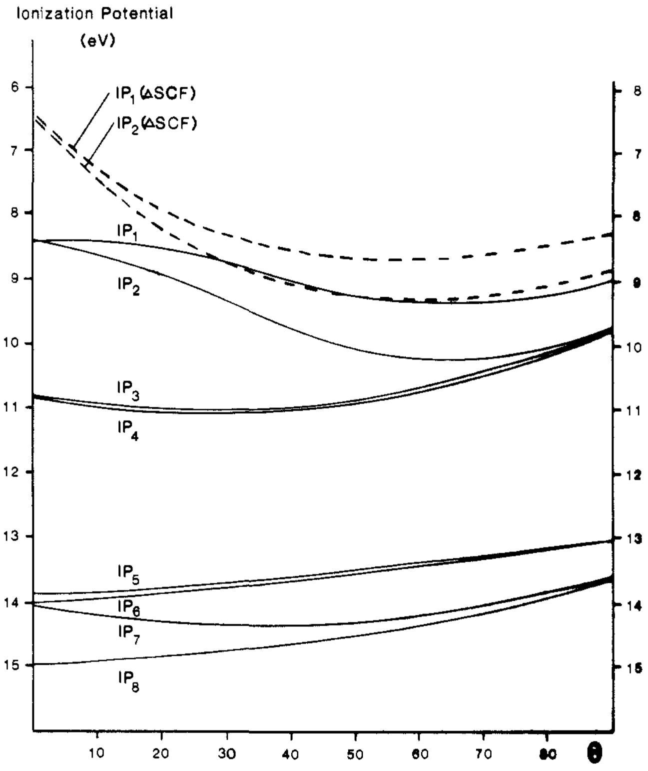

Figure 6. Variation of the first eight ionization potentials with the angle (θ) between the S–O bond and the adjacent ring plane in the double-ring sulfoxide (VI).

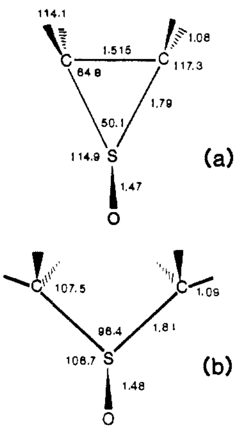

Figure 7. Experimental structures of (a) ethylene sulfoxide[46] and (b) dimethyl sulfoxide.[45]

to the orbitals of the immediate carbon framework and thus cannot interact. However, if the individual rings depart from planarity, the accompanying decrease in the molecular symmetry no longer ensures a strict degeneracy, although the interaction is small unless a substantial ring puckering occurs. As the angle θ increases, the IP's increase, and the orbital splitting begins to appear. When θ reaches 55°, which corresponds to the angle used in the earlier calculations already discussed, both IP's, and hence their separations, are reasonably constant. Therefore, it appears that, provided the value for θ in the geometry adopted was within $\approx$10° of the experimental value, the conclusions reached thus far should be essentially correct.

Turning to the next pair of orbitals, we find that they remain almost degenerate, so that no splitting is expected between the third and fourth IP's, regardless of the out-of-plane angle θ. However, as θ tends toward 90°, it is predicted that these orbitals become very close in energy to the NHOMO, and, consequently, it may be difficult to resolve individual bands in the photoelectron spectrum. A similar feature is observed in the photoelectron spectrum of ethylene sulfoxide, as will be discussed in the next section.

Table VI. Comparison of the Theoretical (Koopmans') and Experimental Ionization Potentials (eV) of Dimethyl Sulfoxide and Ethylene Sulfoxide

ionization potential	dimethyl sulfoxide			ethylene sulfoxide		
	expt	3-21G	DZP	expt	3-21G	DZP
1st	9.01	9.32	9.80	9.66	9.67	10.23
2nd	10.17	10.33	11.14	9.78	9.85	10.37
3rd	$\approx$12.6	13.32	13.96	$\approx$12.9	13.65	14.40
4th		14.80	15.03		14.45	14.63

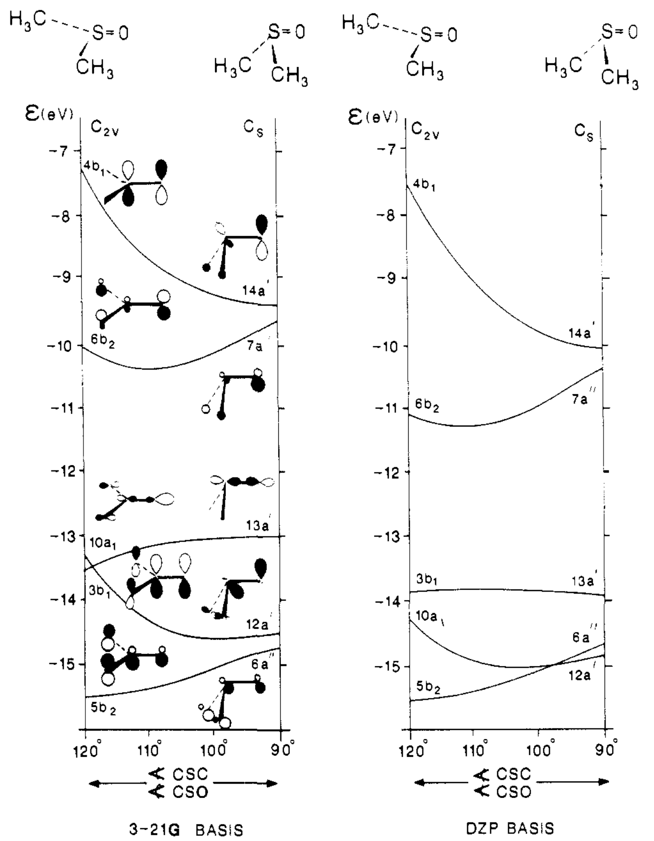

Figure 8. Orbital correlation diagrams for dimethyl sulfoxide calculated with the 3-21G and DZP basis sets.

Dimethyl Sulfoxide and Ethylene Sulfoxide. The orbital assignment and sensitivity of the IP's to variation in the conformation about the sulfur have been investigated by Bock and Solouki[12] for dimethyl sulfoxide and ethylene sulfoxide. As these systems represent two of the simplest stable sulfoxide systems, which would be expected to exhibit behavior similar to that of the various sulfoxides studied here, we though it worthwhile to carry out a comparative study of them.

The experimental structures of dimethyl sulfoxide[59] and ethylene sulfoxide[60] are given in Figure 7. In thiacyclobutane sulfoxide the C–S–C bond angle is $\approx$76°; this angle is larger ($\approx$96°) in dimethyl sulfoxide but smaller ($\approx$50°) in ethylene sulfoxide. The progressive decrease in the C–S–C bond angle is accompanied by a moderate increase in the C–S–O angle from $\approx$107° in dimethyl sulfoxide to $\approx$113° in thiacyclobutane sulfoxide and $\approx$115° in ethylene sulfoxide.

In Table VI the first four experimental IP's of dimethyl sulfoxide and ethylene sulfoxide are compared with the Koopmans IP's obtained with the 3-21G and DZP basis sets. A characteristic feature of the experimental results, also well described by the theoretical treatment, is the collapse of the first two IP's in dimethyl sulfoxide into an effectively single peak in the ethylene sulfoxide. Bock and Solouki[12] investigated this phenomenon using

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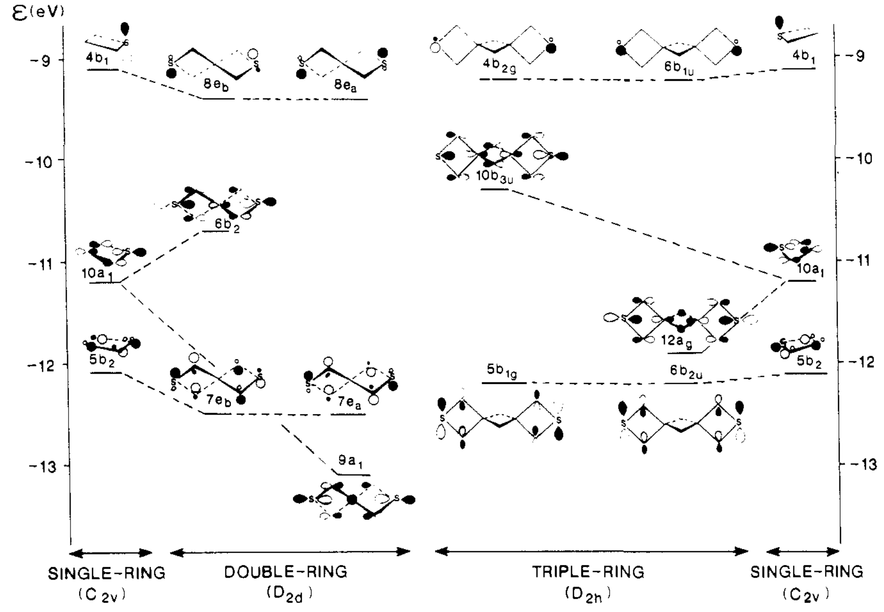

Figure 9. Comparison of the highest lying molecular orbitals in the single-, double-, and triple-ring sulfides.

the CNDO method and calculated an orbital correlation diagram for dimethyl sulfoxide as the C–S–C and C–S–O bond angles are simultaneously varied from 120° to 90°. The corresponding orbital correlation diagrams, obtained at the ab initio SCF level with the 3-21G and DZP basis sets, are given in Figure 8. In agreement with Bock and Solouki,[12] we observe an accidental near degeneracy that occurs for the highest two MO's as the angles decrease toward 90°. However, in contrast with their a_1 symmetry assignment of the HOMO in the C_{2v} conformation, we find this orbital to be of b_1 symmetry and the electronic configuration is ($...1a_2^2...3b_1^2 10a_1^2 6b_2^2 4b_1^2$), in contrast to the electronic configuration ($...1a_2^2...2b_1^2 10a_1^2 6b_2^2 11a_1^2$) given by Bock and Solouki.[12] Comparing the SCF energies of these two configurations calculated at the DZP level, we have found the latter to lie ≈8 eV higher in energy. As the HOMO of the Bock and Soulouki[12] wave function has a very large 3d component, the above calculations were repeated with a DZPP basis, which contains two sets of 3d functions on the sulfur atom, as recommended by Magnusson and Schaefer.[61] The results differ little from those obtained with the DZP or even the 3-21G basis; consequently, it seems most unlikely that the HOMO in this system has a_1 symmetry. The principal components of this orbital derive from an antibonding combination of the out-of-plane p orbitals, which is more consistent with the n_S–n_O assignment given earlier for the disulfoxides than with the n_S assignment of Bock and Solouki.[12] Comparing the orbital correlation diagrams obtained with the 3-21G and DZP basis sets, we find only relatively minor differences between the two. In particular, as the general form of the orbital correlation obtained for the first two MO's is very similar to that obtained with an unpolarized basis, our view that there is only minor d orbital participation in the sulfoxide bond gains additional support.

The orbital correlation diagram (Figure 6) for the double-ring sulfoxide molecule, discussed in the previous section, is with respect to variation in the out-of-plane angle (θ) between the S–O bond and the plane described by the adjacent ring, and it can be directly related to the changes in the C–S–O bond angle used in the orbital correlation diagram for dimethyl sulfoxide. Despite the fact that in dimethyl sulfoxide the bend also involves a simultaneous change in the C–S–C bond angle, the main features of the two systems are quite similar. In the disulfoxide the presence of the two sulfoxide groups results in the pairing of the orbitals into antisymmetric and symmetric combinations. However, by considering the average behavior of each pair of orbitals, we find, in agreement with the orbital correlation diagram for dimethyl sulfoxide, a progressive decrease in the average of the first two IP's as the sulfoxide conformation becomes planar. The third IP in the double-ring sulfoxide molecule is less sensitive to variations in θ and becomes coincident with the second at $\theta \approx 80°$; the analogous accidental degeneracy is also evident in dimethyl sulfoxide. The lower lying levels in these three systems also exhibit a similar behavior, although a detailed comparison becomes more complex.

Discussion

The key to understanding the relationship between the ionization potentials of the various sulfoxide and sulfide compounds (Table I), especially the near constancy of the first IP, lies in understanding the relationship between the highest few occupied SCF MO's in these systems.

To explain qualitatively the behavior of the highest lying molecular orbitals of the disulfoxides, in particular the splitting, two different approaches can be adopted. First, one can consider the parent sulfides and examine the effect of bonding an oxygen atom to each of the sulfurs, or, second, the formation of the double- and triple-ring sulfoxides can be viewed as linking together two single-ring sulfoxides. Since the first view relates directly to the use of the dithiaspiroalkanes as bridging ligands where a metal atom becomes coordinated to the sulfur, this is the preferred approach and will be explored in greater depth.

Formation of the Sulfoxides from the Parent Sulfides. Before considering the addition of oxygen to the sulfides and the formation of the sulfoxides, it is pertinent to examine the nature of the first few molecular orbitals in the parent sulfides. In particular, it is of interest to relate the molecular orbitals of the disulfides to those of the single-ring sulfides. In Figure 9 the orbital energies of the uppermost three occupied molecular orbitals of the single-ring sulfide and of the corresponding top six molecular orbitals of the double- and triple-ring disulfides are plotted, together with schematic illustrations of the molecular orbitals themselves. The calculations have been carried out with the 3-21G basis set, and for simplicity all the rings have been taken to be planar. Such a restriction does not greatly alter the energy or the nature of the orbitals but due to the higher molecular symmetry (C_{2v}, D_{2d}, and D_{2h} point groups for the single-, double-, and triple-ring sulfoxides, respectively) allows for an easier classification of the molecular orbitals. Examining the HOMO of the single-ring sulfide, viz. the $4b_1$ orbital, we find, in line with the experimental conclusions,[9] that it can be considered as a sulfur lone-pair orbital. In the disulfides the two corresponding MO's are the 8e degenerate pair, and in the triple-ring sulfide they are the $4b_{2g}$ and $6b_{1u}$ orbitals that are calculated to be very close (≈0.05 eV) in energy. In addition, the energies of the HOMO's in these three compounds are found to vary by only 0.3 eV, which, if related to the Koopmans ionization potential, agrees with the experimental fact that the

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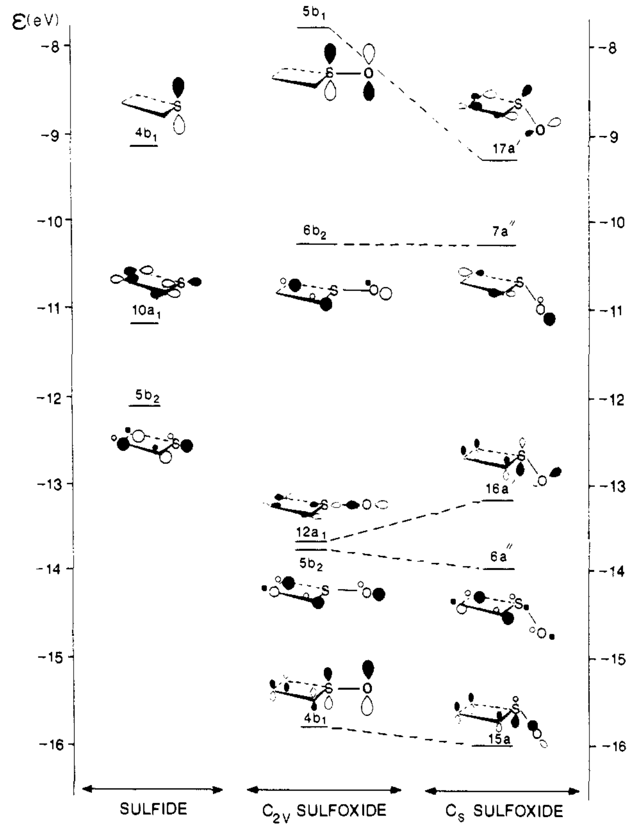

Figure 10. Comparison of the highest lying molecular orbitals in the single-ring sulfide and sulfoxide molecules.

first ionization potentials are nearly the same (Table I). We note also that whereas the CNDO calculations of Stein et al.[9] on the double-ring sulfide did not predict the lone-pair sulfur orbitals to be the highest in energy, there is no such disagreement between experiment and the current ab initio calculations.

A simple characterization of the MO's that may be thought to arise from the interaction of the NHOMO's of the single-ring compound is significantly harder. Although the single-ring NHOMO has a large p_σ contribution from the sulfur atom, it cannot be considered as a pure sulfur σ-type lone-pair orbital, as there is sizable delocalization through the whole ring system. The corresponding two MO's in the double- and triple-ring disulfides are found to be markedly different in energy, the antisymmetric orbital being higher. The separation between these two orbitals is then found to decrease from the double- to the triple-ring system, due mainly to the greater degree of destabilization of the symmetric MO in comparison with the antisymmetric one.

The third highest molecular orbital of the single-ring sulfide is similarly hard to characterize, as it contains contributions from all of the ring atoms. However, in the disulfides two equivalent orbitals can be identified, which relate to the single-ring sulfide in a manner similar to that found for the first two orbitals; i.e., they form degenerate and nearly degenerate pairs in the double- and triple-ring molecules, respectively, and their energies change little across the sequence.

The molecular orbital diagram for the progressive construction of the thiacyclobutane sulfoxide from the parent single-ring sulfide is given in Figure 10. The addition of the oxygen atom has been considered in two stages: first, the sulfur-to-oxygen bond is formed with the oxygen lying in the plane of the ring; second, the oxygen is allowed to bend out of plane to give the experimental angle ($\approx 55°$). Separation of the bond-making process into these two stages allows for comparison with the previously calculated orbital correlation diagrams obtained for the dimethyl sulfoxide (Figure 8).

From the results obtained for the C_{2v} conformation of the single-ring sulfoxide, we find that a simple diagrammatic representation and interpretation of the molecular orbitals becomes progressively harder as the orbital energy decreases. However, we note that the energy of the HOMO in this conformation is significantly higher than that of the HOMO in the parent sulfide. If we now introduce the out-of-plane bending of the S–O bond, the resulting decrease in symmetry allows for a mixing between the orbitals of a_1 and b_1 symmetry, viz. $5b_1$, 12a1, and $4b_1$. As a result, in the C_s conformation the new HOMO, 17a', consists mainly of the original HOMO, $5b_1$, but also contains a significant contribution from the $12a_1$. The fact that the energy of the new HOMO is very nearly the same as that of the HOMO of the parent sulfide system must, to a large extent, be considered as accidental.

Having established the nature of the MO's in the parent sulfides and the formation of the sulfur-to-oxygen bond in the single-ring sulfoxide, we can now consider the formation of the disulfoxides from the disulfides. This can be done as before, i.e. so that the initial disulfoxide formed maintains the full symmetry of the parent disulfide, which is then reduced by allowing the oxygen atoms to move out of the plane of the adjacent ring. The resulting molecular orbital diagram, which for simplicity shows only the out-of-plane bending of the S–O bond, is given in Figure 11. The symmetry

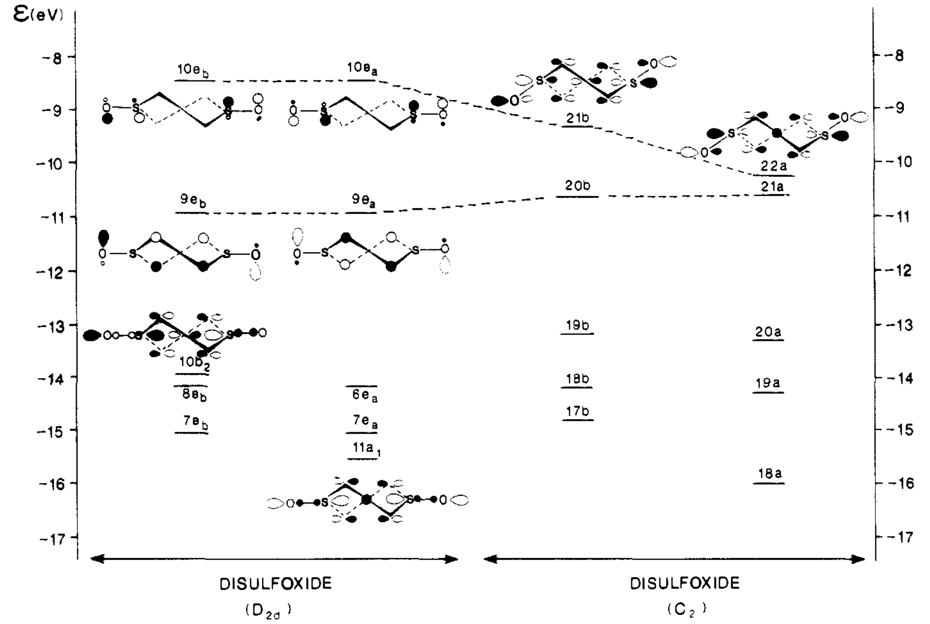

Figure 11. Comparison of the highest lying molecular orbitals of the double-ring sulfoxide assuming D_{2d} and C_2 symmetries.

of each orbital, as well as being labeled according to the irreducible representation of the D_{2d} point group, is further classified as antisymmetric or symmetric with respect to the C_2 axis that is preserved in the final disulfoxide. (We note, in passing, that the relationship between the orbitals of the D_{2d} disulfoxide and C_{2v} monosulfoxide is identical with the previously discussed relationship between the orbitals of the D_{2d} disulfide and C_{2v} monosulfide.) The out-of-plane bending of the S–O bond causes a reduction in symmetry, and thus mixing between all those orbitals, classed as either symmetric or antisymmetric with respect to the final C_2 axis, can occur. Considering the degenerate HOMO's of the molecule with D_{2d} symmetry ($10e_b$ and $10e_a$), it can be deduced, on the basis of the single-ring sulfoxide results, that these orbitals are unlikely to mix greatly with the NHOMO's ($9e_b$ and $9e_a$) since there will be minimal overlap between these orbitals. However, strong mixing would be expected between the degenerate HOMO's and the $10b_2$ and $11a_1$ orbitals, and this has indeed been found to be the case. The nondegeneracy of $10b_2$ and $11a_1$ will allow for a larger interaction between $10b_2$ and $10e_b$ than between $11a_1$ and $10e_a$, which will therefore lift the degeneracy of the HOMO. Furthermore, the new HOMO (21b) will be antisymmetric (with respect to C_2) and lie at approximately the same energy as the HOMO of the single-ring sulfoxide. The latter follows from the observation that the $10e_b$ and $11b_2$ orbitals have almost the same energy as their counterparts $5b_1$ and $12a_1$ in the C_{2v} single-ring sulfoxide (Figure 10), so that interaction will be almost the same.

In considering the triple-ring sulfoxide, it is useful to return to the parent sulfides and in particular to note that the D_{2d} sulfoxide orbitals $10b_2$ and $11a_1$ (Figure 11) are derived, respectively, from the orbitals $8b_2$ and $9a_1$ of the double-ring disulfide shown in Figure 9. In the latter molecule the separation between the $8b_2$ and $9a_1$ orbitals is greater than the separation between the analogous $10b_{3u}$ and $12a_g$ orbitals of the triple-ring sulfide (Figure 9). This is largely due to the energy of the $12a_g$ orbital in the triple-ring system being higher than that of the corresponding orbital in the double-ring sulfoxide, rather than to a significant change in the energy of $10b_{3u}$. As a result the splitting between the two HOMO's in the triple-ring sulfoxide should be smaller than that observed in the double-ring molecule, due primarily to a shift in the energy of the second highest occupied molecular orbital.

Formation of the Disulfoxides from Two Single-Ring Thiacyclobutane Sulfoxides. An alternative approach to the description of the orbital splitting in the disulfoxides is to consider a disulfoxide to result from the combination of two single-ring sulfoxide molecules. Comparing the orbital energies calculated for the sinlge-ring sulfoxide with the corresponding ones for the double-ring sulfoxide (Figures 9 and 10; Tables II and III), we note that there is an intrinsic lowering in the orbital energies as the disulfoxide forms, irrespective of whether the monosulfoxides have planar or nonplanar ring structures. When we focus on the results of the nonplanar sulfoxides, the energy lowering of the second HOMO is approximately 0.4 eV as the double-ring is formed. If a lowering in the center of gravity of the highest two MO's of the disulfoxides is assumed to be roughly the same, then the splitting between the highest two molecular orbitals in the disulfoxides is relative to their lowered center of gravity and results in the antisymmetric combination of monosulfoxide MO's returning nearly to the energy of the HOMO in the original single-ring sulfoxide.

Relative Importance of Through-Space and Through-Bond Interaction. To estimate the importance and magnitude of any through-space interactions, a series of calculations were performed in which the σ framework linking the two sulfur atoms was broken. Initially, this was achieved by placing two dimethyl sulfoxide molecules (effectively constructed from the single-ring sulfoxide, shown in Figure 2a, by the removal of the central carbon atom (C1) and replacing it by two hydrogens) at the same separation and relative orientation as in the relevant disulfoxide. It is possible to go one step further and remove the entire carbon framework and form two dihydro sulfoxide (H_2SO) molecules. In the absence of a direct connection between the two fragments, the separation between the two highest molecular orbitals must be mainly due to through-space interactions. The results show that both calculations predict roughly the same through-space interaction, viz. $\approx$0.5 eV. However, on the basis of the $(H_2SO)_2$ results, the maximum through-space interaction in the double-ring sulfoxide is estimated as 0.42 eV; hence, the through-bond interaction must be at least 0.3 eV. On the other hand, for the triple-ring sulfoxide the splitting appears to be entirely due to through-bond interactions.

Conclusion

Our interest in the electronic structure of dithiaspiroalkanes originated in the experimental findings of facile electron transfer between $Ru^{II}(NH_3)_5$ and $Ru^{III}(NH_3)_5$ groups bridged by these difunctional nonconjugated ligands in compounds II–V.[6–8] As ab initio calculations on the metal complexes are not currently feasible in our laboratory, we have chosen to examine the related disulfoxide systems, for which photoelectron spectroscopic data provide valuable information about the electronic energy levels of the ionized systems and their S–S distance dependence.

An important preliminary question was whether an appropriately deformed s, p basis set is adequate for the determination of relative energies; this suggested an examination of smaller species such as dimethyl sulfoxide and ethylene sulfoxide. We conclude (in agreement with Wallmeier and Kutzelnigg[53]) that d orbital participation in S–O bonding is quite minor and that the bond is best described as semipolar ($>S^{\delta+}$—$O^{\delta-}$) rather than as one involving hypervalent sulfur ($>S{=}O$).

Calculations for dimethyl sulfoxide reveal that the two highest filled levels will be separated by $\approx$3 eV for a hypothetical flat structure (C_{2v} symmetry) but are nearly degenerate when the S–O bond is normal to the C–S–C plane (C_s symmetry). For the experimental intermediate angles of dimethyl sulfoxide and ethylene sulfoxide, the very different experimental $IP_2 - IP_1$ separations of 1.16 and 0.12 eV, respectively, are reproduced to ca. 20% by DZP–SCF calculations, conforming to the above trend.

For the pyramidally bonded thiacyclobutane sulfoxide, as for dimethyl sulfoxide, the principal components of the HOMO are out-of-phase combinations of atomic O and S p orbitals whose axes lie in the plane containing the S–O bond and the bisector of the C–S–C angle, together with minor contributions from carbon orbitals: in the case of thiacyclobutane sulfoxide, the p component at the carbon, which will forms the link in the double-ring system, although small, is crucial for through-bond interaction.

In both the thiacyclobutane sulfoxide and dimethyl sulfoxide, the NHOMO has, as its principal components, an oxygen p orbital with smaller contributions from a sulfur p orbital (both with axes perpendicular to those in the HOMO). When sulfoxides are condensed to form double- and triple-ring disulfoxides, the electron density is split between symmetry-related atoms. The highest molecular orbitals are principally centered on the sulfur and oxygen atoms. The observed near constancy of the first IP of thiaspiroalkane sulfides and disulfides and the *n*-ring disulfoxides (which has been interpreted as indicating that the highest bonding MO in all these molecules is pure atomic sulfur s in character) is found, in fact, to result from an essentially fortuitous cancellation of opposing effects in the disulfoxides.

The splitting of the two highest levels in the *n*-ring disulfoxides, which is a measure of the ligand–ligand interaction in the cation, is calculated to be zero when the ligands lie in the average plane of thiacycloalkane ring; experimental photoelectron values for the pyramidally bonded molecules (0.85, 0.38, and 0.25 eV for n = 2–4, respectively) are approximately reproduced by SCF calculations at various levels, and the appropriateness of a symmetry-breaking approach is discussed. A significant finding is that for the shortest S–S distance (in the double-ring system) the through-space contribution to the energy splitting is roughly the same as that of the through-bond contribution but is zero in the triple-ring (and presumably longer) systems. It follows, first, that an attempt to deduce the form of distance dependence of this splitting for through-bond interaction should not include data for the smallest system, and, second, that the rate of falloff of the through-bond contribution with distance is remarkably slow.

For the bis(ruthenium pentammine)$^{5+}$ complexes II–V of the disulfides, interpretation of the intervalence spectra yields values of the highest orbital splitting, facilitating hole transfer in the mixed-valence ions, in the approximate ratio 1:0.4:0.2, compared with the corresponding ratio 1:0.45:0.29 in the disulfoxides, for n = 2–4 disulfide bridges, respectively (the absolute values are only about 3% of those in the oxygen-linked system). These ratios are quire comparable; we presume that Ru, like O, is bonded to a "pyramidal" sulfur and that we may draw comparative qualitative conclusions about the mechanism of ligand–ligand interaction even though in the former case the Ru atomic orbitals of interest will be predominantly 3d in character.

An interesting discussion of through-bonded interaction via dithiaspiroalkane bridges has been given by Beratan and Hopfield,[62] in which the through-bond propagation of the wave-function tail is calculated with a periodic one-electron potential, the wave function being an eigenfunction of T^J, where T is the translation operator. It is assumed that for the Ru complexes II–V the Ru atoms lie in the plane of the thiacycloalkane ring and that the molecule has two mirror planes containing the metal atoms. In the dithiaspiroalkane disulfoxide series, as remarked earlier, through-bond splitting is calculated to be zero for such a geometry. Since the Ru complexes are in fact expected to be pyramidally bonded, it is not clear what predictions would be made by the periodic potential approach for this geometry, although the strategy is of much interest in general in discussing through-bond interaction via nonconjugated bridges.[63] We note also that in our oxygen-linked calculations—for example, for the double-ring system—the inner-ring coupling is through a p-type C orbital in the HOMO and an s-type orbital in the NHOMO (cf. Figure 5); in the low symmetry of the pyramidal complex, each of these MO's is a product of extensive mixing of the MO's of appropriate symmetry that would characterize hypothetical linearly linked molecules. Thus, it is likely that a rather detailed consideration of the form of the wave functions is necessary for understanding through-bond interaction, and ease of electron or hole transfer, via dithiaspiroalkane bridges.

The conditions under which nonconjugated bridges can facilitate long-range electron transfer have recently begun to be systematically investigated experimentally (e.g. ref 64–70) and theoretically (e.g. ref 71–73). It has been difficult to obtain molecules that, like the dithiaspiroalkanes, are rigid, with little internal rotational freedom, and whose length can be systematically varied. The only other molecules so far studied with these characteristics are the linear saturated hydrocarbons composed of norbornyl-type skeletons, with up to 16 carbon–carbon links along the chain.[75,76] A number of studies of photoinduced and ground-state electron-transfer processes in which these are studies of photoinduced and ground-state electron-transfer processes in which these are used as donor–acceptor bridges have been carried out;[76] photoelectron data[75] for π donors and acceptors are based on the assumption of appreciable orbital overlap between a donor or acceptor π orbital and a bridge carbon σ orbital at the point of attachment as being essential for through-bond transfer. As in the dithiaspiroalkane series, this imposes fairly stringent restrictions on the relative orientation of donor–acceptor and nearest-neighbor bridge atoms; these are borne out directly in photoelectron spectroscopic studies.[75,77] The properties of donor–acceptor systems with both series of nonconjugated bridges thus strikingly illustrate the importance of the geometry at the point of linkage for efficient through-bond electron transfer.

Registry No. VI, 87442-40-8; VII, 87442-41-9; IX, 13153-11-2; ethylene sulfoxide, 7117-41-1; dimethyl sulfoxide, 67-68-5.

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