

Figure 1. Molecular orbital correlation diagram for five-coordinate complexes of the $\{\text{CoNO}\}^8$ group in ligand fields of C_{2v} , C_{4v} , and C_s symmetry. The orbitals are occupied by a total of eight electrons.

side of Figure 2 corresponds to $4a_1 \ll 3e$ and the molecule will have C_{2v} symmetry, a linear MNO group, and a nondegenerate singlet ground state (1A_1). Likewise, the far right-hand side corresponds to $3e \ll 4a_1$ and a molecule with C_s symmetry, a strongly bent MNO group, and a nondegenerate singlet ground state (${}^1A'$). The right- and left-hand extremes of the state diagram are consistent with the conclusions drawn from the molecular orbital diagrams of Figure 1a and 1d and show that the conversion of a linear $\{\text{MNO}\}^8$ group into a bent $\{\text{MNO}\}^8$ group requires the crossing of the $4a_1$ and $3e$ orbitals.

At the crossing point in C_{4v} symmetry (Figure 2), a fivefold degeneracy of the singlet states arising from $(4a_1, 3e)^2$ may exist.⁹ Vibronic coupling can mix these states and lead to a distorted ground state geometry for the CoNOL_4 molecule.^{4b,9,9a} Since there are several degenerate electronic states and several vibrational modes for the CoNOL_4 complex, more than one form of the CoNOL_4 complex may exist whenever $4a_1$ and $3e$ are degenerate. Conversely, the existence of two forms of a CoNOL_4 complex indicates that the complex is near the crossover and that the $4a_1$ and $3e$ orbitals are nearly degenerate. $\text{Co}(\text{NO})\text{Cl}_2[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_2$ exhibits two distinct ν_{NO} bands, and it has been proposed that a TBP complex with a linear CoNO group and a TP complex with a bent CoNO group are both present in equilibrium.^{10a} However, the structure of one of the forms of this complex exhibits an intermediate Co-N-O bond angle (165°) and a very irregular coordination geometry.^{10b} This distorted form of $\text{Co}(\text{NO})\text{Cl}_2[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_2$ is inconsistent with the previous proposal for an interconversion between TBP and TP geometries but is consistent with the vibronic coupling model. The vibronic coupling model precludes the existence of a form of $\text{Co}(\text{NO})[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_2$ with a

(9a) NOTE ADDED IN PROOF. On the basis of extended Hückel molecular orbital calculations, it has been similarly concluded (R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, submitted for publication) that the relative energies of $4a_1$ and $3e$ (Figure 1) are important in determining the ground state geometries of $\{\text{MNO}\}^8\text{L}$ complexes. These calculations also predict intermediate coordination geometries and intermediate M-N-O angles may occur when $4a_1$ and $3e$ are nearly degenerate. The authors thank Professor Hoffmann for providing a preprint of his paper prior to publication.

(10) (a) J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, **93**, 1788 (1971); (b) C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, **12**, 1304 (1973).

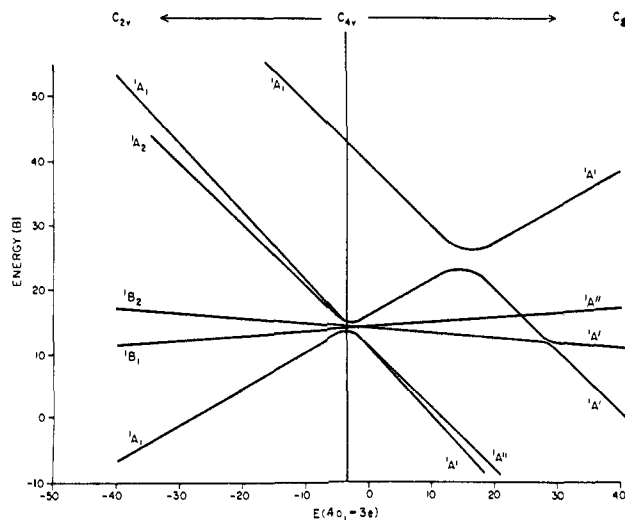
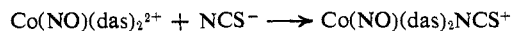


Figure 2. Composite state correlation diagram for C_{2v} , C_{4v} , and C_s symmetries showing the behavior of the singlet states arising from a $(4a_1, 3e)^2$ electron configuration in C_{4v} symmetry.

Co-N-O bond angle of 180° and thus, the second form of this complex should differ primarily in the rotational orientation of the nonlinear CoNO group.^{4b} An equivalent way of describing the two forms of $\text{Co}(\text{NO})\text{Cl}_2[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_2$ is to consider them as vibromers of a somewhat bent CoNO group with a small barrier to rotation.¹¹ To our knowledge, the only well-documented example of the conversion of a linear $\{\text{CoNO}\}^8$ group to a strongly bent $\{\text{CoNO}\}^8$ group by a change in stereochemistry of the metal is the reaction¹²



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(11) This barrier is due to the necessity of rotating the bent CoNO group from the position in which the xz component of $3e$ is doubly occupied to that in which the yz component is doubly occupied. This interchange of xz and yz components can be brought about via the lowest lying ${}^1A''$ excited state and consequently, the energy separation between ${}^1A'$ and ${}^1A''$ represents the barrier to rotation of the bent CoNO group. For complexes with maximum C_{2v} symmetry the energies of the ${}^1A'$ (xz)² and ${}^1A'$ (yz)² states can differ and two distinct conformers are possible.

(12) J. H. Enemark and R. D. Feltham, *Proc. Nat. Acad. Sci. U. S.*, **69**, 3534 (1972).

John H. Enemark, Robert D. Feltham*

Department of Chemistry, University of Arizona
Tucson, Arizona 85721

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Oxathiiranes. Differential Orbital Correlation Effects in the Electrocyclic Formation of Sulfur-Containing Three-Membered Rings¹

Sir:

A structurally simple sulfine, thiopropenal *S*-oxide (**1**), is generated enzymatically from *S*-(1-propenyl) cysteine sulfoxide² in the plant species *Allium cepa* and has been identified as the lachrymatory factor of onions. The compound decomposes within hours at room tem-

(1) Organo-Sulfur Mechanisms. III. For part II see J. P. Snyder, *J. Org. Chem.*, **38**, 3965 (1973).

(2) A. I. Virtanen and C. G. Spare, *Suom. Kemistilehti B*, **34**, 72 (1961); A. I. Virtanen and E. J. Matikkala, *ibid.*, **34**, 74 (1961); T. Moisio, C. G. Spare, and A. I. Virtanen, *ibid.*, **35**, 29 (1962).

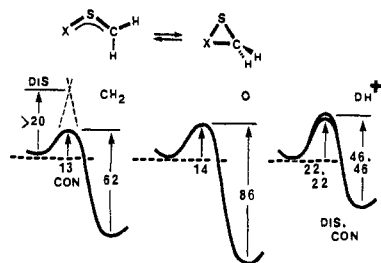
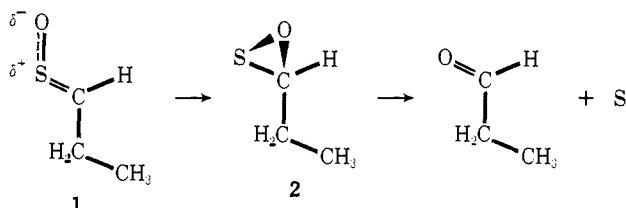


Figure 1. Calculated hyperplanes for the electrocyclic interconversion of **3** and **4**, in kilocalories per mole.

perature producing largely propionaldehyde and sulfur.³⁻⁵ An oxathirane (**2**) has been proposed^{4a} as the



thermal intermediate.⁶ Oxathiranes have likewise been suggested as intervening in the photochemical conversions of synthetic thiocarbonyl *S*-oxides to carbonyl compounds.⁷ Finally a phosphaoxathirane has been mentioned as a plausible intermediate in the peroxy acid promoted transformation of the thiophosphoryl (P=S) function into the corresponding phosphoryl (P=O) moiety.⁸

Although the oxathirane ring has yet to be observed directly, we have undertaken a theoretical study of its electrocyclic formation and that of some isoelectronic sulfur containing rings. O-Protonated species have been included because of reports^{7b,9} that carbonyl compounds are frequent products from the oxidation of thiocarbonyl derivatives to the corresponding *S*-oxides under acidic conditions. The results reveal an interesting deviation from predictions based on a naive application of orbital symmetry conservation rules. Furthermore, a pathway for conversion of oxathirane to carbonyl not requiring the extrusion of a sulfur atom from the ring is outlined.

Structures **3a-c** and the corresponding episulfide (**4a**), oxathirane (**4b**), and protonated oxathirane (**4c**) rings were energy-geometry optimized¹¹ by means of Boyd's MO-SCF-CNDO procedure.¹² Intermediate

(3) C. G. Spare and A. I. Virtanen, *Acta Chem. Scand.*, **17**, 641 (1963).

(4) (a) W. F. Wilkens, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1961; W. F. Wilkens, Cornell Agricultural Experiment Station, Memoir 385, Ithaca, N. Y., Jan 1964; (b) M. H. Brodnitz and J. V. Pascale, *J. Agr. Food Chem.*, **19**, 269 (1971).

(5) J. B. Bredenberg, E. Honkanen, and A. I. Virtanen, *Acta Chem. Scand.*, **16**, 513 (1962).

(6) The decomposition of thiophosgene *S*-oxide has been pictured similarly: J. Silhanek and M. Zbirovsky, *Chem. Commun.*, 878 (1969).

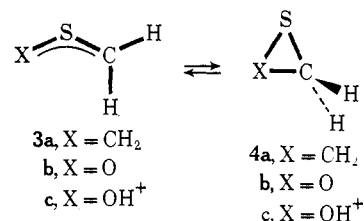
(7) (a) A. G. Schultz, C. D. deBoer, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **90**, 5314 (1968); R. H. Schlessinger and A. G. Schultz, *Tetrahedron Lett.*, 4573 (1969); A. Padwa, *Int. J. Sulfur Chem., Part B*, **7**, 331 (1972); (b) B. Zwanenburg and J. Strating, *Quart. Rep. Sulfur Chem.*, **5**, 79 (1970).

(8) A. W. Herriot, *J. Amer. Chem. Soc.*, **93**, 3304 (1971).

(9) Preliminary experiments with thiocamphor *S*-oxide indicate that the latter's thermal decomposition is complex leading to a variety of products including considerable quantities of camphor and sulfur. The reaction is, however, accelerated by the addition of proton acids;¹⁰ cf. ref 8.

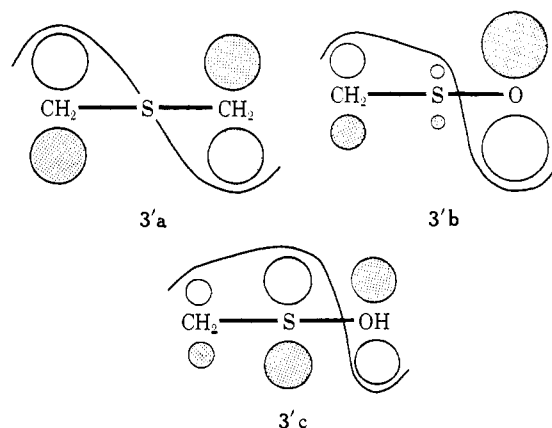
(10) M. Gundestrup (University of Copenhagen), unpublished work.

(11) Cf. J. P. Snyder and D. N. Harpp, *J. Chem. Soc., Chem. Commun.*, 1305 (1972); ref 1.



structures were treated similarly. The attendant ring closure reaction in its stereodistinct modes is depicted as a function of total calculated energy in Figure 1. Conrotatory transformation of thiocarbonyl ylide **3a** is predicted to be an allowed process; disrotatory closure is forbidden.¹³ This result harmonizes in all particulars with experiment¹⁴ and extended Hückel calculations.^{15,16} Oxathirane creation (**3b** → **4b**) is also predicted to be an allowed thermal reaction, although stereochemically uninteresting. Finally we consider the transformation **3c** → **4c**. Changes in the total energy for that portion of the potential surface depicted are virtually independent of rotational variation. Correspondingly *both conrotatory and disrotatory ring closures are calculated to represent allowed¹³ thermal reactions.*

The origin of the latter stereochemical result can be appreciated by considering the relative energy ordering of molecular orbitals for **3** and **4**. Figure 2a illustrates the relationships within the open series. The replacement of CH₂ (**3a**) with O and subsequently with OH⁺ (**3b** and **3c**, respectively) causes a significant decrease in the energy of the π_{HOMO}. Introduction of a strongly electronegative atom at the terminus of the three-atom unit serves to perturb the originally symmetric carbon species by moving the HOMO node from the central sulfur to a position between sulfur and oxygen (**3a'-c'**).



The displacement of electrons onto oxygen undoubtedly makes a major contribution to the stabilization of the π_{HOMO}.

The relative energies of the ring orbitals are likewise affected by oxygen substitution (Figure 2b). The sig-

(12) R. J. Boyd and M. A. Whitehead, *J. Chem. Soc. Dalton Trans.*, **73**, 82 (1972).

(13) Complete correlation diagrams have been constructed for all the reactions discussed. Allowed reactions thus correspond to the familiar definition^{17a} specifying interaction between ground-state levels only. Conversely forbidden processes involve excited molecular states.

(14) R. M. Kellog, S. Wassenaar, and J. Buter, *Tetrahedron Lett.*, 4689 (1970); J. Buter, S. Wassenaar, and R. M. Kellog, *J. Org. Chem.*, **37**, 4045 (1972).

(15) R. Hoffmann, C. C. Wan, and V. Neagu, *Mol. Phys.*, **19**, 113 (1970).

(16) R. Hoffmann, H. Fujimoto, J. R. Swenson, and C. C. Wan, *J. Amer. Chem. Soc.*, **95**, 7644 (1973).

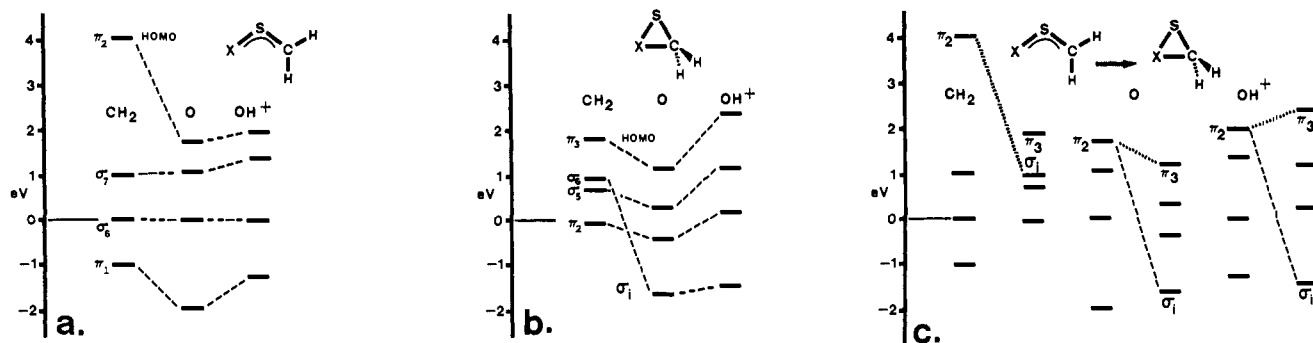


Figure 2. Relative molecular orbital energies of **3** and **4** (the energies of the σ_6 MO's have been arbitrarily equated to zero in Figure 2a, the levels in Figure 2b and c are on the same scale): (a) the open series; (b) the closed series; (c) ring closure. For (a) and (b) the dotted lines connect orbitals of comparable symmetry.¹⁹ For (c) ————— corresponds to the actual correlation; - - - - - corresponds to a permissible but avoided correlation.

nificant alteration in this case is the energy lowering of the MO associated with the in-plane sulfur lone pair, σ_1 . Again relative increasing localization of electron density on atom X can be considered a critical factor in the level stabilization.

Thus by replacing carbon with oxygen the π_{HOMO} of **3** and the σ_1 lone-pair orbital of **4** drop significantly in energy. The remaining MO's are essentially unaffected. The consequence of these changes for the ring closure process is shown in Figure 2c. Analogous to the behavior of the well-studied symmetrical and isoelectronic allyl anion,¹⁷ thiocarbonyl ylide **3a** is transformed to episulfide **4a** while the high-lying occupied orbitals connect by means of a $\pi_{\text{HOMO}}-\sigma_1$ correlation. By contrast thioformaldehyde *S*-oxide (**3b**) and its conjugate acid **3c** ring close by taking advantage of a $\pi_{\text{HOMO}}-\pi_{\text{HOMO}}$ correlation. The $\pi_{\text{HOMO}}-\sigma_1$ interaction is avoided here presumably on energy grounds (Figure 2c).

The existence of a facile ring closure route for thiocarbonyl *S*-oxides has obvious implications for the reverse process. The oxathirane ring can, in principle, open by electrocyclic cleavage of either the C–O or the C–S bond to produce a sulfine or the corresponding keto sulfide, respectively. The latter reaction has been investigated numerically and found to mimic the former in its essential mechanistic features. The presently unknown keto-sulfide system thus may intervene between thiocarbonyl *S*-oxide and product carbonyl. Of significance is the implication that unsymmetrical hetero-substituted sulfur-containing three-membered rings possess an attractive, relatively low energy mechanism for sulfur extrusion not involving the expulsion of a sulfur atom from the oxathirane ring. By contrast episulfides do not possess a similar ground state mechanistic alternative for cleavage of the C–S bond.¹⁸

An important general point arising from these observations is that the introduction of strong asymmetric perturbations, for example, hetero atoms, into a carbon framework can lead to severe reordering of energy levels. In addition electron distribution may be shifted to such an extent relative to the symmetrical model

that symmetry restrictions on orbital interactions are lifted. Concerted reactions can, in principle, then proceed with level correlations quite distinct from those derived by considering an all carbon backbone alone. Any of several orbital correlations¹⁹ may be employed by the system under consideration, the determinant being the combination of lowest energy. By contrast it must be emphasized that symmetrical species such as **3a** and **4a** are constrained to orbital interactions governed by the widely applied orbital symmetry conservation principle.^{17a}

Acknowledgments. We are grateful to Dr. Ulrich Mueller-Westerhoff (IBM Corporation) for helpful advice and to Dr. Russell Boyd (University of British Columbia) for encouragement and counsel. Partial financial assistance was generously provided by the Carlsbergfond (Copenhagen); computer facilities were by NEUCC-Denmark.

(19) The introduction of a strong perturbation naturally prevents a rigorous description of the reaction pathway in terms of symmetry elements alone. In some cases, however, pseudo-symmetry is maintained. In others only a careful stepwise analysis of MO coefficients between potential surface minima permit an orbital correlation to be established.²⁰

(20) The interplay of energy and symmetry considerations obtains for a wide variety of heteroelectrocyclic processes and will be reported shortly; J. P. Snyder and B. Schilling, unpublished work.

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James P. Snyder²¹

Department of General and Organic Chemistry
University of Copenhagen
2100 V Copenhagen, Denmark
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Stereospecific Solid-State Rearrangement of 1,2,5,6-Tetracyano-*anti*-tricyclo[4.2.0.0^{2,5}]octane to 1,2,5,6-Tetracyano-(*Z,E*)-cycloocta-1,5-diene¹

Sir:

Strict application of orbital symmetry rules² to the thermal cleavage of the middle cyclobutane ring of tricyclo[4.2.0.0^{2,5}]octanes, **1**, predicts the formation of (*Z,E*)-cycloocta-1,5-dienes, **2**, by the ($\sigma_{2s} + \sigma_{2a}$) pathway. However, only the (*Z,Z*)-isomers **3a** and **3b** were

(1) A preliminary report of part of this work was presented by one of us (D. B.) at the 3rd International Symposium on Synthesis in Organic Chemistry, Oxford, July 1973.

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(17) (a) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (b) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969); M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4291 (1971), and references therein.

(18) R. Hoffmann, C. C. Wan, and V. Veagu, *Mol. Phys.*, **19**, 113 (1970); O. P. Strausz, H. E. Gunning, A. S. Denes, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **94**, 8317 (1972).