2 H, H_9, H_{10}), 13.24 (s, 1 H, OH). The change in chemical shift, $\Delta\delta$, in the reaction **5** → **6** is 1.26 ppm for H_9 and H_{10} and 0.48 ppm for the aromatic protons.[11] The ^1H NMR as well as ^{13}C NMR of the ions **2** and **6** reveal that a plane of symmetry exists in these protonated dicationic molecules while their precursors **4** and **5** lack this property. The large proton downfield shift in the process **4** → **2** as compared with that of **5** → **6** is attributable to the generation of a diamagnetic ring current in **2** due to its aromatic character. Formally, **2** and **6** may be regarded as trications. However, the slow exchange with the environment of the proton at the carbonyl group even at a relatively high temperature as well as the downfield ^{13}C chemical shift of the carbonyl carbon support the assigned structures. In these structures two positive charges are delocalized and the third charge is localized at the carbonyl function. Transformation of **4** to the protonated cycloocta[*def*] fluorenone dication **2**, at room temperature represents the formation of a polycyclic dication containing the cyclooctatetraene moiety—a 14π-electron aromatic system.

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(11) The ^{13}C NMR spectrum of **5** showed 15 bands pointing to a nonsymmetrical configuration while **6** showed only 8 bands. A total downfield shift of 422 ppm was observed in agreement with a doubly charged species.[9]

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Molybdenum Complexes of Aliphatic Thiols. Isolation and Characterization of Two Isomeric Forms of the Redox Active Binuclear Mo(V) Anion, $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$

Sir:

Research on the coordination chemistry of molybdenum-sulfur compounds has been stimulated by evidence that oxidation-reduction reactions which are catalyzed by molybdoenzymes occur at sites where the molybdenum is coordinated by one or more S atoms.[1] A variety of reactions are now known to produce stable diamagnetic binuclear di-μ-sulfido bridged Mo(V) species in which each Mo atom also is strongly bound to a terminal oxo or sulfido group.[2] As emphasized previously,[3] additional ligands lead to pseudotetragonal coordination geometry about each Mo atom. Two structures (A and B) are possible for two tetragonal pyramids sharing a basal edge.

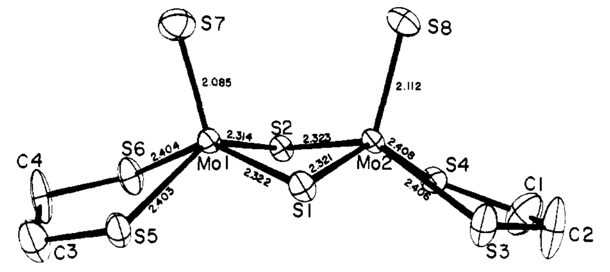


Figure 1. Perspective view of the anion of **1**. The estimated standard deviations of Mo–S bonds are 0.003 Å. Other distances and angles follow: Mo···Mo = 2.863 (2)Å; S1–Mo1–S2 = 99.9 (1), S1–Mo2–S2 = 99.7 (1), Mo1–S1–Mo2 = 76.2 (1), Mo1–S2–Mo2 = 76.3 (1)°. Exclusive of the CH_2 groups the anion has approximate C_{2v} symmetry.

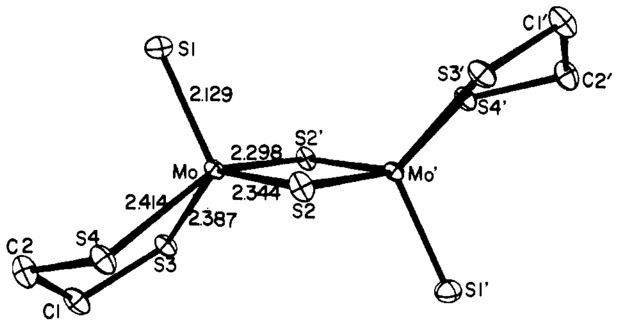
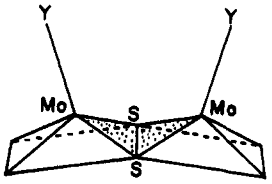
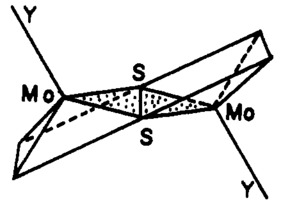


Figure 2. Perspective view of the anion of **2**. Primed atoms are related to unprimed atoms by a center of symmetry. The estimated standard deviations of Mo–S bonds are 0.002 Å. Other distances and angles follow: Mo···Mo = 2.878 (2) Å; S2–Mo–S2′ = 103.38 (7); Mo–S2–Mo′ = 76.62 (7)°. The space group imposes $\bar{1}$ symmetry on the anion. Exclusive of the CH_2 groups the approximate symmetry is C_{2h}.



A



B

Structure A has a bent Mo_2S_2 moiety with a dihedral angle between the two Mo_2 planes of ~150°; structure B has a planar Mo_2S_2 moiety.[4] Several compounds of structure A with Y = S or O are known,[2,3,5] and three cyclopentadienyl derivatives related to B (Y = O,[6] S,[7] and $NC(CH_3)_3$)[8] have been reported. However, there is no prior example of structures A and B both being observed with the same ligands. Herein we describe redox active binuclear Mo(V) complexes of both geometries with Y = S and one 1,2-dimercaptoethanato (dme) ligand per Mo.

Refluxing mixtures of $MoCl_3$, NaHS, $NaOCH_3$, and 1,2-dimercaptoethane in anhydrous oxygen-free methanol produces intractable black solids and dark red solutions. Two forms of diamagnetic crystals of what proved to be tetraethylammonium di-μ-sulfidobis(sulfido-1,2-dimercaptoethanato)molybdate(V)), $[N(C_2H_5)_4]_2[Mo_2S_4(S_2C_2H_4)_2]$, have been isolated from the intensely colored filtrates by adding a saturated methanolic solution of tetraethylammonium bromide. Form **1** has been obtained as red-violet prisms from a 1:2:2:1 molar ratio of the refluxed reagents, and form **2** as small red-violet rhombohedral plates from a 1:1:3:2.25 ratio of reagents. The yields of both reactions are low, 6 and 3%, respectively.[9] Infrared spectra of the two samples (KBr) are similar, but not identical. The strongest bands for **1** and **2** occur

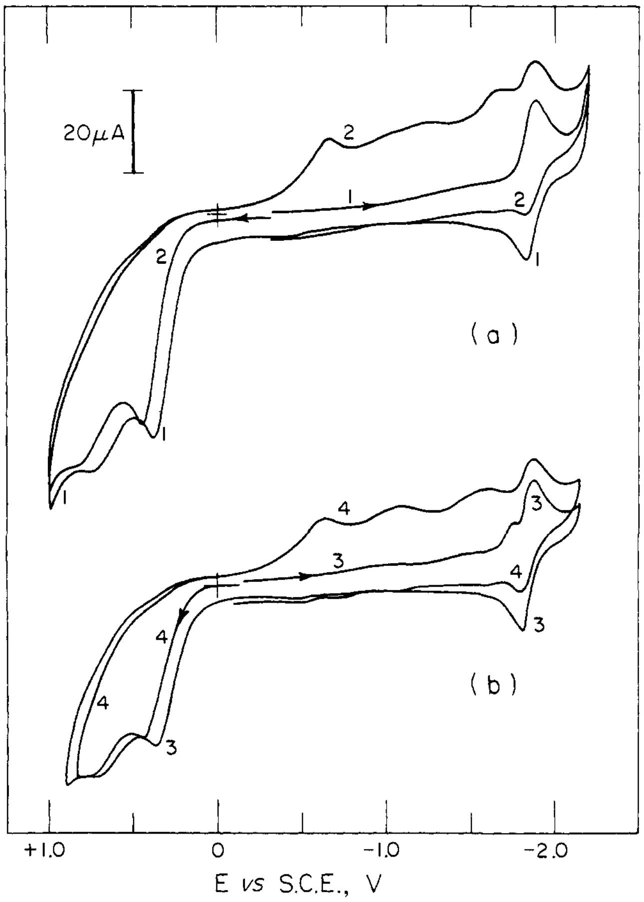


Figure 3. Cyclic voltammograms of 1 mM solutions in 0.1 M tetraethylammonim perchlorate in Me_2SO at a platinum electrode (scan rate, 0.1 V/s): (a) *syn*-$(TEA)_2Mo_2S_4(dme)_2$; (b) *anti*-$(TEA)_2Mo_2S_4(dme)_2$; 1 and 3, initial negative scans; 2 and 4, initial positive scans.

at 508 and 493 cm^{-1}, respectively, and are indicative of terminal sulfido groups.[10] Both bands are equally symmetric. Satisfactory analyses were obtained for C, H, and N, but analyses for S were not reproducible.

Unambiguous identification of **1** and **2** has resulted from single-crystal x-ray structure determinations. Preliminary precession photographs of **1** are consistent with monoclinic space group $P2_1/c$. Crystal data: $a = 10.976$ (4), $b = 19.158$ (6), $c = 17.717$ (7) Å; $\beta = 115.95$ (3)°; $Z = 4$; $d_{calcd} = 1.527$, $d_{obsd} = 1.528$ (4) g cm^{-3}. Preliminary precession photographs of **2** are consistent with monoclinic space group $P2_1/n$. Crystal data: $a = 10.234$ (2), $b = 14.116$ (3), $c = 11.347$ (3) Å; $\beta = 100.40$ (2)°; $Z = 2$; $d_{calcd} = 1.576$, $d_{obsd} = 1.563$ (4) g cm^{-3}. Diffraction data were gathered on a Syntex $P2_1$-Fortran diffractometer by use of graphite monochromated Mo Kα radiation. Form **1** gave 3258 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ and $2\theta \leqslant 50°$. Form **2** gave 1401 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ and $2\theta \leqslant 45$ °. The positions of the Mo atoms and some of the S atoms of **1** and **2** were obtained by direct methods and the remaining nonhydrogen atoms were located by difference electron density maps. Both structures were refined by full-matrix least-squares techniques. In the final cycles all atoms of the anion were refined anisotropically and the atoms of the cations were refined isotropically. No corrections were made for absorption. Refinement of **1** converged to $R_1 = 0.0638$ and $R_2 = 0.0903$; **2** converged to $R_1 = 0.038$ and $R_2 = 0.049$.[11]

The x-ray structural determinations establish that both **1** and **2** have the chemical formula $[N(C_2H_5)_4]_2[Mo_2S_4(S_2C_2H_4)_2]$. Perspective views of the anions of **1** and **2** appear in Figures 1 and 2, respectively. Pertinent distances and angles also are given in the figures and legends. These figures show that **1** and **2** adopt structures A and B, respectively, and hence are the first documented example of syn-anti isomerism[4] in di-μ-sulfido bridged Mo(V) complexes.[12] Both binuclear anions contain Mo atoms ligated by five S atoms in approximately tetragonal pyramidal (TP) coordination geometry. The axial position of each TP is occupied by a terminal sulfido group. Each Mo is displaced from the basal plane of its TP toward the axial S atom (0.72 Å in **1** and 0.66 Å in **2**). The terminal Mo-S distances of 2.085-2.129 Å are close to the 2.14 Å in *anti*-$Mo_2S_4(C_5H_5)_2$,[7] but considerably longer than the 1.937 (6) Å in *syn*-$Mo_2S_4[S_2CN(C_4H_9)_2]_2$.[13] The equatorial Mo-S distances are in the range observed for other di-μ-sulfido bridged Mo(V) complexes.[3,5] The dihedral angle between the two S1-Mo-S2 planes of **1** is 146.8 (1)°, but the Mo_2S_2 bridge of **2** is required to be planar by the space group. Thus, it is surprising that the Mo···Mo distances in **1** and **2** (2.863 (2) and 2.878 (2) Å, respectively) are nearly the same. The bond angles at the bridging sulfido ligands also are nearly identical (76.2 and 76.6°) and similar to the acute bridging angles found in other compounds.[3,5,6,8] The major difference in the Mo_2S_2 fragments of **1** and **2** is that the S2-Mo-S2′ angle in **2** is 3.6° (~35σ) larger than the corresponding angles in **1**.

The cyclic voltammograms of **1** and **2** in Me_2SO are similar (Figure 3). Each isomer undergoes a reversible one-electron reduction at −1.87 V. Both isomers also exhibit two irreversible oxidation waves, each of which appears to involve two electrons per dimer. These are the first electrochemical results for complexes of structure A with Y = S, and the first for any complex of structure B.[14] The reductive behavior of **1** and **2** is consistent with the hypothesis[15] that bridging sulfido groups allow reversible one-electron reductions of binuclear Mo(V) complexes in aprotic solvents.[16]

The two forms of the $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ anion reported here are the first examples of well-characterized redox active Mo complexes of simple nonconjugated biologically relevant thiols in which each Mo atom is ligated exclusively by S atoms. Further studies of molybdenum complexes of simple thiols and of the nature of the oxidized and reduced species of **1** and **2** are in progress.

Acknowledgments. We thank Mr. James J. Houts for experimental assistance. Portions of this work were supported by the National Institute of Environmental Health Sciences (ES00966) and by the National Science Foundation (CHE76-24555). An allocation of computer time from the University of Arizona Computer Center is gratefully acknowledged. We thank Dr. E. I. Stiefel for a preprint of ref 2. We are also pleased to acknowledge National Science Foundation Grant CHE-76-05481 which provided funds for the diffractometer.

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Stereoelectronic Effects in the Hydrolysis of Cyclic Five-Membered-Ring Phosphate Esters. Ab Initio and CNDO Molecular Orbital Calculations on Alkyloxyphosphoranes

Sir:

Strained cyclic five-membered-ring phosphate esters react 10^6- to 10^8-fold faster than their acyclic counterparts.[2,3] Westheimer and coworkers[2] proposed that this rate acceleration was due to relief of ring strain in the five-membered rings. However, as pointed out by Gerlt et al.,[4] the energy released in a strained cyclic ester in going to a "strain-free" cyclic phosphorane transition state is insufficient to explain the total activation energy lowering. As shown[4] in Figure 1 for hydrolysis of ethylene phosphate, **1**, and diethyl phosphate, **2**, the strain energy only accounts for 4-5 kcal/mol of the 10-kcal/mol difference in activation energies between the cyclic and acyclic reactions. Nearly 6 kcal/mol *extra* stabilization of the cyclic vs. the acyclic transition states is unaccounted for by strain theory arguments alone. We wish to propose in this communication that a significant fraction of this 6-kcal/mol difference comes from orbital stereoelectronic effects in the trigonal bipyramid transition states.

Molecular orbital calculations were performed on various conformational isomers of the trigonal bipyramidal, neutral, and dianionic dimethoxyphosphoranes **3** and **4** (Figure 2). Semiempirical CNDO/2 calculations[5] on **3** used idealized geometries based upon x-ray crystallographic structures of appropriate molecules while partial geometry optimization was performed on **4** using the ab initio programs Gaussian 70[6] and a minimal STO-3G basis set.[7] The overlap populations[8] for the axial $P\text{-}OCH_3$ bond obtained in these calculations are shown in Figure 2. As has been previously pointed out for tetracoordinated carbon and phosphorus species the dependence of the overlap populations on conformation about ester bonds derives from an "anomeric"-type effect: an interaction of a trans-antiperiplanar (app) oxygen lone pair with the antibonding orbital on the adjacent bond.[9-12] This anomeric effect strengthens the bond with the oxygen atom bearing the app lone pair and in turn weakens the bond adjacent to the bond containing the lone pair (we assume overlap population changes reflect relative bond strengths[9]).

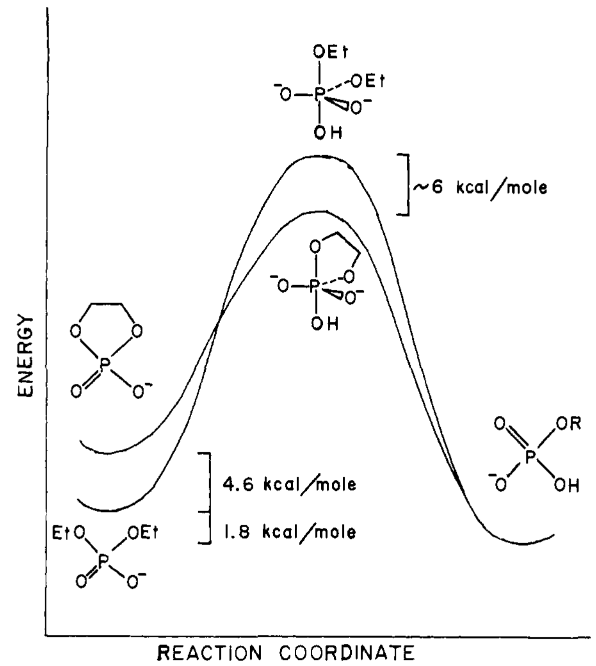

Figure 1. Reaction profiles for ⁻OH-catalyzed hydrolysis of diethyl phosphate, **1**, and ethylene phosphate, **2**. Figure taken from ref 4.

Table I. Summary of Overlap Population Changes in Structures **3a–e**.

A. app Interactions Leading to Bond Weakening

	3a[a]	**3b**[a]	**3c**[a]
Conformation about $P\text{-}O_eR$	spp	g	t
No. of lone pairs app to $P\text{-}O_aR$	(2)[b]	1	0
Net overlap population change	−0.031	−0.020	0

B. app Interactions Leading to Bond Strengthening

	3e[c]	**3d**[c]	**3c**[c]
Conformation about $P\text{-}O_aR$	g	spp	t
No. of lone pairs app to $P\text{-}O_eR$	1	(2)[a]	0
Net overlap population change	0	−0.007	−0.01

[a] Trans apical ester bond. [b] Partial app lone pairs. See footnote 14. [c] Trans equatorial ester bond.

An analysis of the overlap population changes for the axial ester bonds in the neutral phosphoranes, **3**, is presented in Table I. The equatorial ester oxygen in the g_e,t_a conformation, **3b** (see Figure 1 for definition of symbols), has one lone pair app to the axial $P\text{-}OCH_3$ bond, leading to a reduction (relative to the t_e,t_a conformation, **3c**) of 0.020 e in the axial $P\text{-}OCH_3$ overlap population. By contrast, the apical ester oxygen atom in the t_e,g_a conformation, **3e**, has one lone pair app to the equatorial ester bond, resulting in an increase (relative to the t_e,t_a conformation, **3c**) of 0.01 e in the *axial* $P\text{-}OCH_3$ overlap population. The ab initio calculations on **4a–c** demonstrate similar sensitivity of the bond overlap populations to the ester torsional conformations.[13]

To a first approximation these differential effects are only sensitive to the torsional conformation of the bond app to the lone pair. Thus, the additional app lone pair on the equatorial ester oxygen in **3b** (g_e,t_a) vs. **3c** (t_e,t_a) leads to a decrease of