

Table I. Computed Total Energies and Geometric Parameters^a for 1,2-Dihydroxyethylene

	C _{ss}	C _{sc}	C _{cc}	T _{ss}	T _{sc}	T _{cc}
<i>r</i> (C ₁ C ₂), Å	1.3201	1.3183	1.3187	1.3184	1.3176	1.3171
<i>r</i> (C ₁ O ₁), Å	1.4017	1.4023	1.4025	1.4030	1.4034	1.4027
<i>r</i> (C ₂ O ₂), Å	1.4017	1.4023	1.4025	1.4030	1.4034	1.4027
<i>r</i> (O ₁ H ₃), ° Å	0.9899	0.9899	0.9899	0.9890	0.9890	0.9890
<i>r</i> (O ₂ H ₄), ° Å	0.9899	0.9899	0.9899	0.9890	0.9890	0.9890
∠H ₁ C ₁ C ₂ , deg	119.81	121.95	120.96	120.92	121.47	122.48
∠H ₂ C ₂ C ₁ , deg	119.81	121.96	120.96	120.92	121.83	122.48
∠H ₃ O ₁ C ₁ , deg	104.81	105.05	107.79	104.80	104.88	104.65
∠H ₄ O ₂ C ₂ , deg	104.81	103.56	107.79	104.80	104.51	104.65
∠C ₁ C ₂ O ₂ , deg	122.32	119.54	128.44	120.79	120.84	125.76
∠O ₁ C ₁ C ₂ , deg	122.32	124.58	128.44	120.79	125.65	125.76
STO-3G total energy, au	-224.744 91	-224.751 99	-224.746 36	-224.747 05	-224.748 30	-224.750 77
STO-3G rel energy, kcal/mol	4.40	0.00	3.53	2.33	1.55	0.00
4-31G total energy, au ^b	-227.393 61	-227.405 29	-227.396 99	-227.397 61	-227.396 42	-227.397 90
4-31G rel energy, kcal/mol	7.32	0.00	5.21	0.18	0.93	0.00

^a Calculated at the STO-3G level. ^b 4-31G calculation at the STO-3G optimized geometry.

Table II. σ Overlap Populations for Hydroxyethylene and Thiohydroxyethylene

	cis	trans
Hydroxyethylene ^a		
C ₁ -C ₂	0.4075	0.4078
C ₁ -O	0.2649	0.2651
C ₁ -H ₁	0.3873	0.3863
Thiohydroxyethylene ^b		
C ₁ -C ₂	0.4068	0.4072
C ₁ -S	0.2748	0.2737
C ₁ -H ₁	0.3897	0.3890

^a Calculated at the STO-3G optimized geometry.^{4a} ^b Calculated at an approximately optimized geometry.¹

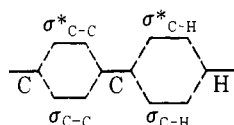
Table III. Atomic Charges for Hydroxyethylene and Thiohydroxyethylene

	cis	trans
Hydroxyethylene ^a		
C ₂	-0.19	-0.17
O	-0.27	-0.28
H ₁	+0.08	+0.06
Thiohydroxyethylene ^b		
C ₂	-0.16	-0.15
S	+0.15	+0.15
H ₁	+0.08	+0.07

^a Calculated at the STO-3G optimized geometry.^{4a} ^b Calculated at an approximately optimized geometry.¹

on oxygen and the vacant antibonding σ^*_{C-C} and σ^*_{C-H} MOs. In the cis conformation the lone pair is syn to σ^*_{C-H} and anti to σ^*_{C-C} , while in the trans conformer the reverse is true. The two factors which control the magnitudes of the various stabilizing interactions follow.

(1) The stabilization energy will increase as ΔE_{ij} decreases, i.e., as the energy of the vacant antibonding σ^* orbital decreases. In general the energy of σ^*_{C-X} decreases as X varies to the right along a row or down along a column of the periodic table.^{38a,b} An unambiguous determination of the relative energies of σ^*_{CC} and σ^*_{CH} is not possible owing to a lack of appropriate model systems. However, a large body of chemical data can be explained by assuming that σ_{CC} lies higher in energy than σ_{CH} ,^{38c-h} something which seems to imply that σ^*_{CC} lies lower in energy than σ^*_{CH} . This argument is illuminated by the interaction diagram shown below.



Accordingly, we shall assume as a working hypothesis that a C-C bond is a better acceptor than a C-H bond.

(2) The stabilization energy will increase as S_{ij} increases. It has been shown^{38a,b} that the absolute magnitude of the overlap between a hybrid AO and an adjacent σ^* MO is larger when the two orbitals are arranged in an anti-periplanar manner as compared to a syn-periplanar arrangement.

By considering these two factors we conclude that the cis conformer of hydroxyethylene will be favored over the trans conformer by σ conjugative interactions.

As σ conjugative interactions involve charge transfer^{38a,b} from a filled nonbonding orbital to a vacant antibonding or-

bital, further consequences of these interactions will be as follows: (1) a greater C₁-O σ overlap population in the cis conformer; (2) a smaller C₁-C₂ σ overlap population in the cis conformer; (3) a smaller C₁-H₁ σ overlap population in the trans conformer; (4) a smaller negative gross atomic charge on the oxygen atom in the cis isomer; (5) a greater negative gross atomic charge on C₂ in the cis conformer; (6) a greater positive gross atomic charge on H₁ in the trans conformer.

In order to test these predictions hydroxyethylene, thiohydroxyethylene, and 1,2-dihydroxyethylene were investigated computationally at the ab initio level.

Ab Initio Calculations

The cis and trans conformations of hydroxyethylene^{4a} and thiohydroxyethylene¹ have previously been investigated at the STO-3G³⁹ level. The various planar conformations of *cis*- and *trans*-1,2-dihydroxyethylene were investigated at both the STO-3G and the 4-31G levels.⁴⁰ All computations were carried out using the Gaussian 70 series of programs.⁴¹ The approximate optimized geometries and total energies are presented in Table I. The specific results pertinent to the qualitative analysis are discussed in the following section.

Results and Discussion

Hydroxyethylene. In accord with the prediction, the cis conformer of hydroxyethylene has previously been shown to be more stable than the trans, both experimentally^{3b} and computationally.^{1,4}

The σ overlap populations for hydroxyethylene are presented in Table II. The C₁-C₂ σ overlap population is larger for the trans conformer as predicted. The C₁-H₁ σ overlap population is larger in the cis conformation, also as predicted. The C₁-O σ overlap populations are, however, anomalous, being slightly

Table IV. σ Overlap Populations for the C_{se} and T_{se} Conformers of 1,2-Dihydroxyethylene^a

	C_{se}	T_{se}
C_1H_1	0.3773	0.3916
C_2H_2	0.4007	0.3951
C_1O_1	0.3907	0.3604
C_2O_2	0.4296	0.4014

^a Calculated at the 4-31G level at the STO-3G optimized geometry.

Table V. Gross Atomic Charges^a for the C_{se} and T_{se} Conformers of 1,2-Dihydroxyethylene

	C_{se}	T_{se}
C_1	+0.07	+0.07
C_2	+0.16	+0.17
H_1	+0.10	+0.18
H_2	+0.11	+0.23
O_1	-0.76	-0.73
O_2	-0.75	-0.73

^a Calculated at the 4-31G level at the STO-3G optimized geometry.

larger in the trans conformer.

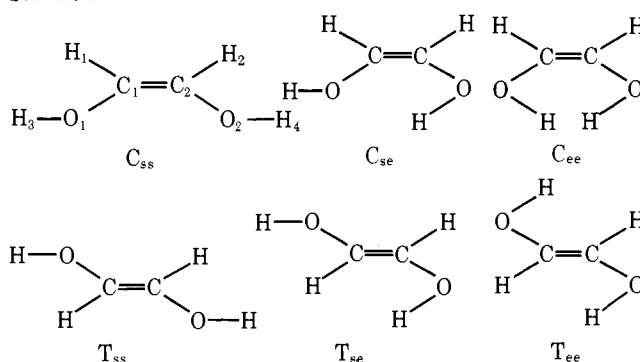
The gross atomic charges presented in Table III are also in accord with the predictions based on the consideration of σ conjugative interactions. The C_2 atom is more negative for the cis conformer while the O and H_1 are more negative for the trans.

Thiohydroxyethylene. As the σ conjugative interactions within thiohydroxyethylene are similar to those within hydroxyethylene, the predictions concerning the relative stabilities of the two conformers, σ overlap populations, and the relative gross atomic charges remain the same.

Thiohydroxyethylene has also previously been found to favor the cis conformation.¹ The σ overlap populations (Table II) and the gross atomic charges (Table III) are also in agreement with the predictions, except that the charge on sulfur is equal in the two conformers.

1,2-Dihydroxyethylene. The various conformations of *cis*- and *trans*-dihydroxyethylene are depicted in Scheme I. By extending the analysis of hydroxyethylene one can easily conclude that the predicted order of stability, based on σ conjugative interactions, is $C_{ee} > C_{se} > C_{ss}$ and $T_{ee} > T_{se} > T_{ss}$.

In the trans isomer the relative stability (Table I) of the conformers decreases in the order $T_{ee} > T_{se} > T_{ss}$. For the cis isomer the relative stability decreases in the order $C_{se} > C_{ee} > C_{ss}$ (Table I). The preference for the C_{se} conformer is probably a result of hydrogen bonding in C_{se} and greater steric repulsion in C_{ee} . However, C_{ee} is found to be more stable than C_{ss} even though the C_{ee} conformer is more sterically crowded. This suggests that the hyperconjugative factor is also at work here.

Scheme I

An inspection of the σ overlap populations and gross atomic charges (Tables IV and V) in the T_{se} and C_{se} conformers of 1,2-dihydroxyethylene illustrates the significance of σ conjugative interactions in these systems. The predictions based on σ conjugative interactions follow: (1) The C-O σ overlap populations are expected to decrease in the order $C_2-O_2 > C_1-O_1$. (2) The C-H σ overlap populations are expected to decrease in the order $C_2-H_2 > C_1-H_1$. (3) The gross atomic charges on the oxygens should become more negative in the order $O_1 > O_2$. (4) The gross atomic charges on the hydrogens should become more positive in the order $H_2 > H_1$.

As can be seen from Tables IV and V all of these predictions are borne out by the calculations except in the C_{se} conformer where O_1 and O_2 have identical charges.

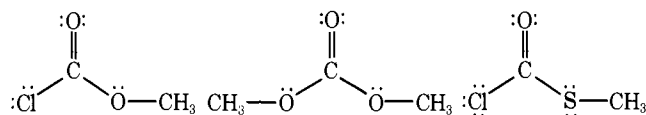
We conclude that the results of our computational investigation support the qualitative hyperconjugative model and that σ conjugative interactions do indeed play a role in determining the conformational preferences of hydroxy-, thiohydroxy-, and 1,2-dihydroxyethylene.

Experimental trends in systems where σ conjugative interactions apply are summarized below.

(1) Vinyl ethers and formate esters prefer the cis conformation.⁸ A summary of key experimental findings is presented in Table VI.

(2) The difference in energy between the cis and the trans conformers is larger for the formate esters than for the vinyl ethers (Table VI). This results from σ^*_{C-O} being lower in energy than σ^*_{C-C} . Therefore, the difference in the stabilization energy between the cis and the trans forms will be larger in formate esters than in vinyl ethers.

(3) Methyl chloroformate^{26,27} and dimethyl carbonates⁸ have been found to be much more flexible than simple formate esters. Even more striking is that a series of chlorothioformates prefer the trans geometry.²⁸ In all of these cases the hydrogen β to the oxygens in methyl formate has been replaced by a Cl

**Table VI.** Experimental Relative Energies (kcal/mol) of the Planar Conformations of H(CX)YR Molecules

	molecule			rel energy		ref
	X	Y	R	cis	trans	
methyl vinyl ether	CH ₂	O	CH ₃	0.00	1.15	17
				0.00	1.44	18
methyl vinyl sulfide	CH ₂	S	CH ₃	0.00	2.30	22, 23
				0.00	2.01-3.01	13
methyl formate	O	O	CH ₃	0.00	~6.0	15
				0.00	2.5	10
ethyl formate	O	O	CH ₂ CH ₃	cis preferred		33b
methyl thioformate	O	S	CH ₃	cis preferred		20, 21, 33c
				cis preferred		33d

or an OR group. Therefore, the stabilization energy difference between the cis and trans conformers is substantially reduced. Since σ^*_{C-Cl} is lower in energy than σ^*_{C-O} , the trans conformer of chlorothioformates and chloroformates is predicted to be preferred on the basis of σ conjugative interactions.

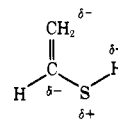
In conclusion, we wish to emphasize that the ideas presented in this and a previous paper^{38a} regarding directionality of hyperconjugation are applicable to a wide diversity of chemical topics such as the stereoelectronic control in the cleavage of tetrahedral intermediates in the hydrolysis of esters and amides,⁴² chemical shifts, coupling constants, etc.

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References and Notes

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- (43) By using arguments similar to those in this work and ref 38a,b, it can be shown that $n-\sigma$ and $\sigma-\sigma$ overlaps are greater in a syn than an anti orientation. Owing to typographical errors, the sense of the discussion in the top seven lines of p 160 of ref 38b is incorrect.