interactions are: a) between S and the axial H attached to C(3) of the molecule at one repeat distance along [010]; b) between the H atoms on C(2) (or C(4)) of one molecule and the H atoms on C(4) (or C(2)) of the symmetric equivalent molecules related by *a* and by *n*.

We express our thanks to Prof. *J. D. Dunitz* (ETH Zürich) for use of the linear diffractometer.

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54. Stereoelectronic Properties of Tetrahedral Species derived from Carbonyl Groups.

Ab initio Study of the Hydroxymethanes

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(10. I. 74)

Summary. Analysis of the electronic structure of the hydroxymethanes provides a consistent picture of stereoelectronic effects in such molecules: The average C—O bond length decreases in the series methanol, methanediol, methanetriol. An oxygen (O′) lone pair, which is *trans*-antiperiplanar (*app*) to another oxygen (O″), shortens and strengthens the C—O′ bond and simultaneously lengthens and weakens the C—O″ bond. This is consistent with solid state structural evidence and with the reactivity patterns of tetrahedral species resulting from nucleophilic addition to a carbonyl group.

Tetrahedral species resulting from nucleophilic addition to carbonyl groups play a central role in the mechanisms and kinetics of many chemical and biochemical reactions. Recent experimental studies have stressed the importance of conformation, in particular the orientation of electronic lone pairs, in controlling the decomposition of such tetrahedral intermediates [1] [2]. The interaction of an antiperiplanar (*app*) lone pair with a σ-bond has been discussed by *Lucken* [3] and has been invoked in the interpretation of the anomeric effect [4] [5].

Following our work on the addition of hydride ion to formaldehyde [6], we have performed non-empirical calculations[2]) on the hydroxymethanes, methanediol (**D**),

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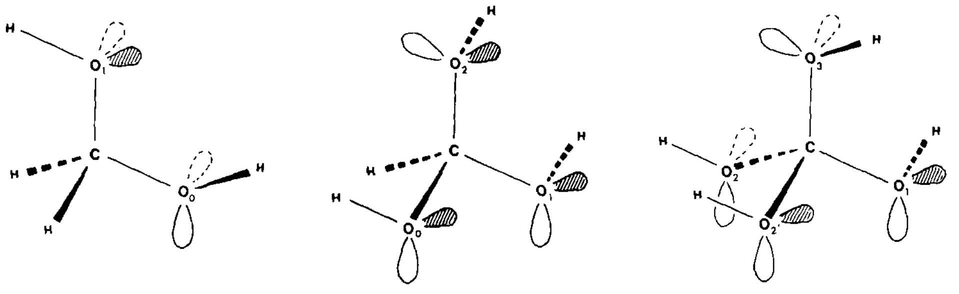
[1]) Part of this work was performed during a stay of *H.-B. Bürgi* in Strasbourg.

[2]) Basis set of gaussian functions: seven s, three p functions on C and O and four s functions on H contracted into three s, two p and two s respectively [6] [7].



D **Tri** **Tet**

(The index of each oxygen atom gives the number of lone pairs antiperiplanar to the corresponding C—O bond)

methanetriol (**Tri**) and methanetetrol (**Tet**) (Fig.) which can serve as models for the tetrahedral species arising from addition of H_2O to ketones or aldehydes, esters and carbonates. Since another theoretical study of **D** has appeared recently [8], the present discussion stresses the general conclusions resulting from the comparison of **D**, **Tri**, **Tet** and methanol. The calculations were performed on staggered conformations of **D**, **Tri** and **Tet** which contain C–O bonds having different numbers of *app* oxygen lone pairs. Except for **Tet** (C–O = 1.40 Å, assumed) the C–O bond lengths were optimized (O–H = 0.97 Å, C–H = 1.095 Å) assuming tetrahedral bond angles.

Species	Bond	Lone pairs *app* a)	Overlap Population Total (lp) b)	Bond Length (optimized) Å	Total energy a.u.
CH_3—OH	C—O	0	0.357	1.450	
D	C—O_0	0	0.412 (–0.010)	1.408	–189.4643
	C—O_1	1	0.331 (–0.098)	1.437	
Tri	C—O_0	0	0.413 (–0.049)	1.386	–264.1487
	C—O_1	1	0.372 (–0.067)	1.408	
	C—O_2	2	0.333 (–0.099)	1.428	
Tet	C—O_1	1	0.483 (–0.026)	1.40 c)	–338.8592
	C—O_2	2	0.450 (–0.068)		
	C—O_2'	2	0.443 (–0.069)		
	C—O_3	3	0.408 (–0.085)		

a) Number of lone pairs antiperiplanar to the C—O bond considered.
b) Sum of the contributions of all localized oxygen lone pairs to the C—O OP.
c) Non optimized value used for all C—O bonds.

The results obtained (Table) lead to the following conclusions:

1. Replacement of a methyl hydrogen of methanol by OH causes a shortening of C–O bond length by 0.03 Å; replacement of a second H by OH causes a further shortening of 0.02 Å. Bond length shortening is accompanied by increase in C–O overlap population (OP). The effect is independent of conformation.

2. The C–O bond lengths and OP.'s show a marked dependence on the number of *app* lone pairs. If, in a given HO–C–OH fragment, a C–O bond is *app* to a lone

pair, it is lengthened by about 0.02 Å and its OP. is decreased by about 0.04 e, while the other C–O bond is shortened by about 0.01 Å and its OP. increased by about 0.015 e. These increments also reproduce bond lengths calculated previously for four different conformations of methanediol [8]. The effect is independent of the presence of other OH groups.

3. The structural and conformational effects on C–O OP.'s are observed even if standard (equal) bond lengths are assumed; thus the pattern of bond properties may be obtained by inspection of OP.'s from a single calculation. For example, in calculations on different conformations of the triol (C–O = 1.40 Å, assumed), rotation about one C–O bond affects the OP.'s of all three C–O bonds qualitatively in the manner described.

4. The four, six and eight nonbonding MO's of **D**, **Tri** and **Tet** respectively are predominantly oxygen lone pairs. The ones higher in energy consist of mainly oxygen p-orbitals, the lower ones are mixtures of oxygen s- and p-orbitals. The C–O bond weakening arises from the p type lone pairs. After localization of the MO's all the localized lone pairs give negative contributions to the C–O OP.'s (Table).

5. For the diol **D**, C–O stretching force constants and the stretch-stretch interaction constant were estimated from calculated energies at twelve points around equilibrium (distance deviations at most 0.03 Å from optimized values). The values obtained are: $k(C–O_0) = 6.0$, $k(C–O_1) = 5.8$ and $k'(C–O_0, C–O_1) = 0.3$ mdyne/Å, *i.e.* the shorter bond is associated with the higher force constant. Asymmetric stretch deformation of the diol is likely to be important in the initial stages of the decay of the diol [9] to a carbonyl compound (acid catalyzed acetal hydrolysis), and the relative magnitudes of the force constants confirm that, at least initially, a reaction path leading to cleavage of the long $C–O_1$ bond is lower in energy than one leading to cleavage of the short $C–O_0$ bond.

6. The above results are in accord with conclusions derived from simple perturbation theory: Interaction between the antibonding σ^* (C–O) MO and a vicinal p type oxygen lone pair [3]–[5], should lengthen and weaken one C–O bond, and shorten and strengthen the other. This interaction is maximal for a coplanar arrangement of the two orbitals, *i.e.* for a conformation of methanediol with a $H–O_0–C–O_1$ torsion angle of 90° (found to be about 2 kcal/mol less stable than **D**[3]), see also [8]); the C–O bond lengths remain the same as in **D** and the $C–O_1$ OP. decreases only very slightly. Thus, there seems to be little orientation effect on $C–O_1$ bond properties in this domain of torsion angles (90° ± 30°) in keeping with the angular dependence of the perturbative overlap between two p-orbitals (on O_0 and on C).

7. The results of the calculations agree with X-ray structural data [8] [9] on bond lengths in derivatives of the model hydroxymethanes studied here and also with the reactivity pattern of C–O bond cleavage in tetrahedral intermediates (oxygen exchange, hydrolysis of esters, transesterification) [1] [2].

8. It is also worth noting that an *app* lone pair *increases* the OP. of a C–H bond. Thus this bond becomes stronger but also, because of and higher electron density,

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[3] The energy changes may of course be larger in substituted derivatives of these model compounds.

more easily attacked by electrophiles like ozone, in agreement with experimental results on the ozonolysis of acetals [12].

Stereoelectronic or conformational effects, which are believed to influence the decomposition of tetrahedral intermediates [1] [2], are thus present in isolated species. Such effects as well as orientation effects [6] [10] may well be important in determining the stereochemical and other specificity of hydrolytic enzymes. Extension to the case of amide hydrolysis should allow to check and to generalize these results [11].

We thank Prof. *J. D. Dunitz* for helpful discussion.

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55. The Reaction of some Carbonyl and Thiocarbonyl Compounds with Prenyl- and Crotyllithium in Tetrahydrofuran Solution

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(11 XII 73)

Summary. Prenyllithium (3-methylbut-2-enyl-lithium) (**1**) and *cis*-crotyllithium (*Z*-but-2-enyl-lithium) (**2**) in tetrahydrofuran solution, prepared according to the method of *Eisch & Jacobs*, react with carbonyl compounds to give the branched alcoholates with moderate to high selectivity, unless access to the carbonyl group is strongly hindered (see the Table). Adamantanethione (**12**) reacts with **1** to give the unbranched thiolate.

Allyllithiums can now be prepared readily, and often more conveniently than the corresponding *Grignards*, by the method of *Eisch & Jacobs* [1–4], by cleavage of allyl phenyl ethers with lithium in tetrahydrofuran. We have studied the reactions of two simple substituted allyllithiums, 'prenyllithium' (3-methylbut-2-enyl-lithium) (**1**) and *cis*-crotyllithium (*Z*-but-2-enyl-lithium) (**2**), made in this way, with a few aldehydes and ketones. These simple addition reactions interested us as possible synthetic steps; prenyllithium (**1**) is a potentially useful synthetic 'isoprene unit'. We also wished to compare these reactions with the related ether [5] [6] and thioether