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Geometry of 1,2-Dihydroxy-1,2-disulphonates

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ABSTRACT

An evaluation of the probability of hydrogen bonding between sulphonate and hydroxyl groups on adjacent carbon atoms of 1,2-dihydroxy-1,2-disulphonates is reported. Using published bond lengths and angles, and allowing free rotation about C–C, C–O and C–S bonds, 2·9% of the possible conformations lead to O–H····O and H····O distances conducive to hydrogen bonding. The significance of the calculated O–H····O and S–O····H bond angles is also considered. These results are discussed in terms of the observation that 1,2-dihydroxy-1,2-disulphonates appear to be more labile than 1-hydroxy-2-oxosulphonates, and the relevance of this result to the inhibition of non-enzymic browning by sulphur dioxide in foods is appraised.

INTRODUCTION

The interaction between sulphur (IV) oxospecies, S(IV), and α-dicarbonyl compounds is important in food preservation by sulphur dioxide: reversible binding contributes to the reduction of free S(IV) in fermented beverages (Burroughs & Sparks, 1973) whilst reversible and irreversible interactions with 3-deoxyosuloses are important in the inhibition of Maillard and ascorbic acid non-enzymic browning (Wedzicha, 1984).

The type of adduct that is formed reversibly between α-dicarbonyl groups and S(IV) has been considered in detail in connection with the mechanism of

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inhibition of non-enzymic browning by S(IV). Knowles (1971) suggested that the reaction of S(IV) with 3-deoxyhexosulose should lead to the formation of a 1,2-dihydroxy-1,2-disulphonate, which is stabilised through hydrogen bonding. The type of structure proposed is illustrated for the dihydroxysulphonate of pyruvaldehyde in Fig. 1 where the relevant atoms of the corresponding sulphonate and hydroxyl groups and the C–C bond are shown co-planar for clarity. Whilst this proposal is attractive and could explain circumstantial evidence for the apparent high stability of the hydroxysulphonate of 3-deoxyhexosulose and 3,4-dideoxy-4-sulphohexosulose (Wedzicha & Imeson, 1977), Salomaa (1956) reports that at pH 7·3 the dissociation of the dihydroxysulphonate of glyoxal takes place much more readily than the dissociation of the monoadduct. There is, in fact, no experimental evidence to support the formation of 1,2-dihydroxy-1,2-disulphonates in food systems, and measurements of S(IV)-carbonyl association constants suggest that in solution the addition stops at the monoadduct (Burroughs & Sparks, 1973; Wedzicha *et al.*, 1985; Wedzicha & Kaban, 1987).

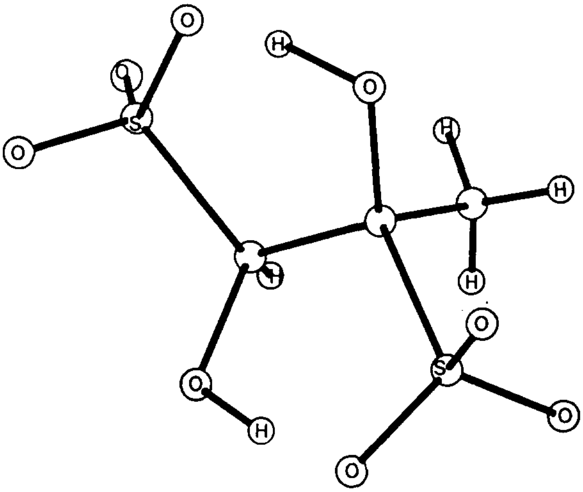


Fig. 1. Model of the dihydroxysulphonate of pyruvaldehyde.

Reasons why the formation of 1,2-dihydroxy-1,2-disulphonates may be less favourable than the formation of monohydroxysulphonates have been advanced (Wedzicha, 1984) in terms of the stability of the hydrogen bond in relation to charge distribution. However, the simplest factor, that of geometry, has not yet been considered in sufficient detail. Here we report a calculation of the geometry of 1,2-dihydroxy-1,2-disulphonates to assess the likelihood of the approach of neighbouring sulphonate and hydroxyl groups in a way suitable for hydrogen bonding.

MOLECULAR DIMENSIONS

The only available data on the crystal structure of an aliphatic hydroxysulphonate were those of Cameron & Chute (1979) for potassium hydroxymethanesulphonate. An important observation made by these workers is that a crystal of this substance consists of potassium ions and a hydrogen-bonded dimeric hydroxymethanesulphonate as shown in Fig. 2.

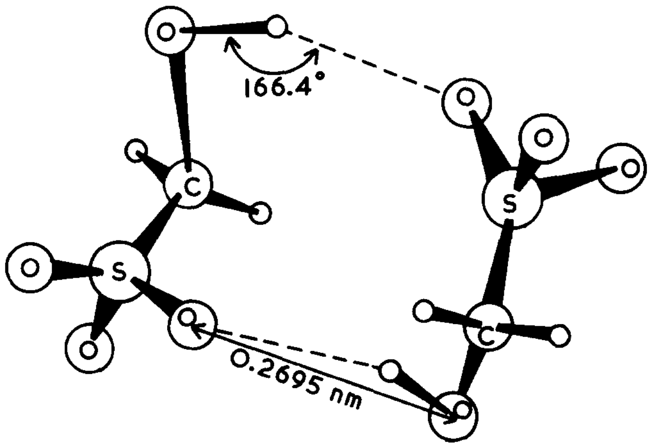
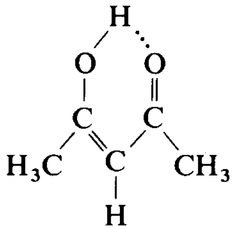


Fig. 2. Hydrogen bonding in hydroxymethanesulphonate ion (Cameron & Chute, 1979).

This demonstrates that hydrogen bonding of the type envisaged in 1,2-dihydroxy-1,2-disulphonates is feasible. Infrared studies on hydroxysulphonates (Frollini *et al.*, 1982) and alkylammonium methanesulphonates (Biaggio *et al.*, 1981) also indicate the feasibility of hydrogen bonding to a sulphonate oxygen.

The dimeric hydroxymethanesulphonate has a total O–H····O distance of 0·2695 nm, which is typical of an O–O separation with a hydrogen bond between the atoms (Coulson, 1961). The ideal hydrogen bond is formed with the O–H····O system linear, but deviations from linearity are frequently observed. For example, the O–H····O angle in Fig. 2 is 166·4°. A well-known hydrogen-bonded structure is that of the enol form of acetylacetone, as follows:



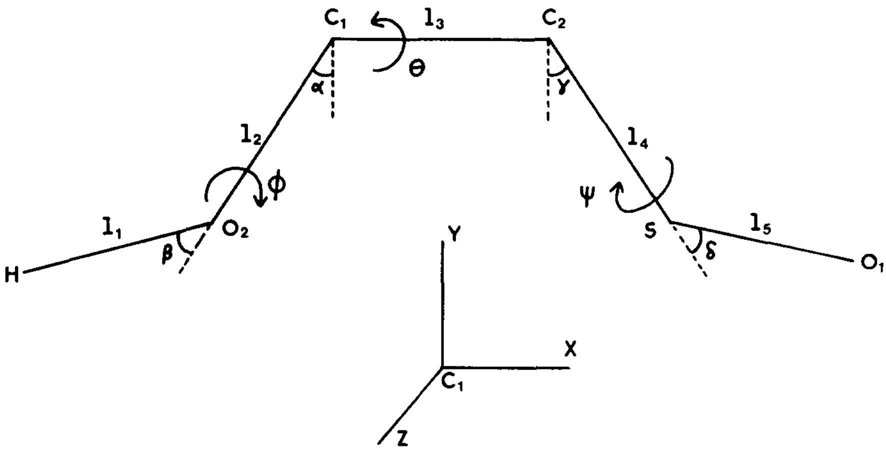


Fig. 3. Dimensions, angles and coordinate axes for calculation of geometry of 1,2-dihydroxy-1,2-disulphonates. Only one OH group and one S–O bond shown for clarity. All bonds are in their reference positions ($\theta = \psi = \phi = 0$).

In this case the O–H····O angle is close to 120°. A further geometrical requirement is that of a sensible S–O····H angle since the tendency of the sulphonate oxygen-to-hydrogen bond will be directional. It is likely that this oxygen will be sp^2 hybridised and an angle of the order of 120° would be ideal.

A diagrammatic structure of a 1,2-dihydroxy-1,2-disulphonate is given in Fig. 3, but showing only one OH and one SO_3^- group. Further, only one of the sulphonate oxygens is shown for clarity since all three oxygens are expected to behave in the same way. Bond lengths and angles used for calculation of geometry in this work are shown in Table 1 where the numbering of atoms refers to that shown in Fig. 3. The length of the S–O bond given (0·1461 nm) is the length of the bond involved in hydrogen-bond formation in hydroxymethanesulphonate. In fact, the three S–O bonds have

TABLE 1

Bond Lengths and Angles for Structure of 1,2-Dihydroxy-1,2-Disulphonates

Bond	*Length (nm)*	*Junction*	*Angle (°)*
$S–O_1$	0·146 1[a]	$O_1–S–C_2$	106·0[a]
$S–C_2$	0·179 0[a]	$S–C_2–C_1$	109[b]
$C_1–C_2$	0·154[b]	$C_2–C_1–O_2$	109[b]
$C_1–O_2$	0·141 2[a]	$C_1–O_2–H$	115·0[a]
$O_2–H$	0·099 4[a]		109 (simple alcohol)[b]

Numbering of atoms refers to Fig. 3.
[a] Cameron & Chute (1979).
[b] Weast (1981).

different lengths: 0·1458, 0·1442 and 0·1461 nm. The mean value, 0·1454 nm, compares favourably with the S–O bond length of 0·1456 nm in $CH_3SO_3^-$ (Charbonnier *et al.*, 1977) where no hydrogen bonding is expected. In this investigation, the preferred length is that of hydrogen-bonded S–O since it is expected that the S–O bond will adjust to a length of this order as the group approaches the OH group. Likewise, the C–S–O bond angle (106°) for a hydrogen-bonded S–O is used. The C_1–C_2 distance is taken as a normal C–C interatomic distance, and bonds around the carbon atoms are assumed to be tetrahedrally arranged. It appears that hydrogen bonding in hydroxymethanesulphonate causes the C–O–H angle to be significantly opened from a normal value of 109° (in methanol). Since this is likely to be a function of the strain in the structure of the dimer of hydroxymethanesulphonate, the preferred bond angle is 109° in this case.

CALCULATION OF GEOMETRY

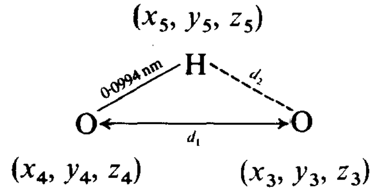
Figure 3 shows the location of coordinate axes, the symbols used for molecular dimensions and angles for the derivation of equations and directions of rotation of the C_1–O, C_1–C_2 and C_2–S bonds by angles ϕ, θ and ψ, respectively. During all rotations C_1, C_2 and S lie in the x/y plane and the atoms which move are, therefore, O_1, O_2 and H. C_1 was placed at the origin of the set of coordinate axes and the coordinates of the remaining atoms are as follows:

$$
\begin{aligned}
C_2:\quad & x_1 = l_3 \\
& y_1 = 0 \\
& z_1 = 0 \\
S:\quad & x_2 = l_3 + l_4 \operatorname{Sin}\gamma \\
& y_2 = -l_4 \operatorname{Cos}\gamma \\
& z_2 = 0 \\
O_1:\quad & x_3 = l_3 + (l_4 + l_5 \operatorname{Cos}\delta)\operatorname{Sin}\gamma + l_5 \operatorname{Sin}\delta \operatorname{Cos}\psi \operatorname{Cos}\gamma \\
& y_3 = l_5 \operatorname{Sin}\delta \operatorname{Cos}\psi \operatorname{Sin}\gamma - (l_4 + l_5 \operatorname{Cos}\delta)\operatorname{Cos}\gamma \\
& z_3 = l_5 \operatorname{Sin}\delta \operatorname{Sin}\psi \\
O_2:\quad & x_4 = -l_2 \operatorname{Sin}\alpha \\
& y_4 = -l_2 \operatorname{Cos}\alpha \operatorname{Cos}\theta \\
& z_4 = l_2 \operatorname{Cos}\alpha \operatorname{Sin}\theta \\
H:\quad & x_5 = -\operatorname{Sin}\alpha (l_2 + l_1 \operatorname{Cos}\beta) - l_1 \operatorname{Sin}\beta \operatorname{Cos}\phi \operatorname{Cos}\alpha \\
& y_5 = -\operatorname{Cos}\alpha \operatorname{Cos}\theta (l_2 + l_1 \operatorname{Cos}\beta) \\
& \qquad\qquad - l_1 \operatorname{Sin}\beta (\operatorname{Cos}\phi \operatorname{Sin}\alpha \operatorname{Cos}\theta + \operatorname{Sin}\phi \operatorname{Sin}\theta) \\
& z_5 = \operatorname{Cos}\alpha \operatorname{Sin}\theta (l_2 + l_1 \operatorname{Cos}\beta) \\
& \qquad\qquad + l_1 \operatorname{Sin}\beta (\operatorname{Sin}\phi \operatorname{Cos}\theta + \operatorname{Cos}\phi \operatorname{Sin}\alpha \operatorname{Sin}\theta)
\end{aligned}
$$

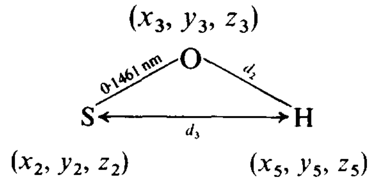
The distance, d, between two points x_m, y_m, z_m and x_n, y_n, z_n is given by:

$$d = [(x_m - x_n)^2 + (y_m - y_n)^2 + (z_m - z_n)^2]^{1/2}$$

In this way, the distances between the atoms involved in hydrogen bonding may be found from the following diagram:



The lengths of the sides of this triangle may be used in the cosine formula to find the angle O–H····O. Similarly, the S–O····H angle may be found by considering the following triangle:



RESULTS AND DISCUSSION

The distances d_1, d_2 and d_3 were calculated at 3° increments of θ, ϕ and ψ (total number of steps = 1 728 000). Combinations of d_1 and d_2 conducive to hydrogen bonding were selected from these results. For a linear O–H····O interaction the O–H bond begins to lengthen when the O–O distance is $<0{\cdot}28$ nm, and this represents the largest O–O separation before O····H interactions become significant (Coulson, 1961). Since, for this deduction, the O–H bond length was taken as 0·096 nm, the maximum O····H distance is 0·184 nm. A short O–O distance (0·25 nm) is found in the β-form of oxalic acid where an extensive hydrogen-bonded structure, over many molecules, occurs. This corresponds to an O····H separation of 0·154 nm if no stretching of O–H takes place. It is also suggested that when the O–O distance is of the order of 0·24 nm, the hydrogen atom is central (Coulson, 1961) and, therefore O····H separations of 0·144 to 0·154 nm are probably the minimum acceptable values, The O····H distance in hydroxymethanesulphonate is 0·171 nm (Cameron & Chute, 1979).

It was found that, of the conformations tried, 16 808 satisfied the conditions $0{\cdot}20 < d_1 < 0{\cdot}28$ and $0{\cdot}15 < d_2 < 0{\cdot}18$. This corresponds to 0·98% of conformations. The range of angles θ, ϕ and ψ for which acceptable distances were found are, respectively, ±63°, 96–267° and 111–252°. These results were obtained with only one S–O bond in the model; with three bonds the condition is therefore satisfied in 2·9% conformations tried. The range of values of ψ is greater than 120° for one S–O bond and therefore the SO$_3^-$ group will be available for hydrogen bonding at any angle of rotation.

Table 2 shows the frequency with which particular S–O····H and O–H····O angles were observed for the 16 808 acceptable conformations. It is apparent that, whilst the distribution of S–O····H angles includes sensible values (say 110–120°), the O–H····O bond shows considerable deviation from linearity. The limiting distances of d_1 and d_2 allow O–H····O angles in the range 83–180°. The largest angle observed, 133°, is therefore not the consequence of the chosen limits of d_1 and d_2. Whilst it is expected that the C_1–O_2–H angle could become more acute with an increase in the O–H····O

TABLE 2

Distribution of Values of Angles S–O····H and O–H····O[a]

	Frequency			*Frequency*			*Frequency*	
Angle (°)	*SOH angle*	*HOH angle*	*Angle* (°)	*SOH angle*	*HOH angle*	*Angle* (°)	*SOH angle*	*HOH angle*
67	8	—	90	346	132	113	212	414
68	62	—	91	328	166	114	178	406
69	122	—	92	306	188	115	180	406
70	212	—	93	326	254	116	174	374
71	264	—	94	268	258	117	152	386
72	334	—	95	320	324	118	138	374
73	439	—	96	286	383	119	128	376
74	531	—	97	298	401	120	112	354
75	472	—	98	248	486	121	108	410
76	514	—	99	312	644	122	78	342
77	580	—	100	246	628	123	70	390
78	572	—	101	266	584	124	44	374
79	690	—	102	258	562	125	30	362
80	596	—	103	270	546	126	4	376
81	526	—	104	236	515	127	0	344
82	470	—	105	242	511	128	0	324
83	452	0	106	238	506	129	0	296
84	396	0	107	248	468	130	0	228
85	396	0	108	212	452	131	0	202
86	372	10	109	228	448	132	0	110
87	368	30	110	206	426	133	0	24
88	394	80	111	237	430	134	0	0
89	306	94	112	199	410	135	0	0

[a] When 0·20 nm $< d_1 <$ 0·28 nm and 0·15 nm $< d_2 <$ 0·18 nm.

angle, it is difficult to see how the change could be sufficiently large to affect, significantly, the outcome.

If only the 564 conformations that give rise to O–H····O angles >130° are considered, it is found that the S–O····H angles are distributed between 74 and 102°, which is probably too small for effective hydrogen bonding. The largest O–H····O angles are therefore associated with small S–O····H angles. It is interesting to note values of θ, ϕ and ψ which lead to the largest O–H····O angles, and the distribution is summarised in Fig. 4. This shows that these conformations are found with O–H and S–O bonds well out of the C_1, C_2, S plane as suggested previously on a semi-quantitative basis (Wedzicha, 1984).

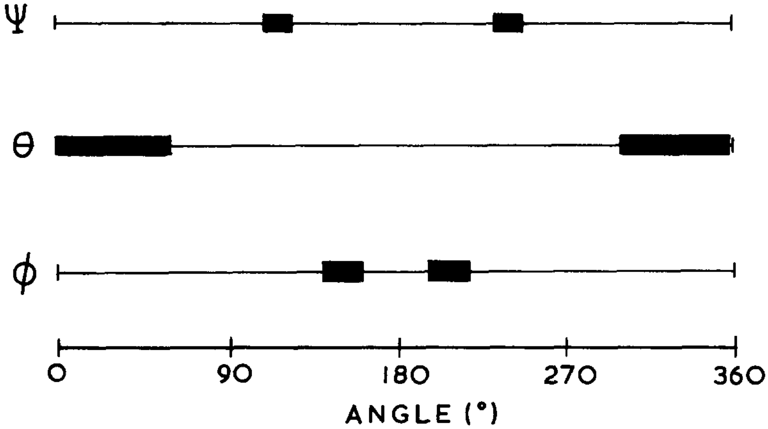
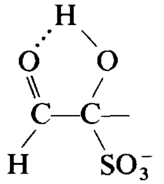


Fig. 4. Distribution of values of ψ, θ and ϕ which satisfy the condition: $0{\cdot}20\,\text{nm} < d_1 < 0{\cdot}28\,\text{nm}$, $0{\cdot}15\,\text{nm} < d_2 < 0{\cdot}18\,\text{nm}$ and O–H····O angle >130°. Ranges of values indicated by bars.

One reason for the apparent lability of 1,2-dihydroxy-1,2-disulphonates has been suggested to be that the monohydroxysulphonate of α-dicarbonyl compounds is stabilised through hydrogen bonding as follows:



Using bond angles and lengths given in Table 1 and a C=O length of 0·122 nm (Weast, 1981), the calculated O····H distance is 0·168 nm with C=O····H and O–H····O angles of 88 and 125°, respectively. Whilst the O····H distance is very reasonable for hydrogen-bond formation, the bond angles are somewhat acute.

CONCLUSION

The detailed geometrical analysis of 1,2-dihydroxy-1,2-disulphonates presented here suggests that the hydrogen-bonded structure is by no means as favourable as suggested previously. These potential diadducts could therefore experience only weak intramolecular hydrogen bonding, which, in solution, could be disrupted as a result of the strong interactions between the sulphonate group and water. It should, of course, be remembered, that the only evidence of hydrogen bonding in hydroxysulphonates is in the solid state. It is also found, and may be relevant to this discussion, that the diadducts of glyoxal and hydroxypyruvaldehyde can be obtained in the solid state (Ronzio & Waugh, 1944; Ingles, 1961).

It is striking that most of the dicarbonyl compounds which are encountered in non-enzymic browning pathways and which are capable of being studied form only monoadducts with S(IV). Examples include L-*erythro*-pentosulose (Burroughs & Sparks, 1973), 3-deoxyhexosulose (Wedzicha & Kaban, 1987), 3,4-dideoxy-4-sulphohexosulose (Wedzicha *et al.*, 1985) and dehydroascorbic acid (Ingles, 1961; Wisser *et al.*, 1970). With the exception of dehydroascorbic acid the lack of a clear stabilising effect in the diadduct with S(IV) is probably accentuated by the participation of one of the carbonyl groups in hemiacetal formation. In the case of dehydroascorbic acid, the five-membered lactone ring prevents free rotation of C–C bonds. Since such rotation is necessary to allow for the largest O–H····O angles in 1,2-dihydroxy-1,2-disulphonates, the possibility of diadduct formation in the case of dehydroascorbic acid is disfavoured.

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