

Structure of Glyoxal Monohydrate

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Summary I.r., Raman, n.m.r., and mass spectral data for glyoxal monohydrate are reported together with cryoscopic data and are interpreted in terms of a dimeric symmetrical tetrahydroxy-*p*-dioxan structure.

THE properties of simple dialdehydes and hydroxy-aldehydes are of considerable chemical and biological significance, being the basis of sugar chemistry. Glutaraldehyde¹ appears to exist in aqueous solution as a complex mixture of forms including the dialdehyde, diol (involving hydration of one or both carbonyl groups) and the dihydroxypyraniforms (I), whereas malonaldehyde² exists mainly in the enol form as either the *s-cis*- or *s-trans*-conformer according to the solvent. This communication considers the structure of the first member of this series glyoxal, which exists in the solid state as a monohydrate. Structural evidence is based on i.r., Raman, n.m.r. [in (CD₃)₂SO], and mass spectra.

The vibrational spectrum of a sample obtained from BDH is reported in the Table. It is immediately apparent that

Vibrational frequencies (cm⁻¹) of glyoxal monohydrate in the solid state

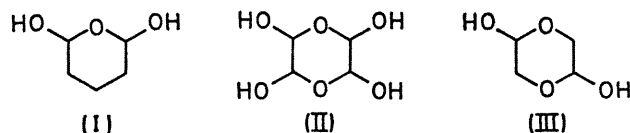
I.r. 3380 vs, 3030 s, 3010 s, 2955 s, 2860 w, 1740 w, 1630 w, 1400 s, 1360 s, 1318 m, 1295 s, 1252 m, 1220 w, 1125 vs, 1075 vs, 1055 vs, 1010 w, 985 vs, 940 vs, 827 vs, 765 s, 615 vs, 580 m, 520 s, 450 s, 385 s, 360 w, 325 w.

Raman. 3344 w, 3030 m, 3011 m, 2946 s, 2810 w, 1420 w, 1350 m, 1300 m, 1265 w, 1240 m, 1212 w, 1170 n, 1108 m, 1075 vs, 1005 vs, 985 w, 945 vs, 825 m, 780 vs, 608 w, 530 m, 475 m, 424 m, 304 s, 180 m.

vs = very strong, s = strong, m = medium, w = weak.

the glyoxal monohydrate is not a molecular complex of glyoxal and water because no carbonyl band is present. The spectrum is considered to support structure (II) since the i.r. and Raman spectra appear to obey the rule of

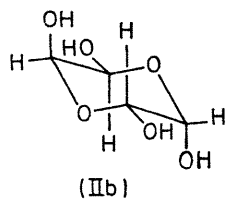
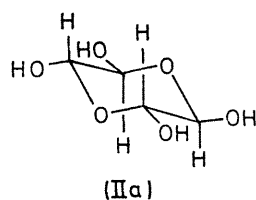
mutual exclusion. Structure (II) would be expected to yield 48 normal modes of vibration. We observe 28 i.r. bands and 25 Raman lines, between which only 9 coincidences of frequency occur; in these cases marked alternation of intensities are observed. It is likely that these coincidences arise *either* from relaxation of selection rules in the solid state *or* from accidental coincidence of frequencies in *g* and *u* symmetry species. We, therefore, conclude that glyoxal monohydrate has a centre of symmetry and suggest (II) as the most plausible structure. The i.r. and Raman spectra bear a marked similarity to those for glycolaldehyde³ in the solid state which has been interpreted in terms of structure (III).



Attempts were made to determine the molecular weight by mass spectrometry using a heated probe. No molecular ion at *m/e* 152 was detected; the highest mass was at *m/e* 58, corresponding to the anhydrous monomer. The base peak was at *m/e* 29 (corresponding to CHO⁺). Weaker peaks corresponded to CO⁺, CH₂O⁺, CO₂⁺, and C₂O₂⁺.

Solutions of glyoxal monohydrate in dimethyl sulphoxide were examined and a molecular-weight determination was attempted cryoscopically. Using dimedone as a standard, the cryoscopic constant was measured in triplicate as $5.47 \pm 0.10 \text{ K mol}^{-1} \text{ kg}^{-1}$. The apparent molecular weight of glyoxal monohydrate was found to be time-dependant; the initial value of 145 falling to 98 after 5 h. This suggests that glyoxal monohydrate exists in solution initially as a dimer and dissociates, probably to the monomer, on

standing. Similar cryoscopic results have been reported by Fenton and Jackson⁴ for glycolaldehyde (III).



The initial n.m.r. spectrum in solution in $(\text{CD}_3)_2\text{SO}$ consisted of a broad resonance at τ 4.85 and a sharp resonance at τ 5.00 which are assigned to the OH and CH resonances respectively. It appears that rapid exchange takes place since no spin-spin splitting was observed and the OH resonance is at higher value than that suggested by Casu *et al.*⁵ for axial or equatorial anomeric protons. This precludes any evidence for the stereochemistry of (II) using

n.m.r. correlations. The n.m.r. shifts may be compared to those in glycolaldehyde.⁶ However, OH splittings are observed in freshly prepared solutions in glycolaldehyde, presumably because of fewer anomeric OH groups. Construction of molecular models suggest forms (IIa) and (IIb) are likely on steric grounds. Both have a centre of symmetry and are, therefore, consistent with the vibrational spectra. It is noteworthy that a ring inversion of (IIa) converts the four equatorial OH groups into four axial groups which are sterically unfavoured; whereas a ring inversion of (IIb) converts this into an identical conformation of two axial and two equatorial OH groups. On energetic grounds we conclude, therefore, that glyoxal monohydrate exists as (IIb). This structure may be understood in terms of hydration of both carbonyl groups in glyoxal to form 1,1,2,2-tetrahydroxyethane followed by condensation of two of these molecules to form symmetrical tetrahydroxy-*p*-dioxan.

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