The spectral data were: ir ($CHCl_3$) 3.22, 3.30, 3.40, 6.27, 6.72, 6.95, 7.27, 9.35, 11.22, 14.32, 15.20 $\mu$; nmr ($CDCl_3$) $\tau$ 2.03–2.88 (m, 15 H, arom), 7.90 (s, 3 H, methyl); uv (ethanol) 234 nm max ($\epsilon$ 52,000), 286 nm max ($\epsilon$ 8000).

*Anal.* Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.96; H, 6.19.

**Direct Irradiation of *cis,trans*-2,3-Diphenyl-1-($\alpha$-styryl)cyclopropane.** A solution of 170 mg (0.574 mmol) of *cis,trans*-2,3-diphenyl-1-($\alpha$-styryl)cyclopropane in 250.0 ml of purified cyclohexane was irradiated for 2.5 hr under deoxygenated nitrogen[14] through a Corex filter ($\lambda \geq 260$ nm) with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. Nmr spectra taken before and after irradiation showed that 50% of the starting material had disappeared and that roughly equal amounts of the *trans,trans*-2,3-diphenyl-1-($\alpha$-styryl)cyclopropane and 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene had appeared.

**Photolysis Apparatus for Quantum Yields.** The "black box" irradiation apparatus[6] used a General Electric AH6 mercury arc in a deep parabolic reflector. The 12-cm beam was filtered through a three-compartment water-cooled solution filter (*vide infra*). The sample cell was maintained at 25 ± 0.2° and deoxygenated nitrogen[14] was bubbled through the photolysis solution.

**Filter Solutions.** Two filter solution systems were used. Filter I: cell 1, 1 *M* nickelous sulfate in 10% sulfuric acid; cell 2, 2 *M* cobalt sulfate in 10% sulfuric acid; cell 3, 0.1 m*M* bismuth trichloride in 10% hydrochloric acid. Transmission was 0% below 260 nm, between 320 and 335 nm, and above 355 nm. It was 2% at 342 nm (max) and 10% at 290 nm (max). Filter II: cell 1, 0.58 *M* nickelous sulfate in 10% sulfuric acid; cell 2, 1.29 *M* cobalt sulfate in 10% sulfuric acid; cell 3, 54.0 m*M* stannous chloride in 10% hydrochloric acid. Transmission was 0% below 310 nm and above 370 nm and 43% at 338 nm (max).[6]

**Actinometry.** Incident light was measured by potassium ferrioxalate actinometry[7] before and after each sample run and was monitored for transmission through the sample cell by an actinometer cell behind the sample cell during the sample run. The quantum yield for ferric ion reduction was taken to be 1.25 for the wavelength used.

**Quantum Yield Irradiations.** The general procedure was as follows. A sample of *trans,trans*-2,3-diphenyl-1-($\alpha$-styryl)cyclopropane was dissolved in purified cyclohexane and freshly recrystallized benzophenone (if any) up to a total volume of 730.0 ml. The actinometry and sample irradiation were then carried out and the solvent removed *in vacuo*. The sample was then analyzed by nmr; 10.0 mg of *p*-dioxane served as an internal standard. Very careful electronic integration of the vinyl proton portion of the nmr afforded an accurate determination of the absolute amounts of the *trans,trans*- and *cis,trans*-2,3-diphenyl-1-($\alpha$-styryl)cyclopropane stereoisomers present. The entire sample was then subjected to reversed-phase polystyrene bead liquid–liquid chromatography (*vide supra*). The two cyclopropane isomers were collected as one peak and again subjected to nmr analysis. Collection and analysis of separate fractions allowed nearly complete separation; however, the analytical results proved more simply obtained by direct assay of the one combined chromatographic peak. The 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene photoproduct was isolated from the chromatogram and assayed by weight. Its mass accounted for the remainder of the photolysis sample. The nmr analysis was calibrated with known mixtures of the cyclopropane isomers.

Specific data for individual irradiations are given below as follows: weight of hydrocarbon and additive (if any), filter system used, amount of light absorbed, quantum yield for the appearance of the cyclopropyl stereoisomer, mass of 1,2,3,4-tetrahydro-1,2-methano-1,3-diphenylnaphthalene isolated, quantum yield for the appearance of the methanonaphthalene, total conversion of starting material.

**Run QY-1.** *trans,trans*-2,3-Diphenyl-1-($\alpha$-styryl)cyclopropane, 293 mg, no benzophenone, filter I, 9.13 mEinsteins, 0.058, 0.029, 62.6 mg of methanonaphthalene, 0.023, 53%.

**Run QY-2.** *trans,trans*-2,3-Diphenyl-1-($\alpha$-styryl)cyclopropane, 302 mg, no benzophenone, filter I, 3.72 mEinsteins, 0.052, 0.023, 25.0 mg of methanonaphthalene, 0.023, 23%.

**Run QY-3.** *cis,trans*-2,3-Diphenyl-1-($\alpha$-styryl)cyclopropane, 298 mg, no benzophenone, filter I, 4.50 mEinsteins, less than 0.0067, less than 0.0067, no detectible methanonaphthalene, less than 3%.

**Run QY-S1.** *trans,trans*-2,3-Diphenyl-1-($\alpha$-styryl)cyclopropane, 295 mg, 4.069 g of benzophenone, filter II, 1.33 mEinsteins, 0.340, 0.340, no methanonaphthalene, 0, 45%.

**Run QY-S2.** *trans,trans*-2,3-Diphenyl-1-($\alpha$-styryl)cyclopropane, 299 mg, 2.989 g of benzophenone, filter II, 0.710 mEinstein, 0.345, 0.345, no methanonaphthalene, 0, 25%.

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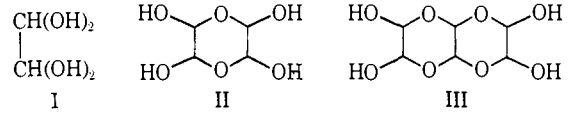
# The Structure of Glyoxal in Water

**Earl B. Whipple**

*Contribution from the Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591.* *Received March 11, 1970*

**Abstract:** The proton magnetic resonance spectrum of aqueous glyoxal is interpreted to show that the principal species present at concentrations below 40% are the hydrated monomer and two dimers whose structures contain a five-membered dioxolane ring.

Glyoxal is generally believed to exist in the form of hydrated oligomers in aqueous solutions, but neither the extent of association nor the structures it produces are known with any certainty. The lowest order oligomers have been assumed, without much evidence, to have the structures I–III.[1]




I II III

The proton magnetic resonance spectrum of aqueous glyoxal (Figure 1), which is partially obscured by the water line unless the temperature is elevated, is quite complicated, giving as many as 12 resolvable lines at 60 MHz and up to 16 in sufficiently strong magnetic fields. None of its lines occurs in the region characteristic of aldehyde protons, and none is affected by isotopic exchange in heavy water. The complex spectrum

(1) H. Raudnitz, *Chem. Ind.*, 327 (1944); "General Chemistry of Glyoxal," Union Carbide Corporation Bulletin 41296A, New York, N. Y., 1967, p 27.

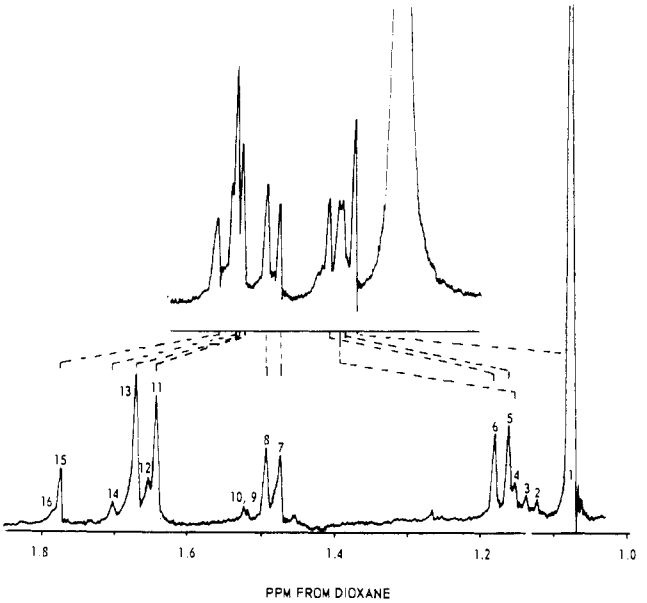



Figure 1. Proton magnetic resonance spectrum of aqueous glyoxal at 60 and 220 MHz. The 220-MHz spectrum was taken at higher dilution, changing the relative intensities of some lines.

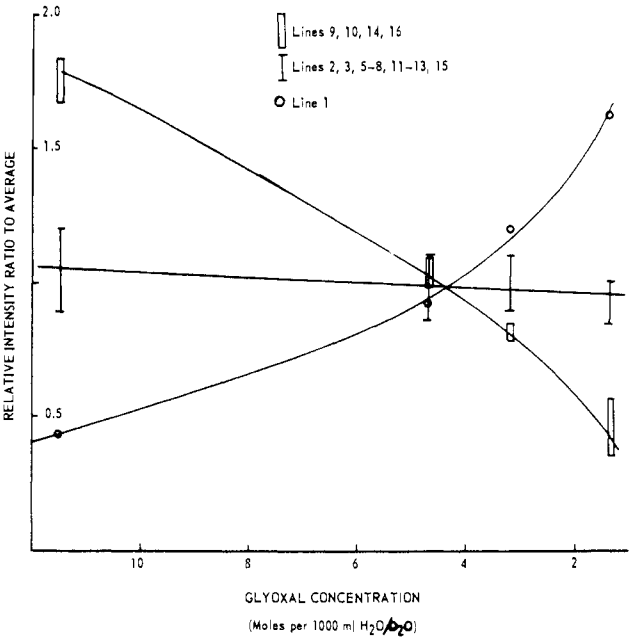



Figure 2. Fractional changes in relative (to line 7) intensities of numbered lines in Figure 1 *vs.* glyoxal concentration.

in Figure 1 must therefore result entirely from hydrated oligomers formed by processes in which no C–H bonds are broken.

The resolved lines can be classified initially according to the degree of oligomerization, based on the reversible changes that occur in their relative intensities when the glyoxal concentration is varied. If the position of the equilibrium

$$nG \rightleftharpoons G_n$$

is defined by

$$K_n = \frac{[G_n]}{[G]^n}$$

and a similar set of definitions applied to an oligomer of degree $m$, then the ratio of concentration of the two species in dilute solutions is given approximately by

$$R_{nm} \equiv \frac{[G_n]}{[G_m]} = K_{nm}[G]^{n-m} \quad (K_{nm} \equiv K_n/K_m)$$

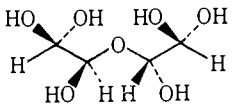
As the solution is diluted the relative concentration of lower order oligomers must increase.[2] The effects of dilution on the intensitites of the resolved lines in Figure 1 are shown in Figure 2, and on the basis of this behavior the lines can be assigned to first-, second-, and higher order species. The single line observed at highest field (line 1 in Figure 1) for the lowest order species can be assigned with confidence to the hydrated monomer, I. No effort will be made presently to assign the four rather weak lines observed for third- or higher order species, since these do not appear to be major components of the solution of glyoxal at concentrations below 40%. Instead, attention is focused on the ten resolved lines assigned to hydrated dimers of glyoxal.[3]

(2) This follows directly from the relation

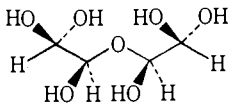
$$\sum_{n=1}^{\infty} n[G_n] = \sum_{n=1}^{\infty} nK_n[G]^n = C$$

where $K_1 = 1$, and $C$ is the glyoxal concentration expressed as monomer.

An exhaustive list of structural possibilities could begin with the open chain dimer, IV, for which there are two structural possibilities corresponding to dl and meso forms, respectively. Each should give rise to an nmr spectrum consisting of two superimposed four-line AB patterns. Cyclization of IV can lead to five

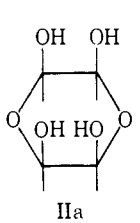


dl
IVa

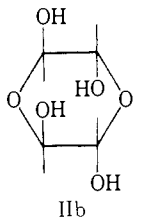


meso
IVb

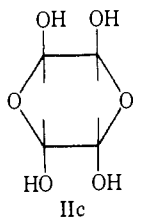
geometrical isomers of structure II. In four of these, IIa–IId, the four ring protons are magnetically equivalent (assuming fast conformational averaging) and each structure should give rise to a single line. The fifth structure contains two nonequivalent pairs of vicinal



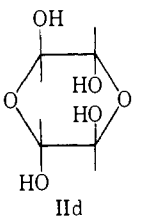
IIa



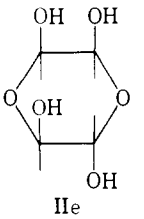
IIb



IIc



IId

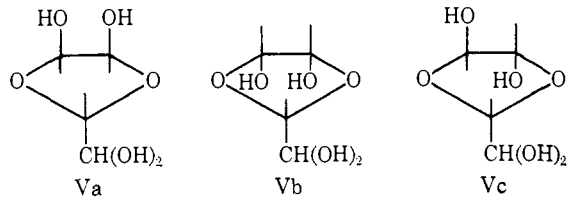


IIe

protons, and its spectrum should consist of two different AB patterns. Still another set of dimeric structures can be generated through cyclic acetal formation at a

(3) The relative intensity of line 4 has been observed to vary in different glyoxal preparations, and it is suspected to be due at least in part to an impurity.

single carbon, the three structures so derived being listed below as Va–Vc. Structures Va and Vb each




contain one equivalent and one nonequivalent vicinal proton pair, while Vc contains two nonequivalent pairs. The structures are classified in Table I according to the

**Table I.** Classification of Glyoxal Dimer Structures According to Proton Equivalence

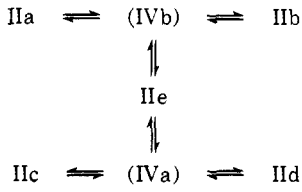
| Structure | Spectrum type[a] |
|---|---|
| IIa–IId | $A_4$ |
| IVa, IVb | AB |
| Va, Vb | AB + $A_2$ |
| IIe, Vc | AB + CD |

[a] J. A. Pople, W. G. Schneider, and H. J. Bernstein "High Resolution Nuclear Magnetic Resonance," McGraw Hill, New York, N. Y., 1959, Chapter 6.

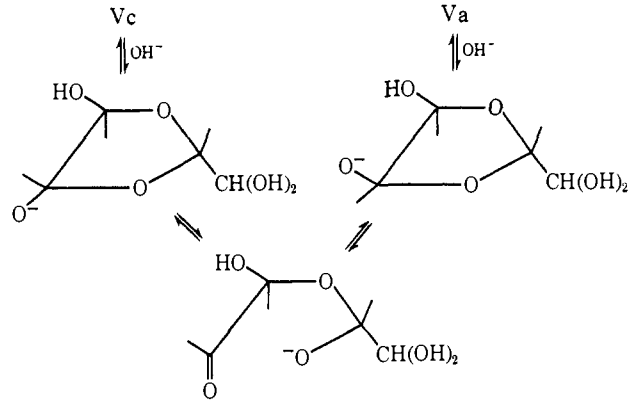
type of nmr spectrum produced by their skeletal protons.

On changing the magnetic field, it becomes apparent (Figure 1) that four of the seven prominent nmr lines from the dimer (lines 5, 6, 7, and 8) form an AB pattern with $J \cong 4$ Hz. Since no other line occurs whose intensity equals the sum of all four members of the AB pattern, these four lines cannot be assigned to structure Va or Vb. The presence of a second AB pattern in the same molecule is ambiguous, since two lines (11 and 13) occur with the necessary intensity, but no field-independent splitting is resolved. However, spin decoupling experiments verify the presence of a weak coupling of line 11 to lines 7 and 8, demonstrating that two AB patterns do occur in the same molecule. The most prominent dimer must therefore have either structure Vc or IIe, and at least one other dimeric species must be present in lesser amounts (lines 2, 3, 12, and 15).

Addition of either acid or base causes pronounced changes in the spectrum. As a broad generalization, the low-field lines are base sensitive, appearing to undergo coalescence into a single, broadened line on addition of hydroxide ion while the high-field region of the spectrum is broadened by acids. The middle region of the spectrum, which consists mainly of one of the prominent doublets (lines 7 and 8), is not very sensitive to pH changes. The temperature-dependent, base-catalyzed coalescence of the low-field lines is shown in Figure 3.[4] The coalescence of the three most prominent low-field lines is indicative of rapid interconversion among at least two chemical structures, and the analogy of the glyoxal oligomers to sugars points to base-catalyzed interconversion processes closely akin to mutarotation. This involves opening one of the acetal bonds followed by rotation and re-formation of the acetal with different configurations about either or both of the carbon atoms attached to one ring oxygen. Assuming that the process involves only one ring oxygen at a time, the possible one-step interconversions among isomers of II are the following. Nowhere in this




scheme, which involves besides IIe only structures in which the two vicinal proton pairs are equivalent, is a means provided whereby the members of one AB group can be permuted without exchanging the other. Structure Ve, on the other hand, provides a natural explanation of the different responses of the low-field and high-field regions of the spectrum to changes in pH. The reactions most sensitive to acid catalysis would be those of the appendent $-CH(OH)_2$ groups, which behave like the hydrated monomer, while base catalysis leads most readily to ring-opening processes that interchange isomers of V, *e.g.*,



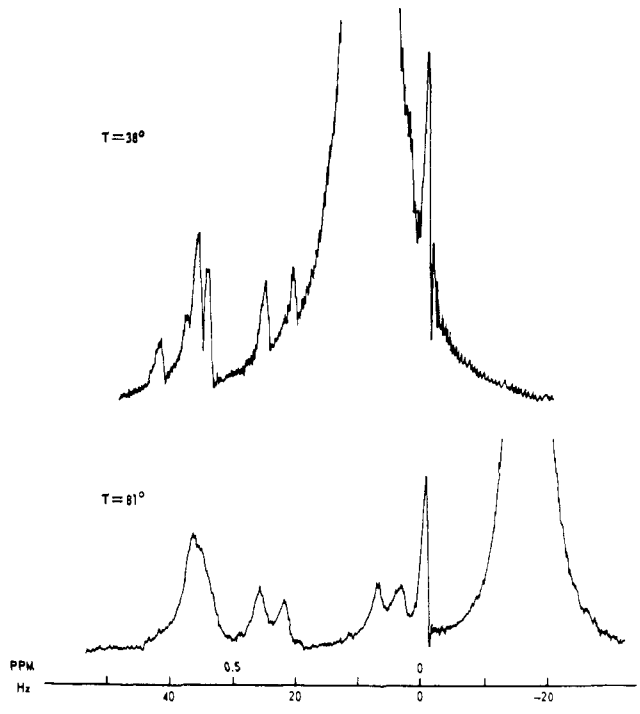




Figure 3. Proton magnetic resonance spectrum (60 MHz) of aqueous 40% glyoxal containing a few drops of 1 *N* NaOH.

(4) The extent to which the solution can be made basic is limited by the conversion of glyoxal to glycolic acid at pH >7.

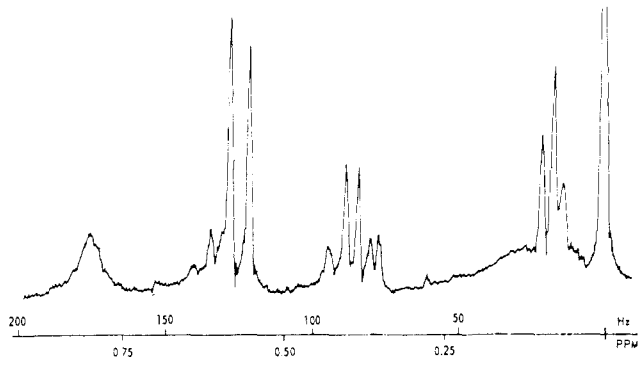



Figure 4. Proton magnetic resonance spectrum (220 MHz) of 40% aqueous glyoxal containing 5% wt added sodium tetraborate.

The rate of mutarotation in sugars is known to be more sensitive to base than to acid catalysis,[5] while acetal formation is catalyzed by acids.

The principal dimer of glyoxal therefore has the structure Vc. A second isomer is present which accounts for line 15 in Figure 1 and has either structure Va or Vb. One member of the AB pattern present in this second structure consists of lines 2 and 3 in Figure 1, while the other doublet is hidden under lines 7 and 8. The magnitude of the vicinal coupling constant (3.0 *vs.* 4.3 Hz in Vc) and the chemical shifts that occur in borate complexes both indicate that this isomer has structure Va, although Vb cannot be rigorously excluded. This dimer is about 20% as abundant as Vc. A third dimer, present in even smaller amounts, is responsible for line 12 and may be due to one of the 1,4-dioxane structures IIa–IId.

Measurements of the monomer and total glyoxal concentrations in a series of dilute solutions yield an approximate value of the equilibrium constant for dimerization of $K_2 \simeq 1.2$. This implies that the monomer predominates at glyoxal concentrations below 1 *M*. At higher glyoxal concentrations, the monomer tends to level off at about 1 *M* due to dimerization and higher order oligomerization, the predominant species in glyoxal solutions between 1 and 10 *M* being dimers.

The assigned dimer structures are confirmed by the changes in the nmr spectrum that occur on the addition of borate salts, as shown in Figure 4. All lines assigned to the cis isomer Va (or Vb) are intensified, shifted, and/or broadened (permitting those hidden under lines 7 and 8 to be observed), while none of the lines assigned to the trans structure, Vc, are affected. The formation of complexes with boric acid is a characteristic reaction of 1,2-diols which is subject to the rather severe steric requirements that the hydroxyl groups involved be approximately coplanar.[6] The fact that the only glyoxal dimer affected by boric acid has the ring hydroxyls in a cis configuration is a necessary consequence of this requirement. Moreover, the remarkable strength[7] of glyoxal–boric acid complexes is, on the basis of the same requirement, much easier to understand if the glyoxal structures are present as five-membered rings rather than six.

The fact that the principal dimers have structures other than those previously thought to exist raises obvious questions about the presumed structures of the trimer.[1] Recent work with model compounds suggests that, of the four trimer lines assigned in Figures 1 and 2, at least two and probably three are due to coupled dioxolane rings.[8]

## Experimental Section

All samples were commercially available (Union Carbide Corporation) and were used without purification. Nmr spectra were recorded on standard (Varian Associates) 60-and 220-MHz spectrometers. The latter instrument is supported by National Science Foundation Grant No. GB12278 and by grants from the Research Corporation and Sloan Foundation to a consortium at the Rockefeller University.

(5) C. Hudson, *J. Amer. Chem. Soc.*, **29**, 1572 (1907).

(6) J. Boseken, *Advan. Carbohydrate Chem.*, **4**, 190 (1949).

(7) B. Pesetsky and N. R. Eldred, *Tetrahedron*, **25**, 4137 (1969).

(8) J. M. Kliegman and E. B. Whipple, unpublished results.