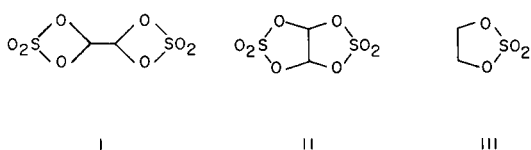


Glyoxal Sulfate. Partial Structure Determination by Dipole Moments

Irene J. Tyminski (1) and Kenneth K. Andersen

Department of Chemistry, University of New Hampshire

The structure of glyoxal sulfate, $C_2H_2O_8S_2$, has never been completely determined; it has been postulated to be I or II with the latter capable of *cis-trans* isomerism, (2, 3).



We wish to present evidence based on dipole moment measurements which excludes structure II with the hydrogens *trans* to one another, *trans*-dihydro-1,3,2-dioxathiole-(1,3,2)dioxathiole-2,2,5,5-tetraoxide, as a possible structure.

The *trans* form of II has a center of inversion. This excludes it having a dipole moment due to cancellation of the various bond moments. The *cis* isomer of II would have a dipole moment which might be calculated from the dipole moment of ethylene sulfate (III).

We have measured the dipole moment of glyoxal sulfate as 5.35 D and of ethylene sulfate as 5.64 D both in dioxane. Taking the dihedral angle between the two five-membered rings of *cis*-glyoxal sulfate (II) as 120° , one calculates its dipole moment, using the moment of ethylene sulfate to represent the group moment of each of the five-membered rings, as 5.64 D in fair agreement with the observed value.

However, structure I is also expected to have a dipole moment even though one of its conformers, the one with the hydrogens *anti*, has a center of inversion and consequently a zero dipole moment. This expectation follows by analogy with 1,1,2,2-tetrachloroethane which has a dipole moment of 1.9 D in benzene (4). Therefore, our measurements cannot rule out structure I as a second possibility.

The dipole moment of ethyl sulfate was measured as 4.43 D in dioxane. It is not a good model for determining the moment of a five-membered cyclic sulfate. Presumably, this is due to the rotational possibilities around the SO bond allowing the methyl groups to assume various orientations. This permits partial cancellation of the CO bond moments which is not possible in a five-membered cyclic sulfate.

EXPERIMENTAL

The dipole moments were determined using a Wissenschaftlich-Technische Werkstätten Dipolmeter Type DMO1 fitted with a DFL2 cell thermostated at $24.90 \pm 0.02^\circ$. The cell was calibrated using nitrogen, cyclohexane, and benzene. The calculations of the dipole moments were carried out by computer (IBM 1620) using the program of Allinger (5) which was based on the procedure of Halverstadt and Kumler (6). Molecular refractivities were calculated as the sum of standard bond refraction constants (7). The dioxane was purified by treatment with alumina followed by refluxing over sodium for several days and was distilled off as needed. Melting points are capillary melting points and are corrected. Infrared spectra were determined on a Perkin-Elmer 337 grating spectrophotometer as mulls in Halocarbon and Nujol and the n.m.r. spectra on a Varian A-60 spectrometer in acetone- d_6 with tetramethylsilane as the internal standard.

Glyoxal Sulfate.

This was prepared as in the literature from 1,1,2,2-tetrachloroethane, mercuric sulfate, and 60% fuming sulfuric acid (8). Recrystallization from ether gave white crystals, m.p. 183° dec., (lit. (3) m.p. $176-177^\circ$), ν max in cm^{-1} 3074 (CH), 1430, 1440, 1240, and 1216 (SO_2) (9), n.m.r., 2.32 τ (singlet), J_{13CH} 217 cps, J_{HH} 4.6 cps.

Anal. Calcd. for $C_2H_2O_8S_2$: C, 11.01; H, 0.92; S, 29.40. Found: C, 11.10; H, 0.92; S, 29.60.

Ethylene Sulfate (III).

Compound III was prepared using a procedure devised by Lichtenberger for other sulfates (10). Sulfuryl chloride (47.9 g., 0.355 mole) was added dropwise with stirring to ethylene glycol (20.8 g., 0.355 mole) at $40-50^\circ$. The temperature rose to $55-65^\circ$ during the addition and the rate of addition was controlled to maintain this temperature. The clear solution was degassed by bubbling in nitrogen for a few minutes. After standing overnight, the mixture was heated to 150° over a 2.5 hour period and held at this temperature for 15 minutes. The dark viscous liquid was sublimed at 80° (1 mm) to give ethylene sulfate (1.62 g., 0.0131 mole) in 3.9% yield. The product was purified by recrystallization from benzene, drying in vacuum, followed by sublimation at 60° (1 mm), m.p. $96.5-97.5^\circ$, (lit. (11) $97-98^\circ$), ν max in cm^{-1} , 3062, 2991, and 2919 (CH), 1373 and 1196 (SO_2) (9), n.m.r., 5.08 τ (singlet) lit. (12) 5.32 in a carbon tetrachloride-chloroform mixture.

Anal. Calcd. for $C_2H_4O_4S$: C, 19.35; H, 3.25; S, 25.83. Found: C, 19.31; H, 3.18; S, 25.74.

Ethyl Sulfate.

A commercial preparation was washed with ice water, dilute sodium bicarbonate solution, distilled under reduced pressure,

dried over Linde Molecular Sieves Type 4A, and redistilled b.p. 85° (7 mm), $n_D^{24.9}$ 1.39850, (lit. (13) b.p. 93.0-93.2 (13 mm) and n_D^{20} 1.40010).

Dipole moment data.

	Glyoxal Sulfate	Ethylene Sulfate	Ethyl Sulfate
α	40.1470	44.3857	27.1439
β	1.2742	0.4432	0.1730
ϵ_1	2.2050	2.2017	2.2084
d_1	1.02826	1.02822	1.02832
$P_{2\infty}$	613.86 c.c.	670.28 c.c.	432.87 c.c.
μ	5.35	5.64	4.43
error	0.04	0.11	0.08

Acknowledgments.

We are indebted to Professor J. J. Uebel for supplying the dipole moment program and for many helpful discussions. The n.m.r. spectrometer was purchased in part by funds from an NSF departmental grant for which we are grateful. The dipolmeter was purchased with funds from the National Institutes of Health, grant number GM-10244.

REFERENCES

- (1) Abstracted from the Ph.D. Thesis of I. J. T., University of New Hampshire, 1967.
- (2) D. S. Breslow and H. S. Skolnik in "The Chemistry of Heterocyclic Compounds, Multi-Sulfur and Sulfur and Oxygen Five and Six-Membered Heterocycles," Part 1, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1966, pp. 25 and 26.
- (3) W. Baker and F. B. Field, *J. Chem. Soc.*, 86 (1932).
- (4) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, 1963, p. 54.
- (5) N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).
- (6) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).
- (7) A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 514 (1952).
- (8) P. Ruggli and E. Henzi, *Helv. Chim. Acta.*, **12**, 362 (1929).
- (9) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 364.
- (10) J. Lichtenberger and R. Lichtenberger, *Bull. Soc. Chim., France*, **15**, 1002 (1948).
- (11) E. T. Kaiser, M. Panar, F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 602 (1963).
- (12) J. G. Pritchard and P. C. Lauterbur, *ibid.*, **83**, 2105 (1961).
- (13) C. P. Smyth and C. S. Hitchcock, *ibid.*, **54**, 4631 (1932).

Received January 2, 1968

Durham, New Hampshire 03824