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THE NMR AND CONFIGURATION OF GLYOXAL OSAZONES

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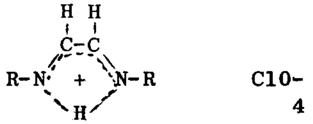
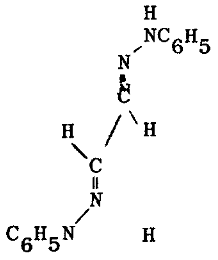
In our recent report we established that the configuration of conjugated 1,2-diimines of glyoxal was *E*-*E*[1]. This was accomplished by analysis of their NMR spectra and by titration with 0.1 N $HClO_4$ in acetic acid. In the former case the appearance of the aldimine proton as a single resonance line precluded a mixture of isomers, i.e. *E*-*Z* , while in the latter, the uptake of 1 mole of $HClO_4$ per mole of diimine to give a planar, highly-stabilized, five-membered ring containing the diimine linkage and an additional proton

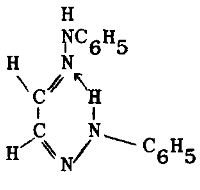


was only allowed sterically if the conformations around the C=N bonds were *E*-*E*.

In a recent paper, Chapman, et al, concluded that the most sterically stable form of osazones is *E* - *E* [2a]. Furthermore from analysis of its NMR spectrum they concluded that glyoxal bisphenylhydrazone exists in a non-chelating[2b], *E* - *E* configuration. In this communication we confirm this conclusion and offer *chemical* evidence for its validity.



non-chelating

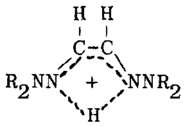


chelating

The glyoxal osazones prepared for this study[3] are given in the table along with the position (in ppm from TMS) in the NMR of their aldiimine resonances, and the result of their titration with 0.1 N $HClO_4$ in acetic acid (as nitrogen equivalents per mole)[4].

Compound	N= C<u>H</u>	Nitrogen eq/mole
$(Me_2NN=CH-)_2$	7.30(s)	0.98
$(C_6H_5NHN=CH-)_2$	7.68(s)	1.00
$(p\text{-}O_2NC_6H_4NHN=CH-)_2$	8.04(s)	1.08
$((C_6H_5)_2NN=CH-)_2$	7.1-7.4 (under arom.)	0.79
$(H_2NN=CH-)_2$	7.57(s)	1.04

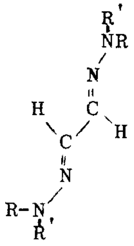
The position of the resonance line in the NMR spectrum for the aldimine protons in these compounds coincides with that observed for mono-hydrazones (7-8 ppm)[5]. The fact that they appear as singlets is evidence that only one isomer, either Z-Z or E-E, is present[6]. Similar to the case of conjugated diimines[1], the uptake of only one proton per osazone linkage is explained by the formation of the following ring system:



ClO_4^-

This structure is only possible if the configuration about the imine groups is E- because rotation of the Z -configuration around the central carbon-carbon bond would be severely restricted by the substituted amino groups.

We therefore conclude from the above that these glyoxal osazones do indeed exist in a non-chelating (when R=H), E-E configuration



Further studies are presently underway to elucidate the conformation about the central carbon-carbon bond by dipole moment measurement.

(1) J. M. Kliegman and R. K. Barnes, Tetrahedron Letters, No. 24, 1953 (1969); Tetrahedron, in press.

(2a) O. L. Chapman, R. W. King, W. J. Welstead, Jr., and T. J. Murphy, J. Am. Chem. Soc., **86**, 4968 (1964).

(2b) cf Ref. 2a in which chelating refers to internal hydrogen bonding.

(3) All compounds prepared are known compounds and had the proper Melting and boiling points.

(4) Titration of Schiff bases with 0.1 N $HClO_4$ in acetic acid represents one of the strongest systems for total basicity, see for example, S. K. Freeman, Anal. Chem., **25**, (11), 1750 (1953).

(5) G. J. Karabatsos and C. E. Osborne, Tetrahedron, **24**, 3361 (1968); G. J. Karabatsos and R. A. Taller, ibid, **24**, 3557 (1968); and references therein.

(6) If the Z-E were present, the aldimine protons would be magnetically non-equivalent and one would expect to see a pattern indicative of an AB pair.