

NUCLEAR MAGNETIC RESONANCE STUDY OF THE STRUCTURE OF GLYOXALDIHYDRAZONE

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Abstract

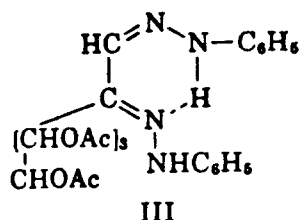
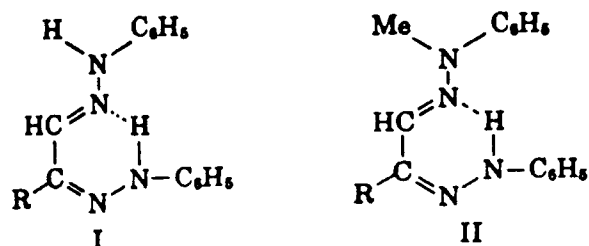
Study of the nuclear magnetic resonance spectra of glyoxaldihydrazone in dimethylsulfoxide and deuteriochloroform leads to the conclusion that this compound exists predominantly in non-chelate structure.

Introduction

Evidence has been presented that sugar phenylosazones contain a chelate ring both in solution and in the crystal [1-4]. Mester [2,5] has favored the chelate structure I on the basis of similarities in properties of glucose phenylosazone (I, $R=C_4H_9O_4$) and glucose 1- methyl- phenyl-2- phenylosazone (II, $R=C_4H_9O_4$). Wolfrom, Fraenkel, Lineback, and Komitsky [3] have favored chelate structure III for

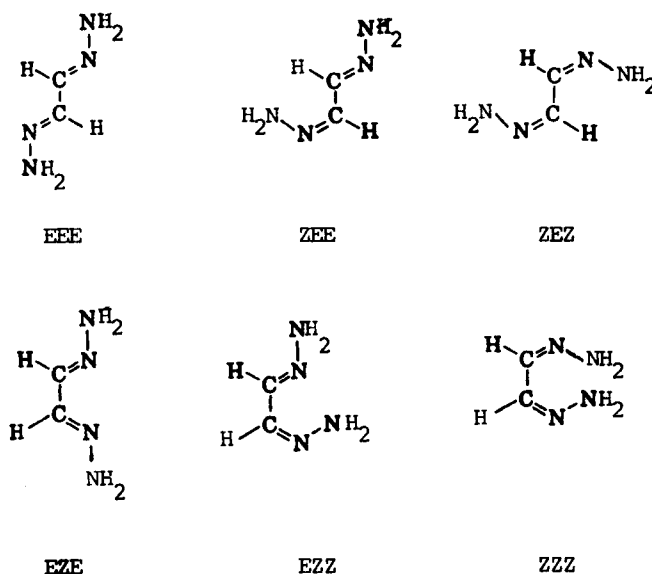
Crystalline xylose p-bromo-phenylosazone shows an arrangement of carbons and nitrogens analogous to I in a two-dimensional X-ray analysis [4].

We have examined the structure of the basic skeleton, glyoxaldihydrazone (IV) in deuteriochloroform, dioxane and especially in dimethyl sulfoxide solutions. Dimethyl sulfoxide is a particularly useful solvent for such studies because of the solubility of glyoxaldihydrazone in this solvent and the reduced rate of exchange of protons bounded to heteroatoms [6,7].



tetraacetylglucose phenylosazone on the basis of nuclear magnetic resonance studies in deuteriochloroform.

Keywords: Glyoxaldihydrazone, Chelating and non-Chelating Conformations



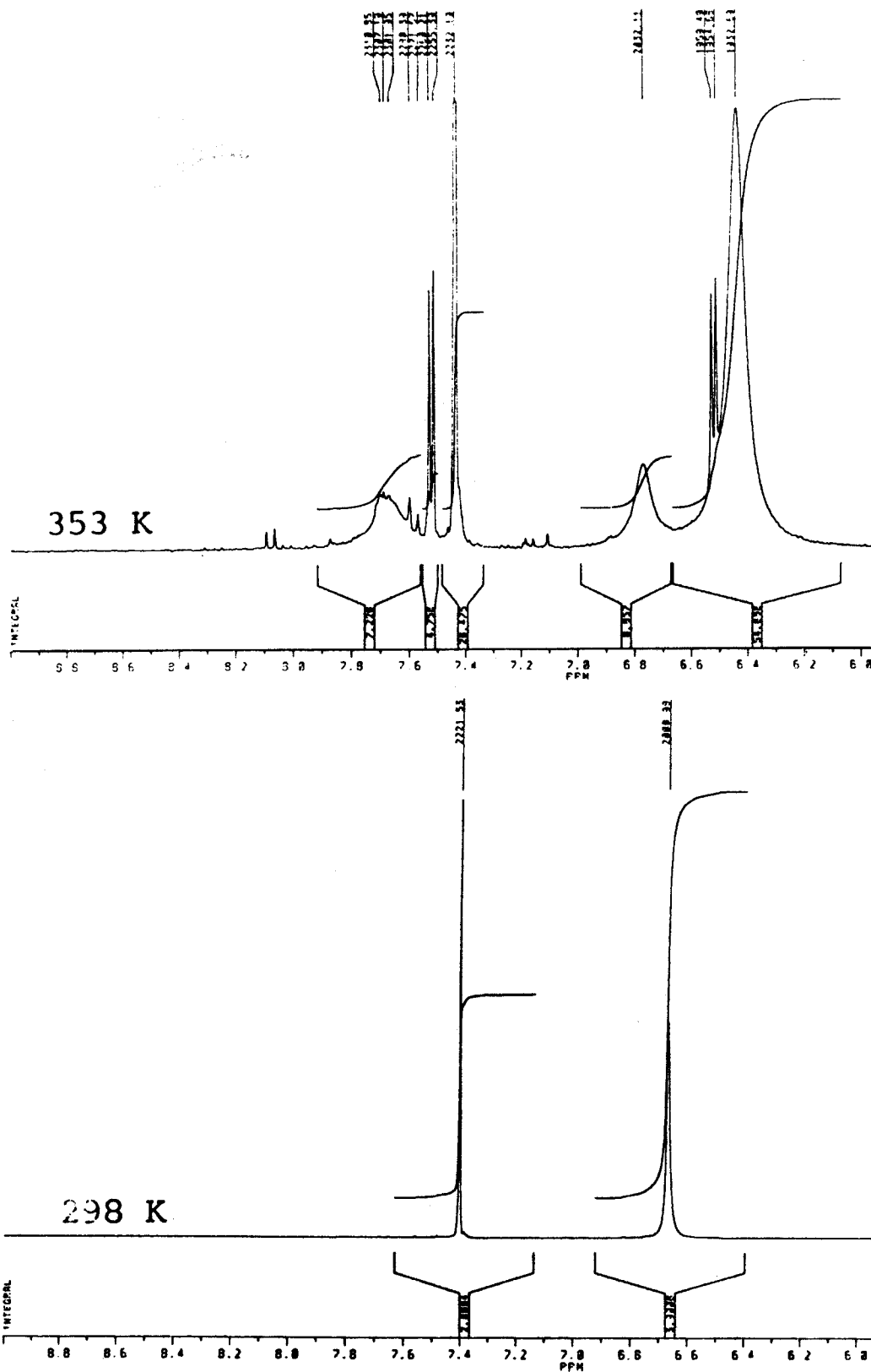


Figure 1. ¹H-NMR spectra of glyoxaldehydehydrazone in DMSO-d₆ at different temperatures.

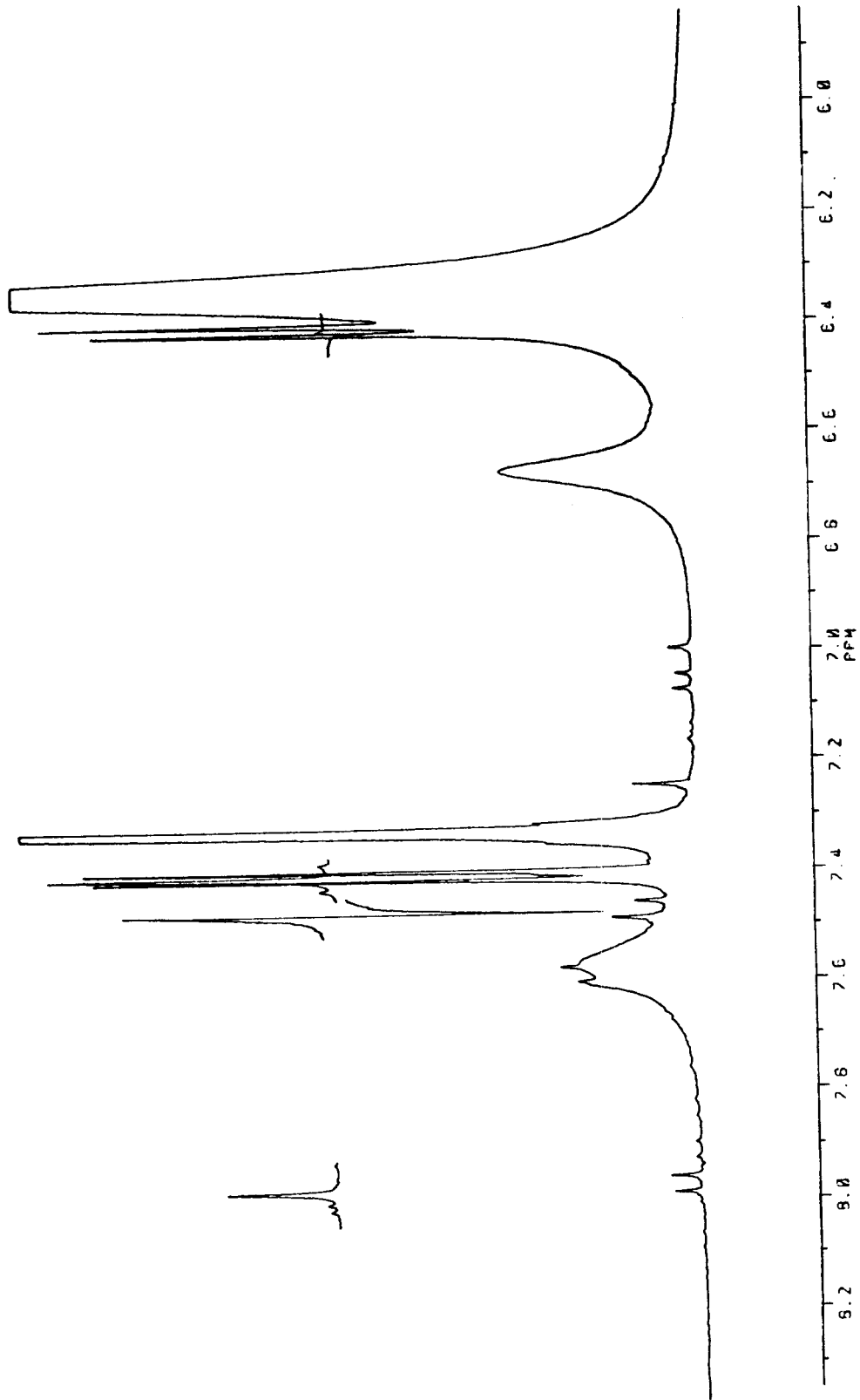


Figure 2. The decoupled spectra of glyoxal dihydrazone at 353 K.

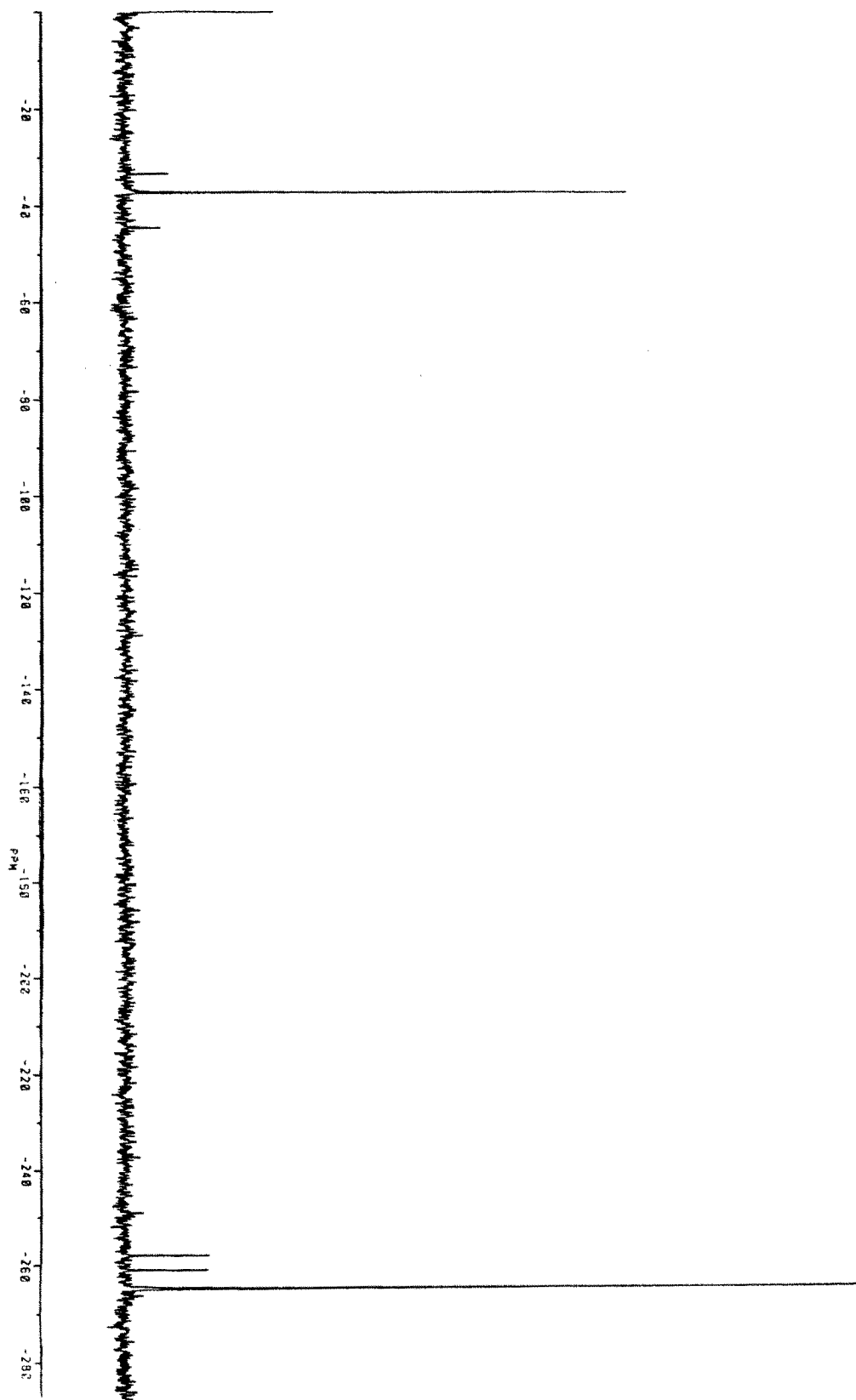


Figure 3. ^{15}N -NMR spectrum of glyoxaldehydehydrazone in DMSO-d_6 at 308 K.

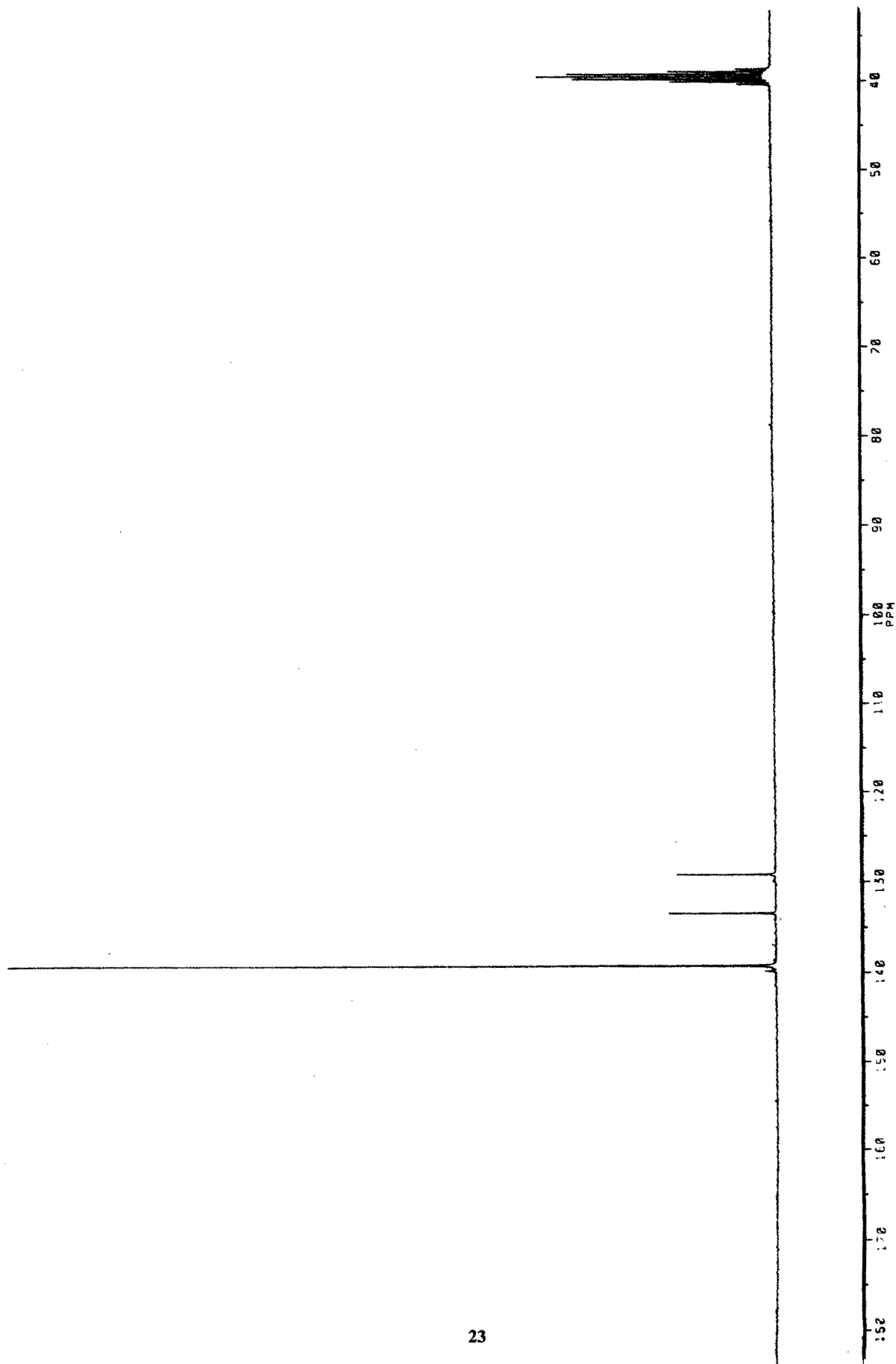


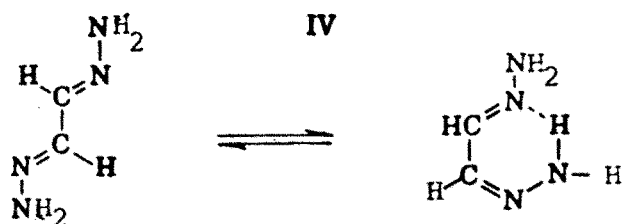
Figure 4. ¹³C-NMR spectrum of glyoxaldihydrazone in DMSO-d₆ at 308K.

Previously, Chapman [8], Kliegman [9], and Pigenet [10], concluded that the most sterically stable form of osazones is E,E. Chapman and his co-workers from the analysis of ^1H -NMR spectrum of the glyoxal bisphenylhydrazone concluded that it exists in a non-chelating E,E configuration. In this work, we confirm the previous conclusion and offer more data on the basis of ^1H -, ^{13}C -, and ^{15}N -NMR spectroscopy.

Results and Discussion

The ^1H -NMR spectra of the title compound at various temperatures in DMSO-d_6 are shown in Figure 1. In the low-temperature region (298 K), the sharp low field singlet at δ 7.40 is assigned to the olefinic protons of the (EEE) conformation and the band at δ 6.66 (temperature dependent) is assigned to the protons on the nitrogens. By raising the temperature (353 K), a set of new lines appear in the spectrum which we have assigned to the new conformation that has been populated by the change of the temperature. Here we have shown that the new conformation is EZZ, which could make internal hydrogen bonding. On the basis of the decoupled spectra at 353 K (Figure 2), the doublets at δ 7.60 ($J=5\text{Hz}$) and δ 6.53 ($J=5\text{Hz}$) are assigned to the olefinic protons and the broad bands at δ 6.75 and δ 7.65 are assigned to the NH_2 protons of the minor conformation that could participate in the hydrogen bonding with solvent. The doublets at δ 7.58 ($J=8.5\text{ Hz}$) and δ 8.05 ($J=8.5\text{ Hz}$) are related to each other and are assigned to the protons that participate in the internal hydrogen bonding. To confirm this minor conformation we have taken the ^{15}N -NMR and ^{13}C -NMR spectra of (IV) at 308K. The only conformation in the S-Cis conformation that shows four nitrogen chemical shifts is EZZ. The ^{15}N -NMR spectrum (Figure 3) shows two lines at -37.3 and -264.9 ppm for $=\text{N}$ - and NH_2 nitrogen chemical shifts respectively, and four lines at -33.4, -44.6, -258.1 and 261.1 ppm for four different nitrogens in the EZZ conformation.

The ^1H -NMR spectrum of IV in CDCl_3 show the same dynamic effects. The only difference between these two solvents is that in the dimethyl sulfoxide at room temperature the minor conformation is not detectable but in the deuteriochloroform at room temperature the minor conformation is detectable (about 5%). The ^{13}C -NMR spectrum of (IV) at 308K in DMSO-d_6 is consistent



with the presence of the two conformations. The major conformation shows a singlet at 139.1 ppm and the minor conformation shows two singlets at 129.1 and 133.4 ppm (Figure 4).

Experimental Section

General. Melting points and boiling points were uncorrected. ^1H -NMR and ^{13}C -NMR spectra were obtained on a Bruker AC 300 P (300 MHz, ^1H ; 75 MHz [^{13}C ; 30 MHz ^{15}N]) with Me_4Si as internal standard.

Glyoxaldihydrazone (IV). Aqueous glyoxal (36 ml of 40%, 0.33 mole) was added dropwise with constant stirring to an excess of hydrazine (approx. 75 ml) cooled by means of an ice bath. The white crystalline product which formed was filtered on a sintered glass filter, washed with a few milliliters of cold 95% ethanol, and dried over P_4O_{10} in vacuo. The product recrystallized from absolute ethanol gave a melting point of 97-99°C; yield, approx. 60%.

Acknowledgements

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References

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