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NUCLEAR MAGNETIC RESONANCE SPECTRUM OF 1,3-CYCLOHEXANEDIONE DIOXIME

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1,3-Cyclohexanedione dioxime has three isomers concerning to the orientation of two hydroxyimino groups as illustrated in Fig. 1.

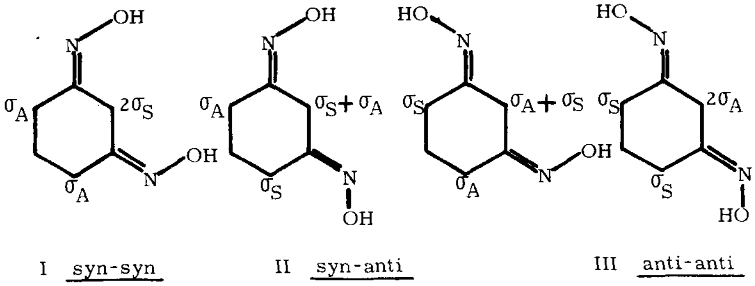

FIG. I THREE ISOMERS OF 1,3-CYCLOHEXANEDIONE DIOXIME

They are denoted as syn-syn, syn-anti, and anti-anti structure with respect to 2-methylene groups, respectively. NMR spectra of these three isomers are expected to give different features considering the paramagnetic and electric anisotropy effect of the hydroxyimino groups. The α-methylene and α-methine proton shift are split into two peaks in monoximes because of the anisotropy effect of the hydroxyimino group[*1]. This anisotropy effect is attributed to the lone pair electrons of the nitrogen atom from the study of oxime hydrochlorides.[1)] In this paper, we wish to report the anisotropy effect due to two hydroxyimino groups of the 1, 3-cyclohexanedione dioxime.

When shielding constants of methylene protons adjacent to a hydroxyimino group are expressed as σ_S and σ_A, the values for 2-methylene group are $2\sigma_S$ for I, $\sigma_S + \sigma_A$ for II, and $2\sigma_A$ for III, where the subscripts S and A denote syn and anti, respectively. Proton shift due to 2-methylene group is expected to be triplet in which each peak is assigned to the structures I, II, and III, respectively.[*2] If the anisotropy effect is the predominant cause of the difference in shielding constants of 2-methylene protons , separations between the peaks of I and II, and of II and III are both expected to be $|\sigma_S - \sigma_A|$, which is 0. 26 ppm in the case of cyclohexanone oxime[1)].

An NMR spectrum of 1, 3-cyclohexanedione dioxime[*3] is given in Fig. 2. Observed peaks of 2-methylene groups are 3. 025, 3. 233 and 3. 475 ppm from TMS. The peak at 3. 233 ppm is definitely assigned to the structure II, but the assignment of the other peaks is not determined because the sign of the value $\sigma_S - \sigma_A$ is ambiguous at present.

[*1] The α-methyl proton is not split into two peaks in ordinary solvents other than the aromatic ones .

[*2] In this paper, mixtures of three isomers described above are studied.

[*3] NMR spectrum of the sample was recorded by a Varian A-60 spectrometer in DMSO-d_6 solution. TMS was used as internal standard.

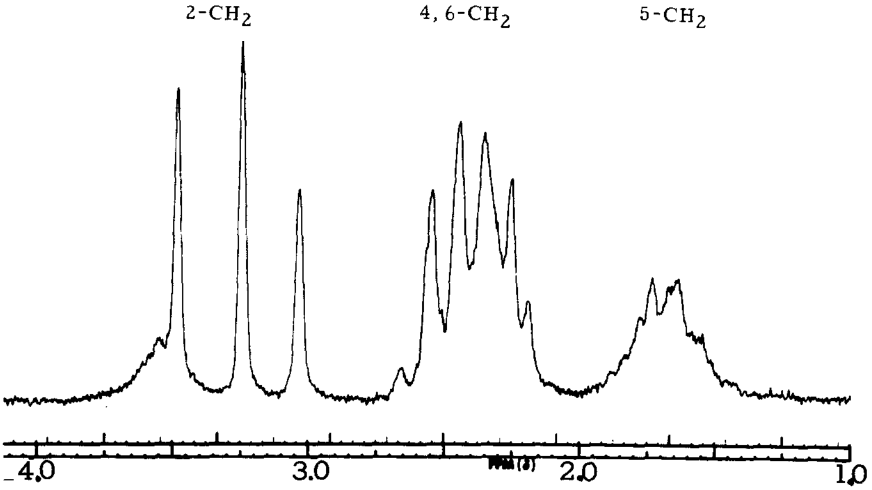

FIG. 2 NMR SPECTRUM OF 1,3-CYCLOHEXANEDIONE DIOXIME. DMSO-$\underline{d}_6$ solution, room temperature, internal standard (TMS)

The evaluation of σ_S and σ_A will be discussed theoretically in the other publication$^{2)*4}$. The separations between both side peaks and central one are 0.208 and 0.242 ppm and the discussion mentioned above is not exactly satisfied. However, the measurement at 150°C shows that both separations become almost equal (0.242 ppm.). It might be concluded that the structure of 1,3-cyclohexanedione dioxime is somewhat twisted with respect to the axis through carbons 2 and 5 in room temperature, since otherwise these separations must be the same. Detailed discussion upon this point will be reported elsewhere.

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* 4 According to the Phillips' assignment of aldoximes$^{3,4)}$ the peaks are assigned to anti-anti, syn-anti, and syn-syn structure in the decreasing order of the magnetic field.

Other methylene signals are very complicated. These are composed of the superposition of the following three groups of peaks : (1) A_4X_2 spin system for structure I, (2) $A_2B_2Y_2$ spin system for structure II, and (3) B_4Z_2 spin system for structure III, where it is expected that the chemical shift between A and B is equal to $|\sigma_S - \sigma_A|$ and that $X \approx Y \approx Z$ [*5].

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[*5] If the long range shielding effect due to the hydroxyimino groups affecting β-methylene protons is negligible, proton shift of 5-methylene group is almost the same for the structures I, II, and III ($X \approx Y \approx Z$). However such a long range shielding effect is practically observed in the NMR spectrum of 1,4-cyclohexanedione dioxime (to be published).