February, 1986] © 1986 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 59, 653—654 (1986) 653

Estimation of Isomer Ratio of 2,3-Alkanedione Dioxime Using High-Resolution ^{13}C NMR in the Solid State

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(Received August 15, 1985)

Synopsis. High-resolution ^{13}C NMR spectra were measured for the CH_3-C(=NOH)-C(=NOH)-R (R=CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9) series in the solid state. A commercially available powder, dimethylglyoxime (R=CH_3), produced two C^2 signals, indicating two isomers: i.e., *s-trans-(E,E)* and *s-cis-(E,E)*. The ratio of *trans*: *cis* was estimated to be 3:1.

Tanaka et al. reported that there are three possible structural isomers for dioximes.[1] Each isomer gave

$$R-\underset{\underset{\text{HON}}{\|}}{C}-\underset{\underset{\text{NOH}}{\|}}{C}-R \qquad R-\underset{\underset{\text{NOH}}{\|}}{C}-\!\!-\!\!-\underset{\underset{\text{HON}}{\|}}{C}-R \qquad R-\underset{\underset{\text{NOH}}{\|}}{C}-\!\!-\underset{\underset{\text{NOH}}{\|}}{C}-R$$

(*E*, *E*) (*Z*, *Z*) (*Z*, *E*)

a different ^1H NMR signal for the NOH proton in DMSO-d_6 solution, and the ratio of the isomers was estimated from the ratio of the peak areas.[1]

On the other hand, a newly developed high-resolution ^{13}CNMR technique (CP/MAS) was applied for coal and oil shale and the aromatic-olefinic fraction was determined by an integration of the solid-state spectra.[2]

In this paper, CP/MAS spectra were measured for the 2,3-alkanedione dioxime (CH_3-C(=NOH)-C(=NOH)-R: R=CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9) series in the solid state. The existence of *trans* and *cis* isomers was identified for a commercially available powder dimethylglyoxime (R=CH_3), and the ratio of the isomers was estimated from the ratio of the peak areas.

Experimental

A commercially available guaranteed reagent, dimethylglyoxime (Wako Pure Chemical Industries, LTD), was used for the measurement. Other 2,3-alkanedione dioximes were prepared as previously described[3] and recrystallized from methanol-chloroform (1:1). A JEOL NM-SH200 spectrometer (50 MHz for ^{13}C) was used for the measurements. All spectra were obtained using magic-angle spinning at room temperature. The spectra were generated from ca. 1000 scans at a rate of one scan per ten seconds. The methylen carbon of adamantane (29.5 ppm from TMS) was used as an external standard.

Results and Discussion

The high-resolution ^{13}CNMR (CP/MAS) spectra of 2,3-alkanedione dioximes are shown in Fig. 1. Also, numerical data are summerized in Table 1. Opella's method was used for the assignment of signals.[4] According to this method, only quarternary and methyl carbons appear as is exemplified for R=n-C_3H_7 dioxime in Fig. 2-a. In the case of R=C_2H_5, n-C_3H_7, n-C_4H_9 dioximes, the ^{13}CNMR spectra in the solid state were similar to those obtained in DMSO-d_6 solution (Fig. 2-b, c). However, as for R=CH_3 dioxime, the C^2 resonance separated into two peaks in the solid state, though it appeared as a single peak in DMSO-d_6 solution (Fig. 3-b, c).

It was reported that carbons directly bonded to nitrogen atoms sometimes showed doublet patterns in CP/MAS spectra.[5] If this is also the case for the dioximes, the C^2 and C^3 resonances of R=C_2H_5, n-C_3H_7, and n-C_4H_9 dioximes should show similar splittings. However, such a phenomenon was not observed (Fig. 1).

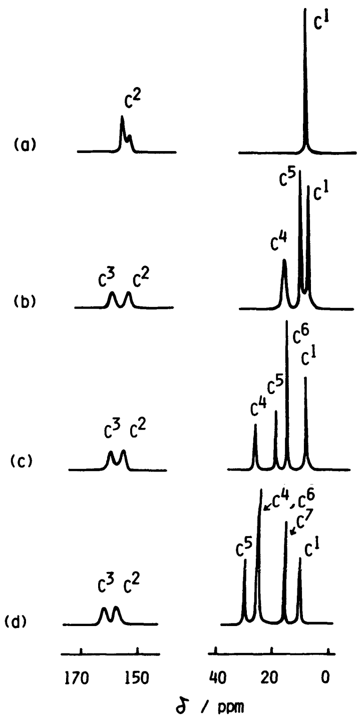


Fig. 1. High-resolution ^{13}CNMR spectra (CP/MAS spectra) of CH_3-C(=NOH)-C(=NOH)-R in the solid state.
(a): R=CH_3, (b): R=C_2H_5, (c): R=n-C_3H_7, (d): R=n-C_4H_9.
Each carbon atom is noted as a following example; C^1H_3-C^2(=NOH)-C^3(=NOH)-C^4H_2-C^5H_2-C^6H_2-C^7H_3.

Table 1. High-Resolution ^{13}C NMR Data of CH_3-C(=NOH)-C(=NOH)-R

R	δ/ppm						
	C^1	C^2	C^3	C^4	C^5	C^6	C^7
CH_3	9.5	155.9 153.6	—	—	—	—	—
C_2H_5	9.3	154.2	159.5	17.6	11.6	—	—
n-C_3H_7	9.6	155.1	159.0	27.5	20.2	16.2	—
n-C_4H_9	9.1	154.5	158.6	23.7	28.3	23.7	14.0

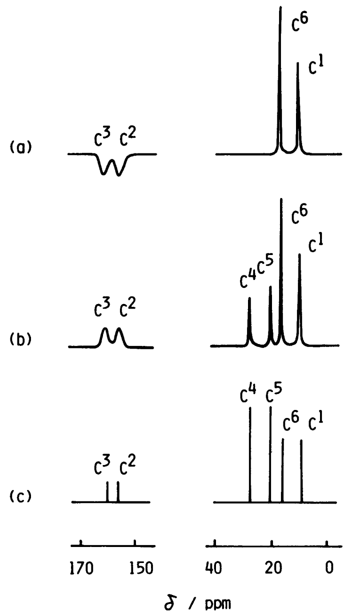


Fig. 2. ^{13}C NMR spectra of $\mathrm{CH_3{-}C({=}NOH){-}C({=}NOH){-}CH_2{-}CH_2{-}CH_3}$.
(a): CP/MAS spectrum using Opella's method (in the solid state), (b): CP/MAS spectrum (in the solid state), (c): in DMSO-d_6 solution.

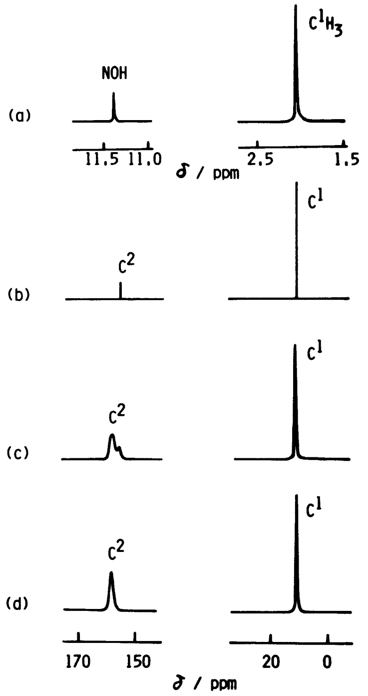
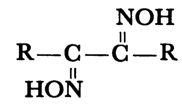


Fig. 3. ^{1}H and ^{13}C NMR spectra of $\mathrm{CH_3{-}C({=}NOH){-}C({=}NOH){-}CH_3}$.
(a): ^{1}H NMR spectrum in DMSO-d_6 solution, (b): ^{13}C NMR spectrum in DMSO-d_6 solution, (c): CP/MAS spectrum of commercial powder compound, (d): CP/MAS spectrum of recrystallized crystal.

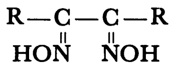
The ^{1}H NMR spectrum of the R=CH$_3$ dioxime showed only one NOH signal in DMSO-d_6 solution (Fig. 3-a), indicating that there are no isomers, such as the previously described *(E,E)*, *(Z,Z)*, and *(Z,E)*.[1] Since the rotation of a C=NOH double bond is inhibited, it is hardly expected that there are such isomers only in the solid state.

The CP/MAS resonance sometimes splits into two peaks based on the "packing effect."[6] According to an X-ray single crystal analysis of R=CH$_3$ dioxime (obtained by a slow evaporation of the solvent ethanol), the R=CH$_3$ dioxime has a *s-trans-(E,E)* conformation and the space group is $P\bar{1}{-}C_i^1$ with one molecule in the unit cell.[7] Therefore, the peak splitting based on the "packing effect" cannot be expected for the R=CH$_3$ dioxime. When commercially available dimethylglyoxime (R=CH$_3$) was recrystallized by a slow evaporation of solvent ethanol or methanol-chloroform (1:1), the splitting of the C^2 resonance was not observed, though the C^1 resonance showed a similar signal as that of the commercial powder compound (Fig. 3-d).

Considering these facts, it is concluded that there were two isomers, i.e., *s-trans-(E,E)* and *s-cis-(E,E)*, in the commercial powder dimethylglyoxime. In solution, these two isomers were indistinguishable since the (HON=)C-C(=NOH) single bond can rotate freely.


$$\mathrm{R{-}\underset{\underset{HON}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}R}$$

s-trans-(E, E)


$$\mathrm{R{-}\underset{\underset{HON}{\|}}{C}{-}\underset{\underset{NOH}{\|}}{C}{-}R}$$

s-cis-(E, E)

The molar fraction of the two isomers was estimated by an integration of the spectra. For a quantitative analysis, the contact time (CT) and the repetition time (RT) must be appropriately chosen.[2] In this study, the CP/MAS spectra were taken while choosing CT=2 ms and RT=10 s. Under these conditions, the dioximes (R=C$_2$H$_5$, n-C$_3$H$_7$ and n-C$_4$H$_9$) gave a peak ratio C^2:C^3=1:1 (Fig. 1), indicating the probability of the quantitative analysis. In the case of the commercial powder dimethylglyoxime (R=CH$_3$), it was estimated from an integration of the corresponding C^2 signals that the ratio *s-trans-(E,E)*: *s-cis-(E,E)* is 3:1. As for R=C$_2$H$_5$, n-C$_3$H$_7$ and n-C$_4$H$_9$ dioximes, these molecules are considered to exist only in *s-trans* or *s-cis* forms in the crystals.

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