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SELF-ASSOCIATION AND RELATIVE STABILITY OF THE ISOMERIC STRUCTURES OF ACETALDOXIME

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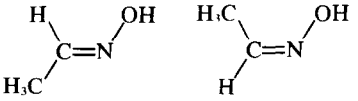
Abstract—The abnormal *syn/anti* ratio for acetaldoxime is explained, on the basis of NMR evidence, in terms of preferred self-association of the *anti* isomer.

INTRODUCTION

In acetaldoxime the *syn–anti* isomerism has been proved by NMR[1] and IR spectroscopy.[2] More recently, the two isomeric forms have been separated by gas chromatography[3]



syn *anti*

and their geometries studied by microwave spectroscopy.[4]

There are also strong indications that acetaldoxime forms associations—dimers and trimers—which are explained in terms of intermolecular H-bonds. Self-association is thought to be present even in gaseous phase.[5]

The relative stability of the *syn* and *anti* isomers in liquid phase has been given by a *syn/anti* ratio of 0.6 obtained from proton NMR spectra.[1] This is a surprising result; in fact one would expect steric and electrostatic effects to make the *syn* isomer more stable than the *anti*. However, we must recognize that what in fact is measured in such circumstances is the "gross" relative stability of polymeric structures and not of the relative stability of the *syn* and *anti* monomers.

Thus, in order to clarify this matter, we have studied acetaldoxime with variable temperature NMR and at different concentration and in various solvents.

RESULTS AND DISCUSSION

The assignment of the proton resonance signals of the two forms of acetaldoxime made by Phillips *et al.*[1] is supported by the values of the one bond ^{13}C–H coupling constant involving the C atom bonded to N. Theoretical[6] and other experimental evidence[7] show that J_{CH} should be larger for the *anti* isomer than for *syn* and in fact the observed values are, respectively, 173 and 160 Hz.

As stated above, there is no obvious reason why the *syn* structure should be less stable than *anti*. In support of this, calculations based on the CNDO/2 method, using the experimental values for bond angles and bond lengths, show that there is no significant difference between the energies of the two monomers.[8]

Self-association involving intermolecular H-bonding is easily revealed by the variation of the OH proton chemical shift with concentration and temperature. Tables 1 and 2 illustrate these variations.

Table 1. ζ-Values for the OH proton of acetaldoxime in CCl_4 as a function of concentration

Concentration	ζ-values	
Pure liquid		−0.70
1.6 M		0.60
0.8		0.64
0.4		0.68
0.2		0.70
0.1	0.94 (*anti*)	1.50 (*syn*)
0.05	1.24 (*anti*)	1.88 (*syn*)
0.025	1.83 (*anti*)	2.50 (*syn*)

Table 2. ζ-Values for the OH proton of acetaldoxime in heptane as a function of temperature (concentration 0.84 M ≡ 50 mg/ml)

Temperature	ζ-values	
238°K	−1.06 (*anti*)	−0.60 (*syn*)
258	−0.94 (*anti*)	−0.48 (*syn*)
278	−0.24	
298	0.00	
323	0.77	
343	1.40	

The ζ-values increase as concentration decreases and as temperature increases, corresponding to the breaking of H-bonds.

It is noted that at low concentration or at low temperature, proton exchange is sufficiently slow for the OH signals of the two isomeric forms to be observed. The OH proton signal for the *anti* form is found to lie at higher frequency than the one for the *syn* isomer. This is consistent with a stronger self-association of the *anti* monomer with respect to *syn*.

Table 3 shows the *syn/anti* ratio of acetaldoxime in various solvents, as obtained from the integrated NMR signals. One finds that such ratio increases substantially as the dielectric constant of solvent increases. That is, as self-association becomes less favorable, the stability of the *anti* form approaches that of the *syn* form, as expected.

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Table 3. *Syn/anti* ratio for acetaldoxime in solvents of variable dielectric constant (ϵ) (concentration 0.84 M ≡ 50 mg/ml)

Solvent	ϵ	*Syn/anti* ratio
Heptane	1.924	0.52
Ciclohexane	2.015	0.56
Carbon tetrachloride	2.228	0.60
Benzene	2.274	0.61
Pure liquid	3.8	0.61
Chloroform	4.806	0.65 ± 0.02
Acetone	20.7	0.72 ± 0.03
Methanol	32.36	0.68 ± 0.04
Acetonitrile	38.8	0.69 ± 0.02
Water	80	0.81 ± 0.02

Nevertheless, the ratio is still well below 1 for highly polar solvents. Although, in these cases, H-bonding to solvent molecules is undoubtly present, this points to a strong tendency of acetaldoxime for self-association.

This is confirmed by Table 4 which shows only a small variation of the *syn/anti* ratio with concentration. This ratio increases upon dilution, that is, the stability of *anti* with respect to *syn* again decreases upon breaking of polymers, as expected. The effect of dilution is, however, quite small.

Table 4. *Syn/anti* ratio for acetaldoxime as a function of concentration (solvent: CCl_4)

Concentration	*Syn/anti* ratio
4.2 M	0.57
2.1	0.58
1.1	0.58
0.5	0.58
0.34	0.58
0.23	0.58
0.17	0.62
0.017	0.64

The variation is much more pronounced when the temperature is varied. This is shown in Table 5. Here, however we have two factors working in the same direction: the breaking of polymeric structures on increasing temperature and the conversion of *anti* structures into the less stable *syn* polymers as temperature rises.

Table 5. *Syn/anti* ratio for acetaldoxime in heptane at various temperatures (concentration 0.84 M ≡ 50 mg/ml)

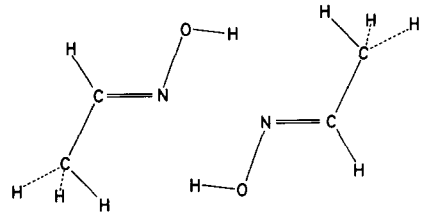
Temperature	*Syn/anti* ratio
258°K	0.47 ± 0.02
278	0.48 ± 0.02
298	0.52 ± 0.01
323	0.55 ± 0.02
343	0.63 ± 0.02
363	0.74 ± 0.02

If we assumed that the whole variation of *syn/anti* ratio shown in Table 5 was due to such conversion, then the overall difference of enthalpy for the *syn* and *anti* isomeric structures found from the variation of the observed ratio (actually its logarithm) with $1/T$ would be 0.9 kcal/mole (the corresponding ΔS value is 1.7 cal/°K). Since there will be a contribution due to breaking of polymeric structures, this will then be an upper limit for ΔH.

CONCLUSIONS

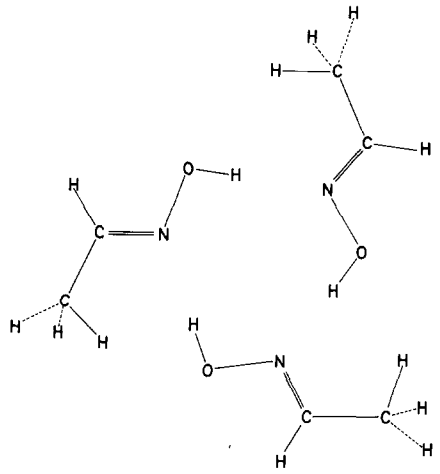
The data and brief discussion in the last section show that it is not right to conclude, from the *syn/anti* ratio of 0.6 given by the NMR spectrum of acetaldoxime, that the monomeric *syn* form is less stable than the corresponding *anti* form. Instead, acetaldoxime forms quite stable polymeric structures, those arising from the *syn* monomeric isomer being less stable than those built from the *anti* isomer; the overall ΔH value is less than 1 kcal/mole.

A possible explanation for these findings may be obtained from scale models of the dimers, e.g.



(1)

and trimers, e.g.



(2)

The *syn* monomer appears as less suitable for such associations, because of steric interaction of the methyl group of each molecule with the OH group of the next molecule.

EXPERIMENTAL

The spectra were run on a Varian spectrometer HA-100 and, for the most dilute solutions, on a Jeol Fourier Transform spectrometer J.N.M. 100 TST.

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