

(b) *Citric acid*. 100 g citric acid, 10 g potassium iodide, and 5 g iodine was dissolved in 150 ml of water. During 10 min, 5 g potassium permanganate in 100 ml water was added. A yellowish precipitate soon appeared. To complete the precipitation the reaction mixture was left at room temperature for 2 h without being stirred. The precipitate was filtered, washed carefully with 200 ml water and dried by suction. It was then dissolved in acetone (100–150 ml) and filtered into water (1–1.5 l) while being stirred. A yellowish precipitate immediately formed which was collected by filtering and washed with 50 ml glacial acetic acid. It was further purified by recrystallization from boiling glacial acetic acid (10 ml/g). 8–12 g of 1,1,3,3-tetraiodoacetone was obtained, m.p. 155.0–156.0°C (d).

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On the Stability of the Rotational Isomers of 2-Furalaldehyde

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2-Furalaldehyde (F) can exist in two rotational isomers, as shown in Fig. 1. Microwave investigation¹ showed that isomer I in the gas phase is more stable than isomer II, and that the energy difference is 0.99 ± 0.20 kcal/mol.

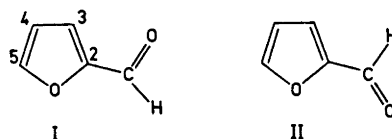


Fig. 1. The two stable rotational isomers of 2-furalaldehyde.

IR and Raman spectra of F show significant dependence on the solvent used.^{2–4} This fact is interpreted as indicating changes in the molar fractions of the two isomers.

No examination of the influence of solvents on the NMR spectrum of F has previously been performed. The most significant change produced in the NMR spectrum of F by variation of solvent or concentration is a change in $J_{\text{CHO}-4}$ and $J_{\text{CHO}-5}$, the coupling constants between the aldehyde proton and the ring protons in 4 and 5 positions, respectively. The coupling constants that we have calculated from the spectra are given in Table 1.

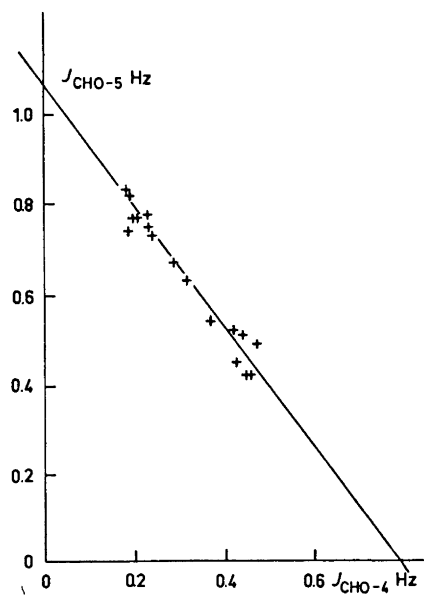


Fig. 2. Plot of the observed coupling constants $J_{\text{CHO}-4}$ against $J_{\text{CHO}-5}$ for 2-furalaldehyde at 31.4°C. The straight line represents the least squares fit.

Table 1. Observed coupling constants and calculated molar fractions of isomer I for different solvents and concentrations.

Solvent	v/v %	$J_{\text{CHO-4}}$ Hz	$J_{\text{CHO-5}}$ Hz	n_I^a	n_I^b
CCl_4	80	0.18	0.83	0.23	0.22
None	100	0.19	0.82	0.24	0.23
CCl_4	60	0.23	0.78	0.29	0.26
CH_3OH	5	0.20	0.77	0.25	0.27
CH_2Cl_2	5	0.21	0.77	0.27	0.27
CCl_4	40	0.23	0.75	0.29	0.29
$(\text{CD}_3)_2\text{CO}$	5	0.19	0.74	0.24	0.30
CDCl_3	5	0.24	0.73	0.30	0.31
<i>p</i> -[D_8]Dioxane	5	0.29	0.67	0.37	0.37
CCl_4	20	0.32	0.63	0.41	0.41
CCl_4	15	0.37	0.54	0.47	0.49
$(\text{C}_2\text{H}_5)_2\text{O}$	5	0.42	0.52	0.53	0.51
CCl_4	10	0.44	0.51	0.56	0.52
C_6H_{12}	5	0.47	0.49	0.60	0.54
CCl_4	5	0.43	0.45	0.54	0.58
C_6H_{12}	2	0.45	0.42	0.57	0.60
CCl_4	2	0.46	0.42	0.58	0.60

^a Calculated from eqn. (1). ^b Calculated from eqn. (2).

There is an obvious increase in $J_{\text{CHO-4}}$ and a decrease in $J_{\text{CHO-5}}$, as the solution is changed from polar to non-polar. $J_{\text{CHO-4}}$ is plotted against $J_{\text{CHO-5}}$ in Fig. 2. The observed linear dependency may be easily interpreted in terms of the coupling constants of the individual isomers I and II. If n_I is the molar fraction of I, we have the equations

$$J_{\text{CHO-4}} = n_I J_{\text{CHO-4}}^I + (1 - n_I) J_{\text{CHO-4}}^{II} \quad (1)$$

and

$$J_{\text{CHO-5}} = n_I J_{\text{CHO-5}}^I + (1 - n_I) J_{\text{CHO-5}}^{II} \quad (2)$$

Dahlqvist and Forsén recorded the NMR spectra of I and II at -115°C , using dimethyl ether as solvent.^{5,6} Making use of arguments concerning anisotropic shielding by the carbonyl group, they assigned the spectra to the two isomers. However, recent discussion of the data,^{7,8} using another theory of anisotropic shielding, reversed the assignment. Combining the experimental data of Dahlqvist and Forsén with the newer assignment, we have the relations

$$J_{\text{CHO-4}}^I = 0.85 \text{ Hz}; |J_{\text{CHO-5}}^I| < 0.2 \text{ Hz} \quad (3)$$

$$|J_{\text{CHO-4}}^{II}| < 0.2 \text{ Hz}; J_{\text{CHO-5}}^{II} = 1.10 \text{ Hz} \quad (4)$$

It follows that the long-range couplings obey the zig-zag rule,⁹ in contradiction

to the first assignment by Dahlqvist and Forsén. However, it also shows isomer II to be the more stable, in contradiction to the gas-phase data mentioned earlier.¹

The two sets of coupling constants must fall along the line in Fig. 2, but because the determination of $J_{\text{CHO-4}}^{II}$ and $J_{\text{CHO-5}}^I$ is so uncertain, plotting of these values would be without value. However, if we postulate that the small coupling constants are equal to zero, as may well be the case,

$$J_{\text{CHO-4}}^{II} = J_{\text{CHO-5}}^I = 0 \quad (5)$$

then the graph yields the following figures:

$$J_{\text{CHO-4}}^I = 0.79 \text{ Hz}; J_{\text{CHO-5}}^{II} = 1.06 \text{ Hz} \quad (6)$$

which values agree well with those of (3) and (4) above. Using the values from (5) and (6), we can calculate the molar fraction of I from (1) and (2); the results appear in Table 1. These results are best illustrated in Fig. 3, where n_I is plotted against the volumetric percentage of F in tetrachloromethane. It is obvious that n_I increases as the solution is changed from polar to non-polar. If the volumetric percentage is extrapolated to zero, we find that $n_I = 0.61$. This means that the most stable isomer in non-polar solutions and in the gas phase is the same. Thus the solution-

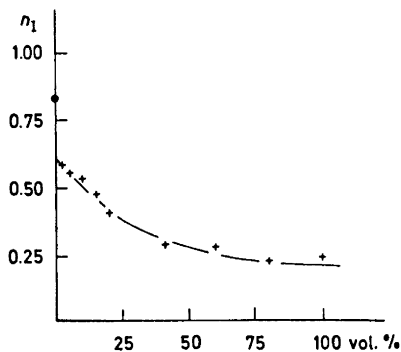


Fig. 3. The calculated molar fraction of isomer I as a function of the volumetric percentage of 2-furaldehyde in tetrachloromethane. ● indicates the gas-phase value for n_1 calculated from the microwave results.¹

phase and gas-phase assessments of isomeric stability offer each other no contradiction.

Experimental. The spectra were recorded on a Varian HA 100 spectrometer at 31.4°C. The coupling constants were calculated using the Fortran IV program LAOCOON III. The necessary change in one coupling constant leading to a doubling of the rms error does not exceed 0.03 Hz.

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Low-Temperature IR- and NMR-Studies of 3,3,6,6-Tetramethylcycloheptanone

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In an earlier publication¹ the synthesis of 3,3,6,6-tetramethylcycloheptanone in nine steps from β,β -dimethylglutaric acid has been described.

As expected for a strained ring with an uneven number of carbon atoms the melting point for this compound was low, -7°C . The entropy and enthalpy of fusion were 11 cal/degree/mol and 3 kcal/mol, respectively. Calorimetric investigations of the melting process unveiled a transition

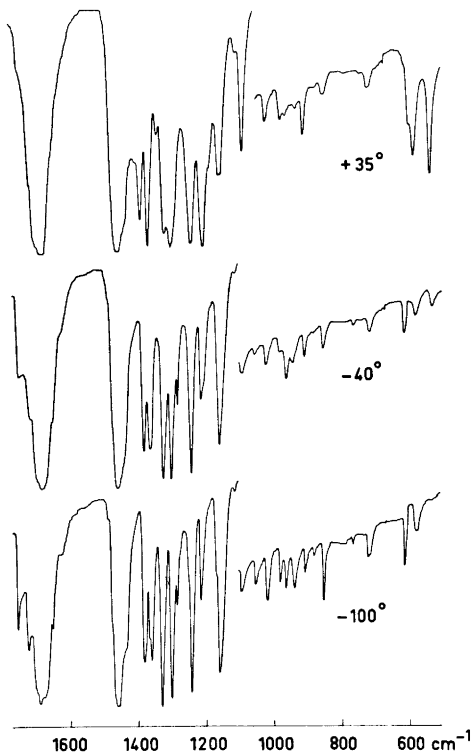


Fig. 1. Infrared spectra of 3,3,6,6-tetramethylcycloheptanone as a liquid (top) and as solid at -40 and -100°C .