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The Barrier to Internal Rotation in 2-Acetylfuran

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The barrier to internal rotation in the $=\overset{|}{C}-\overset{|}{C}=O$ bond and thermodynamic data for the isomer equilibrium I⇄II in 2-acetylfuran have been obtained by proton magnetic resonance studies at 60 and 100 MHz. The rate parameters have been calculated from the line shape of the ring proton in the 3-position at temperatures between +30° and −115°C. Good agreement is observed between the two series of measurements. The rotational barrier in 2-acetylfuran is found to be *ca.* 2 kcal/mole lower than the corresponding barrier in 2-furanaldehyde.

In a previous communication[1] we have reported the barrier to internal rotation in the $-\underset{|}{C}-\underset{|}{C}=O$ bond and thermodynamic data for the isomer equilibrium in 2-furanaldehyde.

The different chemical characteristics of formyl and acetyl groups makes it of interest to investigate the extent to which these differences are also reflected in the rotational barrier of the $=\underset{|}{C}-\underset{|}{C}=O$ bond.

The study of the rotational barrier in 2-acetylfuran by proton magnetic resonance presents much the same problem as in 2-furanaldehyde. In the case of 2-furanaldehyde, however, the temperature-dependent equilibrium between the two conformers could be conveniently followed by means of a stereospecific spin coupling of the aldehyde proton to the ring protons in the 4- and 5-positions. In the case of 2-acetylfuran no such spin couplings are observed, which makes the determination of the conformer equilibrium I⇄II (Fig. 1) somewhat uncertain.

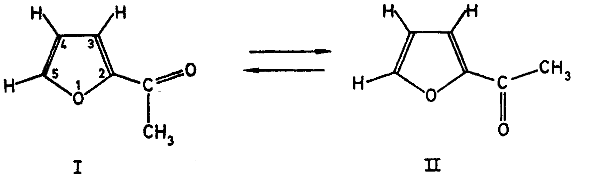

Fig. 1. The two rotational isomers of 2-acetylfuran.

EXPERIMENTAL

2-Acetylfuran was synthesized by the action of BF_3-etherate on a mixture of furan and acetic anhydride.[2] The product was purified by distillation twice. The dimethyl ether used as solvent in the PMR investigation was of commercial quality (The Matheson Co. Inc., USA). The measurements were performed at three different concentrations. A 6.9 % solution was used for the investigation at 60 MHz, whereas the investigations at 100 MHz were performed on a 10.0 % solution in a temperature range −30 to −100°C. At the lower end of this range solubility problems arose which were resolved by the use of a 5.3 % solution in the region −90 to −115°C. In the overlapping temperature range for the two solutions (−90 to −100°C) no significant differences in the 100 MHz spectra were noticed. A few percent TMS was added to all solutions as internal reference.

The investigation at 60 MHz was performed on a Varian A 60 spectrometer. The following instrumental settings were used: scale expansion 1 Hz/cm, sweep rate 0.20 Hz/sec and r.f. field about 0.06 mgauss. The A 60 spectrometer was equipped with a variable temperature controller, previously calibrated with a copper-constantan thermocouple at different flow rates of the heat transfer nitrogen gas.

The investigation at 100 MHz was performed on a Varian HA-100 spectrometer equipped with a V-4333 variable temperature probe and a V-4343 temperature controller. Spectra were recorded with same scale expansion and sweep rate as at 60 MHz and at a r.f. field low enough to avoid saturation. The measurements of the sample temperature were, however, performed in a different way. The temperatures were obtained from the temperature-dependent shift between the methyl and hydroxyl protons in methanol. This solution was sealed in a capillary placed in the centre of the sample tube. The temperature-dependent shift was separately calibrated according to a procedure described elsewhere.[3]

Since the signals from the methyl protons in the solvent dimethyl ether and the methanol in the internal capillary were close to each other with an unfavourable intensity ratio, the small shift between these signals was accurately measured in the temperature region of our experiments. This provided us with a calibrated temperature-dependent shift between the hydroxy proton in methanol and the methyl protons in dimethyl ether which was readily used for the temperature measurements.

At each temperature five or more spectra were recorded and then averaged by hand before fitting to the theoretical spectra.

The chemical shifts were measured by the usual side-band technique using a HP 200 CD Audio Oscillator. The frequencies were measured with a HP 5512 A Electronic Counter. The recordings at low temperatures, especially below −100°C, had to be performed rapidly since the solutions at these temperatures were supersaturated and crystals of 2-acetylfuran were gradually formed. In order to avoid these problems the 5.3 % solution was also used in the low temperature region in the 100 MHz recordings.

MEASUREMENTS AND CALCULATIONS

PMR spectrum. The PMR spectrum of 2-acetylfuran contains four groups of signals. The signal from the acetyl protons is a singlet at 2.36 ppm with no detectable fine structure. The signal from the 5-proton at 7.61 ppm is split

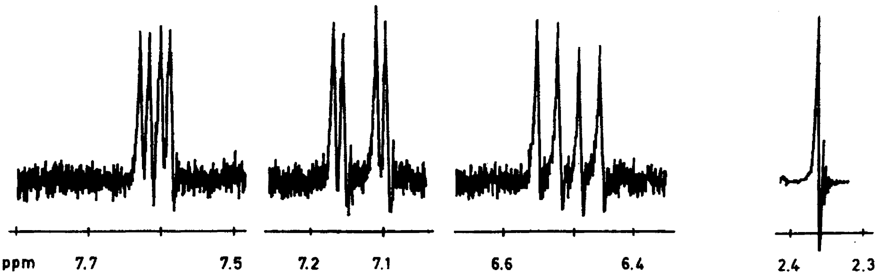

Fig. 2. PMR spectrum of 2-acetylfuran (60 MHz) recorded at room temperature.

into a quartet by coupling to the 3- and 4-protons, (Fig. 2). The 3- and 4-protons also give rise to quartets at 7.14 and 6.51 ppm, respectively.

When the sample was cooled to below -50°C the quartet from the 3-proton began to broaden and was coalesced at -94°C at 60 MHz and at -85°C at 100 MHz. At temperatures below the coalescence point the signal from the 3-proton consisted of two not quite resolved quartets 0.20 to 0.25 ppm apart (Fig. 3). At these temperatures the signal from the proton in the 4-position also became broadened presumably due to the similarity of the 4-proton chemical shifts in the two conformers I and II, which did not allow resolution of the two expected quartets. Shifts and coupling constants at room temperature and -100°C are summarized in Table 1.

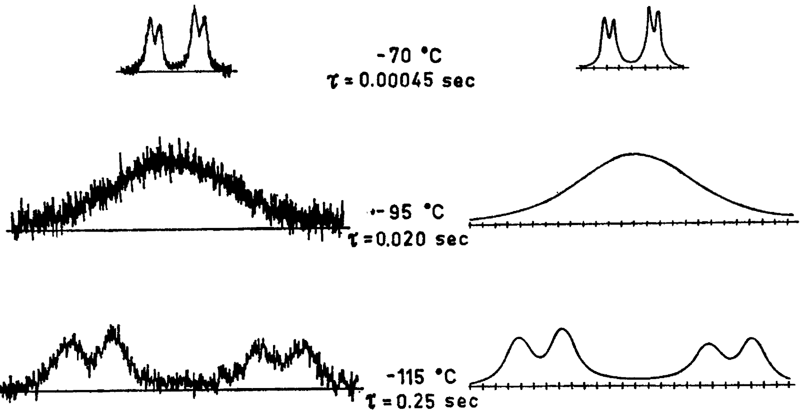

Fig. 3. Examples of experimental and theoretical NMR spectra of the proton in 3-position in 2-acetylfuran.

The acetyl signal remained almost unaffected down to -95°C, where broadening became noticeable. The temperature of maximum broadening was about -105°C, below which two separated acetyl signals a few Hz apart

Table 1. Chemical shifts and spin coupling constants of 2-acetylfuran in dimethyl ether.

T°K	Proton	Shift ppm	Spin coupling constants
303.7 (room temp.)	H-3 H-4 H-5 Acetyl	7.14 6.51 7.61 2.36	$J_{3,4} = 3.5$ $J_{3,5} = 0.75$ $J_{4,5} = 1.7$
173.2	H-3 H-4 H-5 Acetyl	7.34 6.67 7.86 2.42	$J_{3,4} = 3.5$ $J_{3,5} = 0.75$ $J_{4,5} = 1.7$

were obtained. In principle the rate of interconversion of the two conformers of 2-acetylfuran could be obtained from a line shape analysis of both the acetyl signal and the signal from the 3-proton. The small chemical shift between the acetyl signal in the two conformers makes it difficult, however, to obtain accurate rate data from this signal and we have therefore concentrated our efforts on the signal from the 3-proton.

The diamagnetic anisotropy effect of the carbonyl group will cause diamagnetic shielding of nuclei inside a conical surface over and under the trigonal $>C=O$ plane, and nuclei outside this surface will be deshielded [4] (Fig. 4a).

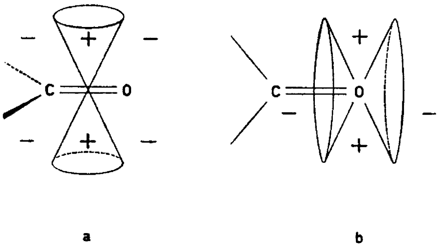

Fig. 4. Two models (see text) of the diamagnetic anisotropy effect of the carbonyl group.

The shape of the surface dividing the region of diamagnetic and paramagnetic shielding effects of the $>C=O$ groups has recently been critically discussed by Karabatsos *et al.*[5] and the authors propose a new model (Fig. 4b).

The conventional model a will give proton 3 a downfield shift in conformer I compared to conformer II. According to model b proton 3 in conformer I will be in the region of pronounced shielding, whereas proton 3 in conformer II will be exposed to about the same shielding effect in both models. Since also microwave studies of 2-furanaldehyde [6] in the gas phase indicate a greater population for the "*trans*" conformer (O—O *trans*) of 2-furanaldehyde, we have ascribed the low field signal from proton 3 to conformer I. If, however, the model for the anisotropic shielding of the carbonyl group given by Karabatsos *et al.*[5] is correct, this assignment must be reversed.

The conformer ratios were calculated by electronic integration (60 MHz) and by cutting out and weighing the curves (100 MHz) recorded below −95°C. The conformer ratios were found to be 1.0 ± 0.1. Since no stereospecific long-range coupling exists, it is not possible to calculate the conformer ratio at higher temperatures.

It appears unlikely that the entropy difference between the two conformers of 2-acetylfuran should be very high. In 2-furanaldehyde ΔS° for the conformer equilibrium was found to be about 2 e.u.[1] If we assume this value to be also valid for 2-acetylfuran we obtain $\Delta H^\circ = ca.$ 0.35 kcal/mole for the enthalpy difference between the conformers. Estimation of the equilibrium constant in the temperature region where rate data may be obtained from the line shape of the 3-proton shows the changes in population of the conformers to have a negligible effect on the evaluated rate constants. We have therefore performed all calculations assuming the equilibrium constant to be unity over the temperature range −70°C to −115°C.

Measurements of the interconversion rate. The shifts and spin coupling parameters given in Table 1 were evaluated from the recorded spectra. The interpretation of the low-temperature spectrum of 2-acetyl-furan is shown in Fig. 5, where the parameters are defined. The zero point ω_0 is an arbitrarily chosen reference, in this case selected to make $\omega_1 = \omega_2$. The shift parameters ω_1 and ω are, however, somewhat uncertain since it was not possible [2] to decrease the temperature below −115°C to verify their independence of temperature.

$$\text{Fig. 5 gives } J_1 = J_{3,4}^{\mathrm{I}},\ J_2 = J_{3,5}^{\mathrm{I}},\ J_3 = J_{3,4}^{\mathrm{II}} \text{ and } J_4 = J_{3,5}^{\mathrm{II}}.$$

No difference could be found within the pairs J_1, J_3 and J_2, J_4.

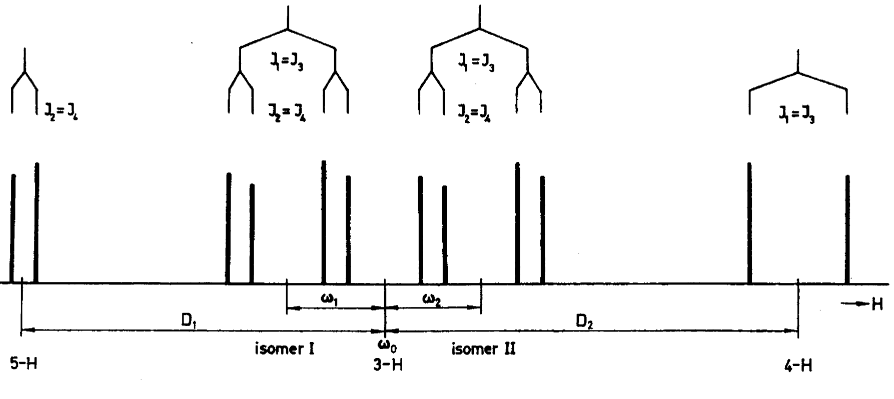

Fig. 5. Interpretation of the low temperature spectrum of 2-acetylfuran and definition of parameters used for the calculations.

In order to describe the quantitative variations of the line shapes with temperature we have used the modified Bloch equations in much the same way as in the case of 2-furanaldehyde.[1]

In order to obtain a more realistic line intensity in the calculated spectra at the slow exchange limit we have weighted the simple first order intensities with a factor correcting for the finite values of $J_{ij}/\delta\nu_{ij}$. This weighting factor was obtained from the line intensities in an AB sub spin system with the appropriate values of spin coupling constants and chemical shifts. This semi-empirical correction of the first order spectra could introduce an error in the evaluation of the rate constants, but a complete density matrix treatment has shown the errors to be quite negligible.[7]

The transverse relaxation time T_2 was determined in different ways at 60 and 100 MHz. At 60 MHz T_2 was calculated from the line width at half height of the TMS signal recorded at each temperature.

In the experiments at 100 MHz the T_2 values were determined from the line width of the 4-proton at temperatures between −30° and −80°C. At lower temperatures, −80° to −115°C, the value was calculated from the hydroxy signal from the methanol capillary since both the 4- and the 5-protons gave signals too broad to all evaluation of T_2. When these T_2 values were plotted against temperature they all fell on a straight line within the limits of error (Fig. 6). In both series of measurements the T_2-values for the theoretical calculations of spectra were the same at the corresponding temperatures.

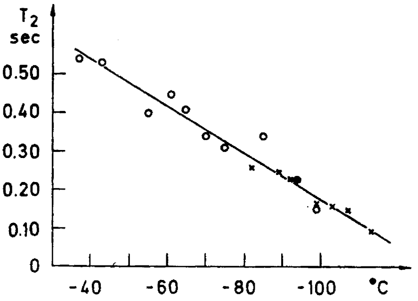

Fig. 6. T_2-values evaluated from different signals at different temperatures. ○ from the proton in 4-position; × from the hydroxyl proton in methanol.

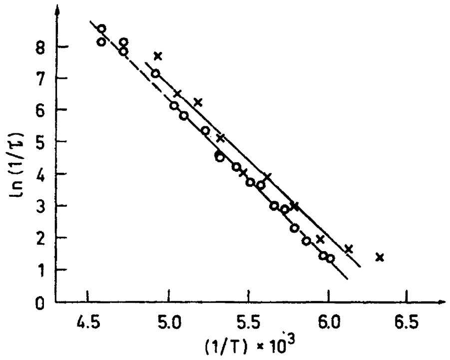

Fig. 7. Plot of ln $1/\tau$ *versus* $1/T$ for 2-acetylfuran. × 60 MHz; ○ 100 MHz.

The remaining parameter, the mean life time τ, was varied until good agreement was reached between recorded and calculated spectra. In the intermediate region, where τ changes from about 0.0005 to about 0.15 sec, τ-values could be determined to within ±10 %. Examples of theoretical and experimental spectra are shown in Fig. 3. The τ-values obtained are plotted as ln $1/\tau$ against $1/T$ in Fig. 7.

The τ-values obtained at 100 MHz are systematically higher by a factor about 1.5 than the values obtained at 60 MHz. The most likely explanation of this fact is a systematic error in the temperature determinations in the series obtained at 60 MHz of somewhat less than 4°C. The random errors in the rate measurements also appear to be higher in the 60 MHz study than in the 100 MHz investigations which is not unexpected considering the different ways the sample temperatures were measured. However, the two series of measurements lead to rather similar values for the evaluated activation parameters.

The activation parameters obtained for 2-acetylfuran at 100 MHz should be the most reliable in view of the improved method for the sample temperature measurements employed in this series.

Table 2. Summary of thermodynamic data and activation parameters for the interconversion of the rotational isomers in 2-acetylfuran and 2-furanaldehyde.[1]

Compound	2-Acetylfuran				2-Furanaldehyde [1]	
Temp. °K	203.2		183.2		216	191.7
NMR freq. MHz	60	100	60	100	60	60
ΔE_{AI} kcal/mole	9.11 ±0.56	9.91 ±0.20	9.11 ±0.56	9.91 ±0.20	11.93 ±0.19	11.93 ±0.19
ΔE_{AII} kcal/mole	9.11 ±0.56	9.91 ±0.20	9.11 ±0.56	9.91 ±0.20	10.88 ±0.21	10.88 ±0.21
ΔH° [a] kcal/mole	$\simeq 0$	$\simeq 0$	$\simeq 0$	$\simeq 0$	1.05 ±0.05	1.05 ±0.05
ΔH_{I}^* kcal/mole	8.71 ±0.56	9.50 ±0.20	8.75 ±0.56	9.58 ±0.20	11.50 ±0.20	11.55 ±0.20
ΔH_{II}^* kcal/mole	8.71 ±0.56	9.50 ±0.20	8.75 ±0.56	9.58 ±0.20	10.45 ±0.21	10.50 ±0.21
ΔF° [a] kcal/mole	$\simeq 0$	$\simeq 0$	$\simeq 0$	$\simeq 0$	0.58 ±0.04	0.63 ±0.05
ΔF_{I}^* kcal/mole	8.87 ±0.57	9.04 ±0.22	8.85 ±0.57	9.14 ±0.23	10.85 ±0.09	10.93 ±0.09
ΔF_{II}^* kcal/mole	8.87 ±0.57	9.04 ±0.22	8.85 ±0.57	9.14 ±0.23	10.27 ±0.09	10.30 ±0.10
ΔS° [a] cal/mole, deg	$\simeq 0$	$\simeq 0$	$\simeq 0$	$\simeq 0$	2.18 ±0.27	2.19 ±0.24
ΔS_{I}^* cal/mole, deg	−0.80 ±0.07	2.31 ±0.07	0.59 ±0.05	2.74 ±0.09	3.00 ±0.06	3.23 ±0.06
ΔS_{II}^* cal/mole, deg	−0.80 ±0.07	2.31 ±0.07	−0.59 ±0.05	2.74 ±0.09	−0.83 ±0.28	1.04 ±0.25

[a] *Cf.* discussion on page 666.

The free energy, enthalpy, and entropy of activation were calculated from the theory of absolute reaction rates assuming the transmission coefficient to be unity. The results are summarized in Table 2 together with the corresponding data for 2-furanaldehyde. The errors indicated in the table are standard deviations, assuming only random errors.

DISCUSSION

The free energy and enthalpy of activation for the internal rotation of the acetyl group in 2-acetylfuran are lower by *ca.* 20 % than the corresponding values in 2-furanaldehyde.

Conjugative interaction between the furan ring and the 2-substituent is expected to favour the planar form of 2-acetylfuran as well as of 2-furanaldehyde. Microwave measurements by Mönnig *et al.*[6] are in agreement with planarity of the two conformers of 2-furanaldehyde in the gaseous phase. Calculations of repulsion potentials have been made [8] according to Hill [9] and Scott-Scheraga [10] using reasonable molecular models of 2-acetylfuran. The parameters used in these calculations are the same as those used by Forsén and Skancke [11] for calculation of nonbonded interactions in benzaldehyde. The two types of repulsion potentials lead to somewhat conflicting results (Table 3) but it appears that the steric interactions between the methyl group and the ring atoms should be fairly small even in the planar conformations, and we may thus infer essentially planar structures for the two conformers. A comparison with the corresponding calculations for 2-furanaldehyde (Table 3) shows that the repulsion between the acetyl group and the furan ring is less than between the aldehyde group and the furan ring. According to these calculations the difference in the barrier to internal rotation between 2-acetylfuran and 2-furanaldehyde can therefore not be explained in terms of increased repulsion between the 2-substituent and the furan ring.

Since the calculations of nonbonded interactions according to Hill gives higher energy for conformer II than for I while the calculations according to Scott-Scheraga gives the opposite result, it is not possible to draw any conclusions about the conformer ratio II/I from these calculations.

The lowering of the rotational barrier in 2-acetylfuran compared to 2-furanaldehyde should thus be attributable to steric interactions in the ground state to only a minor extent and the electronic interaction between the substituent and the ring should be regarded to be the decisive factor.

In 2-acetylfuran the methyl group is expected to donate electrons to the positive carbonyl carbon and make this carbon less apt to attract electrons from the furan ring. This effect is borne out in simple MO calculations of the Hückel type when the methyl group is explicitly considered using either the hyperconjugation model, the pseudo heteroatom model, or the inductive model.[12] The bond order in the $=\underset{|}{C}-\underset{|}{C}=O$ bond is found to be about 0.06 unit lower in 2-acetylfuran than in 2-furanaldehyde. The barriers to rotation calculated with the HMO method as the difference in π-electron energy between the activated and ground states are $-0.56\ \beta$ for 2-furanaldehyde and $-0.49\ \beta$

for 2-acetylfuran. With $\beta \simeq -18$ kcal/mole this difference in π-electron energy between the two compounds corresponds to 1.3 kcal/mole.

More elaborate Extended Hückel calculations give similar results. The change in total energy upon rotation of the carbonyl groups to a plane perpendicular to the ring is decreased from 15 kcal/mole in 2-furanaldehyde to 10 kcal/mole in 2-acetylfuran, the last value slightly dependent on the conformation of the methyl protons in the acetyl compound. The results of the different calculations are shown in Table 3.

Table 3. Summary of calculated nonbonded interactions and electron energy differences in 2-furanaldehyde and 2-acetylfuran (in kcal/mole).

Calculation	Angle of rot.[a]	2-Furanaldehyde	2-Acetylfuran
Repulsion potentials [b]	0°	$+0.521$	$+0.259$ [c] $+0.214$ [d]
acc. to Hill [9]	90°	-0.487	-0.839 [c] -0.832 [d]
	180°	$+0.510$	$+0.422$ [c] $+0.291$ [d]
Repulsion potentials	0°	-0.858	-1.387 [c]
acc. to Scott—	90°	-1.030	-1.669 [c]
Scheraga [10]	180°	-0.924	-1.538 [c]
Hückel, ΔE_π:	0°→90°	10.1 [f]	8.8 [e,f]
	180°→90°		
Extended Hückel, ΔE	0°→90°	14.6	10.8
	180°→90°	15.3	8.5
Experimental values	0°→90°	11.2	9.1
given as ΔH^*	180°→90°	10.1	9.1

[a] The rotation angle is 0° when the oxygen atoms of the ring and the carbonyl group are in a *trans* configuration and 180° in the *cis* configuration.

[b] Negative values represent attraction.

[c] The methyl group staggered with respect to the carbonyl oxygen atom.

[d] The methyl group eclipsed with the carbonyl oxygen atom.

[e] Inductive model,[13] $h_C = -0.5$ for the carbonyl carbon atom.

[f] Using $\beta = -18$ kcal/mole.

As mentioned previously, the rate parameters were obtained from computed spectra utilizing the full line shape of the signals weighted with a set of intensity factors. These factors might have introduced systematic errors into the calculations. In order to estimate these, three 60 MHz spectra recorded at the temperatures $-61°$, $-85°$ and $-106°$C were used as test spectra. A number of spectra were calculated with different τ-values with a (rather time-consuming) density matrix program [6] using the complete Hamiltonian for the spin system of the ring protons. These spectra were fitted to the previously calculated spectra for the three temperatures using the weighted intensity factors. The line shapes calculated with the two programs using a given set of parameters were found to be virtually identical. The error introduced in the τ-values by using the simplified weighting factor treatment is estimated to be less than 3 %.

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