An I.R. Spectroscopic Study of the Conformational Equilibrium in 2-Acetylfuran

Giulio Paliani, Rosario Cataliotti, and Antonio Poletti

Istituto di Chimica Fisica dell'Università, Via Elce di Sotto, 10-06100 Perugia, Italy

(Z. Naturforsch. **31 a**, 1217–1219 [1976]; received May 17, 1976)

The conformational cis/trans equilibrium of 2-Acetylfuran has been studied by i.r. spectroscopy, in various physical states. This equilibrium is strongly influenced by the dielectric constant of the medium. The isomeric energy difference is very small as revealed by the insensitivity of the equilibrium position to temperature changes.

Introduction

Infrared spectroscopy is a well-established technique for investigating conformational equilibria, especially in those cases where the equilibrium between the two conformers is established rapidly.

2-Acetylfuran is an attractive molecule for conformational studies by infrared spectroscopy since its spectrum, from the pure liquid, contains a large number of doublets, suggesting the existence of an equilibrium between two forms. We report such a study and relate the results to those previously obtained by nmr spectroscopy [1–3]. There is little agreement among the nmr studies, especially as regards the percentage of the predominant form present at room temperature.

Experimental

2-Acetylfuran was a commercial product by Aldrich. 2-Acetylfuran-d_3 was prepared with the method reported in Ref. [4], starting from furan and CD_3COCl. Both samples were purified by vacuum distillation and tested for purity by glc on a LAC 728 (diethyleneglycol succinate) column at 180 °C.

Spectra were recorded on a Perkin-Elmer grating spectrophotometer model 521, with 5 × wavelength expansion. NaCl cells of optical path length 0.1 mm were used, connected to thermostated sleeves fed by water from a ultrathermostat, capable of allowing readings of 0.1 °C in temperature. The temperature was measured with a copper-constantan thermocouple in contact with the sample via windows in the cell.

Since the peaks due to the two conformers overlap (Fig. 1) the areas were integrated using the methods reported elsewhere [5].

Reprint requests to Dr. G. Paliani, Istituto di Chimica Fisica, Via Elce di Sotto, *10-06100 Perugia (Italia).*

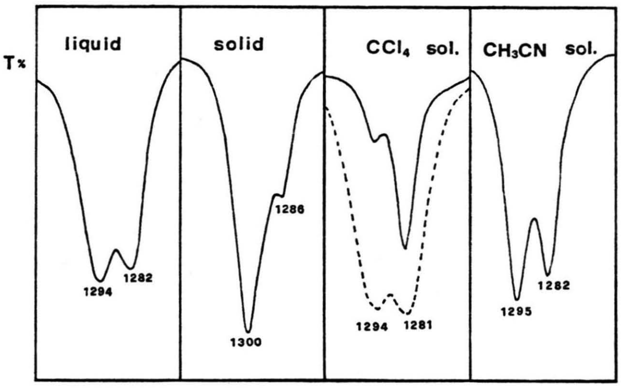
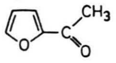


Fig. 1. A typical pattern of doublets of 2-Acetylfuran in various physical states. For CCl_4, the solid line refers to a 0.1 M and the broken line to a 4.5 M solution.

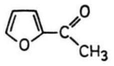
All solvents used were first purified for spectroscopic measurements, as described in [6].

Results and Discussion

Conjugation between the furan ring and the acetyl substituent in position 2 with respect to the heteroatom causes the planar form of 2-acetylfuran to be favoured. Under these conditions, two conformations, i.e., O – O cis and O – O trans, are possible given the electrostatic interactions set up between the heteroatom and the oxygen atom of the acetyl group.



O–O *cis*



O–O *trans*

This indeed appears to be the case, as shown by the large number of doublets in the liquid-state i.r. spectrum of the molecule (1294 – 1282; 1168 – 1163; 1025 – 1010; 968 – 957; 916 – 906; and

$500-492\ \text{cm}^{-1}$) and its deuterated derivative, 2-acetylfuran-d_3, and the differences in relative intensity of the components of these doublets between the liquid and solid state. Thus, in the solid state (at liquid N_2 temperature) the higher frequency components of the doublets are much more intense and, for most of the doublets, those at lower frequency are virtually absent. In solutions of the two isotopic compounds in organic solvents, the intensities in the doublets depend on both the concentration and the nature of the solvent. In particular, in dilute solutions in non-polar solvents the lower frequency component is more intense. On increasing the concentration, the relative intensities tend to shift towards that of the pure liquid, where the doublet components are of about equal intensity. An analogous behaviour is found in solutions of the isotopic compounds in polar solvents such as CH_3CN and CH_3OH, although the higher-frequency component is slightly more intense than the lower frequency one. A calculation of the electric dipole moments, based on known values for group moments, leads to the conclusion that the trans form has the lower electric dipole moment. The dipole moments are estimated to be: $\mu_{\text{cis}} = 3.36$ D and $\mu_{\text{trans}} = 2.74$ D[7].

If we now assume that in solvents of low dielectric constant such as CCl_4 the form with the lower dipole moment predominates, then it follows that the lower frequency components of the doublets should arise from vibrations of the O – O-trans conformer. It may be noted that in the gas-phase spectra only the lower frequency component is observed. If this assignment is correct, it further demonstrates that the trans form predominates in media of low dielectric constant.

With increase in the dielectric constant of the medium (solutions in polar solvents, the pure liquid or very concentrated solutions in non-polar solvents) the predominating form is that having a higher dipole moment, i. e. presumably the cis form. Further, the experimental results indicate that the only forms stable in the solid state, for both isotopic compounds, are the O – O cis forms, the molecular vibrations of which constitute the higher frequency components of the doublets. This conclusion is confirmed by the fact that for a structurally similar molecule, 2-formyl-4-bromofuran, X-ray studies show that the molecule is completely planar and the formyl group is cis with respect to the heteroatom[8].

We have attempted to follow the temperature dependence of the conformational equilibrium, using integrated band intensities, for both isotopic compounds in the pure liquid and in CCl_4 and CS_2 solutions, between $-25°$ and $+60$ °C. However, the relative intensities of the two components of the doublets do not vary with temperature. This fact indicates that the energies of the two conformers are much the same and that ΔH is ca. 0. Similar observations were made by Abraham and Siverns[9] in a study of 2-formyl-furan in non-polar solvents.

The conformational equilibrium constants are found from the relation:

$$K = C_2/C_1 = A_2\,\varepsilon_1/A_1\,\varepsilon_2\,,$$

where the symbols have their usual meaning. However, K cannot be directly calculated using this expression since the absorption coefficients for the two conformers are not known. Hartman et al.[10] have developed a method which allows the ratio $\varepsilon_1/\varepsilon_2$ to be found as the slope of the straight line obtained by plotting the areas A_1 vs A_2 for the isomers at different temperatures. Since in the present case there was no appreciable thermal effect on the areas of the two components, this methods cannot be applied. Nevertheless K could be evaluated, for different solvents, by measuring the ratio A_2/A_1 directly and assuming that, to a first approximation, $\varepsilon_1 = \varepsilon_2$. The validity of this assumption cannot be proved 'a priori', but finds support in the fact that (i) it has been used successfully in many other cases (e. g. see Refs.[11, 12] and (ii) measurements of integrated areas carried out on the pairs of bands at 1291 – 1278 and $1171-1161\ \text{cm}^{-1}$ (in CCl_4) gave values for the equilibrium constant in excellent agreement with one another.

Table 1 lists the K values obtained and the relative percentages of the trans conformer, measured for the pure liquid and in a series of solvents of differing dielectric constant.

It may be noted that the conformational equilibrium constant depends heavily on the nature of the solvent, decreasing greatly with increase in the dielectric constant of the medium *. In addition, for any single solvent, K decreases with increase in solute concentration which, as mentioned above, again corresponds to an increase in the dielectric

---

* The only anomalous solvent, benzene, is well-known to be anomalous in experiments such as these, always behaving as if it were more polar then expected[9, 13, 14]. The reason for this behaviour is unknown.

Table 1. Equilibrium constants and amount of trans form (%) of 2-acetylfuran in various media.

Medium	Dielectric constant	Conc. [a]	$\nu_{\text{cm}^{-1}}$	$K\frac{\text{trans}}{\text{cis}}$	$\nu_{\text{cm}^{-1}}$	$K\frac{\text{trans}}{\text{cis}}$	% trans form
CCl_4	2.24	1.12	1291 1278	3.43	1171 1161	3.40	77
CCl_4	—	45.0	1294 1281	1.06	1169 1162	1.04	51
CS_2	2.64	1.56	1290 1277	2.91	1169 1160	2.83	74
C_6H_6	2.28	1.58	1291 1279	1.97	1168 1160	— [c]	66
CH_3CN	37.50	3.11	1295 1282	0.68	1169 1163	0.72	41
Pure liquid	42.0 [b]		1294 1282	0.80	1168 1163	0.81	45

[a] mole $l^{-1} \times 10$; [b] such value was reported for **2-Formil-furan** [9, 15]; [c] the solvent absorption impedes *K* evaluation in this case.

constant of the medium. These facts demonstrate that the solvent plays an important role in changing the position of the conformational equilibrium, tending to preferentially stabilise particular conformers of the solute molecule. Since the energies of the conformers seem to be virtually identical (there is no thermal effect on *K*, see above) although the polarities of the two forms O – O-cis and O – O-trans are greatly different from one another, we deduce that this solvent effect arises from specific solute-solvent interactions of the dipole type and not to preferential solvation of one of the two forms.

To conclude, the *K* values found here are in considerable disagreement with those in the literature [1–3] (which are also in disagreement with one another). The discrepancies appear to be due to the fact that the literature data were obtained with different physical techniques and at different temperatures, making comparison difficult. In addition, the data have often been obtained in different solvent media and at different concentrations without due account being taken of the effect of the dielectric constant of the medium on the conformational equilibrium in this molecule.

[1] M. L. Martin, J. C. Roze, G. J. Martin, and P. Fournari, Tetrahedron Letters **1970**, 3407.

[2] K. I. Dahlquist and A. B. Hornfeld, Tetrahedron Letters **1971**, 3837.

[3] S. Nagata, T. Yamabe, K. Yoshikawa, and H. Kato, Tetrahedron **29**, 2545 [1973].

[4] Organic Syntheses, Collective **2**, 8 [1943].

[5] G. Paliani, S. Sorriso, and R. Cataliotti, J. C. S. Perkin II, 1976, 707.

[6] Techniques of Organic Chemistry, Vol. VII, A. Weissberger Editor.

[7] H. Lumbroso, D. M. Bertin, F. Fringuelli, and A. Taticchi, J. C. S. Perkin VII, in press.

[8] B. Roques, S. Combrisson, C. Riche, and C. Pascard-Billy, Tetrahedron **26**, 3555 [1970].

[9] R. J. Abraham and T. M. Siverns, Tetrahedron **28**, 3015 [1972].

[10] K. O. Hartman, G. L. Carlson, R. E. Vitkowski, and W. G. Fateley, Spectrochim. Acta **24 A**, 157 [1968].

[11] C. G. Le Fevre, R. J. W. Le Fevre, R. Roper, and R. K. Pierens, Proc. Chem. Soc. **1960**, 117.

[12] L. Pauling, J. Amer. Chem. Soc. **58**, 95 [1936].

[13] R. J. and M. A. Cooper, J. Chem. Soc. B **1967**, 102.

[14] R. J. Abraham, H. D. Banks, E. L. Eliel, O. Hofer, and M. K. Kaloustian, J. Amer. Chem. Soc. **96**, 1913 [1972].

[15] G. Allen and H. J. Bernstein, Canad. J. Chem. **33**, 1055 [1955].