Dependence of the Furan-2-carbaldehyde Conformational Equilibrium on Solvent Dielectric Constant: Direct Evidence from Pulsed (Fourier Transform) Nuclear Magnetic Resonance

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Low temperature pulsed (Fourier transform) n.m.r. measurements on very dilute solutions of furan-2-carbaldehyde in trichlorofluoromethane and carbon disulphide, and on a concentrated solution in deuteriodichloromethane, demonstrate the sensitivity to changes in solution dielectric constant of the position of the conformational equilibrium between *syn*- and *anti*-forms. A previous estimate of the position of the equilibrium in non-polar solvents is close to the results found in the present study.

THE much studied furan-2-carbaldehyde conformational equilibrium (1) provides a useful opportunity for a comparison of the applicability and power of physical methods.[1] In particular, it emphasises the possible inadequacies of the i.r. characteristic group absorption method (where the origin of band multiplicity is often highly controvertible †) and of the room temperature n.m.r. and dipole moment methods where, for such an equilibrium, averaged parameters weighted over all conformations are the only measurable quantities. For solution studies, it seems reasonable to conclude that low temperature n.m.r. measurements, where resonances from individual conformations may be observed directly, are the most reliable method for the determination of the relative concentrations of conformers.

(1)

Unfortunately, for equilibria with low interconversion energy barriers and small chemical shift differences between the n.m.r. signals in the interconverting conformers, the temperatures below which signals for individual conformers are observed ('coalescence' temperatures) are low. (The ^{1}H n.m.r. coalescence temperature for the aldehyde signals of furan-2-carbaldehyde is *ca.* 203 K, for example.) Thus it has not been possible in the past to study such an equilibrium in non-polar solvents (of dielectric constant $<$ *ca.* 5) since such solvents are incapable of holding sufficient material in solution at low temperatures for a satisfactory continuous wave n.m.r. spectrum to be recorded.

Abraham and Siverns[4] were faced with this problem in their study of the dependence of the position of the furan-2-carbaldehyde equilibrium on solvent. Of the observations which they record, two are unequivocal (^{1}H n.m.r. measurements on solutions in dimethyl ether and acetone at low temperatures). The remaining solution data were derived either from dipole moment measurements (carbon tetrachloride and benzene solutions) or room temperature measurements of n.m.r. long-range coupling constants (in dichlorodifluoromethane, dimethyl ether, acetone, and dimethyl sulphoxide solutions): data given for the pure liquid should be discounted since they are based on i.r. measurements. They concluded that the difference in free energy between the *syn*-and *anti*-forms of the aldehyde was strongly dependent on the nature of the solvent, the *anti*-form being more stable than the *syn* in media of dielectric constant $<$ *ca.* 5 and *vice versa* in media of dielectric constant $>$ *ca.* 5. Unequivocal evidence was, however, lacking. In this paper, direct evidence from pulsed Fourier transform ^{1}H n.m.r. studies of very dilute solutions of furan-2-carbaldehyde in non-polar solvents (and,

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† It is ironic that the *syn–anti*-equilibrium was first proposed [2] to explain the doubled i.r. carbonyl stretching band in furan-2-carbaldehyde when the correct explanation is Fermi resonance.[3]

[1] References to much of the work on the furan-2-carbaldehyde conformational equilibrium may be found in C. L. Cheng, I. G. John, G. L. D. Ritchie, P. H. Gore, and L. Farnell, *J.C.S. Perkin II*, 1975, 744. Additional references include B. P. Roques, S. Combrisson, and F. Wehrli, *Tetrahedron Letters*, 1975, 1047; D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin II*, 1975, 13; C. G. Andrieu, C. Chatain-Cathaud, and M. C. Fournie-Zaluski, *J. Mol. Structure*, 1974, **22**, 433; D. J. Chadwick, G. D. Meakins, and E. E. Richards, *Tetrahedron Letters*, 1974, 3183; P. Cremaschi, *Rend. Ist. Lombardo Accad. sci. Lett. A*, 1973, **107**, 735; R. Grigg and M. Sargent, *Tetrahedron Letters*, 1965, 1381; P. Adamek, K. Volka, Z. Ksandr, and I. Stibor, *J. Mol. Spectroscopy*, 1973, **47**, 252.

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

[3] D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Chem. Comm.*, 1972, 742; C. G. Andrieu, C. Chatain-Cathaud, M.-C. Fournie-Zaluski, and B. Roques, *Compt. rend.*, 1972, **C275**, 559.

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

for comparison, evidence from ^1H and ^{13}C n.m.r. studies of a concentrated solution in a more polar solvent) is presented to test the solvent dependence of the aldehyde conformational equilibrium.

EXPERIMENTAL

Commercial furan-2-carbaldehyde was distilled *in vacuo* immediately before use. CCl_3F, CD_2Cl_2, and CS_2 (analytical grade) were dried over molecular sieves (B.D.H. type 3A).

N.m.r. spectra were recorded at 183 K using a Brücker WH90 pulsed Fourier transform spectrometer operating at 90 (^1H studies) or 22.63 MHz (^{13}C studies). For the dilute solution studies, samples were located in a 3 mm tube supported coaxially within a 5 mm tube. Hexadeuterioacetone [containing *ca.* 0.06M-chromium(III) acetylacetonate to reduce the danger of saturation] was used to 'lock' the spectrometer magnetic field and was located in the space between the two tubes. For the concentrated solution (in CD_2Cl_2), ^1H n.m.r. spectra were measured with the sample in a 5 mm tube, and ^{13}C spectra with the sample in a 10 mm tube: the spectrometer was 'locked' to internal CD_2Cl_2. Temperature control was to 1 K.

Solutions were made up by weight using a Mettler S6 balance (accuracy 0.005 mg). Dielectric constants of the dilute solutions at 298 K were calculated using additive volume fractions:[5] possible deviations therefrom are discussed in the text. Literature values of densities (ρ/g cm^{-3}) and dielectric constants (ε) were used: furan-2-carbaldehyde[6] (ρ 1.155, ε 38), CCl_3F[7] (ρ 1.476, ε 2.28), and CS_2[8] (ρ 1.263, ε 2.64). Dielectric constants at 183 K were calculated using the known[8] temperature dependence for CS_2 (ε 2.94) and assuming a similar dependence for CCl_3F (ε 2.60), and the known[7] temperature dependence of the density of CCl_3F (ρ 1.730) and by extrapolation of the literature data[8] for CS_2 (ρ 1.426). Low temperature data for the aldehyde were obtained by extrapolation from room temperature figures[6] and are necessarily approximate.

RESULTS AND DISCUSSION

Of the five solutions examined, four (Table) (three in CCl_3F, one in CS_2) were made up to have very low dielectric constants. The fifth (*ca.* 2.5M in CD_2Cl_2) was expected to have a dielectric constant comparable to those of solutions used in previous low temperature ^1H [4,9] and ^{13}C [1] n.m.r. studies. Deviations (positive or negative) of dielectric constants from the values predicted using volume fractions may occur. In the Table are shown possible negative deviations calculated from the equations described by Decroocq.[5] The small corrections involved are unimportant for the present purposes.

anti : *syn* Ratios for furan-2-carbaldehyde in various solvents

Solvent	CCl_3F	CCl_3F	CCl_3F	CS_2
Weight of aldehyde (mg) per gram of solvent	0.860	4.100	14.750	2.395
ε_{298}	2.32	2.47	2.94	2.73
Possible deviation from ε_{298} (see text)	−0.02	−0.10	−0.35	−0.05
Approximate ε_{183}	2.68	2.96	3.89	3.12
Ratio *anti* : *syn* [a]	1.10 : 1	0.95 : 1	1.00 : 1	0.90 : 1

[a] Integrals accurate to within 5%.

The results require only brief discussion. At 183 K, the n.m.r. signals due to the formyl and 3-H hydrogen atoms and to all ring and carbonyl ^{13}C atoms are split because of the conformational heterogeneity. Whereas in the solution of high dielectric constant the *anti*-isomer is only *ca.* 9% abundant (determined from ^1H and ^{13}C integrals and previously published signal assignments[1,9]), it is found, in agreement with Abraham and Siverns, that this form becomes markedly more favoured relative to the *syn*-form in media of low dielectric constant. However, it would seem that the dielectric constant of the aldehyde solution needs to be somewhat <5 for the *anti*-form to predominate.

I thank Magdalen College, Oxford, for a fellowship.

[5/1286 *Received*, 30*th June*, 1975]

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