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ROTATIONAL ISOMERISM—XIII

ROTATIONAL ISOMERISM IN FURFURALDEHYDE

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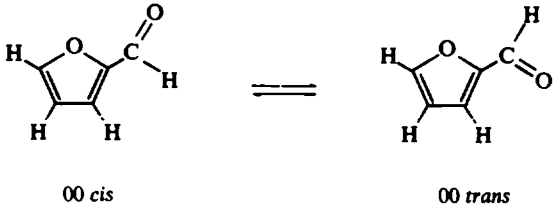
Abstract—The equilibrium between the *cis* and *trans* isomers of furfuraldehyde has been studied by measuring the stereospecific coupling constants between the aldehyde and ring protons in various solvents. These values when combined with the observed values of the couplings in the individual conformers at low temperatures give the energy difference between the *cis* and *trans* forms in these solvents. These values together with other previous measurements demonstrate the large solvent effect on this equilibrium. E(*cis*)-E(*trans*) is +1·5 kcals/mole in the vapour, much smaller in non-polar solvents (+0·3 kcals/mole in CF_2Cl_2), *ca* 0 in $CHCl_3$ and becomes negative in polar media (−1·0 kcals/mole in the pure liquid). This solvent dependence is given a quantitative explanation in terms of a known theory of solvation.

The energy of activation of this equilibrium also shows a pronounced dependence on the medium and this is also quantitatively explained by the same theory.

Finally the vapour state values of the energy difference and energy of activation agree with calculated values based on current MO theories.

THE rotational equilibrium between the two planar forms of furfuraldehyde (I; 00 *cis* → 00 *trans*) has been the subject of numerous investigations and some controversy, since the first demonstration of this equilibrium, by Allen and Bernstein.[1] They found ΔH ~ 1 kcal/mole in the liquid but were unable to observe any temperature dependence of the IR and Raman spectra of the vapour. In agreement with this Karabatsos and Vane from a study of long range coupling constants concluded that only the *cis* form was present in solution.[2]

I



In 1965 two detailed investigations appeared. The microwave spectrum of the vapour gave ΔH −0·99 (±0·2) kcals/mole and also the torsional potential for the rotation (V_2 8·67 kcals/mole).[3] Dahlquist and Forsen succeeded in observing the separate isomers by low temperature NMR in dimethyl ether solution, to give ΔH −1·05 kcals/mole and also an energy of activation (ΔH^*) of 11·5 kcals/mole[4]. Their assignment, based on chemical shift values was the reverse of that of ref 2.

Subsequent values of the energy of activation were V_2 7·0 kcals/mole in the vapour from far IR spectroscopy[5] and ΔH^* 12·1 (± 2) kcals/mole in the liquid from ultrasonic measurements.[6] Also further IR studies[7] showed the *trans* form to be more stable in CCl_4 solution, a conclusion which is also supported by dipole moment measurements.[8]

Recently Roques *et al.* from a comparison of crystal structures and coupling constant data[9] and Martin *et al.* from other NMR studies[10] further supported the assignment of ref 2, and this is now undoubtedly the correct assignment. However, considerable confusion still exists. For example Arlinger *et al.* use the vapour state value of ΔH in support of their assignment of the conformers of 2-acetylfuran[11] even though the comparison is with the NMR of furfuraldehyde in the liquid. Similarly Roques *et al.* dwell at length on the reasons for the preferential thermodynamic stability of the *cis* form[9] when in fact in the vapour it is the trans form which is the more stable.

It is clear that a large part of the confusion in the results stems from the comparison of the results in different media. We have recently derived a general theory for the dependence on the medium of any equilibrium between polar molecules[12, 13] and this has been applied successfully to a variety of systems.[14–16] Thus it is of interest to see whether this theory can be applied in this case.

We present further measurements of the NMR spectrum of furfuraldehyde in a number of solvents and then show how these and the previous results involving both the energy differences and activation energies can be given a satisfactory quantitative theoretical explanation.

THEORETICAL

The theory has been derived elsewhere,[12, 13] thus we give here only the necessary outline, plus the application to furfuraldehyde.

The solvation energy of any polar molecule in state A, i.e. the difference between the energy in the vapour (E^v_A) and in any solvent (E^s_A) of dielectric constant ε, is obtained by calculating the molecular dipolar and quadrupolar electric fields in the solvent by classical electrostatic theory.*

This gives the expression†

$$E^s_A = E^v_A - k_A \, . \, x/(1 - lx) - 3h_A x/(5 - x) \qquad (1)$$

where $x = (\varepsilon - 1)/(2\varepsilon + 1)$, $l = 2(n_D^2 - 1)/(n_D^2 + 2)$, n_D being the solute refractive index, and k_A and h_A are μ_A^2/a^3 and q_A^2/a^5 respectively, μ_A and q_A being the dipole and quadrupole moments of the molecule and the molecular radius. For two equilibrating

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* The calculations are in terms of the potential energy whereas the experimental data are strictly in terms of enthalpy. As we are considering only *differences* between solvents the zero-point energy, contribution of higher vibrational states and PdV terms are expected to cancel out.[17]

† A further term is given in ref 13 which considers explicit dipole–dipole interactions. We have recently extended this to include dipole–quadrupole interactions.[18] As these terms are complex but give only minor corrections to the energy we have for simplicity omitted them here. This does not affect at all our final conclusions.

molecular states (A and B) such as the *cis* and *trans* conformers of furfuraldehyde the equation becomes

$$\Delta E^s = E^s_A - E^s_B = \Delta E^v - kx/(1 - lx) - 3hx/(5 - x) \qquad (2)$$

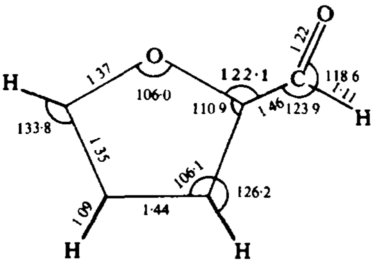
where now $k = k_A - k_B$ and $h = h_A - h_B$.

On our model the dipole and quadrupole moments are calculated by placing point dipoles along and at the centre of the polar bonds and a is given by $4\pi a^3/3 = M_v/N$ where M_v is the molar volume and N Avogadro's number.

Note that the energy difference $E_A - E_B$ need not only be between two stable conformers, any state of the molecule will be affected by the solvent in this manner. Thus the theory can in principle be used to predict the solvent dependence of the barrier to interconversion as well as the conformer energy difference.

In order to quantify this we need to know the molecular geometry and the dipole moments of the three states involved i.e. the *cis* and *trans* conformers and the transition state, which we assume has the aldehyde group twisted 90° out of the plane of the furan ring.

The geometry used (shown below) is taken from the microwave data of furan, the crystal structure determination of the $C.C.CO_2H$ angle in 2-furoic acid and the known geometry of the aldehyde group.[19]



The bond dipole moments were obtained using the microwave determinations of the dipole moments of the *cis* (3·93 D) and *trans* (3·23D) conformers[3] and of furan (0·66D)[8]. Using C═O and C—O dipoles of 3·5 and 0·4D with the above geometry gives values of 3·97 (*cis*), 3·25 (*trans*) and 0·48 (furan) in very reasonable agreement.

It is of interest to compare these values with those from quantum mechanical calculations, which also provide a basis to estimate the dipole moment of the transition state. With the same geometry the CNDO (INDO) MO programme[20] gives dipole moments for the *cis*, 90° and *trans* forms of 3·67 (3·70); 2·73 (2·78) and 2·67 (2·82) D. The *cis* and *trans* values are somewhat lower than the experimental ones but compare reasonably in the relative sizes of the dipoles.

The value for the transition state is virtually identical to that of the *trans* form. A value of the C═O dipole of 2·8 D (the value for an unconjugated CO group) gives the dipole moment of the transition state as 2·93 D, which agrees well with the MO calculations and we will use this value subsequently.

The "C=O bond dipole" decreases from 3·5 D to 2·8 D on rotating the CO group 90° from the furan ring plane, supporting the common representation of the large dipole moment in furfuraldehyde as being due to π electron transfer from the heterocycle to the aldehyde group, which does not operate for the transition state in which the ring and CO π systems are orthogonal.

The remaining parameters needed in Eq 2 are experimentally measured quantities and are given in Table 1 together with the resulting values of k and h.

TABLE 1. MOLECULAR CONSTANTS AND CALCULATED PARAMETERS FOR FURFURALDEHYDE

Isomer	density^{21}	n_D^{21}	Molar volume (mls)	l	Dipole moment (D)	k (kcal/mole)	h (kcal/mole)
cis	1·1598	1·5261	82·84	0·6140	3·97	6·92	16·38
trans					3·25	4·63	13·92
90°					2·93	3·78	9·30

Eq 2 and Table 2 can now be used to evaluate the medium dependence of ΔE and ΔE^*. However we shall first evaluate the NMR measurements performed here, as these provide additional necessary data.

TABLE 2. THE SOLVENT DEPENDENCE OF PROTON–PROTON COUPLINGS IN FURFURALDEHYDE

Solvent	ε (solution)	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}	r.m.s. error
CF_2Cl_2	2·90	0·141 (0·006)	0·469 (0·006)	0·486 (0·006)	3·596 (0·006)	0·779 (0·006)	1·685 (0·006)	0·014
Me_2O	7·90	—	0·310 (0·006)	0·668 (0·006)				0·008
Acetone	19·5	—	0·222 (0·007)	0·782 (0·007)	3·565 (0·007)	0·748 (0·007)	1·697 (0·007)	0·017
DMSO	50·0	—	0·143 (0·001)	0·832 (0·001)				

RESULTS

The results in Table 2, where they overlap, are in good agreement with those of earlier investigations, save that better resolution and increased spectrometer stability provides extra and more accurate information. Thus we find that the aldehyde proton in furfuraldehyde couples to all three protons in the furan ring, the coupling to H_3 (0·14 Hz) only being resolved in CF_2Cl_2 solution. This may be due to the better resolution achieved in this solvent, or to a solvent dependence of the coupling.

The results also provide immediate confirmation of the assignment of ref 2. The decrease of J_{24} and increase of J_{25} with increasing solvent polarity when taken with the general rule that the higher dipole moment form is more stabilized in polar media means that the *cis* conformer has the large J_{25} and small J_{24} and the *trans* conformer *vice versa*.

We wish however to quantify this result to obtain the rotamer couplings and energy differences.

The measured couplings in Table 2 are the weighted mean of the couplings in the *cis* and *trans* forms, i.e. in any solvent S

$$\left.\begin{aligned} J_{24}(S) &= N_c J^c_{24} + (1 - N_c)\, J^t_{24} \\ J_{25}(S) &= N_c J^c_{25} + (1 - N_c)\, J^t_{25} \\ &\text{where from equilibrium I} \\ (1 - N_c)/N_c &= \exp(-\Delta F^s/RT). \end{aligned}\right\} \quad (3)$$

$-\Delta F^s$, the free energy difference in any solvent S, may be replaced by $\Delta E^s(E^s_c - E^s_t)$.* The remaining couplings in the molecule are constant to within the experimental error ($\pm 0{\cdot}03$ Hz) thus we may assume there is no intrinsic solvent dependence of J_{24} and J_{25}. Thus the results in Table 2 with Eqs (3) can provide values of the rotamer couplings and energy differences.

The calculations were performed by two independent methods (a) If Eqs (2) and (3) are combined then as all the parameters in Eq. (2) are known (*cf* Table 1) the solvent dependence of each coupling becomes a three parameter fit in the unknowns J^c, J^t and ΔE^v, the vapour state energy difference.

(b) The two equations for J_{24} and J_{25} may be solved simultaneously. For any solvent this gives two equations in five unknowns (J_{24} and J_{25} in the two conformers and ΔE^s). Each additional solvent adds two more equations but only one more unknown (ΔE in that solvent). Thus the four solvents examined give eight equations in eight unknowns. These therefore may be solved without recourse to the solvent theory of Equation (2).

However, when the errors in the experimental data are included, both methods lead to a range of possible solutions.

Most of these can be eliminated by utilizing the low-temperature measurements on the individual conformers, as follows.

The results of ours and ref 4's measurements give for the low temperature couplings $J^c_{25} = 1{\cdot}08$ ($\pm 0{\cdot}03$) Hz and $J^t_{24} = 0{\cdot}80$ ($\pm 0{\cdot}05$) Hz. The other couplings were not resolved, i.e. J^c_{24} and $J^t_{25} < (0{\cdot}2)$ Hz.

In order to use these values at room temperature the intrinsic temperature variation of the couplings must be considered. The only comparable systems extensively studied both experimentally and theoretically are the substituted ethanes. Schug *et al.*[24] predicted that vibrational averaging will decrease the *trans* oriented coupling and increase the gauche oriented coupling with increase in temperature in any rotamer. This has been observed, e.g. in *t*-Bu CH_2CH_2 Si Me_3 in which only one rotamer is present, the *trans* coupling decreases from 14·0 to 13·2 Hz and the gauche coupling increases from 4·0 to 4·3 Hz over a 200° rise in temperature,[25] in excellent agreement with the theoretical predictions.[14]

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* Replacement by ΔE assumes that (a) we may replace enthalpy by energy (*cf* footnote on page 4) and (b) the entropy difference between the conformers is zero. There seems no reason to suppose otherwise and furthermore the systematic errors in all previous measurements of this equilibrium are larger than the values of ΔS obtained. (*cf* ref 23 for the NMR investigations).

The situation in furfuraldehyde is analogous to that of the trans oriented coupling in ethanes in that vibrational averaging will decrease the couplings. The increased barrier height in furfuraldehyde (10 kcals/mole compared to ~5 for the ethane) is compensated by the lower moment of inertia of the rotating groups thus we may assume an approximately equal proportionate change in the couplings. Thus the room temperature values of the couplings are $J^c_{25} = 1{\cdot}00$, $J^t_{24} = 0{\cdot}70$ both $\pm 0{\cdot}05$ Hz and $J^c_{24}, J^t_{25} < (0{\cdot}2)$ Hz.

All the solutions lying outside these values can be eliminated and this now gives well defined solutions.

Method (a) was solved computationally by varying ΔE^v and obtaining J^t, J^c and the standard deviation of the observed and calculated couplings from the resulting linear equations. In this case the only solution satisfying the conditions for J_{25} was: ΔE^v 1·50 kcals/mole, $J^t_{25} = 0{\cdot}18$, $J^c_{25} = 0{\cdot}96$ Hz standard deviation 0·02 Hz. Above this value of ΔE^v $J^t_{25} > 0{\cdot}2$ (e.g. ΔE^v 1·6, J^t_{25} 0·21, J^c_{25} 0·98 Hz), and below this value J^c_{25} is too small (ΔE^v 1·4, $J^t_{25} = 0{\cdot}13$, $J^c_{25} = 0{\cdot}94$ Hz).

For J_{24} a similar situation holds and for ΔE^v values of 1·5 to 1·8 kcals/mole J^t_{24} ranges from 0·75 to 0·66 Hz and J^c_{24} from 0·05 to $-0{\cdot}02$ Hz.

In this method the two couplings are considered quite separately and therefore the agreement between the values of ΔE^v obtained is very comforting.

Method (b) now involves the solution of eight equations in six unknowns once J^c_{25} and J^t_{24} are known, but a range of solutions is still possible due to the range of values of the two couplings. A solution consistent with the possible values of the couplings is $J^c_{25} = 1{\cdot}00$; $J^t_{24} = 0{\cdot}74$; $J^t_{25} = 0{\cdot}19$ and $J^c_{24} = 0{\cdot}00$ Hz with a standard error of 0·007 Hz. The energy differences in the different solvents which are quite independent of the solvent theory (Eq (2)) are CF_2Cl_2 0·34, Me_2O $-0{\cdot}21$; Acetone $-0{\cdot}55$ and DMSO $-0{\cdot}84$ kcals/mole.

The agreement of the couplings with method (a) is very pleasing. A further check can be made by using Eq (2) with the above energy differences to obtain four independent values of ΔE^v. These are 1·55, 1·71, 1·67, 1·51 kcals/mole in general agreement with each other and the value obtained in method (a).

We may conclude that the room temperature NMR results of Table 2 can be interpreted completely on the basis of Eqs (2) and (3) with values of the conformer couplings of $J^c_{25} = 1{\cdot}0$; $J^t_{25} = 0{\cdot}18$; $J^c_{24} = 0{\cdot}00$ and $J^t_{24} = 0{\cdot}70$ Hz and a value of ΔE^v of 1·5 kcals/mole.

We now wish to consider these results together with the other values of the rotamer energy differences and activation energies in various media.

The observed and calculated solvent effects. The quantitative predictions of Eq (2) can now be checked against the experimental data obtained in this and other investigations. This is given in Table 3.

As previously we replace all enthalpy differences by energy differences thus $E_{cis} - E_{trans}$ $(=\Delta E) = -\Delta H$ for the equilibrium I. Furthermore the enthalpy of activation ΔH^* may be replaced by ΔE^* for these comparative purposes. Note that ΔE^* (*cis* → *trans*) = ΔE^* (*trans* → *cis*) − ΔE. Dahlquist and Forsen[4] give both values but we reverse their assignment to make the *cis* form more stable, as stated earlier. Pethrick and Wyn-Jones[6] derive only ΔE^* (*cis* → *trans*) which has been converted to ΔE^* (*trans* → *cis*) in the Table.

Monnig *et al.*[3] and Miller *et al.*[5] use an alternative description of the equilibrium

TABLE 3. OBSERVED AND CALCULATED ENERGY DIFFERENCES AND ACTIVATION ENERGIES (KCALS/MOLE) FOR FURFURALDEHYDE

Medium	Dielectric Const.	$E_{cis} - E_{trans}$		ΔE^* $(E_{90^\circ} - E_{trans})$		Reference
		obs.	calc.	obs.	calc.	
vapour	1·0	1·0, 1·5, 2·0	(1·5)	8·1, 8·7	(8·5)	3, 5, this work
CCl_4	2·2	0·2	0·56			8
CF_2Cl_2	2·9	0·34	0·29			this work
Benzene	2·2	−0·1	0·54			8
Me_2O	7·90	−0·21	−0·43			this work
Me_2O (−120°C)	12·0	−0·58	−0·60			this work
		−0·60		10·5	10·4	4
Acetone	19·5	−0·55	−0·72			this work
Acetone (−120°C)	37·4	−0·77	−0·84			
P. Liquid	41·9	−1	−0·85	11	10·6	1·6
D.M.S.O.	45·0	−0·84	−0·85			this work

in terms of two potential energies, i.e.

$$V_0 = V_1(1 - \text{cis}\,\theta)/2 + V_2(1 - \cos 2\theta)/2$$

where θ is the dihedral angle between the ring and the CO group and equals 0 for the *trans* form. (Note that this representation ignores all entropy terms). On our definitions above

$$\Delta E = E_{cis} - E_{trans} = V_1$$
$$\Delta E^*\ (trans \rightarrow cis) = E_{90^\circ} - E_{trans} = V_2 + V_1/2$$
$$\Delta E^*\ (cis \rightarrow trans) = E_{90^\circ} - E_{cis} = V_2 - V_1/2$$

Their values of V_1 and V_2 give the only values of ΔE and ΔE^* for the vapour state, except for the present work.

The data in Table 3 is of considerable interest. The value of ΔE^v obtained in the present investigation nicely bisects the values of Refs 3 and 5 (1·0 and 2·0 kcals/mole) and this value is used in Eq 2 to obtain the calculated energies. Similarly the value of ΔE^* of 8·5 kcals/mole in the vapour used for the calculated barriers is merely the average of the two experimental values.

The calculation of any energy difference or activation energy is therefore simply a matter of inserting into Eq (2) the corresponding parameters from Table 1 and the appropriate dielectric constant.

The values of the solvent energy differences are from Refs 1 (Pure liquid); 4 (Me_2O reversing their assignment) and from the previous section by method (b) which did not involve Eq (2). Two other values (dimethyl ether and acetone at low temperatures) are obtained directly from the integrated spectrum and are therefore unequivocal. The values for CCl_4 and benzene are obtained directly from the furfural dipole moment in these solvents (3·54 and 3·63 D respectively)[8] using the conformer dipole moments of Table 1.

Inspection of this data and the corresponding calculated energies show immediately the reason for the confusion in the literature concerning this equilibrium. The energy difference changes sign with solvent, being *ca* 0 for a solvent of dielectric constant *ca* 5 (e.g. chloroform). Thus interpolations even between one solvent and another can result in the wrong assignment. However, the calculated energies are in complete agreement with the observed energies and therefore the theory provides a complete quantitative explanation of the results.

The one anomalous solvent, i.e. benzene, is well known to be anomalous on this picture, always behaving as if it were more polar than expected. In previous studies of this nature[12, 16] benzene gives the result expected for a solvent of dielectric constant 7·0, and this is the case here. The reason for this is unknown.

The theory also provides a quantitative explanation of the various estimates of the energy of activation, though these are inevitably less accurate than the conformer energy differences. The increase in barrier height is simply due to the increased solvation energy of the planar forms. Note that the *cis* conformer is even further stabilised, due to its larger dipole moment, ΔE^* (*cis* → *trans*) changing from 7·0 kcals/mole in the vapour to 12·1 kcals/mole in the pure liquid. Again this is given immediately from Eq (2). It is not necessary to invoke any other factor to account for the differences in the results.

The vapour state energy differences and energies of activation. It is of interest to consider the basic parameters of this equilibrium, i.e. the vapour state values of ΔE and ΔE^*. Arlinger *et al.*[11] have calculated the steric effects in this system, using well known potentials for the non-bonded interactions. The only conclusion which can be reached from their calculations is that all steric terms are negligible. For example steric repulsion in the *cis* and 90° forms relative to the *trans* isomer is *ca* $-0{\cdot}05$ and $-0{\cdot}1$ kcals/mole, the 90° form being the least crowded, as expected. However, dipolar interactions,[26] which could be very large were not included in these calcuations. Also the steric effects of the π electrons was not included and could be a further factor.

Some quantum mechanical calculations have also been performed, e.g. Hückel and extended Hückel calculations[11] give values of ΔE ($0 \rightarrow 90°$) as 10·1 and 14·6 kcals/mole respectively, somewhat higher than the correct value of 8·5 kcals/mole (Table 3). In ref 11 these calculated values are compared with the liquid state value of *ca* 11 kcals/mole which of course give much better agreement.

We have performed CNDO (INDO) calculations, using the programme of Pople *et al.*[20] and the geometries specified earlier. This gives energies of 1·1 (1·0) and 6·0 (5·1) kcals/mole respectively for the *cis* and 90° forms relative to the *trans* form, in excellent, though perhaps fortuitous agreement with the experimental values of 1·5 and 8·5, and thus provide a complete explanation of the equilibrium parameters. It is of interest to note in view of the discussion of the equilibrium in terms of charge repulsions between the two O atoms[9] that the excess electron density on these atoms does decrease on going from the *cis* to the *trans* form, from $-0{\cdot}277$ to $-0{\cdot}284$ (C=O) and $-0{\cdot}177$ to $-0{\cdot}188$ (ring oxygen), which supports this interpretation.

EXPERIMENTAL AND ANALYSIS

Dilute solns of freshly distilled furfuraldehyde in various solvents, with 1% TMS added, were degassed and measured on a Varian A56/60 spectrometer, probe temp 37°. The spectra were measured by the sideband technique averaging 3 or 4 spectra. The r.m.s. errors of all the line positions after averaging were 0·02–0·04 Hz.

The spectra in CF_2Cl_2 and acetone were completely analysed to give all the couplings in the molecule. However, the spectra at 60 MHz are strictly first-order and in the other solns only the aldehyde proton was measured accurately. In all cases the final values of the couplings were obtained using $LAOCN_3$[22] and Table 2 gives these values, their probable errors and the r.m.s. errors obtained from the programme.

The solns in acetone and dimethyl ether were also examined at $-100°$ to measure the separate spectra of the two conformers. Unfortunately furfuraldehyde separated out from CF_2Cl_2 soln at low temps, and also from the other non-polar solvents studied (CS_2, n-hexane) thus it was not possible to obtain directly the conformer ratios in a non polar solvent.

The soln in dimethyl ether at $-100°$ gave aldehyde couplings of $J_{25}^{cis} = 1{\cdot}07$ and $J_{24}^{trans} = 0{\cdot}74$ Hz, which compare well with Dahlquists and Forsen's values of 1·10 and 0·85 Hz.[4] The relative population of the two conformers in these solns were directly measured from the heights of the aldehyde and H_3 protons of the separate spectra. This gave *trans/cis* ratios of 18·6 ($\pm 0{\cdot}5$)% for the dimethyl ether soln and 10·7 (± 3)% for the acetone soln. The dielectric constants of the solns were calculated using additive volume fractions as previously described,[13] and also measured directly in the NMR tube. These values are given in Table 2. The dielectric constants of dimethyl ether and acetone at $-120°$ were calculated from the known temp coefficients.[21]

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