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Hydrogen Bonding of *t*-Butyl Alcohol at Low Temperatures and Concentrations

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The composition of solutions of *t*-butyl alcohol at low concentrations in fluorotrichloromethane has been investigated by IR and NMR spectroscopy at low temperatures. The data obtained have been accommodated to four models for the hydrogen bonded species. The best fit was obtained with a monomer-trimer-hexamer model, with a cyclic trimer and an open-chain hexamer, the end group of which contributes to the band at 3625 cm^{-1}. This model gave for formation of the trimer $\Delta H^\circ = -2.4 \pm 0.4$ kcal mol^{-1}, $^*\Delta S^\circ = -6.5 \pm 0.6$ cal mol^{-1} K^{-1} and for the hexamer $\Delta H^\circ = -6.5 \pm 0.6$ kcal mol^{-1}, $\Delta S^\circ = -19.3 \pm 2.6$ cal mol^{-1} K^{-1}, all per hydrogen bond.

Studies of hydrogen bonding of alcohols in solution are usually performed in non-polar solvents which do not have acceptor or donor groups for hydrogen bonding. Carbon tetrachloride has been particularly popular for such investigations. One disadvantage is that its small temperature range for the liquid state (b.p. 76.8, m.p. −23.0 °C) has restricted its usefulness in thermodynamic studies and resulted in an almost complete lack of data below −20 °C.

In connection with our studies on the conformations of aromatic alcohols, we have found fluorotrichloromethane to be an excellent solvent for studying hydrogen bonding. It has a low melting point (−88 °C) and its interaction with alcohols is as small as or even smaller than that of carbon tetrachloride.[1]

We have now used this solvent in order to obtain the IR and NMR spectra of *t*-butyl alcohol at low temperatures and concentrations (10^{-2} to 10^{-3} M, for NMR also at 1.3 and 3.2 M). The results will be discussed in the light of earlier studies carried out at higher temperatures.[2,3,4]

RESULTS

IR spectroscopy. The spectra of *t*-butyl alcohol at three concentrations were obtained from +15 to −70 °C. The spectra of a 7.8 mM solution showed one band at 3625 cm^{-1} (monomer) down to −25 °C. At this temperature a weak band at 3500 cm^{-1} appeared (dimer or trimer) and at lower temperatures a strong band at 3325 cm^{-1} became the predominant feature. The

* 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

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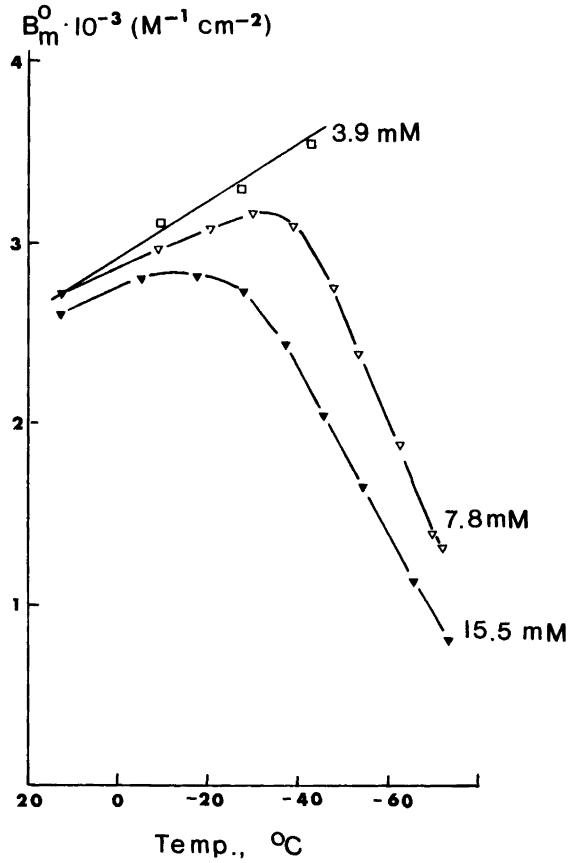

Fig. 1. Integrated molecular absorption at 3625 cm^{-1} of *t*-butyl alcohol in $CFCl_3$ at different temperatures.

same features were shown for the 15.5 and 3.9 mM solutions except in the former case the two low frequency bands appeared at higher temperatures and in the latter case only the band at 3625 cm^{-1} was present down to −40 °C. There was an appreciable increase in the integrated molecular absorption of this band as the temperature was lowered (−0.0053 M^{-1} cm^{-2} K^{-1}) (Fig. 1).[7] The high frequency band shifted from 3625 cm^{-1} at 15 °C to 3615 cm^{-1} at −73 °C. The band at 3500 cm^{-1} (15 °C) moved to 3475 cm^{-1} at −30 °C. At lower temperatures this band merged with the 3300 cm^{-1} band. This band (3325 cm^{-1} at 15 °C) had shifted to 3290 cm^{-1} at −73 °C. The apparent variation of the integrated molecular absorption with the temperature of the 3625 cm^{-1} band is shown in Fig. 1.

NMR spectroscopy. The chemical shifts of the hydroxyl protons at different concentrations and temperatures are shown in Fig. 2. At the lowest concentration, 5.5 mM, the chemical shift increased linearly with decreasing temperature down to −25 °C (−0.0019 ppm K^{-1}). In this region IR spectroscopy showed only the monomeric alcohol to be present. For the 7.8 and 15.5 mM solutions, the curves had a sigmoid shape with the maximum increase in the chemical shift from −40 to −60 °C (−0.1 ppm K^{-1}). The chemical shift of the hydroxyl protons at the highest concentration (3.2 M) showed a linear increase from −50 to −90 °C (−0.007 ppm K^{-1}).

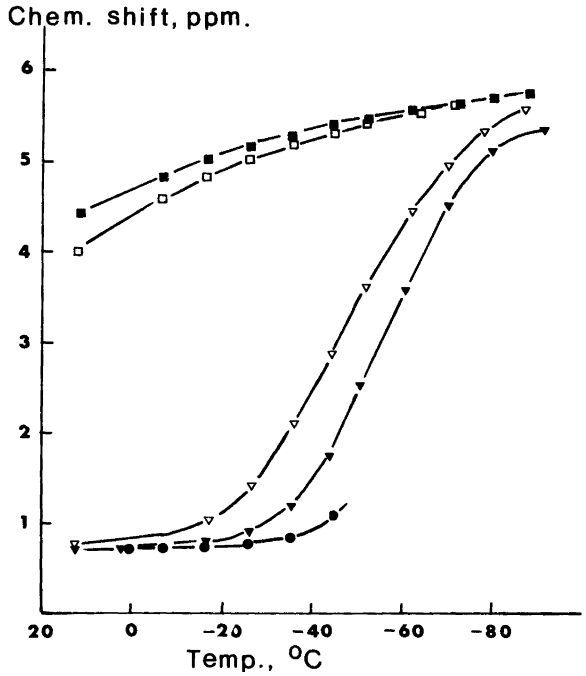

Fig. 2. Chemical shift of the hydroxyl proton of *t*-butyl alcohol in $CFCl_3$ at various temperatures. ■, 3.2 M; □, 1.3 M; ▽, 15.5 mM; ▼, 7.8 mM; ●, 5.5 mM.

DISCUSSION

The nature of the hydrogen bonded species of alcohols in non-polar solvents has been subject of research and discussions for a long time.[2-4] The IR spectra show at least three species, the non-hydrogen bonded alcohol (band at *ca.* 3620 cm^{-1}), a dimer or trimer (band at *ca.* 3500 cm^{-1}) and a polymer (band at *ca.* 3300 cm^{-1}). The hydrogen bonded species have been proposed to be open-chain or cyclic.

There is no *a priori* reason to believe that one single model should fit all the data over extended temperature and concentration ranges. From IR spectra it is clear that the dimer/trimer exists as an important species over a limited temperature range. At lower temperatures or higher concentrations, its IR absorption merges with that of the polymer. Its importance under those conditions can only be found indirectly.

Further, there is no reason to believe that all of the polymers have one single structure over extended temperature or concentration ranges. Intuitively, it appears reasonable that a mixture of several polymers can be present, with differing numbers of monomers and perhaps both of open-chain and cyclic structures. Thus there are unlimited possibilities of different combinations of structures for the polymers, and it is almost certain that more than one combination of these possibilities would fit the experimental results. It is further clear, both from earlier work[2] and from attempts to correlate the IR and NMR data in this work, that the 3625 cm^{-1} band was not caused by the monomer alone. A more difficult question is which other species that contribute to the band, and the integrated molar absorption coefficient of that absorption.

With these points in mind, we have tried four models, in order to see whether the complex situation just described could be represented by a model that would reproduce the experimental results and also give thermodynamic data for the hydrogen bond. The models tried were:

1. Monomer $\rightleftharpoons$ dimer $\rightleftharpoons$ hexamer
$K_2=C_d/C_m^2$; $K_h=C_h/C_dC_m^4$
with an open-chain dimer, its free hydroxyl group contributing to the band at 3625 cm^{-1} and cyclic hexamer.
$C_m^{IR}=C_m+C_d$

2. Monomer $\rightleftharpoons$ trimer $\rightleftharpoons$ hexamer
$K_t=C_t/C_m^3$; $K_h=C_h/C_t\ C_m^3$
with an open-chain trimer and a cyclic hexamer, the free hydroxyl group of the trimer contributing to the band at 3625 cm^{-1}.
$C_m^{IR}=C_m+0.6C_t$

3. Monomer $\rightleftharpoons$ hexamer
$K_h=C_h/C_m^6$
with an open-chain hexamer, its free hydroxyl group absorbing at 3625 cm^{-1}.
$C_m^{IR}=C_m+C_h$

4. Monomer $\rightleftharpoons$ trimer $\rightleftharpoons$ hexamer
$K_t=C_t/C_m^3$; $K_h=C_h/C_tC_m^3$
with a cyclic trimer and an open chain hexamer, its free hydroxyl group contributing to the band at 3625 cm^{-1}.
$C_m^{IR}=C_m+C_h$

where C_m, C_d, C_t and C_h are the concentrations of monomer, dimer, trimer and hexamer, respectively, K's are the equilibrium constants and C_m^{IR} is the appearent concentration of monomer from the 3625 cm^{-1} band.

In addition, a model proposed by Tucker and Becker[2] was tried. This model, obtained from vapour pressure data and IR and NMR spectroscopy, invokes a monomer–trimer–polymer composition of the alcohol, with the polymer being formed by a stepwise addition of monomers to the trimer. The trimer was assumed to be open-chain, the polymer cyclic. From this model eqn. (1) was derived

$$f_a=C_m+3K_t C_m^3/(1-K_\infty C_m) \quad (1)$$

where f_a is the total alcohol concentration, and K_∞ the equilibrium constant for the reaction $(ROH)_{\infty-1}+ROH \rightleftharpoons (ROH)_\infty$. The application of eqn. (1) to our data gave poor fits. This may rather reflect the difficulty in using this model with only two concentrations rather than the unsuitability of the model. However, Tucker and Becker showed that their model gave similar results to those from the monomer–trimer–hexamer model which we have tried (model 2).[2] We therefore believe that the results of this model indicate the suitability of Tucker and Becker's model on our system.

It is convenient to first discuss the results from the IR and NMR studies separately and then try to correlate them with each other and with the four models.

IR. The integrated molecular absorption coefficient of the band at 3625 cm^{-1} (B°_{m}) increased linearly with decreasing temperature (Fig. 1). We have assumed the increase to be linear over the studied temperature range and also to be the same for the contribution to this band from the hydrogen bonded species present (see below). We have used it to adjust the measured absorption of this band for the runs of the 15.5 and 7.8 mM solutions and over the studied temperature range.

From the runs of the 7.8 and 15.5 mM solutions, it was possible to make estimates of the integrated molar absorptions of the dimer/trimer band (at 3500 cm^{-1}, $B^{\circ}_{d/t}$). The estimates are uncertain. The concentrations of the dimer/trimer were found by determining the small changes in the monomer concentrations due to dimer/trimer formation. This results in large uncertainties in the dimer/trimer concentrations and thereby in the $B^{\circ}_{d/t}$,

We estimated $B^{\circ}_{d/t}$ to 60.000±20.000 M^{-1} cm^{-2} for a trimer complex. The limits of error are large. Fortunately, this has only small influence on the determination of the other parameters, because the dimer/trimer was shown to be present in a small molecular fraction over the studied temperature range (Fig. 3).

For their model, Tucker and Becker estimated the integrated molecular absorption coefficient for the "free" end of the open-chain trimer to be approximately half the one of the monomer. In view of the low precision of our estimate of $B^{\circ}_{d/t}$, we have chosen to set the integrated molecular absorption coefficient of the "free" end equal to that of the monomer.

From the two integrated molar absorption coefficients, it was possible for each model to determine the monomer–dimer/trimer–hexamer concentrations, and from these, the equilibrium constants and the thermodynamic parameters. The results are given in Table 1. The molar fractions of the monomer, trimer and hexamer (calculated, model 4) are shown in Fig. 3.

Fig. 3 indicates the concentrations of the trimer to be relatively low at the studied concentration and temperature ranges. Due to the large uncertainties in determining $B^{\circ}_{d/t}$,

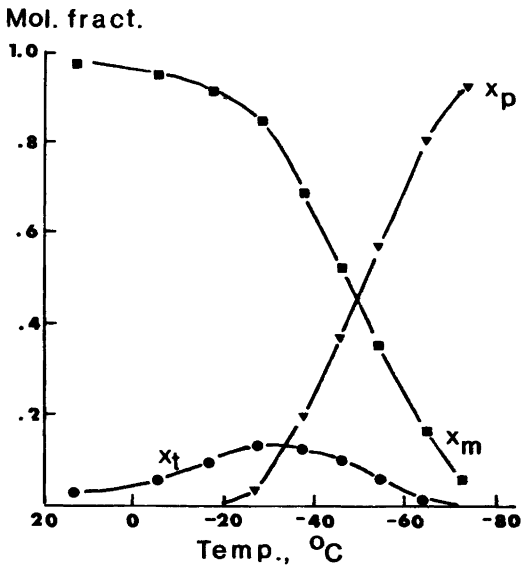

Fig. 3. Molecular composition of 15.5 mM solution of *t*-butyl alcohol in $CFCl_3$, calculated from a 1-3-6 model (Model 4).

Table 1. $\Delta H°$/kcal mol^{-1} and $\Delta S°$/cal mol^{-1} K^{-1} for the proposed models for association of *t*-butyl alcohol in $CFCl_3$ (from IR data).

Parameters from log K *vs.* $1/T$				Parameters *per* hydrogen bond (see text)			
Dimere/trimere		Hexamere		Dimere/trimere		Hexamere	
$-\Delta H°$	$-\Delta S°$	$-\Delta H°$	$-\Delta S°$	$-\Delta H°$	$-\Delta S°$	$-\Delta H°$	$-\Delta S°$
1. $ROH \rightleftharpoons (ROH)_2 \rightleftharpoons (ROH)_6$							
4.7±0.7	15.6±0.2	20.8±1.1	57.8±5.0	4.7±0.7	15.6±0.2	4.3±0.3	12.2±0.9
2. $ROH \rightleftharpoons (ROH)_3 \rightleftharpoons (ROH)_6$							
7.2±1.1	18.0±4.4	14.9±0.5	41.4±2.4	3.6±0.6	9.0±2.2	3.7±0.5	9.9±1.1
3. $ROH \rightleftharpoons (ROH)_6$							
		27.0±1.7	79.0±12			5.4±0.4	15.8±2.4
4. $ROH \rightleftharpoons (ROH)_3 \rightleftharpoons (ROH)_6$							
7.1±1.2	17.6±4.7	25.4±1.9	79.2±8.5	2.4±0.4	5.9±1.6	6.5±0.6	19.3±2.6

larger and smaller values of this was tried. The results were all similar to those shown in Fig. 3 and the variations had only small effects on the calculated thermodynamic parameters. Thus it is not necessary to know the exact value of $B°_{d/t}$ to obtain reliable thermodynamic parameters. The thermodynamic parameters in Table 1 have reasonable limits of error.

NMR. Due to the rapid exchange of the hydroxyl protons in hydrogen bonded complexes, NMR spectra give less qualitative information than IR spectra. In our system with three species present, the chemical shift of each species and its mol fraction are needed to calculate the observed chemical shifts. On the other hand, even if the chemical shifts of all species are known, the molecular composition of such a mixture cannot be determined from the NMR spectrum alone. We will here describe first the determinations of the chemical shifts of the three species present, all three being temperature dependent, and then use these values together with the results from the IR spectroscopy to assess the four models introduced earlier.

(a) *Monomer.* The chemical shift of the monomer hydroxyl proton (δ_m) was determined from the 5.5 mM solution. IR spectroscopy showed only this species to be present from +13 down to *ca.* −35 °C. Over this range, δ_m increased linearly with decreasing temperature. We will assume this relationship to hold for the temperature range studied.

(b) *Dimer/trimer species.* The chemical shift of this ($\delta_{d/t}$) is in principle available from runs where the IR spectra showed only this one and the monomer to be present. By determining the monomer concentration by IR spectroscopy, $\delta_{d/t}$ will be found from the observed hydroxyl proton chemical shift (δ_{obs}). Due to the uncertainties in determining the dimer/trimer concentrations (see above), chemical shifts of the dimer/trimer could only be estimated to 2.7 ppm for the dimer and 4 ppm for the trimer. Other values gave similar results of calculated chemical shifts due to the low concentrations of these species. The temperature dependence of this chemical shift was assumed to be the same as the one for the polymer species.

(c) *Polymer species.* The chemical shift of the hydroxyl protons δ_p was assumed to be the same as those from moderately concentrated *t*-butyl alcohol solutions. From the runs of 1.3 and 3.2 M solutions (Fig. 2), the hydroxyl proton chemical shift increased linearly with

Table 2. Linear regression of calculated *vs.* experimental chemical shifts of the hydroxyl proton of *t*-butyl alcohol, $\delta_{calc}=a\delta_{obs}+b$.

Model	a	b	r^2
1. $ROH \rightleftharpoons (ROH)_2 \rightleftharpoons (ROH)_6$	0.86	0.07	0.991
2. $ROH \rightleftharpoons (ROH)_3 \rightleftharpoons (ROH)_6$	0.86	0.12	0.995
3. $ROH \rightleftharpoons (ROH)_6$	1.07	−0.08	0.995
4. $ROH \rightleftharpoons (ROH)_3 \rightleftharpoons (ROH)_6$	1.03	−0.03	0.994

decreasing temperature from −50 to −90 °C and we have assumed this to hold for the concentration and temperature ranges studied. Neat methanol, often used as a temperature probe in NMR spectroscopy, has a temperature coefficient of −0.008 ppm K^{-1}, constant over at least 100 K. The number of monomer molecules in the polymeric species may vary with both concentration and temperature. However, the environment of each hydroxyl proton in the polymer will be little influenced by the chain length and we therefore believe the above assumption to be reasonable.

Assessment of the proposed models. We have used these chemical shifts to test the four models discussed earlier. The observed chemical of the hydroxyl protons will be [eqn. (2)]:

$$\delta_{obs}=\delta_m \cdot x_m+\delta_{d/t} \cdot x_{d/t}+\delta_p \cdot x_p \qquad (2)$$

where x_m, $x_{d/t}$ and x_p are the molar fractions of the monomer, dimer/trimer and polymer (hexamer) species and the δ's have been defined above.

From the thermodynamic parameters obtained by IR spectroscopy for each model, it is possible to calculate x_m, $x_{d/t}$ and x_p for each temperature at which the NMR spectra have been measured and then calculate the corresponding chemical shift ($\delta_{calc.}$). A plot of δ_{calc} against the observed chemical shift (δ_{obs}) would give a straight line through the origin with slope equal to 1 for a model fitting exactly to the experimental data. In Table 2, the results are given of a linear regression of the calculated *vs.* observed chemical shifts for the investigated models.

We have discussed the difficulties in using only one model for the complex mixtures present. Bearing this in mind, we will use the results in Table 2 to assess the proposed models as for their fitness to reproduce the experimental data. The two models invoking absorption at 3625 cm^{-1} from the end group of dimer or trimer (models 1 and 2) gave calculated chemical shifts for the hydroxyl protons at lower values than those observed (slope 0.86 for both, Table 2). This indicates that the concentrations of monomer (with the smallest chemical shift) have been overestimated by these models, and that those of dimer/trimer or hexamer have been underestimated. In particular, we believe this is the case for the hexamer. This is because variations in the estimates of the dimer/trimer concentrations did not improve the fit of the NMR data. Further, if these concentrations had been underestimated, one would expect the influence of the underestimation to diminish at lower temperatures where the concentrations of the dimer/trimer in any case must diminish. Instead, the results in Table 2 show that the errors increased as the temperature decreased. This leads us to suggest that the polymer has an open-chain structure with the end hydroxyl group exhibiting absorption at 3625 cm^{-1}.

A model with only two species present (model 3) is certainly qualitatively wrong, at least at higher temperatures where the IR spectra clearly show the presence of three species.

However, both the reasonable values for the thermodynamic parameters (see below) and the good correlation of the NMR data, indicate that this model will reproduce the experimental data in an acceptable way. Models 1 and 2 did not do this.

However, model 3 can easily be modified to accommodate the presence of three species. If we assume the dimer/trimer species to be cyclic and the hexamer to be open-chain with absorption at 3625 cm^{-1} of the end hydroxyl group, we have a model which is both quantitatively and qualitatively in accordance with the experimental data in this study (model 4). The correlation of the IR and NMR data is better for this model (slope 1.03, intercept 0.03) than for the two-species model, and far better than those invoking open-chain dimers or trimers.

Our data do not permit us to distinguish between the proposed monomer–trimer–hexamer (model 4) and an analogous monomer–dimer–hexamer model. We prefer the first one, both because of the results of Tucker and Becker,[2] and because a cyclic trimer appears sterically more attractive than a dimer (a six-membered ring *vs.* a four-membered one).

In Table 1, the thermodynamic parameters calculated for the four models are given. There is also given the calculated parameters *per* hydrogen bond. These were calculated using Hess' law and dividing the obtained quantities by the number of hydrogen bonds assumed by the model. Model 4 with a cyclic trimer and an open-chain hexamer gives $\Delta H^{\circ}_{t} = -2.4$ kcal mol^{-1}, $\Delta H^{\circ}_{h} = -6.5$ kcal mol^{-1} per hydrogen bond. That is, a weaker bond for the cyclic species where the angle of the O–H...O bond must deviate more from the optimum 180 ° than in the open-chain hexamer. The weaker bond is also in accordance with the trimer absorbing at a considerably higher frequency than the open-chain hexamer.

In fact, these values of ΔH° with the corresponding values of $\Delta\nu$ (125 cm^{-1} for the 3500 cm^{-1} band and 325 cm^{-1} for the 3300 cm^{-1} band) fit well with the $\Delta H - \Delta\nu$ relationship reported for a large number of alcohols with a number of different bases.[3] With open-chain dimers or trimers it is more difficult to explain why those species should absorb at a different frequency than the cyclic polymer. The steric, and for the trimer also electronic conditions for each hydrogen bond must be very similar in the two species.

Again we stress that model 4 is only one of many that may accommodate the obtained data. From Table 2 for instance, it is clear that at the lowest temperatures, the calculated chemical shifts are larger than the observed ones. This indicates that the model gives hexamer concentrations which are too large. At these temperatures, polymers longer than hexamers probably become important and these will give reduced contribution to the 3625 cm^{-1} band. This will result in an underestimation of the monomer concentration and an overestimation of the polymer concentration by our model. Tucker and Becker's model,[2] which incorporates a continuous increase in the number of monomers in the polymer, may better accomodate the data, but with an open-chain, not a cyclic polymer as proposed.[2] At very low temperatures or high concentrations, the chains will be of such length that only few end hydroxyl groups are present, with no or only weak absorption at 3625 cm^{-1}.

Conclusions. The results of this study of hydrogen bonding in *t*-butyl alcohol, covering a far greater temperature range than has been possible before, can be explained by a 1-3-6 model, the trimer with a cyclic structure, the hexamer an open-chain one. The data could not be fitted into a 1-3-6 model with an open-chain trimer and a cyclic hexamer.

EXPERIMENTAL

Fluorotrichlormethane (Fluka) was distilled and then dried over molecular sieves (3A, activated at 400 °C for 4 h). Solutions of *t*-butyl alcohol were made up in a cold-room, the

solutions manipulated by hypodermic syringes. The solutions were not dried by molecular sieves as introductory experiments showed *t*-butyl alcohol to be slowly adsorbed by these. NMR and IR spectra were run on the same solutions, (7.8 and 15.5 mM). For the NMR spectra, a capillary with $^2H_4$-methanol supplied the lock signal and also served as a temperature monitor.[8] The IR spectra were run on a Beckman IR 4250, with RIIC 1 cm variable temperature cells cooled by a Julabo F 80 cryostate. The area of the bands was determined by Methode I of Ramsay.[9] The NMR spectra were run on a JEOL FX 100 MHz spectrometer. The temperature dependence of B°_m, δ_m and δ_p was measured on 3.9 mM, 5.5 mM and 3.2 M solutions, respectively, in areas with linear increase (See Figs. 1 and 2). The data were treated by a least square regression analysis:

$B^\circ_m = 2700\ (1.034 - 0.0053t)$, $r^2 = 0.965$
$\delta_m = 0.71 - 0.0019t$, $r^2 = 0.973$
$\delta_p = 5.13 - 0.073t$, $r^2 = 0.998$

where t is the temperature in °C.

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