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MOLECULAR MOTION IN SOLID *p*-NITROPHENOL INCLUSION COMPOUNDS OF CYCLOMALTO-HEXAOSE AND -HEPTAOSE: N.M.R. AND DIELECTRIC STUDIES*

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ABSTRACT

^{13}C-C.p.-m.a.s. n.m.r. spectra are reported for two polymorphs of *p*-nitrophenol and its hydrated inclusion compounds with cyclomalto-hexaose (αCD) and -heptaose (βCD). From temperature-dependent ^{13}C-n.m.r. line-widths an activation energy of 50 kJ/mol was obtained for the motion of *p*-nitrophenol in the cavity of αCD. The motion was confirmed to be a two-fold flip of the *p*-nitrophenol molecule about the C-1–C-4 axis by ^{2}H-n.m.r. spectroscopy. Dielectric measurements were used to define a dipole reorientation process with an activation energy of 56.8 kJ/mol for *p*-nitrophenol–αCD, which was attributed to reorientation of the water molecules. The motion of *p*-nitrophenol is faster and less restricted in the βCD complex than in that of αCD and depends strongly on the degree of hydration of the complex.

INTRODUCTION

Cyclomalto-oligosaccharides (cyclodextrins, CDs) can form inclusion compounds with a wide range of guest molecules both in the solid state and in solution[1]. There is considerable interest in these complexes, as often the properties of the guest molecule are modified on inclusion[2,3]. For instance, many compounds that are normally air-sensitive are rendered stable to oxidation when included in a CD. Also, the aqueous solubility of substances can be enhanced by the formation of complexes[2,3]. The formation of inclusion compounds can also modify rates of reaction and distribution of products, and has been used to model enzyme–substrate interactions[4–6].

Many solid CD inclusion compounds have been studied by diffraction techniques[7]. The information obtained shows the relative disposition of the guest and host molecules, as well as the position of the water molecules that impose order on the structures by means of networks of hydrogen bonds. An important

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feature of the host structure is the conformation of the macrocycle of the CD as given by the torsional angles which describe the interglycosidic linkages[7]. Modest success has been achieved in correlating the torsional angles with ^{13}C-n.m.r. chemical shift information[8–12]. Since, in the solid state, separate resonances are observed for crystallographically and chemically non-equivalent nuclei, the ^{13}C-n.m.r. spectrum gives a "fingerprint" of the minimum repeat-unit in the crystal[13].

^{13}C-N.m.r. methods have been used to study molecular motion for CD guest–host complexes in solution[4]. The concept of a dynamic coupling coefficient (ε), defined as the ratio of the motional correlation times for the guest and host, has been explored. Small coefficients (~0.1) imply weak interaction of guest and host, and large coefficients a strong interaction. This concept is difficult to transfer to the solid state, as the host molecule is always static. However, the motion of the guest molecule can be described adequately in terms of an order parameter, and motional correlation times and activation energies.

So far, molecular motion in solid CD complexes has not been studied widely. The presence of relatively slow molecular motion has been inferred[14,15] from severe line broadening of some of the ^{13}C resonances for such guests as *p*-nitrophenol, *p*-hydroxybenzoic acid, and *p*-iodoaniline in αCD complexes. For benzaldehyde in αCD, temperature-dependent c.p./m.a.s. ^{13}C-n.m.r. spectra showed[16] that the benzene ring was static in the cavity below ~220 K, whereas it rotated rapidly with respect to the aldehyde group (which remains static) at >~320 K. Since the X-ray structure[17] shows only a single position for the benzene ring in the crystal lattice, the motion must involve only indistinguishable positions and therefore must be a 180° flip of the aromatic ring about the C-1–C-4 axis.

Molecular motion has been inferred from dipolar dephasing experiments on guests in βCD complexes[15]. Recently, ^{2}H-n.m.r. spectroscopy has been used[18] to develop a detailed model for the molecular motion of biphenyl in βCD.

We now report the use of ^{13}C- and ^{2}H-n.m.r. spectroscopy to compare molecular motion in the inclusion compounds of *p*-nitrophenol with αCD and βCD. Activation parameters for the motion of water molecules in the *p*-nitrophenol–αCD complex have been derived.

EXPERIMENTAL

Inclusion compounds of *p*-nitrophenol and *p*-nitrophenol-d_4 with αCD and βCD were obtained by cooling hot, concentrated, aqueous solutions containing stoichiometric quantities of reagents. ^{13}C-C.p.-m.a.s. n.m.r. spectra were obtained at 45.28 MHz with a Bruker CXP-180 NMR spectrometer. Single cross-polarization contacts[19,20] of 2–5 μs were used with matched r.f. field amplitudes of 70 kHz. Variable temperature spectra were obtained under m.a.s. conditions, using a probe supplied by Doty Scientific. ^{2}H-N.m.r. spectra were obtained at 27.68 MHz with a quadrupole echo sequence[21]. The 90° pulse length was 3 μs and the echo pulse spacing was 35 μs.

For dielectric measurements, powdered *p*-nitrophenol–αCD was pressed in a die to 1.1 kbar, to form a thin disc 1.905 cm in diameter and 0.208 cm thick that was placed between the parallel brass electrodes of a 3-terminal cell[22]. This assembly was placed inside an Andonian cryostat for variable temperature measurements. The temperature was controlled using a Lakeshore Cryotronics DRC-82C temperature controller and a TG-100FP gallium arsenide sensor. The dielectric response was measured using a Hewlett–Packard 4275A multi-frequency LCR meter at frequencies between 10 kHz and 20 MHz.

N.m.r. and molecular motion. — Although broad-line n.m.r. techniques were used to study molecular motion in clathrate hydrates or quinol clathrates[23], this is not feasible for such complex systems as the hydrated complexes of *p*-nitrophenol with αCD and βCD. However, techniques based on natural-abundance ^{13}C-n.m.r. and ^{2}H-n.m.r. spectroscopy of specifically labelled materials have been adapted to study guest–host systems. The more relevant techniques will be briefly reviewed.

(a) ^{13}C-N.m.r. spectroscopy. Highly resolved ^{13}C-n.m.r. spectra can be obtained for crystalline clathrates and inclusion compounds by using solid state techniques such as cross-polarization (c.p.), magic-angle-spinning (m.a.s.), and dipolar decoupling[23]. The dipolar dephasing[24] (interrupted decoupling) technique can be used to detect the molecular motion of proton-bearing carbon fragments. The signals from such carbons, rigidly held in the lattice, disappear from the spectrum when the decoupler is turned off for a short time (~40 μs) prior to the acquisition of data, due to the strong dipolar coupling to the attached protons. Such dipolar couplings are reduced in the presence of sufficiently rapid molecular motion, and signals due to mobile proton-bearing carbons reappear in the dipolar dephased spectrum, often at a reduced intensity which depends on the details of the motion.

Waugh and co-workers[25,26] have shown that motional rates can be derived from n.m.r. spectra when incoherent averaging due to motions interferes with coherent averaging processes such as m.a.s. or dipolar decoupling. Motional-rate-dependent line broadening occurs in spectra where the main broadening interaction is due to the anisotropic chemical shift, with maximum broadening occurring when the motion and m.a.s. have similar rates[25].

Line broadening occurs also when incoherent modulation of the carbon–proton dipolar couplings interferes with coherent averaging caused by the decoupling field. Rothwell and Waugh[26] have developed equation *1*, which relates the degree of broadening directly to the motional correlation time, and

$$1/T_2 = \frac{4\gamma_I^2 \gamma_S^2 \hbar^2}{15 r^6} I(I+1) \left[\frac{\tau_c}{1+\omega_1^2 \tau_c^2}\right], \qquad (1)$$

where T_2^{-1} is proportional to the line-width, γ_I, γ_s are the gyromagnetic ratios for the proton and carbon nuclei, respectively, r is the internuclear vector, ω_1 is the decoupling field amplitude, and τ_c is the motional correlation time. Maximum broadening takes place when $\omega_1\tau_c$ is ~ 1. In the fast-motion limit, $\omega_1\tau_c$ is $\ll 1$ and

$$1/T_2 \propto \tau_c, \tag{2}$$

so that the line width is independent of decoupling field amplitude.

(b) ^{2}H-N.m.r. spectroscopy. This technique can often be used to distinguish between several motional models. For a fully deuteriated, *para*-disubstituted benzene ring fragment (Fig. 1 inset), rigidly held in a crystal lattice, the ^{2}H-n.m.r. spectrum is as shown in Fig. 1. The doublet spliting ($\Delta\nu$) is $\frac{3}{4}\, e^2qQ/h$, where e^2qQ/h is the quadrupole coupling constant.

The principal components of the electric field gradient tensor are q_{xx}, q_{yy}, q_{zz}, with q_{zz} oriented along the C–D bond, q_{yy} at right angles to the ring plane, and q_{xx} in the ring plane at right angles to the C–D bond. In rotating the molecule about the Z′ axis by an angle α (Fig. 1, inset), the electric field gradient components can be written as follows.

$$\begin{aligned} q'_{xx} &= \cos^2\beta \cos^2\alpha\, q_{xx} + \sin^2\alpha\, q_{yy} + \sin^2\beta \cos^2\alpha\, q_{zz} \\ q'_{yy} &= \cos^2\beta \sin^2\alpha\, q_{xx} + \cos^2\alpha\, q_{yy} + \sin^2\beta \sin^2\alpha\, q_{zz} \\ q'_{zz} &= \sin^2\beta\, q_{xx} + \cos^2\beta\, q_{zz} \end{aligned} \tag{3}$$

In the presence of rapid motions, the averaged tensor components can be written

$$\bar{q}_{ii} = \frac{1}{n} \sum_{j=1,n} q_{ii}^{(j)} (\alpha_j), \tag{4}$$

where n is the number of sites and the $q_{ii}^{(j)}$ (α_j) are the electric field gradient components for different values of the rotation angle α. For two-fold flips, $n = 2$, $\alpha_1 = 0°$, $\alpha_2 = 180°$, and

$$\begin{aligned} \bar{q}_{xx} &= \cos^2\beta\, q_{xx} + \sin^2\beta\, q_{zz} \\ \bar{q}_{yy} &= q_{yy} \\ \bar{q}_{zz} &= \sin^2\beta\, q_{xx} + \cos^2\beta\, q_{zz}. \end{aligned} \tag{5}$$

Assuming an axially symmetric field gradient tensor for the rigid lattice, $q_{zz} = q$, $q_{xx} = q_{yy} = -\frac{1}{2}q$, and a value of 60° for the angle β (Fig. 1, inset), a ^{2}H powder pattern is predicted with a large asymmetry parameter $\eta = (\bar{q}_{xx} - \bar{q}_{yy})/\bar{q}_{zz} = 0.6$, with one splitting in the line-shape identical to the rigid lattice case (Fig. 1).

On the other hand, for three or more sites symmetrically disposed about the Z′ axis, $n = 3$, $\alpha_j = 0°, 120°, 240°$, and

$$\begin{aligned} \bar{q}_{xx} &= \tfrac{1}{2} \cos^2\beta\, q_{xx} + \tfrac{1}{2}\, q_{yy} + \tfrac{1}{2} \sin^2\beta\, q_{zz} \\ \bar{q}_{yy} &= \bar{q}_{xx} \\ \bar{q}_{zz} &= \sin^2\beta\, q_{xx} + \cos^2\beta\, q_{zz}. \end{aligned} \tag{6}$$

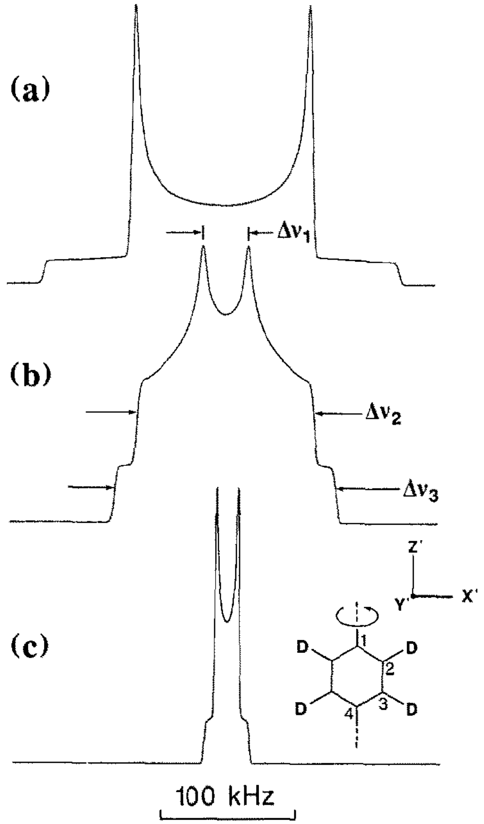

Fig. 1. ^{2}H-N.m.r. spectra for a *para*-disubstituted benzene ring: (a) rigid lattice, (b) rapid 180° flips about the C-1–C-4 axis, (c) rapid rotation about the C-1–C-4 axis, where the order of the axis is ≥3.

If again $q_{zz} = q$, $q_{xx} = q_{yy} = -\frac{1}{2}\, q$, and $\beta = 60°$ are taken, an axially symmetric powder pattern is predicted, but narrower by a factor of 8 as compared to the rigid lattice.

For comparing the motional anisotropy in related systems, it is useful to compare order parameters $S = \bar{q}_{zz}/q_{zz}$ and effective asymmetry parameters $\eta_{\mathrm{eff}} = (\bar{q}_{xx} - \bar{q}_{yy})/\bar{q}_{zz}$. For the two-fold flip model discussed above, $S = 0.625$, $\eta_{\mathrm{eff}} = 0.6$, and, for the *n*-fold rotation, $S = 0.125$, $\eta_{\mathrm{eff}} = 0$.

RESULTS AND DISCUSSION

p-*Nitrophenol.* The sold state ^{13}C-n.m.r. spectra of α-*p*-nitrophenol (from solution) and β-*p*-nitrophenol (from the melt) are shown in Fig. 2a. ^{13}C-N.m.r. spectrum has been reported[14], but the crystal form was not identified and the spectrum was of poor quality. The main reason for the poor quality of this spectrum appears to be an insufficient delay time between successive c.p. cycles, as evidently the ^1H relaxation time is long. The spectrum involved 6000 scans taken with a delay time of 10 s. The spectrum now reported involved only 40 scans taken with a delay time of 2 min.

The asymmetric unit of the crystal of α-*p*-nitrophenol[29] contains one molecule, so that a six-line spectrum may be expected. Only four lines are observed, so that $\Delta\delta$ of the resonances for C-2 and C-6, and C-3 and C-5, were not resolved. The C-4 resonance showed the asymmetric doublet characteristic of a ^{13}C nucleus coupled to a spin $I = 1$ ^{14}N nucleus[30]. The relative broadness of the C-3,5 line can also be attributed to coupling to ^{14}N.

For the metastable β-*p*-nitrophenol, the C-2,6 line was split clearly into a doublet, but its components, as well as all the other lines, were quite broad when compared to the lines for α-*p*-nitrophenol. Most likely, further unresolved multiplicity of the lines must be considered, leading to an asymmetric unit of more than one *p*-nitrophenol molecule for the as yet unreported structure of β-*p*-nitrophenol.

p-*Nitrophenol–αCD trihydrate.* The c.p.-m.a.s. ^{13}C-n.m.r. and ^2H-n.m.r. spectrum of the host lattice region of the *p*-nitrophenol–αCD trihydrate is shown in Fig. 3. The spectrum is in general agreement with published data[12], although the resolution in Fig. 3 was better. The C-1 and C-4 regions are well resolved, and the two groups of six lines expected for the presence of a single guest–host unit in the crystal asymmetric unit[31] can be assigned. The chemical shifts are (intensity in brackets) 104.2(2), 103.2(1), 102.9(1), and 102.4(2) p.p.m. for C-1 and 82.9(2), 81.8(2), 80.5(1), and 78.5(1) p.p.m. for C-4. Most probably the small $\Delta\delta$ values

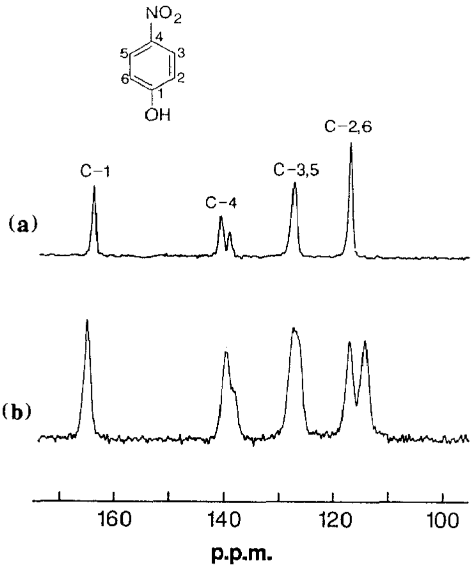

Fig. 2. C.p.-m.a.s. ^{13}C-n.m.r. spectrum of (a) α-*p*-nitrophenol recrystallized from solution, and (b) β-*p*-nitrophenol from the melt.

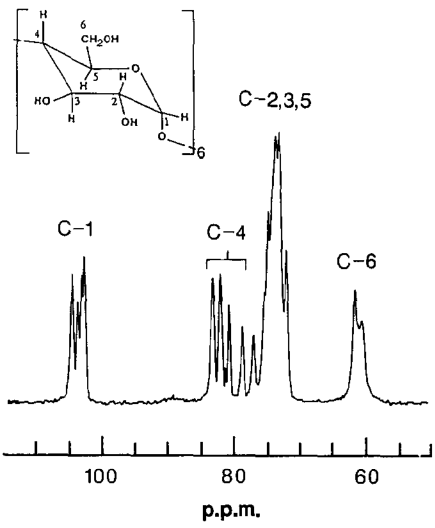

Fig. 3. C.p.-m.a.s. ^{13}C-n.m.r. spectrum of the host lattice region of *p*-nitrophenol–αCD.

within the C-1 and C-4 groups of lines have their origin in differences in the torsional angles which describe the interglycoside linkages[8–12].

The ^{13}C-n.m.r. spectrum of the guest is shown in Fig. 4. At room temperature, only the two non-proton bearing carbon resonances can be seen. The resonance of the phenolic carbon has a small (2.5 p.p.m.), but significant shift to high field as compared to the α form of the solid. This shift probably reflects a change in hydrogen bonding on going from the pure solid to the included molecule. The *p*-nitrophenol molecule resides in the cavity with the nitro group at the primary hydroxyl side and the hydroxyl group protruding from the secondary hydroxyl side and available for hydrogen bonding[31].

The lines for the four proton-bearing carbons C-2,3,5,6 are essentially absent from the spectrum obtained at room temperature, owing to severe line broadening which may have several origins. One origin is the usual line broadening which occurs when the rate of chemical exchange is about equal to the splitting of the lines for the two non-equivalent sites in the absence of exchange. A possible cause for the splitting of, say, the C-2,6 resonances may be simply that their crystallographic non-equivalence arises from the way in which the molecule is inserted in the cavity of the CD. However, this view can be checked by examining the spectrum in the slow motion limit. Fig. 4 shows that discernible splitting of the C-2,6 resonances does not occur even at 223 K.

Therefore, it is assumed that the line broadening observed is caused by the interference of the incoherent modulation of the dipolar couplings due to motion with the coherent dipolar decoupling[26].

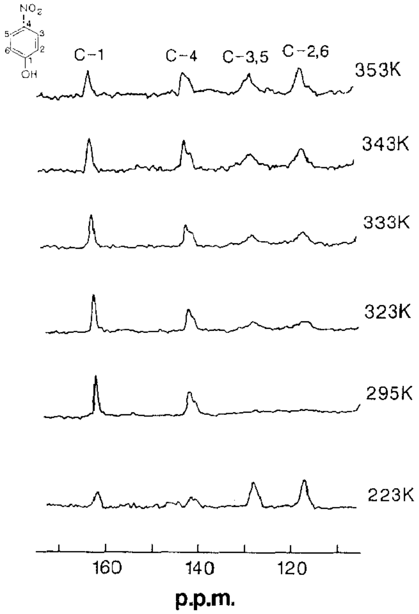

Fig. 4. C.p.-m.a.s. ^{13}C-n.m.r. spectra of the guest region of *p*-nitrophenol–αCD as a function of temperature.

Fig. 4 shows that the line-widths of the C-2,3 and C-5,6 resonances gradually decrease with increasing temperature, confirming the fast limit for the motion. If the line-widths are plotted on a log scale *vs.* $1/T$ (after correcting for the natural line-width), a straight line results (Fig. 5), the slope of which gives an Arrhenius activation energy of 50 kJ/mol. Maximum broadening takes place when $\omega_1\tau_c$ is ~1. Assuming that maximum broadening occurs at 295 K, then a decoupling field strength of 18 kHz yields a frequency factor for the motion of 2.7×10^{-15} s.

The line broadening observed only indicates the presence of fluctuations in the dipolar coupling at a certain frequency. The nature of the motion must be identified by other means and the X-ray structural data[31] are helpful. The *p*-nitrophenol is inserted in the cavity of the CD in a completely ordered way, suggesting that there are no secondary sites. Therefore, the most likely motion is one where the *p*-nitrophenol ring flips about the C-1–C-4 axis by 180°. A motion of this type will lead to indistinguishable situations, and therefore will be able to explain both the X-ray and the n.m.r. results.

As noted above, ^{2}H-n.m.r. spectroscopy can be used to distinguish between different kinds of motional models of a benzene ring fragment. Fig. 6 shows ^{2}H-n.m.r. powder patterns obtained for αCD–*p*-nitrophenol-d_4 obtained at −20° and 80°. The poor signal-to-noise ratio is due to the small quantity of sample available. However, the spectral features are good enough to show quadrupole splitting of 130 kHz, characteristic of static *p*-nitrophenol-d_4 molecules at −20°, and a pattern with a large asymmetry parameter at 80°. The invariant splitting of 130 kHz

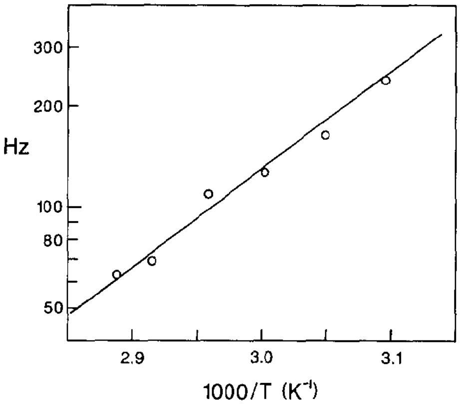

Fig. 5. Arrhenius plot of the line-width of proton-bearing carbons of *p*-nitrophenol in the complex with αCD.

corresponds to the q_{yy} component of the electric field gradient tensor perpendicular to the benzene ring plane.

The ^{2}H-n.m.r. powder patterns therefore confirm the presence of two-fold flips of the *p*-nitrophenol molecule about its C-1–C-4 axis when it is included in the cavity of αCD.

The dielectric data are shown in Fig. 7 in the form of plots of dielectric permittivity (ε') and loss (ε'') at various frequencies as a function of temperature. Broad, but well defined, loss peaks occur between 200 and 320 K, and the associated dispersion in ε' confirms the peaks to be due to loss from dipolar reorientation. The frequency of maximum ε'', when plotted against $1/T$ (Fig. 7), fits Arrhenius behaviour with

$$\nu = \nu_0 \exp(E_a/RT),$$

with $\nu_0 = 2.2 \times 10^{16}$ Hz and $E_a = 56.8$ kJ/mol. The process responsible for the

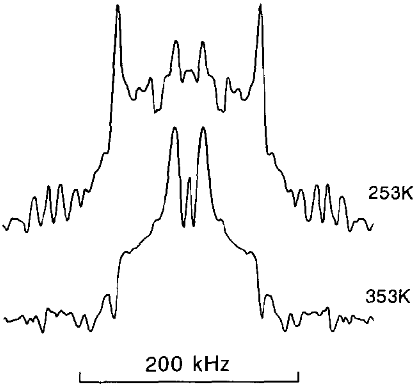

Fig. 6. ^{2}H-N.m.r. line-shapes of αCD–*p*-nitrophenol-d_4.

dielectric relaxation can be ascribed to reorientation of the water molecule and also to the motion of any other mobile dipoles associated with the OH groups of the CD[32]. Although the static permittivity ε^0 can only be estimated, the value derived for $\Delta\varepsilon$ is only 3.5, and is much less than that (33.8) for βCD undecahydrate[32]. This result can be taken to reflect a much lower degree of rotational freedom of the water molecules in the αCD than in materials where there are more extensive networks of hydrogen bonds, such as βCD undecahydrate[32], ice, and clathrate hydrates[33]. However, the similar values for the activation energies in the CDs[32] and ice suggest that the water molecules may have a common mechanism for reorientation. For ice and clathrate hydrates, this has been proposed to be the well-known mechanism of Bjerrum defect migration[33].

Although the activation energies for reorientation of the water dipole and of the *p*-nitrophenol two-fold flip are similar, the frequency factors in the Arrhenius expressions are quite different so that, in general, the motions will have independent correlation times.

βCD. The c.p.-m.a.s. ^{13}C-n.m.r. and ^{2}H-n.m.r. spectra for the *p*-nitrophenol–βCD complex are shown in Fig. 8. The highly resolved spectrum in Fig. 8a was obtained for freshly prepared samples or samples spun with some excess water in the spinner. The spectrum shown in Fig. 8b was obtained after the sample had been exposed briefly to the air, and is similar to that published[15]. This set of spectra again illustrates the critical role played by water in determining the structural and motional properties of the CD complexes. The apparent slight loss of water gives

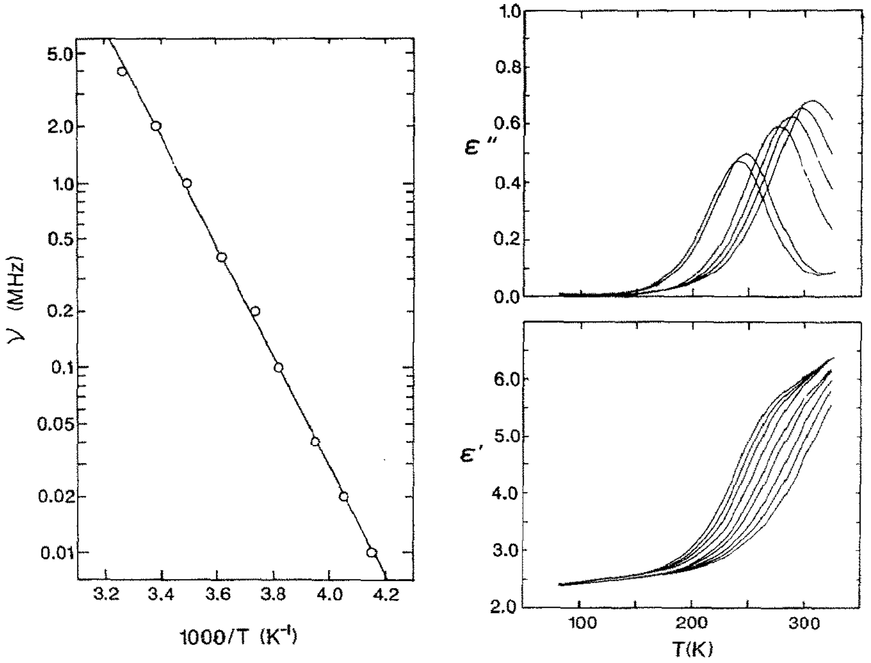

Fig. 7. Dielectric absorption (ε'') and dispersion (ε') of the *p*-nitrophenol–αCD complex as a function of temperature, and the frequency of maximum ε'' *versus* $1000/T$.

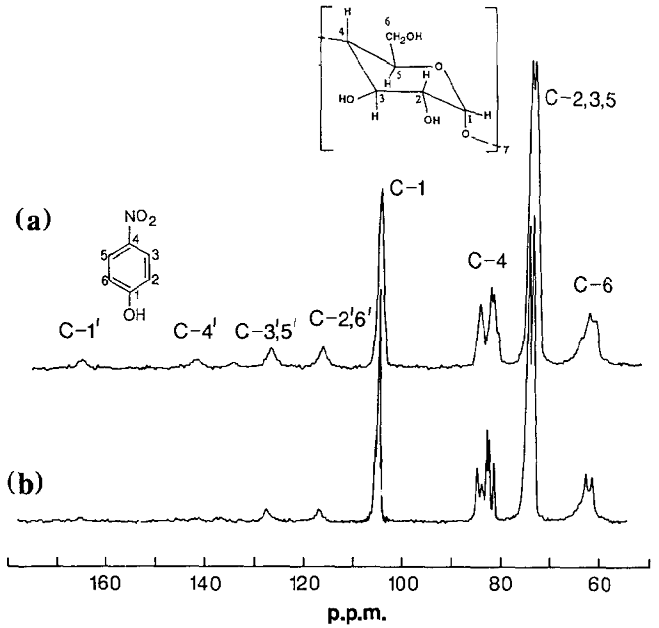

Fig. 8. C.p.-m.a.s. ^{13}C-n.m.r. spectra of samples of *p*-nitrophenol–βCD (a) fully hydrated, and (b) after exposure to ambient atmosphere.

rise to a significant loss of spectral resolution for the host lattice spectrum, and the guest lines appear with increased intensity.

The application of dipolar dephasing shows that *p*-nitrophenol molecules are mobile in the cavity of βCD, although it is not possible to obtain information on the type of motion, or motional rate[15].

Further information can be obtained by examining ^{2}H-n.m.r. spectra as a function of temperature for the βCD–*p*-nitrophenol-d_4 complex (Fig. 9). At 223 K, the spectrum corresponds to a rigid-lattice-powder doublet with a characteristic quadrupole coupling constant of 176 kHz. Spectra go through a "motional fade-out" region and appear above 270 K as axial powder doublets of vastly reduced splitting. The reduction factor is given by $\frac{1}{2}|3\cos^2\theta - 1|$ where θ is the angle between the C–D bond and the rotation axis. For the spectrum at 278 K shown in Fig. 9, the reduction factor is 0.20, which leads to angles of 47 or 63°. The second value being close to 60° would seem to be the logical choice, as it leads to a model where the *p*-nitrophenol molecule rotates about the C-1–C-4 axis (see above Fig. 1C) where the order of the rotation axis is ≥ 3. Since the spectrum shows that all C–D bonds are equivalent within the resolution of the experiment, angles other than 60° would require a much more complicated model. It seems reasonable that the motion of the polar axis of the *p*-nitrophenol molecule is more restricted than motions about the polar axis.

As the temperature increases above 278 K, the spectrum continues to evolve, however, and develops a noticeable asymmetry above ~290 K, which ultimately

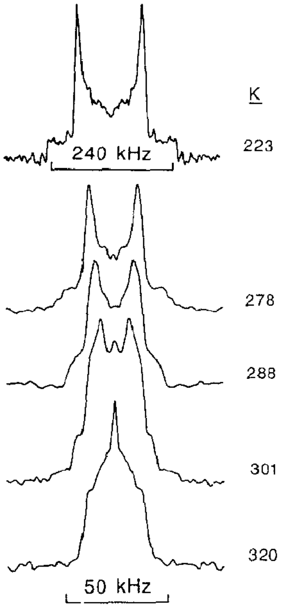

Fig. 9. ^{2}H-N.m.r. line-shapes of βCD–p-nitrophenol-d_4 as a function of temperature.

leads to a completely asymmetric (η = 1) line-shape at 320 K. The line-shapes seem to remain in the fast-motion limit, *i.e.*, there is no other "motional fade-out" region in evidence. This finding suggests that the new motion involves the thermal population of an energetically less-favoured site. Also, one splitting in the spectrum is independent of temperature. Therefore, the motion involves an averaging of only two electric-field-gradient components, those lying along the Z' and one of the X' or Y' axes. This suggests that the motion must be about an axis perpendicular to the C-1–C-4 axis.

Unfortunately, the exact temperature at which the asymmetry set in depended quite markedly on water content. This sensitivity was also noted in the ^{13}C-n.m.r. experiments. Hence, water trapped in the structure must play a critical role not only in determining the local order in the structure, but also the molecular motion.

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