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Different types of urea inclusion compounds have been studied to test the importance of the molecular interactions between the guests. Experimental evidence has been obtained from the EPR spectra of radicals derived from guests by room temperature γ -ray irradiation of the inclusion compounds. The guest–guest intra-channel interactions are very important in the case of tridecanedioic and tetradecanedioic dicarboxylic acid guests which give rise to strong intermolecular hydrogen bonding between the carboxylic groups. It is found that the molecular conformation of the tetradecanedioic acid is strongly distorted to fit in the host channel dimensions. The interactions between guest molecules included in adjacent host channels have been modulated by varying the relative guest composition in a mixed nonadecan-10-one–nonadecane inclusion compound. It is shown that the molecular reorientation of the nonadecan-10-one guest becomes faster by increasing the nonadecane percentage as a consequence of the reduced inter-channel interactions.

Introduction

Urea inclusion compounds (UIC) form a well known class of clathrates in which hexagonal channels formed by hydrogen bonded urea molecules constitute the host matrix.¹ Different types of long chain molecules can be accommodated as guests inside the channels. The most extensively studied UICs are those formed with long chain alkane molecules. However, it is possible to obtain many other families of UICs containing functionalized alkanes, such as ketones, esters and carboxylic acids.

High energy irradiation of the latter type of UICs gives rise to stable radicals originating only from the guests. The radicals are produced by the breaking of a C–H bond near the functional group. In this way radicals very similar to the undamaged guests are introduced into the crystal, and the inclusion compounds can be studied by EPR spectroscopy. In the past many compounds of the latter type have been studied by Griffith.² He analyzed the hyperfine (hf) pattern of the EPR spectra, varying the temperature and the orientation of the crystals in the magnetic field, to obtain a good insight into many of the properties of these compounds. He found that the hf couplings of the two β -protons are markedly non-equivalent and temperature dependent, and he reached the conclusion that this behaviour is related to a distortion of the chain from the all-*trans* conformation. However, today the possibility of accurate simulations of the EPR spectra profiles allows a much more subtle analysis of the spectra. We studied by EPR and ENDOR a series of UICs of long chain acids, ketones and esters, characterizing their inter- and intra-molecular motions.^{3–5}

From the results of our previous studies and of those of other authors with different techniques^{6–8} the following conclusions can be reached. The guest rotational motion around the axis of the hexagonal channels and the interconversion dynamics between different conformations of the chain are apparently uncorrelated. However, the dynamic behaviour of the included molecules should be related to the guest–host and guest–guest interactions. There is evidence that the inter-channel interactions produce a distortion of the host structure, inducing a transition from a phase with hexagonal symmetry to a low temperature orthorhombic phase. In the case of a diketone UIC, strong host–guest hydrogen bonds are formed and a three

dimensionally ordered structure has been obtained.⁹ One would expect, therefore, that long range inter-channel interactions should be effective in determining the guest rotational dynamics.

On the other hand, the internal molecular motion is affected by the formation of hydrogen bonds between guests inside the same channel. This effect was discovered by the study of UICs with, as unsymmetrical guest molecules, acids and ketones whose functional group is located at the end of the carbon chain. These guests can assume two different arrangements inside the channels, head-to-head and head-to-tail, and we have shown that the dynamics and structure of the guest radicals is remarkably different in the two cases.⁵

In this paper we report an EPR study on UICs of hydrocarbon derivatives which is focused on the effects of guest–guest inter- and intra-channel interactions in determining the dynamics and the structure of the radicals. We will show for the first time that the long range inter-channel interactions do affect the dynamic parameters of the molecular motion. By comparing the structure and dynamics of radicals of pure nonadecan-10-one UIC, which we have previously studied extensively,^{3,4} with those of the same radicals included together with different amounts of nonadecane, we determine the effects of the long range interactions, while the radical structure remains the same. Moreover, by studying the EPR spectra of the UICs of two dicarboxylic acids, tridecanedioic and tetradecanedioic acids, we find further evidence that hydrogen bond formation between neighbouring guests lying in the same channel is of paramount importance in determining the average conformation of the radical and the dynamics of conformational interconversion.

Experimental

Methods

Single crystals of nonadecan-10-one–urea doped with two different amounts of nonadecane were grown from a 1:1 methanol–acetone (spectrophotometric grade) solution of the urea and the guests in the chosen ratio. The molar ratio between the total amount of the guests and that of urea was 1:60. The crystals were obtained by cooling $0.01\text{ }^\circ\text{C min}^{-1}$ from $50\text{ }^\circ\text{C}$ to room temperature.¹⁰ The ketone and hydrocarbon were obtained from Aldrich.

The ratio of the two guests in the crystals was measured by NMR spectroscopy on solutions of the clathrates. Two types of

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crystal with respectively 30 and 55% of the guest molar content of nonadecane were obtained. We will refer in the following to the compounds pure nonadecan-10-one-urea and mixed nonadecan-10-one-nonadecane-urea respectively as NDOU and mixNDOU.

Tridecandioic (undecane-1,11-dicarboxylic) and tetradecandioic (dodecane-1,12-dicarboxylic) acids were also obtained from Aldrich, and were purified by recrystallization before use. The inclusion compounds in urea were prepared with the procedure explained above. The urea inclusion compound of the tridecandioic acid is referred to as 13AU and that of tetradecandioic acid as 14AU.

The crystals were irradiated with a dose of 30 kGy (3 MRad) of γ -rays at room temperature. The EPR spectra were recorded using a conventional Bruker ER200D spectrometer interfaced with a Bruker data system ESP1600 and equipped with a Bruker variable temperature unit. The crystals were mounted in a small lucite cube and rotated inside the cavity around three orthogonal axes. The Z axis was chosen to lie along the long prism axis of the hexagonal crystal, and therefore coincident with the urea channel axis.

Analysis of the spectra

The EPR spectra of the guest radicals in the high temperature hexagonal phase of UIC have fast motion lineshapes and were analyzed in the framework of the Redfield-Freed theory.^{11,12} The resonance transition fields are given by the first order expression given in eqn. (1), where a_k are the hf coupling con-

$$B_{\text{res}}\{M\} = B_0 + \sum_k a_k M_k \quad (1)$$

stants. The summation in eqn. (1) is extended to the protons in α - and β -positions with respect to the carbon atom with unpaired spin density. The coupling of the more distant protons of the guest and of the host nuclei have been detected by ENDOR spectroscopy for nonadecan-10-one radical UIC. The EPR spectral profile is given by a superposition of Lorentzian lineshapes [eqn. (2)], whose linewidth can be written as a poly-

$$I(B) = \sum \frac{W\{M\}}{W\{M\}^2 + (B - B_{\text{res}}\{M\})^2} \quad (2)$$

nomial expression [eqn. (3)] in the nuclear spin azimuthal quantum numbers M_k .

$$W\{M\} = A + \sum_k B_k M_k + \sum_{k < k'} E_{kk'} M_k M_{k'} \quad (3)$$

Since the transition lines were partially overlapping we resorted to a best-fitting procedure to obtain the values of the hf splittings and the linewidth coefficients.^{3,13} The latter values were determined by the molecular dynamical processes. In particular, the principal contribution to B_0 arises from the molecular rotation which modulates the dipolar interaction of the α -proton. Therefore, B_0 was strongly dependent upon the orientation of the crystal and it was at a maximum when the magnetic field was orthogonal to the Z symmetry axis.

Results

Mixed nonadecan-10-one-nonadecane UIC

The EPR spectra of the NDOU radical have been described previously.^{3,4} We summarize here the main features. The EPR spectrum is due to the radical $\text{CH}_3(\text{CH}_2)_8\text{CO}\dot{\text{C}}\text{H}(\text{CH}_2)_7\text{CH}_3$ and it is characterized by the hf coupling with three non-equivalent protons, the α -proton and the two β -protons. The spectra do not vary when the magnetic field lies in the crystal XY plane and the hf tensors are axially symmetric for $T > 155$ K. The conclusions are that the spin hamiltonian tensors are averaged by the rotational motion of the radical inside the host

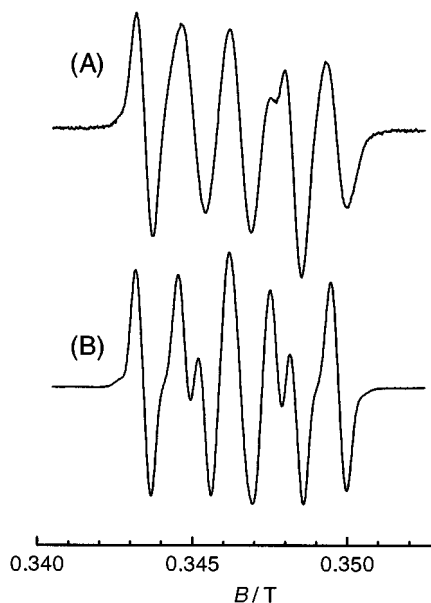


Fig. 1 EPR spectra of NDOU (A) and mixNDOU with 55% of nonadecane (B) measured with the magnetic field perpendicular to the hexagonal symmetry axis at $T = 180$ K

channels. At $T = 155$ K one can detect a transition from the symmetric hexagonal high temperature phase to an orthorhombic one.¹⁴

The isotropic hf coupling of the α -proton is nearly independent of the temperature. The principal values of the α -proton hf tensor are consistent with an orientation of the CH_α bond nearly perpendicular to the long molecular axis. On the other side, the two β -protons are found to be non-equivalent at each orientation and any temperature. The principal values of their hf coupling tensors are noticeably temperature dependent, while the anisotropies are small. The difference between the values of hf couplings of the β -protons indicates the effects of the chirality of the host channel which induces a chiral distortion in the guest molecule. Moreover, the large temperature variation of the β -proton couplings indicates that the latter ones are average values due to a restricted rotation of the methylene group around the $\text{C}_\alpha\text{-C}_\beta$ bond.^{2,3}

The EPR spectra of the two mixNDOU crystals (30 and 55% of the guest molar content of nonadecane) were recorded in the temperature range 160 to 290 K and at different orientations of the Z axis with respect to the magnetic field. The spectra show only the presence of the radical formed from nonadecan-10-one, and their angular dependence is very similar to that obtained from NDOU. On the other hand, the temperature dependence is quite different. In Fig. 1 we report the spectra obtained for the mixNDOU (55%) and for NDOU at the same temperature and at the same orientation in the magnetic field. It can be observed that the spectrum of mixNDOU shows narrower lines as if the averaging motions were faster. In general the spectra of mixNDOU at a temperature T are very similar to those of NDOU at a higher temperature.

The spectra of both mixNDOU compounds have been simulated with the non-linear best fitting procedure described above. The parameters for the fitting procedure were: the hf splittings and the coefficients of the linewidth expression, eqn. (3). The angular and temperature dependence of the hf splittings of the radicals in the mixNDOU crystals are nearly the same as in NDOU and they are not displayed here. The most interesting differences regard the linewidth parameters. The temperature dependences of the values of B_0 for radicals in NDOU and in the two mixNDOU compounds are reported in Fig. 2. As one can see, the B_0 value decreases on increasing the percentage of nonadecane.

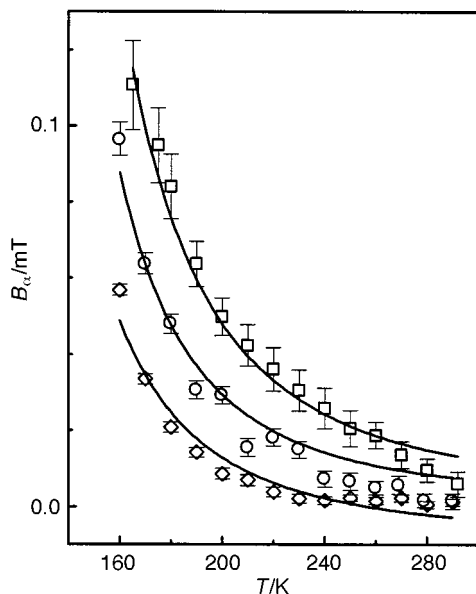


Fig. 2 Temperature dependence of the B_α linewidth parameter for the mixed nonadecan-10-one-nonadecane UIC. The percentage of nonadecane is: 55% (\diamond), 30% (\circ), 0% (\square).

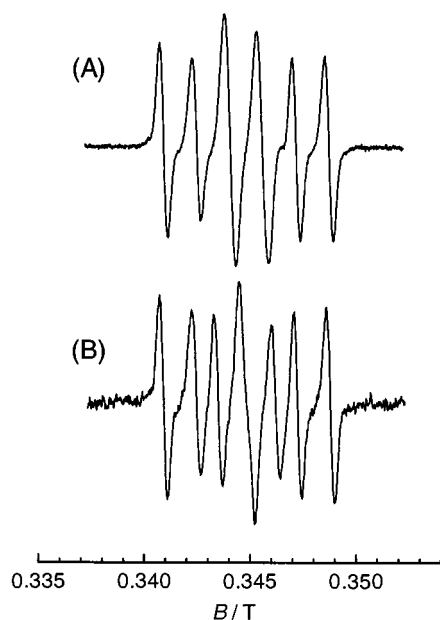


Fig. 3 EPR spectra of 13AU (A) and 14AU (B) measured with the magnetic field perpendicular to the hexagonal symmetry axis at $T = 280$ K.

Dicarboxylic acids

The EPR spectra of both 13AU and 14AU were recorded in the temperature range 150 to 290 K and at different orientations of the Z axis with respect to the magnetic field. For both compounds when $B//Z$ and $B\perp Z$ the EPR spectrum shows the presence of only one radical similar to those observed for the other systems. The spectra show the coupling with three protons, an α -proton and two β -protons, indicating that the unpaired electron is localized on a carbon atom near one of the two functional groups.

The spectra at 280 K for $B\perp Z$ are reported in Fig. 3. Despite the similarity of the guests, the spectra are quite different. As one can see the spectrum of 13AU is given approximately by a doublet of triplets, therefore the hf couplings of the two β -protons are very similar, whereas the spectrum of 14AU is given by a doublet of doublets of doublets, the two central lines by chance overlapping.

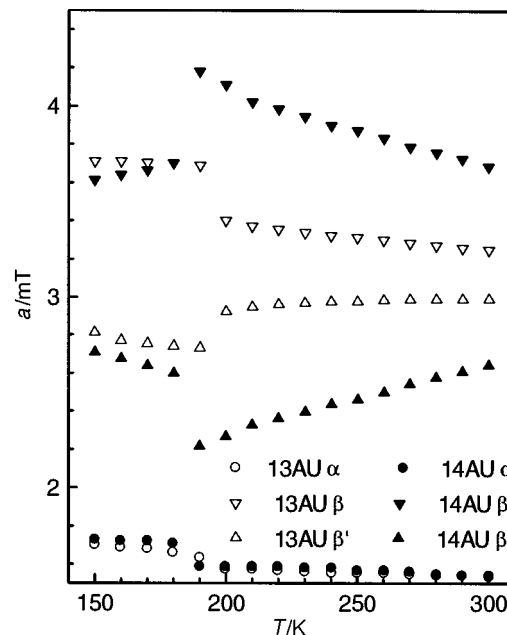


Fig. 4 Temperature dependence of the hf coupling constants for 13AU and 14AU.

We have simulated the spectra for both compounds by the procedure described above. In Fig. 4 the temperature dependences when $B\perp Z$ of the hf coupling constants of the three protons for both 13AU and 14AU are reported. First of all, the phase transitions from the hexagonal to the orthorhombic phase are clearly indicated by the abrupt change in the hf couplings. The temperatures of the transitions are in the range 180–200 K, being slightly higher for 13AU than for 14AU. The hf couplings of the α -protons of the two radicals are very similar, and vary slightly with the temperature. Their values are also similar to those of all the other radicals included in urea channels studied so far. On the other hand, the hf couplings of the β -protons are quite different. For 13AU the two protons have very similar hf couplings, which vary only slightly with the temperature, whereas for 14AU the two hf couplings are very different, and the temperature dependence is much more pronounced. It is worth noting however that, at temperatures below the phase transition the two radicals have very similar hf couplings for the β -protons.

Another particular feature of the EPR spectra of these two irradiated UICs is that the EPR spectra obtained when the magnetic field is not parallel or perpendicular to the Z axis cannot be accounted for by a unique set of magnetic interactions. Since the spectra for $B//Z$ and $B\perp Z$ can be simulated by assuming that only one radical is present, we are forced to conclude that magnetically non-equivalent sites are present in the system, and therefore the hf and/or the g tensors for the radicals in 13AU and 14AU are not axially symmetric.

Discussion

Mixed nonadecan-10-one/nonadecane UIC

The isotropic hf coupling of the β -protons depends on the dihedral angle θ between the π orbital of the unpaired electron and the CH_β bond direction according to eqn. (4)¹⁵ where a

$$a_i = \mathcal{A} \cos^2 \theta_i \quad (4)$$

typical value for the proportionality constant is $\mathcal{A} = 4.3$ mT. In the case of a planar conformation for the carbon chain, the values of the dihedral angles are $\theta_{1,2} = \pm\pi/6$ and the hf coupling constants are equal. For all the nonadecan-10-one UICs the β -protons of the guest radicals have non-equivalent hf couplings. Their temperature dependence indicates unambiguously an

Table 1 Correlation time τ_c at room temperature and activation energy E_a for the rotational correlation motion of the nonadecan-10-one radical in the mixNDOU for different nonadecane guest percentages

%	$\tau_c/10^{-10}$ s	$E_a/\text{kJ mol}^{-1}$
55	1.0	5.8
30	1.2	7.2
0	5.0	7.5

intramolecular motion in which the methylene group oscillates around an average position, locally distorted of an angle γ with respect to the planar configuration. The values of the hf couplings a_β , $a_{\beta'}$ depend on the amount of the distortion and the amplitude of the oscillation. It can be shown that the hf couplings of the distorted radical are related by eqn. (5),^{2,3} where eqn. (6) holds.

$$a_\beta = f(\gamma)a_{\beta'} + \frac{\mathcal{B}}{2}[1 - f(\gamma)] \quad (5)$$

$$f(\gamma) = \frac{\cos^2(\pi/3 + 2\gamma)}{\cos^2(\pi/3 - 2\gamma)} \quad (6)$$

The value of γ can be obtained by fitting eqn. (5) to the experimental data. The unequivalence between the β -proton coupling constants gives a clear indication of the conformation of the guest inside the channel. The variation of the hf splittings between the different mixed UIC is quite small, and we obtain for the average distortion angle the value $\gamma = 25 \pm 3^\circ$. Therefore, we can say that the molecular conformation of the nonadecan-10-one radical does not depend on the composition of the mixed UIC. However, the spectral linewidths are clearly affected by the relative composition of the mixed crystals. The value of the correlation time τ_c for the radical rotational motion inside the host channel is obtained from the linewidth coefficient B_u , measured with the magnetic field in the perpendicular arrangement,⁴ given by eqn. (7) where δg and δA_u are the aniso-

$$B_u \propto \delta g \delta A_u \tau_c \quad (7)$$

tropies of the g and A_u tensors in the molecular xy plane. Since the radical conformation is the same irrespective of the guest composition, we expect that the tensor anisotropies have equal values for the radicals in the different mixNDOU compounds. Therefore, the variation of the B_u value should derive from the radical mobility, increasing with the nonadecan-10-one–nonadecane ratio. From the temperature dependence of the B_u coefficient it is possible to extract the correlation time and the activation energy of the rotational motion, which are reported in Table 1. The radical motion is faster and the rotational activation energy is lower for the inclusion compounds with a greater amount of nonadecane. This effect must be a consequence of the reduced inter-guest molecular interactions in mixNDOU with respect to NDOU. Since the guest molecules differ only in the presence of the carbonyl group, one should ascribe these differences to the variation of the average value of the interactions between the carbonyl groups. These latter interact directly *via* long-range dipolar forces and in an indirect way since the host urea molecules are able to bond to the guest carbonyls in adjacent channels.⁹ We have previously tested with different approaches the effect of the guest–host interactions on the molecular reorientation inside the channel. By EPR experiments,⁴ we found that the rotational rate of the nonadecan-10-one radical in NDOU is considerably slower than that of the nonadecane in its UIC (NDU) as measured by NMR relaxation.¹⁶ By molecular dynamics simulations,¹⁷ we put forward evidence that the ketone carbonyl of NDOU points preferentially towards the sides of the hexagonal walls of the host channel. The origin of this preference is the formation

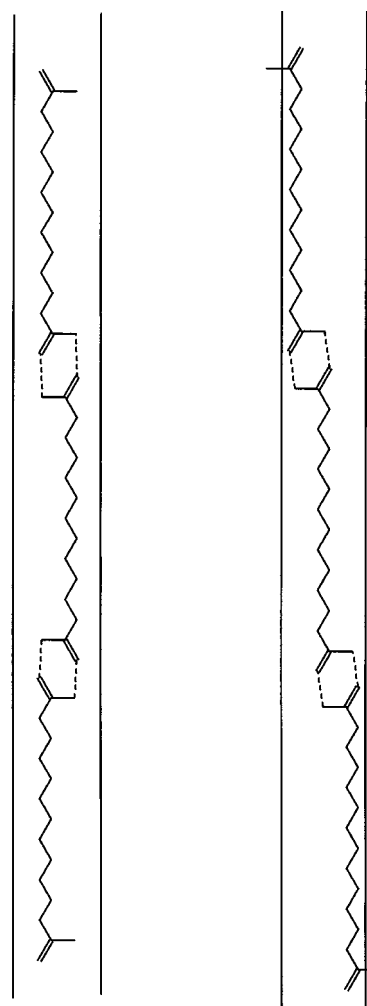


Fig. 5 Hydrogen bonded chains of tridecanedioic (left) and tetradecanedioic acids (right) in all-*trans* conformation

of weak hydrogen bonding with a urea molecule that rotates about its two-fold axis. This latter result explains the experimental difference between NDOU and NDU dynamics. The present data give further insight, since they show that the rotational dynamics of the guest ketone inside a channel depend upon the nature of the molecules hosted by nearby channels. In fact, the probability that urea molecules form hydrogen bonds with guest carbonyls in adjacent channels diminishes as the nonadecane percentage increases. Therefore, we conclude that the inter-channel interactions greatly affect the rotational dynamics of the guests.

Dicarboxylic acids

It is known that the temperature T_c of the transition from the hexagonal to the orthorhombic phase in UICs depends on the length of the chain of the included molecule: the longer the chain, the higher is the transition temperature. For the alkane UICs T_c ranges from 110 K ($n = 10$) to 160 K ($n = 20$) and to 220 K ($n = 40$).¹⁸ For hydrocarbon derivatives UICs the dependence of T_c on the chain length fits very well the latter experimental trend, except for carboxylic acids. In fact for these UICs the T_c value is always higher than that expected on the basis of the chain length. This behaviour has been attributed to their ability to form hydrogen bonds between themselves and, therefore, to form dimers in the case of monocarboxylic acids, and longer chains in the case of dicarboxylic acids.¹⁹

Also in the case of 13AU and 14AU the phase transition temperatures indicate the presence of hydrogen bonded guest molecules, corresponding to chain lengths of 30–40 carbon atoms. Therefore, we can expect that on average three mol-

ecules should be hydrogen-bonded for a time long enough to allow the coupling between the guests and host, which gives rise to the phase transition. Moreover, since it is well known that the guest molecules in UICs are closely packed inside the channels, we can expect that also longer chains of hydrogen bonded molecules can be formed with shorter lifetimes.

In Fig. 5 are shown the chains of three hydrogen bonded molecules in the all-*trans* conformation for 13AU and 14AU compared with the diameter of the host channel (about 5.5 Å). The molecules are oriented in such a way that two facing carboxylic groups belonging to neighbouring molecules can give rise to the tight double hydrogen bond typical of fatty acids. Due to the different symmetries of the chains with odd and even numbers of carbon atoms, in the case of 13AU the axis of the trimer coincides with the axis of each molecule, whereas in the case of 14AU the axis of the trimer is different from that of the single molecule. Therefore, a chain of hydrogen bonded molecules in an all-*trans* conformation fits into the urea channel for 13AU, whereas it does not for 14AU. For this latter UIC we expect that the conformation of each molecule should be chiral, giving rise to a helix bringing the two carboxylic groups in a relative position similar to that of 13AU. This conclusion is in agreement with the results obtained for the β -protons for the two UICs. In the case of 14AU the two hyperfine coupling constants have very different values and they have a marked temperature dependence. This behaviour can be analyzed by the same method we used above for the hf coupling constants of the β -protons of the ketone radical. By plotting a_β versus $a_{\beta'}$, we obtain a linear relationship and the value of the distortion angle $\gamma = 47^\circ$ is obtained. On the other hand, in the case of 13AU the two hyperfine coupling constants of the β -protons have similar values, about 3 mT, and they have a slight temperature dependence. We already observed this trend in the case of the radical formed from the UIC of nonadecanoic acid⁵ and it can be explained by assuming that in these cases the distortion is very small and nearly temperature independent. The value of the static distortion angle is obtained from the ratio $a_\beta/a_{\beta'}$ and in this case it is less than 5° .

The other relevant result to be explained is the presence of radicals in magnetically non-equivalent sites, giving rise to complex spectra when the magnetic field is at any angle with respect to the crystallographic axes. As discussed thoroughly previously,³ this observation can be explained only by assuming that the rotation around the *Z* axis is limited to an angle smaller than 360° . In this case, thanks to the crystal symmetry, the EPR spectra are given by the superposition of three magnetically non-equivalent sites, at 120° from each other. Previous results obtained by ENDOR on the small hf coupling constants of γ and ζ protons in irradiated NDOU have been interpreted by assuming fast rotations spanning an angle of 180° , and much slower ones allowing complete rotation.

The hindering of the molecular reorientation in the channel in the present case could be explained by the larger number of

constraints that the guests in these UICs present thanks to the formation of strong hydrogen bonds with neighbouring molecules. During the lifetime of a hydrogen bonded chain of guests their motions must be strongly correlated. Moreover, each molecule feels the interaction with the walls of the urea channels, and the terminal carboxylic groups of the chain feel the interactions with neighbouring molecules. All these interactions can give rise to a potential hindering the rotation around the *Z* axis and forcing the radical to span an angle smaller than 360° .

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