Structure and dynamics of radicalized hydrocarbon derivatives included in perhydrotriphenylene single crystals

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The radical obtained by γ-irradiation of the nonadecan-10-one/perhydrotriphenylene (10-NDO/PHTP) inclusion compound has been studied by EPR spectroscopy. The radical is formed by removal of one of the protons in the α position to the carbonyl group and the unpaired electron spin is coupled to the α proton and to two equivalent β protons. The hyperfine (hf) coupling constants vary slowly on lowering the temperature until an abrupt change occurs at $T = 150$ K. The radical reorients quickly on the EPR timescale inside the PHTP channels. The reorientational correlation time τ_r is obtained from the linewidth values and it is found to be shorter than the τ_r value measured previously for the same radical included in urea. The EPR spectrum changes in the timescale of weeks and after two months displays the presence of an additional hf coupling with a pair of equivalent protons, the other spectral parameters being unchanged with respect to those of the freshly irradiated radical. This modification is probably due to a folding of the radicalized guest molecule inside the host channel.

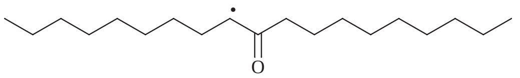
Introduction

Inclusion compounds (IC) with channel-like cavities are among the best studied clathrates.[1,2] In this group one finds IC with urea, thiourea and perhydrotriphenylene (PHTP) as host molecules. When these three substances crystallize in the presence of long chain alkanes or functionalized alkanes—as ketones, esters and carboxylic acid molecules—they give rise to IC in which the guest molecules are included in hexagonal channels. In particular, urea (UIC) and PHTP IC (PIC) have very similar features as regards the shape and the dimensions of the channels, the internal diameter of which is slightly more than 5 Å. On the other hand, they also have important differences which are related to the type of intramolecular interactions that hold together the host matrix: hydrogen bonds for urea and van der Waals forces for PHTP. The interchannel distance *a* is much larger for PIC than for UIC, *i.e.* 14.40 Å instead of 8.22 Å, and the space group is $P6_122$ for UIC[3] and $P6_3/m$ for PIC.[4] In fact, the H-bonded urea molecules form a spiral channel, and each crystal contains channels of the same chirality, whereas the PHTP molecules form non-chiral channels. In general, PHTP is more versatile in including different types of guests. As an example, urea can include linear hydrocarbons only, while PHTP can include both polyethylene and poly-2,3-dimethyl-*trans*-buta-1,4-diene.[4]

The UIC have been studied quite extensively by diffractometric, spectroscopic and calorimetric techniques. In particular, we have recently studied UIC with several types of functionalized alkanes as guest molecules by EPR and ENDOR spectroscopy.[5–8] Single crystals of the desired compound were produced and then γ-irradiated. Stable radicals are produced only on the guest molecules by cleavage of a C–H bond near the functional group. The EPR spectra were recorded at different orientations of the magnetic field and at different temperatures, and a large set of data, the hf splittings and the linewidths, were obtained and utilised to gain an insight into the structural and dynamical properties of the guest radicals. We have shown that in all the radicals formed in irradiated UICs the carbon chain deviates from the planar all-*trans* configuration, assuming a chiral average conformation matching that of the host channels, and that two kinds of motion affect the spin relaxation properties of the radicals: the internal motions of the methylene chain and the uniaxial molecular rotation inside the host channels.

On the other hand, only a few studies on radicals produced in PHTP have been performed to date. Griffith *et al.* studied some radicals of long chain hydrocarbon derivatives included in PHTP X-ray irradiated single crystals. They noticed that the EPR spectra at room temperature for the radicals obtained showed a rapid uniaxial molecular rotation around the channel axis similar to that in UIC, and that their intramolecular motion appeared more free than that in urea inclusion compounds.[9] Sozzani *et al.* studied *via* EPR at room temperature the propagating radicals in the polymerization of diene monomers included in PHTP.[10]

All the previous EPR investigations were performed at room temperature, and therefore the dynamic behaviour of the guests has not been studied. Therefore, we decided to perform an EPR study on a γ-irradiated single crystal of a PIC, with the aim of comparing the properties of the radicals obtained with those of the IC of the same guest in urea. We chose for this study as guest molecule the symmetric ketone nonadecan-10-one (10-NDO) that we had already extensively studied in urea.[5,6]



Scheme 1 Radical from 10-NDO

Experimental

PHTP was kindly supplied by Professor Piero Sozzani and was synthesized and purified according to standard methods.[11] The ketone was obtained from Aldrich. Single crystals of nonadecan-10-one in PHTP (NDP) were grown from a butan-2-one (spectrophotometric grade) solution of the PHTP and the guest in molar ratio *ca.* 1 : 2. The crystals were obtained by slow cooling, 0.01 °C min^{-1} from 48 °C to 0 °C.

The crystals were irradiated with a dose of 30 kGy (3 MRad) of γ rays at room temperature and they were maintained at room temperature during the time between the measurements. 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 PIC channel axis.

For g value calibration, the microwave frequency was measured with a 5342A Hewlett-Packard microwave frequency counter and a LiTCNQ crystal was used as g value standard.

A number of different crystals were grown, under slightly different experimental conditions. All the crystals were hexagonal-based prisms, with dimensions *ca.* 1 × 0.5 mm. The experimental results reported were repeated several times, with similar findings.

Methods

The radicals produced by high energy irradiation of the guest molecules included in urea have peculiar properties. They are very stable since they are confined in a solid matrix. On the other hand, they are fast moving and the anisotropies of their magnetic interactions are partially averaged out and their EPR spectra display a fast motion, first-order lineshape. The case of a radical in UIC can be considered as the limiting situation of a paramagnetic probe oriented in an axially symmetric anisotropic matrix with orientational degree of order $S = 1$. The EPR lineshape is affected in different ways by the short range guest–host interactions and by the long range inter-channel guest–guest interactions. In our previous studies we have shown how the spectral parameters of the included radicals can be exploited to obtain the maximum amount of information about the nature of the intermolecular interactions and the structure and dynamics of the guest molecules in UIC. The main features of the EPR spectra of the NDP radical are quite similar to those of the radical of 10-NDO in urea (NDU). Therefore, in this section the methods of spectral analysis will be briefly reviewed and in the following section the results for NDP will be presented and compared with those for NDU.

The hf splitting of the β protons[12] is very sensitive to the dihedral angle θ of the CH(β) proton with the π orbital of the unpaired electron according to eqn. (1).

$$a_\beta = a_0 \cos^2 \theta \qquad (1)$$

In all the UIC the hf splittings of the two β protons are different since the equilibrium conformation of the guest radicals deviates from the all-*trans* arrangement of the methylene chain. The amount of the distortion depends upon the ability of the guest to form weak hydrogen bonds with the host urea molecules. This result was obtained by comparing the radicals obtained from 10-NDO and nonadecanoic acid.[7] The carboxylic acid molecules are disposed inside the channels in a head-to-head arrangement, so that the CO groups are mainly engaged in forming guest–guest hydrogen bonds and a small distortion is observed. Instead, the ketone carbonyl group interacts more strongly with the urea molecules of the clathrate walls and the average conformation largely deviates from the all-*trans* one. The importance of the guest–host intermolecular interaction in determining the guest conformation was suggested from EPR spectroscopy and has been recently confirmed by a molecular dynamics calculation.[13]

The EPR spectra of the guest radicals in the high temperature hexagonal phase of UIC have fast motion line shapes and can be analysed in the framework of the Redfield–Freed theory[14,15] by taking into account the orienting effects of the anisotropic environment.[16] The width of the transition line corresponding to a set of nuclear spin quantum numbers $\{m_k\}$ is given by the polynomial expression (2):

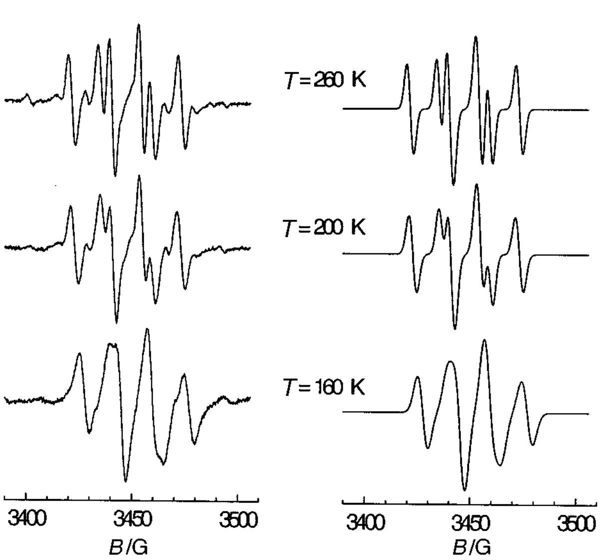


Fig. 1 EPR spectra, at three different temperatures, of the radical obtained by irradiation of the nonadecan-10-one in PHTP, with the magnetic field orthogonal to the hexagonal symmetry axis of the crystal. Left, experimental spectra; right, computer simulations.

$$W\{m\} = A + \Sigma_k B_k m_k + \Sigma_k C_k m_k^2 + \Sigma_{k<k'} E_{kk'} m_k m_{k'} \qquad (2)$$

Since the transition lines partially overlap it is essential to resort to a best-fit procedure to obtain the values of the spectral parameters.[5,17] The adjustable parameters are the centre of the spectrum, the hf splittings and the coefficients of the line width expression (2). The theoretical expressions of the line width coefficients are related to the different molecular dynamic processes, the rotation of the radical inside the channel and its conformational oscillations.[6] In particular, the principal contribution to the linear term $B_\alpha m_\alpha$ arises from the molecular rotation which modulates the dipolar interaction of the α proton. Therefore, B_α is strongly dependent upon the orientation of the crystal and reaches a maximum when the magnetic field is orthogonal to the Z symmetry axis. On the other hand, the modulation of the isotropic coupling constants of the β protons is due to the oscillation of the methylene groups about the equilibrium conformation and this determines the quadratic coefficients in eqn. (2), $C_\beta m_\beta{}^2$, $C_{\beta'} m_{\beta'}{}^2$ and $E_{\beta\beta'} m_\beta m_{\beta'}$. Since for an $I = \frac{1}{2}$ nucleus m^2 is a constant, the cross term $E_{\beta\beta'}$ only brings a non trivial contribution to the line width.

The analysis of the EPR linewidths allows one to obtain information about the long range interactions. This has been shown by studying a series of UIC in which the guest species is a mixture with different concentrations of 10-NDO and nonadecane.[8] The radical is formed on the ketone molecules only, and it is found that the EPR linewidths are smaller and the radical motion faster when the composition of the guest mixture is richer in nonadecane. All the other experimental settings being the same, this result implies that the motion of the 10-NDO radical is affected by the type of molecules occupying the adjacent channels. In fact, the activation energy of the ketone rotational motion is weaker when the non-polar nonadecane molecules are present in the IC.

Results and discussion

The EPR spectra of freshly irradiated NDP are given, for any orientation of the crystal in the magnetic field, by a doublet of triplets. The EPR spectra at three different temperatures and with the magnetic field perpendicular to the hexagonal axis of the crystal are shown in Fig. 1 together with their computer simulation. We attribute this spectrum to the same radical as in irradiated NDU, due to the homolytic cleavage of a

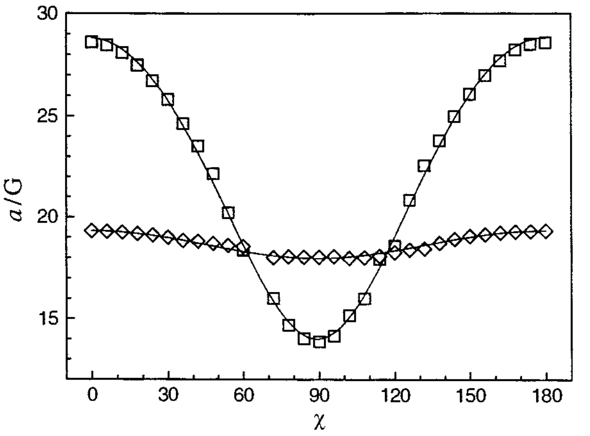


Fig. 2 Hyperfine splittings of the α proton (□) and of the β proton (◇) as a function of the crystal orientation at $T = 180$ K. The continuous lines are the least-square fits to the expression $[a_{\|}^2 \cos^2 \chi + a_{\perp}^2 \sin^2 \chi]^{\frac{1}{2}}$.

C–H bond on one of the two equivalent methylene groups near the carbonyl group. Therefore the hf splitting generating the doublet is attributed to coupling with the α proton, whereas the one corresponding to the triplet is due to coupling with two equivalent β protons.

As in the case of the NDU, the guest is rotating fast around the Z axis of the channel and the spectra are motionally averaged in the XY plane. On the other hand, when the magnetic field B_0 explores a plane containing the Z axis, the shape of the spectrum varies since both the hf splittings and the linewidths are modified.

Hyperfine splittings. Orientation dependence

In Fig. 2 the orientation dependence of the hf couplings of NDP is reported. The striking difference with respect to the NDU reported previously[5] is demonstrated by the hf couplings of the two β protons, which are equivalent in NDP and different at any orientation in NDU. This indicates that in NDP the torsional motion of the β methylene group with respect to the –CO–CH$_\alpha$– fragment must be equally probable for positive and negative torsion angles. This is expected due to the non chiral environment of the radical in the PHTP channel, whereas the chirality of the urea channels gives rise to different energy barriers for the torsional motions in opposite directions and therefore to two different hf splittings for the two β protons in NDU.

Moreover, it is worth noting that the value of the β proton hf coupling in NDP is typical of a freely rotating methylene group, whereas the values of the two different β couplings in NDU can be attributed to the hindered oscillations of the methylene group out of the all-*trans* plane of the methylene chain. Therefore, one must assume that the methylene chain of the guest in NDP can perform, at any temperature, transitions between a large number of different conformations in a time very short with respect to the timescale typical of EPR spectroscopy.

As in the case of NDU, for the α-proton the splitting varies between the averaged value $A_\perp$ when **B** is in the XY plane and the value $A_\|$ for **B** parallel to Z. As discussed in ref. 6, the hf splittings $A_\perp$ and $A_\|$ indicate that the –CO–CH$_\alpha$– fragment is rotating around the axis perpendicular to both the C–H$_\alpha$ direction and the axis of the 2p orbital bearing the unpaired electron.

Hyperfine splittings. Temperature dependence

On decreasing the temperature, the EPR shape evolves as shown in Fig. 1 since the hf splittings change and the lines broaden. Their temperature dependence is reported in Fig. 3 together with the same data for NDU for comparison. The sudden variation at $T = 150$ K suggests the presence of a phase transition. It is well known that in all UIC a hexagonal to orthorhombic phase transition is present at a temperature T_c whose value depends on the length of the methylene chain.[18] In particular, we have observed a discontinuity of the hf splitting of NDU at $T_c = 155$ K, in agreement with the occurrence of a phase plane transition for the nonadecane UIC. No previous observations of phase transitions in PIC have been reported in the literature.

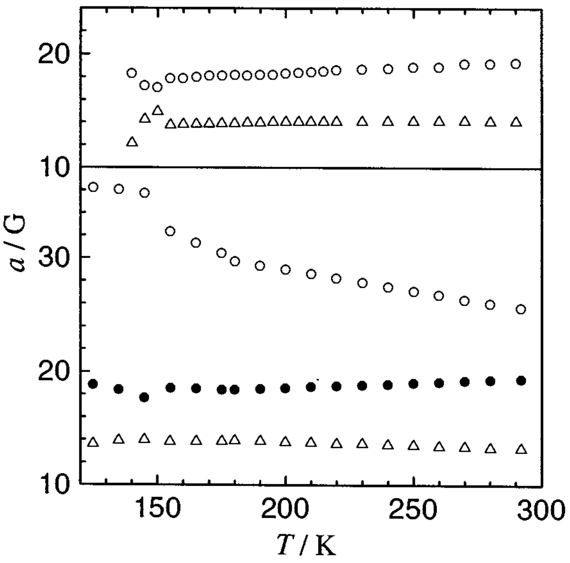


Fig. 3 Temperature dependence of the hf splittings of the nonadecan-10-one radical with the magnetic field perpendicular to the crystal symmetry axis: upper box, included in PHTP, lower box, included in urea. β protons (○); α protons (△).

The temperature variation of all the hf couplings for NDP above 150 K is quite small and that of the β proton couplings is larger than that of the α proton, as in the case of NDU. However, the comparison between the data for NDU and NDP shows that when B_0 is along the Z axis, the hf coupling of the α proton decreases slightly on increasing the temperature in the NDP case, while it is temperature independent in the NDU case. This result indicates, in the case of NDP, a tilting motion of the rotational axis of the guest in the channel, giving rise to an increase of the hf splitting with temperature as the amplitude of the latter motion increases. This is to be expected, since the average direction of the alkyl chain must be modified when the methylene groups undergo conformational transitions.

On the other hand, the temperature dependence of the β proton hf coupling is much more pronounced in the case of NDU than in that of NDP. For NDU, the behaviour of the β proton hf coupling has been explained by assuming that the amplitude of the intramolecular motion of the methylene group with respect to the carbon atom bearing the unpaired electron depends on the temperature. The lesser temperature dependence for NDP indicates that the amplitude of the intramolecular motion does not vary substantially with temperature. These results are confirmed by the data on the dynamic behaviour of the radical which are discussed below. The principal values of the A and g tensor at two different temperatures are reported in Table 1.

Dynamic parameters

As observed in our previous studies on UIC, the librational motion of β protons modulates their isotropic hf interactions and contributes to the quadratic terms in the linewidth expression. When the two protons are equivalent, only the $C_\beta M_\beta^2$ term should be considered in eqn. (2), with $M_\beta = m_\beta + m_{\beta'} = -1$,

Table 1 Principal components of the hyperfine tensors (in G) and of the g tensor for the NDP radical. The standard error is ±0.05 G for the hyperfine components, $\pm 2 \times 10^{-4}$ for the g components

T/K	$A_{\alpha\parallel}$	$A_{\alpha\perp}$	$A_{\beta\parallel}$	$A_{\beta\perp}$	$g_{\parallel}$	$g_{\perp}$
180	28.77	14.02	19.30	17.96	2.0043	2.0050
290	28.34	14.00	20.65	19.21	2.0041	2.0047

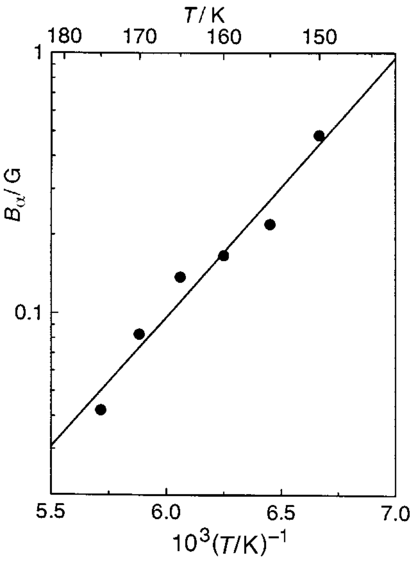


Fig. 4 Temperature dependence of the B_α linewidth coefficient for nonadecan-10-one in PHTP. The straight line is the least-square fit.

Table 2 Rotational mobility τ_r, conformational mobility τ_c (at $T = 290$ K) and rotational barrier ΔE_r obtained from the linewidth coefficients for NDU and NDP

	NDU[6]	NDP (this work)
τ_r/s	7×10^{-10}	3×10^{-11}
ΔE_r/kJ mol^{-1}	7.5	6
τ_c/s	2×10^{-11}	*a*

[a] The intramolecular mobility is too fast to give any linewidth effect.

Table 3 Spectral parameters used for the simulation of the spectra in Fig. 5. The number of equivalent protons is one for a_1 and two for a_2 and a_3. Hyperfine coupling constants in G.

Species	g	a_1	a_2	a_3
A	2.0046	18.7	19.3	–
B	2.0046	18.7	19.3	12.2

0, 1. The linewidth parameter C_β in NDP is found to be very small at any temperature and its contribution to the total linewidth can be ignored. This fact means that the intramolecular motion which averages the spectra is always very fast and its contribution to the transverse spin relaxation is negligible. This observation is in agreement with the value of the β proton hf coupling, which is typical of a freely rotating methylene group, and has a slight temperature dependence, as discussed above.

On the other hand, the parameter B_α is found to be strongly dependent upon the orientation of the crystal, as expected, and its value is a maximum when measured with the magnetic field perpendicular to the Z axis. The logarithmic plot of its variation against temperature is reported in Fig. 4. The value of the correlation time τ_r for the radical rotational motion inside the host channel can be obtained from this coefficient by using eqn. (3):

$$B_\alpha = \tfrac{1}{4}(\mu_B B_0/\hbar^2)\,\delta g\,\delta A_\alpha\,\tau_r \qquad (3)$$

where δg and δA are the anisotropies of the g and A_α tensors in the molecular xy plane.[6] The temperature dependence of the rotation frequency is given by:

$$\tau_r^{-1} = \tau_0^{-1}\exp(-\Delta E_r/k_B T) \qquad (4)$$

where ΔE_r is the rotational hindrance barrier. By assuming that δg and δA_α have the same values as in NDU,[6] we obtain the values for the rotational mobility at room temperature and the rotational barrier in NDP. The values are reported in Table 2, together with those found in NDU. The temperature dependence of B_α gives, for the rotational rate inside the channel, a pre-exponential factor and an energy barrier both smaller than those for the same radical in urea.

Therefore, the conclusion is that both the intermolecular and intramolecular motions in NDP are faster than in NDU. Since the average radius of the channel is the same for the two types of inclusion compounds, this different behaviour must be attributed to the weaker interactions of the guests with the host in the case of NDP. In fact, several experimental studies with different techniques,[19] and a molecular dynamics simulation,[13] have shown the importance of the host–guest H-bonds in determining the dynamic behaviour of the guests in UIC. On the other hand, only van der Waals interactions are to be expected between host and guest in PHTP.

As far as the intramolecular motions are concerned, the large number of conformations that have to be explored by the guest molecule to give rise to a β proton hf coupling typical of a free methylene group must be explained by co-operative motions of the host and the guests, overcoming the steric hindrance due to the small channel radius.

Time evolution of the EPR spectrum

A peculiar property of the EPR spectrum of NDP is that it modifies after irradiation very slowly, on the time scale of weeks. The change can be followed more easily by observing the spectrum with the magnetic field directed at 60° to the Z axis. In fact, for this orientation the hf couplings of the two β protons and of the α proton become nearly equal, as shown in Fig. 2. Therefore, as a consequence of the accidental degeneracy, the spectrum is particularly simple and is approximately represented by a 1:3:3:1 quartet. The evolution of the spectrum over two months is shown in Fig. 5. Let us call the radical observed in the freshly irradiated crystal radical **A**. As one can see, additional EPR lines appear and increase in intensity with time, due to another radical, which we can call **B**. The surprising feature of the new lines is that they are exactly centred at the same field as the old ones.

The spectra have been simulated with the parameters reported in Table 3. The radical **B** has the same g value and the same hf coupling constants as the radical **A**, but it also shows an additional coupling with two other equivalent protons. The relative population p_A/p_B of the two species is 1:0, 3:2 and 0:1 for the spectra (I), (II) and (III) displayed in Fig. 5. This observation result is quite unusual, and we have excluded the possibility that the **B** signal is due to the formation of a new radical involving the host protons since it would be less mobile than radical **A** and its lines would be

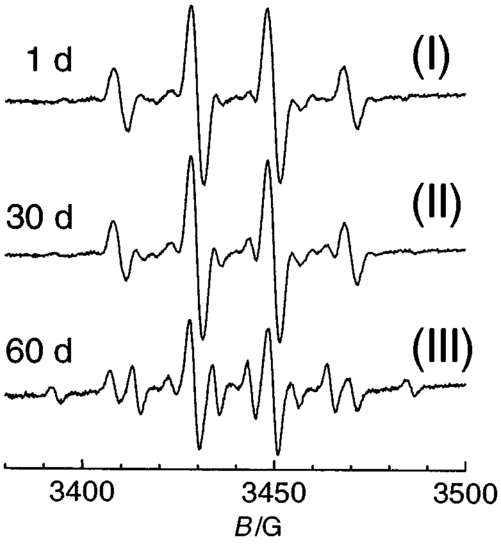


Fig. 5 Evolution of the EPR shape of the nonadecan-10-one radical in PHTP during two months after irradiation. The lag time is: (I) 1 day, (II) 30 days, (III) 60 days.

much wider. We propose instead that the radical **B** is in fact the same radical species as radical **A**, but assuming a different molecular conformation that allows another pair of methylene protons of the guest to be coupled with the unpaired electron. Our hypothesis is also based on the results of an X-ray conformational analysis of the *n*-hydrocarbon PIC. In fact, it was shown previously that the PHTP channel allows the inclusion of guest alkyl chains with *gauche* as well as *trans* conformations.[20] Moreover, our observation that the methylene group is almost freely rotating points out the capacity of the guest to assume a large number of different conformations.

The existence of through-space or through-bond interactions between non directly bonded atoms (proximity effect) has been revealed in organic radicals by EPR spectra in many cases, thanks to the variation of the electron spin distribution which is very sensitive even to tiny interactions.[21] We have, therefore, examined all the conformations that the 10-NDO guest molecule could assume inside a cylindrical cavity within the dimensions of the PHTP channel. The allowed conformations have been generated by a computer program and their statistical weights have been assumed on the basis of the rotational isomeric (RIS) state model.[22] According to this model, the increase in potential energy with respect to the all-*trans* arrangement of an alkyl chain with n_g methylene groups in the *gauche* conformation and n_p sequences g_+g_- which produce a local overlap of the chain (the so-called pentane effect) is given by eqn. (5):

$$E = n_g E_g + n_p E_p \qquad (5)$$

The usual values for the energy parameters are $E_g = 2$ kJ mol^{-1} and $E_p = 7.5$ kJ mol^{-1}. These values are used to obtain the probability of the different conformations.

The conformations generated by the program have been selected by taking into account the steric hindrance of the host channel and by choosing those which bring a pair of methylene protons in close proximity to the sp^2 carbon atom. In the conformation reported in Fig. 6, the folding of the carbon chain brings the carbon atom bearing the unpaired electron to 2.5 Å with respect to that in the η position (six C–C bonds away). The distance between the methylene protons and the unpaired electron allows a weak through-space homoconjugative interaction between the carbon 2p orbital and the hydrogen 1s orbitals.

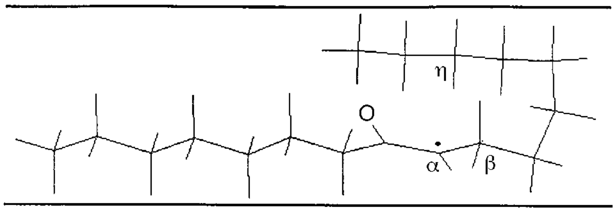


Fig. 6 Folded conformation of the nonadecan-10-one radical in PHTP in aged irradiated crystals. The EPR spectrum (see Fig. 5) shows the coupling of the unpaired electron with the protons in the α, β and η positions. The latter hyperfine coupling is due to a through-space homoconjugative interaction.

A restricted Hartree–Fock calculation with the MOPAC 6.0 package[23] was performed in order to obtain an indicative value of the spin density on the two H_η atoms for this conformation. The results are $\rho\ (H_{\eta 1}) = 0.015$, $\rho\ (H_{\eta 2}) = 0.007$, corresponding, respectively, to hf couplings of 7.6 and 3.5 G. These values are indicative of possible spin density transfer through weak homoconjugative interactions between non bonded atoms.

Conclusions

We have studied by EPR spectroscopy the inclusion compound of radicalized nonadecan-10-one in the host formed by PHTP. The structural and dynamic properties of this system have been compared with those previously observed for the same radical included in the urea host matrix. They differ to a significant degree because of the different chirality of the host matrices and because of the weaker host–guest interactions in PHTP. The radical in PHTP reorients rapidly at any temperature between a large number of non chiral conformations, whereas in urea the reorientation was between chiral conformations slightly different from the all-*trans* one. The rotational motion inside the channels is much faster for the radical in PHTP. Moreover, the EPR spectrum of the radical in PHTP evolves over a time scale of weeks, until it stabilises in a pattern that we attribute to a folded conformation of the original radical.

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