Proton Spin-Rotational Interaction in Crystalline 1-Hydroxy-2,4-Hexadiyne

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The amplitude and temperature dependence of the longitudinal proton spin relaxation time T_1 in crystalline 1-hydroxy-2,4-hexadiyne is caused by the activated process of the CH_3-group reorientation. The low hindering barrier of 4.4 kJ/mole leads above 200 K to relaxation contributions by spin-rotational interaction, which are comparable to the dipolar interaction.

Introduction

Diacetylenes have been extensively studied because of their natural occurence[1] and their ability to produce macroscopic conjugated polymer molecules by solid state polymerisation[2]. So far there have been relatively few N.M.R. studies[3] as most of the reactive monomers have large complex end groups. We have studied the simpler diacetylene 1-hydroxy-2,4-hexadiyne (HH), which offers the possibility of observing the methyl group motion. From sterical considerations we expect that the intramolecular hindering barrier for the CH_3-group reorientation will be small and, therefore, that at higher temperatures relaxation contributions due to SR-interaction occur, as found recently in crystalline methylnaphthalenes[4].

Experimental

HH was prepared by the method due to Armitage et alies[5]. The product was a polycrystalline material with measured composition C 76.1%, H 6.45% (theoretical C 76.6%, H 6.38%). HH sublimes at 44 °C, which limits the temperature range of observation. The samples were slightly pink in colour, indicating a polymer content some what less than 1%, too small to effect the N.M.R.-experiments.

T_1 was measured at 44 and 22 MHz with 90°-τ-90° pulse sequences in the temperature range from 300 to 20 K. The magnetisation decay was not a single exponential. A small component of about 20% of the total magnetisation, for which T_1 was always shorter than for the majority of spins, was present. Solution molecules or paramagnetic centers may cause this effect, because spin-spin interaction should be fast enough to equalize the spin temperature of the whole molecule.

Results and Discussion

In Fig. 1 the high temperature behaviour of T_1 is represented. No dispersion within 44 and 22 MHz was found between 300 and 60 K, which implies the extreme narrowing case ($\omega\tau \ll 1$) at least for $\omega \geqq 22$ MHz. Below this temperature range T_1 exhibits a minimum at 50 K (44 MHz) and a shoulder at 58 K which is due to a tunneling process[6], very similar to the T_1-results found on β- and 2,6-MN[7].

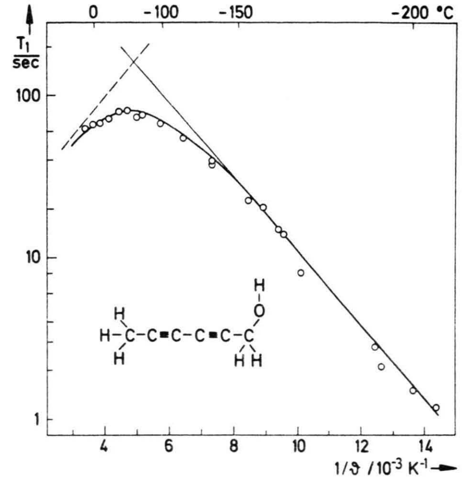

Fig. 1. The temperature dependence of T_1 in crystalline 1-hydroxy-2,4-hexadiyne at 44 MHz. The broken line represents the relaxation contribution of the SR-interaction, the continuous line the dipolar part.

The decrease in T_1 with increasing temperature between 200 K and room temperature is specific for relaxation by spin-rotational interaction of symmetric top molecules, as found for crystalline methylnaphthalenes[4]. The reorientation of the molecule as a whole can be excluded by steric considerations and the lack of magnetic field dependence in this temperature range.

The total relaxation rate T_1^{-1} is composed of contributions from dipolar and SR-interactions:

$$T_1^{-1} = T_{1\,\mathrm{DD}}^{-1} + T_{1\,\mathrm{SR}}^{-1} \,. \tag{1}$$

For fast CH_3-reorientation ($\omega\tau \ll 1$) these rates were determined to be

$$T_{1\,\mathrm{DD}}^{-1} = 3 \cdot 10^{10} \left(\frac{n_{\mathrm{CH_3}}}{n_{\mathrm{H}}}\right) \tau_{\mathrm{DD}}\ \mathrm{sec}^{-1} \qquad (2)^{8}$$

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and $$T_{1\,\mathrm{SR}}^{-1} = 3 \cdot 10^{-15} \left(\frac{n_{\mathrm{CH_3}}}{n_{\mathrm{H}}} \right) \tau_{\mathrm{DD}}^{-1} \sec^{-1} \qquad (3)^{4}$$

($n_{\mathrm{CH_3}}/n_{\mathrm{H}}$ = ratio of CH_3-protons the total number of protons, τ_{DD} = correlation time of the CH_3-reorientation.) The value of Eq. (3) is based on Boden and Folland's[9] model of fast uncorrelated jumps of the CH_3-group between discrete potential minima with mean jump angles of 120°.

The evaluation of Fig. 1 with respect to Eq. (1) yields for the dipolar (continous line) and the SR-interaction (broken line) the values given in Table 1.

Table 1. Experimental values for the dipolar ($T_{1\,\mathrm{DD}}^{-1}$) and SR-interaction ($T_{1\,\mathrm{SR}}^{-1}$) in 1-hydroxy-2,4-hexadiyne. The activation energies E were derived from the slopes of the curves and the frequency constant τ_{∞} was determined by the minimum condition $\omega\,\tau = 0{,}62$ at 50 K (44 MHz). The corresponding results on β-MN are given for comparison.

HH	β-MN (from Ref. 4)
$T_{1\,\mathrm{DD}}^{-1} = 2 \cdot 10^{10} \frac{n\mathrm{CH_3}}{n\mathrm{H}} \tau_{\mathrm{DD}} \sec^{-1}$	$T_{1\,\mathrm{DD}}^{-1} = 3 \cdot 10^{10} \frac{n\mathrm{CH_3}}{n\mathrm{H}} \tau_{\mathrm{DD}} \sec^{-1}$
$T_{1\,\mathrm{SR}}^{-1} = 8.8 \cdot 10^{-15} \frac{n\mathrm{CH_3}}{n\mathrm{H}} \cdot \tau_{\mathrm{DD}}^{-1} \sec^{-1}$	$T_{1\,\mathrm{SR}}^{-1} = 10.4 \cdot 10^{-15} \frac{n\mathrm{CH_3}}{n\mathrm{H}} \cdot \tau_{\mathrm{DD}}^{-1} \sec^{-1}$
$\tau_{\mathrm{DD}} = \tau_{\infty} \cdot \exp \{E_{\mathrm{DD}}/R\,\vartheta\}$	
$\tau_{\infty} = 5.2 \cdot 10^{-14}$ sec	$\tau_{\infty} = 8.8 \cdot 10^{-14}$ sec
$E_{\mathrm{DD}} = 4.4$ kJ/mole	$E_{\mathrm{DD}} = 3.8$ kJ/mole
$E_{\mathrm{SR}} = -4.6$ kJ/mole	$E_{\mathrm{SR}} = -3.8$ kJ/mole

The slopes of the dipolar and SR-curve are the same in magnitude and of opposite sign as expected, a good confirmation of the assumption, that both relaxation effects are due to the same thermally activated motion with an activation energy of 4.4 kJ/mole. It is worth mentioning, that a similar barrier height was estimated by neutron diffraction experiments on dimethylacetylene[10] (4.3 kJ/mole), in which the intramolecular potential of the methyl-group should be the same as in HH.

Whereas the small difference in the amplitude of the dipolar interaction for HH and that determined in previous experiments for MNs can be explained by larger distances between the protons of the adjacent molecules in HH than in methylnaphthalenes, the discrepancy between the determined SR-interaction and the calculated value of Eq. (2) is still open to discussion, as in other works[11].

The most striking point is the excellent agreement of the results on HH and β-MN as shown in Table 1. The only similarity between these substances is the occurence of CH_3-groups with similar barriers, while the molecular skeletons and the lattice structure are quite different. This means first, that the assumption of relaxation by the CH_3-group only in HH was correct, and secondly that the SR-interaction does not depend on the molecular skeleton. Therefore, we are able to predict similar relaxation phenomena in all crystalline materials, in which the CH_3-group possesses comparable potential with at most C_{3v} symmetry. Smaller jump angles of the CH_3-group in glassy non crystalline materials lower the SR-interaction efficiency, and prevents observation of this effect[12].

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