between B'' and B' is small, but it has been proved to be positive by a more appropriate graphical analysis.

Except for the center of the Q branch, the recorded absorption band agrees well with the computed one. The slight deviation from the exact symmetric top causes the greatest discrepancies when K is small, because it is there that the strongest components of the parallel type band exist, and these transitions are allowed for in an asymmetric top molecule [5, 6].

The author wishes to thank Dr. R. ANTTILA for great help in recording the spectra and Prof. P. TUOMIKOSKI for suggesting the topic. This work was financially supported by Neste Oy and the National Research Council for Sciences which are gratefully acknowledged.

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Radiation-Induced Conformation Changes of the Pyrimidine Ring in a Single Crystal of Dihydrothymine

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Radiation-induced radicals in a single crystal of dihydrothymine were studied with EPR. It was found that the 5-thymyl radical is the dominant radical species at room temperature. The orientation dependence of the hyperfine couplings can only by explained if one assumes that $C_{(5)}$, $C_{(6)}$ and $C_{(7)}$ lie in the plane defined by the rest of the nonhydrogen atoms of the ring. The highly disordered structure of the ring in the undamaged crystal is ordered if a proton bound to $C_{(5)}$ is removed.

Radiation damage of several dihydropyrimidines in powder and solution has been studied with electron paramagnetic resonance (EPR) [1]. No similar investigation in single crystals of any of these compounds has been done. In the present paper we report an EPR study of the structure of free radicals in a gamma-irradiated single crystal of dihydrothymine. The crystal and molecular structure of this compound has been reported by FURBERG and JENSEN [2]. In contrast to thymine [3, 4], the pyrimidine ring in the crystal of dihydrothymine is highly disordered. From the EPR study of the radiation induced radicals in a single crystal of dihydrothymine it is possible to determine whether or not the disordered structure of the ring remains unchanged after the molecule has been damaged by irradiation.

Experimental

The crystals were grown by slow evaporation of an aqueous solution at 20 °C. No good quality crystals of moderate size could be found. Fortunately, dihydrothymine is very sensitive to irradiation and the crystal $1 \times 1 \times 0.2\ \mathrm{mm}^3$ in size was sufficient for the EPR analysis. The external configuration and the crystallographic axes of the crystal used in this study are shown in Fig. 1. The axes were identified with X-ray diffraction analysis. The crystal is orthorhombic and the dimensions of the unit cell are $a = 7.336$, $b = 23.474$ and $c = 7.034$ Å (l. c. [2]). There are eight molecules in the unit cell.

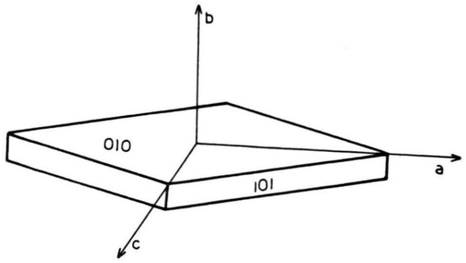

Fig. 1. External configuration and the crystallographic axes of the single crystal of dihydrothymine.

The crystal was irradiated in air at room temperature to a dose of about 5 Mrads by ^{60}Co gamma rays, at a dose rate of 0.3 Mrads/hour. The crystal was aligned in the EPR cavity so that one of the crystallographic axes was perpendicular to the magnetic field. The spectra were recorded at room temperature with a

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Varian E-3 spectrometer at 10° or 15° intervals as the crystal was rotated in the magnetic field. A similar procedure was adopted to record the spectra about the other two axes of the orthogonal set.

Identification of Radicals

The irradiated single crystal of dihydrothymine gave spectra which did not change rapidly when the crystal was rotated in the magnetic field, H. The total splitting of the lines was always close to 135 gauss. Figure 2 shows the resonances (first derivative curves) for the magnetic field parallel to b and c crystallographic axes. From the total splitting and the structure of the resonance pattern it is possible to conclude that the most pronounced resonance, indicated by the solid lines under the spectra, is due to the $-C(CH_3)CH_2$-radical. In dihydrothymine it is radical I.

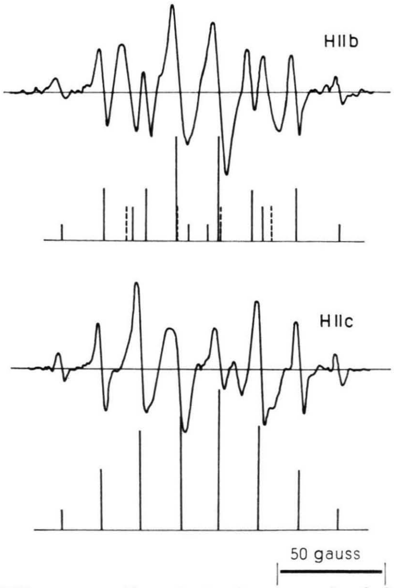
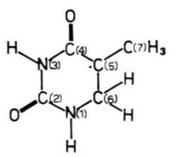
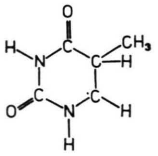


Fig. 2. EPR spectra (first derivative curves) of the dihydrothymine crystal, for the magnetic field parallel to b and c crystallographic axes. The bars under the spectra indicate relative intensity and the positions of the resonance lines.



I



II

It is formed by the abstraction of the hydrogen atom from $C_{(5)}$. The hyperfine splitting is caused by the coupling of the unpaired electron with three equivalent methyl protons and a larger coupling with two methylene protons. From the three equivalent couplings of 20 gauss of the methyl protons one concludes that the methyl group is rotating and that he unpaired spin is largely localized. In spite of the fact that it is a part of the conjugated system, its density is about 0.8 on a single atom – $C_{(6)}$.

The same radicals have been identified in the powdered specimens of dihydrothymine either irradiated with gamma rays [1, 5] or bombarded with thermal hydrogen atoms [5, 6]. 5-thymyl radicals were first observed and interpreted in the thymine base of DNA [7, 8] and analyzed in more detail in a single crystal of thymidine [9]. In the latter compounds radical I is formed by a hydrogen atom addition on $C_{(6)}$ of thymine.

As judged from the spectra in Fig. 2, 5-thymyl radicals are not the only ones present. Additional resonance, indicated by the dotted lines under the spectrum, may belong to radical II. This type of radicals could not be analysed in any detail and will not be discussed here.

Conformation of 5-thymyl Radical

The present experiments enable us to gain more information on the structure of radical I and on the conformation changes of the pyrimidine ring in irradiated dihydrothymine. Figure 3 shows the varia-

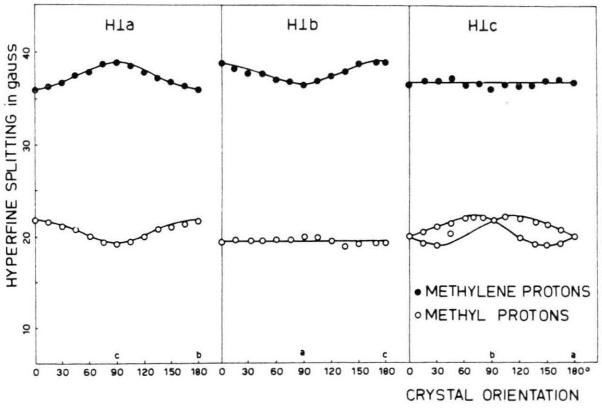


Fig. 3. Angular variation of the methyl and methylene couplings in three orthogonal planes.

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tion of the hyperfine splittings for the methylene and methyl protons in three orthogonal planes. The couplings of the methyl protons were directly measured from the spectra. The methylene proton couplings were deduced from the total splitting. β-hydrogen couplings are often quoted to be nearly isotropic [9–11]. We observe a slight but for our purposes very significant variation of the couplings. From Fig. 3 one can see that the methyl proton coupling, A^{CH_3}, is approximately constant in the $a\,c$ plane, and has a maximum in the direction almost parallel to b axis. Thus, A^{CH_3} is approximately an axially symmetric tensor. Similarly, the coupling tensor for the methylene protons is found to be axially symmetric with the axis of symmetry in z direction. Nearly axial symmetry of the rotating methyl protons has also been observed by other investigators [12, 13] and the coupling has been treated theoretically by REITBÖCK [14]. The axis of symmetry coincides with the axis of rotation. For this symmetry, the hyperfine coupling for each proton can be described by the equation

$$A = A_f + A_d (3\cos^2 \Theta - 1) .$$

A_f is the isotropic coupling, A_d is the unisotropic dipolar coupling and Θ is the angle between H and the symmetry axis. For both methyl and methylene protons $A_f \gg A_d$.

For the axial symmetry the coupling tensor is defined by two parameters, $A_{\parallel}$ and $A_{\perp}$. For dihydrothymine, however, these parameters could not be accurately evaluated. Namely, from the known space group, P $b\,c\,a$, of the dihydrothymine crystal [2] one expects four magnetically distinct molecules in a unit cell. In addition to that, there are two enantiomorphs, making in total eight magnetically distinct groups of molecules. Each of them gives at least three quartets of lines, what makes almost a hundred lines in total. Generally, it is not possible to analyze a pattern of such complexity in a solid specimen, thus it is impossible to determine the hyperfine coupling tensor elements. In the particular case of dihydrothymine two facts make at least some analysis possible. First, only β-protons are involved in the hyperfine coupling, making it rather isotropic. Second, all the unpaired electron-proton directions are close either to y direction (methyl protons) or to z direction (methylene protons). Thus, although we measure only the average coupling of all methyl protons or all methylene protons, a remarkable angular variation of the couplings is observed (see Fig. 3). Two distinct groups of methyl couplings are found only in the $a\,b$ plane. The "average" coupling parameters are given in Table 1. The maximum values are in the directions 25° from b axis and in the $a\,b$ plane, indicating the orientation of the $C_{(5)} - C_{(7)}$ bond. That is approximately in the plane defined by all nonhydrogen atoms of the undamaged molecule except $C_{(5)}$, $C_{(6)}$ and $C_{(7)}$. This fact suggests that originally very distorted molecule [2] becomes planar or almost planar after the proton bound to $C_{(5)}$ is removed. Probably both enantiomorphs become equivalent in the radical form. The probable conformation change is shown in Fig. 4.

Group	$A_{\perp}$	$A_{\parallel}$	Axis of symmetry
$-CH_3$	19.5	22.0	25° from b axis in $a\,b$ plane
$-CH_2-$	36.5	39.0	in c axis

Table 1. Hyperfine couplings, in gauss, of methyl and methylene protons.

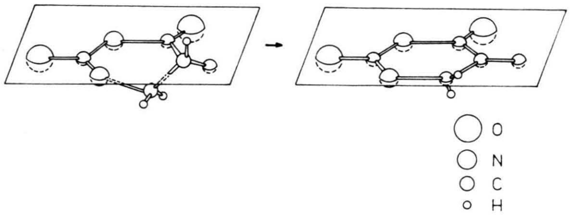

Fig. 4. Radiation-induced conformation changes of the pyrimidine ring in the crystal of dihydrothymine.

Additional evidence for the ordering of atoms comes from the couplings of the methylene protons. For the rotational conformation of the $-CH_2-$ group this coupling depends on the angle, Φ, defined by the π orbital of the unpaired electron and the projection of the C – H bond to the plane through $C_{(5)}$, $C_{(6)}$ and the π orbital as [15]

$$A = B \cos^2 \Phi$$

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where B is a constant. Although the two methylene couplings in radical I could not be determined exactly, it is possible to conclude that they do not differ for more than 4 gauss. Using $B \cong 50$ gauss and assuming that the angle $\sphericalangle H_{(1)}C_{(6)}H_{(5)}$ remains approximately the same as in the undamaged molecule (108°), one finds that the angles Φ_1 and Φ_2 corresponding to the $C_{(6)}-H_{(1)}$ and $C_{(6)}-H_{(2)}$ bonds, respectively, do not differ by more than 5°, in contrast to the very large difference in the undamaged molecule. If one assumes the rocking conformation of the $-CH_2-$ group, $|\Phi_1-\Phi_2|$ is even smaller [16]. Equivalence of the two methylene protons proves their symmetric arrangement with respect to the unpaired electron localized on $C_{(5)}$, hence to the plane defined by $C_{(5)}$, $C_{(6)}$ and $C_{(7)}$. Since $C_{(5)}-C_{(7)}$ bond lies in the ring plane one safely concludes that in the 5-thymyl radical the whole pyrimidine ring is approximately planar.

The help of Dr. B. Kojić-Prodić in the X-ray crystal analysis is gratefully acknowledged. This investigation was supported by the Yugoslav Federal Research Fund and by the Research Fund of Croatia.

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Optically Thin Hydrogen Plasma with Self-Consistent Electron Velocity Distribution

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Occupation numbers of the atomic levels and degree of ionization of a stationary optically thin hydrogen plasma are calculated for temperatures in the range 8000 °K $\lesssim T \lesssim$ 16000 °K and for electron densities in the range 10^9 cm$^{-3} \lesssim n_e \lesssim 10^{17}$ cm^{-3}. The electron velocity distribution is not supposed to be Maxwellian, rather, it is obtained in a self-consistent way from the corresponding kinetic equation which is solved simultaneously with the equations that describe the statistical steady-state of the atomic levels. Besides spontaneous radiative bound-bound transitions and radiative recombinations, inelastic electron-atom collisions as well as elastic electron-electron and electron-atom collisions are taken into account. Hydrogen atoms are approximated by model atoms having four bound levels and a continuum. The numerical results show that for temperatures $T \lesssim$ 10000 °K the tail of the electron distribution function differs markedly from that of a Maxwell distribution, except in the case of high electron densities. Likewise, the self-consistently calculated values of the atomic occupation numbers and of the degree of ionization there deviate strongly, up to several orders of magnitude, from those obtained by assuming a Maxwellian velocity distribution of the electrons.

1. Introduction

The principle of detailed balancing ensures that in the case of thermal equilibrium the loss of electrons out of the tail of the distribution function due to excitation or ionization collisions with atoms is exactly compensated by the production of such electrons due to the corresponding deexcitation or three-body recombination collisions. If the upper level of any atomic transition is underpopulated relative to the Boltzmann or Saha value ("departure from thermal equilibrium"), this balancing is perturbed, resulting in a net flux of electrons from the high energy tail into the low energy body of the distribution function. In a stationary state, this net flux is then counterbalanced by elastic electron collisions which tend to fill up the tail of the distribution function to its Maxwellian values. Departures of the atomic occupation numbers from their thermal values thus result in departures of the electron velocity distribution from a Maxwell distribution.

This shows that in determining the spectroscopic state of a plasma a self-consistent procedure has to be applied. For the atomic occupation numbers depend on the collision rates and hence on the electron velocity distribution, which, in turn, depends on the occupation numbers through the mechanism described above. Only in the case of prevailing elastic collisions is the electron distribution function independent of the interaction with the atoms; it is then approximately Maxwellian

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