

Communication

# ENDOR evidence for the quantum exchange of the methylene protons

Janko N. Herak \*

*Department of Pharmacy and Biochemistry, University of Zagreb, Ante Kovačića 1, 100001 Zagreb, Croatia*

Received 16 April 2007; revised 14 November 2007

Available online 5 December 2007

## Abstract

ENDOR spectroscopy was used for studying methylene proton couplings in the 6-yl (or H-addition) radical in a single crystal of 1-methyluracil at 4.2 K. The two methylene protons were magnetically equivalent in all crystal (radical) orientations in the magnetic field, indicating proton quantum exchange. The two protons compose magnetically single entity with spin  $I = 1$ . The observed small ENDOR line splittings of about 0.60 MHz agree well with the theoretical expectations for such a system.

© 2007 Elsevier Inc. All rights reserved.

*Keywords:* ENDOR; Methylene protons; Quantum exchange

## 1. Introduction

In the study of organic radicals by EPR and ENDOR spectroscopies, the proton hyperfine interactions give important information on the structure and dynamics of the radicals studied. It has been known for long time that the magnetically equivalent protons give rise to the level splitting and consequently to the splitting of the EPR or ENDOR lines. The proton equivalence is brought about by molecular motion, like originally observed with EPR for the ethyl radical in solution [1] and with ENDOR for the rotating methyl group in a solid [2]. Since the line splitting is very small, it could be observed only for the systems giving rise to very narrow resonance lines and rather large proton couplings.

Accidental equivalence of the two methylene protons in a radical in solid was first treated by Gloux [3]. The equivalence was observed only for some orientations of the radical in the magnetic field, for the orientations in which the corresponding energy levels were expected to cross. Subsequent EPR and ENDOR studies of the so-called 5-yl or H-addition radicals in thymidine [4,5] and thymine [6,7] undoubtedly demonstrated individual character of the

two methylene protons; they exhibited two distinct coupling tensors. The only report which might illustrate complete equivalence of the two methylene protons is that on the 6-yl or H-addition radical in 1-methyluracil [8], although not completely recognized at the time of the report. In the present report we present the evidence for quantum exchange of the methylene protons in that system, independent of the crystal and radical orientation in the external magnetic field.

## 2. Results and discussion

In order to rule out the molecular motion as a source of averaging out the magnetic properties of the two methylene protons, the ENDOR measurements were done at 4.2 K, by immersing the ENDOR resonance cavity with the sample into liquid helium. The high-frequency resonance lines corresponding to the methylene proton couplings were recorded in various directions of the crystal (and the radical) in the external magnetic field. Fig. 1 shows the doublet of the closely spaced resonance lines recorded for a selected direction of the magnetic field in the crystallographic *ac* plane. The experimental data for the complete *ac* plane are presented in Fig. 2. The *ac* plane is selected for presentation, because in the earlier study at room temperature [8], for most directions of the magnetic field in that plane, the lines

\* Fax: +385 1 4856 201.

E-mail address: [jaherak@pharma.hr](mailto:jaherak@pharma.hr)

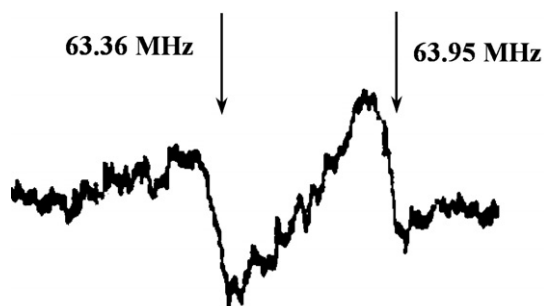


Fig. 1. ENDOR resonance lines attributed to the methylene protons in the H-addition radical of 1-methyluracil. The spectrum was recorded for the magnetic field in the  $ac$  crystal plane,  $70^\circ$  from  $\langle a \rangle$ , for  $\nu_e = 9.14 \times 10^9$  Hz and  $\nu_p = 14.28$  MHz.

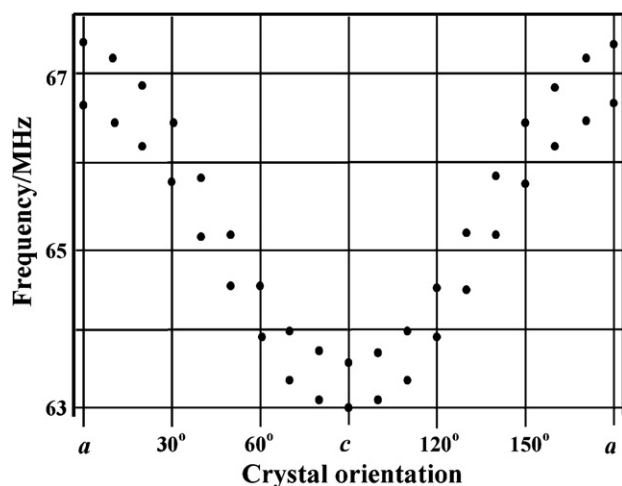


Fig. 2. Angular variation of the methylene proton resonance lines in the H-addition radical of 1-methyluracil, in the  $a,c$  plane of the crystal lattice. The measurements were done at 4.2 K, for  $\nu_e = 9.1 \times 10^9$  Hz and  $\nu_p = 14.28$  MHz.

corresponding to the methylene proton couplings could not be observed. The spacing between the lines in the doublet is 0.55–0.68 MHz, being larger for larger proton couplings. That observation obviously demonstrates correlated behavior of the two methylene protons. They might be considered to compose a single entity with nuclear spin  $I = 1$ .

The energy levels for the system composed of an unpaired electron ( $S = 1/2$ ) and a nuclear entity of spin  $I = 1$  in the magnetic field ( $B$ ) could be derived by solving the corresponding secular equation [9]. Instead of referring to the exact solution, for the present purpose it is convenient to present the three high-frequency energy levels ( $M_S = -1/2$ ,  $A > 0$ ) in frequency units in a power series expansion to the second order:

$$E_{-1} = -\frac{1}{2}\nu_e + \nu_p + \frac{1}{2}A,$$

$$E_0 = -\frac{1}{2}\nu_e - \frac{1}{2}\frac{A^2}{\nu_e + \nu_p},$$

$$E_{+1} = -\frac{1}{2}\nu_e - \nu_p - \frac{1}{2}A - \frac{1}{2}\frac{A^2}{\nu_e + \nu_p}.$$

Here  $\nu_e$  and  $\nu_p$  refer to the EPR and the proton NMR resonance frequencies, respectively, and  $A$  is the orientation-dependent proton coupling. The corresponding transition frequencies are:

$$\nu_1 = \nu_p + \frac{1}{2}A, \quad (1)$$

$$\nu_2 = \nu_p + \frac{1}{2}A + \frac{1}{2}\frac{A^2}{\nu_e + \nu_p}. \quad (2)$$

The two transitions differ in the second order term,

$$\Delta = \frac{1}{2}\frac{A^2}{\nu_e + \nu_p}. \quad (3)$$

Since in our experiments  $\nu_e = 9.1 \times 10^9$  Hz and  $\nu_p = 14.28$  MHz, for the direction of the magnetic field in the  $c$  crystallographic axis the observed resonances at  $\nu_1 = 63.00$  MHz and  $\nu_2 = 63.57$  MHz give  $A(c) = 97.44$  MHz and the line splitting of 0.57 MHz. For the magnetic field in the  $ac$  plane,  $70^\circ$  from  $\langle a \rangle$ , the resonances appear at 63.36 and 63.95 MHz, respectively (Fig. 1). Likewise, for  $B \parallel a$ , the values are  $\nu_1 = 66.60$  MHz and  $\nu_2 = 67.25$  MHz, giving  $A(a) = 104.64$  MHz and the line splitting of 0.65 MHz. According to Eq. (3) the corresponding theoretical line splittings are  $\Delta(c) = 0.52$  MHz and  $\Delta(a) = 0.60$  MHz, what is in good agreement with the experiments. The experimentally observed splittings (recorded with the error of  $\pm 0.02$  MHz) are systematically slightly higher than the theoretical values. A part of the explanation might lie in the use of the approximation in deriving Eqs. (1)–(3).

### 3. Conclusions

It is concluded that the two proton spins in the H-addition radical in the crystal of 1-methyluracil form the triplet state in all orientations of the crystal (and the radical) in the external magnetic field. For certain orientations the coupling of the two protons, if they were independent, would differ by as much as 10 MHz. This means that the exchange interaction between the spins is larger than 10 MHz and forces the spins to be strongly correlated. To our opinion, the proton spin correlation lies in the symmetry of the system. In the highly symmetric crystal lattice [10] the hydrogen atom that adds to 1-methyluracil upon radical formation makes the two hydrogens of the newly formed methylene group symmetrically placed with respect to the pyrimidine ring and equivalent in the immediate surroundings. They might be considered to compose the pseudo-orbital composed of the two hydrogen  $s$  orbitals,  $\varphi = (1/2)^{-2} \cdot [\varphi(A) - \varphi(B)]$ . Pseudo-orbital  $\varphi$  has the same symmetry as the atomic  $p_z$  orbitals and participates on equal terms in composing the molecular  $\pi$  orbital and in the spreading of the unpaired electron. The two methylene protons occupy the same “orbital” and consequently are not discriminated. In other related systems studied [3–7], the two methylene protons are not equivalent in their crystal environment.

## Acknowledgments

This work was supported by the Croatian Ministry of Science, Education and Sports (Grant No. 006-006117-1237).

## References

- [1] R.W. Fessenden, Second-order splittings in the ESR spectra of organic radicals, *J. Chem. Phys.* 37 (1962) 747–750.
- [2] S.F.J. Read, D.H. Whiffen, ENDOR studies on a rotating methyl group, *Mol. Phys.* 12 (1967) 159–164.
- [3] P. Gloux, Effet de second order pour des protons de méthylène en ENDOR, *Mol. Phys.* 21 (1971) 829–839.
- [4] H.C. Box, E.E. Budzinski, W.R. Potter, ENDOR characterization of the free radicals in irradiated thymidine, *J. Chem. Phys.* 61 (1974) 1136–1139.
- [5] E.O. Hole, E. Sagstuen, W.H. Nelson, D.M. Close, Primary reduction and oxidation of thymine derivatives. ESR/ENDOR of thymidine and 1-methylthymine X-irradiated at 10 K, *J. Phys. Chem.* 95 (1991) 1494.
- [6] A. Dulčić, J.N. Herak, Crystal structure dependence of radiation-induced radicals in thymine. An ESR study, *Radiat. Res.* 47 (1971) 573–580.
- [7] E. Sagstuen, E.O. Hole, W.H. Nelson, D.M. Close, Radiation-induced free radical formation in thymine derivatives. EPR/ENDOR of anhydrous thymine single crystals X-irradiated at 10 K, *J. Phys. Chem.* 96 (1992) 1121–1126.
- [8] J.N. Herak, C.A. McDowell, ENDOR study of long-range spin interactions in molecular crystals. I. 1-methyl uracil, *Chem. Phys.* 61 (1974) 1129–1135.
- [9] A. Dulčić, J.N. Herak, Fine phenomena in ENDOR spectra of equivalent nuclei, *Fizika* 8 (1976) 217–223.
- [10] R.K. McMullan, B.M. Craven, Crystal structure of 1-methyluracil from neutron diffraction at 15, 60 and 123 K, *Acta Crystallogr.* 45 (1989) 270–276.